Stabilisation of Isocyanate Cross Linked Polybutadiene Binder

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Doctor of Philosophy

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April1998

Summary

Isocyanate cross-linked hydroxyterminated polybutadiene is used as a binder for solid rocket propellant. Rocket motors containing this propellant require a storage life of at least 20 years. During storage it has been found that the important rubbery properties of the binder can be lost due to oxidative cross-linking of the polybutadiene chains. This could cause catastrophic failure when the rocket motor is required. At present the bis-hindered phenol Calco 2246 is used as a thermal oxidative stabiliser, but it's performance is only adequate. This has led to the search for a more efficient stabiliser system.

To hasten the evaluation of new antioxidant systems the use of dynamic thermal analysis was investigated. Results showed that a tentative relationship existed between predictions by thermal analysis and the long term oven ageing for simple single antioxidant systems. But for more complex systems containing either autosynergistic or mixed antioxidants no relationship was observed suggesting that results for such an "accelerated" technique cannot be used for the purpose of extrapolation for long term performance. This was attributed to the short time and more aggressive condition used (higher temperature and oxygen rich atmosphere in thermal analysis) altering the mechanism of action of the antioxidants and not allowing time for co-operative effect of the combined antioxidant system to form.

One potential problem for the binder system is the use of an diisocyanate as a cross-linking agent. This reacts with the hydroxyl hydrogen on the polymer as well as other active hydrogens such as those contained in a number of antioxidants, affecting both cross-linking and antioxidant effectiveness. Studies in this work showed that only antioxidants containing amine moieties have a significant affect on binder preparation, with the phenolic antioxidants not reacting. This is due to the greater nucleophilicity of the amines.

Investigation of a range of antioxidant systems, including potentially homo, hetero and autosynergistic systems, has highlighted a number of systems which show considerably greater effectiveness than the currently used antioxidant Calco 2246. The only single antioxidant which showed improvement was the partially unhindered phenol γ-Tocopherol. Of the mixed systems combinations of the sulphur containing antioxidants e.g. DLTP with higher levels of chain-breaking antioxidants, especially Calco 2246, were the most promising. Also the homosynergistic mix of an aromatic amine and a phenol was seen to be very effective but the results were inconsistent. This inconsistency could be explained by the method of sample preparation used. It was shown that the efficiency of a number of antioxidants could be dramatically improved by the use of ultrasound during the mixing stage of preparation. The reason for this increase in performance is unclear but in the case of the homosynergistic amine/phenol mix both more efficient mixing and/or the production of a novel mechanism of action are suggested.

Key Words : Polybutadiene, Antioxidants, Thermal oxidation, Thermal analysis

To
Mum & Dad

Acknowledgements

I gratefully acknowledge the help and advice I received from my supervisors Dr. S Al-Malaika and the late Dr. A Davis, and from my many colleagues in the research group, especially Dr. H. H. Sheena.

I am indebted to the DRA for their generous financial support for the project, and invaluable knowledge.

I thank the technical and support staff throughout the department for their help in use, development and maintenance of numerous equipment. Also for their often invaluable advice.

Finally to all the people who have kept me sane during both the practical and writing up periods of this project. This especially includes my long suffering parents and Andrea.

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List of Abbreviations

HTPB:-	Hydroxyterminated polybutadiene
IPDI:-	Isophorone diisocyanate
AO:-	Antioxidant
HPLC:-	High performance liquid chromotography
CB-A:-	Chain breaking acceptor
CB-B:-	Chain breaking donor
PD:-	Peroxide decomposer
CLD:-	Cross-link density

CHAPTER ONE

1 INTRODUCTION

1.1 Solid Propellants for Rocket Motors

A long history of solid propellant rockets has led to the development of composite rocket propellants. Propellants are composed of a rubber binder which is highly filled (up to 90% of total mass) [1, 2] with finely ground aluminium and crystalline oxidisers such as ammonium perchlorate to produce the required burn properties [3]. In addition to its role the binder has two main functions; as a fuel, burning after firing to produce low molecular weight gases which are then vented via a nozzle, to protect the motor from stresses imposed during firing where operating pressures of 1000 psi and temperatures of 3000°C are seen [1, 3]. An insulator is required to protect the motor casing, usually high strength aluminium or steel, from combustion gases. If the propellant also functions as the insulator it can be directly bonded onto the case, thus producing weight savings [3]. This is possible since the combustion radiates from the star shaped centre (fig. 1) of the propellant .

The propellant is normally case bonded (fig. 1), i.e. cast in the case so the propellant adheres to the internal surface [4]. This produces two main storage stresses on the case propellant interface [5, 6], both caused by the different thermal expansion coefficients of the binder and case. The first stress occurs because of cooling to ambient temperature after the curing at 60°C, the second from diurnal temperature cycling. Besides storage loads the propellant has to withstand very high stresses caused by acceleration during firing. These require the binder to have a high tensile elongation [6] and remain flexible at low ambient temperatures for the complete potential life-span of the rocket, which could be as long as twenty years [1]. The tensile strength and flexibility of the binder can be lost through oxidation, therefore antioxidants are used to prevent this.

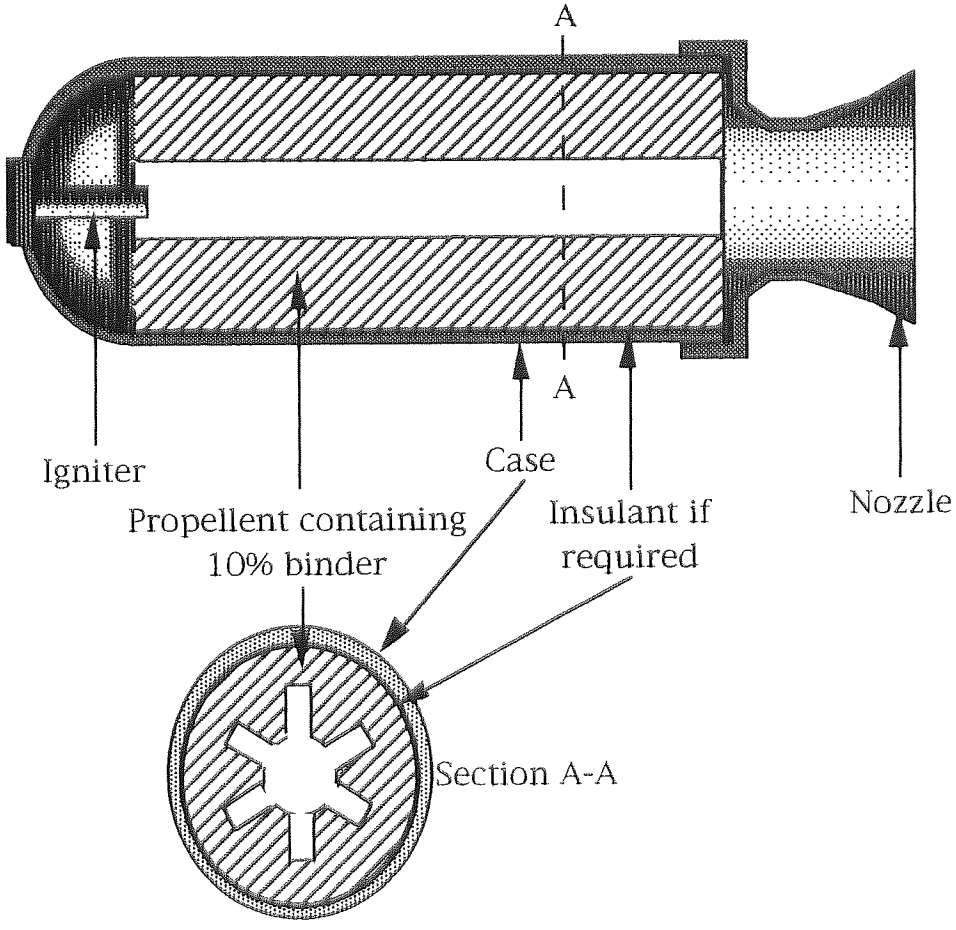
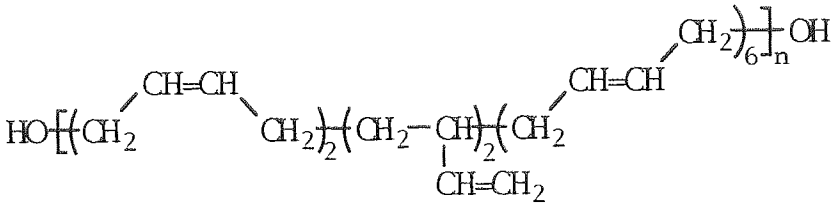


Figure 1-1 Diagram of a typical solid propellant rocket motor

1.2 Preparation of the Binder

1.2.1 General Binder Information

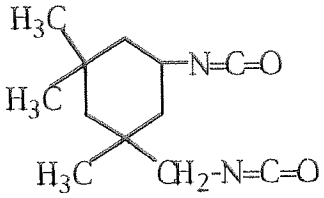
Hydroxyterminated polybutadiene (HTPB) is the most commonly used prepolymer to produce the binder due to its unsurpassed mechanical properties [5]. The hydroxyterminated polybutadiene is prepared by Arco from butadiene [7] by a free radical mechanism [8] using H_2O_2 as the initiator in a mixed aqueous-organic medium to ensure solubility of both monomer and initiator. This produces a polymer, known as Arco R-45M, with a microstructure containing: 20% cis 1,4; 60% trans 1,4; 20% vinyl 1,2 double bonds as shown in structure I.



Cis 1,4 Vinyl 1,2 Trans 1,4

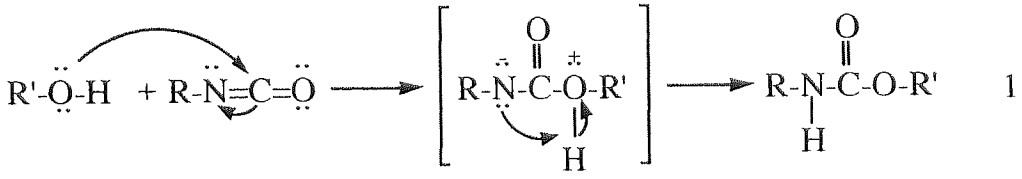
I, Arco R-45M HTPB

The binder is a polyurethane which is prepared by cross-linking the low molecular weight (approx. 3000) hydroxyterminated polybutadiene with isophorone diisocyanate (3-isocyano-methyl-3,5,5-trimethylcyclohexyl-isocyanate, IPDI (II)).

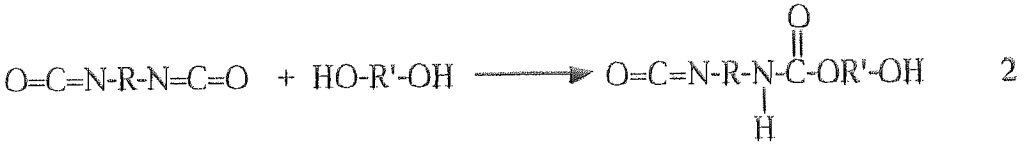


II, IPDI

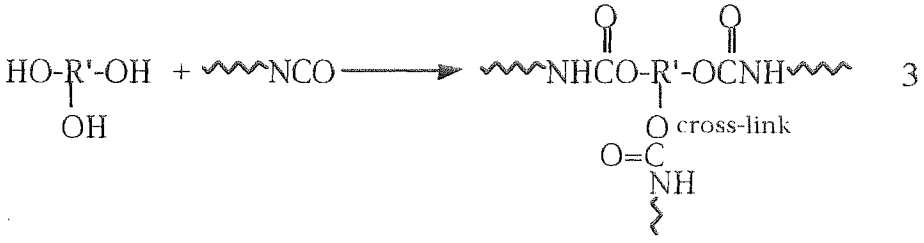
This reacts with the hydroxy group on the hydroxyterminated polybutadiene to form a urethane linkage, reaction 1 [9].



The initial step of binder preparation is the reaction between a molecule of diisocyanate and a molecule of hydroxyterminated polybutadiene this forms the urethane link and a difunctional product (reaction 2). This can then react with either another diisocyanate, another hydroxyterminated polybutadiene or another difunctional molecule that causes the growth of a long chain polymer.



Cross-linking occurs as the OH functionality of the hydroxyterminated polybutadiene is slightly higher than 2 implying some hydroxyterminated polybutadiene molecules contain 3 OH groups. The extra OH is located on a vinylic segment and allows the bridging of two chains as shown in reaction 3 to produce the loosely cross-linked binder.



The ratio of -OH and -NCO is closely associated to the initial cross-link density (CLD) of the binder. The theoretical relationship is shown in figure 2 where percentage soluble material is plotted against NCO:OH ratio [10]. The ideal ratio contains the lowest proportion of isocyanate to hydroxyterminated polybutadiene to produce a cross-linked binder and is in the range of 0.7 to 0.9 [11]. After addition of a calculated amount of IPDI to the hydroxyterminated polybutadiene the mixture is cured in an oven at 60°C for seven days where it forms a gel with a specific CLD.

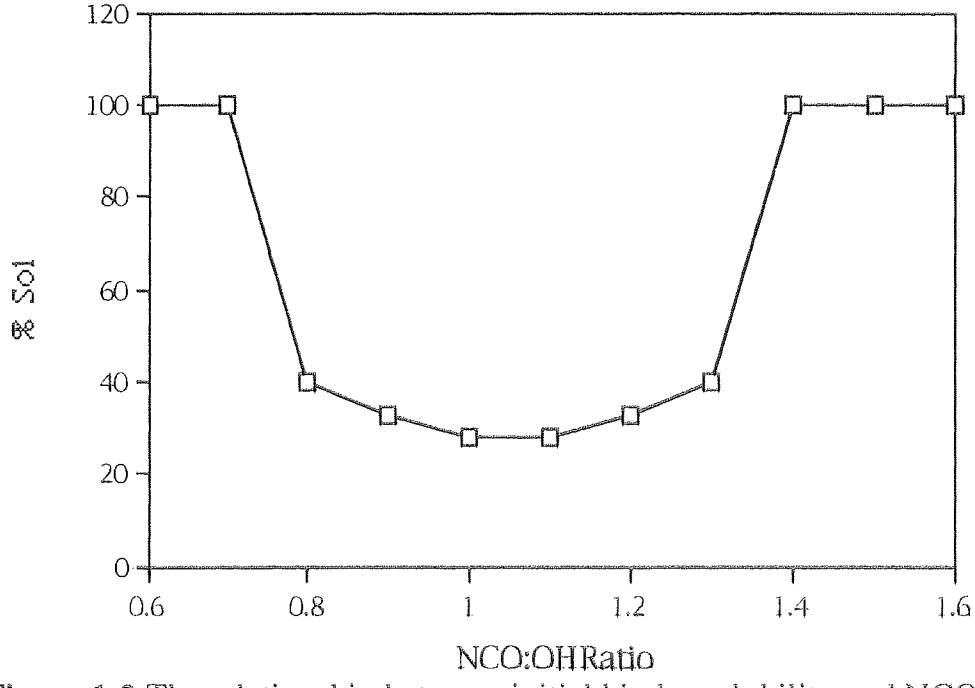
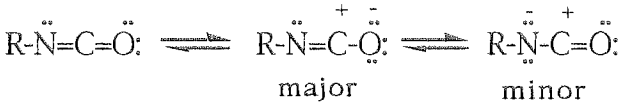


Figure 1-2 The relationship between initial binder solubility and NCO:OH ratio

1.2.2 Isocyanate Chemistry

Isocyanates contain the highly reactive -N=C=O group that can react with many compounds including itself. Its electronic structure allows the formation of two resonance possibilities [12, 13].



The overall effect of these resonance structures is to give the carbon the highest net positive charge, the oxygen the highest net negative charge and the nitrogen an intermediate net negative charge. Reactions with compounds which have an active hydrogen therefore occur via the attack of a nucleophilic centre on the electrophilic isocyanate carbon as in reaction 1. The proof that the active hydrogen compound is acting as a nucleophile is shown by the effect electrophilic groups in the compound have on its reaction with the isocyanate. These groups pull electron density from the active hydrogen site making it a poorer donor and thus decreasing the rate of reaction [12].

A reaction will occur in appropriate conditions between an isocyanate and OH containing compounds unless strong steric hindrances are present. Primary alcohols react readily at room temperatures, secondary alcohols are less reactive and tertiary even less so. The reaction is strongly catalysed by mild and strong bases which help stabilise the intermediate [14] and weakly by acids. This also means the reactant molecule can act as a catalyst altering the rate of the reaction. The rate of the reaction affects the stability of the urethane formed with slow reaction rates generally producing a more stable product. Also urethanes produced from aliphatic isocyanates are more stable than those from aromatic isocyanates.

The urethane can decompose in three ways [13]: dissociation back to the isocyanate and alcohol; formation of a primary amine and olefin as shown in reaction 4; or formation of a secondary amine as in reaction 5.

$$RNHCOOCH_2CHR' \longrightarrow RNH_2 + CO_2 + R'CH{=}CH_2 \quad 4$$

$$RNHCOOR' \longrightarrow RNHR' + CO_2 \quad 5$$

Reaction 4 occurs at temperatures of approximately 200°C and can produce reasonable yields of products, in the case of urethanes prepared from phenols decomposition can be as low as 150°C [12]. Urethanes prepared from tertiary alcohols decompose readily at temperatures as low as 50°C via reaction 5, whereas those prepared from primary and secondary alcohols only decompose slowly at 150 to 200°C. The formation of secondary amines by reaction 5 only occurs at temperatures above 300°C. The presence of catalysts and other reactants also greatly influences the stability.

Isocyanate also reacts with water to form amines and carbon dioxide (CO_2), the reaction proceeding via the formation of an unstable carbamic acid (reaction 6). This reaction is the basis behind the formation of polyurethane foams.

$$RCNO + H_2O \longrightarrow \underset{\text{carbamic acid}}{[RNHCOOH]} \longrightarrow RNH_2 + CO_2 \quad 6$$

The amines formed are then even more reactive to the isocyanate and disubstituted ureas are formed (reaction 7).

$$RNCO + R'NH_2 \longrightarrow RNHCONHR' \quad 7$$

1.2.3 Mechanical Properties of Polybutadiene

Polybutadiene (PBD), as with most diene rubbers, has good rubbery properties, such as resilience and high recoverable elasticity [15]. The high resilience is a consequence of high chain flexibility, which also accounts for polybutadiene's low glass transition temperature (Tg). The flexibility is due to

the carbon single bond being free from steric hindrance. The double bonds enhance this low steric hindrance so although not being flexible themselves lead to a net reduction in Tg. An increase in the number of vinylic double bonds causes an increase in steric hindrance which leads to an increase in the polybutadiene's Tg, but the ratio of cis and trans bonds has no effect [16]. The use of an aliphatic isocyanate for cross-linking does not affect this high chain flexibility [3].

The presence of double bonds is also a disadvantage as it introduces a point of weakness into the polymer backbone. This double bond is susceptible to oxidation which leads to cross linking causing the binder to become rigid. When this occurs the binder made from polybutadiene loses its critical stress strain behaviour and is no longer able to adhere to the rocket casing during storing and firing. This could lead to failure during firing and thus a potential catastrophe. Therefore oxidation of the binder has to be minimised.

1.3 Oxidation of Hydrocarbons.

1.3.1 Overview of General Reactions.

The reaction of oxygen with organic materials is an important process. It has many positive uses including the production of energy both in internal biological systems and in the burning of fossil fuels [17]. It is also the main reason for the deterioration of foodstuffs and polymers via oxidative degradation.

Oxidative degradation occurs in most polymers during processing at high temperatures and in subsequent service conditions [18]. The oxidation of organic materials is caused by a radical chain reaction initiated by heat, light energy or impurities [19]. In the case of solid polymers mechanical stresses can also induce oxidation [20, 21]. The kinetics of this oxidation are made more complex by the production of primary products, which may have a different

sensitivity to oxidation, and irregularities in polymer chain structure [19]. Also temperature and oxygen pressure [22] linked to diffusion in solid polymers [23 - 26] affect polymer degradation. This means the mechanisms involved in oxidative degradation are complex.

The basic mechanism for the radical degradation of hydrocarbon polymers is shown in scheme 1 [27]. This is an autocatalytic process which starts slowly, possibly with an induction period, after which the rate increases slowly until it becomes constant [28]. The chain mechanism consists of three basic steps, initiation, propagation and termination.

Initiation.

Source	$\longrightarrow$	$R^{\bullet}$	(a)

Propagation.

$R^{\bullet} + O_2$	$\longrightarrow$	$ROO^{\bullet}$	(b)
ROOH	$\longrightarrow$	$RO^{\bullet} + {}^{\bullet}OH$	(c)
2ROOH	$\longrightarrow$	$RO^{\bullet} + RO_2^{\bullet} + H_2O$	(d)
$ROO^{\bullet} + RH$	$\longrightarrow$	$ROOH + R^{\bullet}$	(e)
$RO^{\bullet} + RH$	$\longrightarrow$	$ROH + R^{\bullet}$	(f)
$HO^{\bullet} + RH$	$\longrightarrow$	$H_2O + R^{\bullet}$	(g)

Termination.

$R^{\bullet} + R^{\bullet}$	$\longrightarrow$		(h)
$R^{\bullet} + ROO^{\bullet}$	$\longrightarrow$	None Radical Products	(i)
$ROO^{\bullet} + ROO^{\bullet}$	$\longrightarrow$		(j)

Scheme 1-1 Radical mechanism of oxidative degradation [27].

1.3.2 Initiation

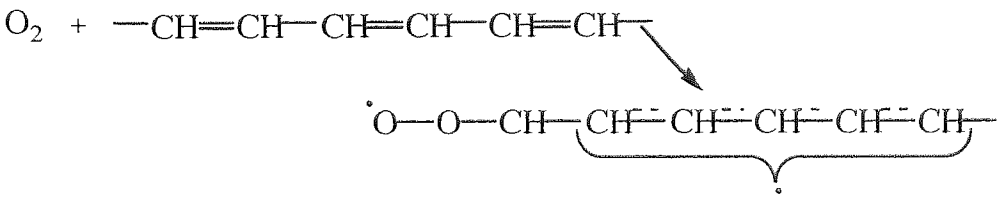
The microradicals which cause the onset of oxidation can be initiated thermally, photochemically, by impurities [19] and in the case of solid polymers

by mechanical stressing during processing and service [20, 21]. These factors can cause the breaking of bonds in the polymer to produce free radicals. These free radicals can then react with oxygen to begin the chain mechanism [21]. The rate of initiation of oxidation at ambient temperature in the dark in most polymers is low [29].

A possible route for chemical initiation is the production of free radicals via the direct reaction between molecular oxygen and the organic material (reaction 8). Since atmospheric oxygen is paramagnetic it shows the characteristics of a biradical [30]. This direct reaction is actually both thermodynamically and kinetically unfavourable having an activation energy of approximately 125 - 188 kJ mol^{-1} [31, 32]. Thus it only is likely to occur in groups with very labile hydrogens which then form stable radicals and cause the termination of the reaction [30]. The rate of this reaction becomes moderate at temperatures above 100 °C [29].

$$RH + O_2 \longrightarrow R^{\bullet} + {}^{\bullet}OOH \qquad 8$$

It is also possible for ground state oxygen to react with conjugated double bonds as in reaction (9), but this is also energetically unfavourable.



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Other oxygen species which have been implicated in initiation are; superoxide radical anions formed by the addition of an electron to O_2, (reaction 10), singlet oxygen or ozone [30]. Only ground state oxygen and superoxide can participate directly in radical reactions as they contain unpaired electrons. The importance of singlet oxygen has been questioned [30], as it is not normally a component of the atmosphere and is easily quenched. Ozone (IIIa-c) does not contain an

unpaired electron but has resonant structures with (IIIa) and (IIIb) being the most important in oxidation initiation.

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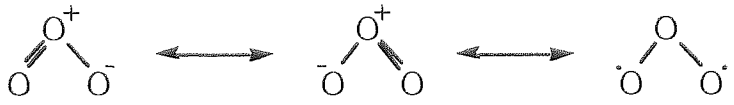

IIIa IIIb IIIc

Various atmospheric pollutants can also cause initiation of oxidation, the most important of which are sulfur dioxide and the oxides of nitrogen. In the presence of light, both are able to form species which react with organic materials [30], although some of the products from the reactions are able to act as antioxidants.

Another method of chemical initiation is by impurities (B) found in the organic material. Even extremely pure polymers contain trace amounts of impurities which may act as initiators via reactions 11 and 12.

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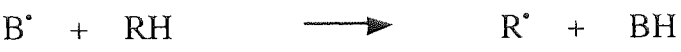


12

Polymers may also contain chemical modifications in the backbone due to side reactions during polymerisation, catalyst residues or peroxides all of which can lead to initiation of oxidation.

During processing of polymers stresses are caused by milling and shearing and in use polymers are subject to flexing, tensile stress and compression. These can all cause the breaking of bonds producing free radicals [20].

1.3.2.1 The Importance of Hydroperoxides in Oxidation

During the oxidation of both acyclic and cyclic alkenes [33, 34] the primary oxidation products were found to be a mix of hydroperoxides and polymeric peroxides, also present were aldehydes and ketones formed by cleavage at double bonds. It is also known [29] that during the induction period prior to autoxidation of polymer there is a build up of hydroperoxides via reaction (b) scheme 1.

As hydroperoxide concentration increases during oxidation its degradation becomes the most energetically important initiation step [29]. Their dissociation into free radicals via reactions (c) and (d) scheme 1, increase the rate of oxidation, leading to a characteristic autocatalytic rate of oxygen absorption and peroxide decomposition as shown in figure 3.

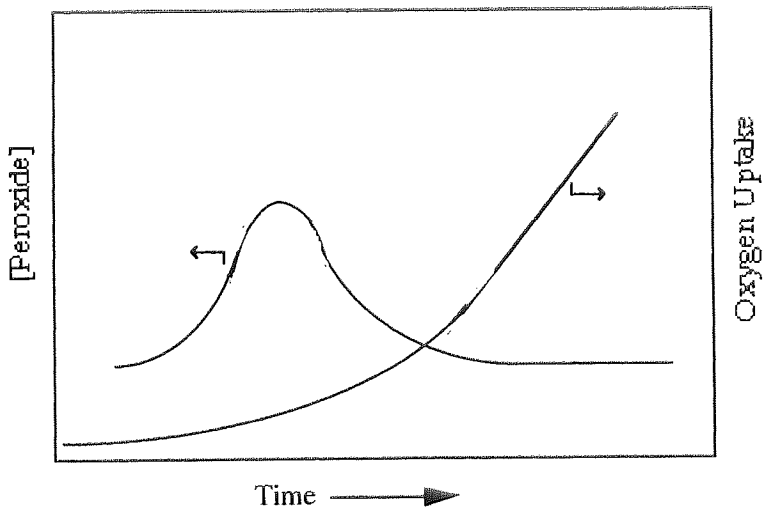
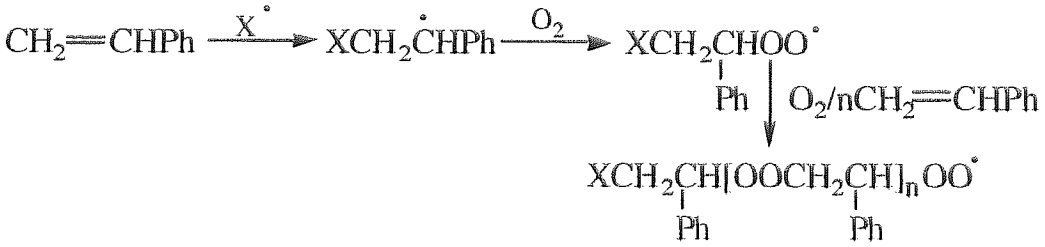


Figure 1-3 Relationship between hydroperoxide decomposition and rate of oxidation

The rate of formation of a peroxide via reaction (b) scheme 1 depends partly on the radical structure, the more stable the radical the lower the rate [35-37]. This reaction is also reversible in cases where oxygen pressure is low, the temperature high or the radical is highly stabilised [38]. The ceiling temperature, for the point when concentrations of carbon and peroxyl radicals are equal, is lower the more stable the radical [38]. The peroxyl radical can then

abstract a hydrogen from another molecule via reaction (e) scheme 1. The rate of abstraction is associated with the radical stability, the more stable the R˙ radical, the higher the yield of hydroperoxide [39-41]. Peroxyl radicals are relatively selective electrophilic species abstracting allylic and tertiary hydrogen's in preference to secondary and primary. In the case of conjugated olefins co-polymerisation with oxygen can occur to give polymeric peroxides (reaction 13) [30].



13

The bond dissociation energy of the hydroperoxide oxygen-oxygen bond is about 175 kJ/mol (40 kcal/mol) [29]. This makes the O-O bond the weakest in the hydroperoxide group which will undergo scission forming powerful oxidising alkoxyl and hydroxyl radicals. These radicals then become the most important initiators of oxidation. The total hydroperoxide concentration affects the molecularity of the decomposition [42, 43]. At low oxygen pressures, corresponding to low hydroperoxide concentrations the oxidation rate of various hydrocarbons follows first order kinetics decomposing via reaction (c) scheme 1. With increasing oxygen pressure the bimolecular decomposition via reaction (d) scheme 1 becomes more important. A strong hydrogen bond association between hydroperoxide molecules has been shown [44] and it has been proposed that, at high hydroperoxide concentrations, radical formation occurs via a hydrogen bonded dimer (reaction 14). This change from first order to second order was also accompanied by a lowering of the activation energy from 91 kJ/mol to 84 kJ/mol.

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Once the radical has been formed it is able to induce the further decomposition of the hydroperoxide, this occurs by both oxidative and reductive reactions (reactions 15 and 16).

$$ROOH + RO^{\bullet} (^{\bullet}OH) \longrightarrow ROO^{\bullet} + ROH\,(H_2O) \qquad 15$$

$$16$$

In the case of tert-butyl hydroperoxide in a oxidisable solvent a pair of reaction cycles, one oxidative and one reductive, have been proposed [30]. Also mediums containing acetic acid have been shown to catalyse the decomposition of hydroperoxides [45] where the acid is thought to act as reversible hydrogen donor [31].

The oxidisability of the solvent can greatly affect the hydroperoxide decomposition even where chain breaking antioxidants have been used to decrease the rate of the redox reactions [46]. The solvent induced decomposition can not therefore be caused by alkylperoxide radicals and experiments have shown the effect to occur in oxygen rich conditions where alkyl radical concentration would be negligible [46]. This has lead to the conclusion that in the main reaction the solvent acts as a reducing agent (reaction 17) [30].

$$ROOH + R'H \longrightarrow RO^{\bullet} + H_2O + R'^{\bullet} \qquad 17$$

Other agents which are considered to promote peroxide decomposition are metal ions, often found as catalyst residues. The dominant reaction in metal catalysed decomposition are the redox reactions 18 and 19 [46]. The combination of these two reaction is equivalent to reaction (d)(scheme 1).

$$ROOH + M^{n+} \longrightarrow RO^{\bullet} + OH^{-} + M^{(n+1)+} \qquad 18$$

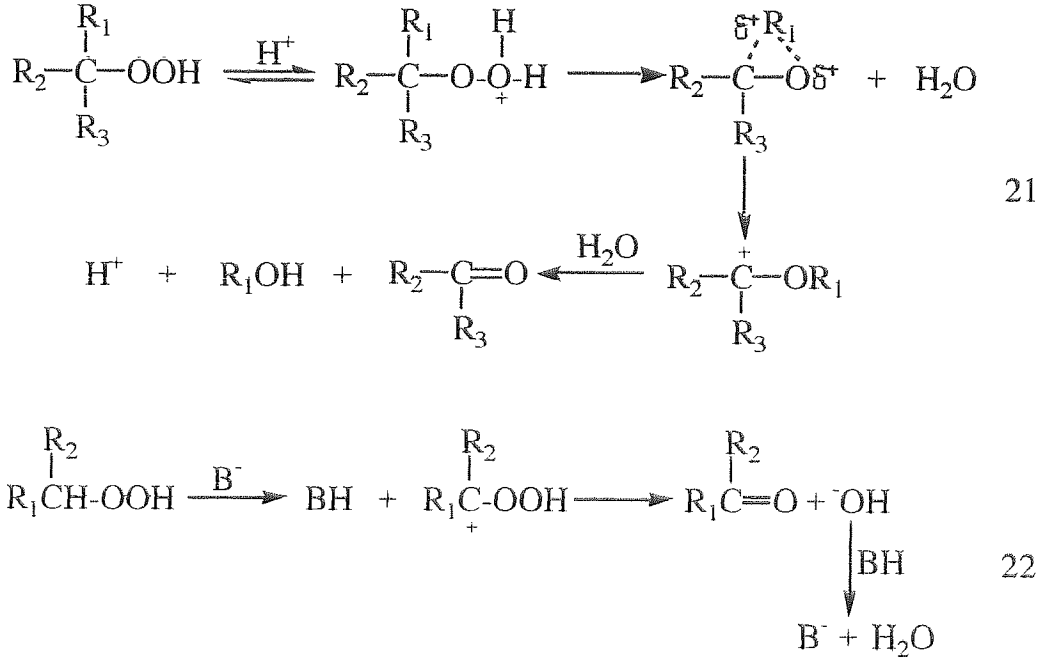
$$ROOH + M^{(n+1)+} \longrightarrow ROO^{\cdot} + H^{+} + M^{n+} \qquad 19$$

The catalytic reaction is only observed where there is comparable stability for both oxidation states, if this is not the case stoichiometric decomposition occurs [29]. The activation energy of the decomposition is reduced from 170-191 kJ/mol for thermal decomposition to 42.5-85 kJ/mol by metal catalysis. For metals which cannot exist in two valance states it is proposed a complex between the M ion and the hydroperoxide is formed in which the peroxide is polarised towards homolytic fission [48]. This mechanism of metal catalysis would suggest the relative activity of a series of metals should be independent of the substrate and depend on the redox potentials of the metals. This has not been found [49]. An explanation could be that the catalytic entity is a metal complex with the substrate, the redox potential for which is substrate dependant and is a reflection of the complex stability [49]. There is also evidence [50-52] that at higher concentrations transition metal ions, particularly in their lower valance states act as antioxidants.

In conditions where organic materials are exposed to light it can be a major cause of oxidative degradation. The photolysis of hydroperoxides via reaction 20 is one of the most powerful initiators of photo oxidation [30]. The hydroperoxides are photolysed by ultra violet (U.V.) light with a quantum efficiency of 1.

$$ROOH \xrightarrow{h\nu} RO^{\cdot} + {}^{\cdot}OH \qquad 20$$

In certain conditions the decomposition of hydroperoxides can lead to the production of non radical products which will not then contribute to further oxidation. This can occur via acid catalysed and base (B^{-}) catalysed decomposition as shown in reactions 21 and 22.



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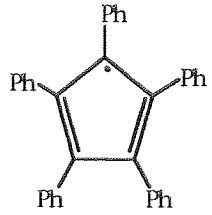
22

Therefore the first radicals are most likely produced by impurities, stressing or thermal or light energy. These radicals quickly react with oxygen to form hydroperoxides which build up before decomposing by a variety of mechanisms to initiate the autoxidation of the substrate.

1.3.3 Propagation

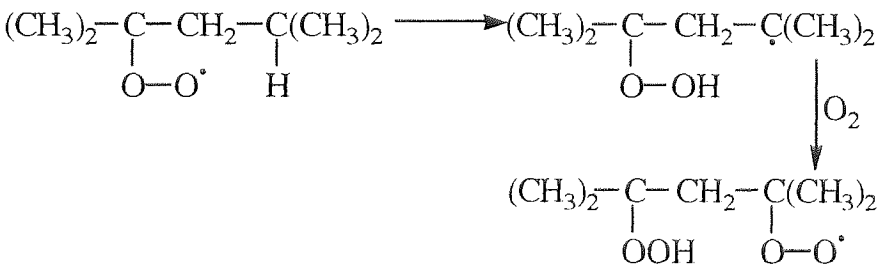
Alkyl radicals formed in an initiation step react immediately with oxygen (a biradical) in a rapid radical coupling reaction (reaction (b) scheme 1) [53]. The rate of this reaction has been found to be in the order of 10^9 M^{-1} s^{-1}. As mentioned earlier, high temperatures and low oxygen pressures can cause the reversal of this reaction [38], but generally at oxygen pressures above 50 mm [54] the rate of oxidation becomes insensitive to variations in oxygen pressure. This suggests the radical coupling reaction is occurring freely. There are exceptional cases where reaction (e) scheme 1 competes with reaction (b). This mainly occurs where the alkyl radical is highly resonance stabilised as with the pentaphenylcyclopentadenyl radical (IV) [29].



(IV)

The most important step in autoxidation is hydrogen abstraction by the peroxyl radical (reaction (e) scheme 1). This is the rate determining step as it requires a higher activation energy than the radical coupling reaction discussed above. An increase in the rate of this reaction increases the oxidation rate, the hydroperoxide concentration and the length of the propagating chain. The propagating chain is defined as the number of oxygen molecules reacting per initiation step [55].

Intermolecular hydrogen abstraction is the most common reaction of this type but peroxyl radicals can participate in intramolecular abstraction (reaction 23) [29, 35]. This phenomena occurs most frequently in aliphatic systems which contain reactive hydrogens in the 1,3 or 1,4 positions [56] and in a number of branched alkanes [57].



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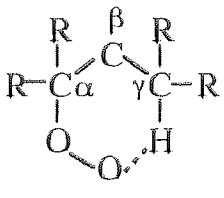
The intramolecular reaction mainly proceeds via a six membered cyclic transition state, V, on the γ - carbon atom.



V

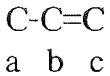
The ratio of intra and inter molecular hydrogen abstraction is therefore related to the hydrocarbon structure.

The other important propagation reaction is the addition reaction. This occurs mainly with substrates with unsubstituted double bonds in the 1-ene position (reaction 24).

24

In the case of styrene this reaction always occurs in such a way to produce the most stable β-peroxyl alkyl radical (24) [29]. The radicals then can continue to react and form polymeric peroxides (reaction 13).

The structure of the reacting peroxide affects both the rate and type of propagation reaction. In a study of a large number of olefins [58], represented by VI, the effect of various types and positions of substitution on ease of hydrogen abstraction were analysed and a number of general rules were deduced.



VI

Replacement of one or two of the hydrogen atoms at positions a or c increases the rate of abstraction, while replacement of hydrogens at position b has no effect.

Replacement of a hydrogen from position a with a phenyl group increases the rate by 23 times and if the unsaturated group Alk-CH=CH is used the rate increases by 107 times.

An allylic system in a cyclic structure has a greater rate of abstraction than in an acyclic structure.

The reasons for these differences are the relative stabilities of the resulting alkyl radicals.

The position of the double bond can also affect the amount of hydroperoxide produced due to competition between the abstraction and addition reactions (scheme 1 (e) and 24). The amount of hydroperoxide (rather than polyperoxide) formed follows the trend of the reactivity of the corresponding α-methylenic hydrogen [29], i.e. the more reactive the hydrogen, the more likely abstraction rather than addition will occur. The effect of structure in the rate constant for addition of the peroxyl radical to a double bond (reaction 24) depends mainly on the stability of the β-peroxyl alkyl radical formed [33, 34, 59]. So in cases where the double bond is conjugated with groups such as aromatics, vinyls, nitriles or carbonyls addition is favoured over abstraction.

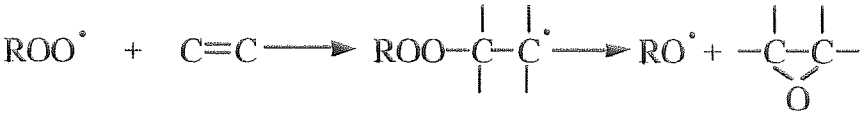
Further work has shown that both steric and polar effects can influence propagation reactions [29]. In general peroxyl radicals will abstract tertiary hydrogens rather than secondary or primary ones, especially at lower temperatures. Also primary and secondary peroxyl radicals are much more likely to abstract hydrogen than tertiary ones. This means that effects which make the α-methylenic hydrogen atoms more reactive, leave the derived alkenyl radical less reactive. Thus the more likely the abstraction reaction (scheme 1 (e)) the less likely the biradical reaction with oxygen will occur (scheme 1 (b)). This narrowing of the difference in rate of the two reactions is reflected in the fact that oxygen pressure can exert an effect on the oxidation rate over a much wider range [54]. These differences can mostly be attributed to steric effects but polar effects can influence the rate of hydrogen abstraction [60]. It was found that both strong and weak electron withdrawing groups had little effect on remaining α-hydrogens. Thus the resonance stabilisation of the formed radical is not the only influence on the rate of abstraction. The dipolar contribution to the transition state (VII) of the reaction is thought to offset the increase in reactivity expected from resonance stabilisation of the radical formed.

$$ROO^{\bullet\delta-} \quad H \quad R^{\bullet\delta+}$$

VII

Increases in peroxyl radical reactivity has also been found when electron withdrawing groups have been substituted on to the α carbon [29].

In cases where there are no structural features to stabilise the derived peroxyl radical, such as terminal olefins, the radicals oxidise mainly to an epoxide and ketone (reaction 25). This reaction is much faster than scavenging for oxygen [29, 53].



25

Epoxide is also produced by olefins which normally oxidise to give mainly peroxides when oxidised at high temperatures or with low oxygen pressures.

Another reaction which occurs during oxidation is chain scission [54]. This reaction is relatively unimportant in simple olefins but can have a strong influence on degradation of polymers.

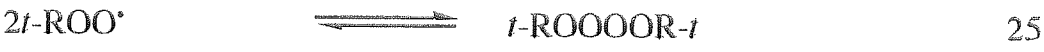
Therefore the most important reactions which propagate the oxidation are the hydrogen abstraction from the substrate by the peroxy radicals formed during initiation.

1.3.4 Termination

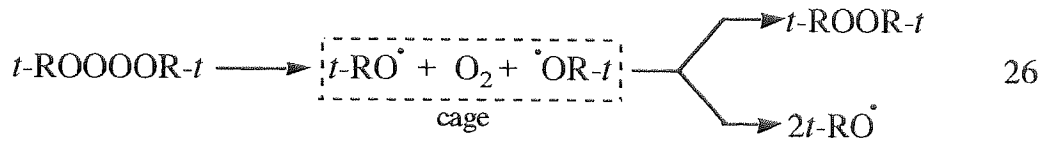
Termination occurs when free radicals react with each other to form inactive products (scheme 1 (h)-(j)). During oxidation under atmospheric pressure and ambient temperature with most olefins alkylperoxyl radicals are the major product and chain termination occurs almost exclusively through their combination (scheme 1 (j)). As oxygen pressure is lowered or in the case of

very stable alkyl radicals, termination reactions scheme 1 (h) and (i) become more important until eventually at very low oxygen levels scheme 1 (h) becomes dominant.

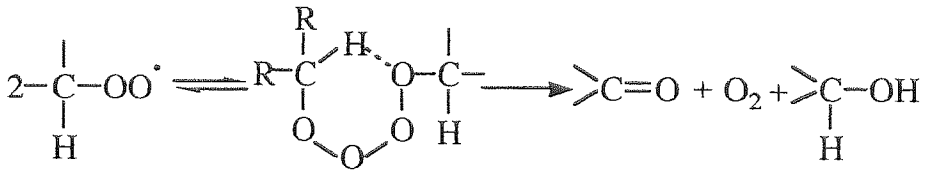
It has been shown [61-63] that the rate of the termination reaction between two peroxyl radicals changes depending on structure. The rate increases in the order, tertiary peroxyl < secondary peroxyl < primary peroxyl, with rate for primary and secondary being 10^3 times higher than for tertiary radicals. The lower rate constant for termination of tertiary peroxyl radicals is attributed to the high activation energy required for decomposition of the tetroxide which is believed to exist in equilibrium with peroxyl radical (reaction 26) [64].



The tetroxide decomposes irreversibly to give two caged alkoxyl radicals and oxygen. Most of the alkoxyl radicals escape from the cage to continue the propagation reaction with a small amount recombining to give a peroxide (reaction 26).



The formation of a cyclic transition state, VIII, has been suggested in the termination of the primary and secondary peroxyl radicals. Experimental observations and the presence of an isotope effect have supported this mechanism where one of the α-hydrogens is transferred to give ketone, alcohol and oxygen (reaction 27)



27

VIII

A mechanism for the reaction between an aldehyde and a hydroperoxide involving an intramolecular bond rearrangement has also been proposed [72-74] (reactions 28-30). This mechanism does not require the involvement of free radicals. Evidence for this mechanism was shown by the decomposition of n-butyl hydroperoxide to give butyric acid and hydrogen rather than butyraldehyde or butylalcohol as would be expected via the homolytic mechanism [65-67].

28

29

30

The termination mainly occurs through the decomposition of unstable peroxide products, formed during propagation, to produce more stable oxygen containing products [29].

1.3.5 The Effect of Temperature on Oxidation

As temperature increases the rate of most reactions also increases as more energy is supplied. The dependence of increase of rate with temperature varies depending on the reaction but can be expressed in the terms of an activation energy [68] (Eqn. 1).

$$E_a = RT^2 \left(\frac{\delta \ln k}{\delta T} \right)_v \qquad 1$$

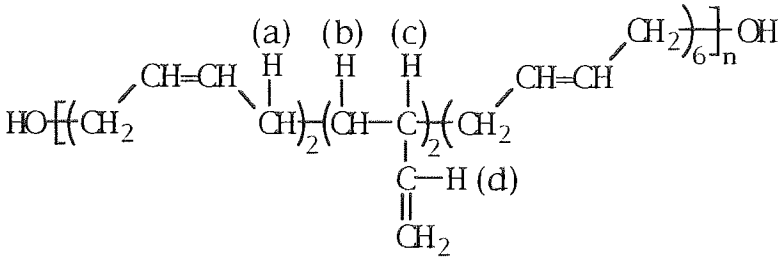
This shows that the higher the activation energy, the stronger the temperature dependence of the rate constant. This relationship means prediction of long term ageing behaviour of organics from accelerated ageing results can be difficult.

It has been suggested that as temperature increases so does the abstraction / addition ratio [22], this indicates the activation energy for abstraction is greater than for addition. Also suggestions of reversibility of the addition reaction [22] would favour abstraction at higher temperatures. As noted earlier, increase in temperature can also decrease the number of peroxide radicals formed, thus at higher temperatures the proportion of reactions occurring via the alkyl radical will increase.

1.4 Oxidation of Polybutadiene

1.4.1 Structure of Polybutadiene

The polybutadiene main chain contains trans-1,4, cis-1,4 and vinyl-1,2 double bonds, in a ratio of trans:cis:vinyl 6:2:2. (IX)



cis-1,4 1,2 vinyl trans-1,4

IX, HTPB

The reactivities of these bonds varies due to steric effects and delocalization of the π electron cloud. Heats of hydrogenation [69] and hyperconjugation energy [42] show stability of these double bonds decreases in the order

$$\text{trans-CH=CH-} > \text{cis-CH=CH-} \gg \text{-CH=CH}_2$$

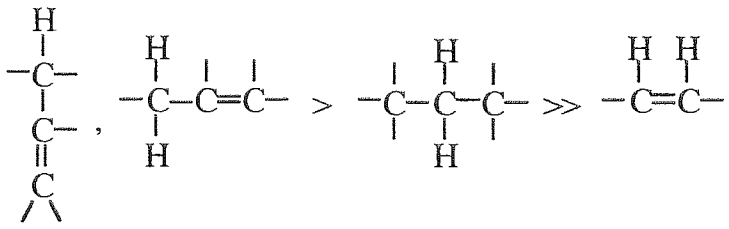
Table 1-1 Energies associated with some olefins with structures relating to polybutadiene [31]

Olefin	Heat of Hydrogenation	Hyperconjugation Energy
CH_2=$CHCH_3$	126.1 kJ/mol	11.3 kJ/mol
Cis- CH_3CH=$CHCH_3$	119.8 kJ/mol	17.6 kJ/mol
Trans- CH_3CH=$CHCH_3$	115.6 kJ/mol	21.8 kJ/mol

The main polymer chain also contains two carbon-carbon single bonds. The single bond adjacent to the double bond is stronger than the single bond which is more distant. This is due to the sp^2-sp^3 orbital overlap being better than the sp^3-sp^3 orbital overlap [69], thus breaking of the polymer backbone is more likely to occur at the sp^3-sp^3 bond.

Also contained in the polybutadiene structure are four different types of hydrogen-carbon bonds: allylic hydrogen (a) bonded to a secondary carbon, non-allylic hydrogen (b) bonded to a secondary carbon, allylic hydrogen (c) bonded to a tertiary carbon and vinylic hydrogen (d). The allylic hydrogens are the most reactive since the formed allyl radical can be stabilised via a resonance hybrid.

Between the two allyl radicals formed, the tertiary radical formed by the abstraction of the hydrogen from IX(c) will be most stable due to the greater delocalization of the electron cloud. The vinylic hydrogen-carbon bond IX(d) is the most stable as it is formed from by sp^2-s orbital overlap which produces a shorter bond length than the sp^3-s overlap in the allylic and non allylic hydrogen carbon bonds. This means the ease of abstraction of hydrogen from polybutadiene decreases in the order:



1.4.2 General Oxidation of Polybutadiene

Polybutadiene undergoes oxidative degradation in the presence of oxygen, heat, UV-light and stress [48]. It was shown [70] that the basic mechanism of degradation is the same whether initiated by heat or light, the only difference occurring in relative amounts of carbonyls formed due to the subsequent photoreaction of the initial oxidation products. The reaction mechanisms for the oxidation of polybutadiene are only partially understood for a number of reasons [71]. The reaction is heterogeneous and normally controlled by the rate of diffusion of oxygen into the sample, which in turn is dependant on the size, geometry and history of the sample. Identifying the products of the primary oxidation reaction is difficult as such material undergoes further oxidation. Furthermore, the oxidised polybutadiene becomes rapidly insoluble due to cross-linking, rendering a large number of techniques unusable.

1.4.2.1 Initiation of Oxidation

The polybutadiene used extensively in the preparation of rocket binders is R-45M, this is prepared via a free radical mechanism where H_2O_2 is used as an initiator [8]. Therefore once the liquid polybutadiene is prepared a low concentration of radical species are likely to remain. These radicals would then be able to initiate the subsequent oxidative degradation of the binder via reaction with oxygen, abstraction of hydrogen or attack on unsaturation. It has also been reported [72] that in the case of acrylonitrile-butadiene-styrene (ABS) copolymer oxygen was able to abstract hydrogen directly. This was attributed to the unsaturation contained in the butadiene regions and the C-H on the α-carbon being particularly easy to oxidise.

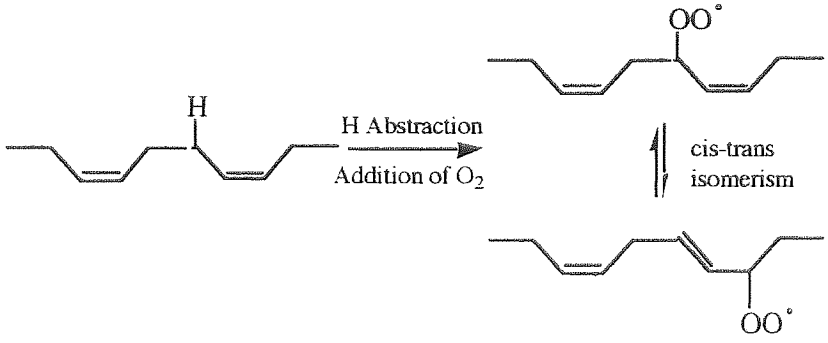
Initiation can also occur in rocket motor binders via physical force. Cooling after curing and the diurnal temperature cycling which motors experience can cause fatigue as discussed in section 1.1. This may cause the fracturing of the polymer backbone to produce radical species.

The presence of the solid fillers in the propellant may also be expected to cause initiation, however this has not been found [1] and is also outside the scope of this work.

As is common with most oxidation processes under oxygen sufficient conditions an induction period has been observed [73] before the decay of unsaturation and formation of stable oxidation products occurs. During this time a low rate of oxygen is absorbed and hydroperoxides are formed [31]. It has been shown that oxidised polybutadiene is more unstable than unoxidised due to the high concentration of peroxides which decompose to produce radicals.

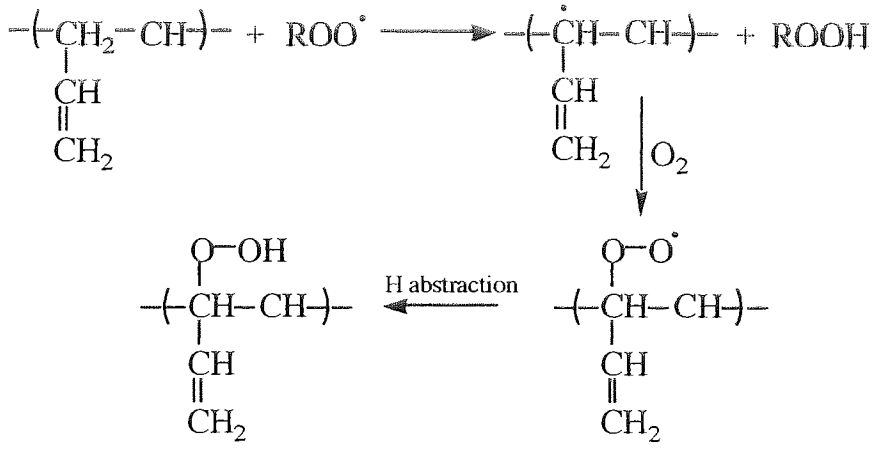
1.4.2.2 Propagation of Oxidation

In the case of polybutadiene the most important part of the autoxidation process is the abstraction of a hydrogen, rather than the addition of oxygen to the carbon double bond [48]. Those prone to abstraction are the allylic hydrogens IX(a) and IX(c) on the α-carbon (with respect to the double bond). This is due to the increased stabilising effect of the double bond on the radical produced [48] thus in the case of a 1,4- cis double bond oxidation will occur via reaction 31 [71].



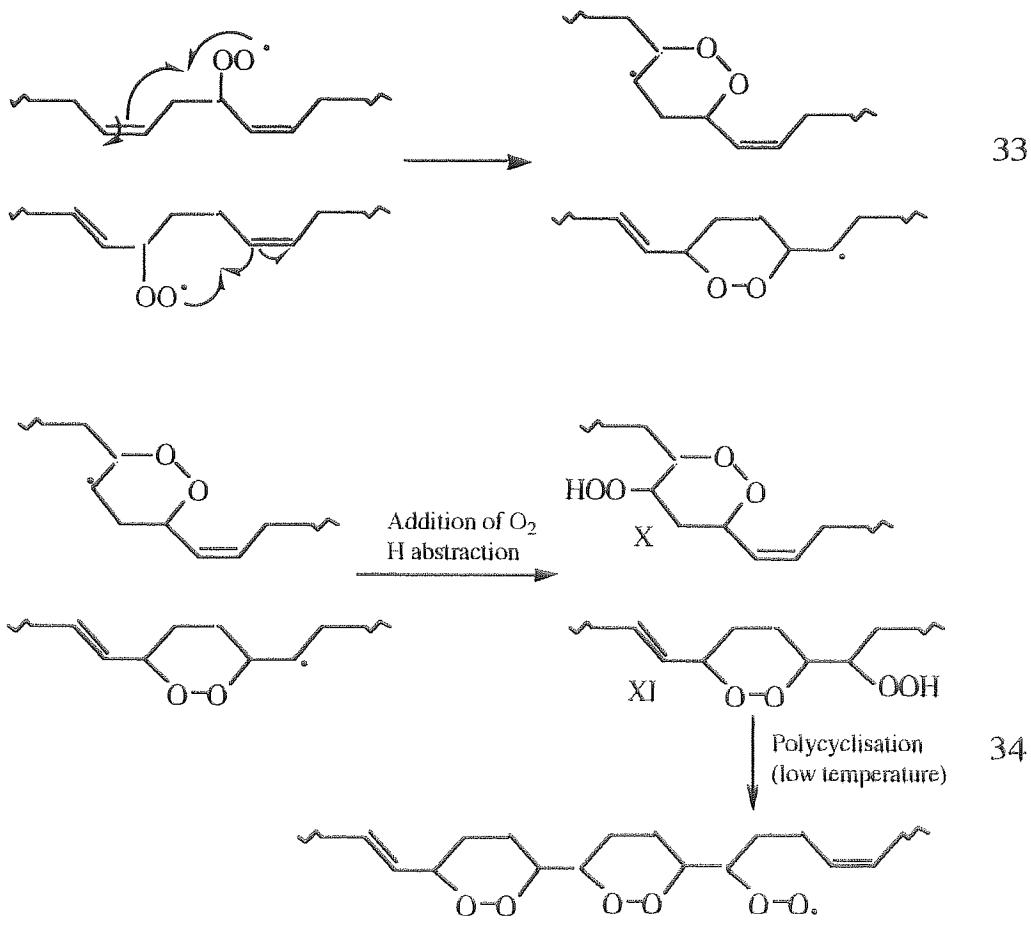
31

The alkyl radical formed has two resonant structures, either of which can react with molecular oxygen. This produces peroxy radicals with different structures, one retaining the original cis form the other containing the trans form. In cases where high cis content polybutadiene has been oxidised [74] the formation of trans double bonds has been observed as an oxidative reaction. The vinyl units are oxidised in a similar manner (reaction 32) with abstraction of the most reactive hydrogen from the tertiary carbon [70].



32

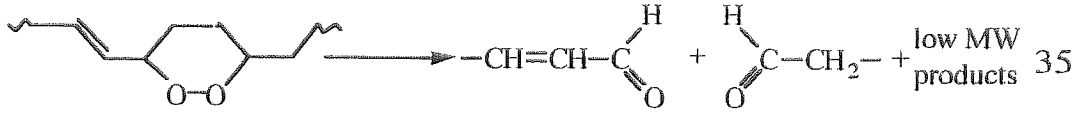
Once formed the alkyl peroxide radicals can then react via abstraction of an α-methylenic hydrogen thus continuing the propagating chain. Alternatively intramolecular cyclization with a neighbouring double bond is possible. This can progress to produce polycyclised products [71, 73] (reactions 33 to 34).



The cyclization can produce two types of cyclic peroxides, one with the radical inside the ring and one with the radical outside (reaction 33). Further oxidation of these radicals (reaction 34) produces polybutadiene analogues (X, XI) of intermediates proposed during polyisoprene oxidation [74]. Once formed the peroxides can react further or decompose to produce the secondary oxidation products.

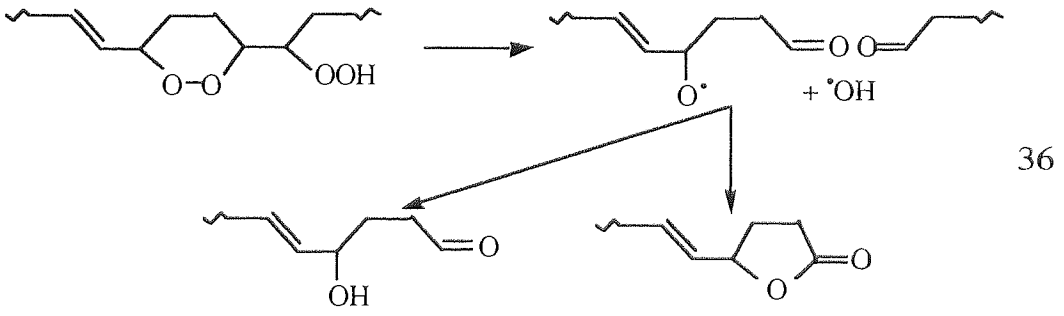
Infra-red analysis of polybutadiene oxidation by several workers have shown a number of similarities. At low temperatures (0 and 25°C) [72, 74] initial increases in the C-O absorbance at 1090 cm^{-1} and O-H absorbance at 3400 cm^{-1} indicated the formation of peroxides. Also observed during this time was a decrease in cis-methine groups [73] shown by the loss of the α-methylenic H absorbance at 3007 cm^{-1} in a cis-1,4 polybutadiene. As oxidation continued strong carbonyl absorptions formed in the regions 1650 to 1810 cm^{-1}; the appearance of weak absorbance at 1810 cm^{-1} has been attributed to acid peroxide

material [71] and the absorptions at 1720 and 1695 cm^{-1} to saturated and α,β-unsaturated carbonyls respectively, the latter also being observed during U.V. analysis [71]. It has been suggested [73] that cleavage of the O-O bond along with β-scission of the alkoxy radical X or XI would produce an α,β–unsaturated aldehyde XII and a saturated aldehyde XIII (reaction 35). This reaction would also cause scission of the polymer backbone.



XII XIII

Continuing oxidation showed the peak at 1720 cm^{-1} becoming the major carbonyl product and the appearance of an absorption at 2720 cm^{-1} which also suggested the presence of the aldehydic species [73]. Shoulders formed at 1776 and 1177 cm^{-1} have been attributed to 5 membered lactone rings [73] possibly formed from the decomposition of polymeric cyclic peroxides via reaction 36.



Decreases in the total number of olefinic peaks was observed but at later stages of oxidation resolution of the peaks became difficult due partly to formation of water during oxidation [71, 75]. Plots made of changes in absorbance at 3400 cm^{-1} indicating OH, 1720 cm^{-1} indicating C=O and 1090 cm^{-1} indicating C-O showed a sigmoid curve type typical of autocatalytic processes [71, 73].

At higher temperatures the final products of oxidation are similar to those found at lower temperatures. A range of carbonyls were again formed and the formation of the OH absorbance was shown to be caused only by alcohol groups

bound to the polymer, these are likely to have been formed via reaction (f) scheme 1 [70, 71]. At 60°C the band observed at 1090 cm^{-1} corresponding to C-O is weak and carbonyls formed almost immediately via reaction 36, this suggests that at the higher temperature ROOH converts rapidly to R=O [73]. Thermal analysis of polybutadiene samples oxidised at low (0°C) temperature [71] showed an exotherm present at about 90°C which was not present in those oxidised at higher temperatures (100, 150, 200, 250°C). This exotherm was attributed to the decomposition of peroxide materials which were presumably unstable at the higher temperatures. Further inferring concentrations of peroxides were very low in samples oxidised at higher temperatures. The presence of absorbencies at 1120 and 1070 cm^{-1} corresponding to C-O groups at the higher temperatures were thought to be caused by stable polyether groups. These bonds were also observed in the later stages of oxidation at low temperatures where they may have been caused by a mix of both polyethers and hydroperoxide bridging bonds [71].

It has been suggested [75] that polybutadiene undergoes both cross-linking and chain scission during oxidation at about 120°C, the scission just about exceeding the cross-linking until a limiting gel content is reached. However the fact that there was an increase in gel content in most cases suggested cross-linking is dominant [48, 71, 78]. Analysis of the soluble extract from thermally oxidised urethane cross-linked polybutadiene [31] showed evidence of the formation of some lower molecular weight species not present after initial curing. During this time the cross-link density of the polybutadiene was seen to increase indicating both cross-linking and chain scission were occurring, cross-linking being the more prevalent.

One method of cross-link formation is by the direct combination of radicals as in reactions (h) and (i) scheme 1 and 37 and 38.

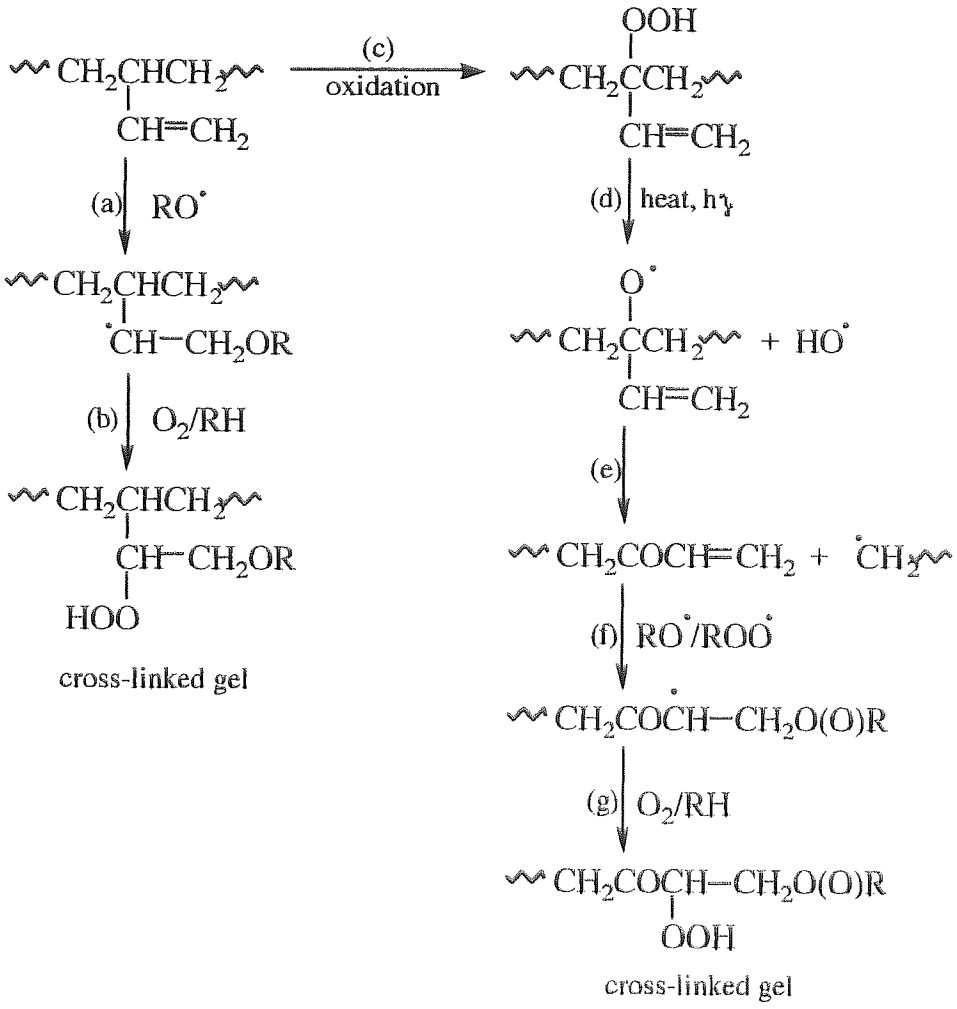
$$RO^{\bullet} + R'O^{\bullet} \longrightarrow ROOR' \qquad 37$$

$$RO^{\bullet} + R'^{\bullet} \longrightarrow ROR' \qquad 38$$

These reactions are unlikely to cause a rapid increase in cross-link density as observed in polybutadiene as the probability of two species being in close enough proximity to bond is low.

During the oxidation of polybutadiene the increase in cross-links has been accompanied by a decrease in unsaturation [76-79]. It is thought that cross-linking is more common in polybutadiene than in natural rubber due to the more unstable polybutadienyl radical formed by α-hydrogen abstraction [80, 81]. This will more readily add to a double bond and it has been inferred [82] that intermolecular addition of peroxyl radicals in polybutadiene, causing cross-links, is at least one quarter as frequent as hydrogen abstraction.

Two mechanisms for the cross-linking reaction were proposed after the study of the photo-oxidative behaviour of some polybutadiene blends [76, 77] (scheme 2). One is the addition of peroxy or alkoxy radicals to 1,2-vinyl groups (reactions (a)-(b)), the other is from the decomposition of an alkoxyl radical to produce a conjugated carbonyl (reactions (c)-(g)).



Scheme 1-2 Proposed mechanisms of cross-linking reactions during the photoxidation of polybutadiene

For these mechanisms to proceed the presence of either vinyl groups or conjugated double bonds is required. Another reaction, which is reported to occur regardless of vinyl groups [81], was observed during the peroxide vulcanisation of polybutadiene under vacuum [80, 81, 83]. A radical chain reaction initiated by alkoxyl radical was seen to occur, the addition of RO• to a double bond gave rise to a secondary alkyl radical (reaction 39). This, as mentioned earlier, is highly reactive due to the lack of resonance stabilisation [80, 81] and can then react with a neighbouring chain by addition to a double bond (reaction 40 (a)) or hydrogen abstraction (reaction 40(b)). If reaction 40(a) predominates then rapid formation of a polymer network will occur.

$$RO^{\bullet} + RCH{=}CHR \longrightarrow RO\text{-}RCH\text{-}C^{\bullet}HR \qquad 39$$

$$RO\text{-}RCH\text{-}C^{\bullet}HR + RCH{=}CHR \longrightarrow \underset{\text{Cross-linked Gel}}{RO\text{-}RCH\text{-}CHR\text{-}RCH\text{-}C^{\bullet}HR} \quad 40a$$

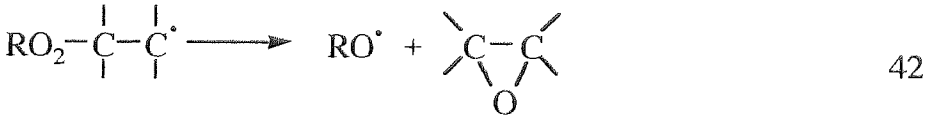
$$RO\text{-}RCH\text{-}C^{\bullet}HR + RCHR \longrightarrow RO\text{-}RCH\text{-}CH_2R + RC^{\bullet}R \quad 40b$$

Where the rate of diffusion of oxygen into the sample is rapid, causing a high dissolved concentration, the $RO_2^{\bullet}$ radical is likely to be involved in producing cross-links [71] (reaction 41). These would be unstable peroxide cross-links which may degrade to produce other products.

$$RO_2^{\bullet} + RCH{=}CHR \longrightarrow RO_2\text{-}RCH\text{-}C^{\bullet}HR \quad 41$$

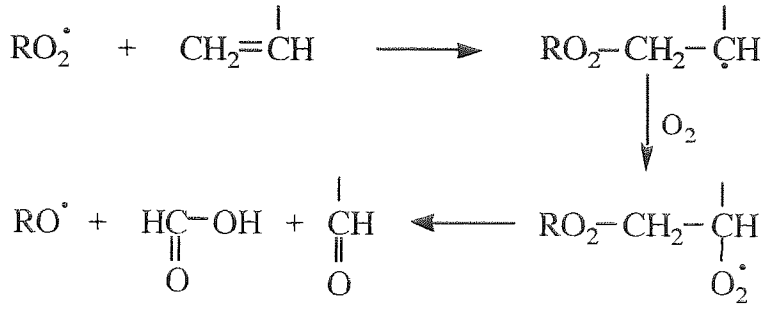
Analysis of the three types of unsaturation during oxidative cross-linking has shown that they all degrade via a first order reaction, but with differing rate constants [31, 76]; 1-2 vinylic having the largest, 1-4 trans the smallest. Under oxygen deficient and oxygen free conditions a decrease in unsaturation does not occur [31].

During oxidation at higher temperatures (90-180°C) it has been suggested that [85] epoxides formed 30 to 50 % of oxidation products via reaction 42 but their presence has not been observed by a number of other workers [70, 71, 73, 75].



42

Another commonly found product during the oxidation of polybutadiene is formic acid. It has been suggested that this is due to oxidation of the vinyl group (reaction 43) which would not produce chain scission [86]. This is questionable as the same yield of formic acid has been found in polybutadiene oxidation regardless of the concentration of the vinyl groups Furthermore, it was shown [75] that in the case of polyisoprene, formic acid is formed as a product of main chain scission.



43

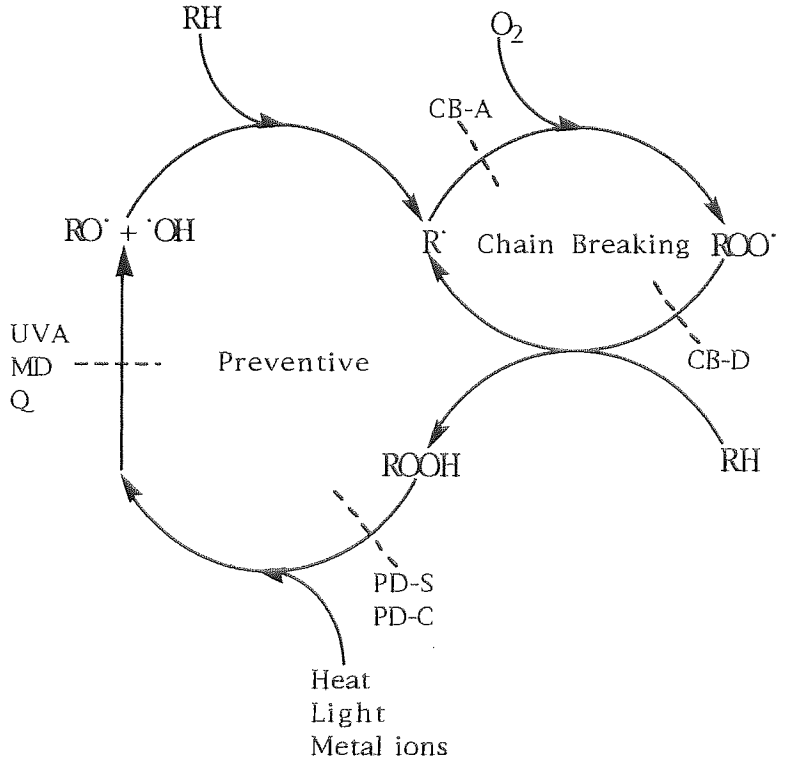
1.4.2.3 Termination of Oxidation

As discussed earlier termination of oxidation usually occurs by the combination of radical species. In oxygen rich conditions this will usually occur by reaction (j) scheme 1 with the influence of reaction (i). In the case of polybutadiene, since cross-linking occurs during the oxidation the diffusion of oxygen is restricted as oxidation continues. This can mean reactions (h) and (i) scheme 1 are more important.

1.5 The Role of Antioxidants and their Mechanisms of Action

1.5.1 General Overview of Antioxidants

In order to improve the long term performance of organic materials attempts have been made to prevent oxidation, to this end additives have been developed which retard the autoxidation reactions. These additives are known as antioxidants. The extensive study of autoxidation retardation has led to the classification of two distinctive classes of antioxidants [87]. Scheme 3 shows the basic mechanisms of action of the two classes of antioxidants, the chain breaking (CB) and the preventive. Chain breaking antioxidants (CB AO) operate by interrupting the main oxidative cycle by removing the main propagating radicals R· and RO_2·. Preventative antioxidants prevent the introduction of the chain initiation radicals into the material, of these the peroxide decomposers (PD) are the most important and operate via stoichiometric (PD-S) or catalytic (PD-C) pathways [88].



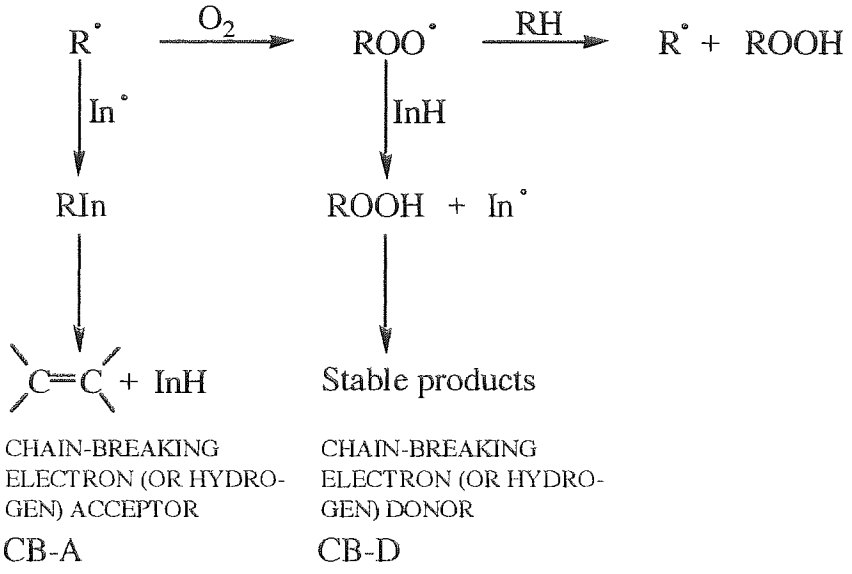
Key

CB-A	Chain Breaking Acceptor
CB-D	Chain Breaking Donor
PD-S	Peroxide Decomposer (Stoichiometric)
PD-C	Peroxide Decomposer (Catalytic)
UVA	Ultra Violet Absorber
MD	Metal Deactivator
Q	Quencher

Scheme 1-3 Oxidative degradation processes and antioxidant mechanisms[89]

1.5.2 Chain Breaking Antioxidants.

The CB antioxidant are the best known and most frequently used class of antioxidants. These can be further divided into chain breaking donors (CB-D) which donate electrons (or hydrogen) and chain breaking acceptors (CB-A) which accept electrons (to oxidise or spin trap R˙ in the absence of oxygen) [90, 91]. Scheme 4 summarises these processes. In certain conditions it can be possible for CB-A and CB-D mechanisms to operate together in a catalytic mechanism.



Scheme 1-4 Summary of the chain breaking mechanisms of antioxidant action [90, 92]

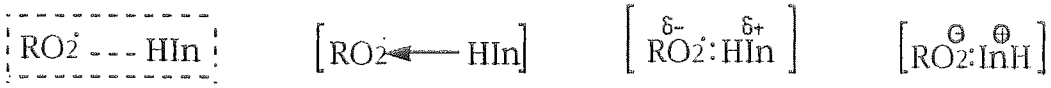
1.5.2.1 Chain Breaking Donor Antioxidant Mechanisms.

Chain breaking donor antioxidants (e.g. InH) [90] operate by deactivating the electrophilic propagating $RO_2^{\cdot}$ radical, giving rise to a more stable antioxidant radical ($In^{\cdot}$) as in reaction 45. The total number of $RO_2^{\cdot}$ radicals deactivated by each antioxidant molecule is known as the stoichiometric coefficient (f). Reaction 44 implies that for CB-D antioxidants f has a value of one, i.e. one InH molecule breaks one oxidative kinetic chain. However antioxidant transformation products may also react with $RO_2^{\cdot}$ and in most cases, for a single InH f approaches 2. Examples of CB-D antioxidant are hindered phenols and aromatic amines.

$$\underset{\text{Antioxidant}}{RO_2^{\cdot} + InH} \longrightarrow ROOH + \underset{\text{Stable radical}}{In^{\cdot}} \qquad 44$$

The rate of reaction 44 proceeds much faster than the corresponding hydrogen abstraction oxidation reaction (scheme 1 reaction (e)) [91]. The difference between the O-H (463 kJ mol^{-1} [93]) or N-H (388 kJ mol^{-1} [93]) bond strength and that of the C-H bonds (412 kJ mol^{-1} [93]) does not explain the large difference in activation energies of the two reactions. The kinetic deuterium

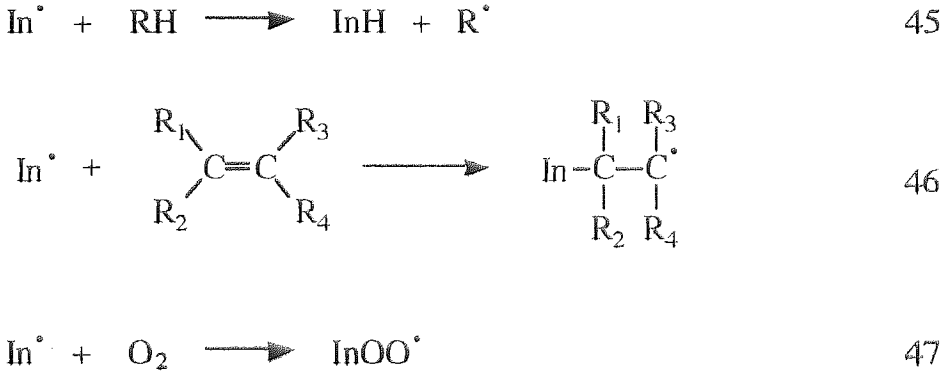
isotope effect [94, 95] has shown that the transfer of the hydrogen is the rate determining step of the stabilisation reaction. This suggests that decrease in activation energy of reaction 44 over the oxidative hydrogen abstraction reaction is due to the nature of the transition state during the transfer of the hydrogen. This transition state may be formulated [91] as (a) a caged intramolecular H bonded species, (b) as a loose Pi complex, (c) as a state with partial charge separation [96, 97] or (d) in terms of complete separation of charges [98].



(a) (b) (c) (d)

The geometry of the reaction is influenced by the steric environment of the reaction site, the strain energy of the ortho substituents in phenols affecting the rotational barrier [99]. If InH is sterically hindered the transfer is in a direction perpendicular to the plane of the aromatic ring [100]. If at least one of the ortho groups is not bulky the process is most likely to occur via a coplanar transition state which can be assumed to be longer lived.

In principle, a number of hydrogen donors are able to participate in reaction 44. Only those which react to give stable radical products which do not continue the chain transfer (reactions 45 and 46) or react with oxygen (reaction 47) are practically important.



45

46

47

Reactions 46 and 47 have been shown to be retarded or eliminated by bulky substituents on the nitrogen of the amine [31] and with sterically hindered and

dihydric phenols [91]. Also even the most reactive amino radicals have been seen to be inefficient at abstraction of H from RH [101, 102]. Reaction 45 is regarded as the major source of initiation in the early stages of inhibited oxidation [91], but as its activation energy is very high for most antioxidants it only proceeds at high InH concentration and rather high temperatures [103].

Once formed the $In^{\cdot}$ can undergo a number of other reactions. In cases where $RO_2^{\cdot}$ is derived from an alcohol the original InH may be regenerated by reaction with another hydroperoxy radical [91] (reaction 48) and another similar regenerative reaction has been proposed [91] (reaction 49).

$$\text{>C(OH)OO}^{\cdot} + In^{\cdot} \longrightarrow \text{>C=O} + InH + O_2 \qquad 48$$

$$In^{\cdot} + HO_2^{\cdot} \longrightarrow InH + O_2 \qquad 49$$

Theoretical studies [104] have also predicted the possibility of reaction 50 which is the reverse of reaction 44 occurring. In practice this has been completely ruled out for sterically hindered phenoxyls [90], although as with reaction 45 it may occur in unhindered cases.

$$In^{\cdot} + ROOH \longrightarrow InH + ROO^{\cdot} \qquad 50$$

One of the main reactions of the $In^{\cdot}$ radical is its dimerisation as in reaction 52, this can produce a complex range of products which will be discussed further in later sections.

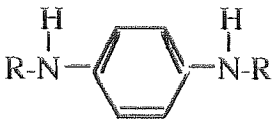
$$2In^{\cdot} \longrightarrow \text{Products} \qquad 51$$

1.5.2.1.1 Aromatic Amine Antioxidants.

Aromatic amines are probably the most important class of antioxidants with respect to unsaturated elastomers [105], the mechanisms involved in the antioxidant activity being similar to those discussed above. All aromatic amines

are able to scavenge $RO^{\bullet}$ and $RO_2^{\bullet}$ radicals but they can also be effective against flex cracking and ozone cracking [105] making them particularly useful.

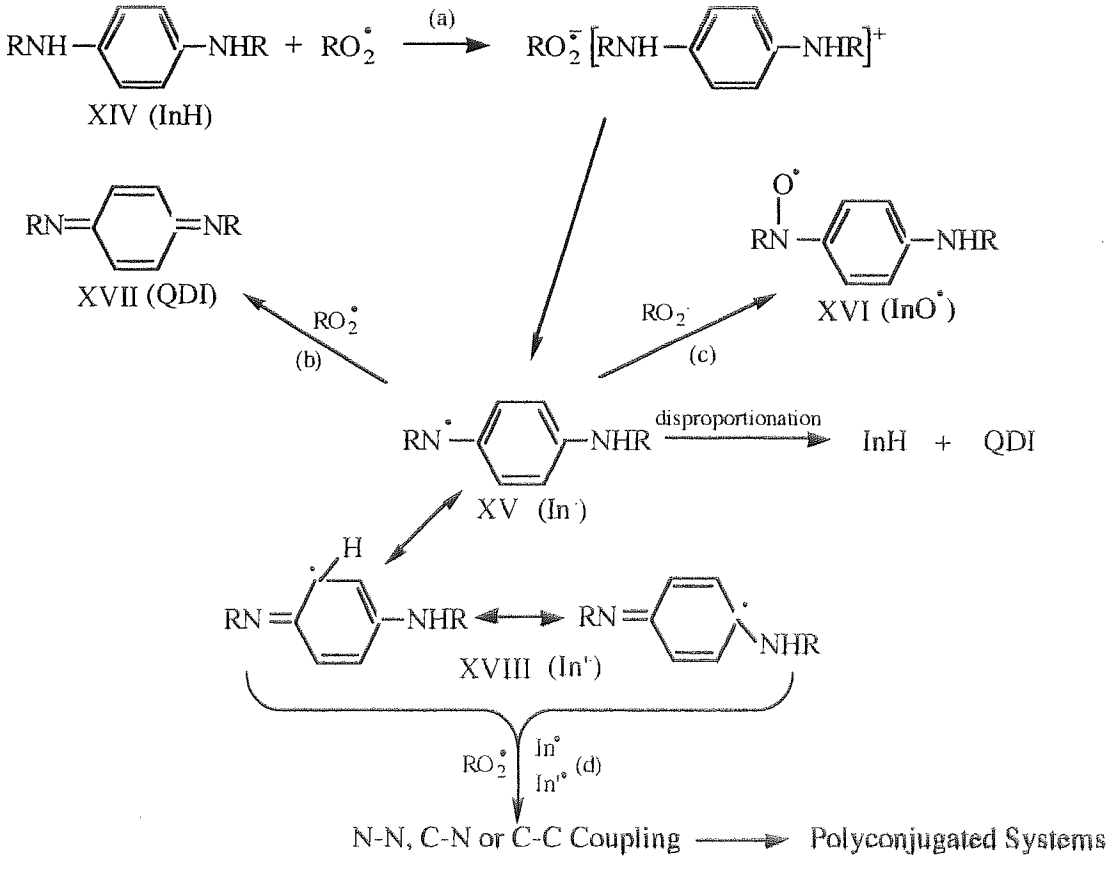
The most important aromatic amine species used as antioxidants are the N,N-disubstituted 1,4-phenyldiamines (PD) with the general structure XIV, part of the bifunctional secondary amine group. Other species are; the bifunctional primary amines, which have week antioxidant properties, and the monofunctional secondary amines, of which diphenylamine (DPA) and its alkylated or arylalkylated derivatives are strong antioxidants. N-phenyl-2-napthylamine and it's 1 isomer are the most used of this group. Also, the tertiary amines are efficient antioxidants.



XIV

The production of the aminyls ($In^{\bullet}$) by hydrogen transfer is the rate determining step shown by the kinetic isotope effect [95, 97, 106, 107] where partial charge separation has been observed during the reaction [97, 106]. The effect decreases with increasing concentration and efficiency of InH and temperature [95]. Evidence for the formation of $In^{\bullet}$ during stabilisation has been obtained from ESR and the strength of the N-H bond has been seen to play an important role in the amine equivalent of reaction 45, the stronger the bond the lower the efficiency [108]. The reactivity of the amines has also been related to their structure [31], more efficient amines having: (a) effective delocalization of the unpaired electron formally resident on the nitrogen, (b) high electron density on the nitrogen to facilitate electron transfer to the alkylperoxy radical and (c) sufficient steric protection of the nitrogen atom to reduce chain transfer by the arylamino radical. Electron donating groups attached to the aromatic ring can increase the reaction rate. However the probability of the undesirable reaction 50 increases at the same time [97, 106, 108] although as stated above bulkier substituents limit this reaction. The presence of N-phenyl groups or N-alkyl

groups which are branched at the α position also increase antioxidant activity due to their ability to delocalize the unpaired electron of the aminyl radicals [36]. It has also been observed that N,N'-diaryl and N-alkyl-N'-aryl-1,4-PD are stronger antioxidants in rubbers than N,N'-dialkyl derivatives [105] and their retarding action continues after the induction period. Investigation [105] into the effect of various substituents on the effectiveness of N,N'-disubstituted 1,4-PD in liquid hydrocarbons did not indicate any generally valid relationship between structure and activity. The influence of the N,N'-disubstitution is seen to be more dependant on reactivity of the substrate and method of evaluation. The maximum reaction rate of aromatic amine with $RO_2^{\cdot}$ was shown to occur with aromatic amines having redox potential of about 0.4 V [105]. It is also known that transformation products play an important role in the effectiveness of amine antioxidants. Scheme 5 shows some of the transformations involved when a secondary amine as an antioxidant.



Scheme 1-5 Some transformations of aromatic secondary diamines during the ageing of hydrocarbons

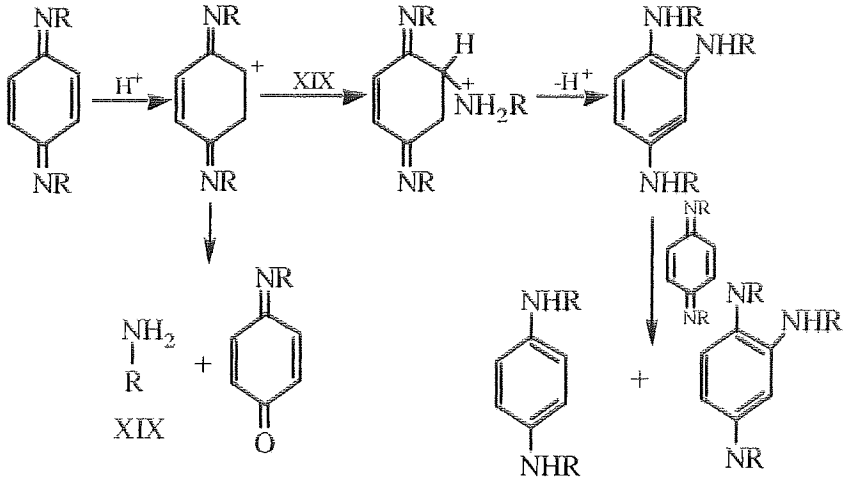
Aminyl radicals, (XV) formed by reaction (a) scheme 5, are stable towards oxygen but are weak oxidants. Ones of lower activity are generally derived from the more efficient antioxidants. This is mainly due to the stabilising effects of the other groups in the molecule, for example In$^{\cdot}$ formed from monoamines are much more reactive than those from phenyldiamines [105] due to the lack of conjugation in the former. As can be seen from scheme 5 once formed the XV can undergo a range of further reaction to produce a number of transformation products, these can have major effects on the antioxidant ability of the compound.

The initial aminyl can form a number of other mesomeric structures (XVIII), these can then react to form N-N, C-N and C-C coupled products [109, 110]. This may be limited by steric factors but may continue to produce highly coloured polyconjugated systems. These reactions may be catalysed by metal ion impurities [105].

The benzoquinone diimine (BQDI)(XVII) formed via reaction (b) scheme 5 and from the disproportionation of In$^{\cdot}$ are considered to be the most important of the transformation products [105]. They are formed stepwise from the onset of either thermal or photoxidation and most phenyl diamines are transformed to BQDI by the end of the induction period [111], thus BQDIs are involved in retarding oxidation after the induction period. They are very reactive species and can be involved in hydrolytic, substitution and redox reactions [105].

N,N'-Disubstituted BQDIs are able to be hydrolysed, this being catalysed by weak acids. Hydrolysis occurs more easily with C=N-alkyl than C=N-aryl, with N,N'-diaryl derivatives being relatively stable. The aromatic amine moiety is split off hydrolytically to produce amine (XIX) which participates in nucleophilic attack on the quinone nucleus, various redox and cyclization reactions can then occur leading to a mixture of products. The reaction is

initiated by the addition of a proton. Scheme 6 shows a number of the reactions and a route to regenerate the initial phenyldiamine, which may partly explain the stabilising affect of BQDI. Stabilisation is further explained by the radical scavenging ability of BQDI, [105] during which process BQDI may be incorporated into an unsaturated polymeric chain potentially causing cross-links due to its bifunctionality. It is reported that the antioxidant activity of BQDIs is lower than that of the initial phenyldiamine [105] and is also concentration dependent.



Scheme 1-6 Transformations of quinonediimines.

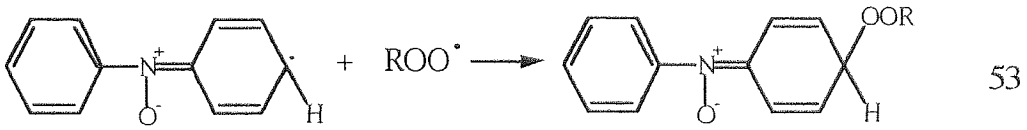
Reactions of the aminyl radicals with alkylperoxyl radicals and alkylhydroperoxides reaction (c) scheme 5 are important as secondary and tertiary diamines are oxidised to nitroxyls, InO$^{\bullet}$(XVI). In the case of the secondary amines in the PD series the evidence for the formation of nitroxyls is contradictory. It has been suggested [112] that direct formation of BQDI occurs as a consequence of immediate oxidation of the second NH group, forming a bisnitrone rather than a dinitroxyl (reaction 52).

52

In other work the formation of nitroxyls by the PD secondary amines has been shown to occur [113-115] and has also been synthesised to be used [31, 114, 115]. In the case of diphenyl amines there is evidence by ESR of the formation of nitroxyls [116]. Although, in the case of diaryl amines if one of the aryl groups is polyconjugated the $RO_2^{\cdot}$ will preferentially attack this system leading only a small amount of nitroxyl formation [116].

Once formed nitroxyl radicals can play an important role in the action of amine antioxidants. The aromatic nitroxides have delocalized free electrons which can produce mesomeric forms XX and XXI [105] and can inhibit radical chain process due to their ability to react with species with an unpaired electron [117]. They are able to react with both alkyl and alkylperoxyl radicals via the two forms. The XXI form is able to react with $RO_2^{\cdot}$ via reaction 53 [117], to produce nitrones, this product can then be irreversibly consumed by reaction 54.

XX XXI



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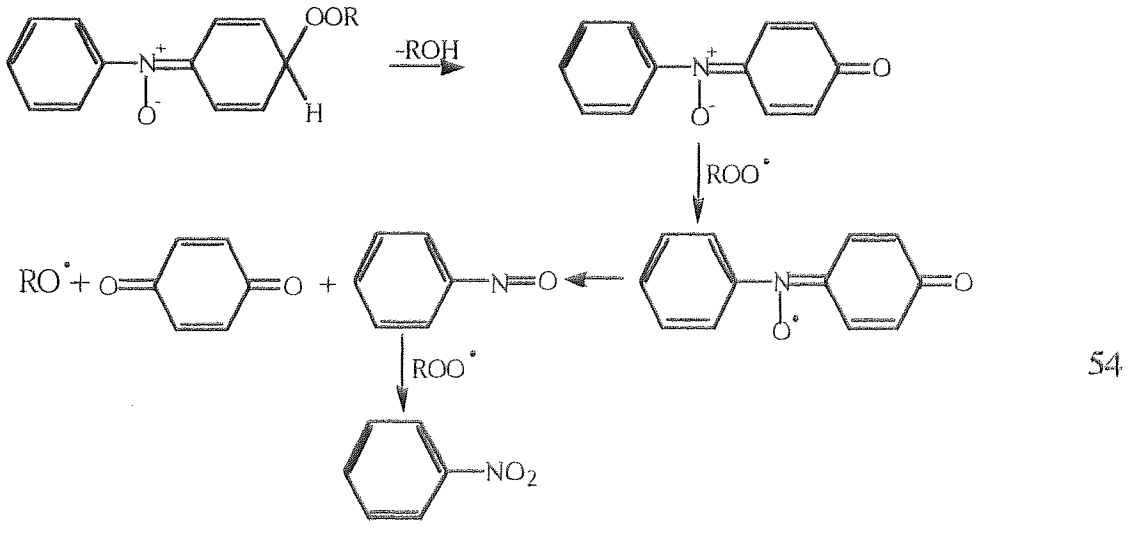
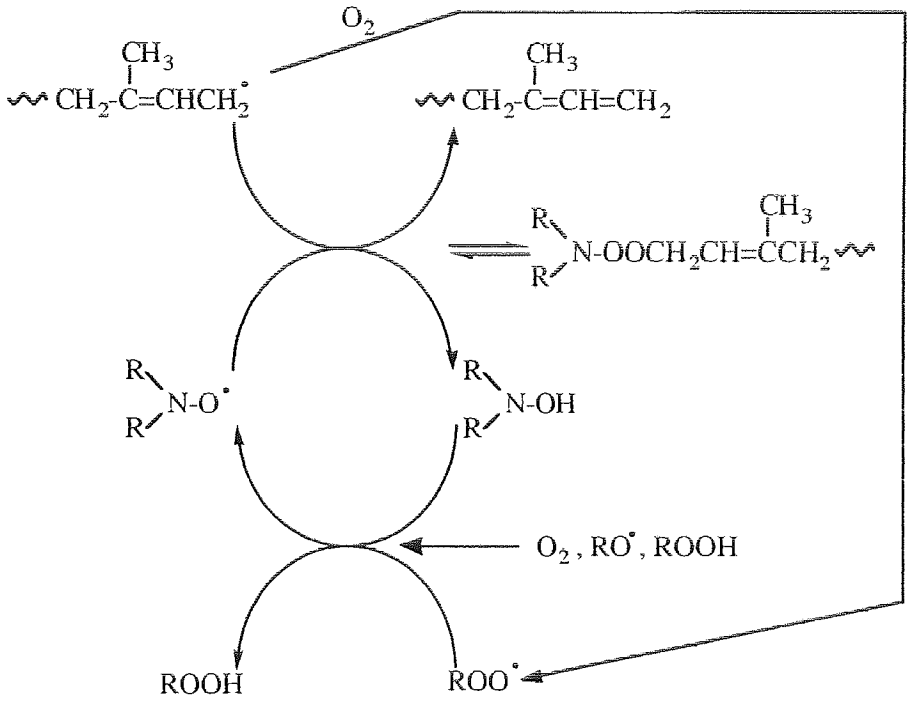


54

It has been shown that the nitroxyl radicals react with alkyl radicals (R$^{\cdot}$) via reaction 55 leading to the corresponding O-alkyl hydroxylamines [118].

55

The disproportionation of the O-alkyl hydroxylamines is possible to give the corresponding olefin and hydroxylamine InOH which is in turn able to scavenge an alkylperoxyl radical leading to the regeneration of the InO$^{\cdot}$. Hence this leads to the proposal of a regenerative cycle in various polyolefins involving a series of CB-D and CB-A steps as shown in scheme 7 [113-115].



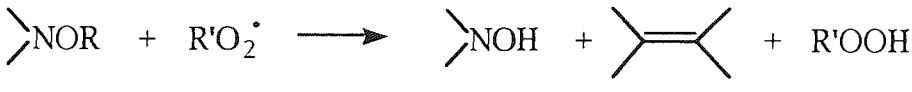
Scheme 1-7 The regenerative cycle of nitroxyls

Another important part of the efficiency of nitroxyl radicals as inhibitors is due to their regeneration from the ethers or hydroxylamines, reaction 56.

56

The regeneration leads to the high values found for the number of chains terminated per nitroxyl radical (f). This value increases during the course of the

reaction due to an increase in the rate of reaction 56 as the product from reaction 55 accumulates. It has been found [117] that aromatic amine antioxidants terminate a much smaller amount of chains per molecule compared to hindered aliphatic amines. This is probably due to the side reaction 54 which aromatic nitroxyl radicals can undergo, leading to their irreversible consumption. Other methods of regeneration of the nitroxyl radicals have been proposed [119] such as reactions 57 and 58, but there is still controversy about the mechanism of regeneration of the >NO˙ radical.



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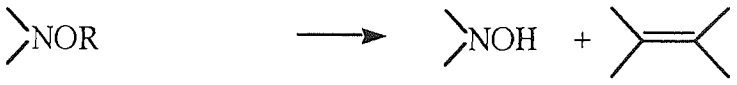
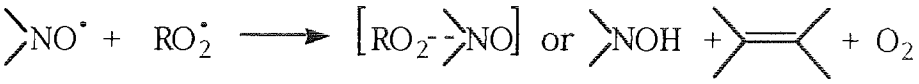


58

Nitroxyl biradicals have, in principle, the same inhibiting properties as monoradicals and it is thought that these decompose to the corresponding monoradicals prior to inhibition. Another reaction possible by nitroxyl radicals with RO_2˙ is 59 [117].

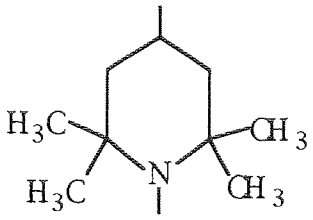


59

1.5.2.1.2 Sterically Hindered Amine Antioxidants.

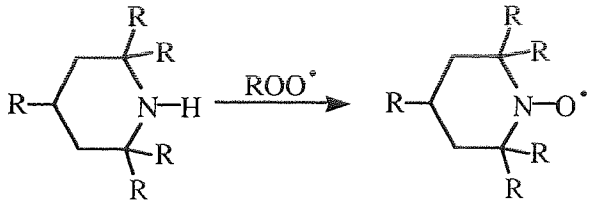
Sterically hindered amines (SHA) have been seen to be a highly efficient class of polymer stabilisers which act by a CB-A mechanism [119]. They are mainly related to piperidine derivatives with the structural group (XXII) with a hydrogen atom as the usual substituent at the nitrogen. They were initially

thought to work only as photostabilisers but further investigation has shown them to be thermal stabilisers also [120].



XXII

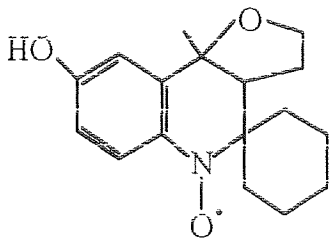
The effect of SHA's as CB-D's is very limited as the N-H bond strength is quite large, 364 $kJmol^{-1}$ in piperidine, compared to other CB-D antioxidants. However, the important reaction for SHA's is their ability to be oxidised by a variety of oxidants including the peroxyl radicals to produce stable nitroxyl radicals (reaction 60). The hydrogen abstracting ability of the nitroxyl is only slight as the energy of the corresponding O-H bond is only 303 $kJmol^{-1}$.



60

A major difference between the reactions of aromatic amine nitroxyls and those formed from SHA's is that the latter only react with alkyl radicals [119, 120, 121]. The reactions of the nitroxyl radicals are similar to those discussed earlier with the regenerative reactions proposed in scheme 1-7 again thought to operate. In the cases of the SHA the values of (f) can be as high as 600 although both the substrate structure and temperature can have a large effect on this. The fact that large increases in (f) have been observed when increasing the temperature from 65 to 130°C suggests that at least one step in the catalytic cycle has a fairly high energy of activation [120]. The thermal stability and lack of undesirable reactions (reaction 54) leading to the destruction of the SHA's nitroxyl are thought to be the reason why the values of (f) are larger than those for the aromatic amines [105, 120].

Spirane nitroxyl of the type (XXIII) also reacts with both alkyl and alkylperoxyl radicals, the product of which does not react further with $RO_2^{\cdot}$ but acts as a CB-A [117].



XXIII

1.5.2.1.3 Hindered Phenol Antioxidants.

Hindered phenols are the other major class of CB-D antioxidants often preferred for polyolefins due to their non-staining behaviour. This is less of an issue for the coloured elastomers. There has been a large amount of research into the relationship between structure and activity for phenols. The level of hindrance can be defined as: [122]

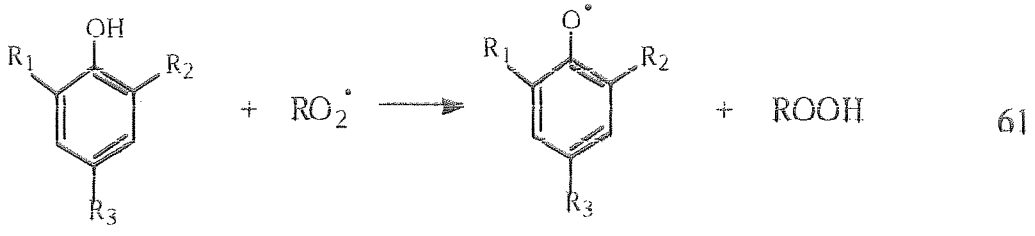
(a) hindered phenols - possess both ortho positions substituted with the same or different bulky substituents;

(b) partially hindered phenols - with only one bulky substituent in the ortho position and an H or CH_3 in the second;

(c) partially unhindered phenols - with a methyl group in one or both of the ortho positions;

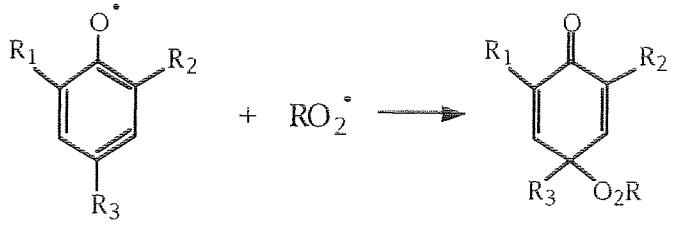
(d) unhindered phenols - without substitution in the ortho position.

The chain breaking donor step for a hindered phenol is shown in reaction 61.



XXIV XXV Phenoxyl Radical

Again the value for f is close to two which is explained by reaction 62, where by the produced phenoxyl radical (XXV) reacts with a second alkylperoxyl radical [91].



62

XXVI

A study [122] into the rate of formation and the stability of the phenoxyl radicals produced from a number of phenolic structures, including some methylene and sulfur bridged compounds, led to some general conclusions being drawn about the antioxidant activity [90].

(i) The activation energy of the hydrogen abstraction by an alkylperoxyl radical increases and the stability of the phenoxyl decreases with decreasing steric hindrance i.e. moving from (a) to (d) above.

(ii) Substitution of the α-hydrogens in a 4-alkyl group by alkyl substantially increases the stability of the phenoxyl and hence CB-D activity.

(iii) Increasing bulk of the 4 substituent decreases the ability of the phenoxyl to deactivate a second alkylperoxide (reaction 62).

(iv) The incorporation of an alkylidine bridge in the 2 or 4 positions decreases the tendency of the initially formed phenoxyl to disproportionate with loss of the second phenolic group.

(v) The presence of a sulfur bridge increases the delocalization of the unpaired electron, thus permitting a lower degree of steric hindrance without sacrificing CB-D activity.

Other generalisations have been made linking the nature of the 2, 4 and 6 substituents to the antioxidant efficiency [90].

(vi) Electron releasing groups (methyl, methoxy, alkylamino, etc.) in the 2 and 4 positions increase antioxidant activity, whereas electron attracting groups reduce activity.

(vii) Groups in the 2 and 4 position which delocalize the unpaired electron on the derived radical (notably aryl) increase antioxidant activity.

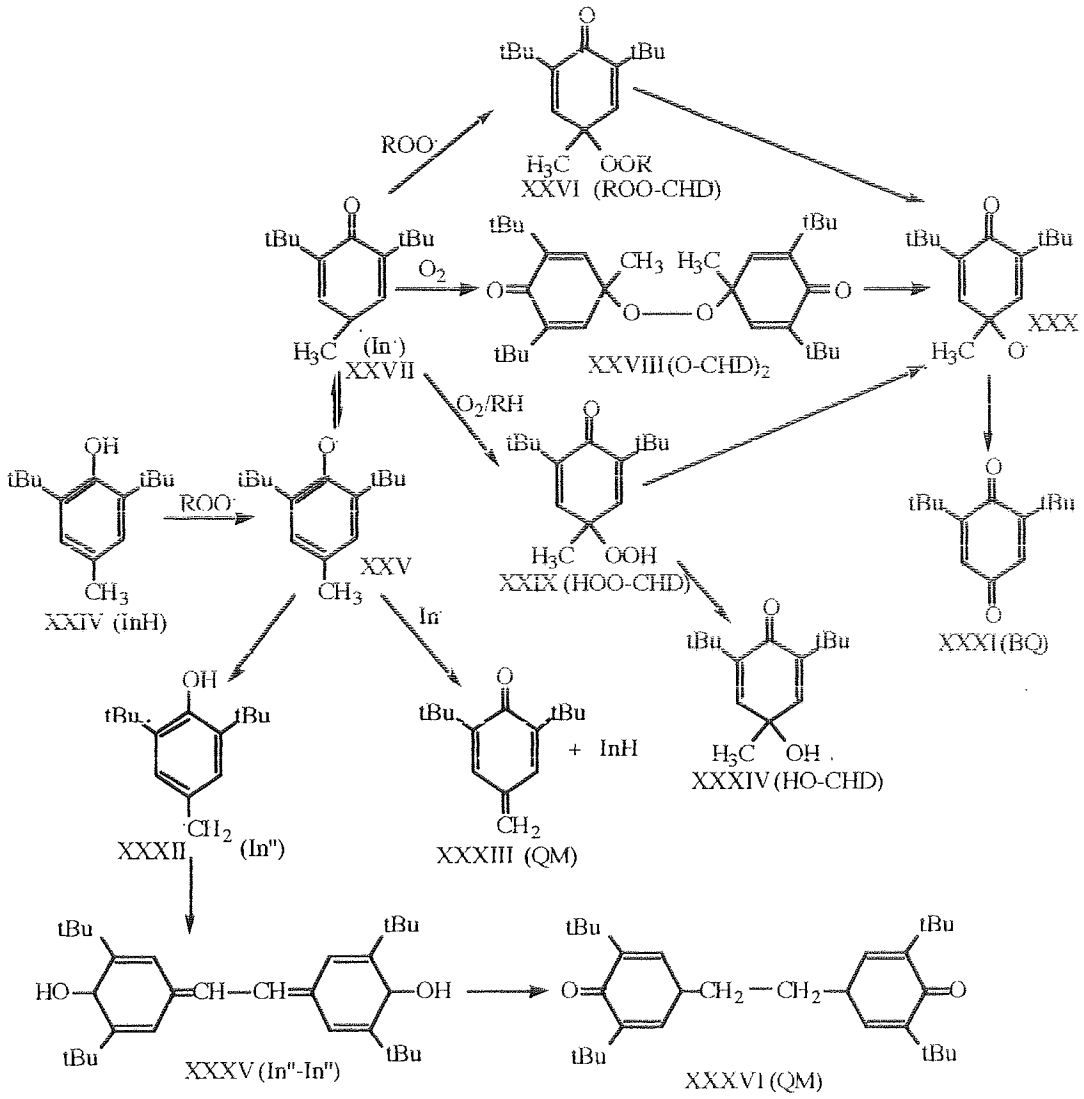
(viii) Branched chain alkyl groups in the 2 and 6 positions increase antioxidant activity.

The generalisations (vi) and (vii) can be explained by the stability of the transition state. The fact that the alkylperoxyl radical is an electron acceptor, thus having a partial negative charge in the transition state, means that the aromatic ring becomes partially electron deficient, therefore substituents in the 4 position which donate electron density can stabilise the transition state. Also substituents in the 2 or 4 positions which can delocalize the electron density will decrease the transition state energy [90]. The fact that alcohols and aliphatic amines have virtually no antioxidant activity is due to the unpaired electron formed by hydrogen abstraction being very localised. This allows the radical species to act as an effective transfer agent.

The amount of steric hindrance plays an important role in the activity of an antioxidant, the fully hindered phenols produce the most stable phenoxyl radicals but this is at the expense of the hydrogen transfer reaction. Also as mentioned in (iii), increased steric hindrance in the 4 position decreases the reaction with the second alkoxyl radical, the optimal effect being shown by the methyl group [90].

In addition to the initial oxidation product (the phenoxyl radical XXV), many other transformation products are formed during the antioxidant function

of hindered phenols by a variety of routes [91]. The main routes being dimerisation and reaction with oxygen containing radicals [90]. These products may have either pro-oxidant or antioxidant activity [88]. Scheme 1-8 shows an overview of the reactions undergone by the commercial antioxidant BHT.

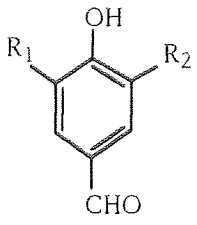


Scheme 1-8 Oxidation of a hindered phenol by alkylperoxyl.

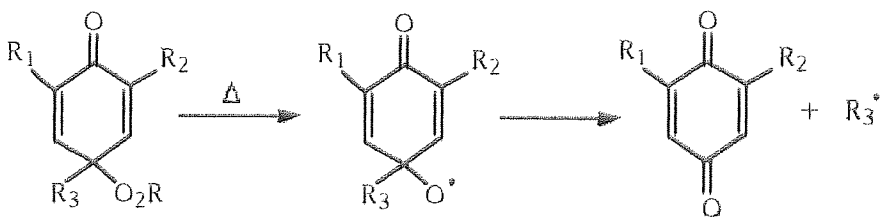
One of the initial reactions is the production of quinone methide (QM) (XXXIII) and regeneration of the initial InH by disproportionation. This quinone is highly reactive and readily undergoes further reactions such as dimerisation via a radical intermediate (XXXII). In the case of phenoxyls O-O dimerisation is not known [123] therefore the reaction proceeds via the mesomeric cyclohexadienonyl radical (XXVII) or the isomeric form benzyl

radical (XXXII). Compounds of the In''-In'' (XXXV) type prevail in the mixture of the transformation products [91], and are as effective antioxidants as the initial phenol [90]. They act as hydrogen donors and are eventually oxidised to a quinomethinoid system (XXXVI). This is also able to function as an antioxidant but via a CB-A mechanism [90] making use of an extensive system of conjugated bonds [91]. 2,6-Disubstituted phenols give rise to biphenyldiols, HIn-InH, which participate further in the inhibition process [91] leading to diphenoquinones. With polynuclear InH more complicated systems are produced such as phenolic oligomers which are difficult to characterise [90]. These oligomers are the main route for the removal of the In$^{\cdot}$ from the system.

At high $RO_2^{\cdot}$ concentrations alkylperoxycyclohexadienones ROO-CHD (XXVI) form and are thermally and photochemically unstable due to the O-O bond. One of the breakdown products from ROO-CHD has been seen [124] to be RO$^{\cdot}$ thus the structure may act as a prooxidant [90]. Decomposition to initiate oxidation can occur at temperatures as low as 75°C for 2-ROO-3,5-CHD and all derivatives of 4-ROO-2,5-CHD strongly accelerate oxidation above 100^{0}C [91]. Complex mixtures of products are produced from this decomposition, such as stilbenequinones (XXXVI) hydroxybenzaldehydes (XXXVII) [91] and alkyl elimination via reaction (63) leads to the formation of benzoquinoid compounds (XXXI)[31].



XXXVII



XXVI XXX XXXI

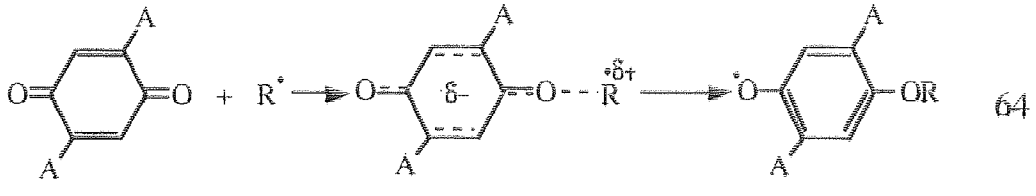
63

Benzoquinone compounds can participate in further reactions in a very complex manner. They are able to trap R• radicals through the Π bond system and to form donor acceptor systems [91]. Testing has shown [91, 125] that the retarding properties of benzoquinones are structurally sensitive, but the differences decrease with increasing temperature. Also concentrations of benzoquinones higher than the original phenols from which they have been derived may be pro-oxidative [91]. Their structure allows them to participate in photochemical processes where transformations can act as either as inhibitors or initiators [91].

1.5.2.2 Chain Breaking Acceptor Antioxidant Mechanisms.

The importance of the chain breaking acceptor (CB-A) mechanism has only been quite recently recognised. It was understood that the effectiveness of a CB-A antioxidant must depend on its ability to compete with oxygen in reacting with the alkyl radical [90]. This fact is true in cases where diffusion of oxygen to the reactive site is rapid such as in liquid hydrocarbons, but in solid polymers the rate of diffusion can be 100 times slower [126]. This leads to alkyl radicals having much longer lifetimes and it has been calculated that the ratio of $R^{\bullet}/RO_2^{\bullet}$ in polypropylene was $2x10^{-3}$ compared to $5x10^{-6}$ in a hydrocarbon under the same conditions [125]. It is clear then that in solid polymers it is possible for alkyl radicals to be involved in the inhibition process and it was studies in such systems which has led to much of the evidence for the CB-A mechanisms.

The classes of stabilisers which perform as CB-A antioxidants include quinones, nitro compounds and stable free radicals such as nitroxyls and phenoxyls. The transition state for the reaction of a quinone and an alkyl radical involves charge separation and the reaction proceeds via reaction 64 [88].



64

Electron withdrawing and delocalizing groups in positions A increase the alkyl radical affinity and thus the antioxidant activity. It is found [88, 90] that most of these types of antioxidants have no significant activity in hydrocarbons where they are unable to compete with oxygen for alkyl radicals, but in solid polymers they have been shown to be much more effective.

1.5.3 Preventative Antioxidants

Preventive mechanisms also have an important role to play in stabilisation of organic materials. As can be seen in scheme 1-3 there are a number of types of preventative mechanisms. The metal deactivators, which mainly work by co-ordinating with metal ions to prevent them participating in the catalytic hydroperoxide decomposing reactions 18 and 19. The absorption or screening of UV light and the decomposition of hydroperoxides to non-radical products [127]. The first two types are only of limited effectiveness as they retard the formation of free radicals from hydroperoxides rather than inhibit it. The peroxide decomposers which decompose hydroperoxides by a chemical mechanisms to produce non free radical products (the peroxidolytic mechanism) are thus the most important of the preventative antioxidants. These can be split into two groups, stoichiometric and catalytic decomposers.

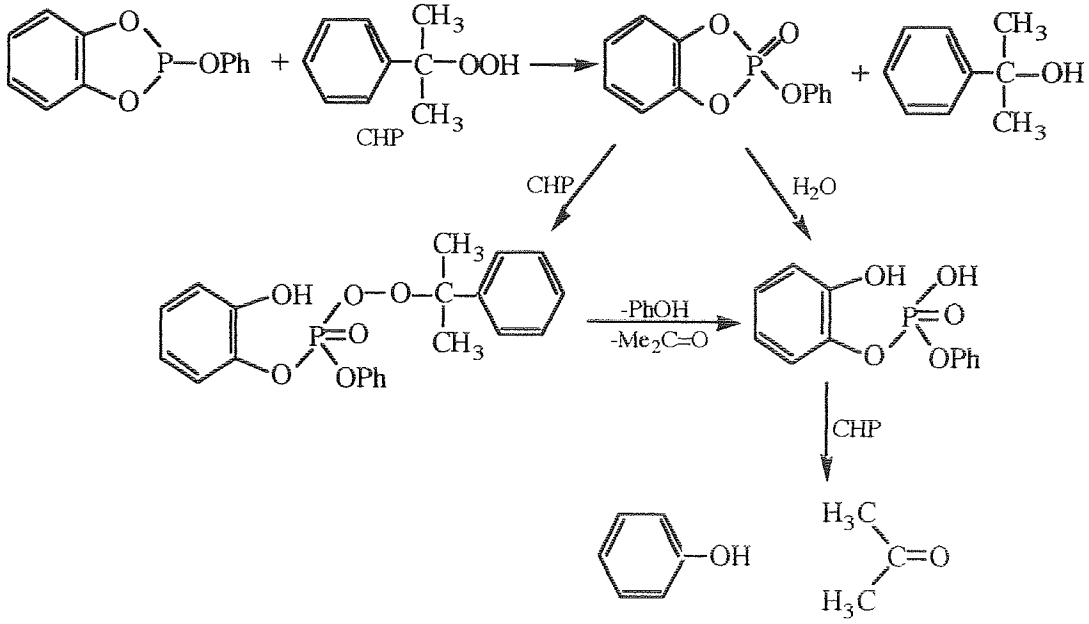
1.5.3.1 Organic Phosphorus Compounds.

Organophosphorus compounds are examples of stoichiometric peroxide decomposers [128]. They are widely used as antioxidants in both polyolefins and elastomerics and an important reason for their use is there ability to preserve the inherent colour (or colourlessness) of the polymers in which they are used. The basic reaction involved in their action as peroxide decomposers is represented in reaction 65 where hydroperoxides are reduced to alcohols [128].

$$R'OOH + (RO)_3P \longrightarrow [R'\dot{O}H\dot{O}P(OR)_3] \longrightarrow R'OH + O{=}P(OR)_3 \quad 65$$

This reaction can either occur via a non-radical or a radical route. At lower temperatures the reaction mainly proceeds via a non-radical mechanism due to the high energy of activation required to produce the radical pair. If the temperature is increased the rate of the radical reaction increases more rapidly than the non-radical reaction. So at higher temperatures the contributions of both routes then become comparable [127]. An interplay of these mechanisms can lead to a situation where the reaction with the hydroperoxide can become an important source of radical formation. The reactivity to hydroperoxides is governed by both steric and polar effects of the groups bound to the phosphorus atoms, reaction rates decreasing with increasing bulk and electron acceptor ability.

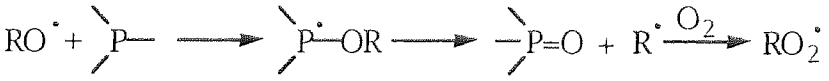
The five membered catechol phosphites have been shown to decompose hydroperoxides [128] by the ionic catalytic pathway shown in scheme 1-9 when reacted with cumene hydroperoxide. The initial structure is transformed by oxidation of the hydroperoxide to a cyclic phosphate which is a powerful Lewis acid. This can then react by a slow reaction with hydroperoxide, via an unstable peroxyphosphate or by a rapid reaction with water, to produce the open chain hydrogen phosphate. This open chain phosphate acts as the catalyst decomposing the peroxides to phenols and ketones.



Scheme 1-9 Mechanism of catalytic hydroperoxide decomposition by the cyclic phosphites

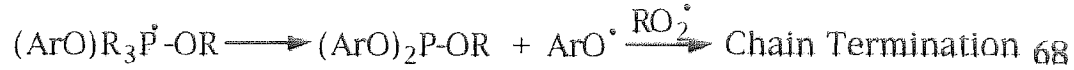
In the presence of $RO_2^{\bullet}$ radicals phosphites can be 'self oxidized' by the chain process as shown in reactions 66 and 67 [128]. This can lead to the complete consumption of the phosphite, but if it can be suppressed the effectiveness of inhibition increases.

66



67

The chain is much shorter for the aromatic phosphites, particularly for those with sterically hindered phenoxyl groups, than for the trialkyl phosphites. The reason for this is a change in the chain termination mechanism which proceeds via reaction 68 with the formation of an aryloxyl radical.



68

The sterically hindered aryloxy radical can then act as a chain-breaking antioxidant to effectively trap the alkylperoxide radical. This allows the

sterically hindered aryl phosphites to act as chain-breaking antioxidants, but with rate constants two orders of magnitude lower than those of sterically hindered phenols.

1.5.3.2 Organic Sulfur Compounds.

Another variety of widely used peroxide decomposers are the sulfur containing compounds which are examples of catalytic peroxide decomposers [130]. A number of organic sulfur compounds, including alkyl and aryl sulfides (XXXVIII), disulfides (XXXIX) [131] and metal dithiocarbamates (XL) [132], have been shown to be active.

R-S-R	R-SS-R	$[R_2NCS_2]_nM$
XXXVIII	XXXIX	XL

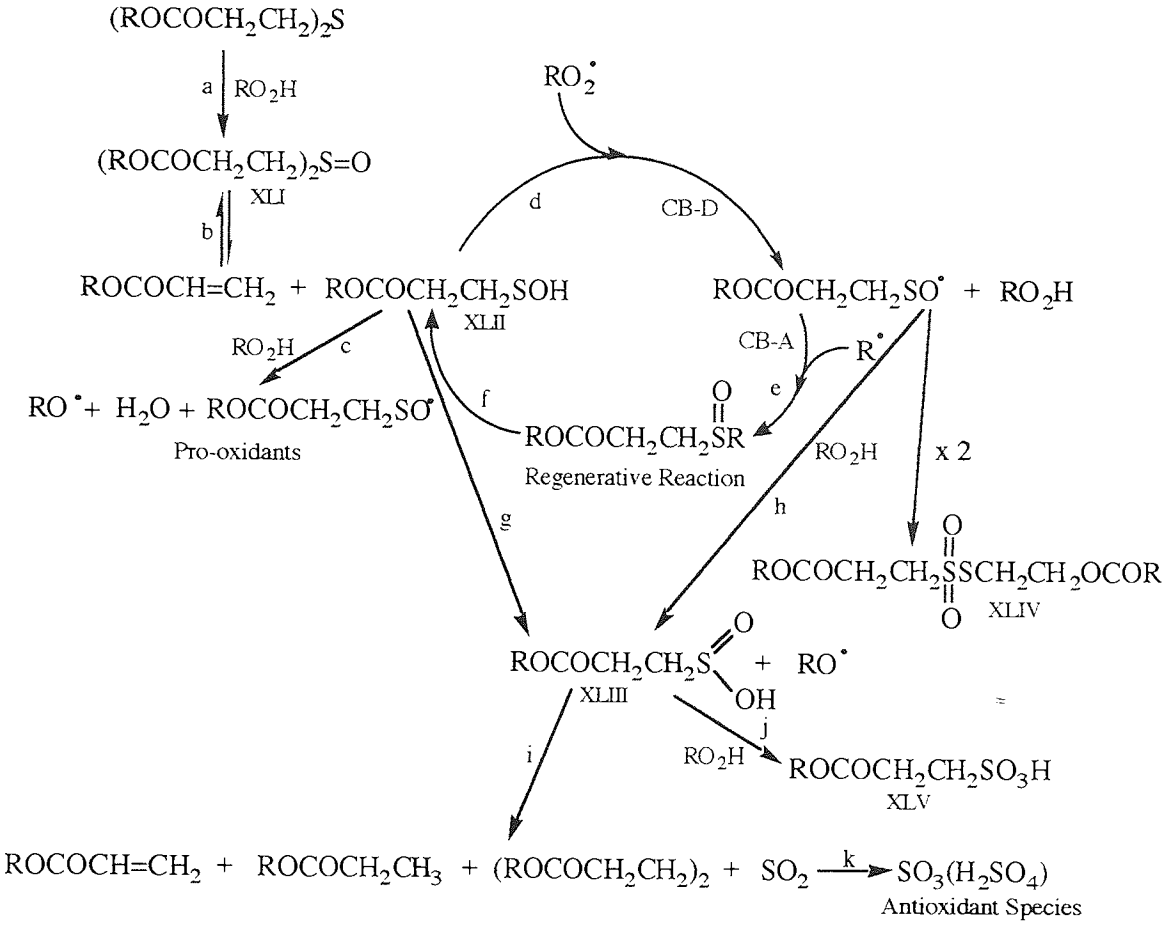
Studies of the mechanisms of these compounds have shown a number of similarities [131].

(i) The effective antioxidant is not the parent sulfur compound but an oxidation product formed from it in the autoxidizing medium.

(ii) In all cases, the effective antioxidant is the catalyst for the ionic decomposition of hydroperoxides.

(iii) The antioxidant stage is frequently preceded by a pro-oxidant stage which varies in intensity. Hence the oxidations are generally autoretarding.

Scheme 1-10 shows the typical reactions which the commonly used dialkyl thiodipropionates undergo.



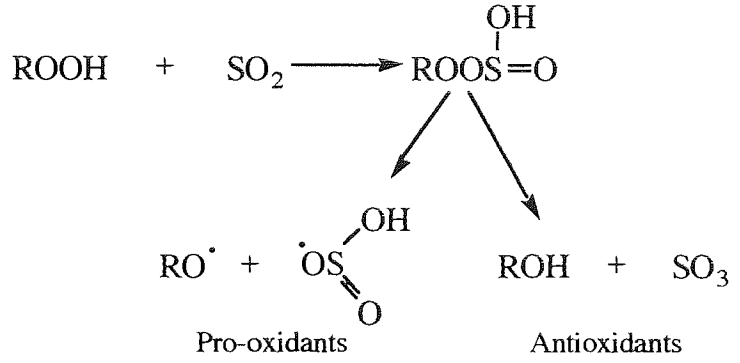
Scheme 1-10 Antioxidant mechanism of dialkyl thiodipropionates in the presence of hydroperoxide

The initial reaction is between the parent alkyl sulfides and a hydroperoxide, this produces a thermally unstable sulfoxide (XLI). If this has one or more hydrogens on a β carbon to the sulfonyl group it can undergo thermal decomposition (scheme 10 b). This occurs at relatively low temperatures to give a sulfenic acid (XLI) and olefin by a stereospecific cis-elimination [130]. The fate of the sulfenic acid depends on the surrounding hydroperoxide / sulfonic acid ratio. At low peroxide ratios decomposition of the hydroperoxide occurs (scheme 10 c) to produce an alkoxyl radical. This is thought to be the reason why a pro-oxidant stage is often observed during the early stages of stabilisation [127]. Where the ratio of hydroperoxide is high the sulfenic acid is oxidised to sulfinic acid (XLIII) which is relatively stable at room temperatures but rapidly disproportionates at 60°C to give thiosulfonate (XLIV) and sulfonic acid (XLV) (scheme 10 j). At high temperatures sulfinic

acid undergoes homolysis to produce sulfur dioxide and various other products (scheme 10 i).

The three sulfur compounds, the sulfinic acid (XLIII), sulfonic acid (XLV) and sulfur dioxide, are able to catalyse the ionic decomposition of hydroperoxides. Studies of the rate of the reaction showed [133] that sulfur dioxide and the sulfinic acid were the much more active.

In the case of sulfur dioxide studies [134] have shown that although sulfur dioxide is a more effective catalyst for the decomposition of hydroperoxides it cannot survive the oxidising conditions of autoxidation. It is suggested that the effective catalysts are either sulfur trioxide or sulfuric acid. The sulfur trioxide is formed by the ionic breakdown of an unstable peracid as shown in scheme 1-11.



Scheme 1-11 Reactions of sulfur dioxide with hydroperoxide

In addition to the peroxidolytic action the sulfur compounds (sulfenic, sulfinic and sulfonic acid and sulfur dioxide) were found [133] to operate by chain breaking mechanisms, the presence of an acidic hydrogen being responsible for this action. The formed radical appears to be incapable of continuing the chain reaction. A regenerative mechanism has also been proposed (scheme 10 d-f).

1.5.4 Synergistic Antioxidant Mechanism

The prediction of the practical performance of antioxidants in polymer systems is difficult. This is not only due to physical properties such insolubility or volatility but also due to interference from other chemicals either as impurities initially present or deliberately added to the polymer. This is important in real antioxidant systems as the addition of two antioxidants to a polymer rarely gives an additive effect and in practice the result usually better or worse than predicted [135]. If the result is better than additive this is synergism and is advantageous, if it is worse this is antagonism and is disadvantageous. Synergistic antioxidant combinations have become very important in the stabilisation of polymers. Three mechanistically distinct types of synergism have been described: [135]

(i) homosynergism - interaction of two antioxidants acting by the same mechanism, generally in a single electron cascade;

(ii) heterosynergism - two antioxidants acting by different complementary mechanisms;

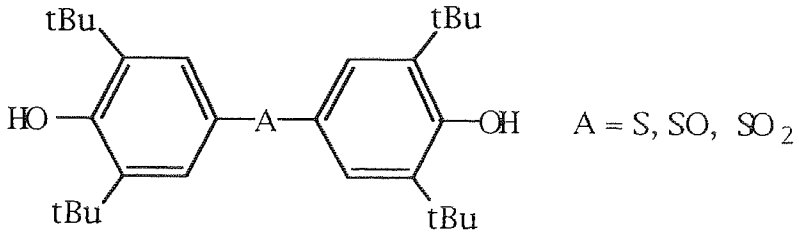
(iii) autosynergism - synergism resulting from two different moieties in one molecule.

Homosynergism has been reported to occur by the mutual interaction between structurally different phenols and between phenols and amines [135]. The effect is generally greatest when the activity of one of the antioxidants is stronger than the other. The more reactive inhibitor will efficiently scavenge the peroxyl radical by a chain breaking donor mechanism, the radical formed from the antioxidant can then be regenerated by the less reactive inhibitor (reaction 69) which forms a stable radical. Thus, the less reactive antioxidants act as reservoir of available hydrogen extending the efficiency of the stabilisers [136].

$$\underset{\text{More reactive inhibitor}}{In^{\bullet}} + \underset{\text{Less reactive inhibitor}}{In'H} \longrightarrow \underset{\text{Regenerated Inhibitor}}{InH} + In'^{\bullet} \quad 69$$

Heterosynergism [137] involves two or more antioxidants acting via different mechanisms. The best examples of which are the combination of peroxide decomposers with chain breaking antioxidants. In the case of synergism between CB and peroxide decomposing antioxidants the heterosynergistic mechanism will be due to the free radical chain stopping action of the CB (e.g. CB-D) antioxidants which will retard the formation of peroxides by termination of the free radical chains. However, at least one molecule of peroxide will be formed during the CB-D action and this can react with the peroxide decomposer to form non-radical products. The PD will thus reduce peroxide initiation to a negligible source of free radicals so the CB-D will have fewer radical chains to terminate, thus the reaction can inhibited over a much longer period.

Autosynergism can occur in a stabiliser molecule which can function in more than one way as an antioxidant. The most obvious compounds are phenolic antioxidants which contain phosphorus or sulfur groups such as the case with thiobisphenols (XLVI).



XLVI

One problem with combining different antioxidants is that synergism is rarely maximised at ratios of 1:1, thus extensive work is required to find the most efficient combination of antioxidants.

1.6 Objectives and Scope of Present Work

The overall aim of this work is to develop a more effective stabiliser system for the polybutadiene binder used in solid composite propellant rocket

motors. Earlier work [31] has suggested the use of synergistic antioxidant combinations which led to improved stabilisation over the currently used antioxidant 2,2'-methylene-bis(4-methyl-6-tert-butylphenol) (Calco 2246).

The main objectives of the work are :

Investigation into the role of specific synergistic antioxidant systems which are based on combinations of chain breaking and peroxide decomposing antioxidants.

The investigation of thermal analysis as a method which could more rapidly give information on the potential effectiveness of antioxidant systems.

To investigate the extent of interaction of antioxidants with the curing agent, isocyanate, leading to antioxidant-inactive moieties. The importance of steric hindrance in phenolic antioxidants in such non-useful side reactions will be examined.

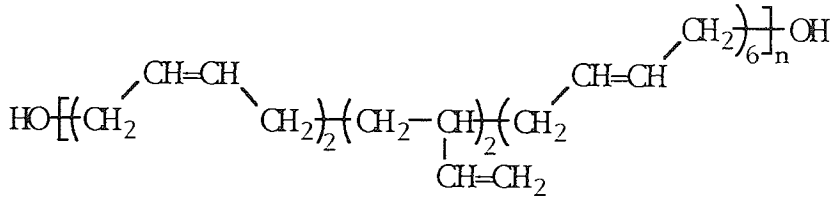
A study of the extent of retention of the antioxidant during ageing and the nature and effect of transformation products formed during this time.

CHAPTER TWO

2 EXPERIMENTAL WORK

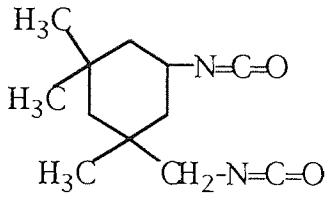
2.1 Materials

The polymer used in this work is hydroxyterminated polybutadiene, HTPB (RM45) supplied by the Defence Research Agency (DRA). This is a viscous clear colourless liquid with the specifications shown in Table 1 [138] and the chemical structure XLVII.



XLVII HTPB

The solid rubber binder is produced by cross-linking the HTPB via the OH groups with isophorone diisocyanate, IPDI (3-isocyanato-methyl-3,5,5-trimethylcyclohexyl-isocyanate). This is a clear colourless low viscosity liquid which is miscible with many organic compounds but is practically insoluble in water. The physical properties of IPDI are shown in Table 2 [138, 139] and the chemical structure is XLVIII.



XLVIII, IPDI

The role of a variety of commercially available antioxidants and synthesised antioxidants [140] has been examined. The antioxidant's structures are shown in Table 3.

The FTIR analyses were obtained using a 1710 Perkin Elmer FTIR instrument with IBM computer control. KBr discs were prepared for solid samples and NaCl plates were used for liquid samples. The UV analyses were obtained using

a Hewlett Packard diode array UV-Vis spectrophotometer with IBM computer control. Dichloromethane (DCM) was used as a solvent and a 1 cm^3 quartz cell was used throughout.

Table 2-1 DRA specification of HTPB.[138]

Test	Limit	Method
Volatile matter	0.5% Max.	M898
Hydroxyl content	0.73±0.05% meq/g	M898
Viscosity at 30°C	5.0±1.0 Pas	M898
Water Content	0.1% Max.	M898
Unsaturation type		
Trans	52% Min. - 57% Max.	
Cis	22% Min. - 27% Max.	
Vinyl	19% Min. - 24% Max.	
Total peroxides as H_2O_2	500 ppm Max.	M898
Trichloroethlyne insolubles	0.2% Max.	M898
Relative Density at 20°C	0.87 Min	BS 4522
Colour	50 Max.	M898
No. average molecular mass	~3000	
Hydroxy functionality	2.1-2.4	

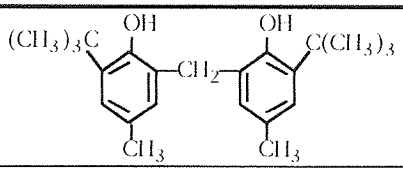
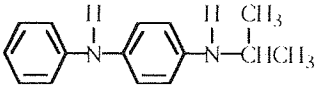
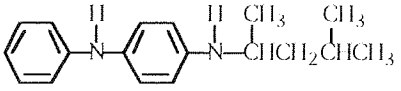
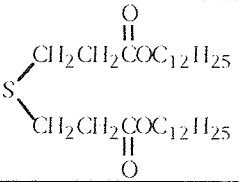
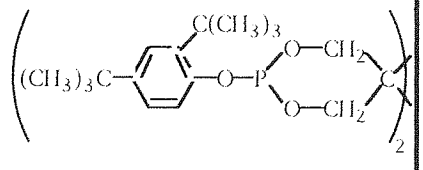
Table 2-2a Physical properties of IPDI.[139-140]

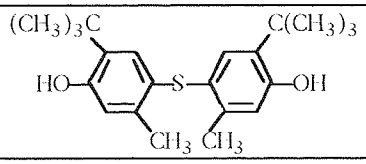
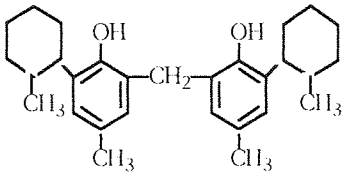
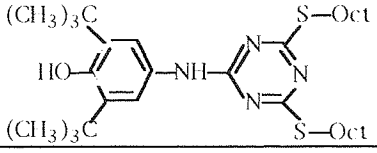
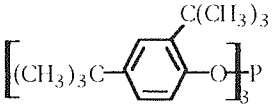
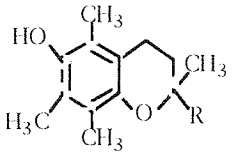
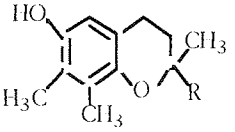
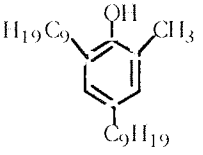
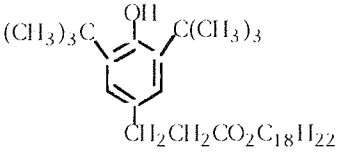
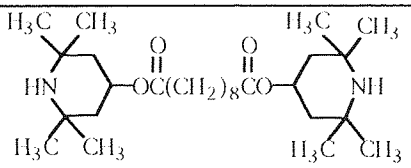
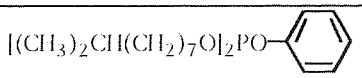
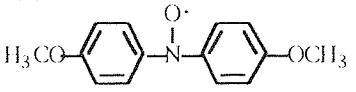
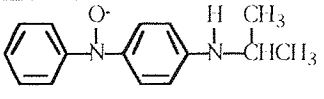
Test	Conditions	Value
Refractive index		1.4825
Vapour pressure	at 20°C	0.0003 mmHg
	at 50°C	0.007 mmHg
Boiling point	at 10 mmHg	158°C
	at 20 mmHg	170°C
Density	at 15°C	1.062 g/cm^3
	at 20°C	1.058 g/cm^3
Viscosity	at -20°C	150 cps
	at -10°C	78 cps
	at 0°C	37 cps
	at 20°C	15 cps
Flash point (open cup)		163°C
(according to DIN51584)		
Ignition temperature		430°C
(according to DIN51794)		

Table 2-2b Safety information for IPDI.[139, 140]

Handling	Use safety goggles, rubber gloves and rubber aprons in well ventilated room. Breathing filters to be used otherwise.
Storage	Exclude all moisture, keep containers carefully sealed in well ventilated room.
Combustibility	Stored according to regulations for combustible liquids. For small fires use powder or CO_2 extinguishers. Wear suitable protection as isocyanate containing vapours are produced.
Physiological Effects	Can irritate body but low vapour pressure prevents large atmospheric concentration. Will cause irritation on prolonged contact to skin. If swallowed stomach tract will be corroded but poisoning by absorption is unlikely. Drink copious amounts of water then take up to 40 charcoal tablets. See physician. If large amounts of vapour are inhaled see physician immediately
Spillage Procedure	Wash off any skin contamination, remove contaminated clothing. Treat spill with mix of :- 30 parts MeOH 70 parts H_2O 1 part conc. NH_4OH

Table 2-3 Structures of Antioxidants Examined.

Chemical Name / Source	**Molecular Structure**	**Code/State, Colour**	**Mpt/^{o}C RMM**
2,2'-Methylenebis(4-methyl-6-tert-butylphenol) / USA Cynamide		Calco 2246 / Yellow	120 - 124 340
N-iso-propyl-N'-phenyl-para-phenylenediamine/ Vulnax		IPPD / Black	74 - 76 226
N-Phenyl-N'-1,3-dimethylbutyl-para-phenylenediamine / Vulnax		6PPD / Brown	268
Dilauryl thiodipropionate / Robinson Brothers		DLTP / White	38 - 44 514
Bis (2,4-di-t-butylphenyl)pentaerythritol diphosphite / General Electric		Ultranox 626 / White	177 - 178 641

Chemical Name / Source	Molecular Structure	Code/State, Colour	Mpt/°C RMM
4,4'-Thiobis(2-tert-butyl-5-methylphenol) / Ciba-Geigy		Santonox R / White	154 - 158 358
2,2'-Methylenebis(4-methyl-6-(1'-methyl-cyclohexyl)phenol)) /		WSP / Light Yellow	130-133 420
Phenol-4(4,6-bis(octylthio)1,3-triazine-2-yl)amino-2,6-bis(1,1-dimethylethyl) /Ciba-Geigy		Irganox 565 / White	100 - 103 589
Tris (2,4-ditert-butylphenyl) phosphite /Ciba-Geigy		Irgafos 168 / White	180 - 186 646
2,7,8-Tetramethyl-2(4',8',12'-trimethyltridecyl)chroman-6-ol / Hoffmann La Roche		α-Tocopherol / Orange	Liquid 400
2,5,7,8-Tetramethyl-2-(4',8',12'-trimethyltridecyl)chroman-6-ol / Hoffmann La Roche		γ-Tocopherol / Dark Brown	Liquid 386
2-Methyl-4,6-dionylphenol / Monsanto		Santowhite 54 / Orange	Liquid 360
3,5-Bis(1,1-dimethyl-4-hydroxy-octadecyl ester / Ciba Geigy		Irganox 1076 / White	51-52 515
Bis(2,2',6,'-tetramethyl-piperidinyl)sebacate / Ciba-Geigy		Tinuvin 770 / White	80 - 85 417
Diiso-decylphenylphosphite/ Akzo		P310 / Colourless	Liquid 440
4,4'-Dimethoxydiphenyl-nitroxyl/Synth. in earlier work[31]		DMDP-NO· / Purple crystals	Does not melt 244
P-(N-isopropyl)diphenyl-nitroxyl/Synth. in earlier work[31]		IPPD-NO· / Brown crystals	Does not melt 241

2.2 Preparation of Binders [31, 141]

Scheme 1 shows the method used for the preparation of the binder. The HTPB was first dried in a rotary evaporator at 60°C for 2 hours using an oil bath for heating and then allowed to cool in a desiccator. The glassware was also dried at 120°C and cooled in a desiccator. The required amount of antioxidants were weighed into beakers to which the HTPB was added, this mixture was then either stirred vigorously or mixed using ultrasound. An L & R Maxomatic Ultrasonic Bath was used to perform the ultrasound. The correct amount of curing agent (IPDI) was then added according to equations 2 and 3.

$$\text{NCO : OH} = \frac{\text{weight IPDI(g) x 2 x 1000}}{\text{weight HTPB (g) x hydroxy content (meq/g) x 222}} \qquad (2)$$

Since a NCO:OH ratio of 0.85 was required and IPDI has a molar mass of 222 and contains 2 NCO groups per molecule and HTPB has a hydroxyl content of 0.73 meq/g (table 1), the actual mass of IPDI can be then calculated by reducing equation 2 to equation 3.

$$\text{weight IPDI(g)} = 0.73 \text{ x } \frac{222}{2 \text{ x } 1000} \text{ x } 0.85 \text{ x weight HTPB(g)} \qquad (3)$$

After stirring the binder was then poured into either glass tube or plastic dish moulds. These were then loosely covered and placed in an oven at 60°C for 7 days for curing (cross-linking), see scheme 1.

Table 2-4 Typical weights used for preparation of binder samples

	Mass HTPB (g)	Mass IPDI (g)	Total Mass (g)
Tube Sample	10	0.689	10.689
Dish Sample	1.57	0.108	1.678

2.3 Accelerated Oven Ageing and Testing of Binder

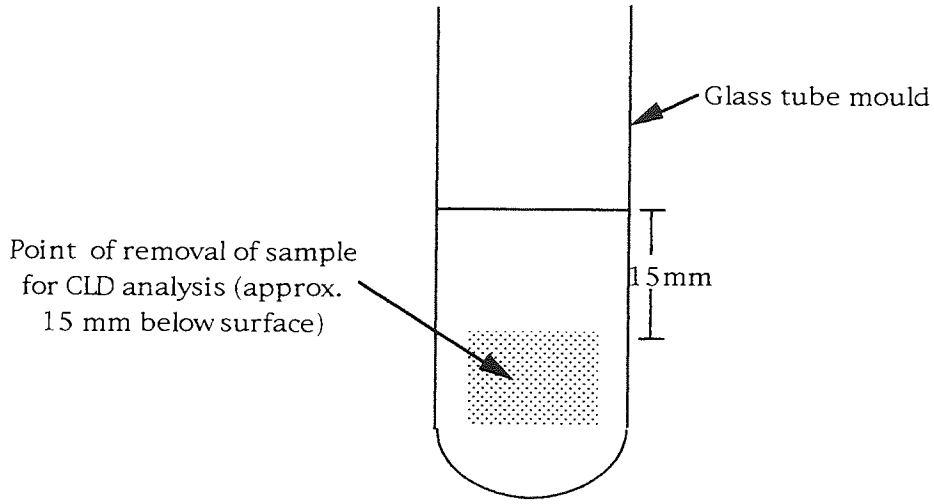
After curing, the binder samples containing different antioxidants were thermally aged at 60°C or in some cases at 80°C in ovens which allowed the free circulation of air. Single samples were removed at various times for binder testing [142].

The measurement of percent soluble materials (% sol) and cross-link density (CLD) after Soxhlet extraction with dichloromethane (DCM) was used as a measure of binder degradation. These extractions and measurements were carried out in duplicate. Alumina extraction thimbles (h x w=80 x 20 mm) were dried in a vacuum oven at 60°C for 3 hours and then cooled in a desiccator until a constant weight was obtained (W1, g). Tubes containing the cured sample were broken and 0.3 ±0.005 g of binder was removed from the sample at the positions shown in figure 2-1 and added to a thimble, in the cases of the dish moulds the sample was removed as a single layer which was cut up before analysis. The thimble containing the sample was then reweighed (W2, g). The binder was extracted in a Soxhlet extractor for at least 16 hours with 250 mls of DCM (H.P.L.C. grade if required for further analysis). The thimble was removed and placed in a fume cupboard to allow excess solvent to evaporate before being placed in a vacuum oven overnight at 60°C and then cooled in a desiccator. The thimble containing the dry undissolved solid was weighed again (W3, g) and equations (4) and (5) [143] were used to calculate % sol and CLD. Equation (5) was derived by the D.R.A. from the Charlesby-Pinner equation and is their standard method of relating % sol to CLD. In cases where the extract was required for further analysis, excess solvent was removed by rotary evaporation and the extract was kept in a freezer.

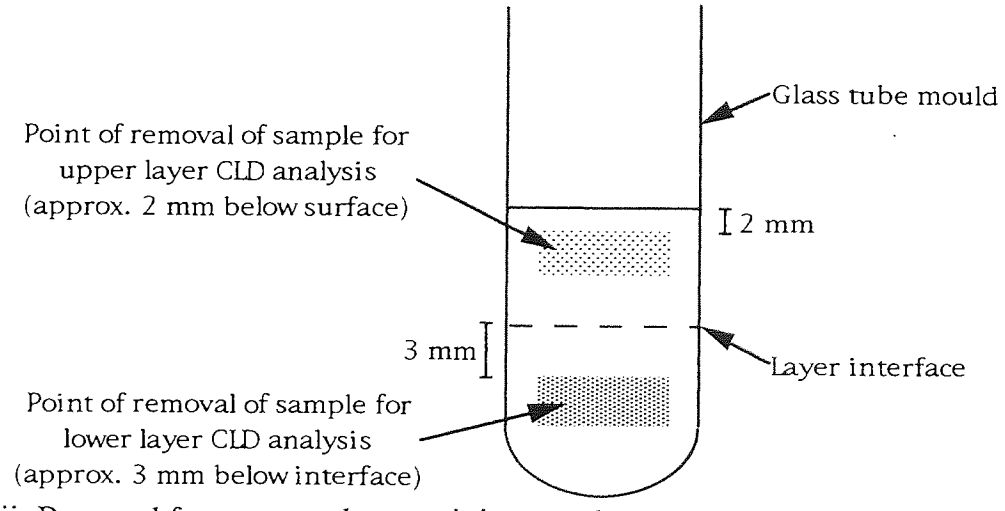
$$\text{Sol fraction \% (s)} = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \qquad (4)$$

$$\text{Cross-link Density} = \frac{(1-s)[2-(s+s^{0.5})]}{s+s^{0.5}} \qquad (5)$$

In the case of certain samples distinct colour layers were seen to form after curing. If it was possible the CLD of both layers was analysed using the method explained above. Figure 1 shows the regions in which the binder was tested. In cases where two layers did not form the sample for testing was removed only from the lower region.



i. Removal from a sample containing one layer



ii. Removal from a sample containing two layers.

Figure 2-1 Relative locations of solvent extracted samples within the glass moulds

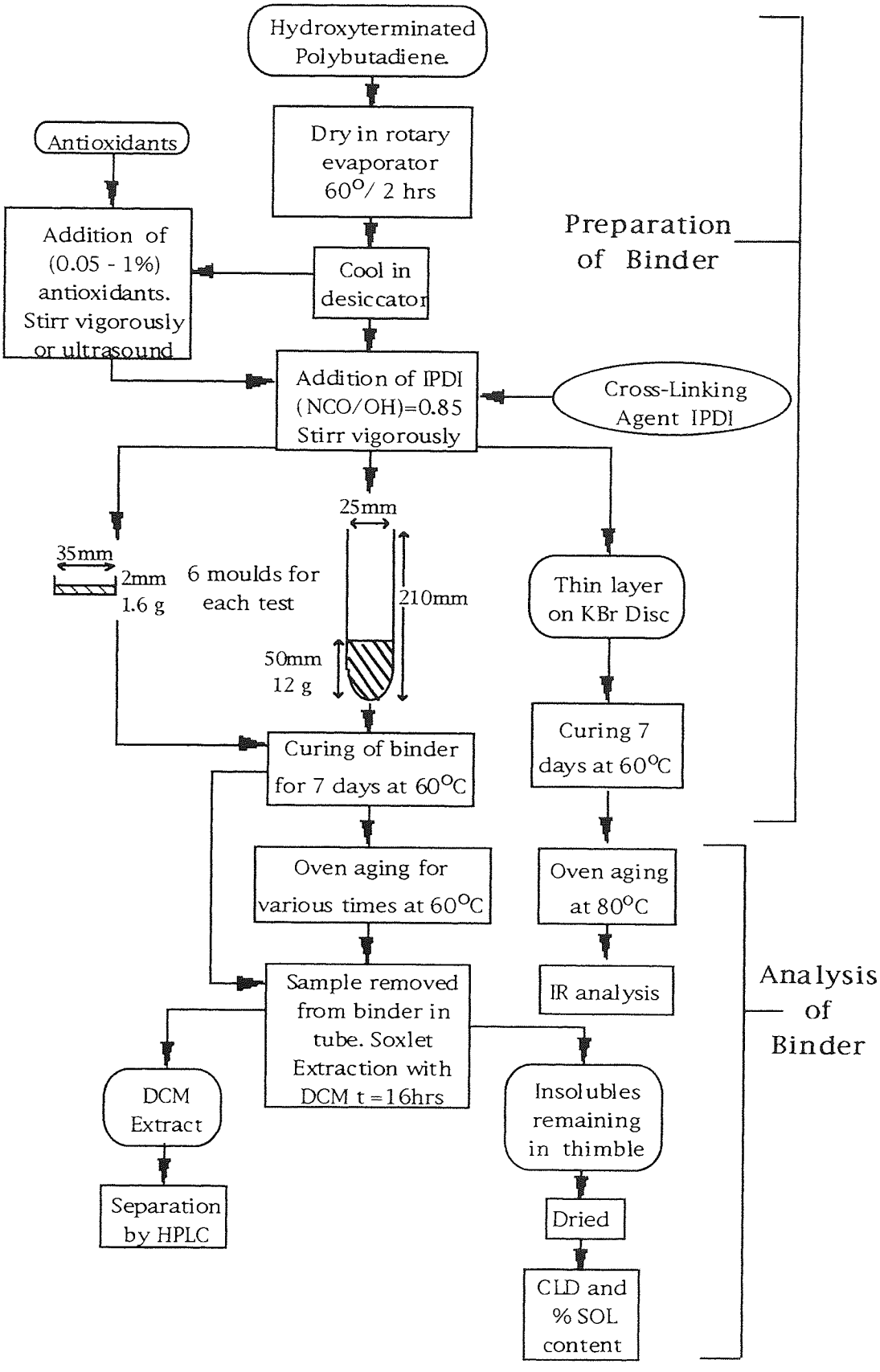
2.3.1 Method of Infra Red Analysis of Samples.

Thin layer samples prepared on KBr disks were cured at 60°C then aged at 80°C. After curing infra red analysis was performed on the samples then at various times during ageing. Peak areas were measured using the Perkin Elmer IRDM software provided with the Infra Red instrument's control software. After conversion of the spectra into absorbance, points either side of the peak of interest were marked on the spectra. The software then drew a line between the marked points and using this as the baseline calculated the peak area. Table 5 shows the peaks investigated.

Table 2-5 Baselines used for peak measurements

Peak Assignment	Absorption Max. υ^{-1}	Absorption Envelope υ^{-1}
O-H	3300	3650 - 3180
C=O	1700	1800 - 1660
C=C	1640	1655 - 1620
C-H Trans	965	988 - 938
C-H Vinyl	910	934 - 890
C-H Cis	730	760 - 650
Reference Peak	3090	3122 - 3052

To normalize the peak areas a reference peak is used. The peak chosen in this case is a peak corresponding to CH groups in the sample. The area of the measured peaks were divided by the area of reference peak to remove errors caused by variation in sample thicknesses.



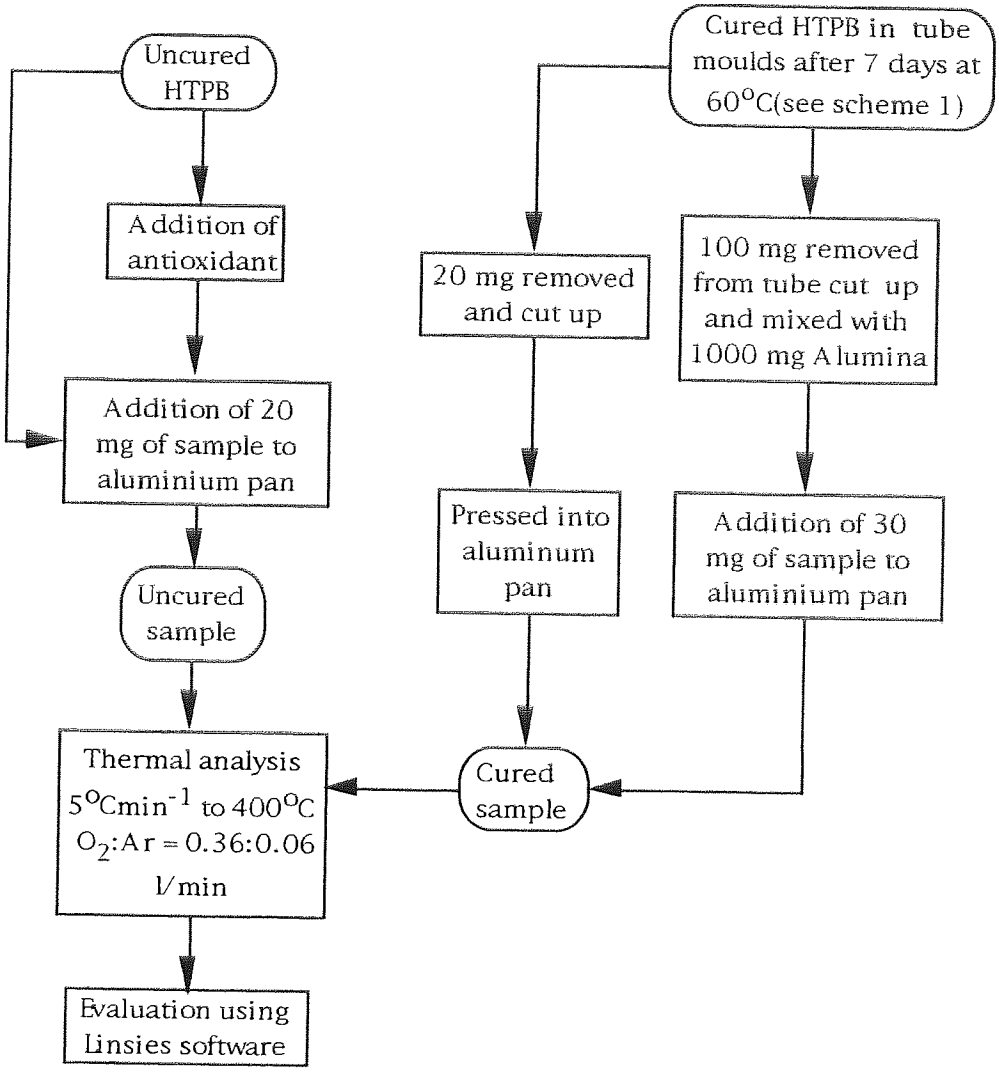
Scheme 2-1 Preparation and measurement of CLD of the binder.

2.4 Rapid Evaluation of Binder Samples Using Thermal Analysis

The instrument used for thermal analysis was a Linseis thermal analyser with thermal gravimetry (TG) and differential thermal analysis (DTA). This had a horizontal balance with a range from 1 to 1000 mg and was controlled by Linseis own software. The DTA used a platinum rhodium thermocouple and a pair of aluminium pans, one as a control the other as a sample container. The conditions used for the dynamic temperature binder analysis were: a heating rate of 5°C per minute up to a temperature of 400°C in a mixed atmosphere of flowing oxygen and argon (0.36 0.06 l/min respectively). Both uncured and cured binder samples were analysed, these were prepared for analysis by different methods. For analysis of the uncured binder the appropriate amount of antioxidant was added to 5 grams of HTPB and was stirred until the antioxidant was well mixed. These samples did not contain the curing agent IPDI and were therefore not cross-linked. 20 mg of sample was then used with no reference material for the thermal analysis. A sample of pure HTPB was also ran under a flowing atmosphere of argon only. Cured samples were prepared by two methods. The first was to take 20 mg of sample from a tube mould and cut it using a scalpel into small pieces, these were then pressed into an aluminium sample pan. The second method was to take 100 mg of cured sample from a tube mould which had been cured for 7 days. This was then cut into small pieces and mixed with 1000 mg of alumina powder. These are ground in a pestle and mortar until a fine consistent powder was produced, i.e. no lumps of binder can be detected. A mass of 30 mg of this powder was then placed into a sample pan which was tapped on the bench 3 times to settle the powder. Alumina powder was used as a reference in the control pan for thermal analysis. Scheme 2 shows the preparation and testing of the samples by thermal analysis.

The analysis of the results produced by all methods was performed using Linseis software. This includes a 'peak evaluation' section which produces an 'onset temperature' which corresponds to the point at which the peak starts to

form. The software also produces other information including 'offset temperature' at the point the peak disappears a 'peak maximum' and a 'reaction temperature'. A peak area was also produced.



Scheme 2-2 Thermal analysis of the binder.

2.5 Method of Preparation and Analysis of Binder Samples Used to Investigate the Reaction Between Isocyanate Cross-Linker and Antioxidants.

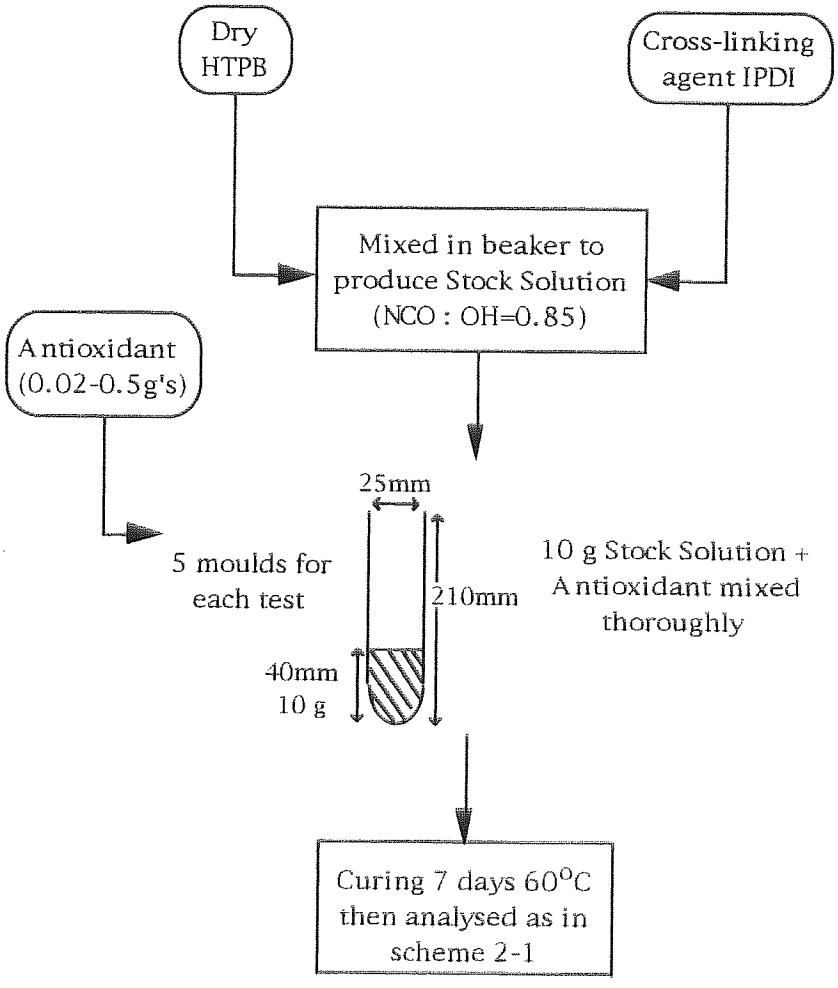
Two separate methods have been used to prepare binder samples for analysis of the effect of antioxidants on CLD. The first involved varying the NCO:OH ratio and keeping to antioxidant concentration constant, in the second method the NCO:OH ratio was kept constant while the antioxidant concentration was varied. After preparation the samples were cured and analysed by the standard method described in section 2.3.

2.5.1 Preparation of Samples with Varying NCO:OH Ratio

For each analysis six NCO:OH ratios were used, each one containing 10 g of HTPB and 0.2% antioxidant, table 6 shows the exact ratios and masses used. Before the preparation all the equipment and chemicals were dried as explained in section 2.2. The antioxidant was then weighed into a test tube to which the dried HTPB was added. This was then stirred vigorously using a glass rod to dissolve the antioxidant before the required amount of IPDI cross-linker was added. The samples were then cured and analysed by the method explained in section 2.3. See scheme 3 for an overview of the preparation technique.

Table 2-6 Quantities required to prepare samples containing varying NCO:OH ratios.

NCO : OH Ratio	Mass HTPB / g	Mass IPDI / g	Mass AO / g
0.6	10.00	0.48	0.0210
0.8	10.00	0.65	0.0213
1.0	10.00	0.81	0.0217
1.2	10.00	0.97	0.0220
1.4	10.00	1.13	0.0223
1.6	10.00	1.30	0.0226



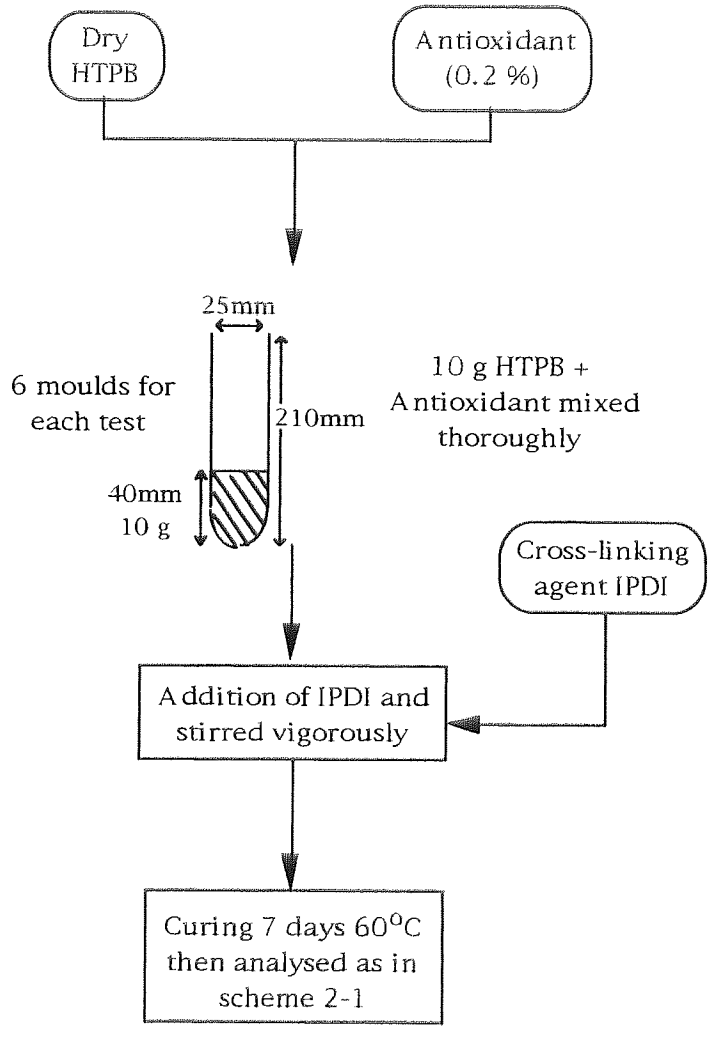
Scheme 2-3 Preparation of binder samples with varying NCO:OH ratios.

2.5.2 Preparation of Samples with Varying Antioxidant Concentration

For each analysis five antioxidant concentrations were used, table 7 shows the exact percentages and masses used. As with other binder preparations all chemicals and equipment were dried before use. Then a stock solution of binder with a NCO:OH ratio of 0.85 was prepared (a typical quantity used; 120g HTPB, 8.28g IPDI). The antioxidant was placed in a test tube and 10 g of the stock binder was added. The samples were then stirred vigorously with a glass rod, cured and analysed by the method explained in section 2.3. See scheme 4 for an overview of the preparation technique.

Table 2-7 Quantities required to prepare samples containing varying antioxidant percentages

% Antioxidant / w/w	Mass Antioxidant / g	Mass of Binder / g
0.2	0.0200	10.00
0.8	0.0800	10.00
1.5	0.1500	10.00
2.5	0.2500	10.00
5.0	0.5000	10.00



Scheme 2-4 Preparation of binder samples with varying antioxidant concentrations.

2.6 Method of Infra Red Analysis of Reaction Between Isocyanate Cross-Linker and Antioxidants

To analyse the reaction between the cross-linker, IPDI, and antioxidants, antioxidant or HTPB was dissolved in 20 mls of spectroscopic grade chlorobenzene in a 2 neck 100 ml flask. In a fume cupboard IPDI (0.3462 g) was added and the solution was then placed in a silicone oil bath at 80°C for up to 8 hours. A magnetic flea was used to stir the solution via a magnet in the oil bath and a condenser was fitted to prevent solvent loss. Samples were then removed from the solution using a syringe which could then be used to inject the sample into a fixed path KBr liquid cell. This was analysed using a Perkin Elmer FTIR. Samples were taken at the beginning of the analysis and then at 1 hour intervals for a period of up to 8 hours. Peak areas were then measured using Perkin Elmer's IRDM Windows software. A sample containing just HTPB with no antioxidant was also ran under the same conditions and used as controls. All chemicals and apparatus were dried fully prior to use. The method for this analysis is shown in scheme 5.

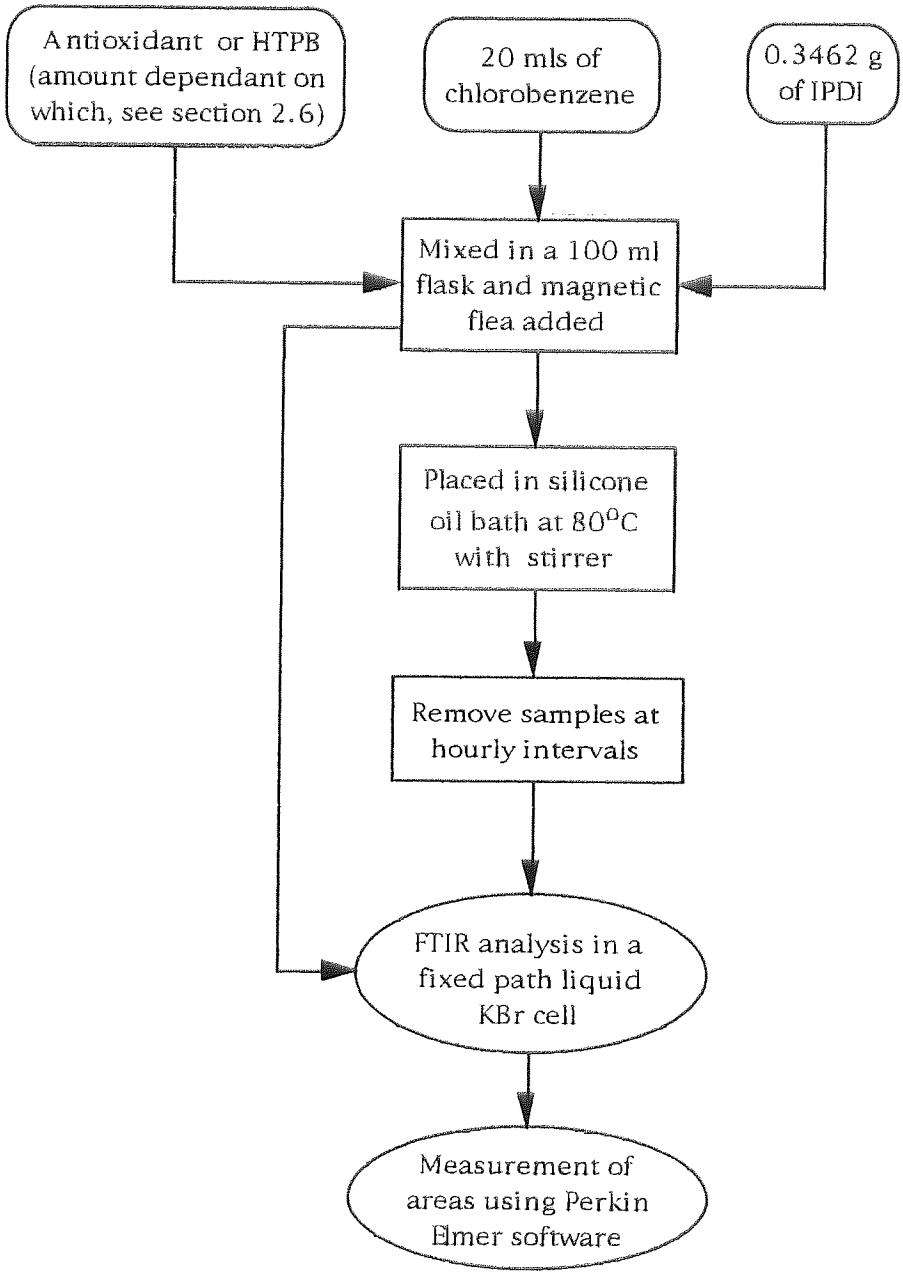
2.6.1 Method of Peak Area Measurement and Peak Ratioing

Peak areas were measured using the Perkin Elmer IRDM software provided with the Infra Red instrument's control software. After conversion of the spectra into absorbance, points either side of the peak of interest were marked on the spectra. The software then drew a line between the marked points and using this as the baseline calculated the peak area.

Table 2-8 Baselines used for peak measurements

Peak Assignment	Absorption Max. υ^{-1}	Absorption Envelope υ^{-1}
NCO	2264	2376 - 2186
CO	1729	1755 - 1675
NH	3431	3480 - 3326
OH	3612	3647 - 3558
Reference Peak	1788	1755 - 1840

To normalize the peak areas a reference peak is used. The peak chosen in this case is present in the solvent and was checked to make sure it did not change during the experiment. The area of the measured peaks were divided by the area of reference peak to remove errors caused by variation in sample thickness.



Scheme 2-5 Analysis by infra red of cross-linker antioxidant interaction.

2.7 Chromatographic Analysis of the DCM Binder Extract

Scheme 6 shows the method of analysis of binder extract by High Pressure liquid Chromatography (H.P.L.C.) The H.P.L.C. analysis was carried out on a Phillips PU4100 chromatograph with a Phillips PU4120 Diode Array Detector. The control of the equipment and manipulation of the results was accomplished using Phillips own Windows compatible software. A gradient elution method shown in table 9 was developed from a method which had been shown to separate a large number of antioxidants [144]. An octadecylsilica (ODS) column (25 x 0.4 cm 5μ), a flow rate of 1 ml/min and a 20μl sample loop were used. A variety of known concentrations of antioxidant standards in acetonitrile (AcN) were analysed in order to produce calibration curves, at a wavelength of 284 nm, so amounts of antioxidant present in samples could be calculated. This wavelength was chosen as it showed large peaks for the antioxidants with the least interference from solvent and HTPB extract (see chapter 5 for further details). The masses and relevant peak areas for Calco 2246 and IPPD are shown in tables 9 and 10 respectively and plots of these values are shown in figures 2 and 3.

Table 2-9 Masses and peak areas related from Calco 2246 standards.

Mass/mg	Calco 2246 peak area (33 min)	Peak A area (35 min)
1.168E-02	514.4	11.725
9.344E-03	411.9	9.1
7.475E-03	337.7	10.1
3.887E-03	210.8	4.5
1.555E-03	68.5	0.34
6.219E-04	27.6	

Table 2-10 Masses and peak areas related from IPPD standards.

Mass/mg	IPPD peak area (24 min)	Peak C area (21 min)	Peak D area (23 min)	Peak E area (26 min)
4.000E-03	810.4	146.3	6.539	30.911
1.600E-03	173.8	71.7	2.086	6.062
6.400E-04	82.9	41.6	0.96	2.225

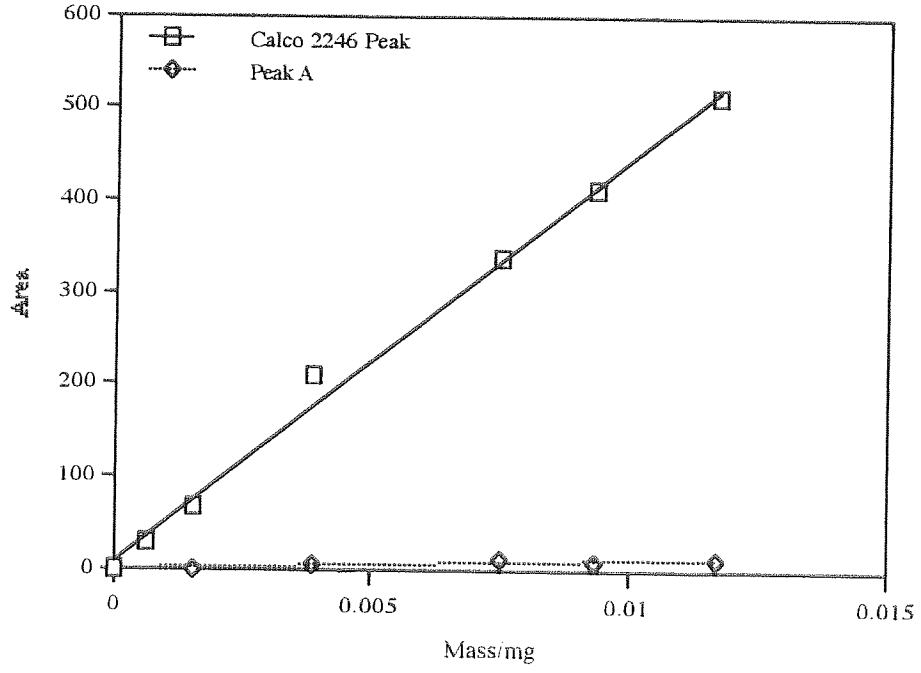


Figure 2-2 Plot of peak areas at 284 nm vs. mass injected for peaks found in Calco 2246 standard.

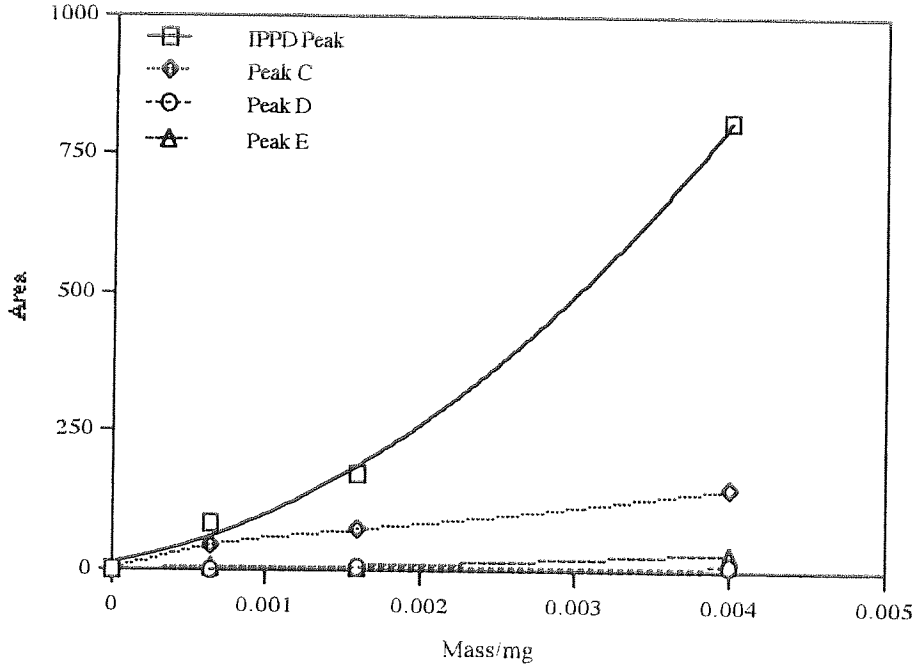


Figure 2-3 Plot of peak areas at 284 nm vs. mass injected for peaks found in IPPD standard.

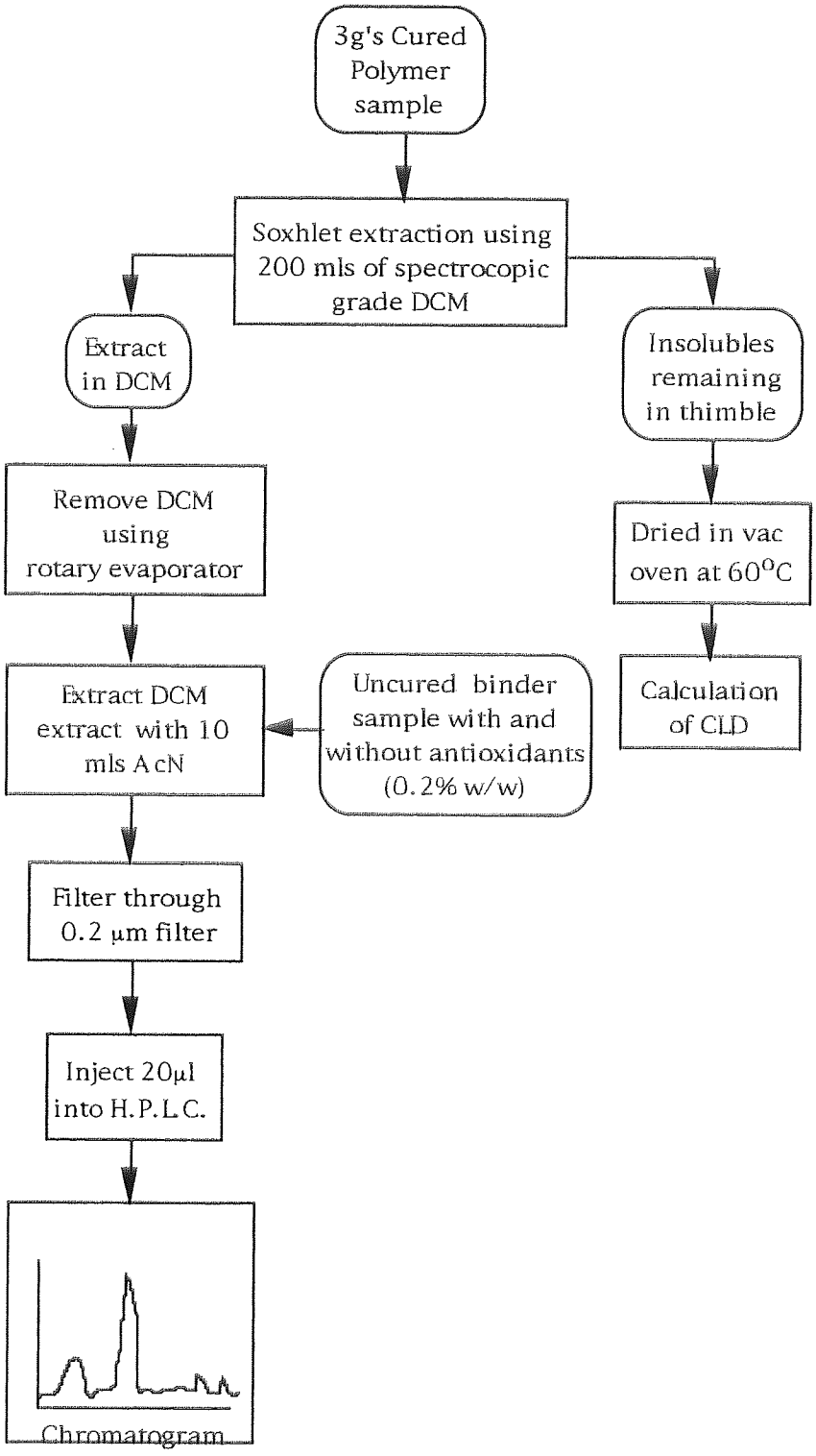
Samples from both cured and uncured binder were prepared. For analysis of uncured binder, a known mass of sample was placed in a vial with a lid and a known volume of H.P.L.C. grade AcN was added. This was then placed on a

shaker for 4 hours. After shaking, the liquid was decanted then filtered through a 0.2 μm PTFE Whatman filter. Known volumes of AcN were then used to rinse out the sample vial and the AcN was then filtered using the PTFE filter. The AcN extracted sample was then stored in the freezer until required for analysis.

Analysis of the cured binder first required the extraction of approximately 3 grams of binder removed from the tubes using 150 mls of H.P.L.C. grade DCM. This was performed in the same way as described in section 2.3 using 250 ml flasks. The extracts from the thimbles (silica, as used in section 2.3) of the same sample were combined and the DCM was removed using a rotary evaporator. Once the sample was completely dry 5 mls of H.P.L.C. grade AcN was added to the flask. The flask was then placed on a shaker for 4 hours after which the liquid was decanted into a sample vial. A further 2 mls of AcN was added and the flask placed back on a shaker for 30 minutes. The liquid was then decanted again into the sample vial and this procedure was repeated for a further 2 mls of AcN. Finally the flask was rinsed using 1 ml of AcN which was added to the sample vial.

Table 2-11 Conditions used for H.P.L.C. gradient analysis.

Time/min	H_2O/%	AcN/%
0	90	10
30	0	100
60	0	100
70 (reset 10 min)	90	10
75 (equilibration 5 min)	90	10



Scheme 2-6 Method of analysis of binder by H.P.L.C.

CHAPTER THREE

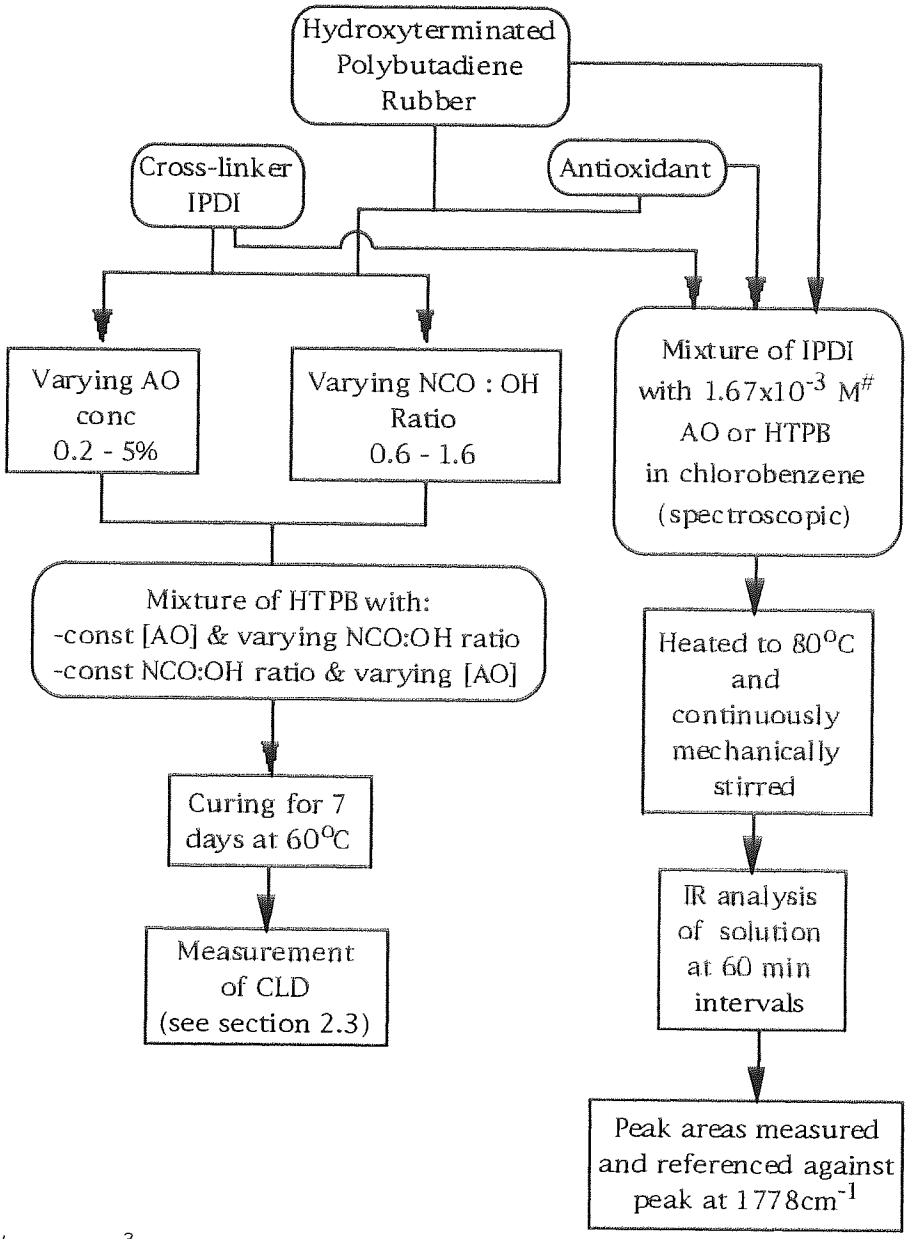
3 INITIAL ANALYSIS OF ANTIOXIDANT SYSTEMS USING RAPID TEST METHODS

3.1 Object and Methodology

3.1.1 Analysis of Interaction Between Antioxidants and the Cross-linking Agent IPDI

A potential problem with the antioxidant systems used to stabilise the binder is the possible reaction of the antioxidant and the cross-linker IPDI. Since the IPDI is designed to react with the hydroxy group in the liquid polymer it may also be able to react with groups present in some of the antioxidants. This could have two unfavourable effects: the production of a binder that does not meet required cross-link density; and/or inactivation of the antioxidant. Factors which affect the possibility of a reaction between the IPDI and antioxidants include the antioxidant's steric hindrance [12], the strength of the carbon bond attached to the active hydrogen in the antioxidant [105] and the nucleophilicity of the group attached to the hydrogen [150]. It was therefore important to assess the likelihood of reactions between the antioxidant (for structures see table 3.1) and the IPDI. This was examined using two methods.

In the first method infra red spectroscopy was used to monitor the changes in functional groups involved in the reactions of polybutadiene or the antioxidant with the cross-linker IPDI in an inert solvent. The second method relied on the analysis of changes in the cross-link density of the binder either in the presence of varying antioxidant concentration or varying cross-linker ratio (for experimental method see section 2.6). Scheme 1 shows the various methods used to assess the effect of antioxidants on the cross-linking reaction.



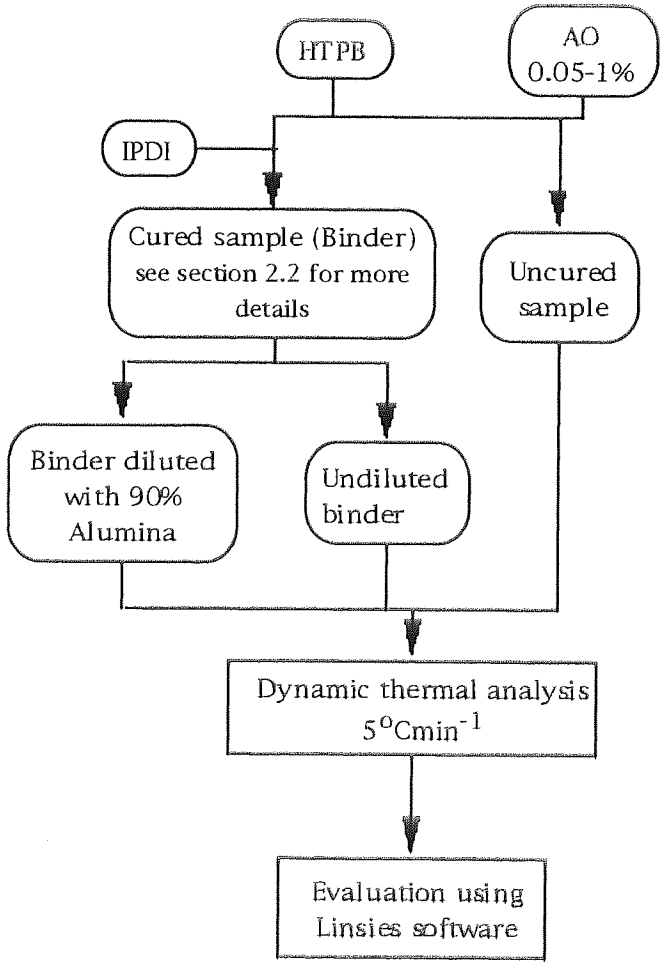
#(1.67x10^{-3} M of HTPB was calculated assuming a molecular mass of 3000.)

Scheme 3-1 Overview of the methods of analysis used in determination of effect of antioxidants on the cross-linking reaction.

3.1.2 Use of Thermal Analysis

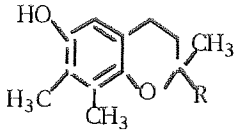
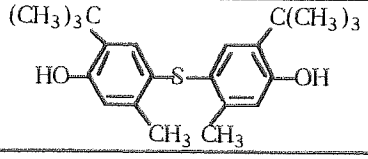
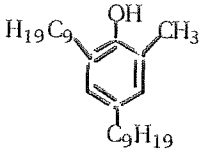
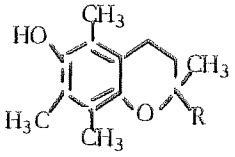
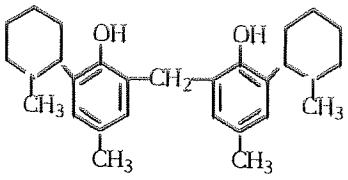
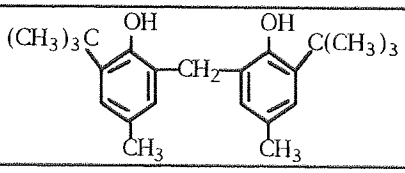
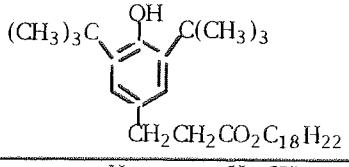
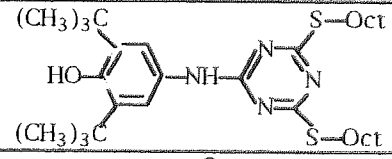
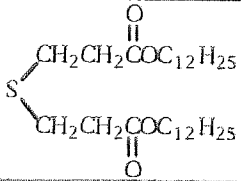
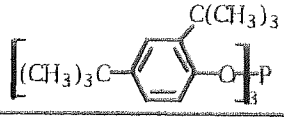
Evaluation of antioxidant effectiveness in polybutadiene has been examined in earlier work [31], using a long term oven ageing technique. It has been suggested [145 - 148] that thermal analysis could be used as a more rapid evaluation method. In most cases this has been performed by either Differential Scanning Calorimetry (DSC) or Thermal Gravermetry (TG) using both isothermal and dynamic heating methods.

The equipment available for this work allowed combined Differential Thermal Analysis (DTA) and TG. This has the advantage of producing results of both sample energy and mass change simultaneously, thus allowing easier interpretation of results. Thermal analysis was performed on both liquid uncured polybutadiene samples (prepared as described in section 2.4) and cured solid binder samples. The cured binder samples were prepared by two methods; in the first method small pieces of samples were analysed with no further treatment, in the second alumina was used as an inert diluent. The diluent was used to produce a more regular surface area to volume ratio for the samples, it also allowed oxygen to diffuse more easily into the samples. The samples were analysed by a dynamic heating method as outlined in section 2.4. Results from these short term analyses could then be compared with results obtained from the long term oven ageing experiments performed in earlier work [31]. Scheme 2 shows the different types of samples examined used thermal analysis.



Scheme 3-2 Overview of the samples analysed by thermal analysis

Table 3-1 Structures of the phenolic and other antioxidants examined for reactions with the cross linker IPDI.

Name	Structure	Active Groups
γ-Tocopherol Two Layers		Phenol
Santonox R Two Layers		Phenol & Sulfur
Santowhite 54 Two Layers		Phenol
α-Tocopherol Two Layers		Phenol
WSP Two Layers		Phenol
Calco 2246 Two Layers		Phenol
Irganox 1076 One Layer		Phenol
IPPD Two Layers		Amine
Irganox 565		Phenol, Amine & Sulfur
DLTP Two Layers		Sulfur
Irgafos 168 One Layer		Phosphite

3.2 Results

3.2.1 Effect of Antioxidants on Cross-Link Density of the Binder

3.2.1.1 Spectroscopic Analysis of Reactions of IPDI with HTPB and Antioxidants

Figure 3 shows the infra red spectrum of the spectroscopic grade chlorobenzene used as solvent during the spectroscopic analysis. Figure 4 shows the infra red of the isocyanate IPDI.

Figures 5 to 14 show both plots of the peak ratios against time and the corresponding IR spectrum for the important peaks in the reaction of IPDI with either pure HTPB or with various antioxidants. These peaks correspond to: the -OH group on the HTPB or antioxidant in the region 3647 - 3558 cm^{-1}; the -NH group on the formed urethane link in the region 3480 - 3326 cm^{-1}; the -NCO group on the IPDI in the region 2376 - 2186 cm^{-1}; the -CO group in the formed urethane link in the range 1755 - 1675 cm^{-1} (see section 2.6.1 for more detail on method of measurement). In all cases the number of active hydrogens available in the solution are equivalent e.g. if an antioxidant has 2 active hydrogens then only half the number of moles was used as an antioxidant with one active site. The experiments were carried out at 80°C in a spectroscopic grade chlorobenzene solution (see section 2.6 for experimental set up).

The values for peak ratios were produced by normalizing the areas of the peaks of interest to a reference peak (1755 - 1840 cm^{-1}) from the solvent on each spectrum. This enhances the accuracy of the results by eliminating refractive index effects. The peak areas were produced using the tangent baseline method [149].

3.2.1.2 Comparison of NCO Peak Ratios

Figures 15 to 17 show the results from the analysis of the NCO peak ratios verses time produced from peak area in the range 2736-2186cm^{-1}.

3.2.1.3 Comparison of CO Peak Ratios

Figures 18 to 20 show a comparison of the results from the analysis of the CO peak ratios against heating time produced from the area of the peak in the range 1755-1675 cm^{-1}.

3.2.1.4 Comparison of NH Peak Ratios

Figures 21 to 23 show a comparison of the results from the analysis of the NH peak ratios against time produced from the area of the peak in the range 3480-3326 cm^{-1}.

3.2.1.5 Comparison of OH Peak Ratios

Figures 24 and 25 show a comparison of the results from the analysis of the OH peak ratios against time produced from the area of the peak in the range 3647-3558cm^{-1}.

3.2.1.6 Effect of Antioxidant Concentration on Cross-Link Density

The fact that all the antioxidant may be removed during Soxhlet extraction with dichloromethane could lead to a lower than actual calculated cross-link density. Figure 26 shows the calculated (from equation 5) predicted theoretical error (assuming no antioxidant polymer bonding) in cross-link density measurement if all the added antioxidant was removed as well as the soluble polymer. If changes greater than this theoretical calculated CLD are observed it is probable that this is due to the antioxidant affecting the cross-linking reaction. Figures 27 to 29 show the effect of increasing the concentration of a variety of antioxidants on the CLD after 7 days curing at 60°C. The level of antioxidant was increased from 0.2 to 5% (w/w).

3.2.1.7 Effect of NCO : OH ratio on Cross-Link Density

Figures 30 to 34 show the effect of changing the NCO : OH ratio from 0.6 to 1.6 on the CLD of the binder. This experiment has been performed in the absence and presence of various antioxidants to examine their effect on the CLD. In a number of samples two distinct layers (see sec. 2.3) were produced as shown in figure 30, in these cases the CLD of both layers were tested and both sets of results are shown.

3.2.2 Thermal Analysis

3.2.2.1 Effect of Atmosphere and Antioxidants on Thermograms

Figures 35 to 45 show thermograms produced from the thermal analysis of both uncured HTPB and cured polybutadiene binder. The thermograms contain a trace corresponding to the DTA analysis (a) and one corresponding to the TG analysis (b). Figures 35 and 42 were performed under an atmosphere of argon whereas the rest were performed under an oxygen rich atmosphere. These are examples of the types of thermograms produced by thermal analysis. Exotherms are recorded on the DTA which correspond to the oxidation of the polymer. Analysis of the exotherms was performed using Linseis software provided. This produced values for peak onset, reaction, maximum and offset temperatures as well as peak area, see figure 36.

3.2.2.2 Comparison of Peak Maximum and Onset Temperatures of Uncured Samples

Figures 46 and 47 and tables 4 and 5 show the effect of various (individual and some mixed) antioxidants have on the 'peak maximum and onset temperatures' observed during thermal analysis. The mechanism of action and type of functional group responsible for the antioxidant activity are shown in the tables. The difference between the two temperatures gives an indication of the sharpness of the exotherm produced which is related to how rapidly the reaction

proceeds once it has been initiated. In these cases the analyses were performed on uncured HTPB containing 0.2% (w/w) antioxidant in figure 46 and table 4 and 0.3% (w/w) in figure 47 and table 5. The results are shown in ascending order with respect to peak maximum temperature. The reproducibility of results from this method is high with an error of only ± 2.5°C as shown on the graphs. These results show that the peroxide decomposing antioxidants are least effective with the chain breaking amines being the most effective.

3.2.2.3 Comparison of Peak Maximum and Onset Temperatures of Cured Samples

Figures 48 and 49 and tables 6 and 7 show the effect of various individual and combinations of antioxidants (0.2 % tot. w/w unless otherwise stated) on the 'peak maximum and onset temperature' observed during thermal analysis of cured polybutadiene samples. The mechanism of action and type of group responsible for the antioxidant activity are shown in the tables. Figure 48 and table 6 show results from analyses of cured samples which were diluted with 90% alumina (see sections 2.4 and 3.1.1). The errors in this method were ± 5 °C due to the production of reproducible surface areas during sample preparation. This has also affected the exotherms making them much larger due to the greater surface area available for reaction. Figure 49 and table 7 show results from cured samples which were prepared without dilution (see sections 2.4 and 3.1.1). The errors produced by this method of analysis were relatively large ± 7.5 °C due to the potential variation in surface areas produced by sample preparation. Again results are shown in ascending order but for the diluted samples onset temperature is used rather than peak maximum due to the change in peak shape. The overall results reveal that peroxide decomposing antioxidants are inefficient stabilisers under these conditions and again the chain breaking ones being the most efficient. Results from mixed antioxidant systems are inconclusive.

3.2.2.4 Change in CLD Measured Using Oven Ageing Techniques

Figures 50 to 53 show results (reproduced from earlier work in our laboratory [31]) of change in CLD during thermal ageing in air ovens with time for various individual antioxidants. They are shown here so that a comparison can be made with results obtained from the thermal analysis used in this work. The antioxidant concentration in all oven aged samples was 0.1% (w/w) and the temperature used for ageing was 60°C (figures 50 to 52) and 70°C (figure 53) [31].

3.2.2.5 Analysis of a Potential Antioxidant Synergistic Combinations

Figures 54 to 56 and table 8 show results from combinations of IPPD and DLTP obtained from various method of analysis. Figures 54 and 55 show the 'peak maximum and onset temperatures' produced by the thermal analysis of uncured HTPB and undiluted cured polybutadiene binder respectively. Figure 56 contains results obtained from earlier work [31] of oven ageing for similar samples. These earlier results suggested the occurrence of synergism with certain ratios of IPPD and DLTP.

3.2.2.6 Effect of Antioxidant Concentration on 'Peak Maximum' Temperature

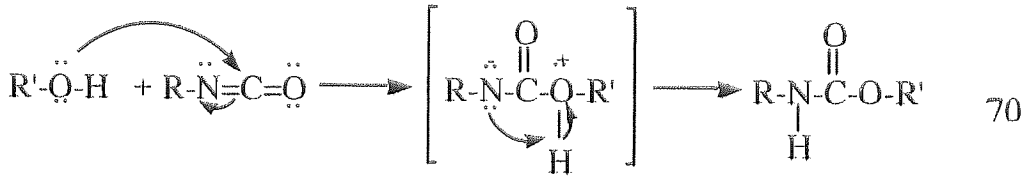
Figure 57 shows the effect of increasing the concentration (w/w) of the antioxidants Calco 2246 and IPPD on the 'Peak Maximum' temperature. All analyses were carried out on uncured HTPB in a flowing mixed atmosphere of argon and oxygen. The amine IPPD has a much greater effect than the phenol Calco 2246, but with both samples concentrations above 0.5% (w/w) produced a disproportionately small increase in stabilisation.

3.3 Discussion

3.3.1 Effect of Antioxidants on Curing Reaction

3.3.1.1 Spectroscopic Analysis of Reactions Occurring Between Antioxidants and IPDI

The formation of the solid binder from the liquid hydroxyterminated polybutadiene is achieved by the use of a diisocyanate as a cross-linking agent [5]. The reaction occurs by a nucleophilic addition, the nucleophilic oxygen on the terminal end of the diol polymer attacking the electrophilic carbon in the isocyanate group (reaction 70).



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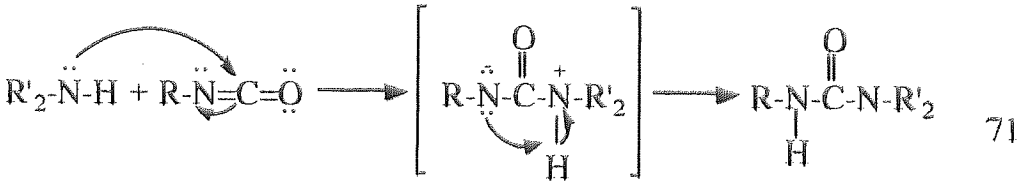
The carbon in the isocyanate is surrounded by two groups which are more electronegative, the oxygen and the nitrogen, these draw electron density from the carbon leaving it susceptible to attack by an electron donating nucleophile. The fact that the attacking species is acting as an electron donor not a hydrogen donor is confirmed by the effect electron withdrawing groups have on the nucleophilic species. These will slow the rate of the reaction by reducing electron density on the active hydrogen site making it a poorer donor [12].

It is known that isocyanates can react with a range of nucleophiles including phenols and amines [13]. The reaction with amines follows the same route as those with the hydroxide but this produces a urea rather than a urethane (reaction 71).



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Urea

Since the chain breaking class of antioxidants have a nucleophilic nature and an active hydrogen there is potential for these to react with the diisocyanate during curing. The general trend in reactivity of isocyanates with a variety of groups is shown below [150].

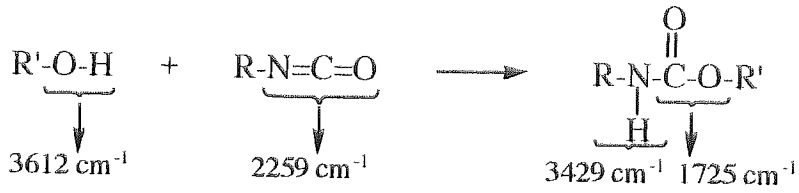
Aliphatic NH_2 .> aromatic NH_2 > primary OH > water > secondary OH > tertiary OH > phenolic OH

A number of experiments have been performed to assess the potentially likelihood of an antioxidant preferentially reacting with the IPDI cross-linking agent. The phenolic antioxidants examined (see table 1 for structures) contained a wide variety of groups surrounding the active OH group thus giving a range of steric hindrance effects. Space filling molecular models were constructed for these phenolic antioxidants, and a qualitative order of steric hindrance around the hydroxyl group was determined as follows:

γ-Toc. < Santo. R < Santo. 54 ≈ α-Toc. < WSP < Calco 2246 < Irg. 1076

Chlorobenzene was selected as a solvent for the spectroscopic analysis as the electron withdrawing action of the chlorine deactivates the ring making it relatively unreactive. However, chlorobenzene has a complex infra-red spectrum (fig. 3) which may be co-incident with other peaks. The cross-linker IPDI has a very distinctive peak corresponding to the isocyanate NCO group at 2260 cm^{-1} (fig. 4). This peak, which is much larger than any other peak in the corresponding region in the chlorobenzene spectrum, is the most important for following reaction of the antioxidants with the isocyanate. As the reaction commences and the isocyanate reacts, the size of the NCO peak is expected to decrease. A decrease in the small carbonyl peak at 1765 cm^{-1} is also expected but peaks in the chlorobenzene spectrum prevent this peak from being observed. If a reaction has occurred between the isocyanate and a hydroxyl group the formed urethane would be expected to show a single peak in the region of 3350 cm^{-1} which corresponds to the formation of a secondary amine [151]. Also, since

the nature of the carbonyl group would change compared to that of an ester, a new peak would be expected in the region of 1730 cm^{-1} [152] but unfortunately chlorobenzene also absorbs in this region (fig. 3) and this may mask the formation of the carbonyl absorption. It may also be possible to follow the disappearance of the OH peak on the group reacting with the isocyanate. Reaction (72) shows the main changes expected in the peaks during the formation of a urethane.



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No reaction took place, within the experimental time, between IPDI and the chlorobenzene solvent used for this investigation (fig. 5), although after two hours a brief increase in the area of both the NCO and CO peak was observed. This brief increase was also observed in a number of other samples and analysis of the infra-red spectra revealed that at this time a new peak on the shoulder of the carbonyl peak appears (see fig. 5e). This peak, at 1715 cm^{-1}, is another carbonyl and since it only occurs occasionally then disappears it is thought to be due to acetone. During the cleaning between analysis, acetone was used as a final rinse for the sealed spectroscopic cell. Compressed air was then used to dry the cell but if any acetone remained this would produce a carbonyl peak at the position found in these experiments, acetone also has a small wide peak at approximately 2200 cm^{-1} which would have caused an increase in the NCO peak.

Analysis of the reaction between the hydroxyterminated polybutadiene and IPDI resulted in a gradual decrease in the NCO peak (fig. 6a and d) from the isocyanate of the cross-linking agent which corresponded to a decrease in the OH peak of the rubber (fig. 6c). This indicates the hydroxyterminated polybutadiene and IPDI reacted to form a urethane (reaction 70), the concomitant increase in NH peak (fig. 6c) and the appearance of a CO (fig. 6e)

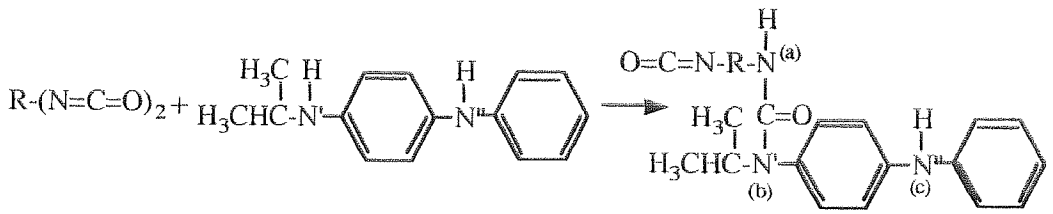
peak at 1729 cm^{-1} is also in agreement with the formation of a urethane. In this case the formed ester carbonyl peak was obvious above the chlorobenzene peak at 1730 cm^{-1}, but also present were peaks at a lower absorption caused by acetone. It can be seen that the reaction proceeded quite rapidly and after the 7 hours of the experiment the peak corresponding to the isocyanate NCO group had reduced considerably (fig. 6d).

Analysis of the results for the various phenolic antioxidants (figures 7 to 13) indicated that there was no reaction between the OH groups of the phenol and the isocyanate during the time of the experiment (7 h at 80°C). Comparison of the peak ratios for the NCO peak, which would decrease if a reaction took place, (fig. 15 & 16) indicates only the hydroxy groups on the polybutadiene has reacted. The decrease in NCO peak observed in the case of Santowhite 54 (fig. 10 and 16) is caused by the presence of acetone as an impurity. This is shown by two effects: since the same ratio of chlorobenzene to IPDI was used for all the samples the peak ratio for the NCO peak would be expected to be the same for all samples and after the initial decrease the ratio of the NCO peak for Santowhite 54 settled to the same level as the other samples; also in contrast to the results from the reaction of the NCO group with HTPB, no gradual increase in the peak corresponding to formation of a carbonyl (fig. 18) or amine was observed which would indicate the formation of a urethane (reaction 70). Further analysis of all the peaks studied (fig. 18 & 19 CO peaks, fig. 21 and 22 NH peak & fig. 24 and 25 OH peak) confirmed that the formation of a urethane had not occurred.

These results may be expected as it is known that phenols react more slowly with isocyanate than aliphatic alcohols [12]. The phenols are stronger acids due to the stabilising effect of the aromatic ring on the phenoxide anion [153], this will tend also to decrease the nucleophilicity of the phenol as the electron density is shared around the benzene ring.

Also the increased steric hindrance of the phenols over the polybutadiene probably has some effect in preventing the formation of the urethane. But, since even the least hindered phenol did not react this probably has less effect than the stabilisation by the aromatic ring.

In previous work the amine antioxidant, IPPD (see table 1 for structure), was suggested to undergo a reaction with IPDI [31] but no experimental evidence was given. Spectroscopic analysis of a mixture of this antioxidant with IPDI (fig. 14) confirms a reaction did occur as a rapid decrease in NCO peak ratio was observed. In this case instead of urethane being formed an urea is formed (reaction 73) and the corresponding carbonyl peak forms at the lower wavelength 1690 cm^{-1} (fig. 14b).



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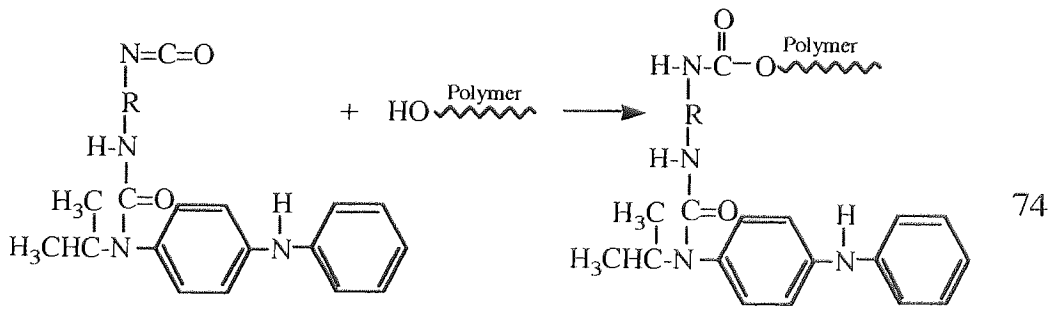
The reaction also creates a new secondary amine (a) a tertiary amine (b) and has a secondary amine (antioxidant functioning) remaining. This makes the interpretation of the infra-red around the amine region complex as secondary amines are both being destroyed in the antioxidant and formed in the urea. The decrease in the concentration of the amine peak analysed (fig. 22) implies that this peak corresponds to the secondary amine on the antioxidant.

Comparison of the rate with which the NCO peak in the isocyanate reduced during the reaction between the amine IPPD and IPDI and polybutadiene and IPDI (fig. 17) showed that the IPDI reacted more rapidly with the antioxidant IPPD than the rubber. Since the O-H bond strength is approximately 361.9 ± 8 $kJmol^{-1}$ and the amine approximately 368.2 ± 8 $kJmol^{-1}$ (N-H bond in aniline) [154] this would have had little effect on the reaction. Both the amine and the aliphatic hydroxyl groups are relatively unhindered so

steric effects are also unlikely to have been important. This suggests that the amine acts as a stronger nucleophile than the aliphatic alcohol with its increased base strength [155]. The initial reaction with the IPPD may be expected to occur via the amine with the aryl alkyl substituents (reaction 73) as the electron pair is less stabilised than by the two aromatic groups.

This suggests that IPPD would not be an effective antioxidant for the cured binder as most of it would be destroyed during the curing process of the binder. However earlier experimental work [31] reported that IPPD was as effective as the commercial hindered phenol Calco 2246. This may be explained if the reaction between the IPPD and IPDI cross-linker occurred as in reaction 73 above. This may cause the urea group to become bonded to the polymer via the second isocyanate (reaction 74), this bonded group would still have antioxidant properties as the NH between the aromatic rings, which is the active centre in preventing oxidation [105] is more likely to remain intact due to its lower nucleophilic nature.



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3.3.1.2 Effect of Increasing Antioxidant Concentration on Cross-Link Density

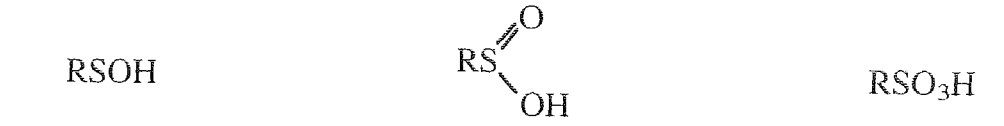
The spectroscopic analysis of mixtures of antioxidants and IPDI indicated no reaction occurred between the phenolic antioxidants and the cross-linking agent IPDI in an inert solvent (section 3.3.1.1). In the case of the aromatic amine, a rapid reaction occurred with the cross-linker IPDI to form urea (reaction 71). To see if similar results were obtained during real binder

preparation, where antioxidant transformation products could also be present, the effect of increasing the antioxidant concentration on the binder cross-link density was examined. If the active groups on the antioxidant reacted more rapidly than the hydroxyl groups on the polybutadiene with the cross-linker IPDI, then increasing the antioxidant concentration should lead to a reduction in the CLD of the binder. A slight decrease in measured CLD with increasing antioxidant concentration would be expected because the antioxidant will be extracted along with the soluble polybutadiene during measurement of cross-link density (see section 2.3). The effect is similar for a range of starting CLD (fig. 26) thus even if no reaction is occurring between an antioxidant and the cross-linker a decrease in observed CLD is expected.

A number of antioxidants were analysed with concentrations in the cured binder varying between 0.2 and 5% w/w. In the spectroscopic results discussed in section 3.3.1.1 it was shown that phenolic antioxidants do not react with the cross-linker but an amine containing antioxidants do react. This is in agreement with that observed when the effect of antioxidants on the curing of the full binder was investigated (see figs. 27 to 29). In fact it is clear that at high concentrations of the amine antioxidant IPPD the curing of the binder is prevented, this concurs with the observation made in the previous section (3.3.11) that the rate at which the amine reacts with the NCO in the isocyanate is more rapid than the hydroxyl on the polybutadiene.

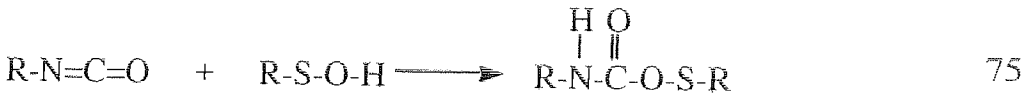
Two peroxidolytic antioxidants, a sulfur based antioxidant DLTP and a phosphite ester, Irgafos 168, (for structures see table 1) which were not analysed by the spectroscopic method were analysed in the binder (fig. 29). The mode of action of both is mainly one of peroxide decomposition rather than hydrogen donation (see section 1.5.3.2 for further information). In the case of DLTP there is no active hydrogen available but Irgafos 168 does contain hindered phenol groups. As with the other hindered phenols no decrease in CLD would be expected by reaction of the antioxidant with the cross-linker, this is not the case

with the sulfur containing DLTP antioxidant (fig. 29 vs. 26). It is well known [130] that transformation products of sulfur containing antioxidants are the main peroxidolytic catalysts. The transformation products of the sulfur compounds such as DLTP have been shown to include [130] various thio acids including sulfenic, sulfinic and sulfonic acid.



Sulfenic acid Sulfinic acid Sulfonic acid

These species contain an active hydrogen and thus could react with the NCO group in the isocyanate cross linker (reaction 75).



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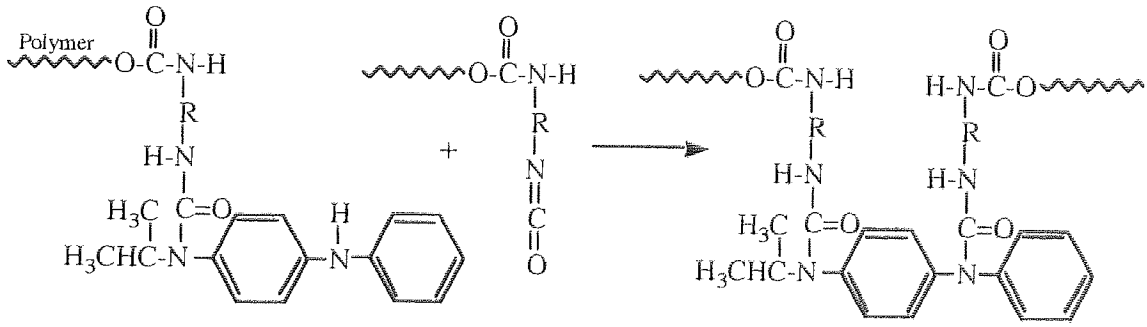
The more acidic, thus less nucleophilic, nature of these sulfur acids compared to the hydroxyl groups in the polybutadiene would suggest that the effect on CLD would not be expected to be as dramatic as that of the amine. However since the thiol acid products are expected to take time to form, even in the presence of very high concentrations of the original antioxidant, their amount is not high enough to react with all the added cross-linker.

Another antioxidant which causes a decrease in the binder CLD is the autosynergist Irganox 565 (for structure see table 1). This molecule contains a number of moieties including both sulfur and an amine. The amine is surrounded by two aromatic groups which would suggest that it would react less with the isocyanate than with the alkyl aryl amine present on IPPD due to the extra stabilisation of the nitrogen lone pair. The presence of the sulfur group in the molecule could also lead to the formation of transformation products which could react with the isocyanate as discussed above. These two factors, although

having a lesser effect than the amine IPPD, do seem to have a small effect on the formation of the cross linked network of the binder.

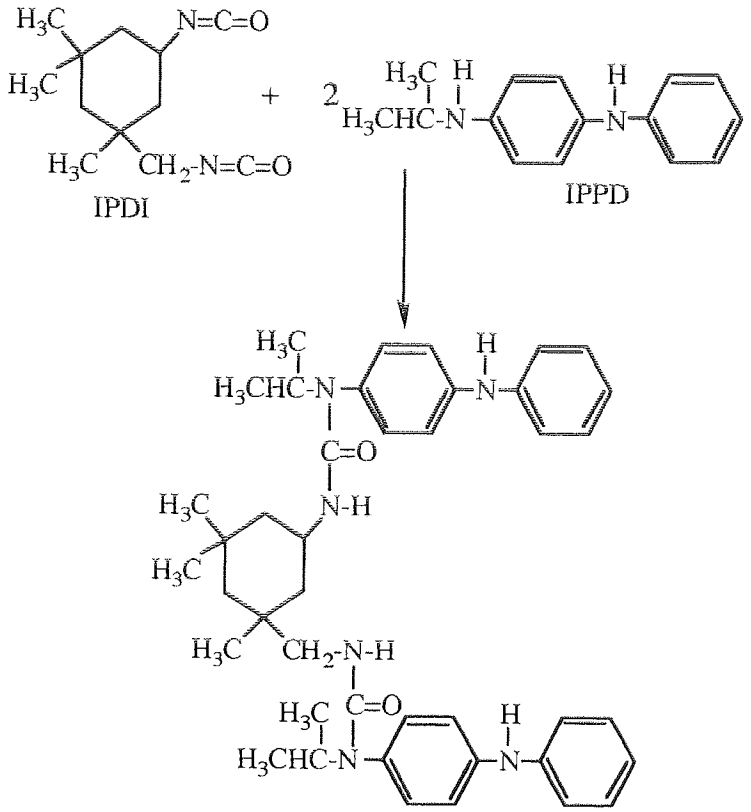
Since the antioxidant is used at a concentration of no higher than 1% in the real binder system [3] it is clear that the only antioxidant which will have any effect on initial binder CLD is the amine IPPD (fig. 29). The actual effect in this work where 0.2% was generally used is expected to be minimal. What is of much greater importance is the effect the reaction of the amine with the isocyanate has on IPPD's effectiveness as an antioxidant. As was discussed earlier the IPPD was found to have an antioxidant effect during oven ageing [31]. Under normal binder preparation, with a NCO:OH ratio of 0.85, 0.031 moles of IPDI would be used per 100 g of binder. It is clear that when using up to 2.5 % (or 0.011 moles) of IPPD that there is still sufficient IPDI in the pre-binder mixture to react with all the IPPD and then promote a degree of cross-linking. Thus at 0.2 % IPPD where only 0.0009 moles are present this would be expected to react fully with the IPDI with enough IPDI remaining to complete the cross linking reaction. This is observed (see fig. 29). The results from this analysis also support the suggestion that only one of the two amine groups in the IPPD molecule react with the isocyanate to leave the active antioxidant amine site available to provide some oxidative stability. If both groups react cross linking would still occur with IPPD acting as a 'chain extender' (reaction 76).



76

This would not be expected to lead to such a rapid decrease in binder CLD with increasing IPPD concentration thus the IPPD must be acting as a chain terminator. Below a ratio of about 0.7 NCO:OH [3] (see section 3.3.1.3) too few

cross-links are formed to prevent the binder being completely dissolved during extraction. Table 2 shows the calculated remaining NCO:OH ratio after either: one molecule of IPPD reacts with two of IPDI (reaction 76); one molecule of IPPD reacts with one of IPDI (reaction 75); two molecules of IPPD react with one of IPDI (reaction 77).



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From the table it can be deduced that if one mole of IPPD had reacted with two moles of IPDI (reaction 76) then the binder would be expected to become completely soluble between 0.2 and 0.8 % IPPD as it is between these points that the theoretical NCO:OH ratio drops below 0.7. Similarly if one mole of IPPD had reacted with one mole of IPDI (reaction 75) the binder would be expected to become completely soluble between 0.8 and 1.5 % and finally if two moles of IPPD reacted with one mole of IPDI (reaction 77) then the binder would be expected to become completely soluble soon after 1.5 % of IPPD was added. This suggests that two molecules of IPPD react with each molecule of IPDI where the initially added concentration of IPPD is high enough. At lower concentrations, some IPPD may become bound to the HTPB (reaction 75) as

there may not be a second molecule of IPPD available to bind to in close proximity to bind to the second NCO group.

Table 3-2 Theoretical effect of increased IPPD concentration on NCO : OH binder ratio.

% by mass IPPD added	No. of moles IPPD Added / 100g HTPB	Initial no. moles IPDI / 100g HTPB	No. moles IPPD react with each IPDI	Theoretical no. of moles IPDI remaining	Theoretical remaining NCO:OH ratio
0.2	0.0009	0.0311	0.5	0.0293	0.80
			1	0.0302	0.83
			2	0.0306	0.84
0.8	0.0036	0.0311	0.5	0.0239	0.67
			1	0.0275	0.75
			2	0.0292	0.80
1.5	0.0067	0.0311	0.5	0.0176	0.48
			1	0.0243	0.68
			2	0.0277	0.76
2.5	0.0113	0.0311	0.5	0.0084	0.22
			1	0.0197	0.54
			2	0.0254	0.69

3.3.1.3 Effect of NCO:OH ratio on Cross-Link Density

It has been shown that there is a strong relationship between initial binder cross-link density and NCO:OH ratio [5] (fig. 1). Below a ratio of approximately 0.7 the concentration of NCO groups is too low to produce a cross-linked gel, above a ratio of 1.5 there are too many NCO groups available. This excess of NCO groups means that a high proportion of the diisocyanates will react with only one polybutadiene hydroxyl group leaving many polybutadiene molecules terminated with isocyanate groups with no other hydroxyl group to react with, this will reduce the number of cross-links.

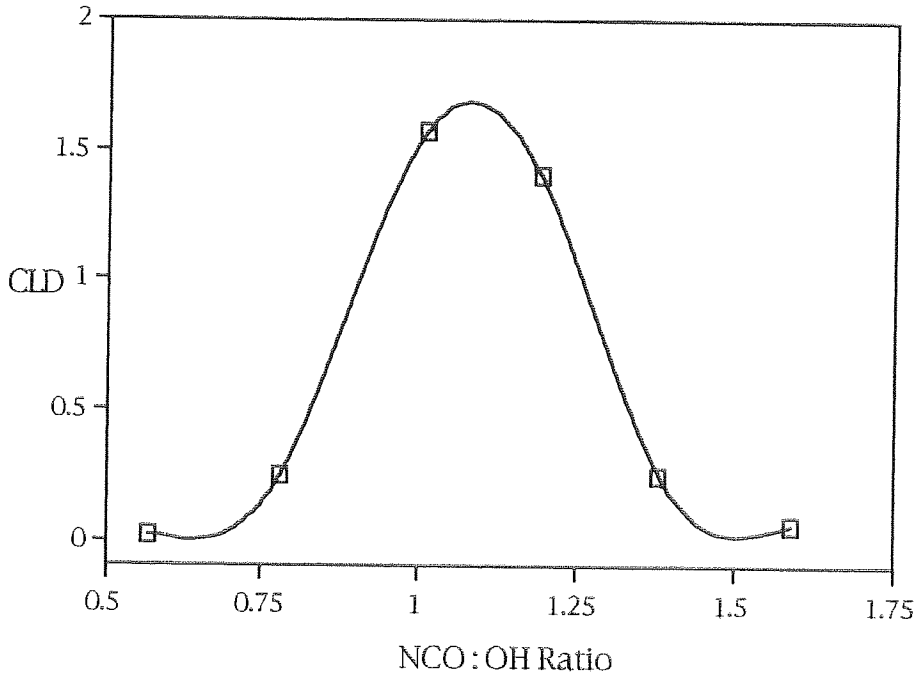


Figure 3-1 Theoretical effect of varying the NCO:OH ratio on binder cross-link density.

An investigation into the effect of antioxidants on this relationship was performed as it would be expected that the ratio at which cross-linking would occur would be higher if the antioxidant reacted with some of the isocyanate. The initial sample prepared containing no antioxidant produced the expected graph (compare fig. 1 with Pure HTPB in fig. 30). In both this and previous work [31] samples with no antioxidant prepared in deep tube moulds were found to be homogenous. In this work, it was found that in samples containing certain antioxidants two distinct coloured layers formed (samples which formed 2 layers are indicated in table 3). These layers had not been mentioned in earlier work [31] but this may have been due to the types of moulds used to prepare samples in that work where binder samples containing antioxidant were prepared in thin layers (approx. 5 mm thick) in small plastic petri dishes, in which the two layer may not have been observed.

Table 3-3 Analysis of percentage occurrence of two layers for different antioxidants.

Antioxidant	Active Group/s	No. times used over or equal to 0.1 % (w/w) in binder	Percent of times two layers formed	No. times used under 0.1 % (w/w) in binder	Percent of times two layers formed
Calco 2246	Phenol	14	75	13	8
WSP	Phenol	1	100	2	0
α-Tocopherol	Phenol	4	75	2	0
γ-Tocopherol	Phenol	4	0	1	100
Santonox R	Phenol & Sulfur	3	0	2	0
Irganox 565	Phenol Sulfur & Amine	4	0	2	0
IPPD	Amine	22	9*	5	0
DLTP	Sulfur	7	14*	12	9
Irgafos 168	Phosphite	5	0	1	100
Irgafos 626	Phosphite	4	75*	3	66

Results taken from samples prepared for oven ageing in chapter 4 and are for mixed as well as single systems. (* The two layers always occurred in mixed samples with low levels of phenols present.)

For the samples in which no layers could be observed the variation in CLD with NCO:OH ratio was similar to that of HTPB containing no antioxidant (compare Pure HTPB fig. 30 with Irg. 1076 fig. 31 and Irgafos 168 fig. 34) It was also shown that for samples containing no antioxidant [31], below a highly cross-linked thin surface layer, the CLD is constant. These two results are in agreement with the results produced by the experiments reported in the previous sections suggesting the antioxidant has no effect on the cross-linking reaction. The CLD of the samples containing two layers was measured for both layers and the results showed that in most cases the layers were different not only in colour but also in their physical properties (see figs. 30 to 34).

In the samples where two layers were formed, both layers show a variation in CLD with NCO:OH ratio of a similar shape to the pure HTPB sample but the peak cross link density occurs at a higher ratio in the upper layer than in the lower layer (see fig. 31), the shift in CLD peak also looks to be

symmetrical around a NCO:OH ratio of approximately 1.15. This is close to the peak observed for samples containing no layers (e.g. pure HTPB fig. 30). These results suggest that the difference in CLD is caused by the polybutadiene isocyanate mix being destabilized by the presence of the antioxidant. This would lead to the isocyanate sinking as its density (1.058 g/cm^2 [139]) is greater than that of the polybutadiene rubber (0.87 g/cm^2 [138]). This sinking of the IPDI into the lower layer would account for the differences in observed relationship of NCO:OH ratio to CLD. In the lower layer a higher concentration than expected of IPDI would be present for a homogeneous sample, thus the CLD peak would appear earlier. In the upper layer, where there would be a lower concentration of IPDI than expected, the peak would appear later. In line with the experimental results the two peaks would be expected to be symmetrical about a central point as the increase in concentration in the lower layer would be equal to the decrease in concentration in the upper layer. These results indicate that although the antioxidants in most cases are not actually reacting with the curing system they are interfering with it.

Further work (see table 3) has shown the formation of two layers occurs most often in binder samples containing hindered phenol type antioxidants, in fact the formation of two layers was never observed unless a phenolic antioxidant was present. In the case of the amine IPPD (fig. 34) the difference between the CLD of the two layers was only small and other samples prepared (see table 3) suggest the formation of two layers is uncommon with this antioxidant.

The reason for this 'destabilization' of the polybutadiene isocyanate mix by phenolic antioxidants is not fully understood. The fact that the very hindered Irganox 1076 (fig. 32) did not form two layers suggested the destabilization may be caused by hydrogen bonding between the hydroxyl group on the polybutadiene and the phenol (fig. 2). This could retard the reaction between the

isocyanate and the polybutadiene allowing the isocyanate which is a much polar molecule to separate and sink.

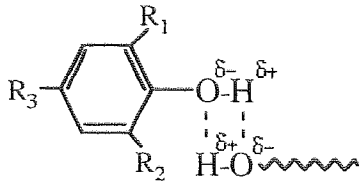


Figure 3-2 Hydrogen bonding between hydroxyl groups of polybutadiene and antioxidants.

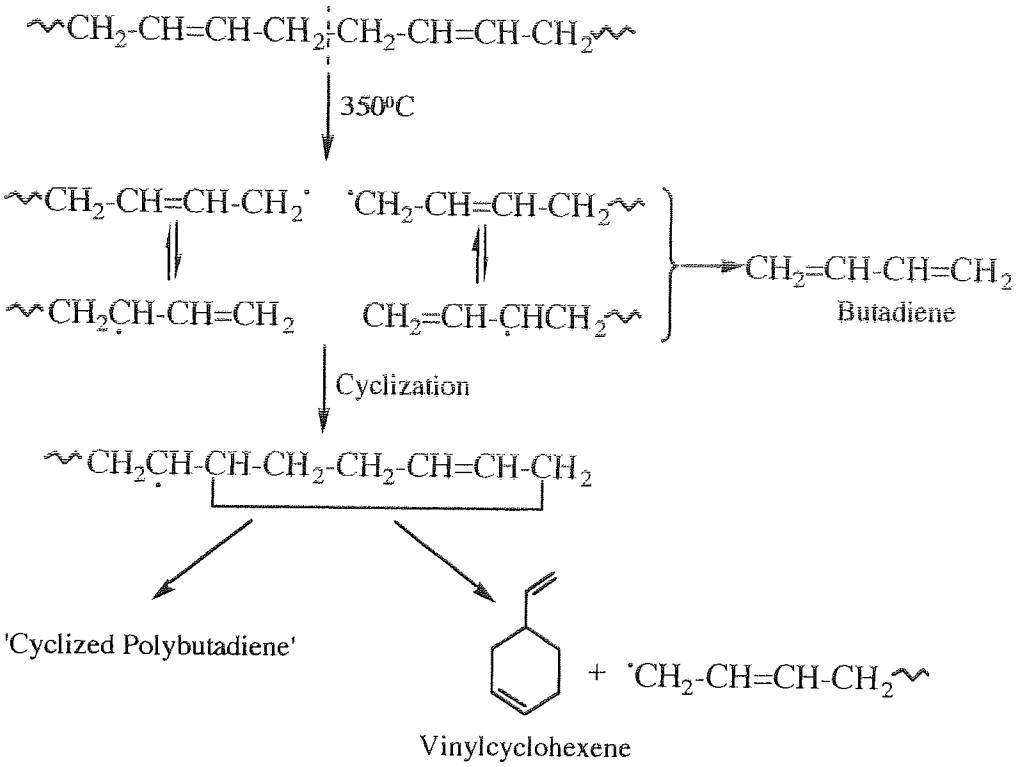
In the full propellant system the high level of filler (90%) in the binder [1] will probably mean the separation of the IPDI and polybutadiene would not occur.

3.3.2 Assessment of Thermal Analysis as a Rapid Screening Technique for Antioxidant Effectiveness

3.3.2.1 Interpretation of Thermograms

A marked difference was observed between the thermograms of uncured liquid HTPB in argon and oxygen rich atmospheres in both DTA (a) and TG (b) traces (compare fig. 35 & 36). Under an argon atmosphere both DTA and TG traces show no thermal events below 280°C after which an exotherm and a corresponding loss of 10 % of mass were observed (fig. 35). This is in agreement with observations made by other workers [79, 156-158] and appears to be independent of polybutadiene microstructure [156]. The exotherm is due to a positive energy balance from endothermic depolymerisation and cis trans isomerism and exothermic cyclization and cross-linking [156, 158]. The heating rate can alter the percentage of mass loss during this stage from 10% at 5 to 10°C/min to 50% at 100°C/min [156]. This is thought to be due to the amount of cross-linking which occurs during the heating of the sample, the slower the rate the greater the time allowed for cross-links to form [159] which reduce depolymerisation. During this mass loss butadiene and vinylcyclohexene are volatilised [158-160] (scheme 4 [78]). Initiation is due to main chain scission

producing radical chain ends which can then either react to eliminate butadiene or cyclize and then eliminate vinylcyclohexene. They can also abstract hydrogen from other polybutadiene molecules to produce a radical which can attack unsaturation and produce cross-links or cyclization in a typical radical chain mechanism. The saturated cross-linked and cyclized residue degrades at a higher temperature (above 450°C [157]) endothermically to produce a complex mix of products.



Scheme 3-3 Mechanism of polybutadiene degradation during thermal analysis

Analysis of uncured liquid hydroxyterminated polybutadiene in an oxygen rich atmosphere (fig. 36), on the other hand, produces another large exotherm (DTA trace) at about 170°C together with a slight increase in mass. This type of exotherm has been observed in a variety of polymers including carboxyl-terminated polybutadiene [146-148] and has been attributed to oxidation of the polymer. The slight mass increase occurring simultaneously is caused by addition of oxygen to the polymer matrix during the oxidation process. As was discussed in section 1.4.2.2, oxidation of polybutadiene produces similar

products whether it occurs at high (100 to 250°C) or low temperatures, the main difference being the level of peroxides structures [71]. In the case of oxidation during thermal analysis there may be some peroxide build up during the initial heating but these would decompose rapidly above about 90°C. These reactions, if occurring, are doing so at low levels as they are not registered by the thermobalance. At higher temperatures (above 100°C) in the presence of oxygen it is possible for oxidative initiation to occur by direct reactions between hydrocarbons and molecular oxygen (reaction 78) [29].

$$RH + O_2 \longrightarrow R^{\bullet} + {}^{\bullet}OOH \qquad 78$$

Therefore this type of initiation may have occurred during thermal analysis. Once the peroxide radicals have been produced, in the case of a sample with no stabiliser present, it would be expected that autoxidation would proceed rapidly. The mechanism of the propagation may also be affected by the high temperatures involved in thermal analysis as the rate of the abstraction reaction increases more rapidly than that of the addition reaction. Also the reversibility of the addition reaction means at higher temperatures abstraction becomes more prevalent [22].

The atmosphere has no effect on the decomposition of the sample at higher temperature, a similar exotherm at about 360°C leading to a loss of approximately 10 % of mass was observed in samples analysed in argon or oxygen (fig. 34 and 35). This mass loss was also observed by workers studying carboxyterminated polybutadiene who analysed samples after thermal analysis in air and found the samples had also lost most of their unsaturation [146]

The presence of an antioxidant, e.g. Calco 2246, in the uncured liquid hydroxyterminated polybutadiene leads to a shift of the oxidation peak to a higher temperature, the peak also becoming sharper (fig. 37 and 38). This behaviour has been observed by other workers [146-148] and is attributed to the antioxidant delaying the onset of the autoxidation. Since antioxidants prevent

the onset of propagation reactions by reacting with the initiating species (free radicals or peroxides, see section 1.3.1), only when all the antioxidant has been consumed or removed will oxidation occur. The shift in the temperature at which the oxidation peak appears is therefore related to how long the antioxidant remains effective under these conditions. The peak is likely to become sharper if the onset of oxidation is shifted to a higher temperature as even if the same oxidation reactions are occurring they will be more rapid due to the higher temperature. It has been seen that the second peak corresponding to the cross-linking and cyclization shifts to a higher temperature during thermal analysis under nitrogen in the presence of chain breaking type antioxidants [146]. This effect is expected as the chain breaking type of antioxidants will inhibit any free radical reactions. It is noticeable that this shift is not observed in this work for samples analysed under oxygen, this would be expected if the antioxidant was consumed during the initial delaying of the onset of oxidation.

Analysis of cured binder samples in the absence and presence of antioxidants (fig. 39 to 40) showed similar characteristics to those of uncured hydroxyterminated polybutadiene, with an exotherm corresponding to oxidation which occurred at a higher temperature with the addition of antioxidants. The second exotherm corresponding to the decomposition also shifted to a slightly lower temperature although still constant for the cured samples. This is likely to be due to the urethane cross-link formed during curing, these decompose before the polybutadiene [158]. The information from the analysis of cured samples was important as it would show the effect of the curing agent and solid samples on the antioxidants ability to delay the oxidation. It is well known that sample preparation is very important in thermal analysis and the initial analysis of cured samples (prepared as in section 2.4) produced quite high variation in results when compared to those of the uncured samples. This is most likely caused by a variation in surface area to volume ratio with the solid samples which would not occur with the liquid samples.

In an attempt to increase the reproducibility of the cured binder results the use of alumina as an inert diluent (see fig. 42 to 45) was investigated since powdering of samples led to a more regular but larger surface area. Only 1.8 mg of binder the was used (30 mg total sample size) instead of 20 mg used in the absence of diluent, this reduced amount produced a measurable response and use of larger samples produced too vigorous reactions in oxygen. The increase in sample surface area to volume ratio is the reason for the much stronger reaction.

Results of the thermal behaviour under argon of cured binder diluted with alumina showed no obvious exotherms corresponding to either oxidation or decomposition, although mass loss was observed (fig. 42). However when an oxygen rich atmosphere was used for the analysis of diluted (by alumina) cured binder samples both with and without antioxidants (e.g. fig. 43 to 45) the exotherm produced was very different from that produced from the analysis of undiluted cured and uncured samples (e.g. fig. 43 vs. 39 or 36). In the presence of diluent the DTA trace typically showed an exotherm with 2 parts (e.g. fig. 44), the first part corresponds to the oxidation peak since a mass increase is observed at the same time. The second peak occurred in conjunction with a mass loss and was unaffected by the presence or nature of the antioxidants (see fig. 44 and 45). This peak, therefore, is most likely to correspond with the decomposition of the polymer, but as was discussed earlier the presence of the urethane cross-link effects the temperature of decomposition. It was shown that the urethane begins to decompose at temperatures as low as 220°C [158] after which the parent diisocyanates volatilize, the remaining polybutadiene will then act as if it has never been cross-linked. The much increased surface area to volume ratio found in the diluted sample appears to have altered the amount and rate of material volatilised, with a steady loss being observed from 230°C up to 400°C where the analysis ends. This is different from the more sudden mass loss observed in the undiluted cured and uncured samples (e.g. fig. 43 vs. 39 or 36). The amount of mass lost in the diluted samples is also affected by the oxygen atmosphere as in argon a much smaller loss was observed (see fig. 42 and 43).

The diluted samples would allow much easier diffusion of oxygen in and products out, these products may be trapped and further reacted in the undiluted samples.

Another striking difference in the thermograms produced from analysis of diluted samples compared to those from undiluted samples was the effect antioxidants have of the temperature at which the peak occurs. In both cured and uncured undiluted samples antioxidants caused the onset and maximum peak temperatures to shift considerably (see fig. 46 to 48) but with diluted samples there was much less movement in onset temperature although the peak max. temperature changed considerably (fig. 49) altering oxidation peak sharpness (compare fig. 44 with 45). In this case the shift to a higher temperature causing the reactions to proceed more rapidly does not explain the sharper peak, as in the case of pure binder the peak maximum temperature is lower than that of the binder containing 0.2 % of the antioxidant IPPD (fig. 43 vs. 45) although the onset temperature was higher, this will be discussed further in a later section.

3.3.2.2 Comparison of Results Obtained From Thermal Analysis and Oven Ageing

As discussed in the last section and by a number of other workers [145-148] thermal analysis can be used to detect the effect of an antioxidant on the thermal oxidative stability of a polymer. However the usefulness of these results in predicting the long term stability of a polymer has been questioned a number of times [160, 161]. Large discrepancies in the predicted lifetimes between oven ageing and thermal analysis have been noted [161]. Although thermal analysis may have its uses as a method for quality control its use as a method for prediction is limited [161]. A practical reason for this inconsistency is the small size of samples used for thermal analysis, usually less than 20 mg, thus any incomplete mixing will cause discrepancies. Also, bulk polymers may contain random 'weak spots' at which oxidation is most likely to initiate, e.g. remaining catalyst. If these are not included in the thermal analysis sample an over

estimate of the polymer stability's will be obtained [160]. This is generally seen [161]. Another error occurs with the change of state of the sample from solid to liquid during analysis, especially with polyolefins [160, 161]. If the sample is crystalline below the melting point its oxidation rate will be considerably less in this state than in the liquid state during thermal analysis. The reason for this is that the rate of diffusion in the crystalline material is lower than that in amorphous or liquid material. This is due to the higher densities of the crystalline material [28]. Fortunately this is not relevant to this work as even the solid samples were above their glass transition temperature. Physical loss of additive can also affect the long term stability of polymers, this can either occur by diffusion or blooming and is related to the mass and solubility of the antioxidant. These effects will occur gradually over the lifetime of the polymer and thus decrease the real lifetime. They are not likely to occur to the same extent during thermal analysis due to the short analysis time producing artificially high results.

In an attempt to clarify the usefulness of the thermal analysis results from this work, the predictions of effectiveness from thermal analysis were compared to results for oven aged samples from earlier work in this laboratory [31] (fig. 48 to 51). Sample representing each type of antioxidant mechanism were chosen (tables 4 to 8), these are: Chain breaking donor antioxidants which interrupt the propagating radical chain by production of a more stable radical; chain breaking acceptor antioxidants which combine with the alkyl radicals to produce a more stable product; peroxide decomposers which decompose peroxides via non radical pathways to harmless products (see section 1.5.1 for a more detailed information).

It is clear from the thermal analysis of both the uncured polybutadiene and diluted cured binder, that the peroxide decomposer antioxidants are inefficient at delaying the onset of the oxidation (see tables 4 to 6 and figures 46, 47 and 49). In fact with DLTP, a sulfur containing antioxidant (see table 1 for

structure), the temperature at which oxidation occurs is lowered. These results may be expected as it is known that both types of peroxide decomposer, the sulfur containing and the phosphites, are not very efficient antioxidants in the polybutadiene when used alone [31] and although the results from earlier work on oven ageing (fig. 52) do not clearly confirm this further analysis did [31]. In the case of the sulfur containing antioxidants a pro-oxidant stage is often observed during the early stages of stabilisation due to the formation of an alkoxyl from sulfenic acid, an early transformation product (reaction 79). This generation of radicals, which would cause early initiation, could explain the lowering of the oxidation peak.

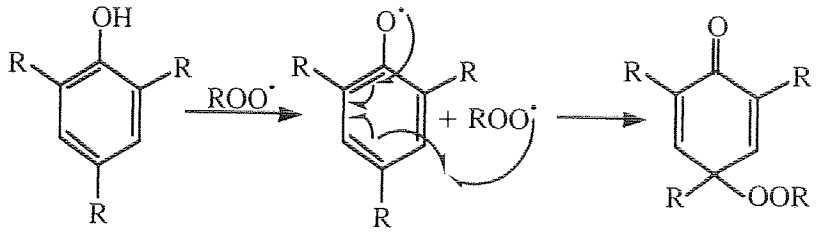
$$ROCOCH_2CH_2SOH + \underset{\text{low level}}{ROOH} \longrightarrow RO^{\bullet} + H_2O + ROCOCH_2CHSO^{\bullet} \quad 79$$

Below is listed the order of effectiveness that chain breaker antioxidants examined in earlier work [31] showed in preventing oxidation during oven ageing tests.

IPPD = Calco 2246 = WSP > Tinuvin 770 > Santowhite 54 > Irganox 1076 > Pure HTPB

This order shows some agreement with that predicted by thermal analysis for both liquid uncured and solid undiluted samples. The results from the diluted cured samples are less easy to interpret and will be discussed further below. The most obvious difference between the predicted effectiveness of the chain breaking antioxidants by thermal analysis and the results of the oven ageing are in the case of the phenyl diamines. These are predicted to be much more effective than any other antioxidants by thermal analysis (see figs. 46 to 49) in this and other laboratories [162]. In general terms aromatic amines have been seen to impart better oxidative protection than phenolic antioxidants [105, 162] due to the mix of high molecular weight transformation products, including nitroxyls, formed, so the results from thermal analysis may be expected. However during oven ageing this much greater effectiveness is not shown by

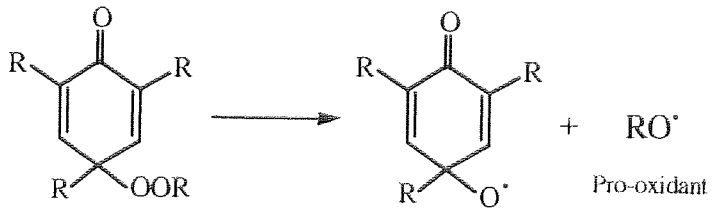
binder samples containing aromatic amines, where the amines are no more effective than phenols (fig. 51). This may be explained by the results from section 3.3.1 which show that the amines are likely to react with the cross-linking agent during curing thus reducing their effectiveness. But even in the cured samples the IPPD delays the onset of the oxidation peak considerably over the best of the phenols Calco 2246 (see fig. 48) which also suggests thermal analysis produces conditions which are particularly unfavourable for phenols. A reason for this may be the formation of peroxydienones as transformation products by the phenols (reaction 80).



Peroxydienone

80

Peroxydienone are formed to some extent by most phenolic antioxidants [163] especially when high $RO_2^{\cdot}$ concentrations are present. In conditions of ambient temperatures and dark they are relatively stable compounds but at elevated temperatures, above 100°C, they decompose to produce initiating radicals (reaction 81) [164].



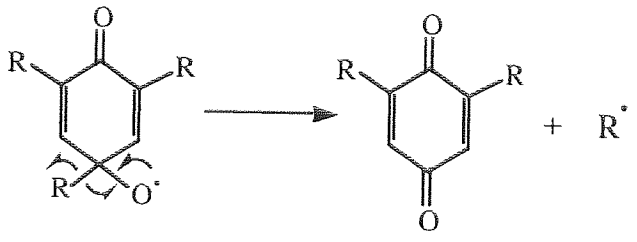
Peroxyidenone

Pro-oxidant

81

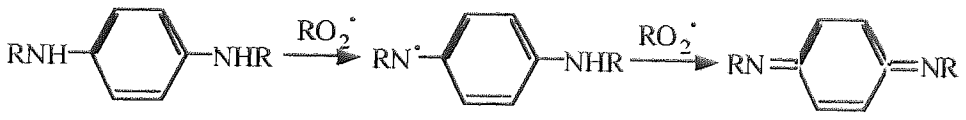
In the case of easily oxidisable substrates such as tetralin initiating effect of can the peroxydienones be stronger than that of dicumylperoxide [164], but in the case of more stable substrates, such as polypropylene, the effect is reduced [112]. In less stable substrates the further antioxidant transformation products from the peroxydienones, such as benzoquinone (reaction 82), are not able in the

time available to build up a large enough concentration to affect the rapid substrate oxidation.



82

But with more stable substrates the general slower rate of initiation will allow the transformation products, which can act as antioxidants, to build up thus inhibiting further oxidation. If very high concentrations of peroxydienones are present they will even have an affect on more stable substrates [124]. Since polybutadiene is quite susceptible to oxidation then it might be expected that peroxydienones formed by early transformations of the phenolic antioxidants will decompose as the temperature of thermal analysis increases to initiate oxidation. In the case of the phenyldiamine used, the initially produced aminyl radical formed, rapidly reacts with another $RO_2^{\cdot}$ to form a benzoquinone diimine (reaction 83) [132] without the production of initiating radicals. Under the gradual heating conditions of thermal analysis the oxygen rich atmosphere allow peroxydienones to build up, these will then rapidly decompose at the higher temperature to cause initiation.



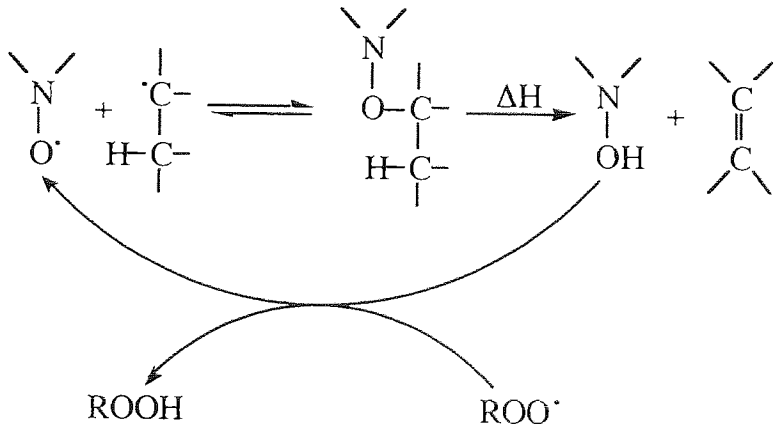
83

Thus rather than the thermal analysis making the phenyl diamines look more efficient than they are at lower temperatures it may be making phenols look less efficient than they would be at lower temperatures.

It would also be expected that the effectiveness of an antioxidant at delaying the onset of oxidation would decrease if the sample was aged for a time

before analysis. This would be due to some of the antioxidant being consumed in stabilisation during the initial ageing. A sample of cured binder, containing 0.2% Calco 2246, tested before ageing and then after ageing at 60°C for 200 days did not show any difference in thermal analysis (fig. 48) even though during this time the increase in cross link density of this sample showed some oxidation had occurred.

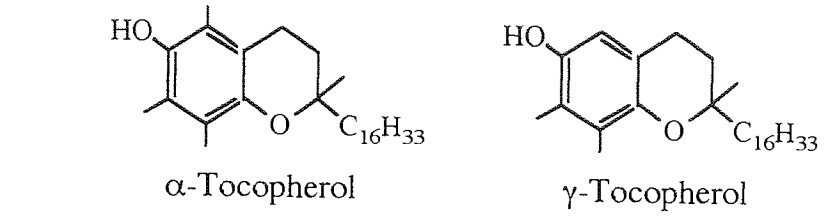
Other results which do show agreement between the oven ageing and thermal analysis are samples containing the chain breaking acceptor antioxidants DMDP-NO· and IPPD-NO· (compare fig. 47 & 53). The formation of nitroxyl radicals as transformation products from amines is thought to be one reason for their effectiveness due to their ability to inhibit radical formation by a cyclic mechanism (scheme 5). It has been suggested that in the case of phenyl diamines the nitroxyls play only a small part and the quinone diimine is much more important [112]. One problem with the prepared nitroxyls is their low solubility in polybutadiene, particularly in the case of IPPD-NO·, which limits their antioxidant ability and may explain the difference between the nitroxyl antioxidants.



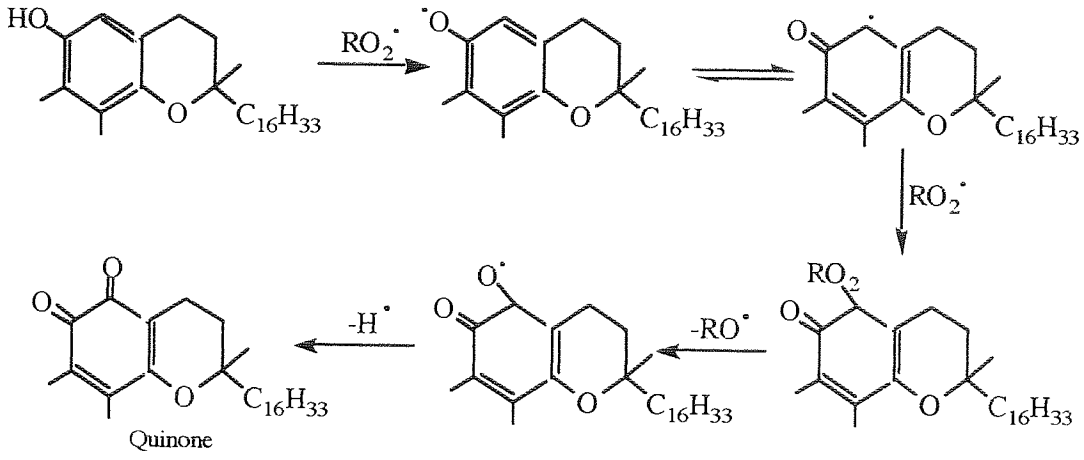
Scheme 3-4 Regenerative mechanism of nitroxyl antioxidants.

Another interesting finding is the greater effectiveness of γ over α-Tocopherol which has been seen with other elastomers during ageing [165]. The difference between these two phenols is the lack of a methyl group ortho to the

phenol. This allows the formation of a quinone (reaction 84) as a transformation product, which has antioxidant properties and explains the high efficiency of the γ-Tocopherol [166].



α-Tocopherol γ-Tocopherol



84

When onset temperatures for thermal analysis of diluted cured samples are compared (fig. 49) some similarities in order of effectiveness to the undiluted samples are seen (fig. 49 vs. 47). Again the peroxide decomposer type antioxidants are the least effective showing a pro-oxidative effect and the amine IPPD is the most effective of the chain breaking antioxidants. But the differences in onset temperatures are much smaller than the undiluted samples and the peak maximum temperatures do not increase with the peak onset temperature (compare Pure Binder i with IPPD on fig. 49). Also, in most cases the difference between the peak onset temperature and the peak maximum temperature is much larger than with undiluted samples. This implies that the oxidation was proceeding much more slowly after the samples were diluted. If this occurred with all samples then diffusion of oxygen to the binder could explain the decrease in reaction rate, but the diluted samples containing peroxide decomposers and IPPD did not show slower oxidation and the method of sample

preparation would not be expected to inhibit the ingress of oxygen therefore this explanation is not valid.

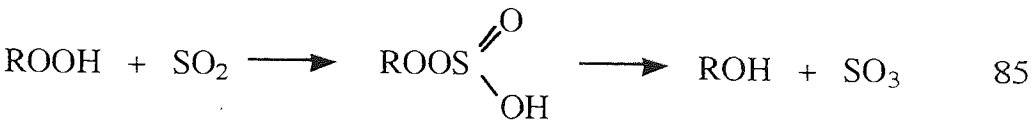
One effect dilution has on the analysis is to dissipate the heat generated by reactions due to the inert material absorbing some of the heat, this means reactions are less likely to accelerate themselves by the heat they generate. This type of problem is more particular to DTA than DSC as in DSC when the reaction generates heat the equipment reduces its heating accordingly to prevent overheating, DTA does not thus 'explosive' reactions can occur as was occasionally observed during the higher temperature decomposition of undiluted samples. Therefore the rates of oxidation observed with the diluted samples may be closer to natural rate without acceleration by the heat generated by the reaction. This suggests that IPPD does retard the onset of the oxidation but once oxidation has commenced the products from the antioxidant promote the oxidation of the binder as do the peroxide decomposer antioxidants as the oxidation occurs more rapidly than the binder containing no antioxidant.

An antioxidant which was suggested to be particularly effective in polybutadiene [167] is the potentially autosynergistic Irganox 565. The thermal analysis of samples containing this and another potentially autosynergistic antioxidant Santonox R (figs. 46 & 47) showed no greater effectiveness over the chain breaker antioxidants containing a single moiety.

Other mixed antioxidant systems which have been seen to show a synergistic effect [31] during oven ageing were the heterosynergistic mixture of IPPD and DLTP at a ratio of 2:1. The thermal analysis of various combinations of these antioxidants was performed both on uncured HTPB and undiluted binder samples (fig. 54 and 55 respectively & table 8). When these results were compared to those from oven ageing in earlier work on similar mixtures (fig. 56 [31]) a number of discrepancies were seen. In the case of the uncured HTPB sample the difference between synergism for the 2:1 IPPD:DLTP ratio and

similar performance to DLTP alone for the 1:2 ratio is not observed and for the cured binder sample no sign of synergism was shown (fig. 55).

This may highlight a general problem with using such an accelerated test to detect synergistic combinations, whether they be of auto or hetero type. It is known [90] that transformation products are very important in dictating the effectiveness of an antioxidant and their interaction with other antioxidants which can produce synergism [135]. There may be insufficient time in this rapid analytical method to allow the important products to form. In the case of mixtures of the chain breaker antioxidant IPPD and the sulfur containing peroxide decomposer DLTP one of the main roles of the IPPD [52] is to suppress the pro-oxidant initial stage of the DLTP. After this the catalytic degeneration of the hydroperoxide by sulfur transformation products can occur. In the case of thermal analysis the pro-oxidative effect seen in samples containing only DLTP (fig. 46, 47 & 49) is removed by addition of even a low level of IPPD. The steadily increasing temperature and conditions of thermal analysis do not allow the co-operative mechanisms to develop. One of the transformation products which is known to be effective in sulfur containing antioxidants at high temperature is sulfur trioxide [134] formed via reaction (85) but this is likely to be lost rapidly during thermal analysis.



85

During thermal analysis the effectiveness of the mixed antioxidant sample is seen to increase more by the increase in IPPD concentration than any co-operative effect.

The difficulty in relating results from thermal analysis to other ageing techniques has been discussed [161] and in this work the results suggest great caution is required. Also the results for the amines IPPD and 6PPD during

thermal analysis are very different from those during oven ageing. The analysis on the solid binders were very inconclusive as was that on mixed samples and it would be unwise to use these results to predict antioxidant efficiency.

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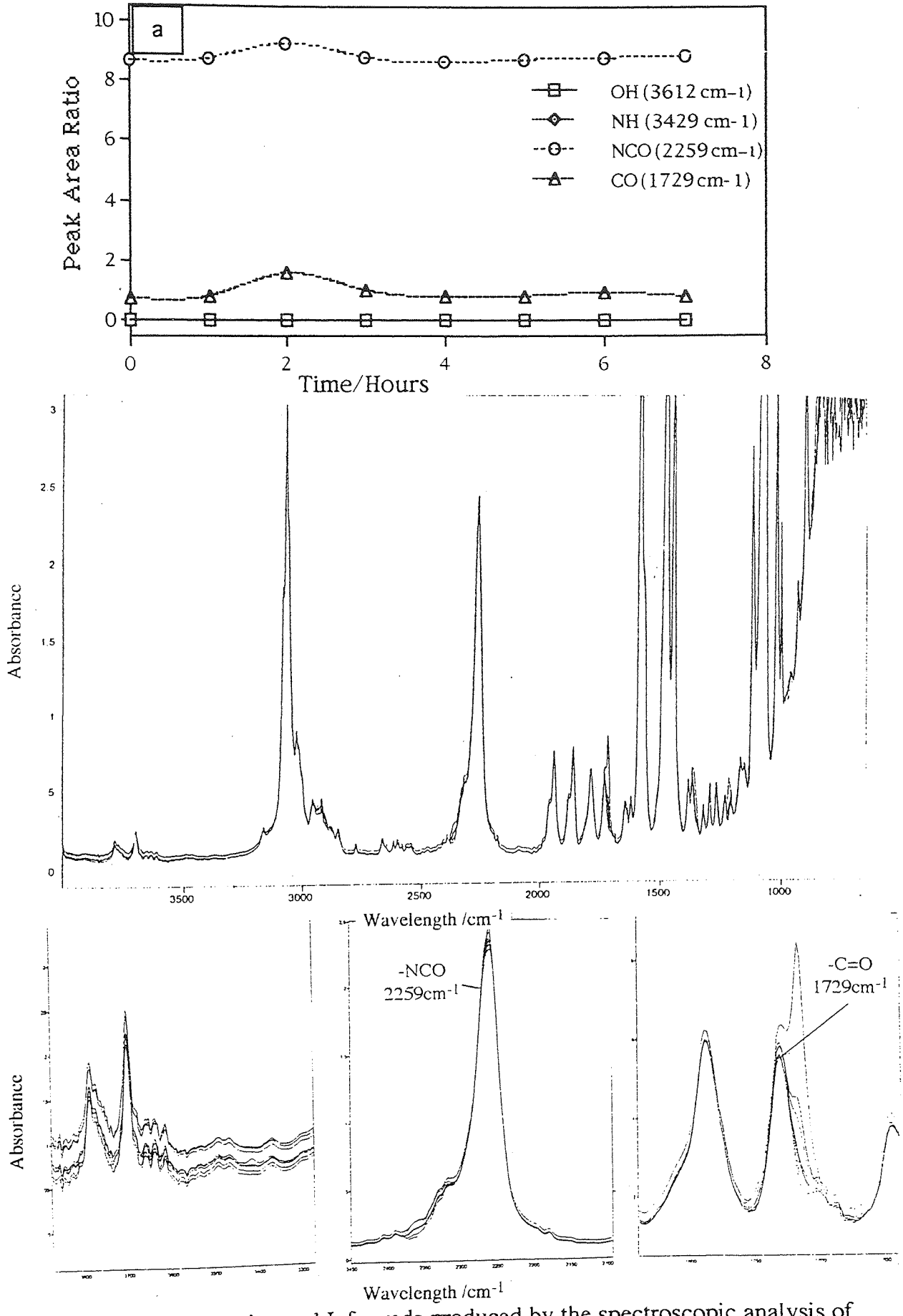


Figure 3-5 Peak ratios and Infra reds produced by the spectroscopic analysis of IPDI (0.3462 g) in chlorobenzene (20 ml) heated at 80°C.

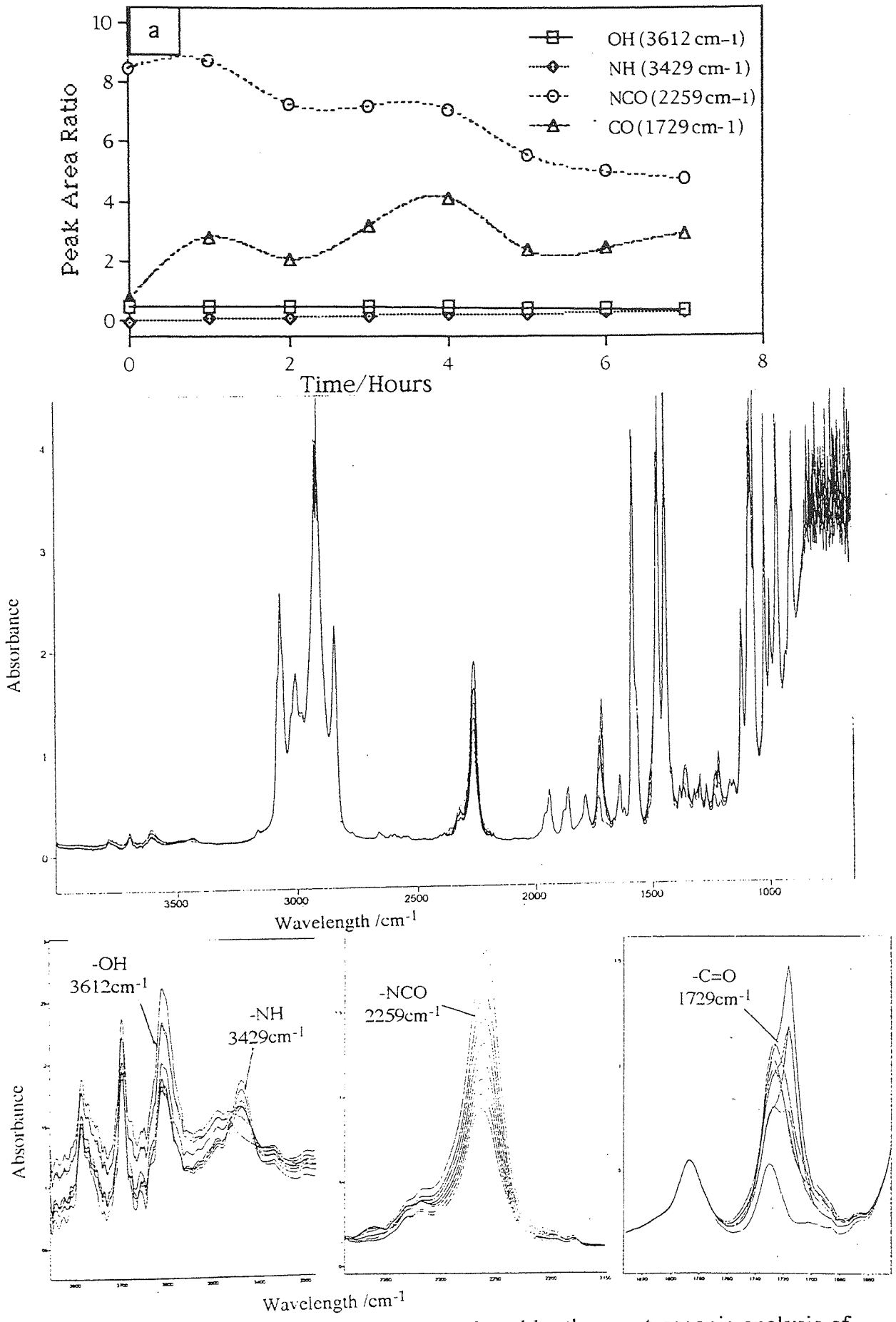


Figure 3-6 Peak ratios and infra reds produced by the spectroscopic analysis of IPDI (0.3448 g) mixed with HTPB (5.0377 g) in chlorobenzene (20 ml) heated at 80°C.

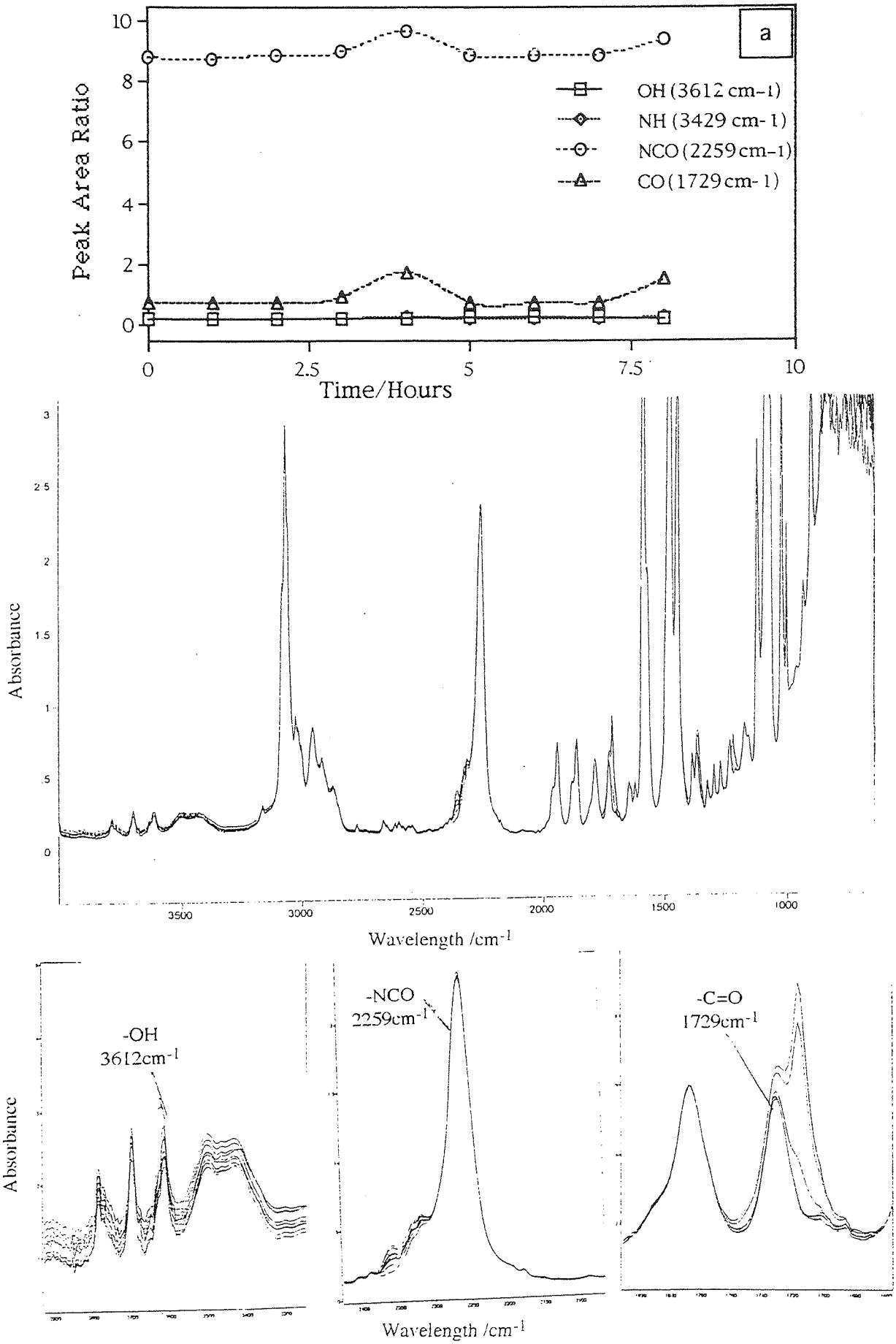


Figure 3-7 Peak ratios and Infra reds produced by the spectroscopic analysis of IPDI (0.3487 g) mixed with Calco 2246 (0.5678 g) in chlorobenzene (20 ml) heated at 80°C.

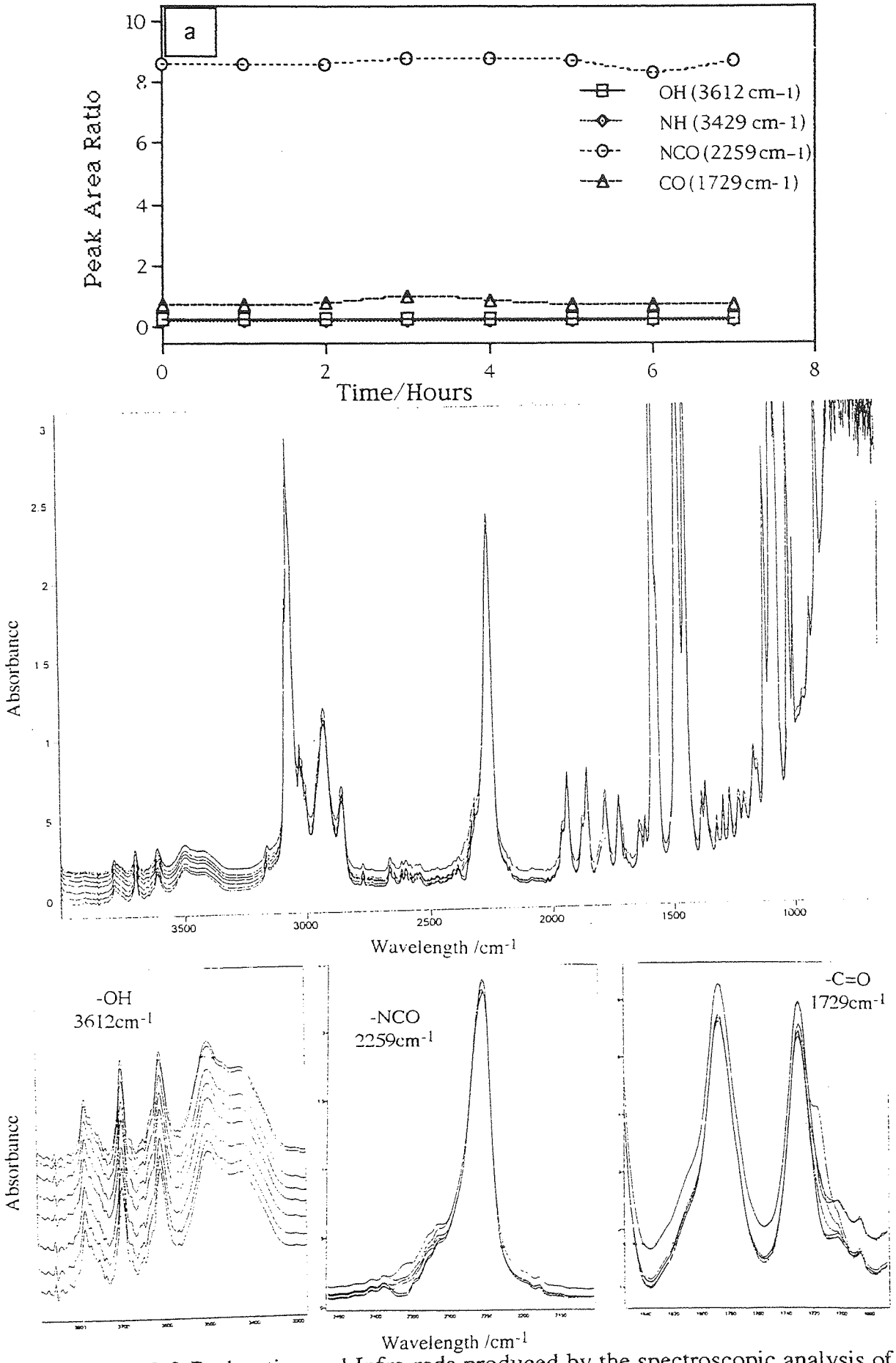


Figure 3-8 Peak ratios and Infra reds produced by the spectroscopic analysis of IPDI (0.3467 g) mixed with WSP (0.7016 g) in chlorobenzene (20 ml) heated at 80°C.

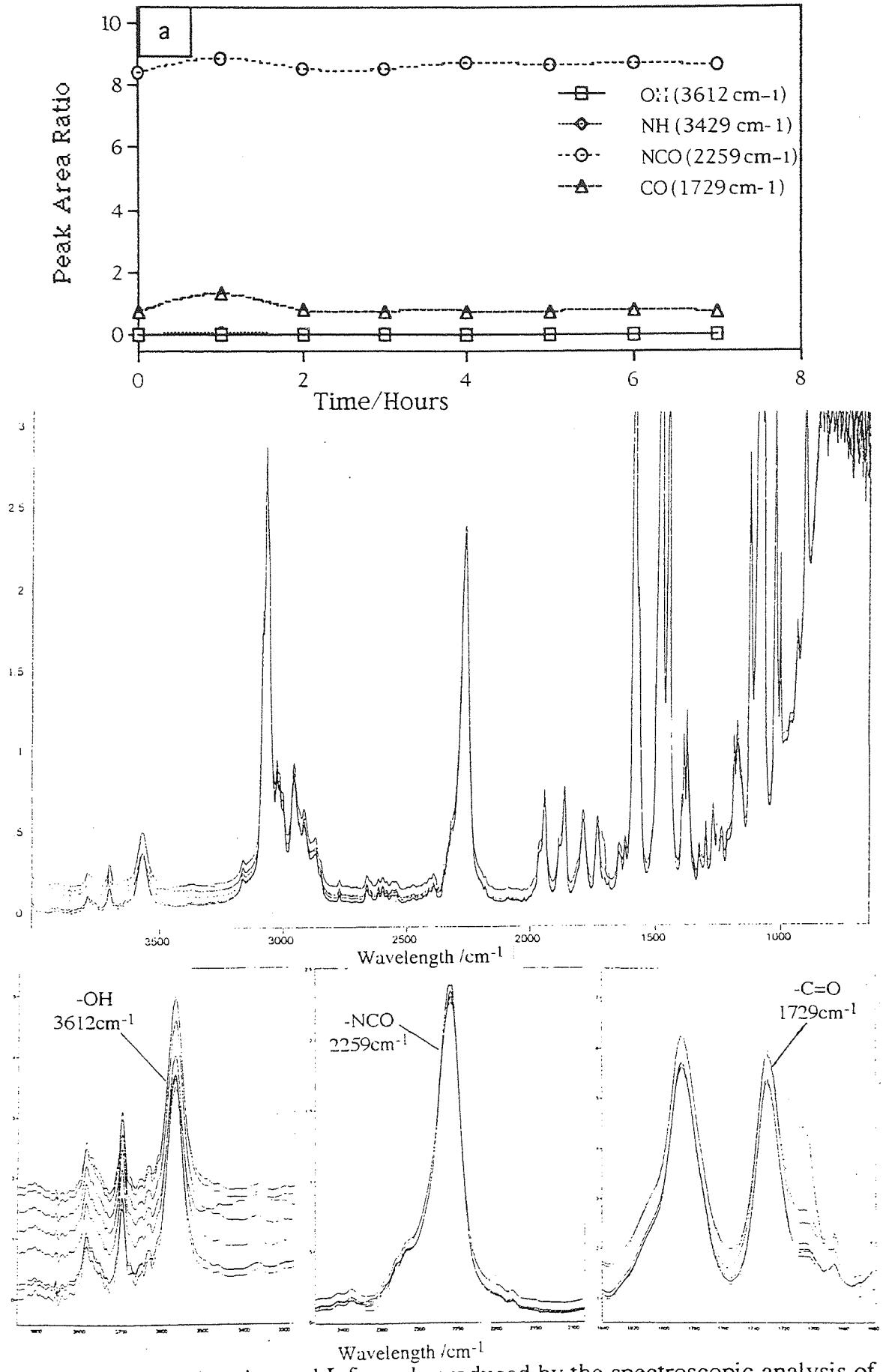


Figure 3-9 Peak ratios and Infra reds produced by the spectroscopic analysis of IPDI (0.3448 g) mixed with Santonox R (0.5977 g) in chlorobenzene (20 ml) heated at 80°C.

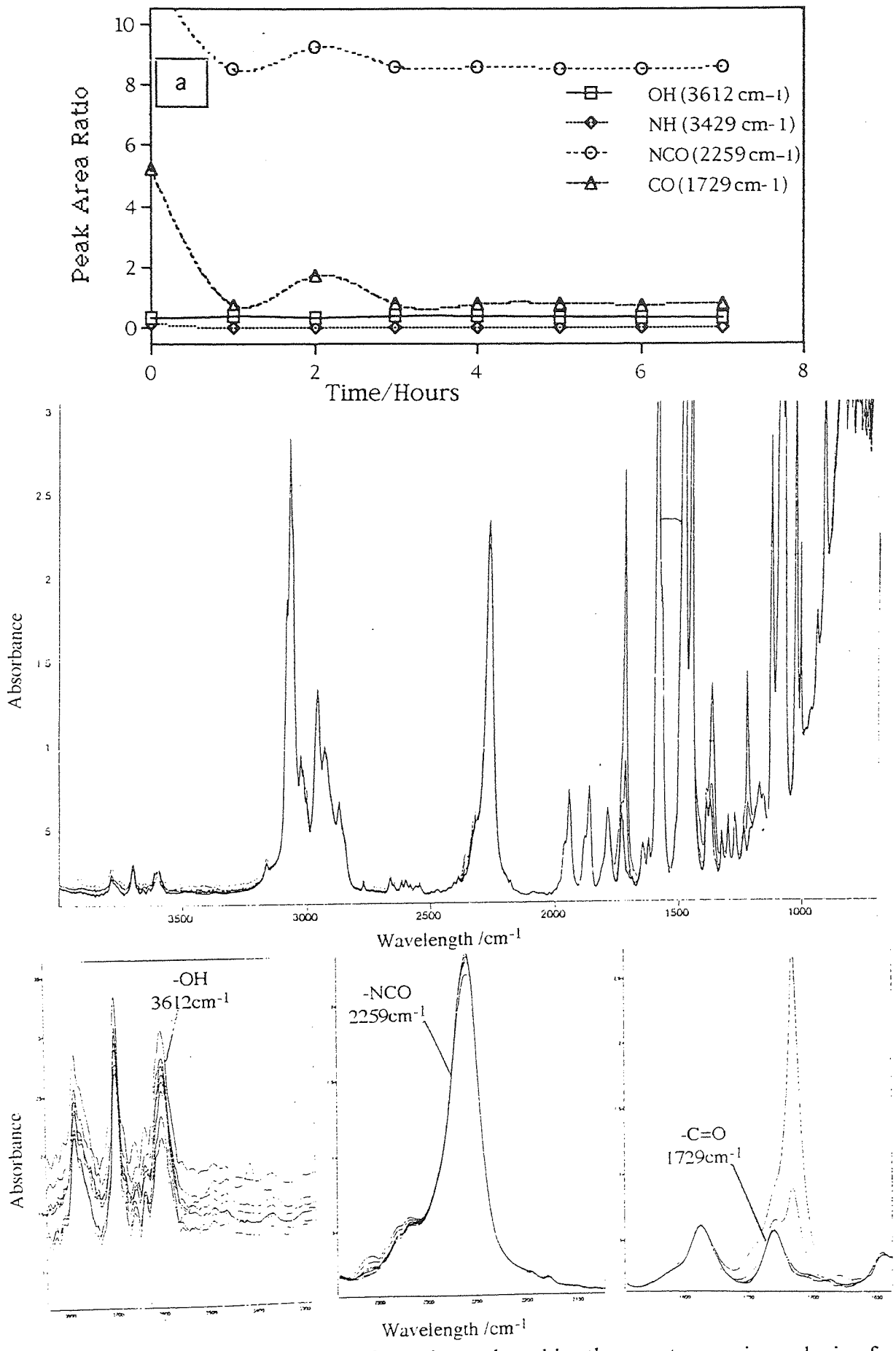


Figure 3-10 Peak ratios and Infra reds produced by the spectroscopic analysis of IPDI (0.3497 g) mixed with Santonox 54 (0.6003 g) in chlorobenzene (20 ml) heated at 80°C.

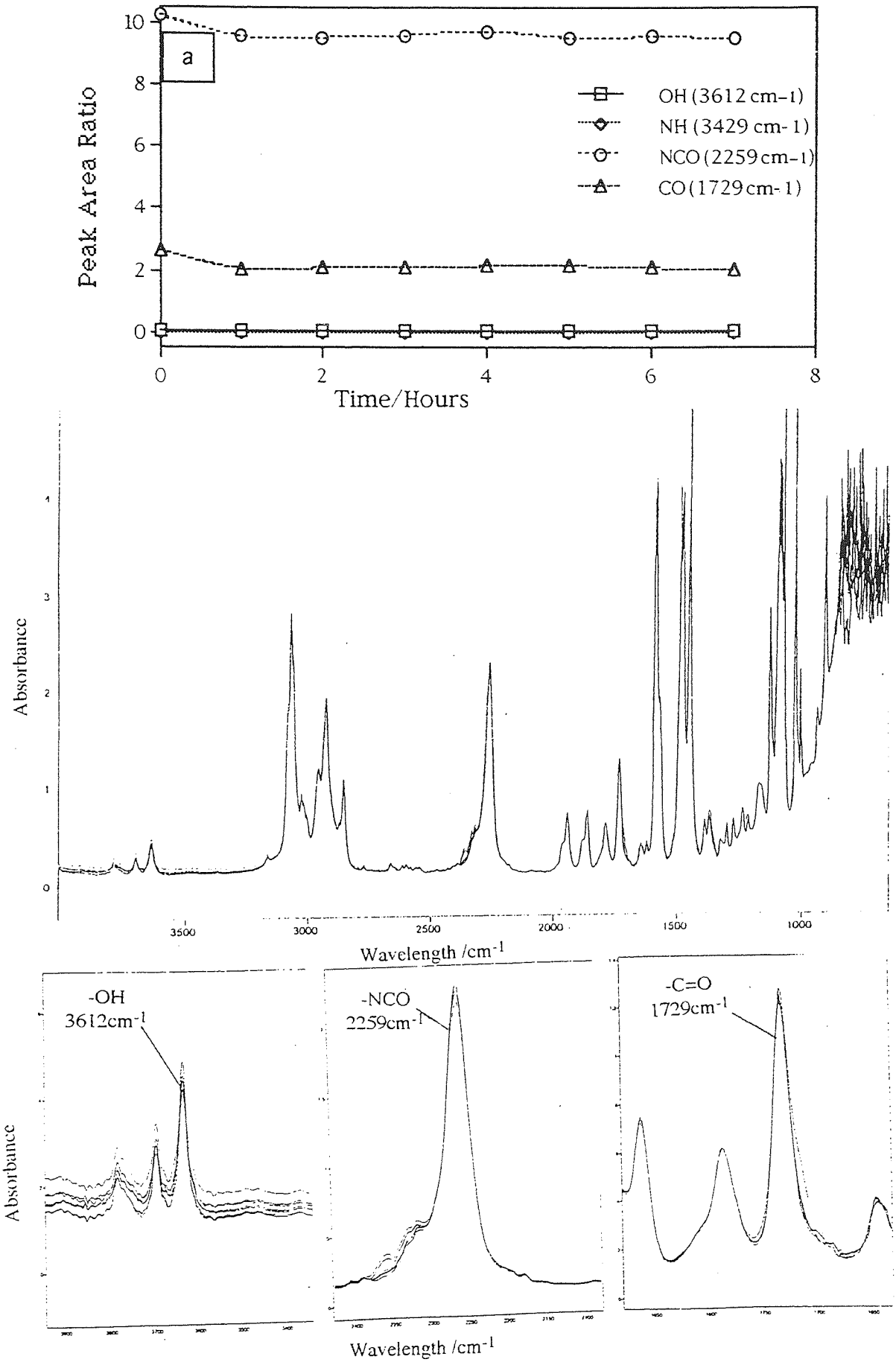


Figure 3-11 Peak ratios and Infra reds produced by the spectroscopic analysis of IPDI (0.3459 g) mixed with Irganox 1076 (0.8575 g) in chlorobenzene (20 ml) heated at 80°C.

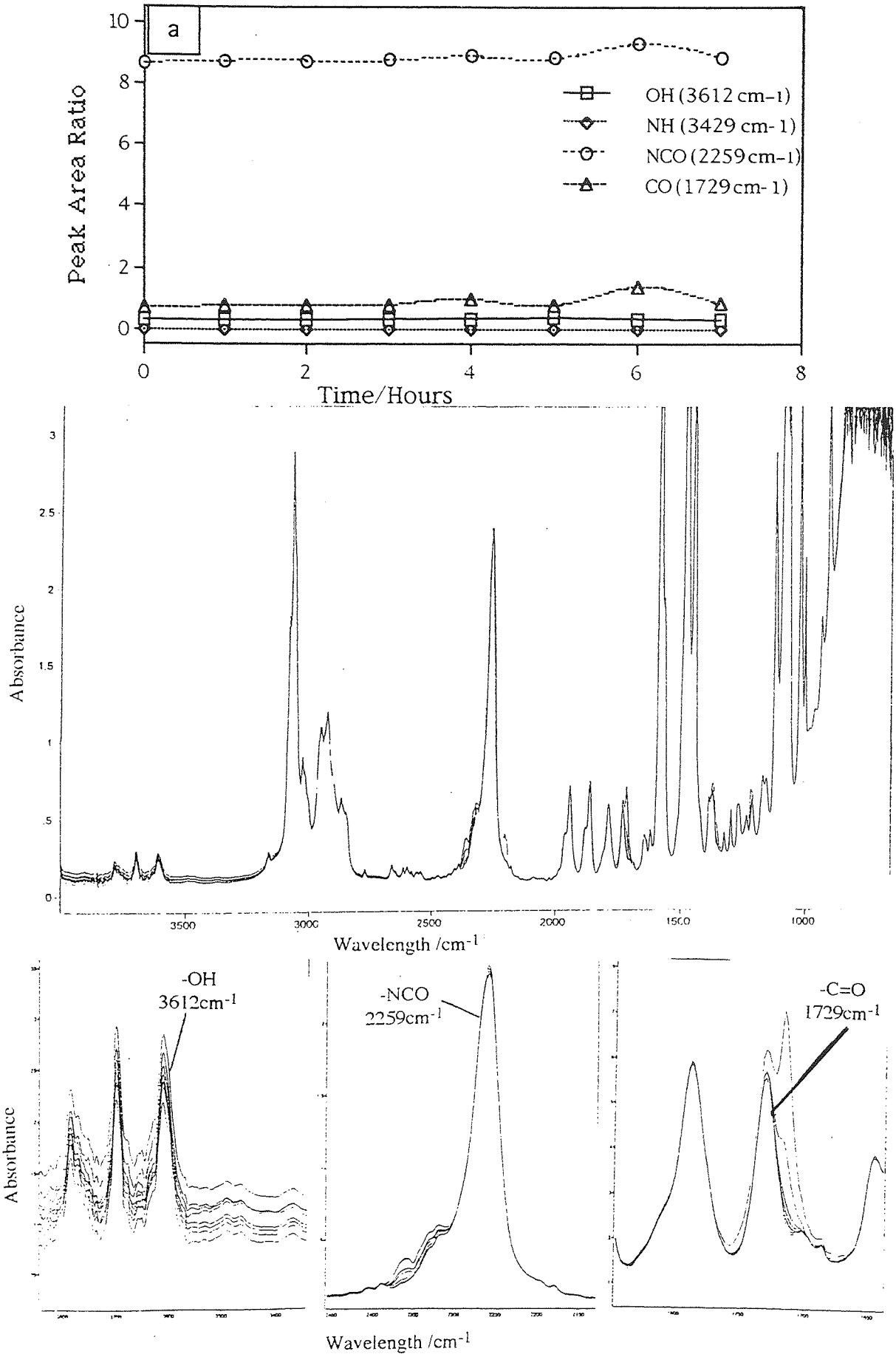


Figure 3-12 Peak ratios and Infra reds produced by the spectroscopic analysis of IPDI (0.3510 g) mixed with α-Tocopherol (0.6687 g) in chlorobenzene (20 ml) heated at 80°C.

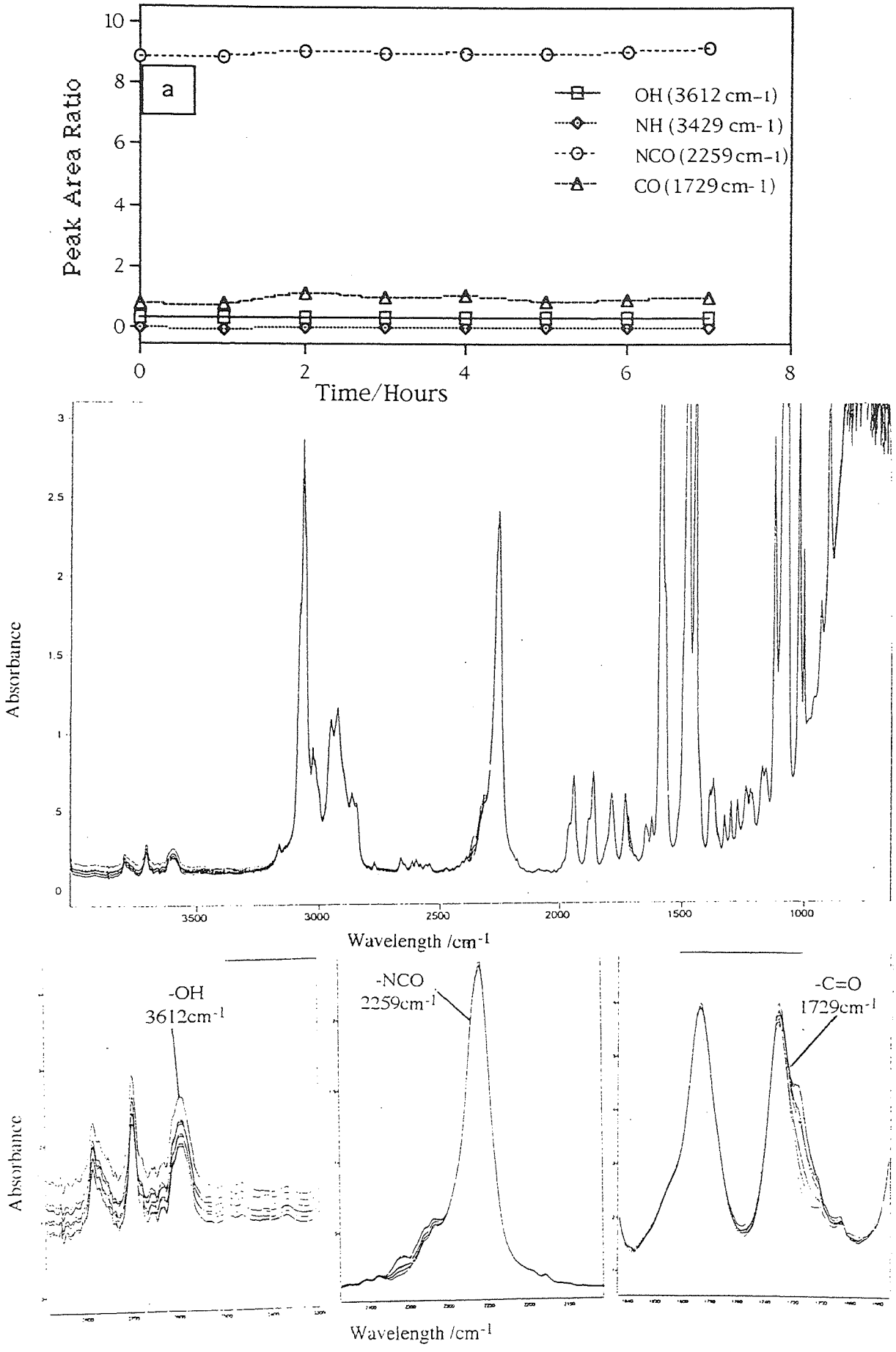


Figure 3-13 Peak ratios and Infra reds produced by the spectroscopic analysis of IPDI (0.3566 g) mixed with γ-Tocopherol (0.6444 g) in chlorobenzene (20 ml) heated at 80°C.

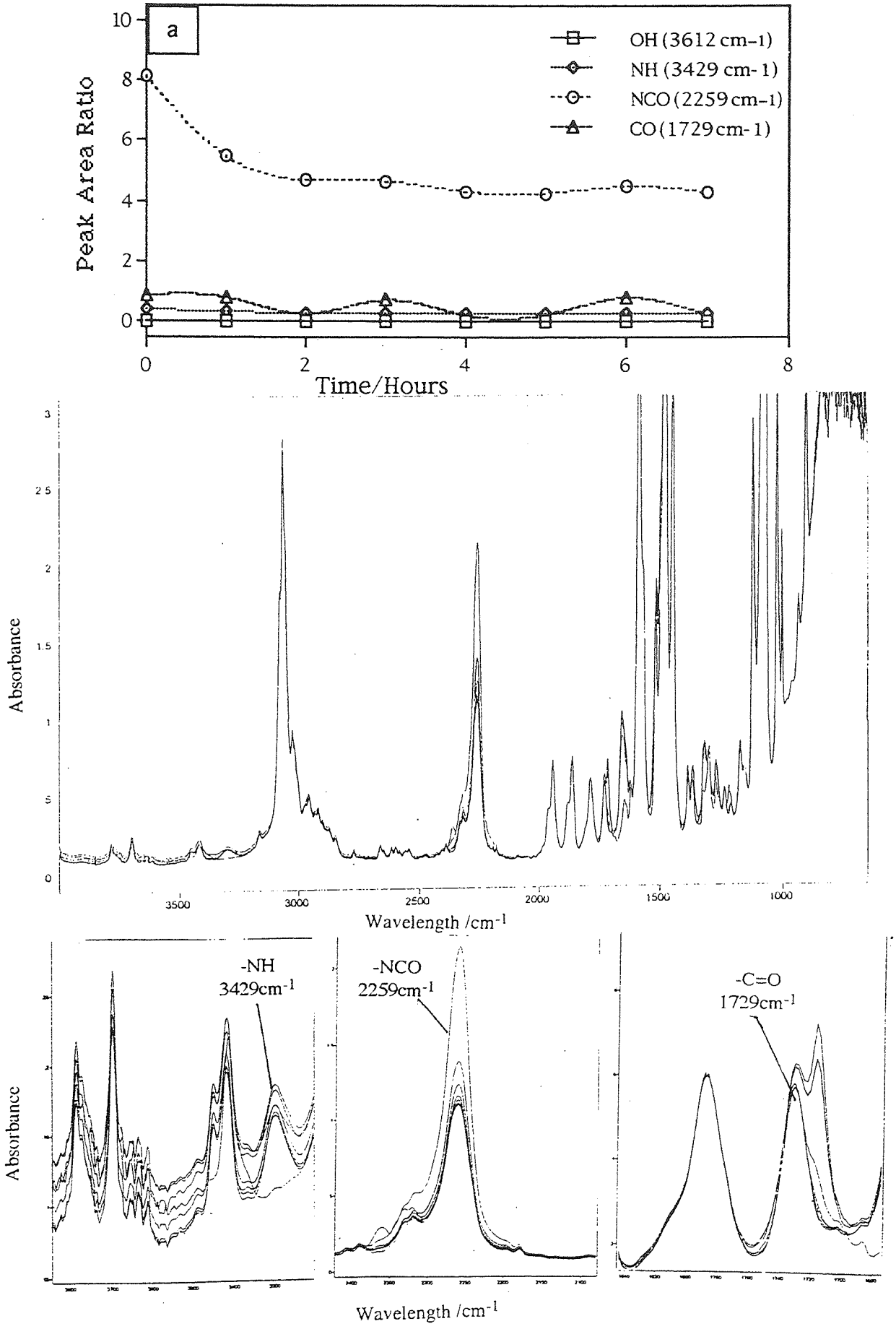


Figure 3-14 Peak ratios and Infra reds produced by the spectroscopic analysis of IPDI (0.3487 g) mixed with IPPD (0.5678 g) in chlorobenzene (20 ml) heated at 80C.

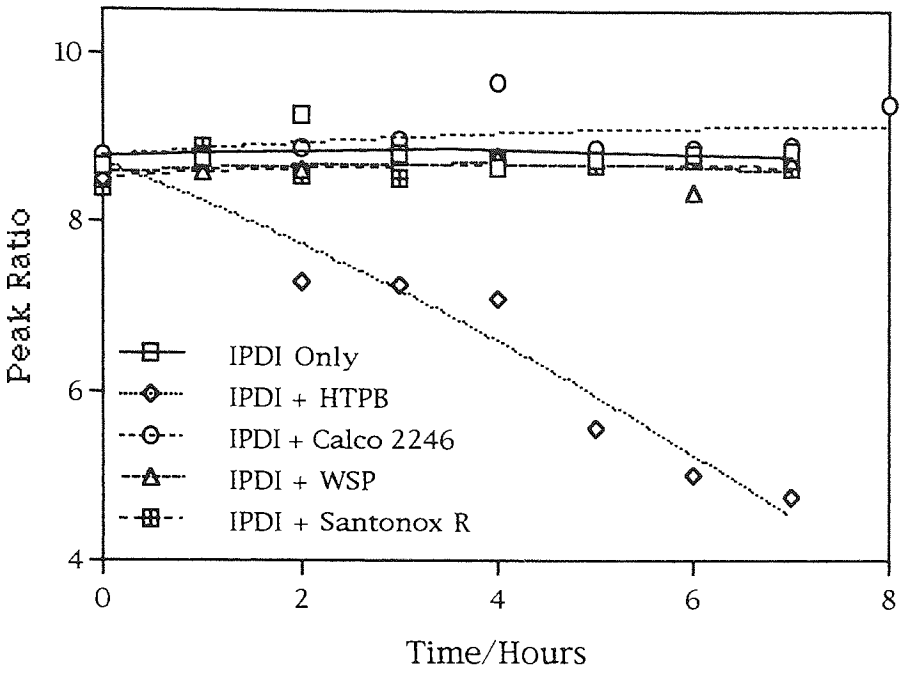


Figure 3-15 Comparison of NCO peak ratios produced from spectra of various antioxidants mixed with IPDI in chlorobenzene.

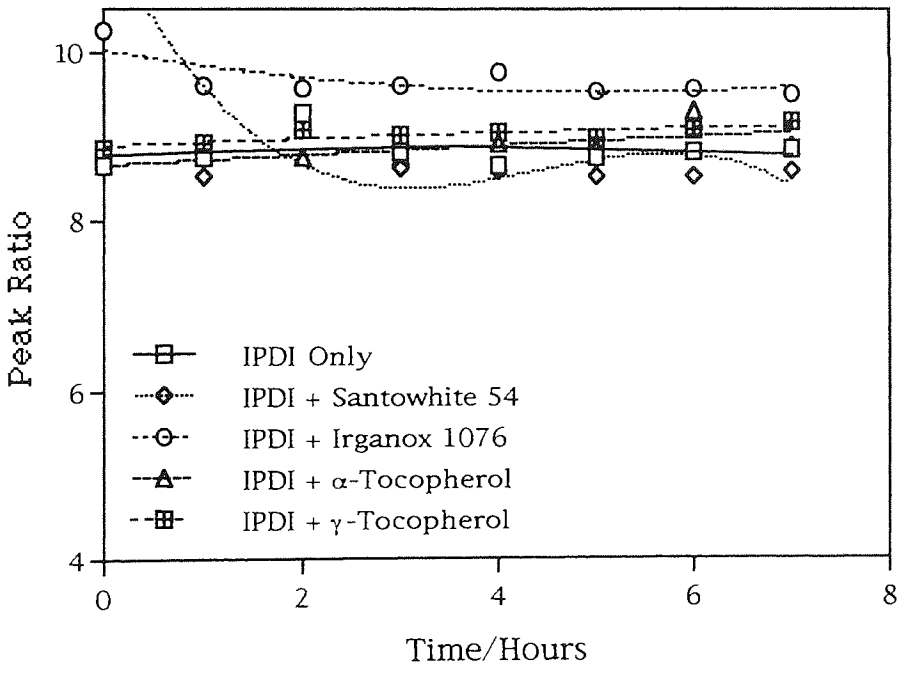


Figure 3-16 Comparison of NCO peak ratios produced from spectra of various antioxidants mixed with IPDI in chlorobenzene.

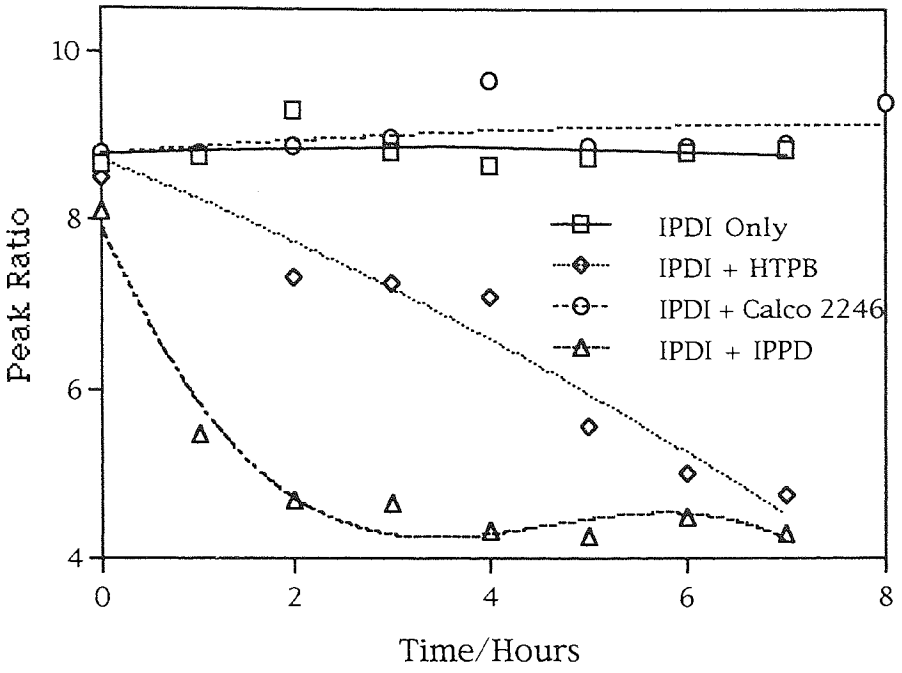


Figure 3-17 Comparison of NCO peak ratios produced from spectra of various antioxidants mixed with IPDI in chlorobenzene.

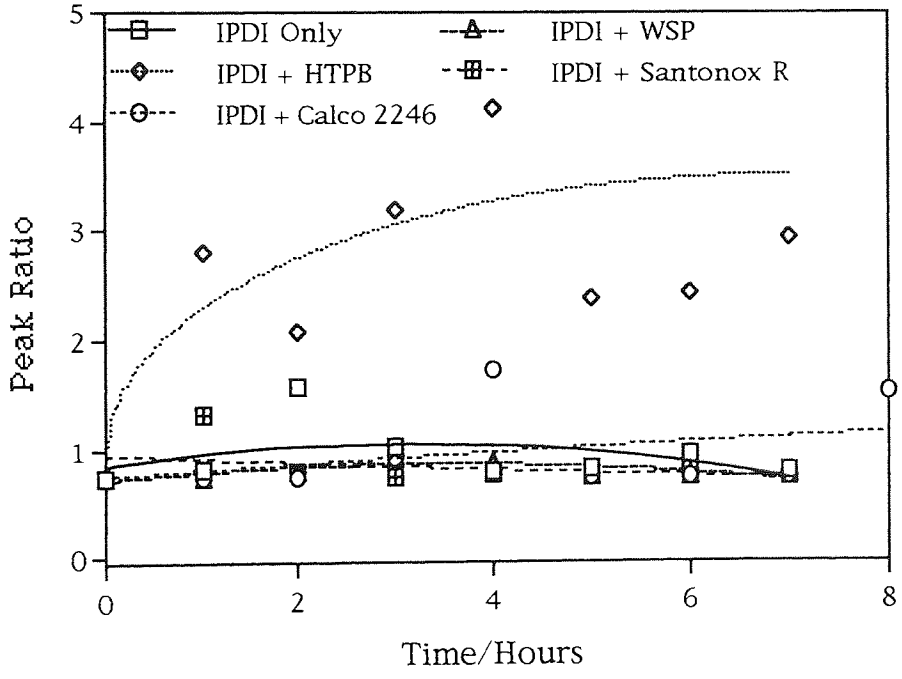


Figure 3-18 Comparison of CO peak ratios produced from spectra of various antioxidants mixed with IPDI in chlorobenzene.

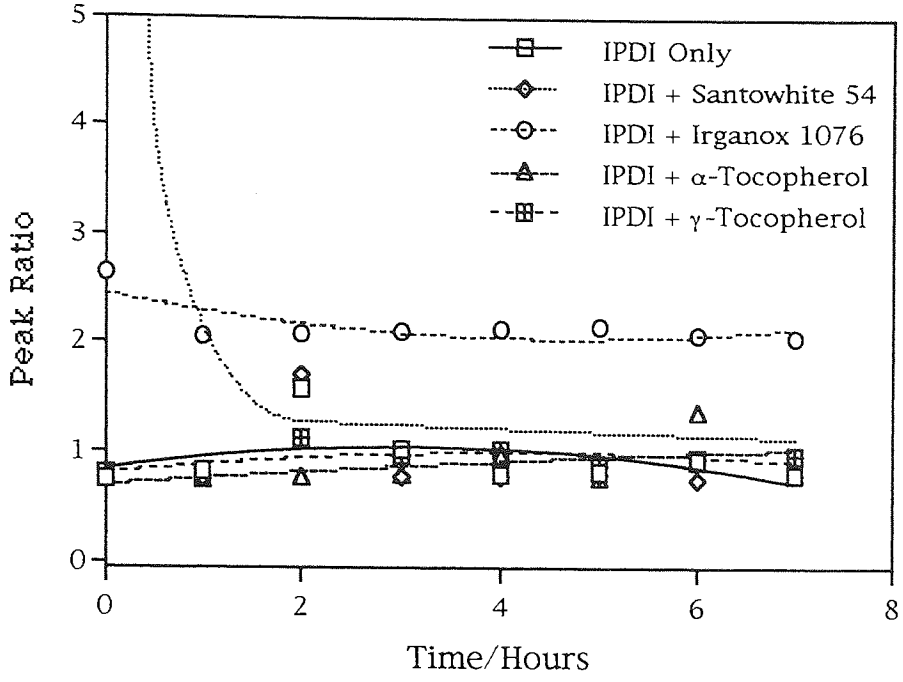


Figure 3-19 Comparison of CO peak ratios produced from spectra of various antioxidants mixed with IPDI in chlorobenzene.

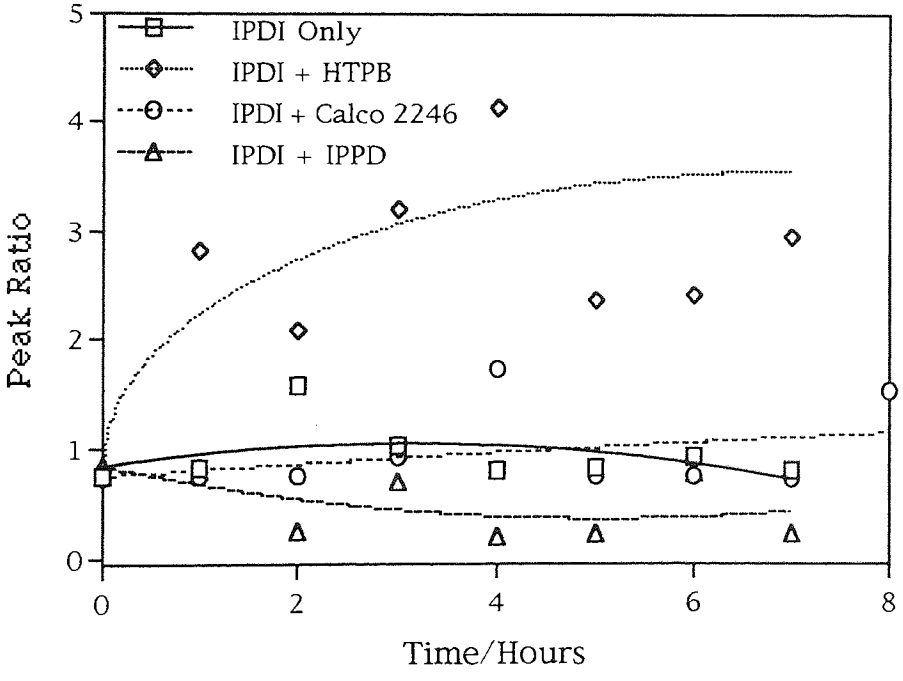


Figure 3-20 Comparison of CO peak ratios produced from spectra of various antioxidants mixed with IPDI in chlorobenzene.

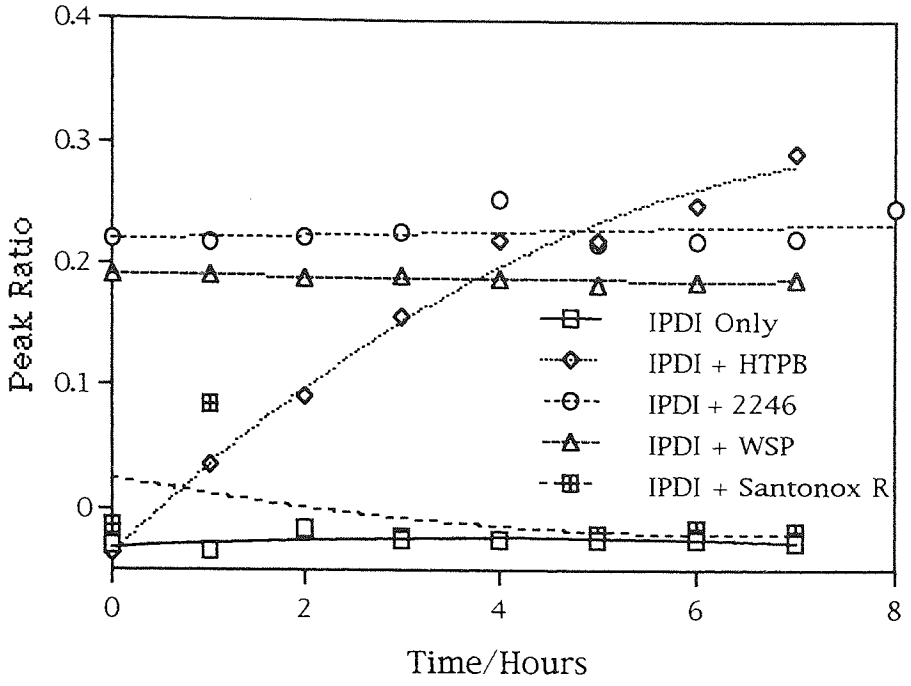


Figure 3-21 Comparison of NH peak ratios produced from spectra of various antioxidants mixed with IPDI in chlorobenzene.

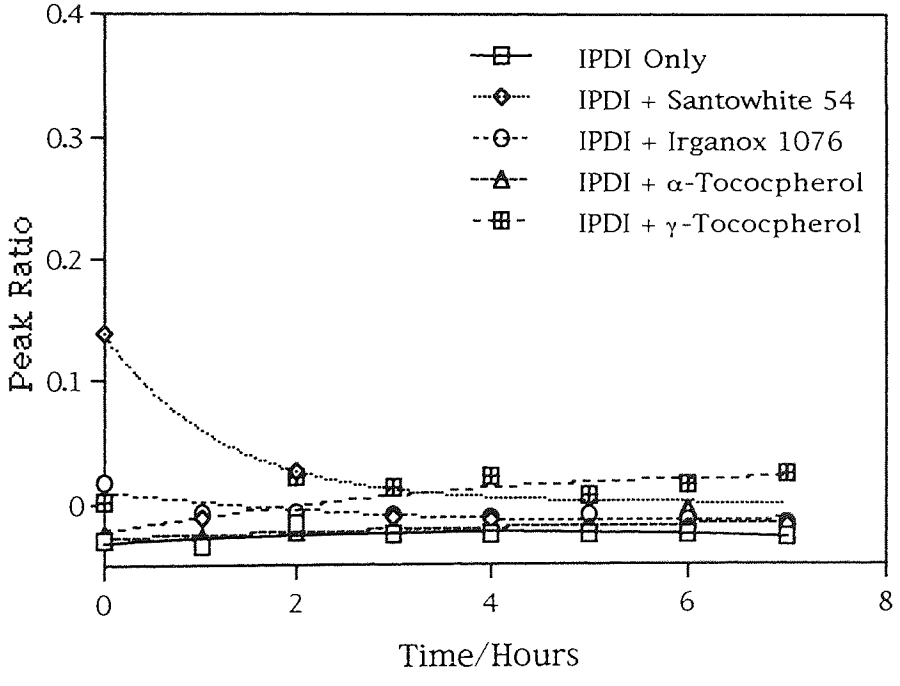


Figure 3-22 Comparison of NH peak ratios produced from spectra of various mixed with IPDI in chlorobenzene.

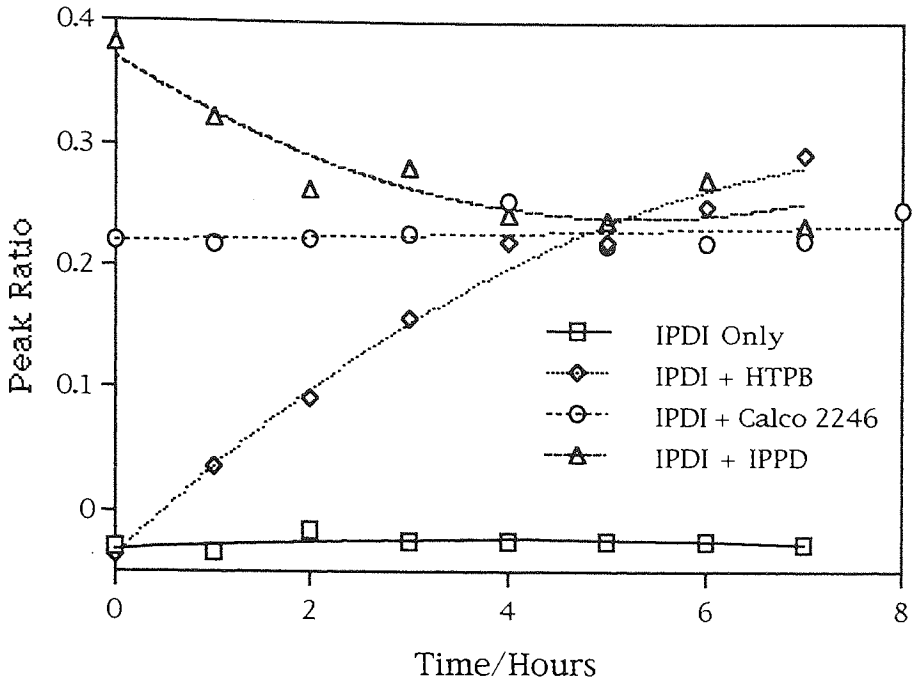


Figure 3-23 Comparison of NH peak ratios produced from spectra of various antioxidants mixed with IPDI in chlorobenzene.

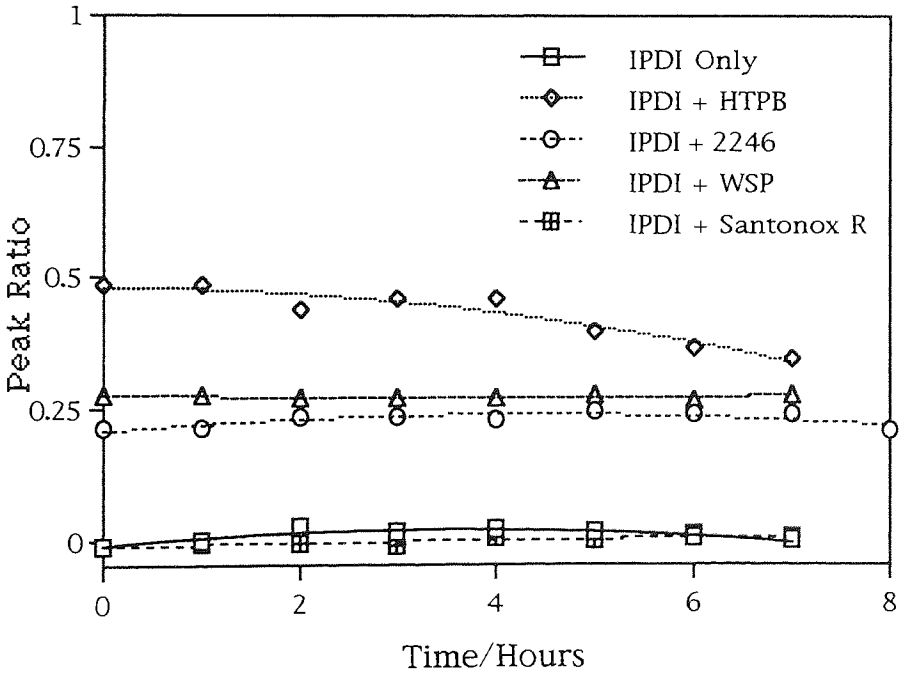


Figure 3-24 Comparison of OH peak ratios produced from spectra of various antioxidants mixed with IPDI in chlorobenzene.

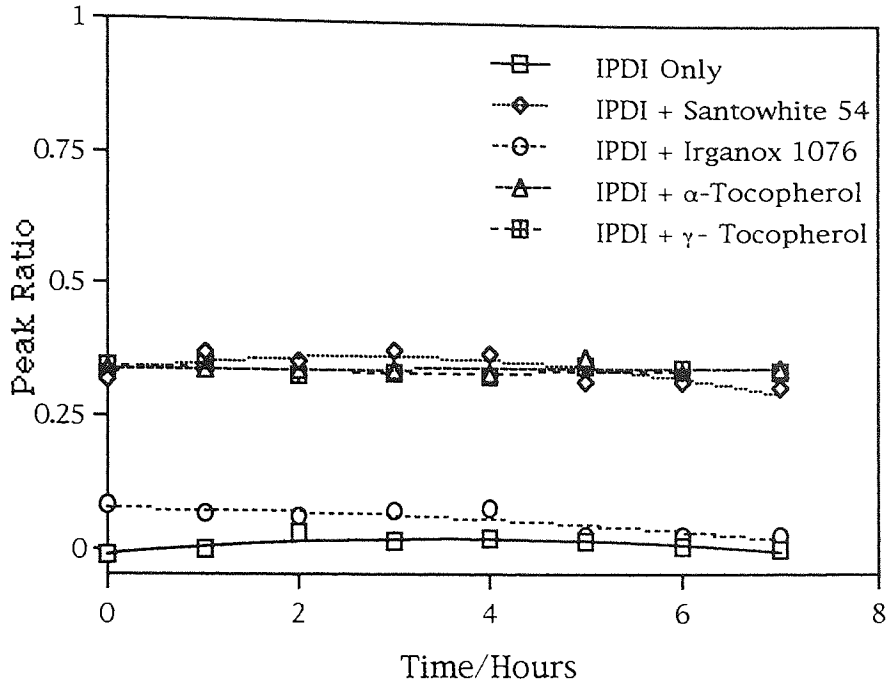


Figure 3-25 Comparison of OH peak ratios produced from spectra of various antioxidants mixed with IPDI in chlorobenzene.

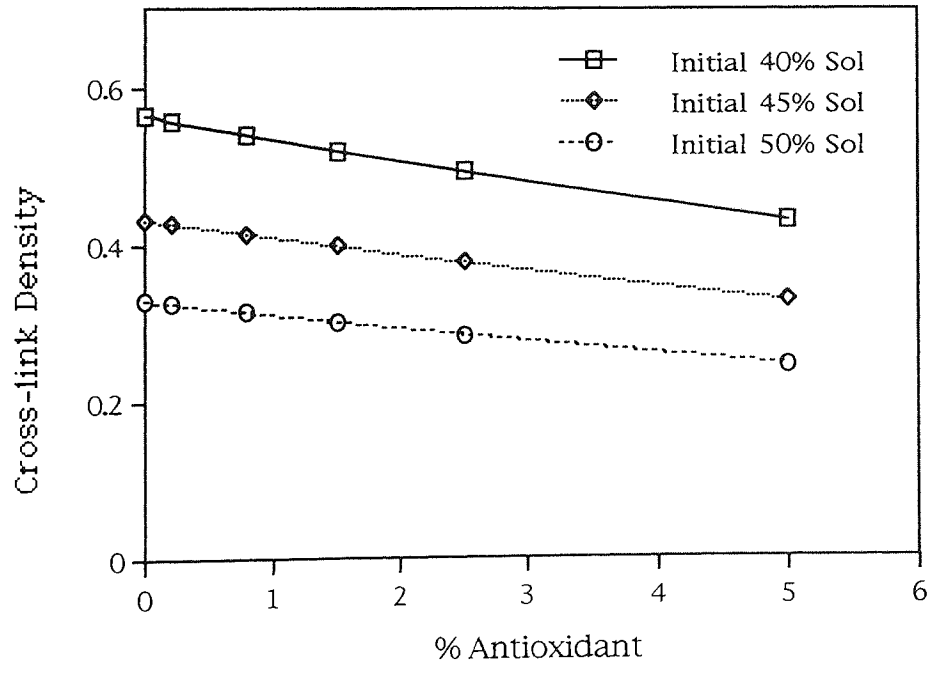


Figure 3-26 Theoretical effect of an increasing concentration of an inert filler on measured cross-link density at 3 different initial % Solubility's.

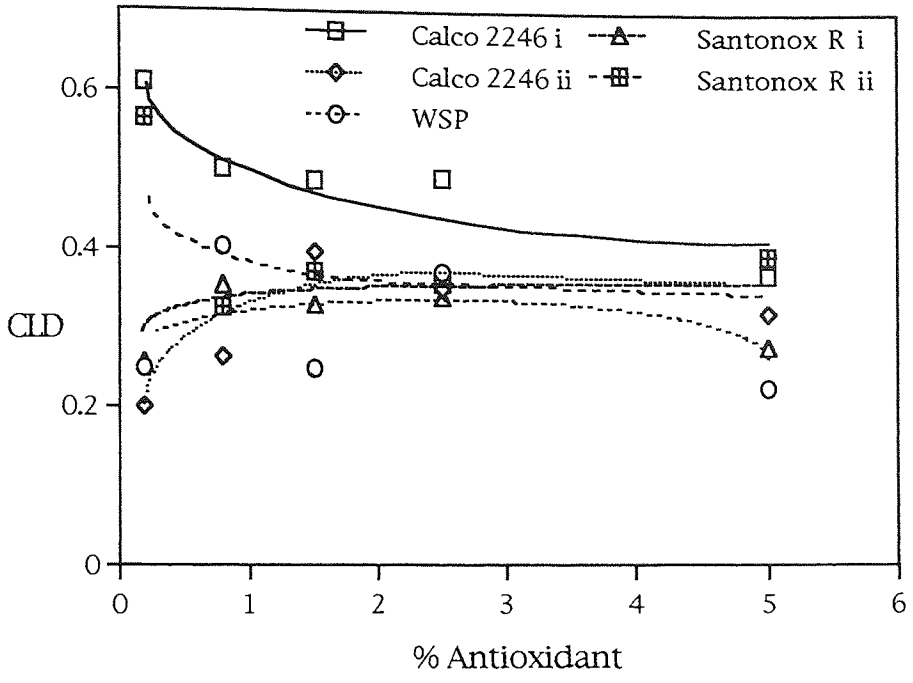


Figure 3-27 Effect of increasing concentration of antioxidants on the cross-link density of polybutadiene binder prepared in tube moulds.

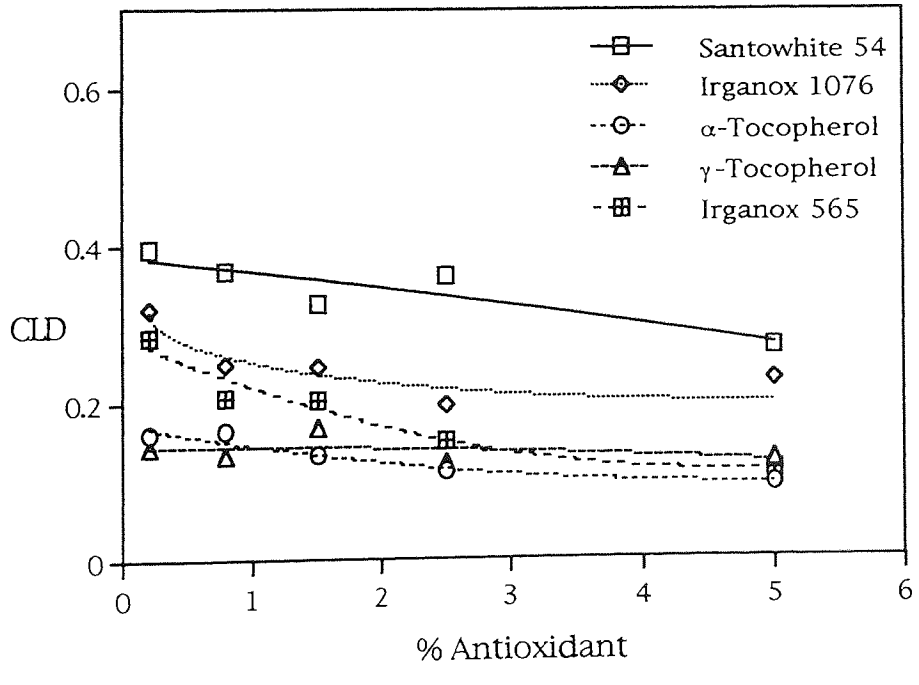


Figure 3-28 Effect of increasing concentration of antioxidants on the cross-link density of polybutadiene binder prepared in tube moulds.

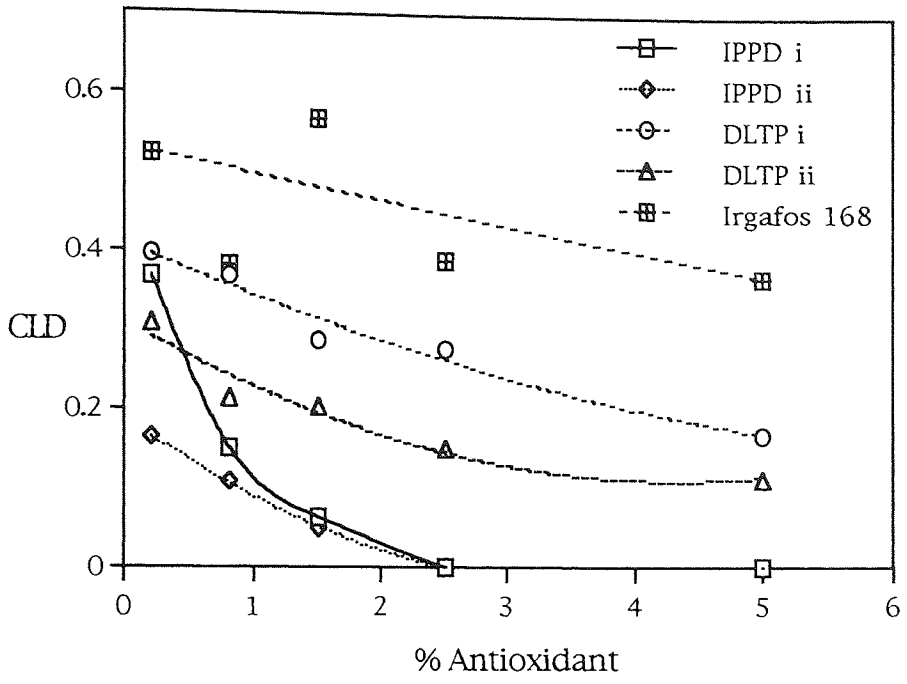


Figure 3-29 Effect of increasing concentration of antioxidants on the cross-link density of polybutadiene binder prepared in tube moulds.

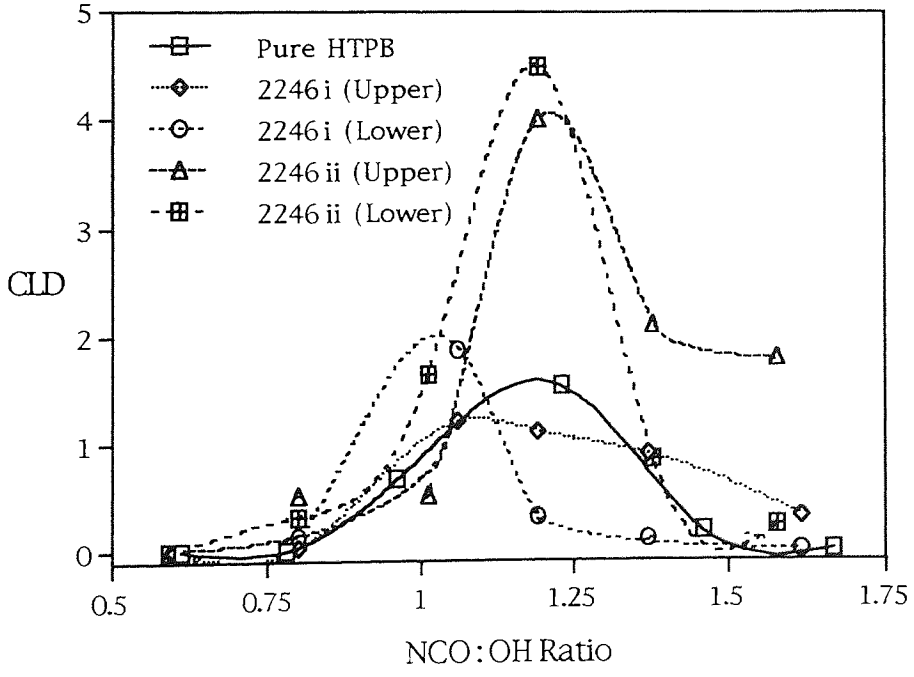


Figure 3-30 Effect of NCO:OH ratio on the initial cross-link density of polybutadiene binder prepared in tube moulds without and with 0.2% w/w antioxidants.

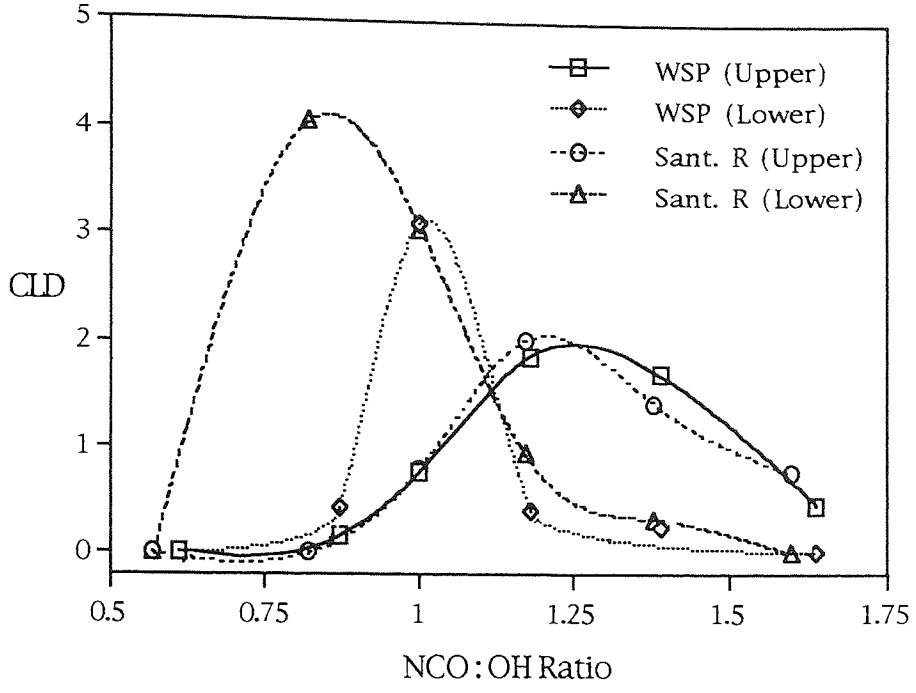


Figure 3-31 Effect of NCO:OH ratio on the initial cross-link density of polybutadiene binder prepared in tube moulds containing 0.2% w/w antioxidants.

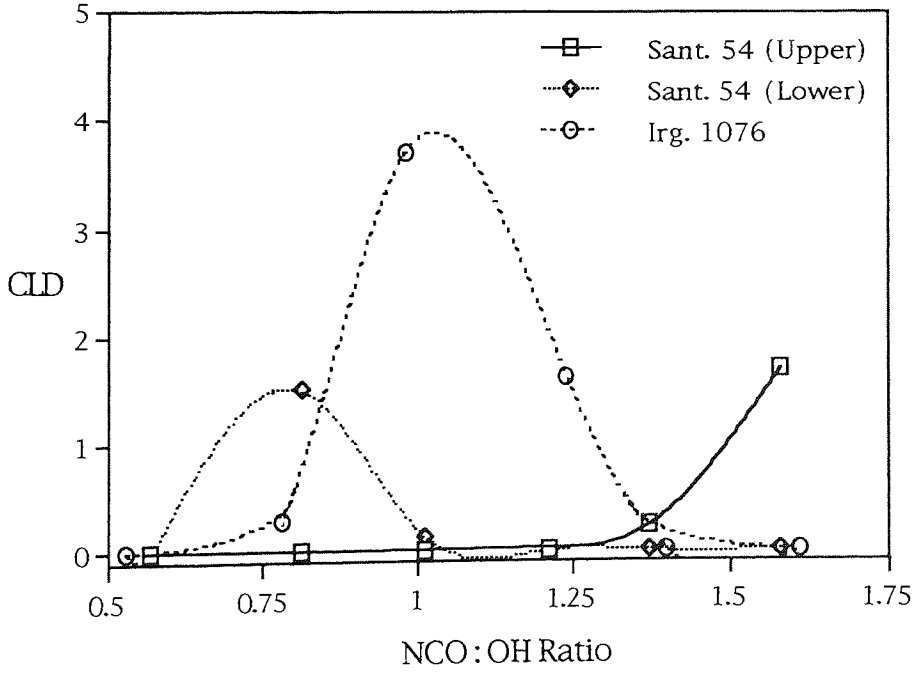


Figure 3-32 Effect of NCO:OH ratio on the initial cross-link density of polybutadiene binder prepared in tube moulds containing 0.2% w/w antioxidants.

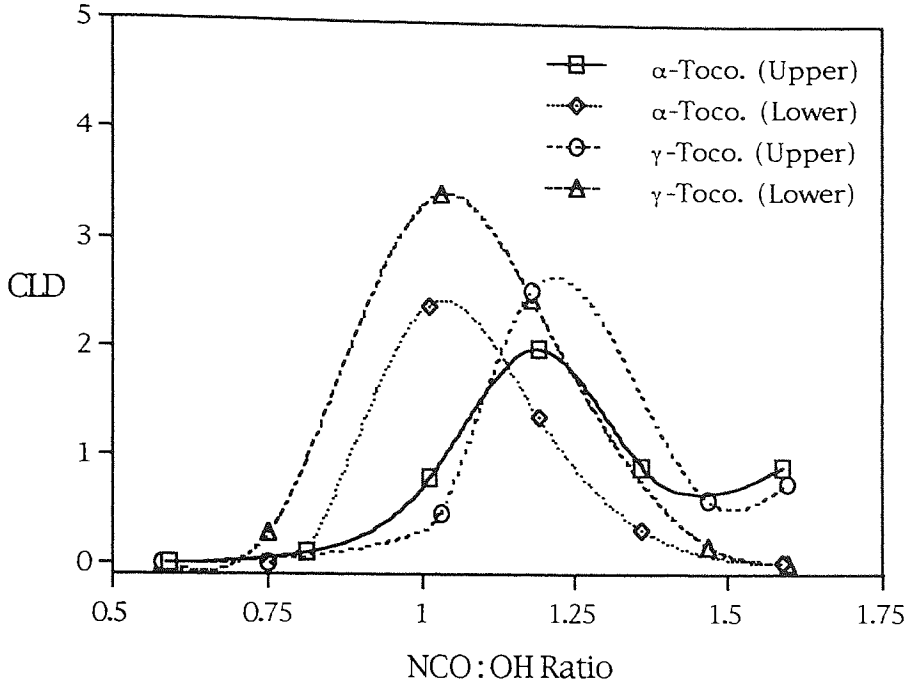


Figure 3-33 Effect of NCO:OH ratio on the initial cross-link density of polybutadiene binder prepared in tube moulds containing 0.2% w/w antioxidants.

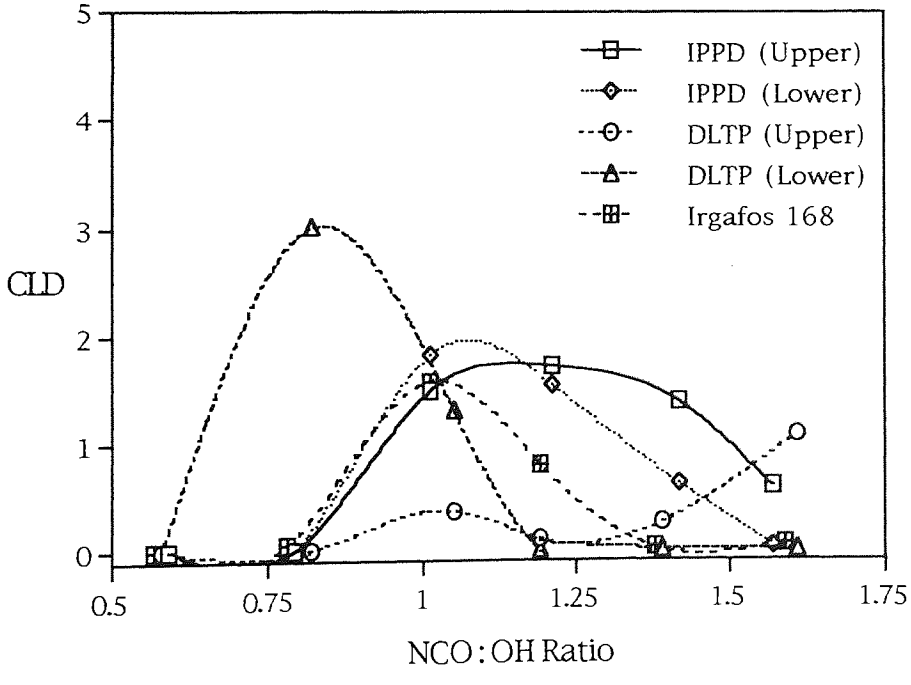


Figure 3-34 Effect of NCO:OH ratio on the initial cross-link density of polybutadiene binder prepared in tube moulds containing 0.2% w/w antioxidants.

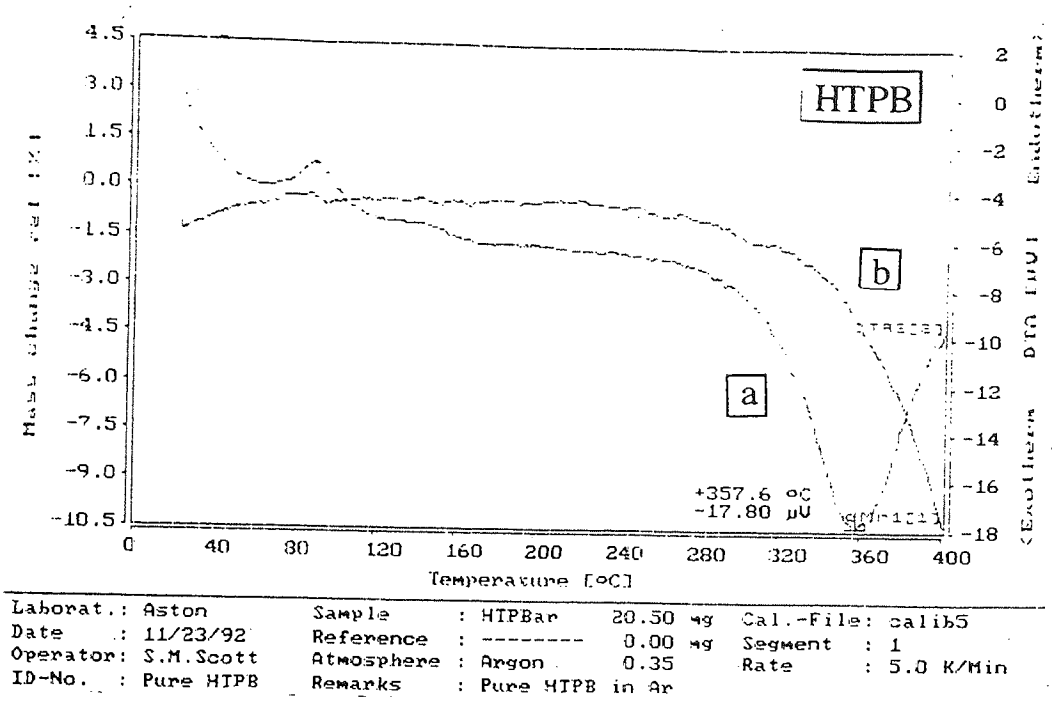


Figure 3-35 Thermogram of uncured HTPB analysed in a flowing argon atmosphere (0.35 l/min) dynamically with a heating rate of 5°C/min.

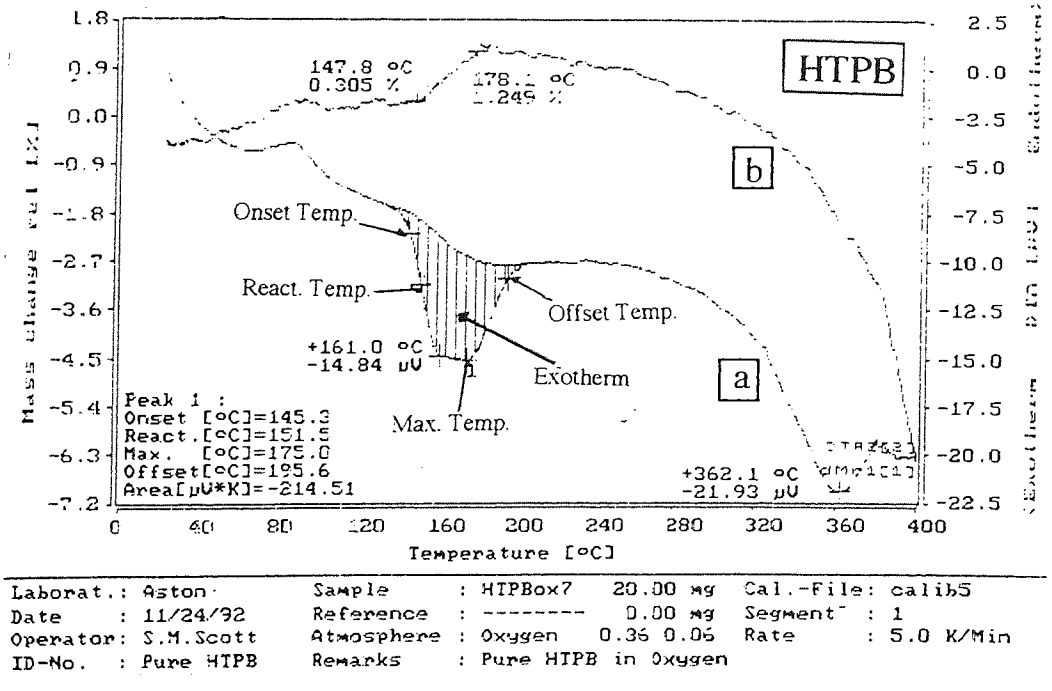


Figure 3-36 Thermogram of Uncured HTPB analysed in a mixed flowing oxygen (0.36 l/min) and argon (0.06 l/min) atmosphere dynamically with a heating rate of 5°C/min..

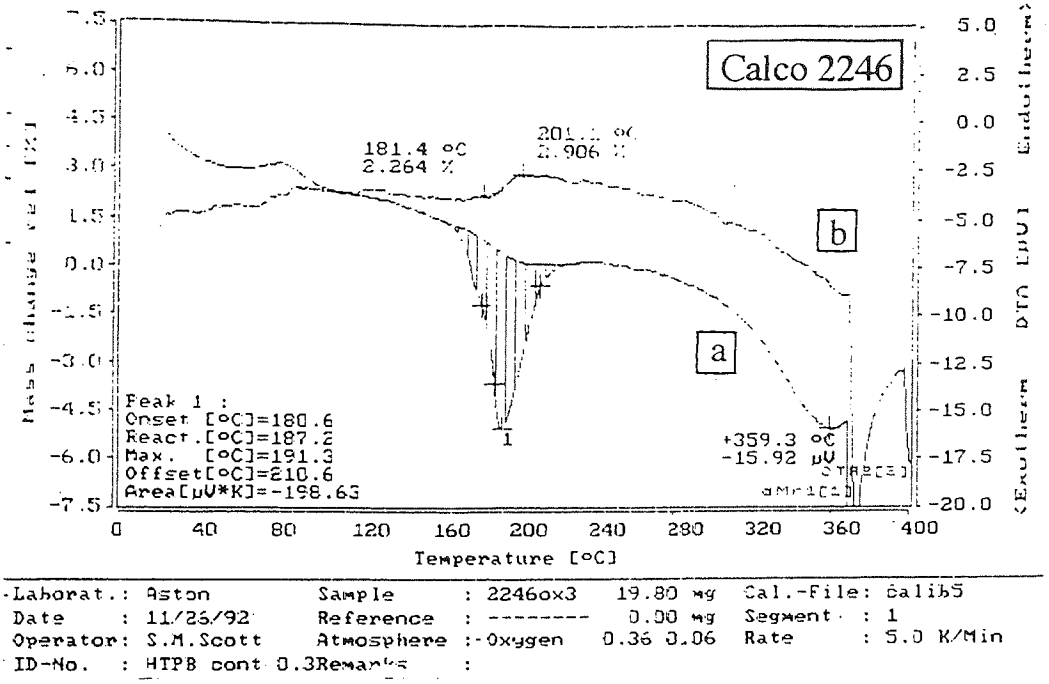


Figure 3-37 Thermogram of uncured HTPB containing Calco 2246 (0.2% w/w); analysed in a flowing mixed oxygen (0.36 l/min) and argon (0.06 l/min) atmosphere dynamically with a heating rate of 5°C/min.

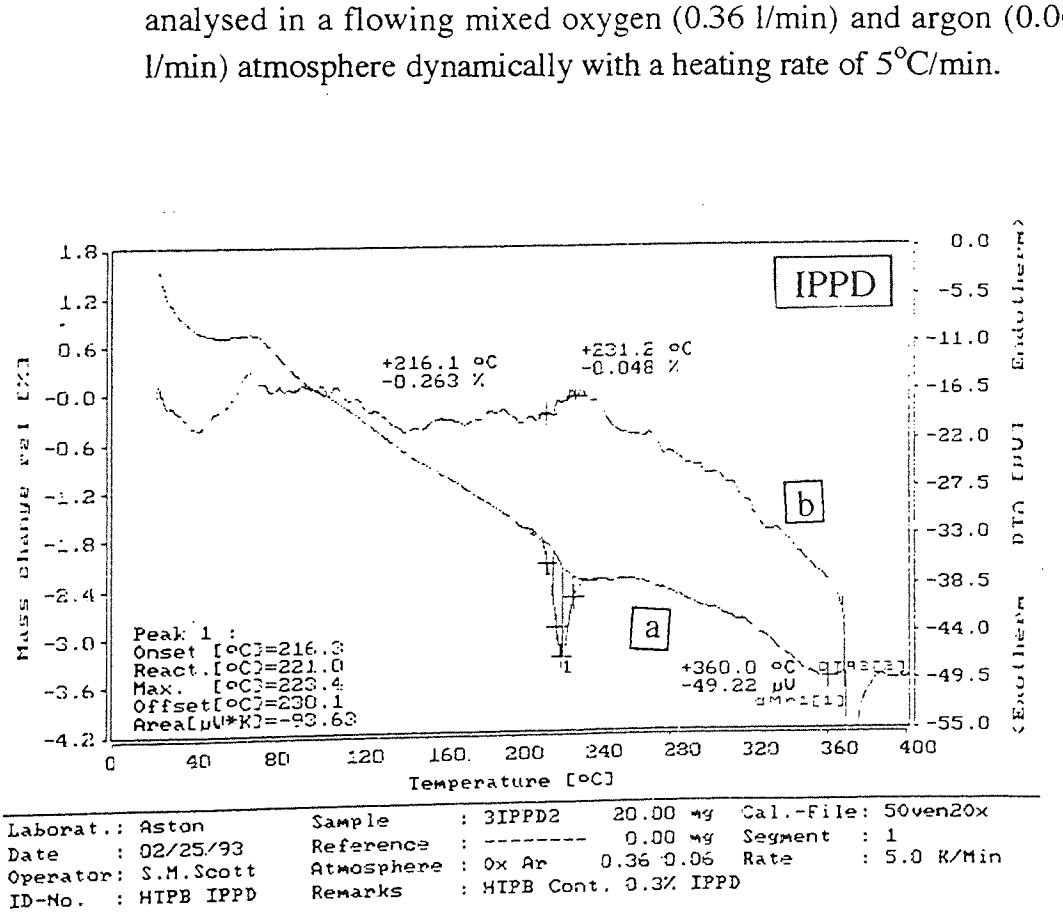


Figure 3-38 Thermogram of Uncured HTPB containing IPPD (0.2% w/w); analysed in a flowing mixed oxygen (0.36 l/min) and argon (0.06 l/min) atmosphere with a heating rate of 5°C/min.

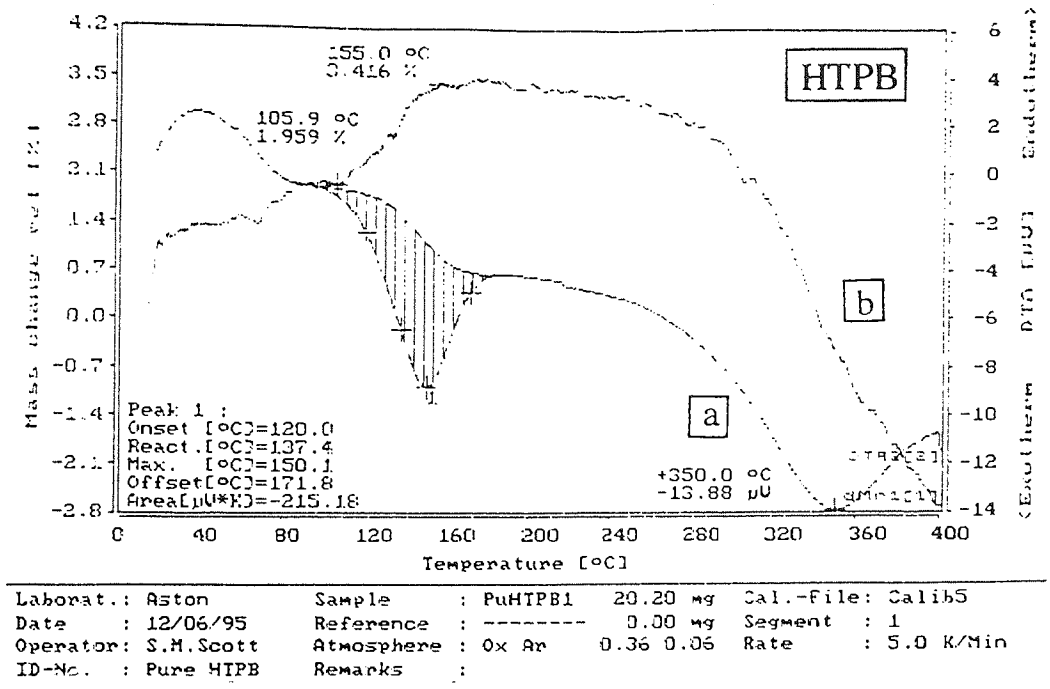


Figure 3-39 Thermogram of cured polybutadiene analysed in a flowing mixed oxygen (0.36 l/min) and argon (0.06 l/min) atmosphere with a heating rate of 5°C/min.

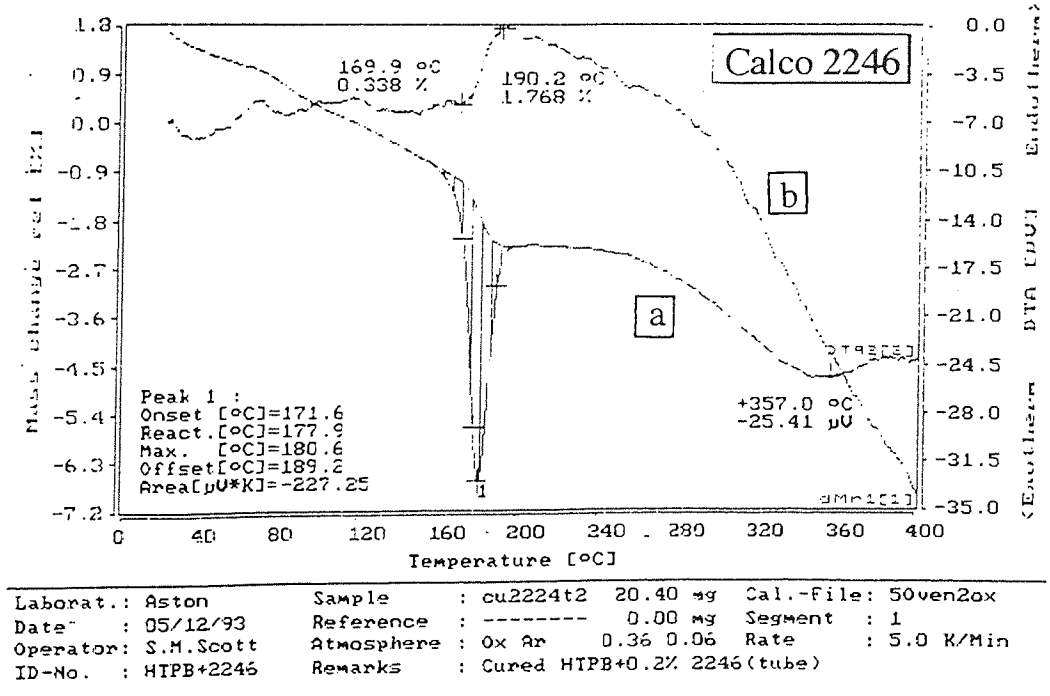


Figure 3-40 Thermogram of cured polybutadiene containing Calco 2246 (0.2% w/w) analysed in a flowing mixed oxygen (0.36 l/min) and argon (0.06 l/min) atmosphere with a heating rate of 5°C/min.

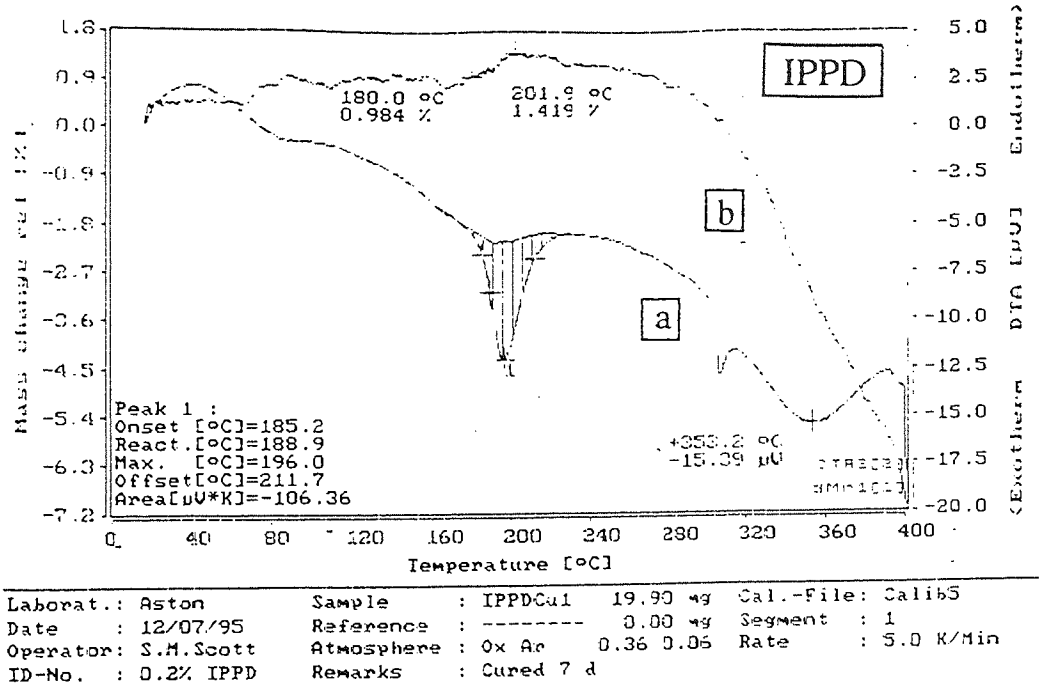


Figure 3-41 Thermogram of cured polybutadiene containing IPPD (0.2% w/w); analysed in a flowing mixed oxygen (0.36 l/min) and argon (0.06 l/min) atmosphere with a heating rate of 5°C/min.

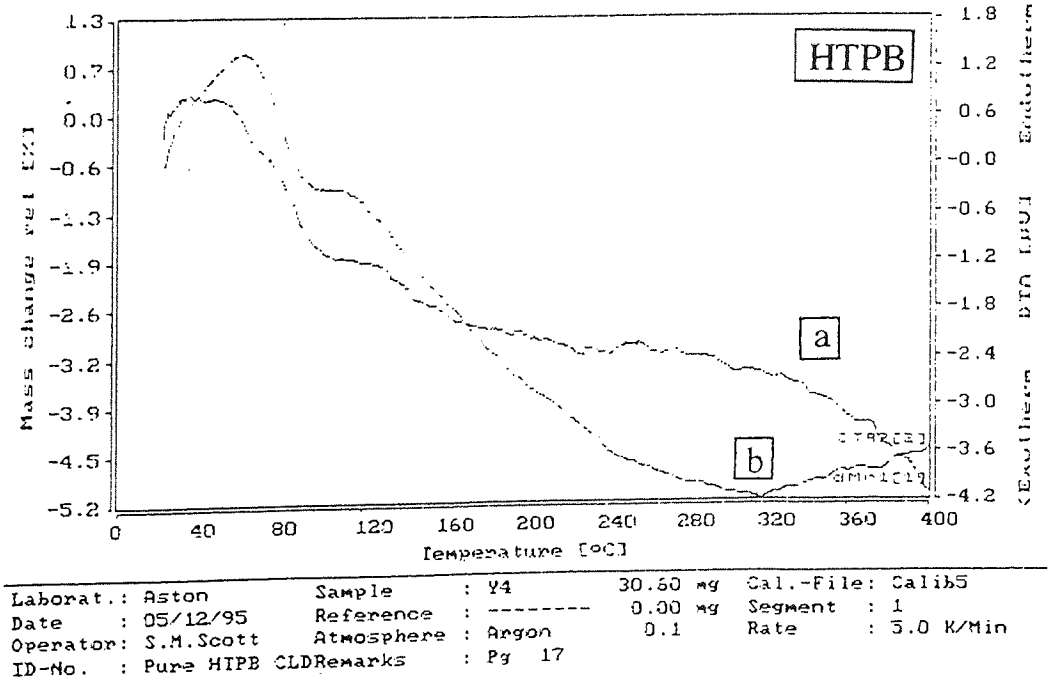


Figure 3-42 Thermogram of cured polybutadiene diluted with 90% alumina analysed in a flowing argon; (0.1 l/min) atmosphere with a heating rate of 5°C/min.

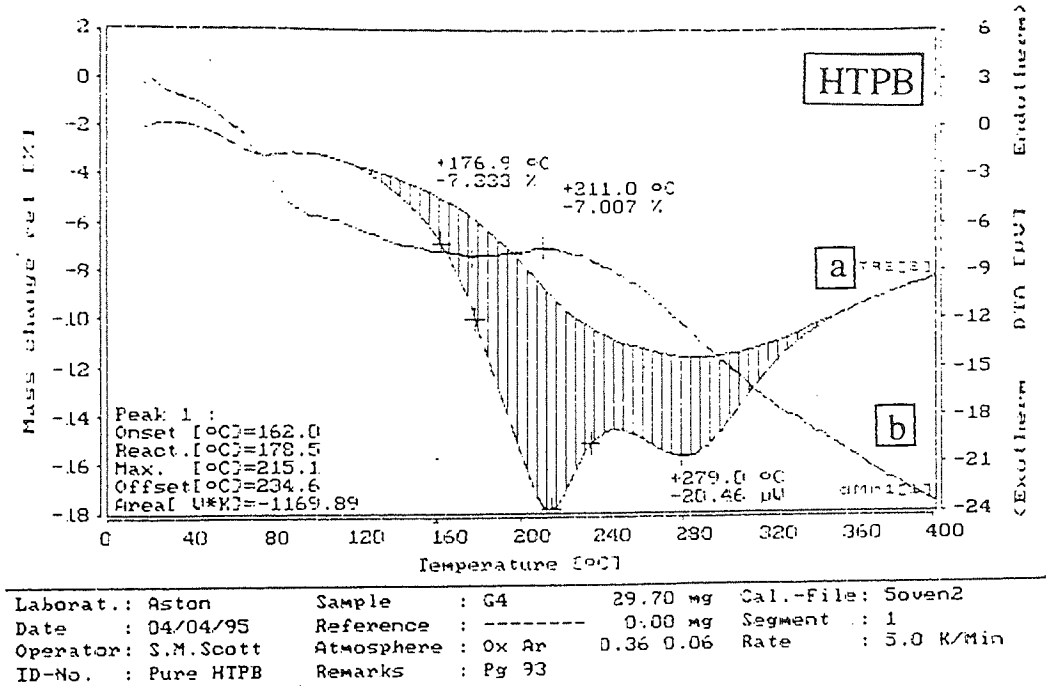


Figure 3-43 Thermogram of cured polybutadiene diluted with 90% alumina analysed in a flowing mixed oxygen (0.36 l/min) and argon (0.06 l/min) atmosphere with a heating rate of 5°C/min.

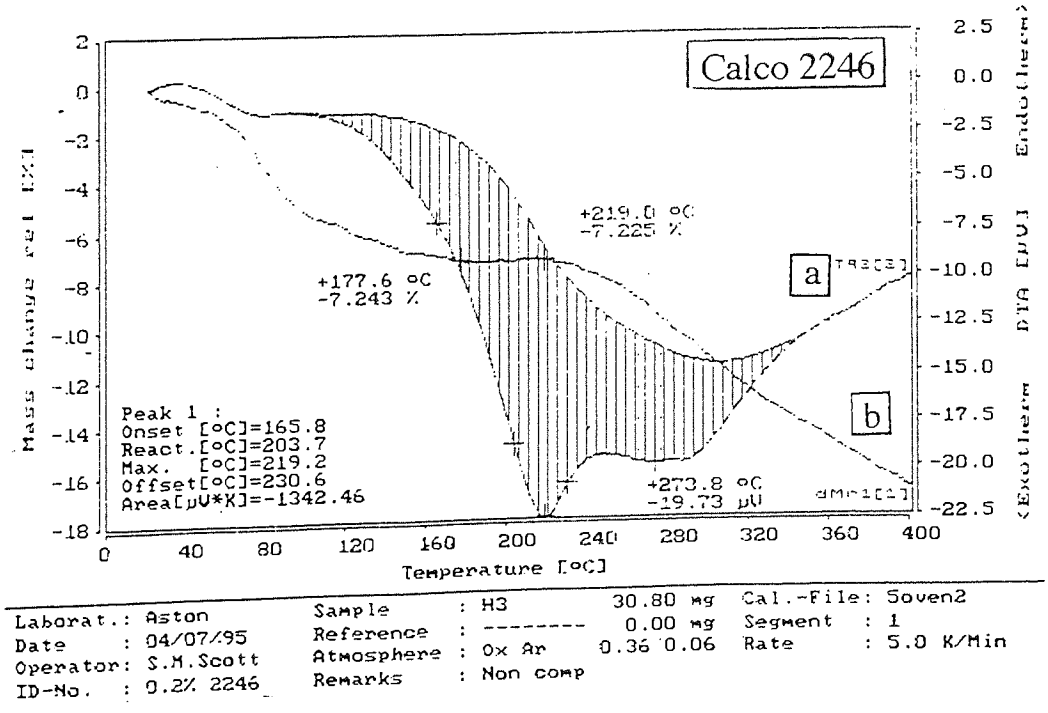


Figure 3-44 Thermogram of cured polybutadiene containing Calco 2246 (0.2% w/w); diluted with 90% alumina analysed in a flowing mixed oxygen (0.36 l/min) and argon (0.06 l/min) atmosphere with a heating rate of 5°C/min.

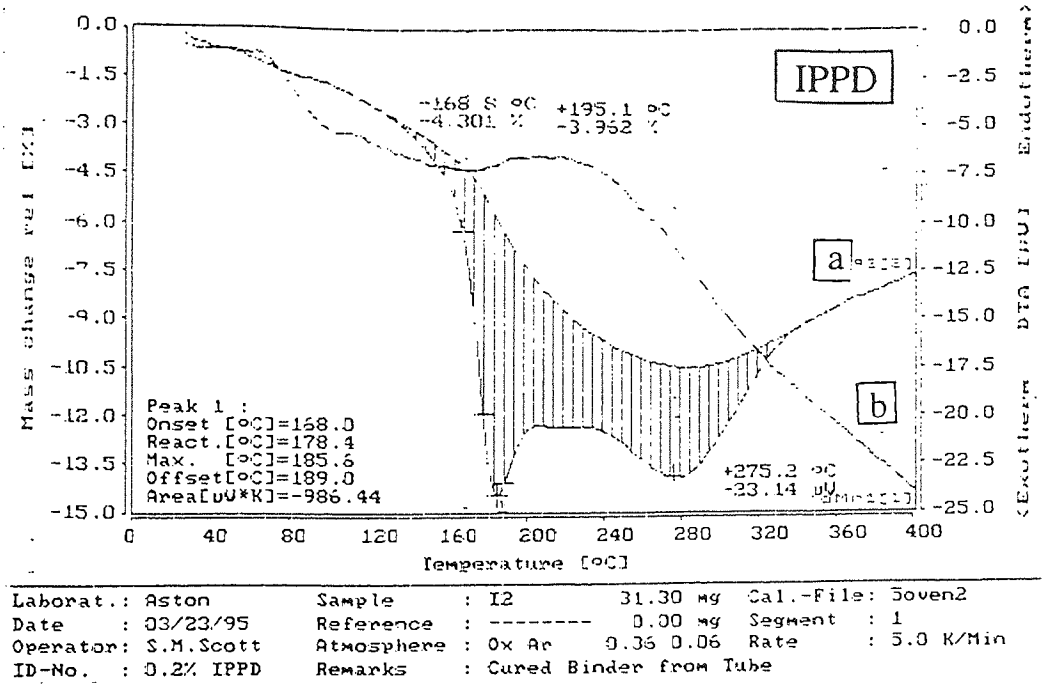


Figure 3-45 Thermogram of cured polybutadiene containing IPPD (0.2% w/w); diluted with 90% alumina analysed in a flowing mixed oxygen (0.36 l/min) and argon (0.06 l/min) atmosphere with a heating rate of 5°C/min.

Table 3-4 The effect of antioxidants (0.2% w/w) on the 'peak maximum and onset temperatures' produced by thermal analysis of uncured HTPB in oxygen listed from lowest 'peak maximum' to highest.

Sample	Mechanism of Antioxidant Action	Moiety Responsible	Peak Max. Temp. °C	Onset °C
DLTP	PD	Sulfur	173.8	144.6
Pure HTPB	-	-	176.1	144.4
Irgafos 168	PD	Phosphite	176.7	143.7
Irgafos 626	PD	Phosphite	177.9	149.4
Santowhite 54	CB-D	Phenol	181.9	159.4
α-Tocopherol	CB-D	Phenol	182.0	166.4
Irganox 1076	CB-D	Phenol	182.7	161.1
Santonox R	CB-D & PD	Phenol & Sufhur	186.6	172.5
WSP	CB-D	Phenol	189.0	177.7
Irganox 565	CB-D & PD	Phenol Amine & Sufhur	189.0	178.3
Calco 2246	CB- D	Phenol	191.1	177.3
γ-Tocopherol	CB-D	Phenol	192.0	180.6
6PPD	CB-D	Amine	220.2	212.2
IPPD	CB-D	Amine	221.2	212.1

Table 3-5 The effect of antioxidants (0.3% w/w) on the 'peak maximum and onset temperatures' produced by thermal analysis of uncured HTPB listed from lowest 'peak maximum' to highest.

Sample	Mechanism of Antioxidant Action	Moiety Responsible	Peak Temp. °C	Onset °C
DLTP	PD	Sufhur	168.6	147.8
P310	PD	Phosphite	174.2	149.4
IPPD-NO·	CB-A	Nitroxyl	174.2	159.7
Pure HTPB	-	-	176.1	144.4
Irganox 565	CB-D & PD	Phenol Amine & Sufhur	186.6	177.1
α-Tocopherol	CB-D	Phenol	182.0	166.4
Irganox 1076	CB-D	Phenol	182.7	161.1
Tinuvin 770	CB-D	Amine	190.4	163.9
Calco 2246	CB- D	Phenol	192.6	183.8
DMDP-NO·	CB-A	Nitroxyl	193.0	178.0
3:1 2246:DLTP	CB-D & PD	Phenol & Sufhur	194.4	185.2
Santonox R	CB-D & PD	Phenol & Sufhur	200.5	190.0
1:1:1 IPPD:Sant. R:Irg. 168	CB-D & PD	Amine Phenol & Phosphite	205.1	198.1
2:1 Irg. 565:IPPD	CB-D & PD	Phenol Amine & Sufhur	216.2	211.3
IPPD	CB-D	Amine	222.6	214.9

Table 3-6 The effect of antioxidants (0.2% w/w unless otherwise stated) on the 'peak maximum and onset temperatures' produced by thermal analysis of undiluted cured binder listed from lowest 'peak maximum' to highest.

Sample	Mechanism of Antioxidant Action	Moiety Responsible	Peak Temp. °C	Onset °C
Pure Binder	-	-	150.1	120.4
0.05 % Irganox 565	CB-D & PD	Phenol Amine & Sufhur	165.4	149.4
1:1 2246:DLTP	CB-D & PD	Phenol & Sufhur	171.0	156.3
0.05 % Irganox 565 + 0.4% Irgafos 168	CB-D & PD	Phenol Amine Sulfur & Phosphite	171.0	159.2
Calco 2246 i	CB-D	Phenol	175.8	166.8
Calco 2246 ii (200 days)	CB-D	Phenol	176.1	166.7
3:1 2246:DLTP	CB-D & PD	Phenol & Sulfur	179.3	164.2
Calco 2246 ii	CB-D	Phenol	180.3	169.3
IPPD	CB-D	Amine	196.0	184.9
3:1 IPPD:2246	CB-D	Amine & Phenol	197.7	188.4
1% Calco 2246	CB-D	Phenol	204.3	195.0
3:1 IPPD:2246 (200 days)	CB-D	Amine & Phenol	205.3	198.3

Table 3-7 The effect of antioxidants on the 'peak maximum and onset temperatures' produced by thermal analysis of alumina diluted cured binder listed from lowest 'peak onset' to highest..

Sample	Mechanism of Antioxidant Action	Moiety Responsible	Peak Temp. °C	Onset °C
DLTP i	PD	Sulfur	168.5	146.9
Irgafos 168	PD	Phosphite	182.6	152.2
DLTP ii	PD	Sulfur	179.6	158.4
γ-Tocopherol	CB-D	Phenol	206.3	158.4
Pure Binder i	-	-	215.6	160.6
Pure Binder i	-	-	205.9	161.4
1:1 2246:DLTP	CB-D & PD	Phenol & Sulfur	218.1	162.3
Calco 2246 ii (low)	CB- D	Phenol	207.5	162.7
Calco 2246 i	CB- D	Phenol	218.3	165.0
Calco 2246 ii (upp)	CB- D	Phenol	212.6	165.4
IPPD	CB-D	Amine	186.0	167.5
3:1 2246:DLTP	CB-D & PD	Phenol & Sulfur	217.8	168.0
3:1 IPPD:2246	CB-D	Amine & Phenol	183.2	168.7

Table 3-8 The effect of combinations of IPPD and DLTP on the 'peak maximum and onset temperatures' produced by thermal analysis of uncured HTPB and cured binder.

Sample	AO Conc. % w/w	Cured	Peak Temp. °C	Onset Temp. °C
IPPD	0.05	N	188.9	179.7
DLTP	0.05	N	175.4	142.0
1:1 IPPD:DLTP	0.05	N	194.3	186.0
2:1 IPPD:DLTP	0.05	N	200.1	192.7
1:2 IPPD:DLTP	0.05	N	191.4	182.8
Calco 2246	0.05	N	180.5	157.3
IPPD	0.1	Y	206.1	199.5
1:1 IPPD:DLTP	0.1	Y	187.8	176.4
2:1 IPPD:DLTP	0.1	Y	190.0	174.0
1:2 IPPD:DLTP	0.1	Y	178.0	165.2

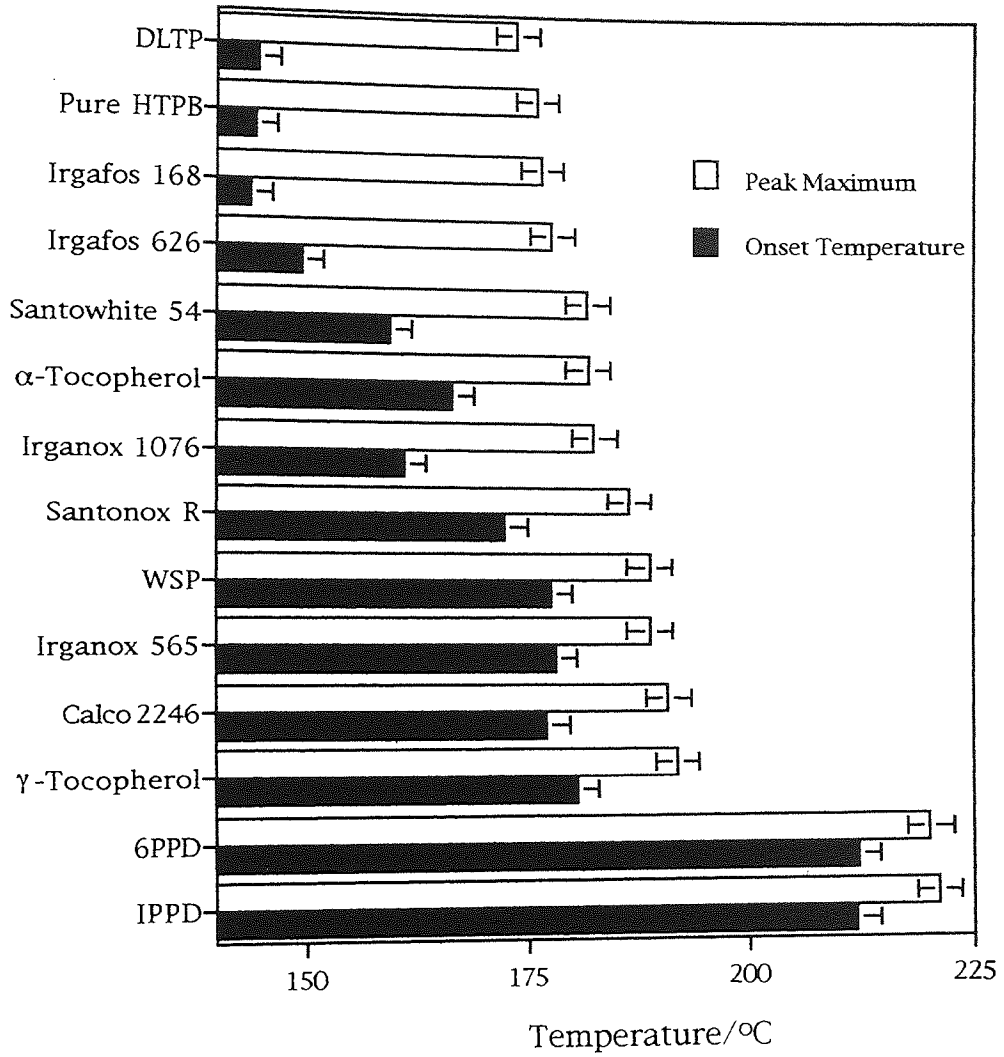


Figure 3-46 Effect of various antioxidants (0.2% w/w) on the 'peak maximum and onset temperatures' observed during thermal analysis of uncured HTPB. (Flowing O_2/Ar atmosphere 0.36/0.06 l/min, respectively)

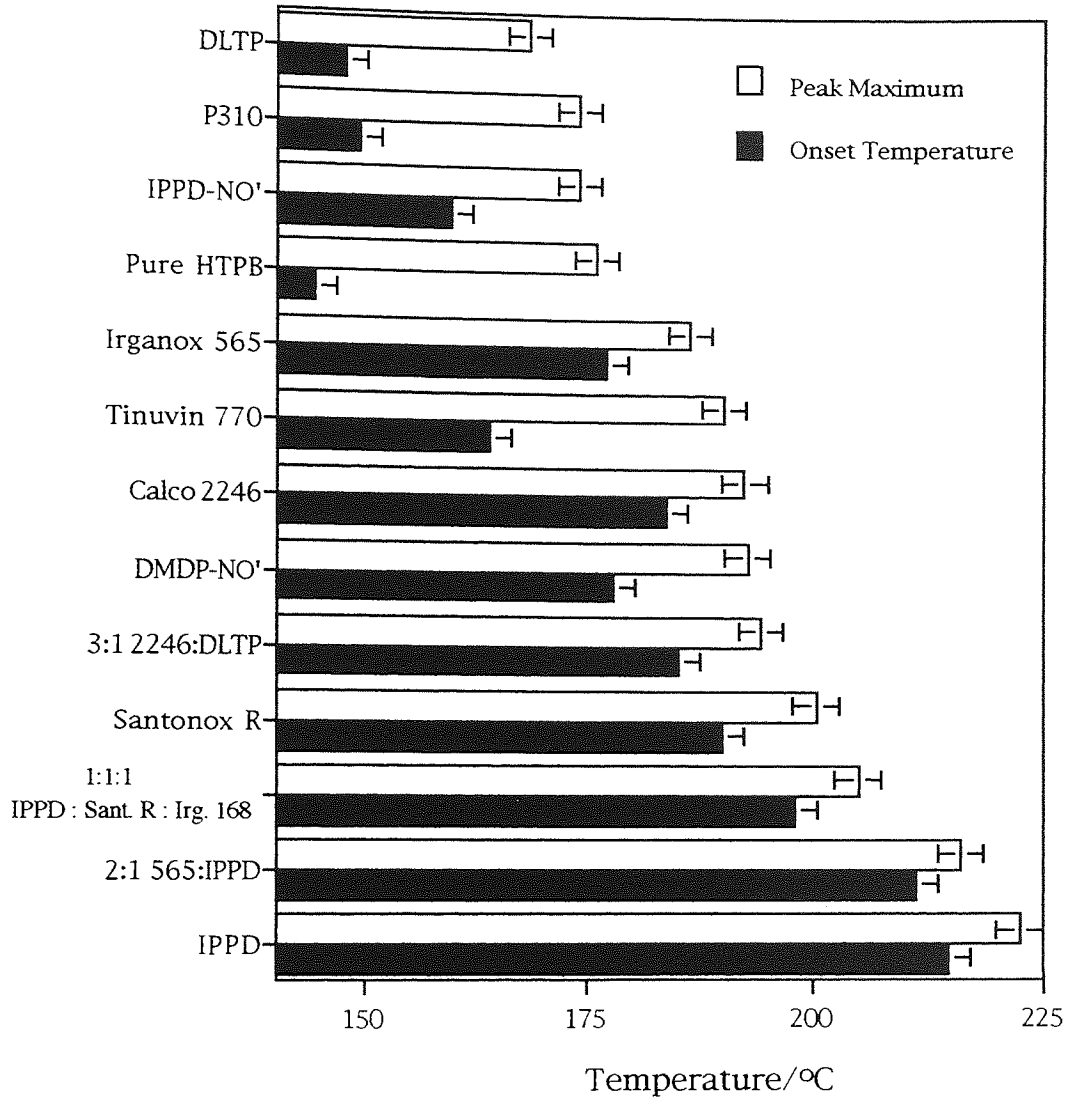


Figure 3-47 Effect of various antioxidants (0.3% w/w) on the 'peak maximum and onset temperatures' observed during thermal analysis of uncured HTPB. (Flowing O_2/Ar atmosphere 0.36/0.06 l/min, respectively)

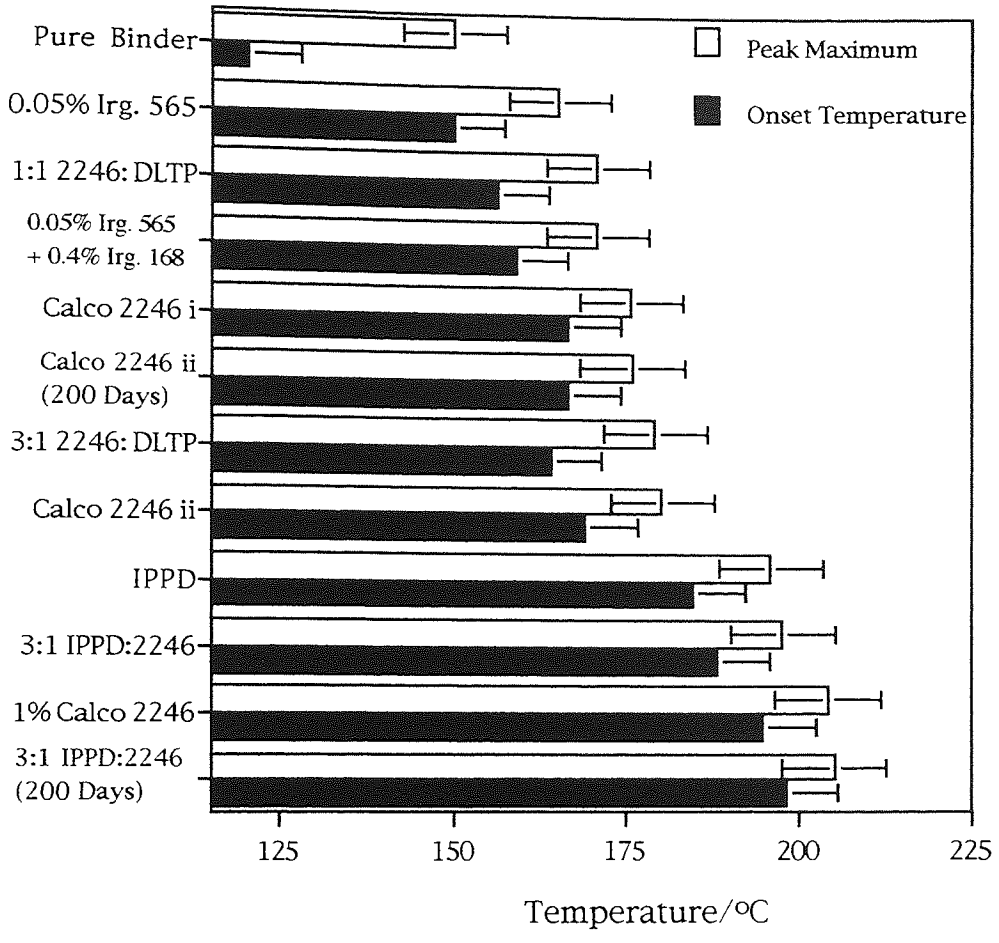


Figure 3-48 Effect of various antioxidants (0.2% tot. unless otherwise stated w/w) on the 'peak maximum and onset temperatures' observed during thermal analysis of undiluted cured polybutadiene binder. (Flowing O_2/Ar atmosphere 0.36/0.06 l/min, respectively). i and ii represents analysis on similar samples prepared at different times. Samples marked 200 days represents samples re-tested after ageing for 200 days at 60°C

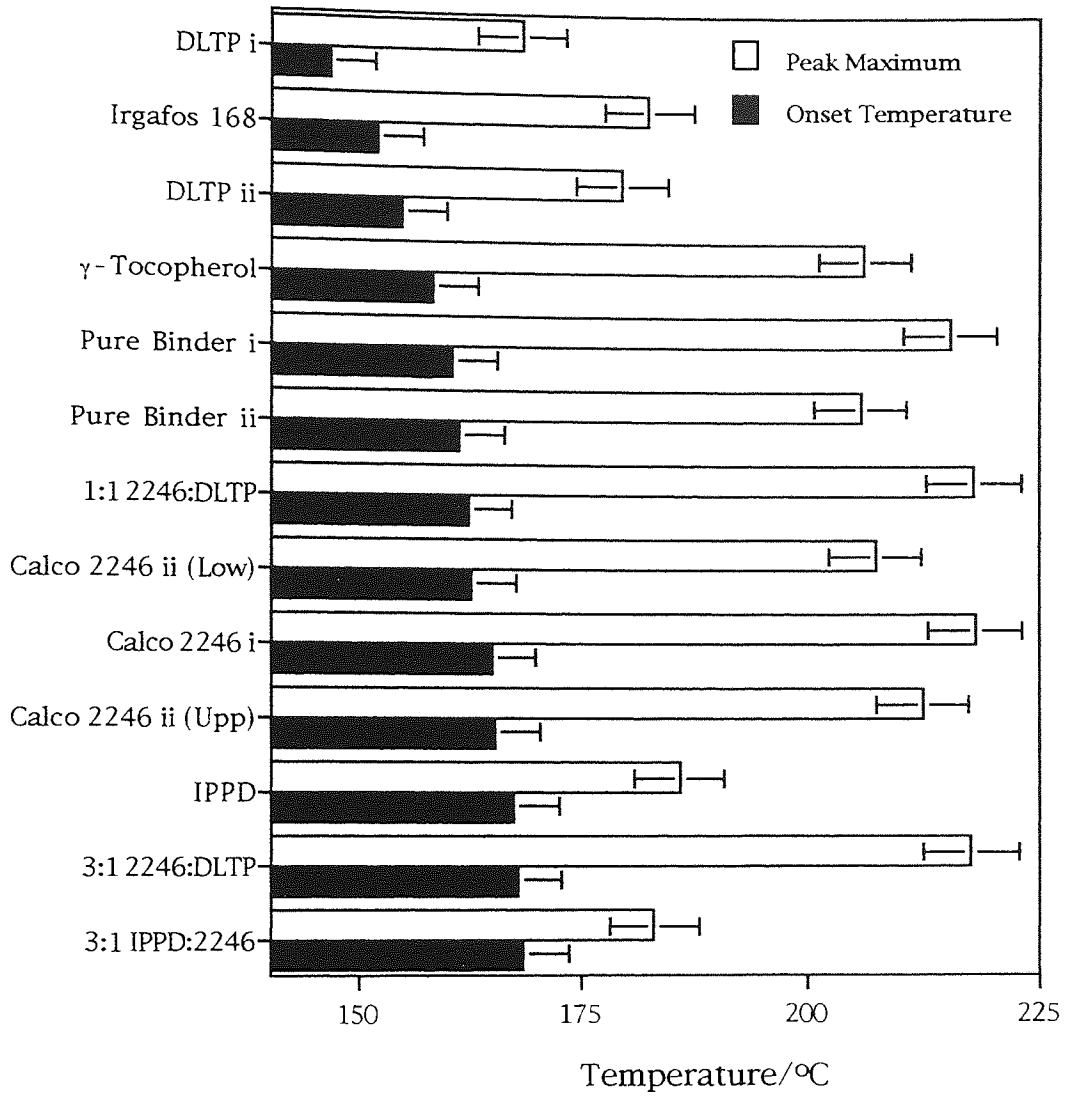


Figure 3-49 Effect of various antioxidants (0.2% w/w tot.) on the 'peak maximum and onset temperatures' observed during thermal analysis of cured polybutadiene binder diluted with 90% Alumina. (Flowing O_2 Ar atmosphere 0.36 0.06 l/min respectively). i and ii represents analysis on similar samples manufactured at different times. Upp and Low represent analysis of upper and lower layers of a sample

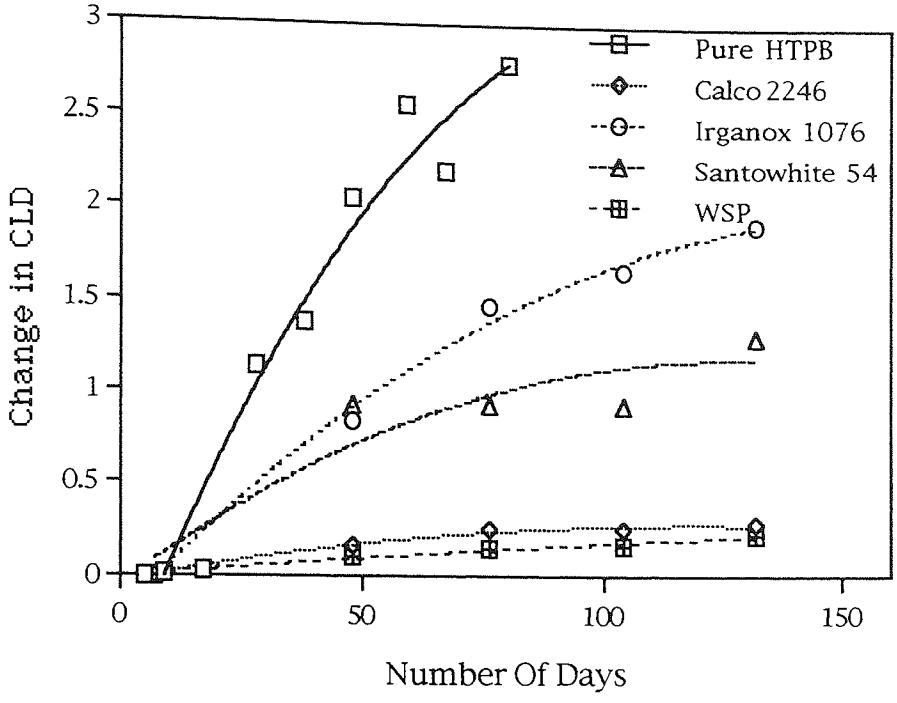


Figure 3-50 Effect of various antioxidants (0.1% w/w) on the CLD of polybutadiene binder in a 5 mm film aged at 60°C. [Reproduced from ref. 31 with permission]

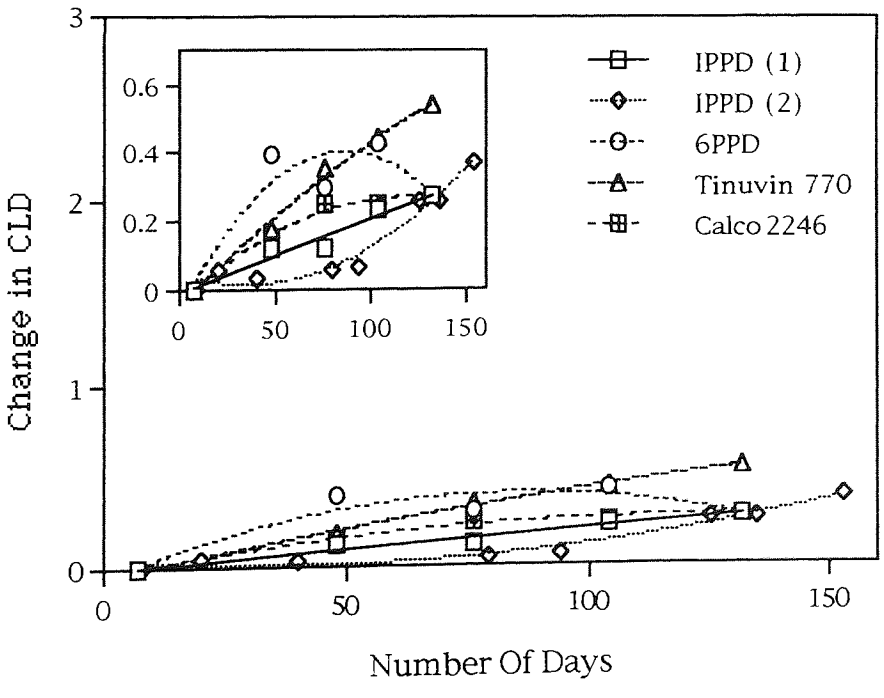


Figure 3-51 Effect of various antioxidants (0.1% w/w) on the CLD of polybutadiene binder in a 5 mm film aged at 60°C. [Reproduced from ref. 31 with permission]

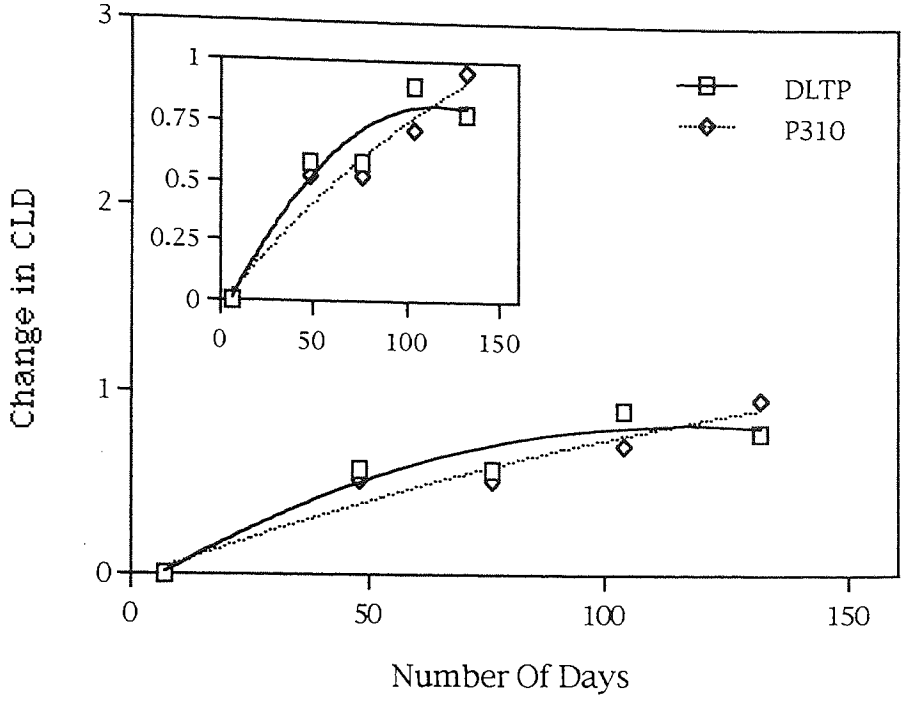


Figure 3-52 Effect of various antioxidants (0.1% w/w) on the CLD of polybutadiene binder in a 5 mm film aged at 60°C. [Reproduced from ref. 31 with permission]

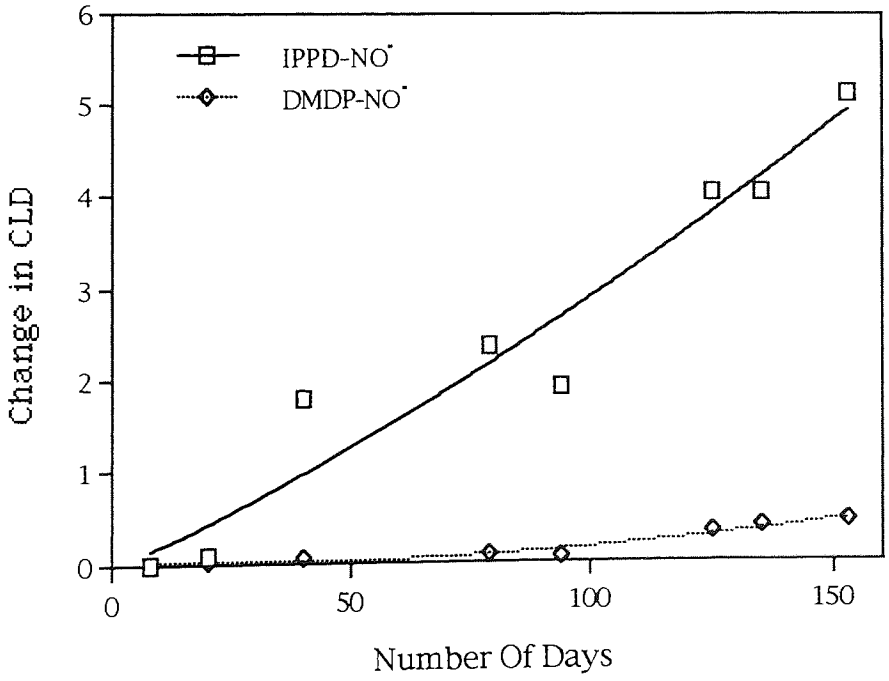


Figure 3-53 Effect of various antioxidants (0.1% w/w) on the CLD of polybutadiene binder in a 5 mm film aged at 70°C. [Reproduced from ref. 31 with permission]

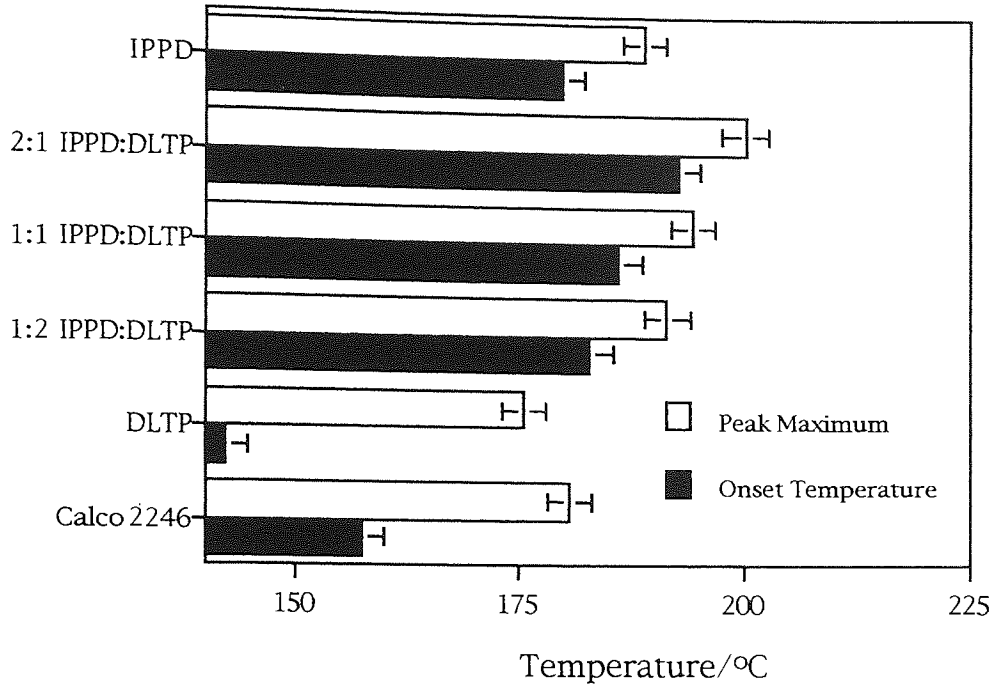


Figure 3-54 Effect of combinations of IPPD and DLTP (0.05% w/w total concentration) on the 'peak maximum and onset temperatures' observed during thermal analysis of uncured HTPB.

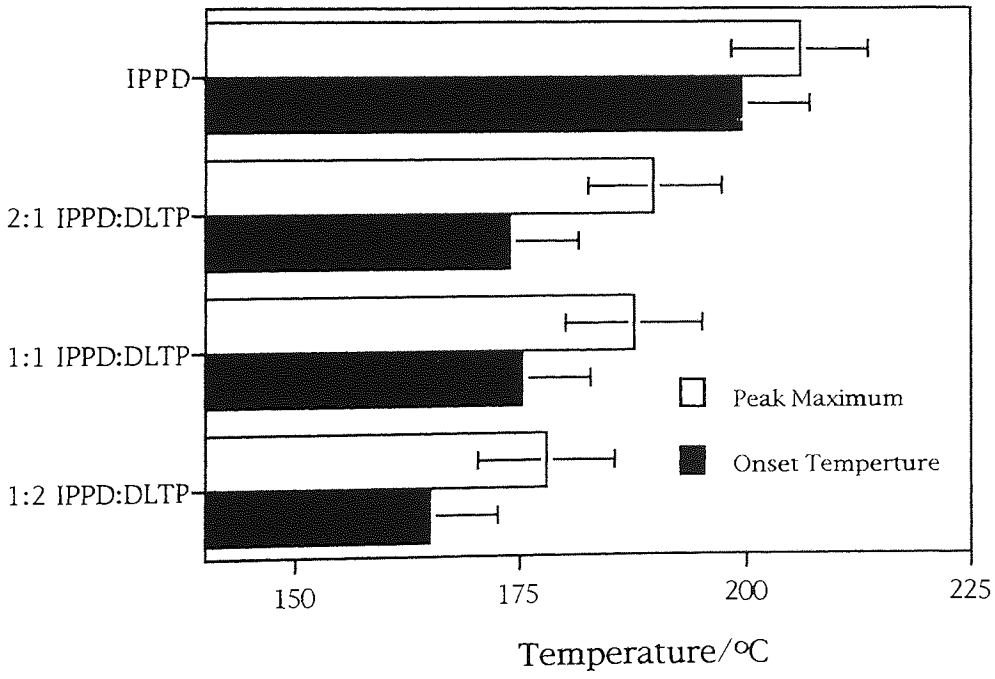


Figure 3-55 Effect of combinations of IPPD and DLTP (0.1% w/w total concentration unless stated) and other antioxidants on the 'peak maximum and onset temperatures' observed during thermal analysis of undiluted polybutadiene binder.

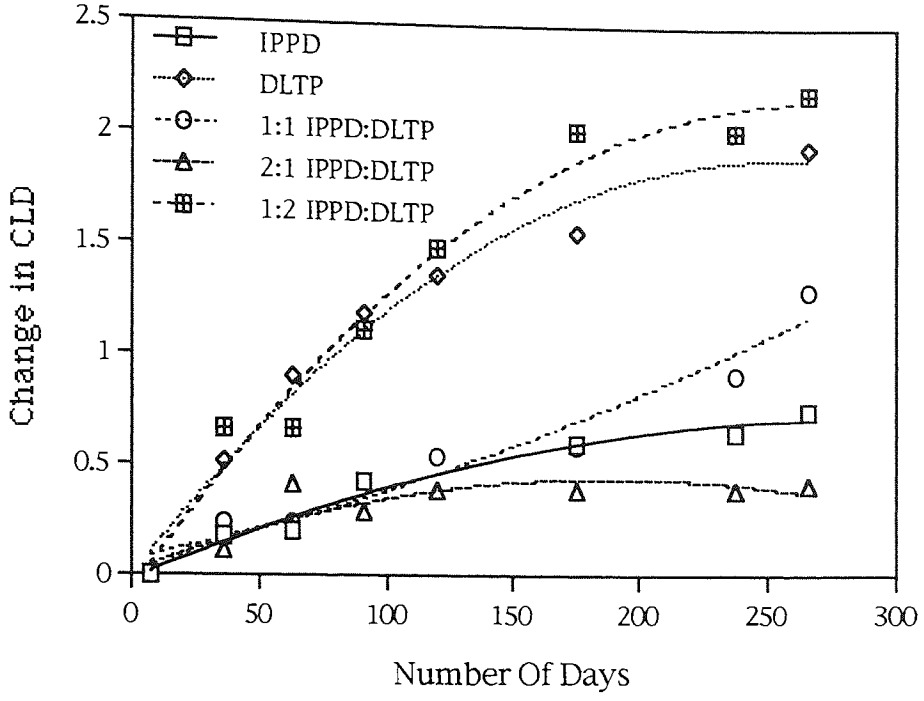


Figure 3-56 Effect of combinations of IPPD and DLTP (0.1% w/w) on the CLD of polybutadiene binder in a 5 mm film aged at 70°C. [Reproduced from ref. 31 with permission]

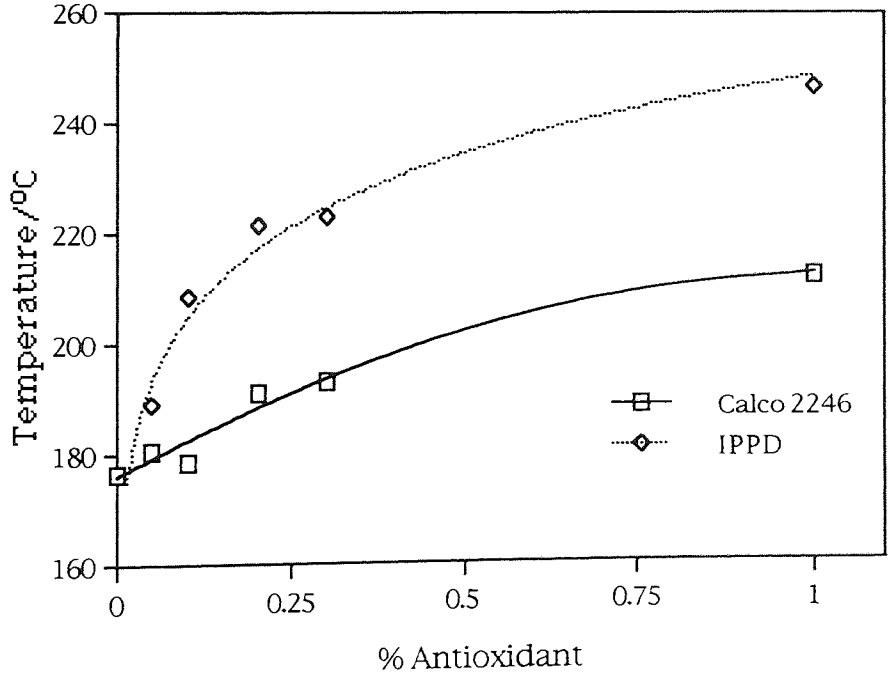


Figure 3-57 Effect of varying concentration of Calco 2246 or IPPD antioxidants on the 'peak maximum temperature' observed during thermal analysis of uncured HTPB.

CHAPTER FOUR

4 ANALYSIS OF ANTIOXIDANT SYSTEMS USING LONG TERM OVEN AGEING

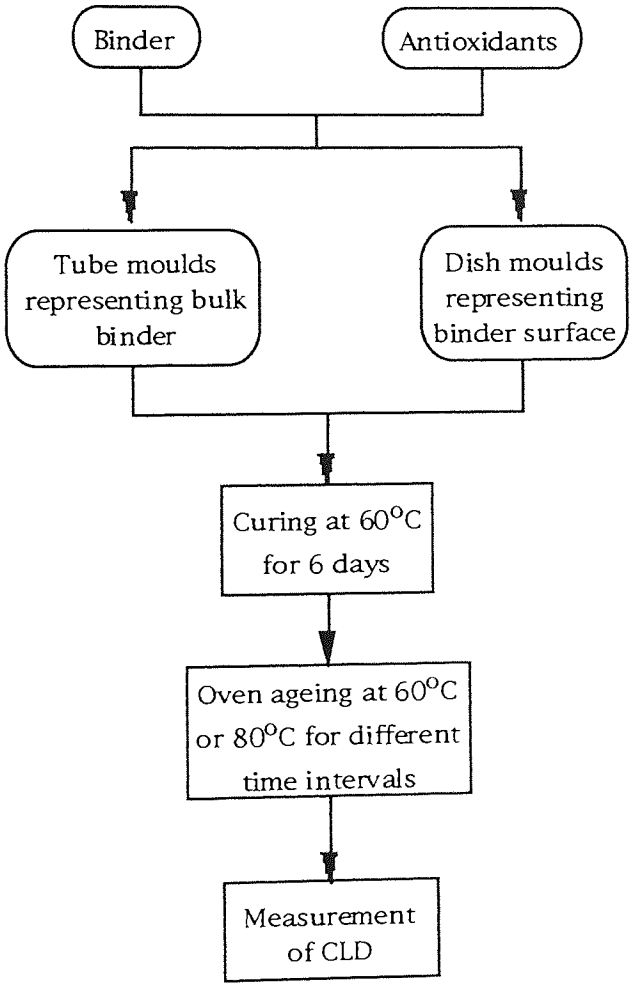
4.1 Object and Methodology

During long term storage it has been found [3] that hydroxyterminated polybutadiene binder undergoes degradation, even at low temperature. This reduces the important rubbery properties of the binder. Work at Aston [31] has illustrated that cross-linking reactions in the presence of oxygen were the main cause of this degradation and the effect of antioxidants on this low temperature (below 80°C) degradation was investigated [31]. It was shown that the use of selected synergistic antioxidant systems could improve the potential lifetime of the binder. The first systems investigated [31] were based on a combination of chain breaking donor (CB-D) and peroxide decomposer (PD) antioxidants which, depending on composition, showed either antagonistic or synergistic effects.

In this work the roles of different antioxidant systems, which could potentially lead to synergism, have been investigated and results are compared to those obtained from the bis-phenol Calco 2246 (for structure see table 2-3) currently used as the preferred antioxidant by the DRA. Also included are further evaluation of the systems used in earlier work [31] and investigation into different systems based on either homo-, hetero- or auto-synergistic combinations. Two types of moulds were used to analyse the efficiency of these antioxidant systems. Dish moulds, which were used in earlier work [31], representing the binder skin where conditions of oxygen excess are simulated. On the other hand, tube moulds were used to represent the bulk binder under the skin where oxygen deficient conditions may exist.

Six individual moulds of each sample were prepared and cured at 60°C for seven days. One mould was then removed and a measurement of initial cross-link density was made. The remaining moulds were aged in an oven open

to air at 60°C, or in a few cases 80°C and were removed at various time intervals for cross-link density measurement. Where two layers were formed during curing, each layer was analysed separately. To estimate the analytical error a number of replications were made. Because of the very long term nature of these tests, replication was carried out only on the 'important' samples, where time allowed. Scheme 1 shows an overview of the methods used.



Scheme 4-1 Overview of the types of samples analysed in the determination of effect of antioxidants on the cross-link density

4.2 Results

4.2.1 Single Antioxidants

Figures 1 to 7 show the effect of various single antioxidants on the cross-link density of the binder. The graphs show the change in cross-link density

from an original cross-link density measured after the seven days curing time. Figures 1 to 4 and 7 are results from thick layer (tube) moulds aged at 60°C and 5 and 6 are from thin layer (dish) moulds aged at 80°C. Figure 1 shows replicate results of 0.2% Calco 2246. Some of these samples contained 2 layers, both of which were analysed. The formation of two layers as discussed in chapter 3, is associated with slightly differing initial cross-link densities which averaged out during the ageing of the sample. It was seen that in the case of Calco 2246 (figure 1) the difference in the cross-link density of the layers is much lower than the change in cross-link density caused by the oxidation of the polymer. Also, during sample preparation, even though a constant NCO:OH ratio was used a variation in initial cross-link density between 0.2 and 0.5 was common. The reason for this variation is unclear but moisture in the atmosphere [31] has been implicated and also the formation of the two layers could cause variations. It is clear from the results of replicate samples containing Calco 2246 (figure 1 where initial cross-link densities vary between 0.2 and 0.5) that these factors do not affect the subsequent change in cross-link density results with reproducibility being within ± 10%. This suggests the initial difference in cross-link density of the samples does not alter the diffusion rate of oxygen through the samples. Earlier work [31] using very thin layers (~1 mm) of binder with cross-link densities greater than two showed that at these high cross-link densities diffusion of oxygen through the samples was greatly reduced.

As was seen in earlier work [31] the antioxidants tested here singularly are all less effective than Calco 2246, with the exception of γ-Tocopherol which shows better overall performance (see fig. 4.3).

4.2.2 Combinations of CB and PD Antioxidants

Figures 8 to 13 show the effect of a number of different combinations of CB and PD antioxidants on the change in cross-link density. Some

combinations were prepared with a number of different ratios in an attempt to establish the optimum combination.

4.2.3 Combinations of Two CB or CB with Autosynergistic Antioxidants

Figures 14 to 17 show the effect a variety of combinations of 2 CB antioxidants at a number of ratios have on the cross-link density of the binder. Figure 16 is from thin layer moulds aged at both 60 and 80°C.

Figures 18 and 19 show the effect of a mixture of a CB and an autosynergistic antioxidants have on the binder cross-link density.

4.2.4 Combinations of two CB and a PD Antioxidant

Figure 20 shows the effect of a mixture of 3 antioxidants which contain the same moieties as an autosynergistic antioxidant on the binder cross-link density.

4.2.5 Repeats of Effective Antioxidant Systems

Figures 21 to 23 show repeats of some antioxidant combinations which were particularly effective at preventing increases in cross-link density. Figures 21 and 22 show results from 2 ratios of a combination of Calco 2246 with DLTP which were reproducibly more effective than Calco 2246 alone. Figure 23 shows repeat analysis of a ratio of 3:1 IPPD:Calco 2246, the reproducibility of results from this combination is low but this is due to the methods of experimental preparation as discussed later, see chapter 5.

4.2.6 Comparison of the Most Effective Stabilising Antioxidant Combinations with Calco 2246

Figures 24 to 27 compare the results of change in cross-link density for a number of promising samples with the results from Calco 2246 all with a total antioxidant concentration of 0.2%. It is clear that a number of mixed samples, including both homo- and hetero-synergism, can be more effective than the commercially used Calco 2246. But also the natural hindered phenol, γ-Tocopherol, is shown to be very effective when used alone.

4.2.7 Thermal Analysis of Some Antioxidant Combinations

Figures 28 to 30 show results from thermal analysis of a number of antioxidant combinations which have also been analysed in tube moulds. Samples from figure 28 were uncured hydroxyterminated polybutadiene and those in 29 and 30 were undiluted cured binder. The results show little agreement with the result obtained from oven ageing.

Figures 31 and 32 are thermograms of polybutadiene binder containing 0.2% 3:1 IPPD:Calco 2246 diluted with alumina. Figure 31 was from the sample prepared on 24/3/94 and 32 from the sample prepared using ultrasound on 28/7/93 which was particularly effective at preventing cross-linking. The ultrasound was used to help dissolve the sparingly soluble IPPD, a small ultrasound bath (L & R Maxomatic Ultrasonic Bath) was used for 30 minutes with stirring at regular intervals.

4.3 Discussion

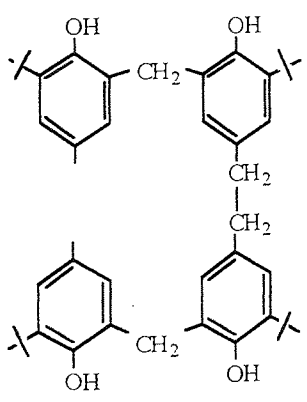
4.3.1 Effectiveness of Single Antioxidants

For study of the antioxidants a constant ratio of 0.2 % weight to weight antioxidant to binder was chosen. This ratio was chosen following consideration

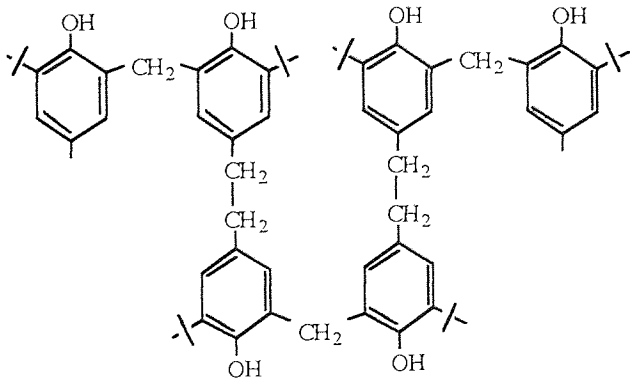
of the results of increasing concentration on thermal analysis (fig 3-57) and from analysis of the effect of concentration of Calco 2246 on oxidation of rubber by other workers [169]. Both suggested that above a value of 0.2% little extra stabilisation was obtained.

Results from this and previous work [31] have shown that the bisphenol Calco 2246 is one of the most effective antioxidants for the binder when using a single antioxidant system. The effectiveness of this bis phenol when used in model systems has been demonstrated [169] and was attributed to the two hydroxyl groups being non equivalent thus having different rate constants for the hydrogen transfer reaction. Hydrogen bonding between the two hydroxyl groups was proposed as the mechanism which caused this difference and other workers [170] have shown the presence of this hydrogen bonding by infra red analysis. However additionally, they suggest that the antioxidant efficiency increases with the level of free (unbound) hydroxyl groups which is in turn related to the bridge structure in bis-phenols [170], the methyl bridge in Calco 2246 being one of the most efficient.

Other extensive studies on the antioxidant activity of Calco 2246 have shown that unlike the fully hindered phenols the partially hindered Calco 2246 does not give a stable primary phenoxyl radical [171]. Instead, the unstable radical is rapidly converted into the dimer (IL), which has similar activity to the initial 2246, and the trimer (L), which has slightly lower activity.

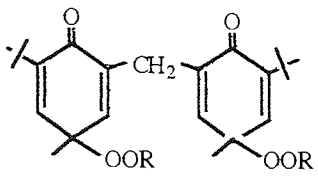


IL

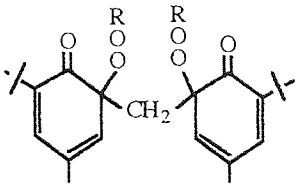


L

Furthermore, the formation of the pro-oxidant, alkylperoxycyclohexadienones (LI & LII), is seen only to occur in conditions where excess hydroperoxide is present [171]. Thus, during inhibited oxidation the concentration of these initiators should be low.



LI



LII

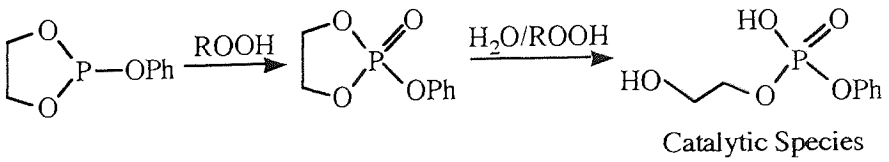
The formation of these dienones may be the reason for the lower effectiveness shown by Calco 2246 in the thin layer samples aged at 80°C (fig. 5) when compared to the amine IPPD. Here high levels of peroxides would be expected to occur due to the ease of diffusion of oxygen throughout the sample. Also the increased temperature could cause the more rapid decomposition of the dienones to initiating radicals.

The effectiveness of the amines IPPD and 6PPD in both the deep and thin moulds (fig. 2 & 5) re-enforces the conclusion from chapter 3 that the cross-linking agent only reacts with one of the amines leaving the other to perform an antioxidant function. Generally amines are thought to be more effective antioxidants than phenols [90], this is attributed to the transformation products formed. Therefore, in the case of these amines the low effectiveness observed (fig. 2) may be due to the reaction with the cross-linker IPDI preventing the formation of some of the important transformation products of the parent antioxidant.

Antioxidants which show lower changes in cross-link density in the deep moulds than Calco 2246 are; γ-Tocopherol, the autosynergist antioxidant Santonox R (fig. 3) and the peroxide decomposers DLTP and Irgafos 168 (fig. 4). In the case of the autosynergist and peroxide decomposers, examination of the samples and the results from the thin layer moulds (fig. 6) showed a rapid

increase in cross-link density at the surface of the deep sample. It has been shown [31] that highly cross-linked binder has a very low oxygen permeability, thus rapid formation of a 'skin' of this impervious binder on the sample surface will prevent more oxygen diffusing into the bulk. Any free radicals or peroxides produced before the protective layer has formed would be prevented from producing a chain reaction by the remaining antioxidant which although not very effective would be able to cope with the low pro-oxidant levels involved. The formation of a protective skin in this way could be seen to be advantageous but in the real system where temperature cycling is an important factor [31] cracking and debonding from the case would occur. This would then allow oxygen access to the polymer bulk, hence restricting this advantage.

The rapid increase in cross-link density at the surface of the samples containing the two peroxide decomposers is expected. It is known that phosphites such as Irgafos 168, which act stoichiometricly, are not very efficient antioxidants when used alone, although Irgafos 168 may have some CB-D effect as well due to the presence of phenol groups. The other phosphite, Ultranox 626, shows greater antioxidant efficiency as, although the increase in cross-link density is greater in the deep moulds, no 'skin' forms. It has been suggested [172] that the cyclic nature of the latter phosphite may allow the formation of species similar to that formed by other cyclic and catechol phosphites (reaction 86) which are known to decompose peroxides catalytically [127].



86

This has been discounted by other workers [173] and the increase in effectiveness of the cyclic phosphite is attributed to the less bulky alkyl groups compared to the aryl groups in Irgafos 168.

In the case of the sulfur containing DLTP, a pro-oxidant stage is often observed before the formation of the antioxidant species [131]. This is caused by the reaction of sulfenic acid, formed by reaction 87, with low concentrations of hydroperoxide (reaction 88) producing an alkoxyl radical.

$$(ROCOCH_2CH_2)_2S{=}O \longrightarrow ROCOCH_2CH_2SOH + ROCOCH_2{=}CH_2 \qquad 87$$

$$ROCOCH_2CH_2SOH + ROOH \longrightarrow RO^{\cdot} + H_2O + ROCOCH_2CH_2SO^{\cdot} \qquad 88$$

This will rapidly initiate oxidation in the easily oxidisable binder before the catalytic antioxidant sulfur species can form thus causing the formation of the heavily cross-linked 'skin'. However, once this pro-oxidant stage is over there is autoretardation (see fig. 6), typical behaviour of sulfur compounds such as DLTP.

The ineffectiveness of the autosynergist Santonox R (see fig. 6) which has two phenol moieties joined by a sulfur bridge can be similarly explained. It is known [112] that fragmentation at the sulfur occurs and the following sulfur transformations are similar to those shown by other sulfur containing species which are likely to include the production of pro-oxidants. The thiobisphenols have been shown to be excellent stabilisers under certain conditions [112, 163] especially high temperatures where the sulfur peroxide decomposing activity becomes very efficient. But in this case, with the highly oxidisable binder and relatively low temperature, the strength of the phenolic antioxidant moiety is not great enough to prevent the initial pro-oxidant activity of the sulfur moiety causing rapid oxidation.

The other autosynergist examined Irganox 565, is suggested to be a very effective antioxidant for butadiene rubber [167]. It contains sulfur groups as well as both phenols and amines and although it is more effective than Santonox R it is no better than Calco 2246 (fig. 3). Again, the sulfur moieties are likely to cause a pro-oxidant stage but the other moieties seem to be able to prevent initiation of oxidation. In the binder system some of the effectiveness of 565

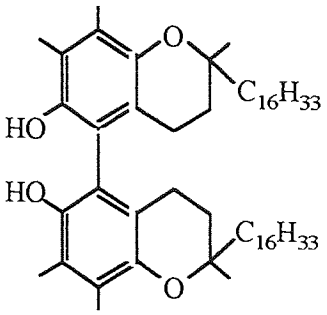
may be reduced due to a reaction between the amine group and the cross-linking agent.

The only antioxidant which outperforms Calco 2246 is the natural hindered phenol γ-Tocopherol (fig. 3) (where no skin forms during ageing). This is an unhindered phenol so may be expected to react rapidly. It also shows considerably more effectiveness than α-Tocopherol which has been shown to be a very efficient antioxidant during processing of polyolefins [174] but was less effective than Calco 2246 in polybutadiene as shown in this work. A pro-oxidative effect of α-Tocopherol has been shown at 25°C in fat at concentrations above 0.2% and has been attributed to both the reaction of the antioxidant (AH) with hydroperoxide (reaction 89) and the direct abstraction of hydrogen by the unhindered alkyl radical formed (reaction 90) [175].

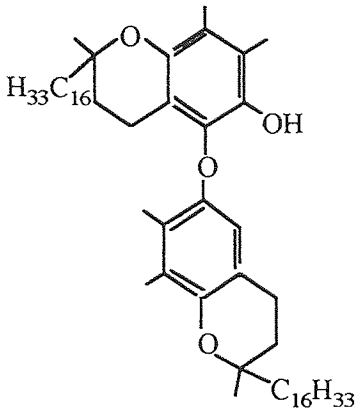
$$AH + ROOH \longrightarrow RO^{\bullet} + A^{\bullet} + H_2O \qquad 89$$

$$A^{\bullet} + RH \longrightarrow R^{\bullet} + AH \qquad 90$$

It may be expected that the less hindered γ-Tocopherol would produce more of a pro-oxidant effect after the initial radical has been formed, but the lack of the extra methyl group in γ-Tocopherol allows the formation of some unique transformation products [175] which are effective antioxidants. Both α- and γ-Tocopherol form a range of transformation products including dimers and trimers a number of which have little antioxidant activity [166]. In the case of γ-Tocopherol in an oxidisable substrate the main transformation products were shown to be biphenyl dimer derivatives (LIII) which retained antioxidant properties. Another product, the tocopherol ether dimers (LIV), also contain considerable antioxidant activity. In contrast, the main product formed from α-Tocopherol were shown to be substrate bound tocopherol ethers containing no antioxidant activity [175].

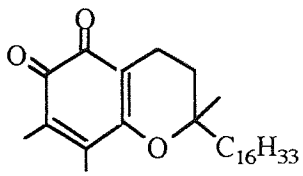


LIII



LIV

Another product unique to γ-Tocopherol is the chroman-5,6-quinone (LV) which retains some antioxidant properties [166]. The formation of quinone structures is important in binder stabilisation as these are known to react with carbon centred alkyl radicals, which are likely to form in the sample lower layers, via a CB-A mechanism [126]. So the ability to react with both alkoxyl and alkyl radicals lead to an enhanced overall stabilising effect.



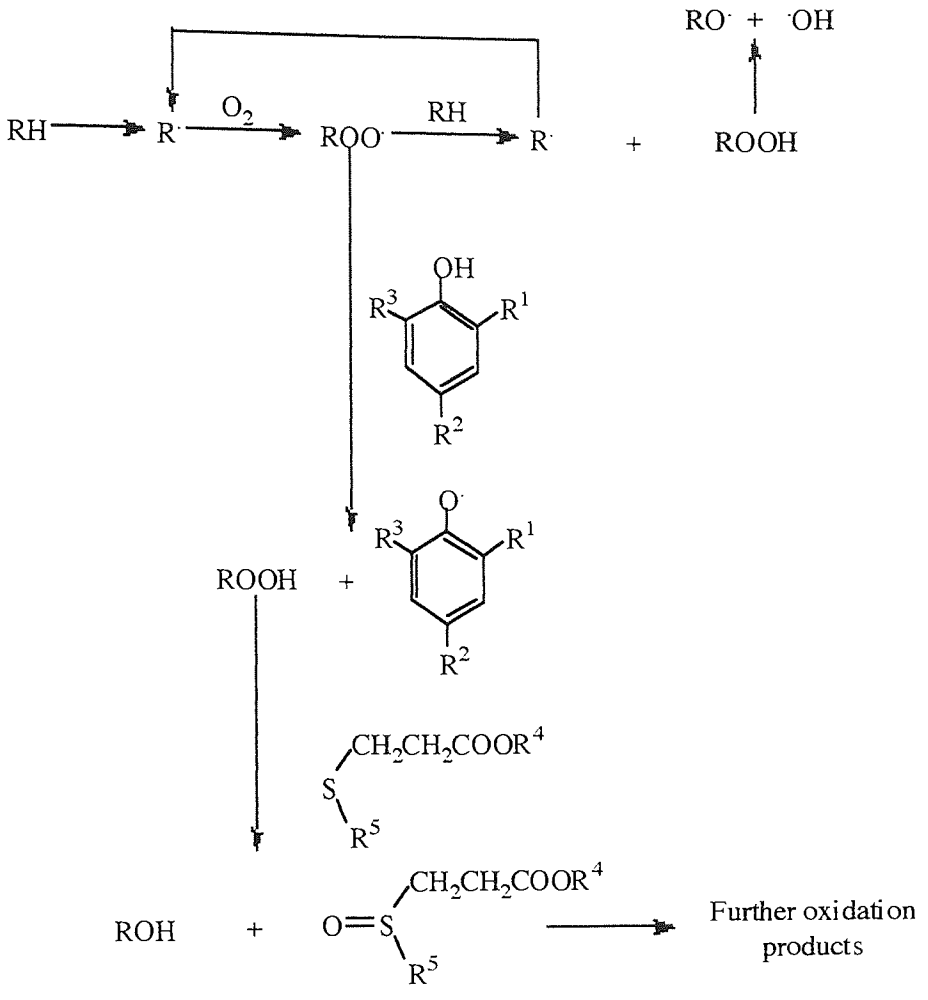
LV

4.3.2 Combinations of CB and PD Antioxidants

Results from earlier work [31] suggested that a mixture of the CB-D Calco 2246 and the PD-C DLTP antioxidant in a 2:1 ratio could produce a synergistic stabilisation effect. Further investigation into this type of heterosynergistic combination was therefore concentrated on samples containing either an equal or a higher ratio of the CB-D antioxidant to DLTP. This is different from the ratio employed in polyolefin stabilisation where the most effective stabilisation is usually found at a ratio containing high levels of the sulfur containing DLTP [135, 176]. This difference is due to the oxidisability of the substrate, polyolefins, e.g. polyethylene, are more oxidatively stable than polybutadiene. This means that initiation, by pro-oxidant species produced

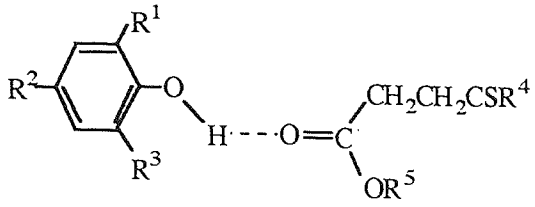
during the early transformations of the DLTP (reaction 88), of autoxidation in the polyolefin occurs only slowly. Therefore only a low level of CB-D antioxidant is required to deactivate the potentially initiating alkoxyl radicals before formation of the catalytic peroxide decomposer. In polybutadiene, the radicals initiate autoxidation rapidly thus more CB-D is required to terminate the more numerous oxidation chains. This explains the [31] pro-oxidant effect in the binder when using ratios containing higher levels of DLTP than phenol as the phenol is not able to deactivate the initial pro-oxidants rapidly enough to prevent initiation. Once the catalytic peroxide decomposer species have formed from the DLTP the co-operative mechanism shown in scheme 2 can operate with remaining CB-D antioxidant.

Synergism between a CB-D antioxidant and DLTP appears to occur quite readily with both phenolic and amine antioxidants (see fig. 24). It also appears to occur to an equal amount at a number of ratios (see figs. 8, 10 &11). This suggests that once a level of CB-D activity has been reached where early initiation by the pro-oxidants produced by DLTP is prevented then synergism occurs quite readily. This is similar to that observed in polyolefin systems [135, 176] where most mixes of a phenolic CB-D and DLTP produce synergism at all but the extreme ratios, a maximum effect usually occurring at a high level of DLTP. A proposed mechanism for this type of synergism is shown in scheme 2 [176], where the role of the phenolic CB-D antioxidant is to trap the peroxyl radical by hydrogen donation. This causes the formation of a hydroperoxide which can subsequently be decomposed to harmless products by the peroxide decomposer thus augmenting the action of the phenol.



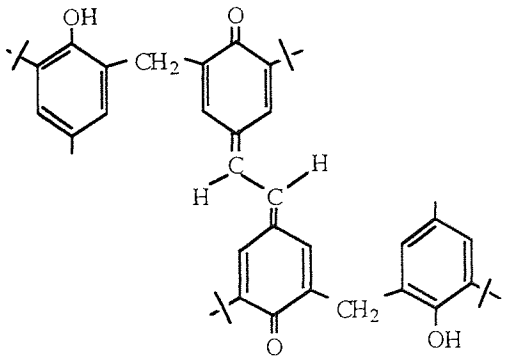
Scheme 4-2 Proposed synergistic mechanism between hindered phenolic and thiopropionate antioxidant.

It has been suggested [176, 177] that the strength of the synergistic effect in the phenol - thiopropionate systems is related to molecular interaction between the antioxidants. With a partially hindered phenol, hydrogen bonding between the hydroxyl group and the carbonyl in the thiopropionate antioxidant keeps the two species in close proximity (scheme 3). It is suggested that this facilitates the rapid destruction of the hydroperoxide formed by the CB-D action. Although the interaction does appear to occur [176, 177] the effect it has on synergism is questionable as the real peroxide decomposing catalyst are the transformation products and not the parent thiopropionate.



Scheme 4-3 Interaction between phenols and thiopropionate.

These mechanisms infer that it is the phenol which is the most important part of the synergistic system. The result from this work and others [52] suggest that it is the sulfur containing antioxidant which is the main stabiliser and the major role of the CB-D antioxidant is to prevent the early initiation. In the binder samples the peroxide decomposer will be very important at the surface, as there will be a high level of peroxides. If alkyl radicals form deeper in the sample then since the level of oxygen will be lower the reaction may occur via a mix of oxygen and carbon centred radicals. In this situation the CB antioxidant will become more important especially if it can also act via a CB-A mechanism (see section 1.5.2.2). It is known that the nitroxyl of the amine IPPD is formed during fatigue [114], this then reacts as a CB-A antioxidant and can produce a regenerative cycle as shown in scheme 1-7. Furthermore the phenol Calco 2246 is known to form quinones (LVI) [171] which can act as CB-A antioxidants. This suggests a number of mechanisms would be occurring at different positions in the samples.



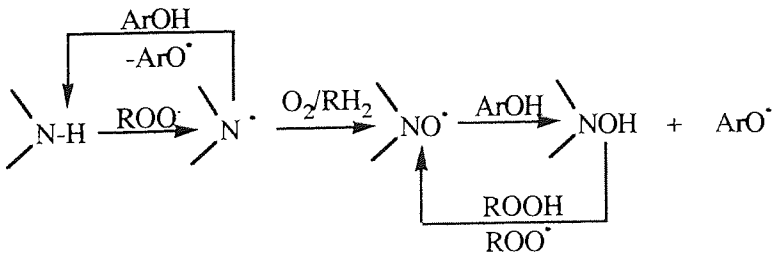
LVI

Replicate samples containing both 1:1 and 3:1 ratios of Calco 2246:DLTP (fig. 21 & 22 respectively) show that these reproducibly produce substantially better stabilisation than Calco 2246 alone (see fig. 24 for comparison).

Another example of homosynergism occurs with a mix of the Phenolic CB-D type antioxidants with the phosphite PD antioxidants [176](see fig. 10-13). The main mechanism of synergism between these antioxidants is that explained earlier in scheme 2. The use of these systems is quite widespread but is due mainly to the increased resistance to discolouration afforded [176]. This reduction of discolouration is thought to occur via a change in the transformation mechanisms, which reduce the percentage of highly coloured quinone structures [176, 178]. A major difference between the sulfur containing and the phosphite PD antioxidants is the lack of an initial pro-oxidant stage in the latter, this makes the choice of ratios less critical as is shown by mixes of Calco 2246 and Ultranox 626 (fig. 10) where very different ratios produce similar results. The actual efficiency of the best synergistic mix of phosphite and phenol is not as high as that with the sulfur containing antioxidant (see fig. 11) due to the lack of a highly efficient catalytic peroxide decomposing mechanism by the phosphites. Also phosphites tend to be less efficient at low concentrations and in highly oxidisable substrates [173] making them a less attractive PD in this system. It would be expected that binder containing mixes of phenols with Ultranox 626 would be more effective than those containing Irgafos 168 due to 626's greater efficiency when used alone. This is seen when synergism is found with α-Tocopherol (fig. 11) but in the case of γ-Tocopherol the 626 seems to act as an antagonist (fig. 12). The fact that the phosphites can change the type of transformation products produced could explain this. The more active 626 may be preventing a particularly effective transformation of γ-Tocopherol being produced, thus reducing its activity. The less rapidly reacting 168 may still allow the formation of this product thus not reducing the activity of the γ-Tocopherol. However, further work is needed to shed more light on the co-operative action of these systems.

4.3.3 Combinations of Two CB or CB with Autosynergistic Antioxidants

The combination of 2 CB antioxidants is potentially very effective due to the possibility of regenerative mechanisms. Earlier work [31] briefly investigated some CB - CB antioxidant combinations and found no evidence of synergism. These results are supported by other workers [179] using IPPD and the weak phenol 2,6-di-tert-butylphenol. In this work the overall stabilising effect of mixtures of phenyldiamines (IPPD & 6PPD) and phenols (Calco 2246, WSP and α- tocopherol) using a number of combinations and ratios (see figs. 14, 15 & 17) in polybutadiene lead to slightly enhanced stabilisation over the performance of the antioxidants when used alone. Homosynergism in CB-CB antioxidant combinations has been explained [135] by the regeneration of the more effective antioxidant by the less effective one which, in turn, acts as a reservoir for the more effective antioxidant. In the case of mixes of aromatic amines [135] and hindered phenols, as in this study, the normal reservoir is the phenol which regenerates the aromatic amine antioxidant or the derived nitroxyl (scheme 5).



Scheme 4-4 Mechanism of regeneration of amine derivatives by hindered phenol antioxidants

In this case of stabilisation of polybutadiene binder, all the antioxidants are 'strong antioxidants' so it would not be expected that the phenol would simply act as a reservoir to regenerate the amine. Furthermore, the overall reactions are also complicated by the interaction between the IPPD and the cross-linker IPDI used in the binder.

Repeat analysis of samples containing 0.2% IPPD:Calco 2246 at a ratio of 3:1 (fig. 23) showed a large variation in the change in cross-link density. Almost no increase in cross-link density was observed in the case of the sample prepared on the 28/7/93, but a change equal to that of Calco 2246 alone was observed for the sample prepared on the 27/9/94 (fig. 26). During the preparation of the stable sample dated the 28/7/93 ultrasound was used to help dissolve the IPPD. Before addition of the cross-linker the uncured hydroxyterminated polybutadiene containing the IPPD and Calco 2246 was placed in an ultrasonic bath for approximately 15 minutes. After this the sample was prepared as normal. An attempt to repeat this method of preparation on the 12/10/94 (fig. 23) failed to produce similar excellent results. Another sample in which ultrasound was used for preparation was the combination of three antioxidants Calco 2246:IPPD:DLTP in a ratio of 6:1:1. This sample also showed very little increase in cross-link density during ageing (fig. 27). Thermal analysis was performed on samples of uncured polybutadiene in which the antioxidants had been dissolved using ultrasound. These showed no difference in peak onset or peak maximum temperatures from samples prepared by vigorous stirring (fig. 28). But comparison of thermal analysis of the diluted sample prepared on the 27/9/94 (fig. 31) and the sample prepared using ultrasound on the 28/7/93 (fig. 32) did show a difference in peak shape a sharper peak was produced by the sample prepared using ultrasound.

At the same time as the preparation of the 3:1 ratio dated 28/7/93 a 4:1 ratio was also prepared using ultrasound. This sample underwent ultrasound for a longer period but then failed to cure and it was not possible, therefore, for it to be tested.

It is obvious that the ultrasound has had an effect on the performance of the stabilisers. This effect seems difficult to reproduce and may even have a detrimental effect on curing. Further investigation into the effects of ultrasound on stabilisation are discussed in chapter section 5.3.1.1.

The addition of a efficient chain breaking antioxidant to the autosynergist Santonox R led, as expected, to an improvement the performance of the latter stabiliser. The heavily cross-linked 'skin' which formed when Santonox R was used alone did not form when IPPD was also added, but the overall efficiency of a number of ratios of Santonox R and IPPD was no greater than that of either Calco 2246 or IPPD alone (fig. 18). The increase in performance when the Santonox R:IPPD combination was used over Santonox R alone, is attributed to the higher level of CB-D type antioxidant, which prevents initiation of oxidation by early prooxidant transformation products of the sulfur moiety in Santonox R [112]. As discussed in section 4.3.2 there appears to be a minimum threshold level of CB-D type antioxidant required to prevent initiation by the sulfur species. In the heterosynergistic cases discussed earlier, once this level was overcome synergism occurred quite readily. In the case of mixes of the Santonox R and IPPD strong synergism does not (fig. 18) occur but samples containing the same three moieties (S, NH, and OH) in individual antioxidants do show improved ageing (fig. 20). In polyolefins it was shown [112] the strongest stabilisation effects of antioxidants containing phenolic sulfides such as Santonox R, occur at high temperatures; at ambient temperatures such antioxidants become no more effective than a hindered phenol alone. In the case of this work, the highly oxidisable polybutadiene is prone to initiation by low levels of prooxidants formed by initial sulfur transformations, but the production of the sulfur antioxidant species at the low temperature involved was too slow to be effective thus the amine and phenolic moieties interacted as week homosynergists.

Similar observations could be made for mixes of the autosynergist Irganox 565 and IPPD, again only small improvement in ageing performance is shown over the single antioxidants alone.

4.3.4 Comparison of the Most Effective Samples with Results From Thermal Analysis.

As was discussed in chapter 3 one aim of this work was to evaluate the use of thermal analysis as a potential rapid screening technique for the action of antioxidants in polybutadiene. The comparison of some of the most promising antioxidant combinations from oven ageing (figs. 24 to 27) with results from thermal analysis of related uncured samples (figs. 28 & 29) re-enforced the difficulties of correlating such results. The most obvious inconstencies occurred with the samples containing mixes of CB-D and PD antioxidants such as Calco 2246 and DLTP (figs. 24 and 29) or γ-Tocopherol and Irgafos 168 (figs. 25 and 28). In these cases thermal analysis does not predict the synergism observed during oven ageing. As discussed in chapter 3 there are a number of reasons why the results from thermal analysis may be inaccurate. These include the changing of mechanisms due to the high temperatures involved in thermal analysis and probably more important in hetero combinations the lack of time (thermal analysis is conducted over very short time periods compared to oven thermal ageing) for synergistic transformation products to form and have their effect.

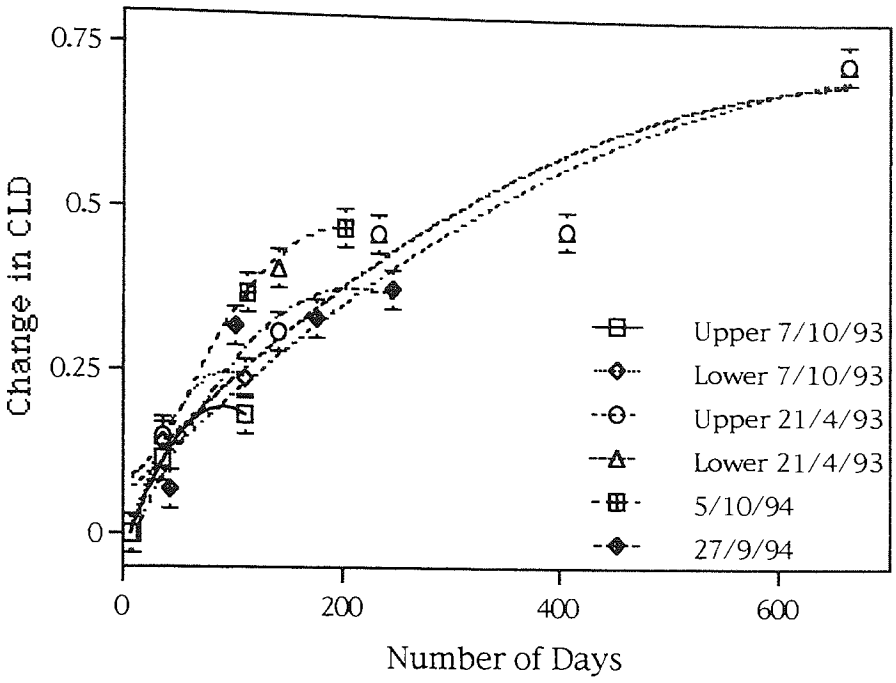


Figure 4-1 Comparison of the cross-link density for repeat samples of binder containing Calco 2246 (0.2% w/w) in tube moulds aged at 60°C

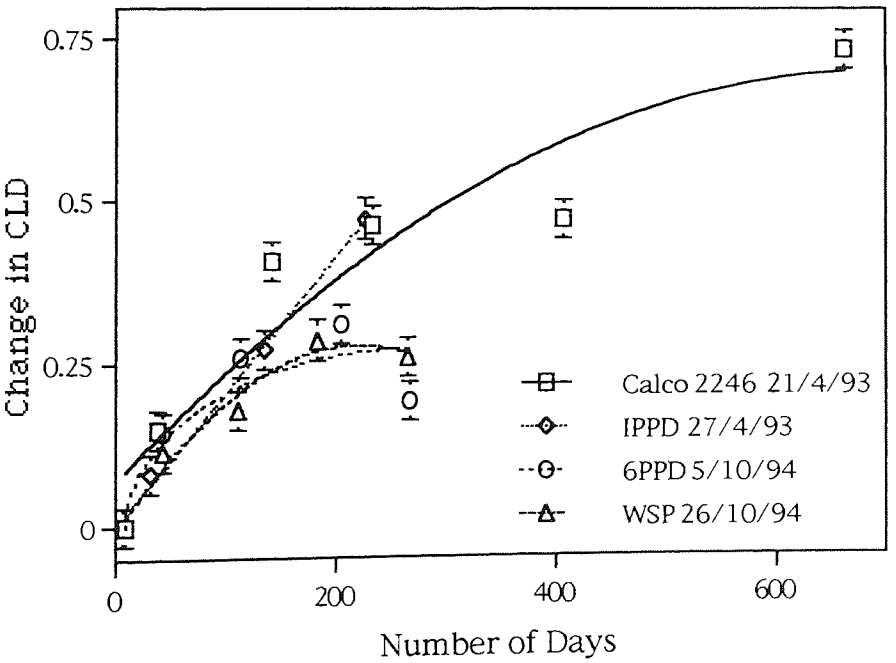


Figure 4-2 The effect of various single antioxidants (0.2% w/w) on the cross-link density of binder in tube moulds aged at 60°C

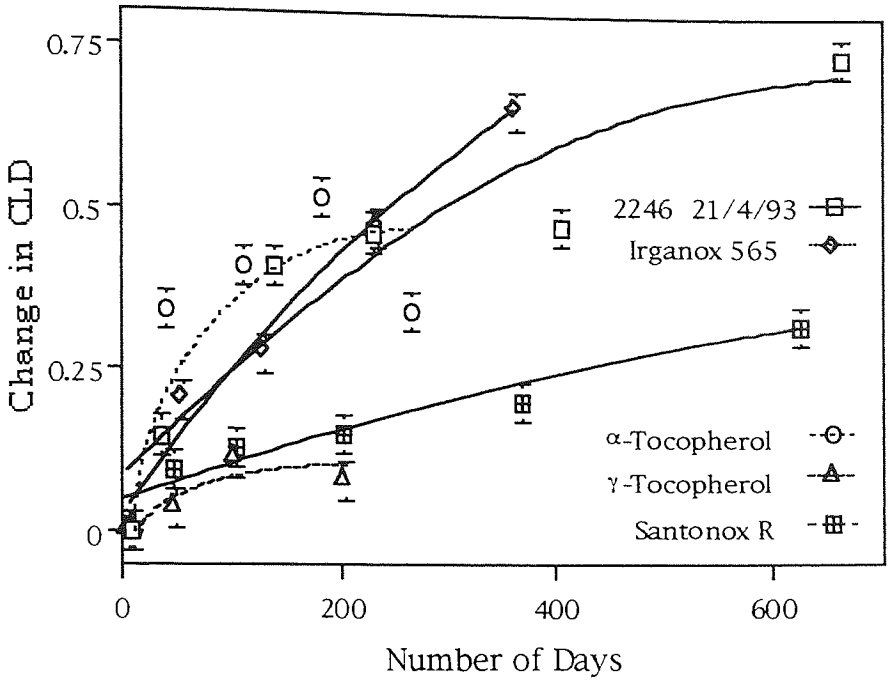


Figure 4-3 The effect of various single antioxidants (0.2% w/w) on the cross-link density of binder in tube moulds aged at 60°C

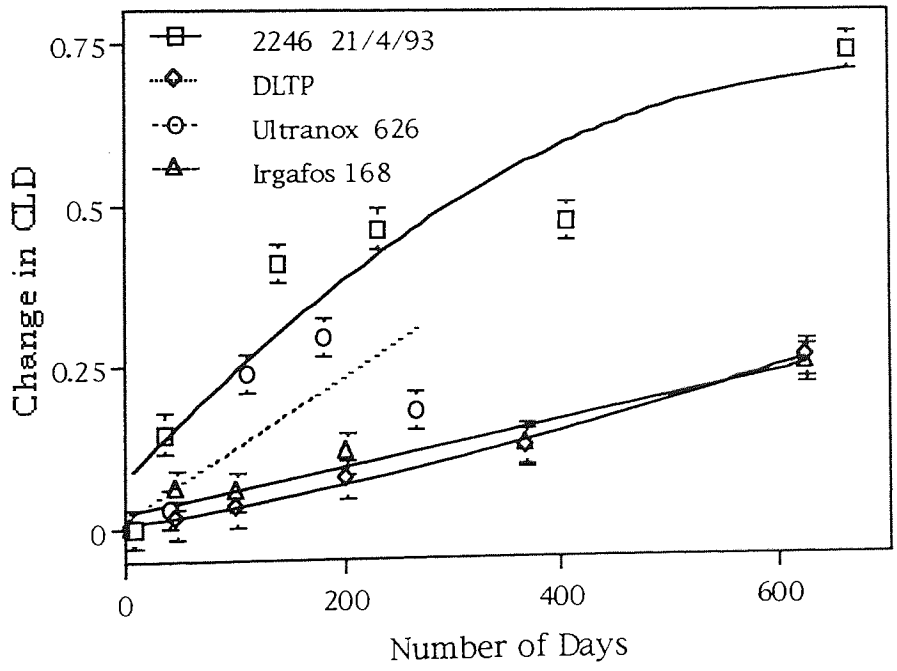


Figure 4-4 The effect of various single antioxidants (0.2% w/w) on the cross-link density of binder in tube moulds aged at 60°C

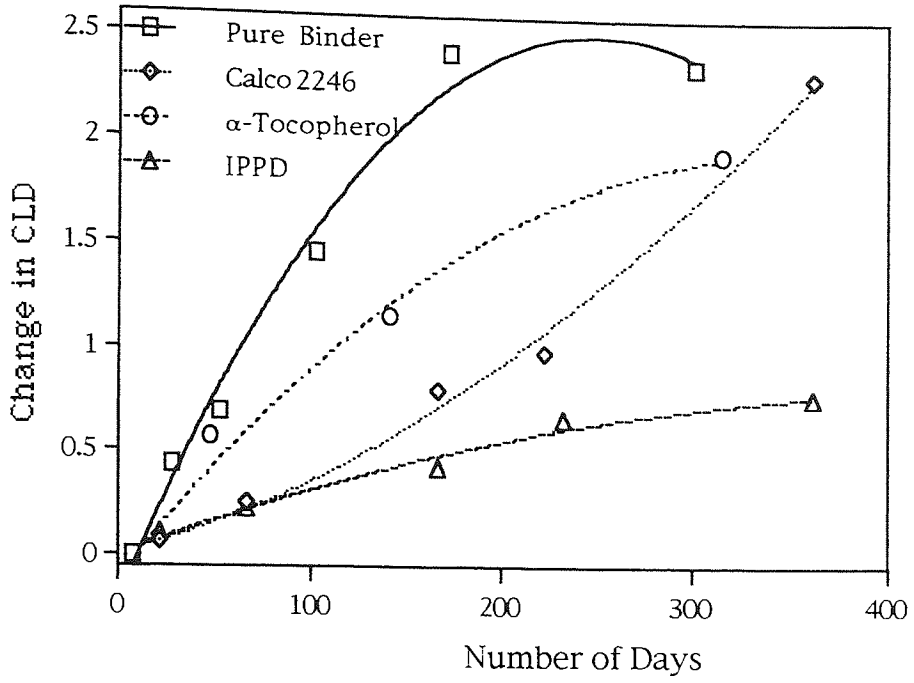


Figure 4-5 The effect of various single antioxidants (0.2% w/w) on the cross-link density of binder in dish moulds aged at 80°C

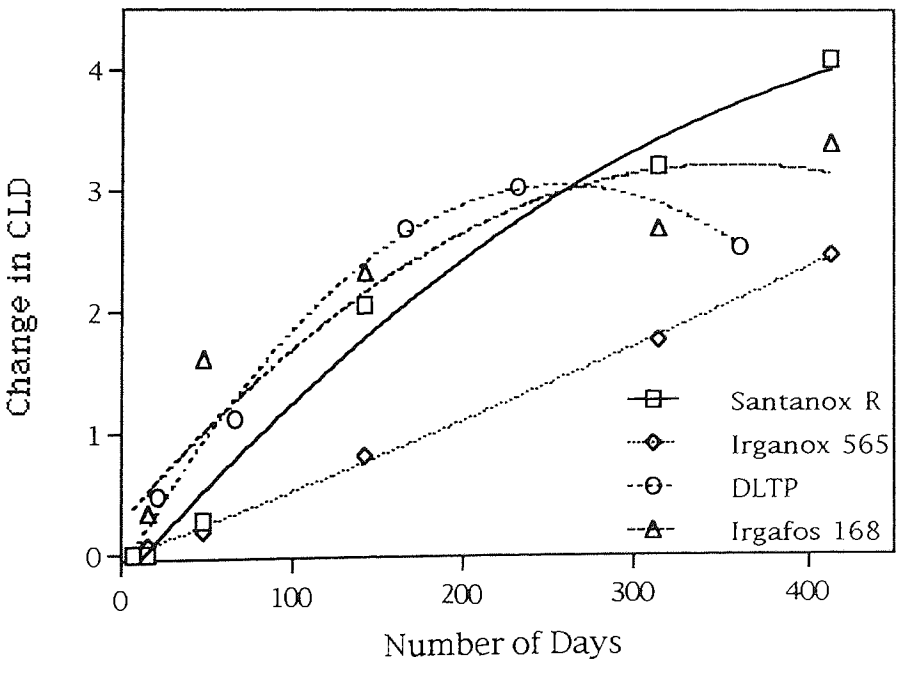


Figure 4-6 The effect of various single antioxidants (0.2% w/w) on the cross-link density of binder in dish moulds aged at 80°C

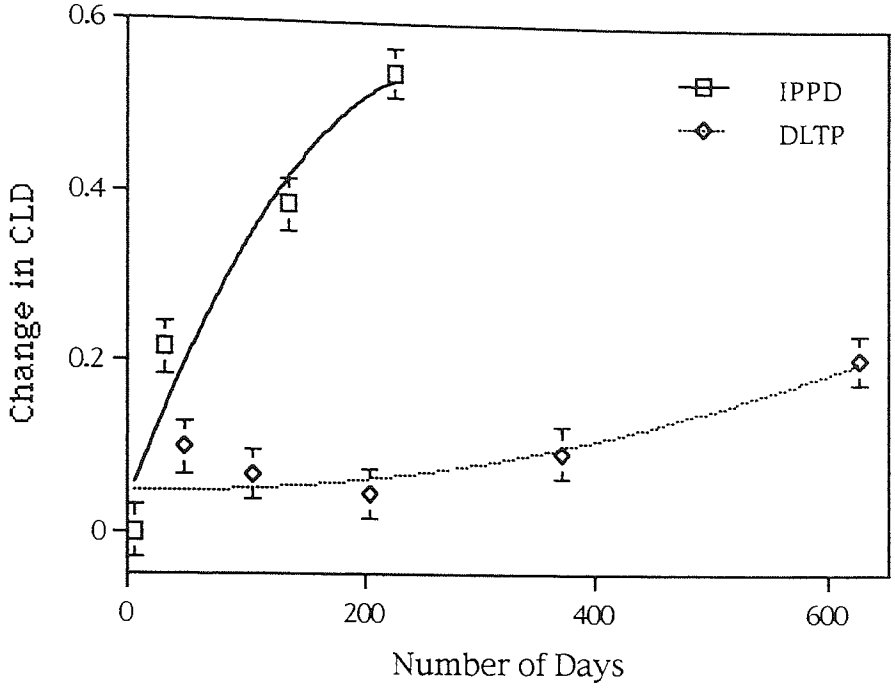


Figure 4-7 The effect of various single antioxidants (0.4% w/w) on the cross-link density of binder in tube moulds aged at 60°C

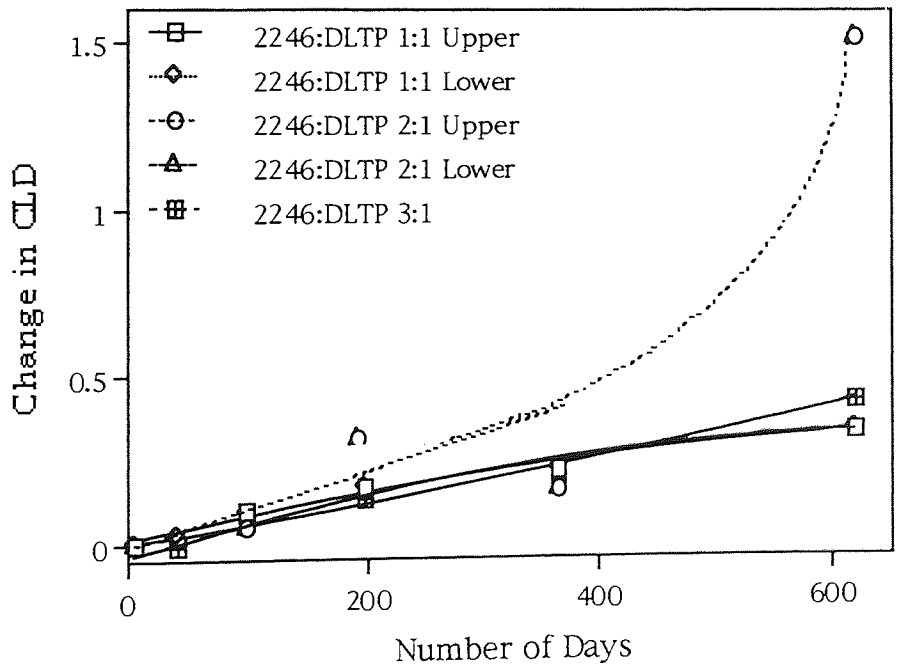


Figure 4-8 The effect of combination of Calco 2246 and DLTP (Tot. 0.2% w/w) on the cross-link density of binder in tube moulds aged at 60°C

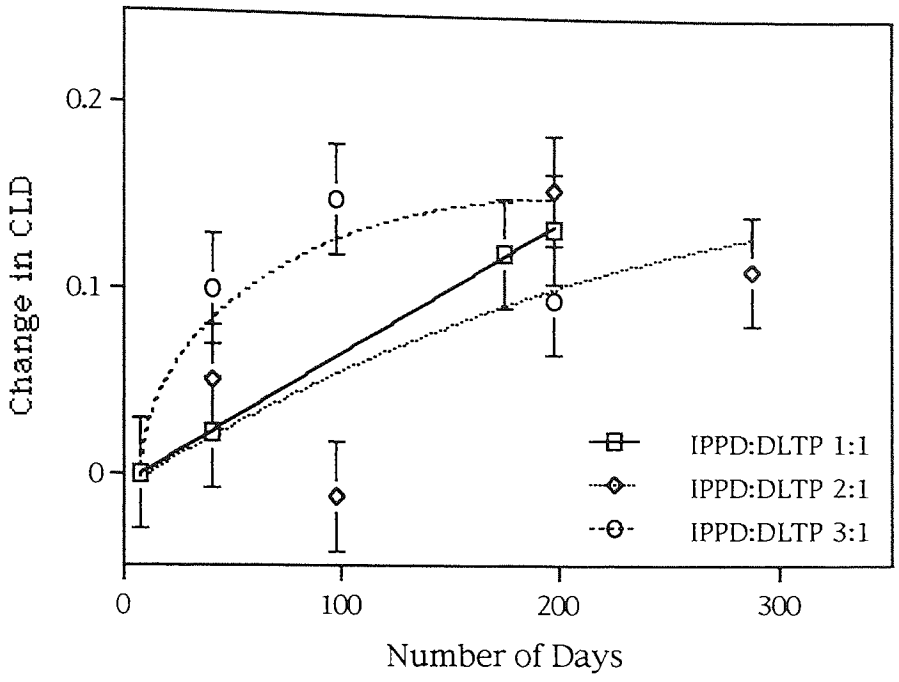


Figure 4-9 The effect of combination of IPPD and DLTP (Tot. 0.2% w/w) on the cross-link density of binder in tube moulds aged at 60°C

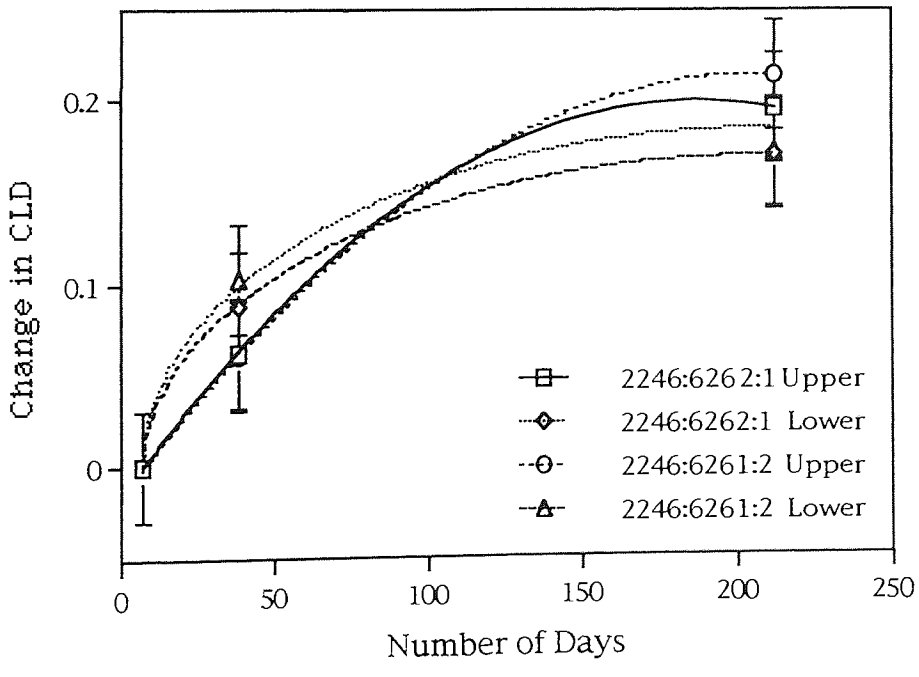


Figure 4-10 The effect of combination of Calco 2246 and Irgafos 626 (Tot. 0.2% w/w) on the cross-link density of binder in tube moulds aged at 60°C

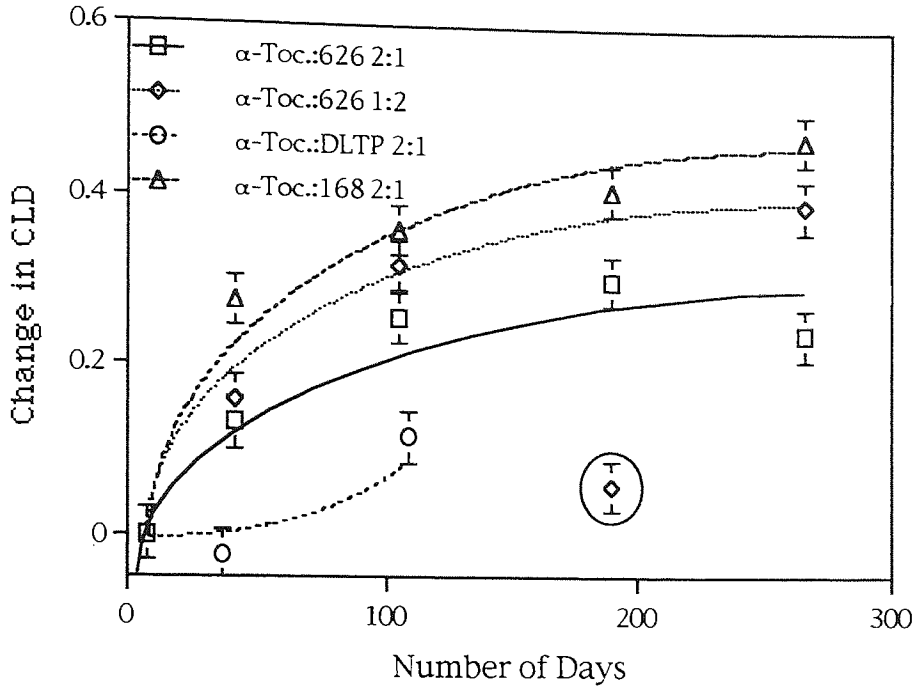


Figure 4-11 The effect of combination of α-Tocopherol and either Irgafos 626, DLTP or Irgafos 168 (Tot. 0.2% w/w) on the cross-link density of binder in tube moulds aged at 60°C. The circled point has been ignored as an experimental error

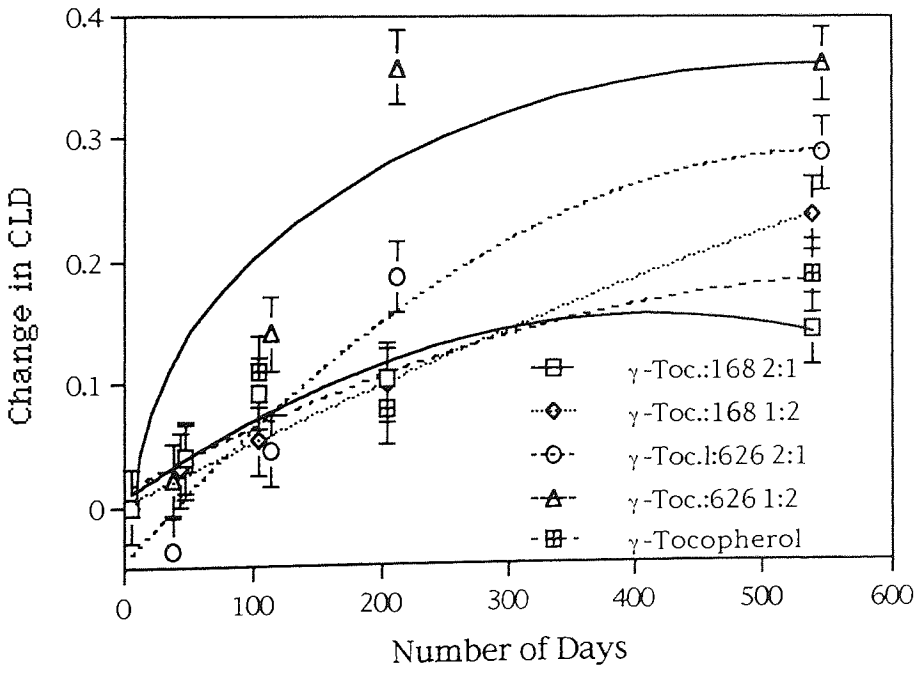


Figure 4-12 The effect of combination of γ-Tocopherol and either Irgafos 168 or Irgafos 626 (Tot. 0.2% w/w) on the cross-link density of binder in tube moulds aged at 60°C

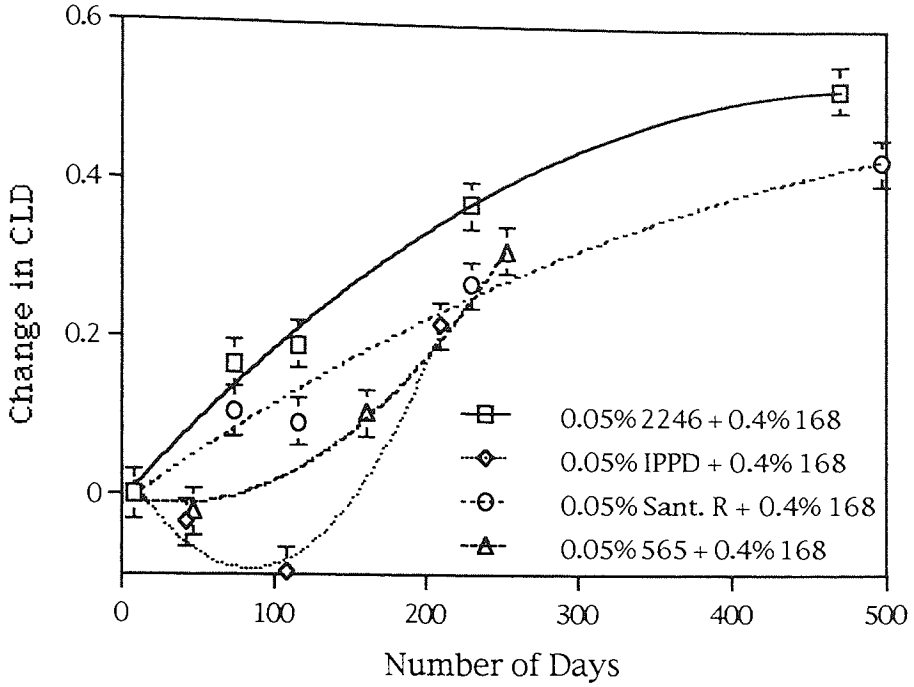


Figure 4-13 The effect of combination of a CB or autosynergistic antioxidant (0.05% w/w) and Irgafos 168 (0.4% w/w) on the cross-link density of binder in tube moulds aged at 60°C

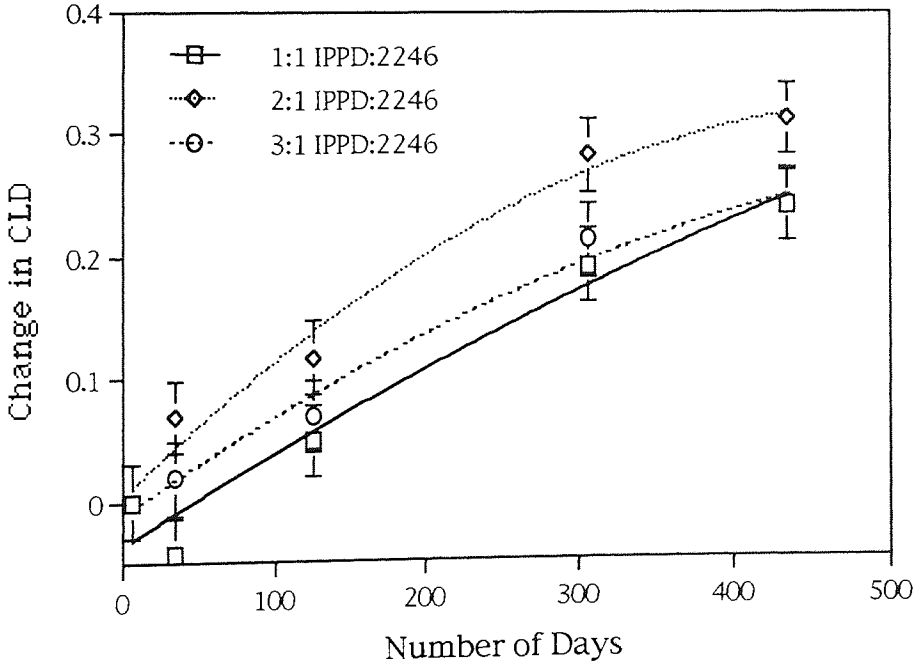


Figure 4-14 The effect of combination of IPPD and Calco 2246 (Tot. 0.2% w/w) on the cross-link density of binder in tube moulds aged at 60°C

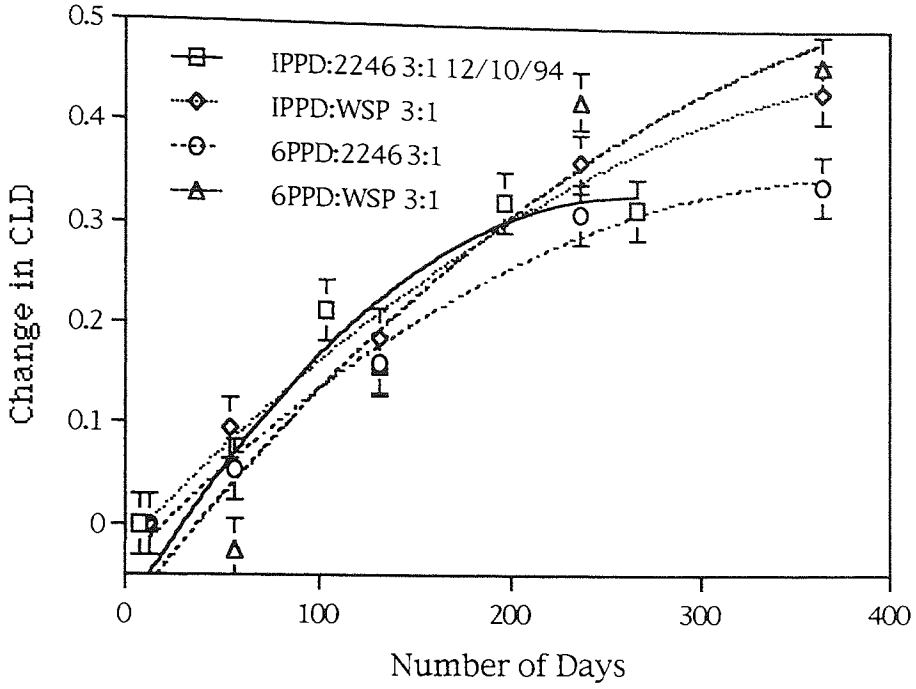


Figure 4-15 The effect of combination of IPPD or 6PPD with Calco 2246 or WSP (Tot. 0.2% w/w) on the cross-link density of binder in tube moulds aged at 60°C

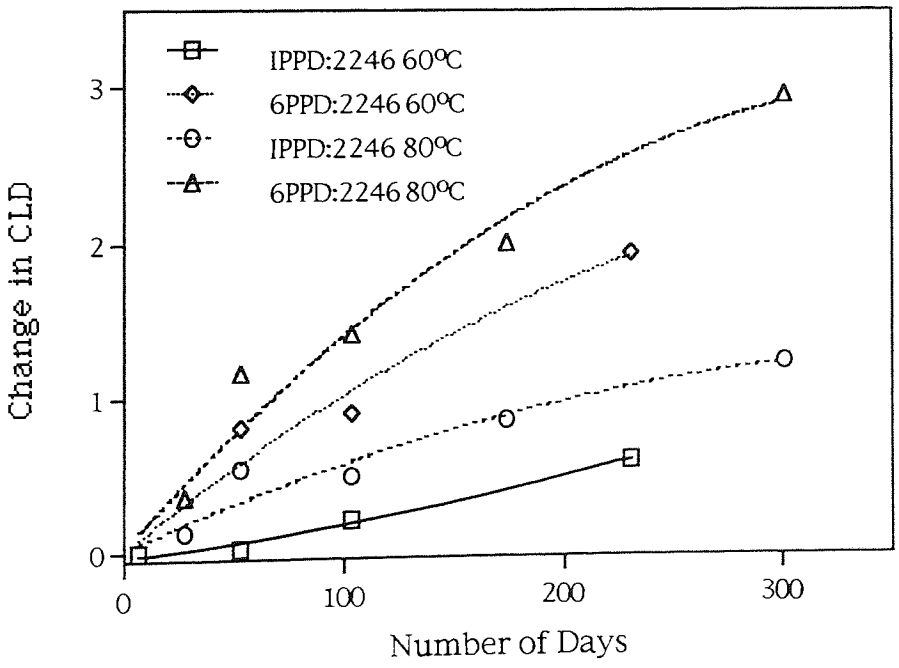


Figure 4-16 The effect of combinations of IPPD or 6PPD with Calco 2246 or WSP (Tot. 0.2% w/w) on the cross-link density of binder in dish moulds aged at 60°C and 80°C

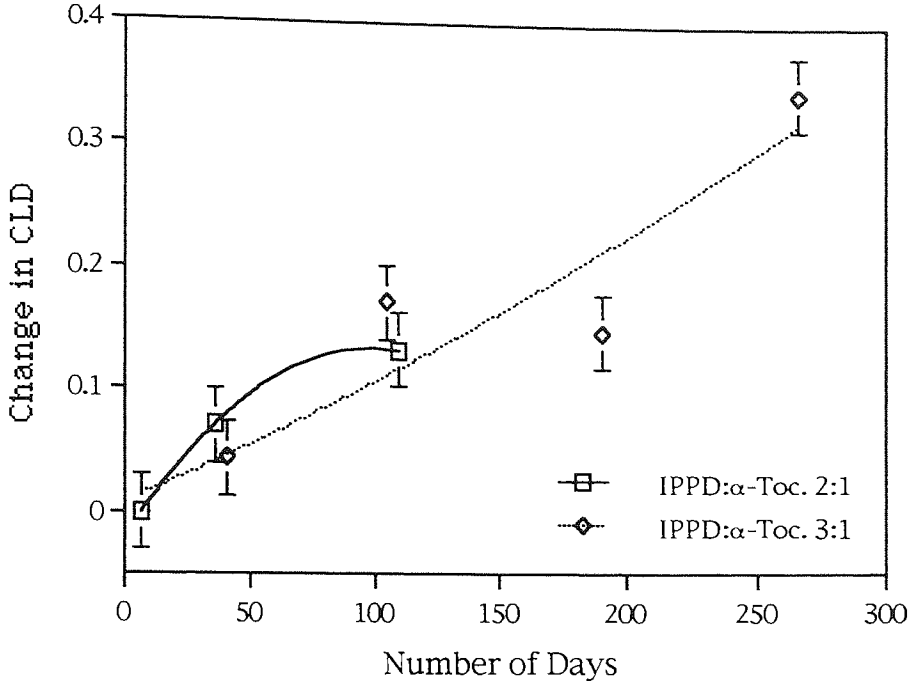


Figure 4-17 The effect of combinations of IPPD and α-Tocopherol (Tot. 0.2% w/w) on the cross-link density of binder in tube moulds aged at 60°C

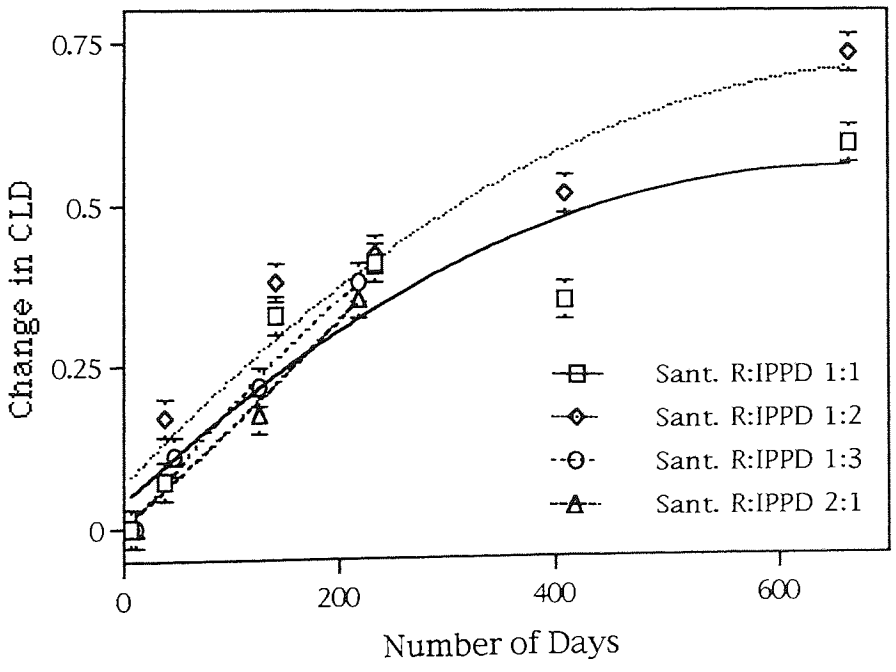


Figure 4-18 The effect of combinations of Santonox R and IPPD (Tot. 0.2% w/w) on the cross-link density of binder in tube moulds aged at 60°C

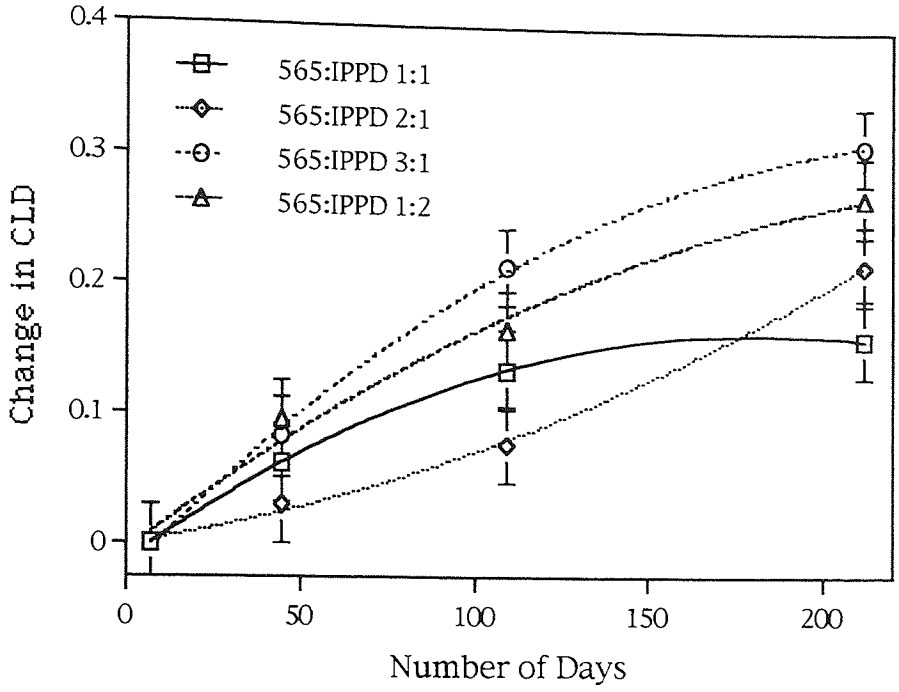


Figure 4-19 The effect of combinations of Irganox 565 and IPPD (Tot. 0.2% w/w) on the cross-link density of binder in tube moulds aged at 60°C

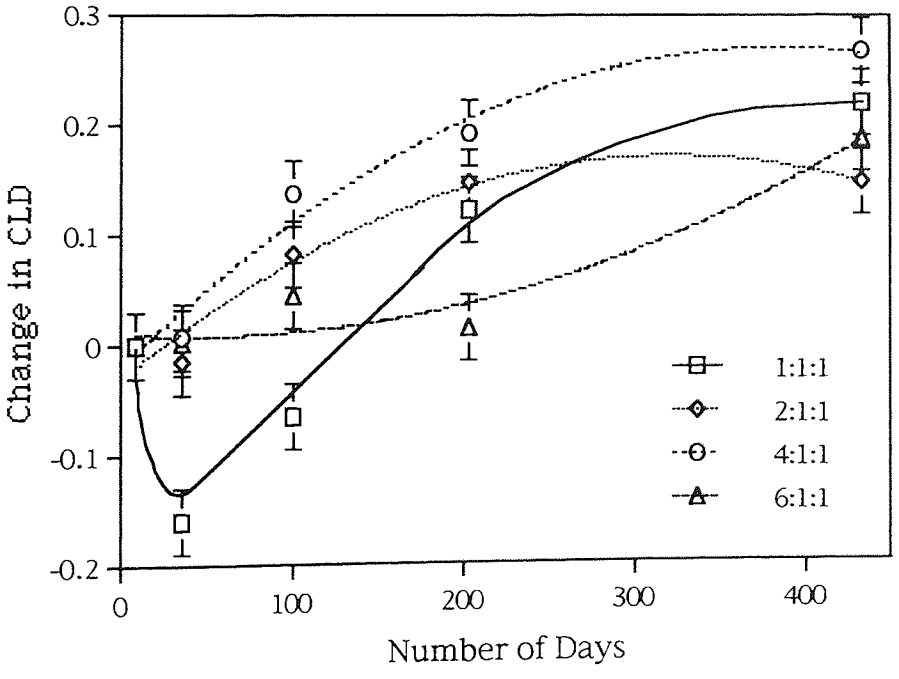


Figure 4-20 The effect of combinations of IPPD, Calco 2246 and DLTP (Tot. 0.2% w/w) on the cross-link density of binder in tube moulds aged at 60°C

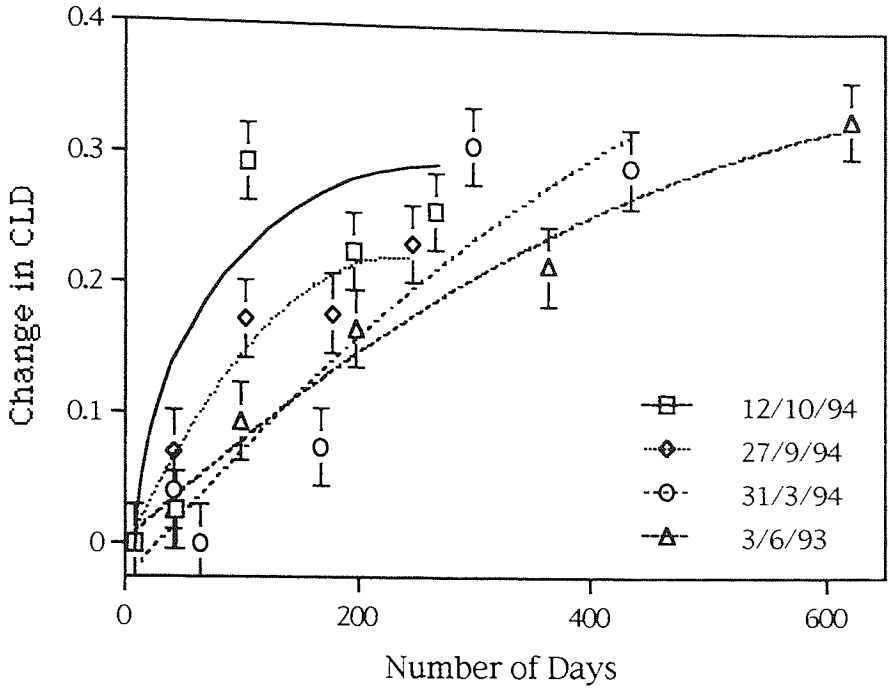


Figure 4-21 Comparison of the cross-link density for repeat samples of binder containing 1:1 Calco 2246:DLTP (0.2% w/w) in tube moulds aged at 60°C

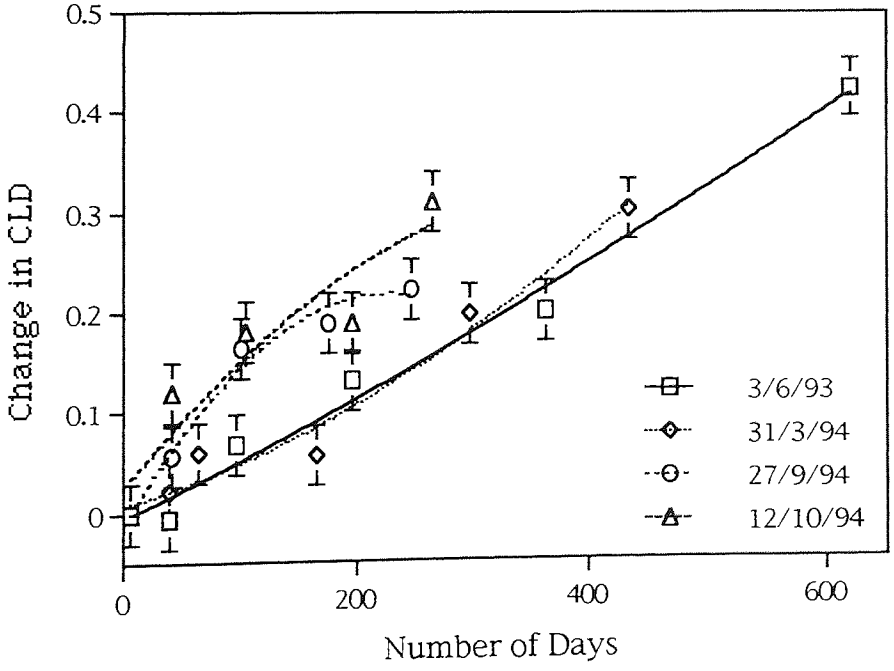


Figure 4-22 Comparison of the cross-link density for repeat samples of binder containing 3:1 Calco 2246:DLTP (0.2% w/w) in tube moulds aged at 60°C

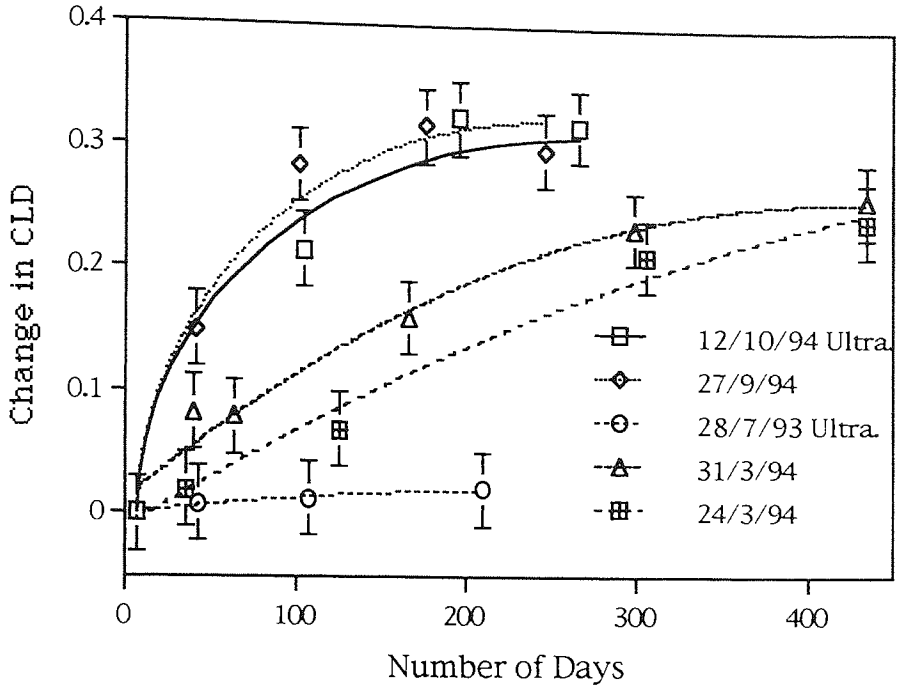


Figure 4-23 Comparison of the cross-link density for repeat samples of binder containing 3:1 IPPD:2246 (0.2% w/w) in tube moulds aged at 60°C (Ultra indicates ultrasound was used during preparation)

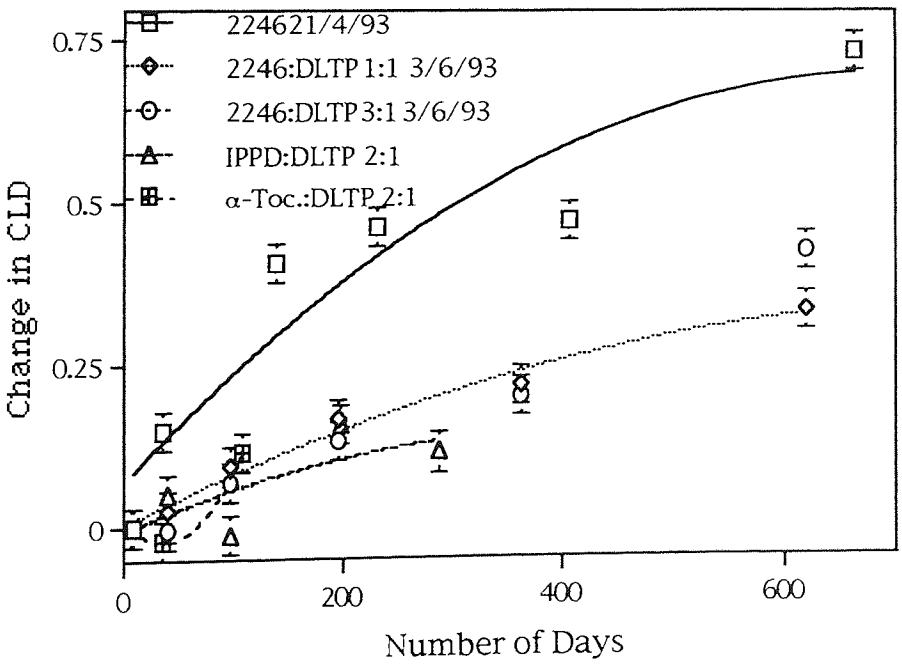


Figure 4-24 Comparison of the cross-link density for some of the best mixed antioxidant systems with Calco 2246 (0.2% w/w) in tube moulds aged at 60°C

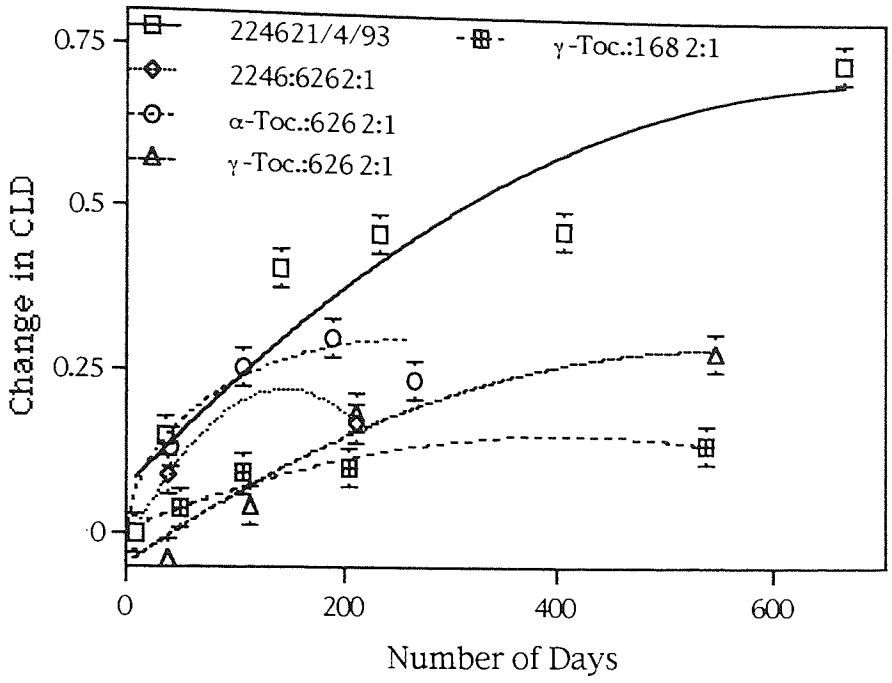


Figure 4-25 Comparison of the cross-link density for some of the best mixed antioxidant systems with Calco 2246 (0.2% w/w) in tube moulds aged at 60°C

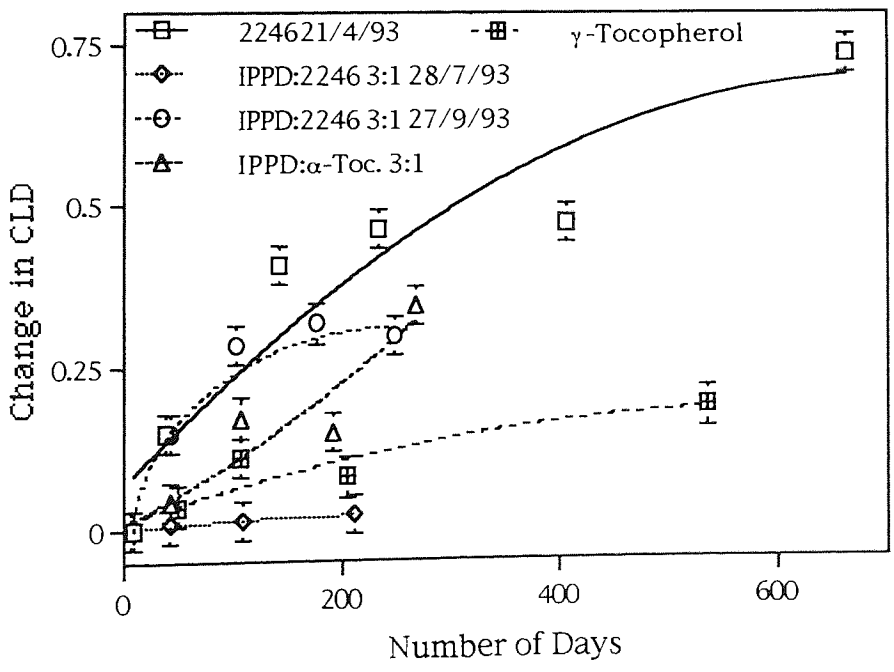


Figure 4-26 Comparison of the cross-link density for some of the best mixed antioxidant systems with Calco 2246 (0.2% w/w) in tube moulds aged at 60°C

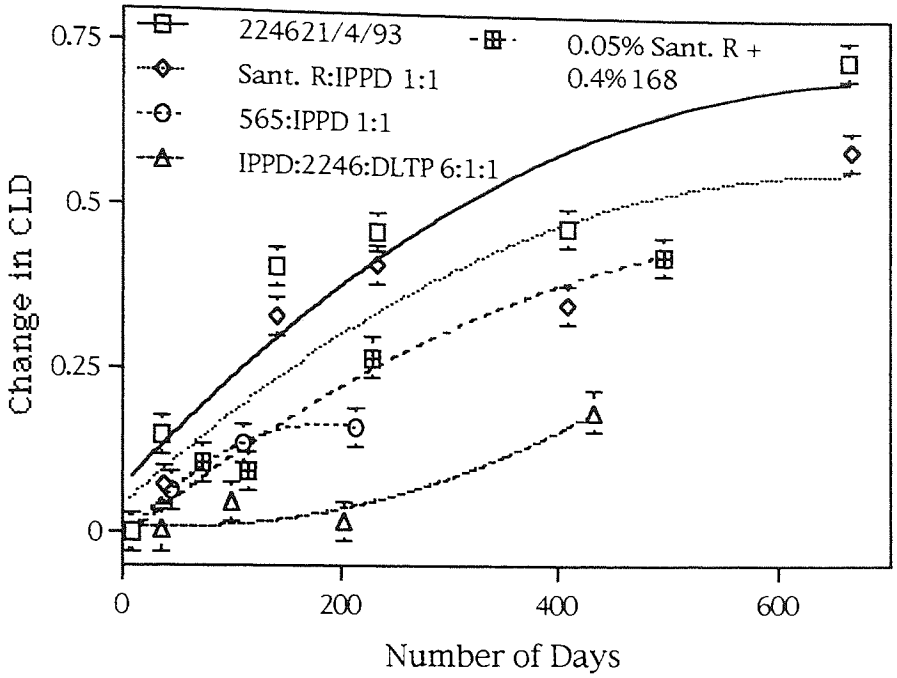


Figure 4-27 Comparison of the cross-link density for some of the best mixed antioxidant systems with Calco 2246 (0.2% w/w) in tube moulds aged at 60°C

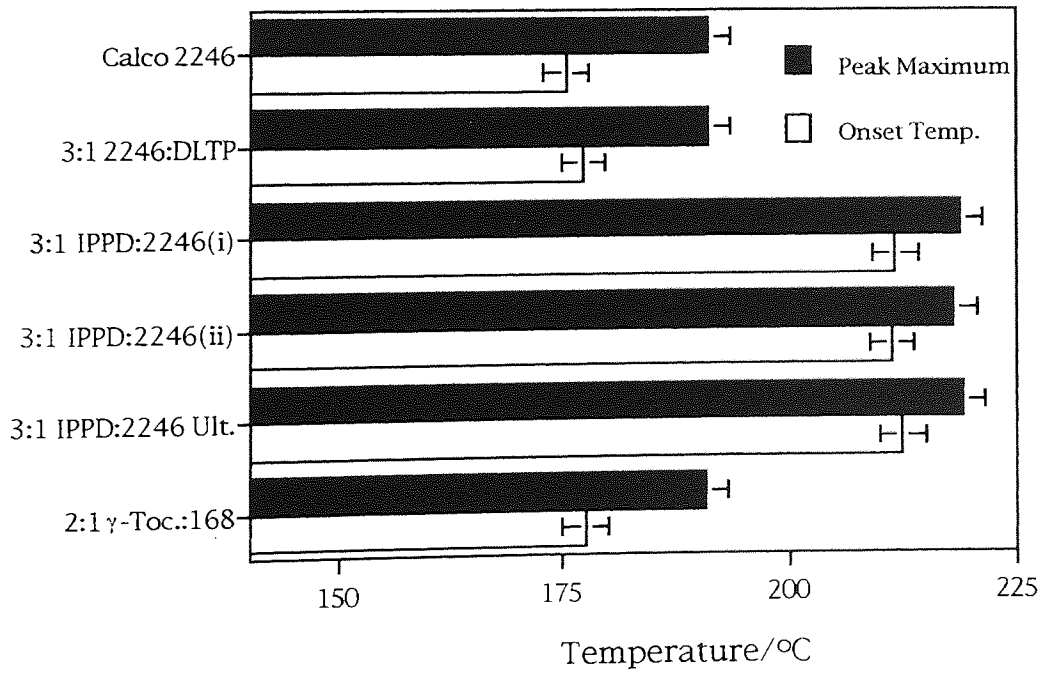


Figure 4-28 Effect of some of the best antioxidant system (0.2% w/w) on the 'peak maximum and onset temperatures' observed during thermal analysis of uncured hydroxyterminated polybutadiene.

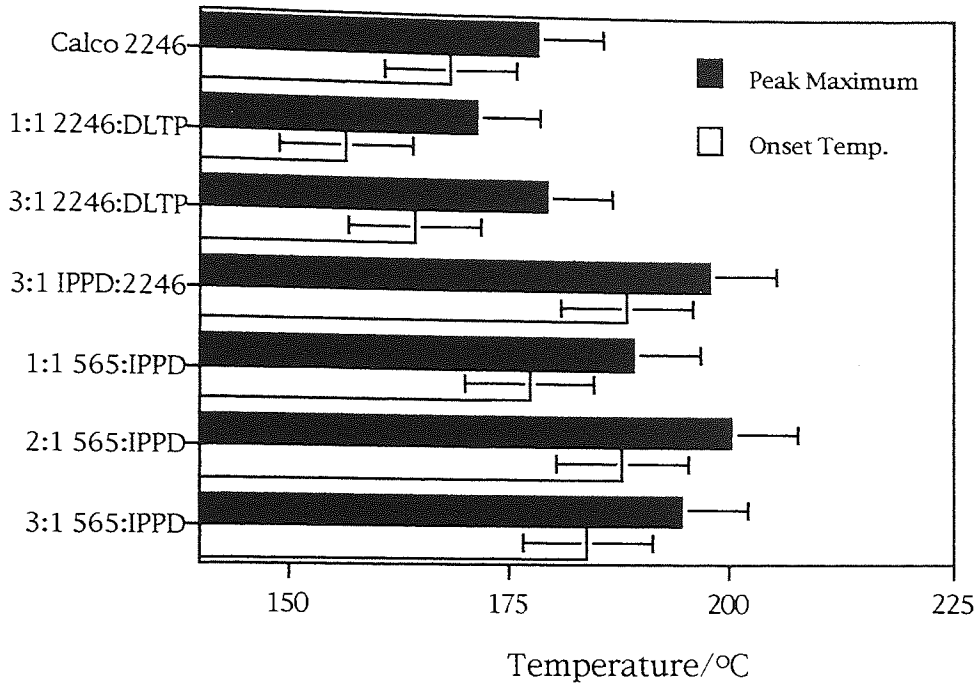


Figure 4-29 Effect of some of the best antioxidant system (0.2% w/w) on the 'peak maximum and onset temperatures' observed during thermal analysis of undiluted polybutadiene binder.

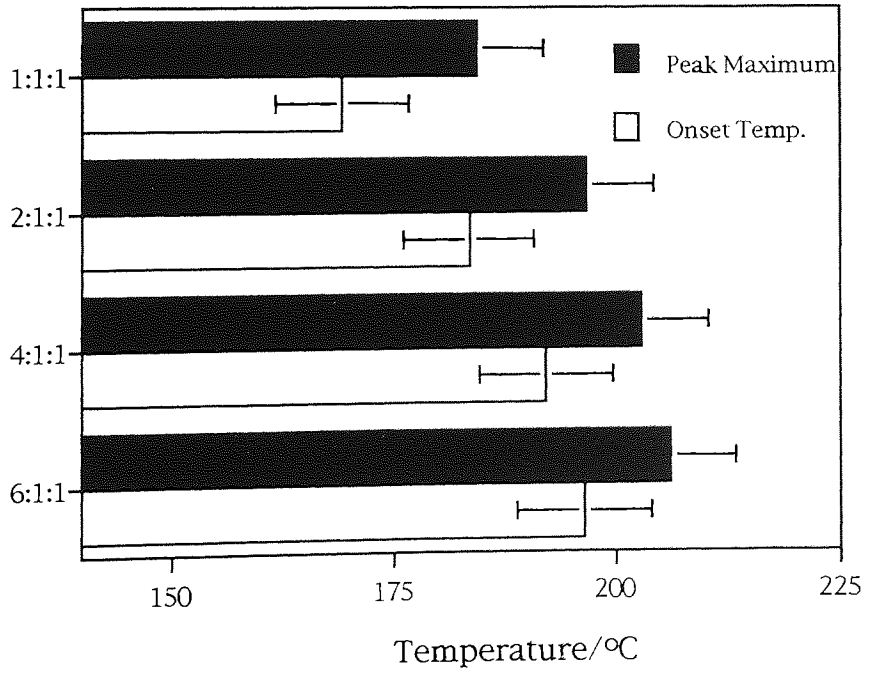


Figure 4-30 Effect of combinations of IPPD, Calco 2246 and DLTP (0.2% w/w) on the 'peak maximum and onset temperatures' observed during thermal analysis of undiluted polybutadiene binder.

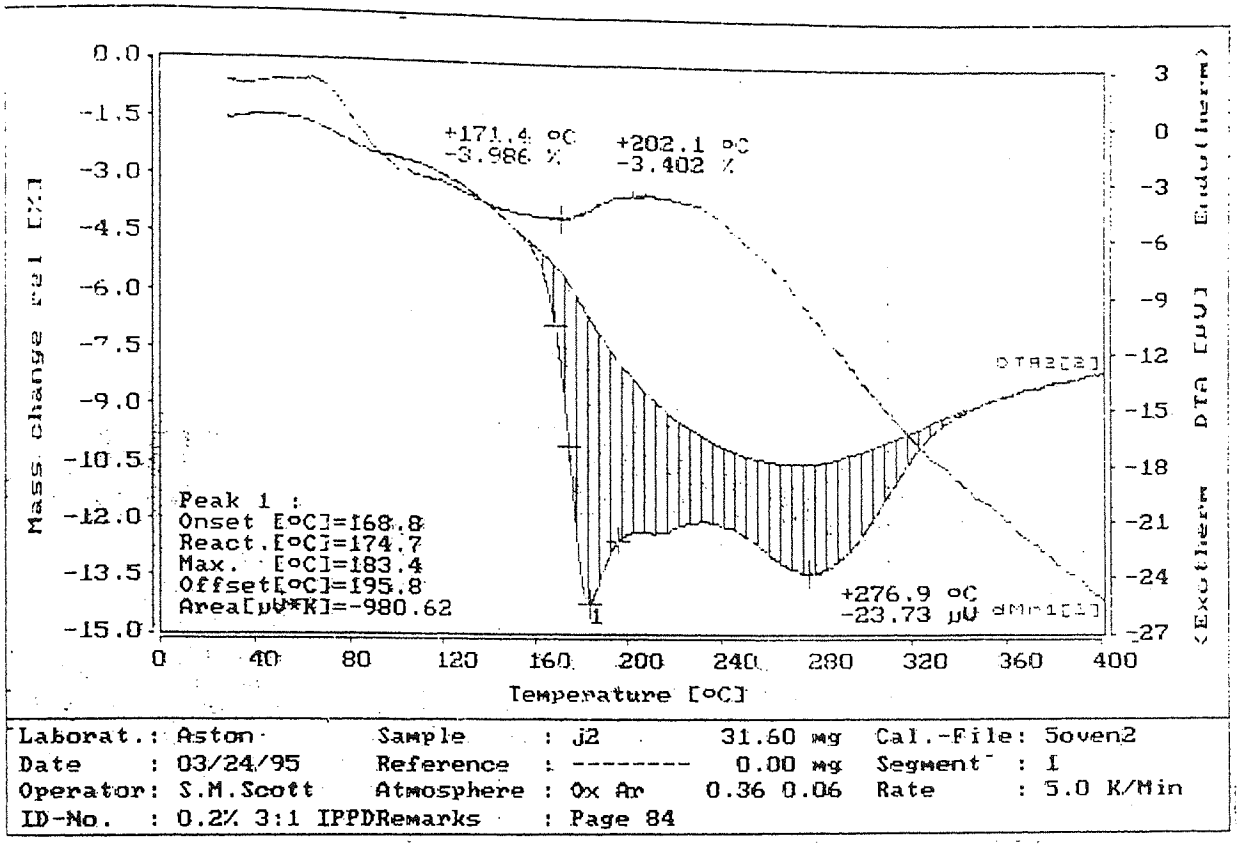


Figure 4-31 Thermogram of cured polybutadiene containing 3:1 IPPD:2246 (0.2% w/w) diluted with 90% Alumina analysed in a flowing mixed oxygen (0.36 l/min) and argon (0.06 l/min) atmosphere with a heating rate of 5°C/min.

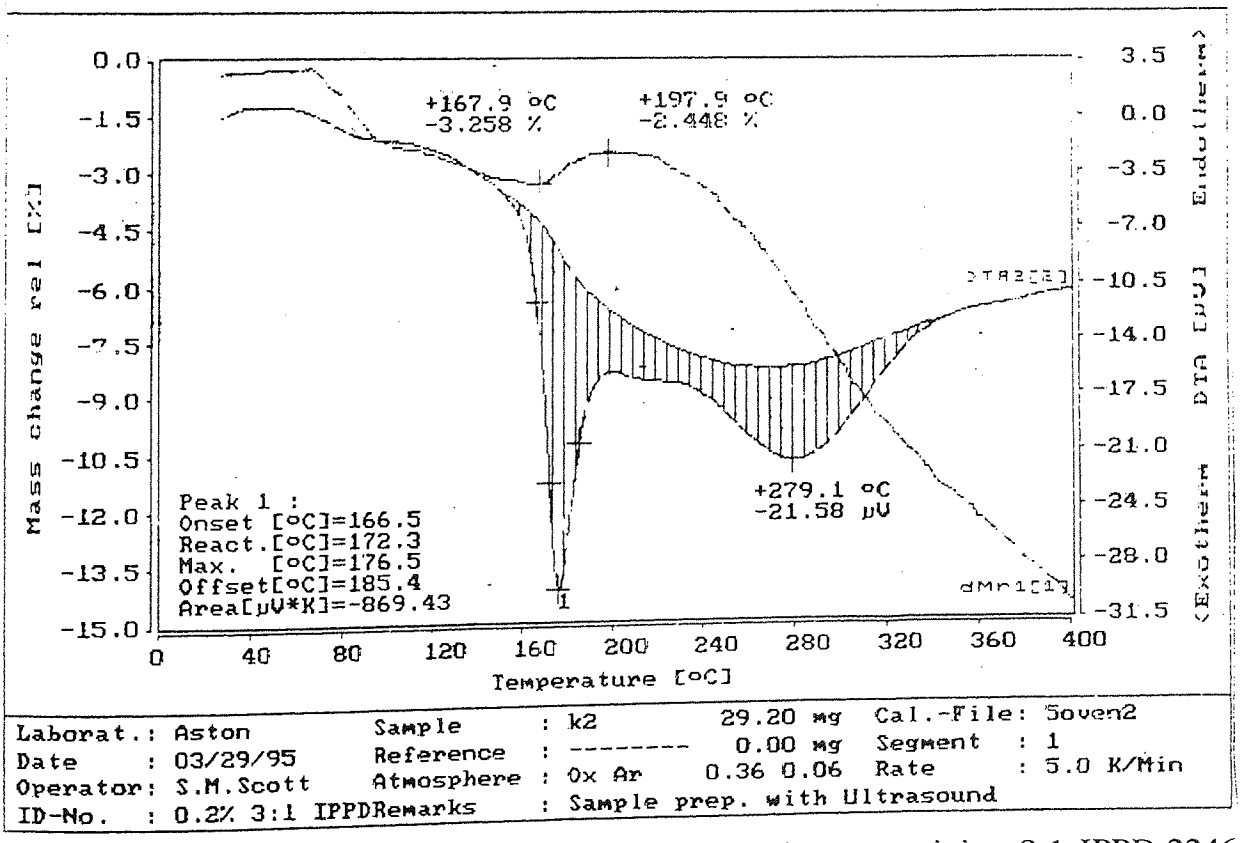


Figure 4-32 Thermogram of cured polybutadiene containing 3:1 IPPD:2246 (0.2% w/w) which had ultrasound performed on it during preparation diluted with 90% Alumina analysed in a flowing mixed oxygen (0.36 l/min) and argon (0.06 l/min) atmosphere with a heating rate of 5°C/min.

CHAPTER FIVE

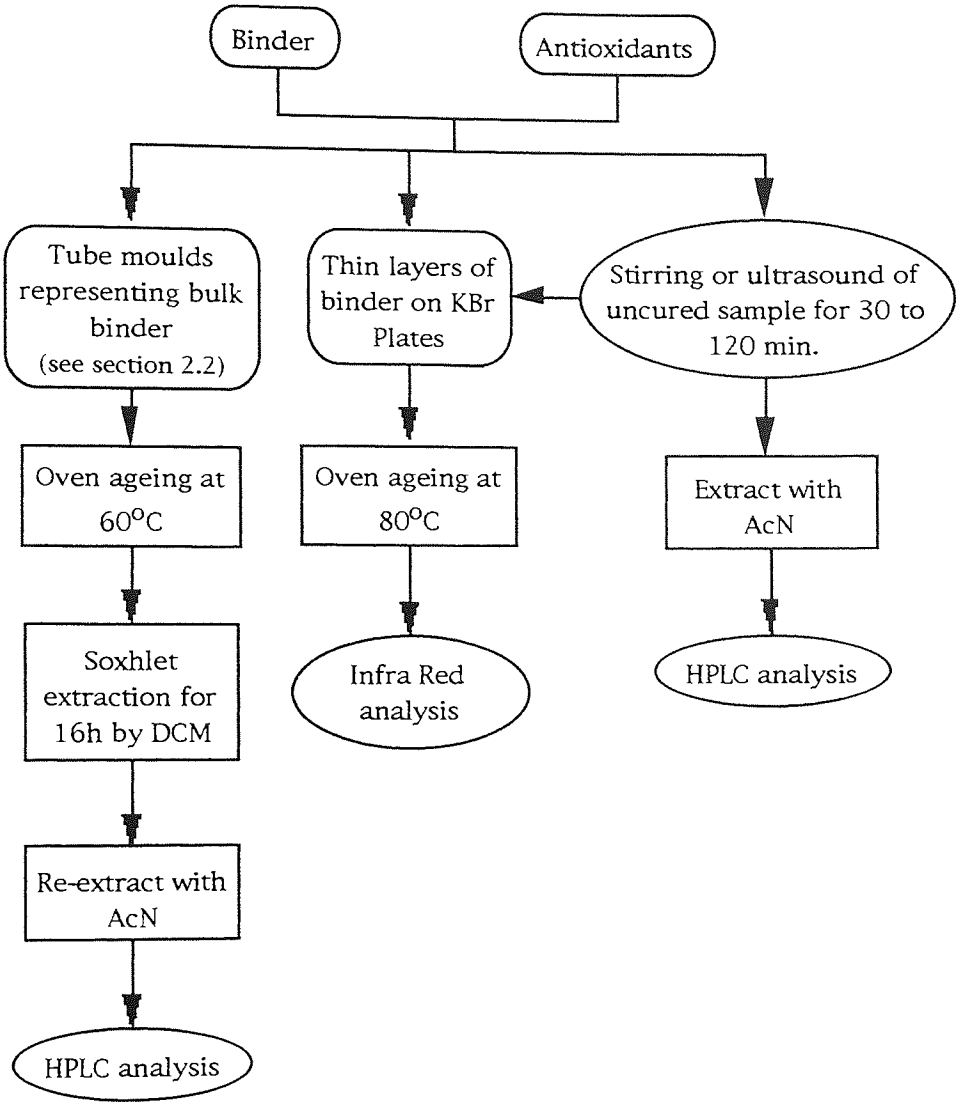
5 STUDIES OF ANTIOXIDANT MECHANISMS.

5.1 Object and Methodology

In chapter 4 a number of interesting hetero and homo synergistic systems were examined. Also the use of ultrasound to help mix antioxidants was seen to affect their efficiency. To try to gain more information about the mechanisms involved, some of the antioxidant systems were further analysed, the use of ultrasound during the preparation of samples was further investigated.

It is expected that oxidation of polybutadiene would lead to changes in its structure. These changes were followed by infra red spectroscopy using thin layers of the cured binder aged at 80°C. Samples prepared both by stirring and ultrasound were analysed, the ultrasound being performed both before and after addition of the cross-linking agent IPDI. Also H.P.L.C. analysis was performed on samples during ultrasound treatment in an attempt to gauge the effect on the antioxidant.

Attempts were made to gain information on the fate of some of the antioxidants by the use of H.P.L.C. analysis. This was also performed on the extracts of a number of the oven aged samples, including the 3:1 IPPD:Calco 2246 samples prepared using ultrasound. Scheme 1 shows an overview of the methods for this investigation.



Scheme 5-1 Overview of the methods used to further investigate the effect of antioxidants on binder ageing.

5.2 Results

5.2.1 Infra Red Analysis of Binder Samples With and Without Antioxidants

Figures 1 to 14 show both plots of the peak ratios against time and the corresponding IR spectra for the important peaks representing the ageing of thin layer binder samples at 80°C. The peaks correspond to: hydroxyl groups in the region 3650 - 3180 cm^{-1}; carbonyl groups region 1800 - 1660 cm^{-1}; the carbon double bonds in the polybutadiene in the region 1665 - 1620 cm^{-1}; C-H groups related to trans double bonds in the region 988 -934 cm^{-1}, vinyl double bonds in the region 934 - 890 cm^{-1} and cis double bonds in the region 760 - 650 cm^{-1} [156] (see section 2.3.1 for more detail on method of measurement). Graphs

were not produced for samples of the pure binder with no antioxidant (fig. 1) and binder containing 0.2 % DLTP (fig. 12) as it is clear these samples have oxidised fully during the 7 days curing at 60°C.

The values for peak ratios were produced by normalizing the areas of the peaks of interest to a reference peak (3122 - 3052 cm^{-1}) from the base polybutadiene on each spectrum. This enhances the accuracy of the results by removing the effect of varying sample thickness. This was a particular problem with this analysis as the samples could not be analysed through the same point in the sample each time. The reference peak was chosen as it did not appear to be largely affected by sample oxidation, but as found by other workers [71] once oxidation occurs the peaks indicating the finer structure became poorly resolved making accurate measurement difficult. The peak areas were produced using the tangent baseline method [149].

Figures 15 to 19 are graphs comparing the increase in OH peak during oxidation of various samples. Figures 15 and 17 to 19 show repeats of samples containing similar antioxidants either prepared using ultrasound or by stirring. These show the ageing in the case of the single antioxidants Calco 2246 (fig. 15) and IPPD (fig. 17) is reproducible and in both cases the sample prepared using ultrasound performed better. In the case of the samples containing 3:1 IPPD:2246 (fig. 18) the results are not as reproducible but again the samples prepared using ultrasound showed improved performance. Figure 16 compares the increase in OH peak of samples containing Calco 2246, 1:1 Calco 2246:DLTP and 3:1 Calco 2246:DLTP. Figure 19 shows the effect ultrasound had on a number of samples prepared at the same time as those using just stirring. During the preparation of these samples small amounts were removed which were subjected to H.P.L.C. analysis (for method see section 2.7).

5.2.2 H.P.L.C. Analysis of Uncured Samples Mixed Using Ultrasound.

Figure 20 shows the 3D and single wavelength (284 nm) chromatographs produced by the gradient H.P.L.C. method (see section 2.7) for injection of the solvent used for extraction AcN. This shows a peak only at about 3 minutes in the single wavelength chromatogram that is likely to be the pure AcN peak. The baseline change is due to the slight change in U.V. absorbance of the eluent during the gradient change, this is exaggerated by the small scale used. Figures 21 and 22 show the chromatograms produced by analysis of the antioxidants Calco 2246 and IPPD. The peaks for the antioxidants are clearly visible in both the 3D and the single wavelength spectra. Also visible are a number of other peaks (A-E) which have been labelled. Figure 23 shows the chromatograms produced by extraction of uncured hydroxyterminated polybutadiene by AcN. The 3D spectra shows a number of peaks in the lower wavelength region representing various HTPB molecules. These do not appear in the single wavelength chromatogram so should not interfere with analysis of the levels of the antioxidants present.

Figures 24 to 26 show graphs of the percent of added level detected by H.P.L.C. analysis of samples containing 0.2 % (w/w) of antioxidants that were mixed by stirring or by ultrasound. In the case of the stirred samples only one sample was analysed to compare with the results from ultrasound. The values for percent of expected level were calculated using the calibration curves determined from standards data (see section 2.7) except for peak B where no calibration curve could be plotted so peak area observed normalised by sample mass were plotted. After 120 min. of ultrasound both the stirred and ultrasound treated samples were cured and the results from infrared analysis of the samples during ageing are shown in figure 19.

5.2.3 H.P.L.C. Analysis of Cured Deep Mould Binder Samples During Oven Ageing at 60°C.

Figure 27 shows the chromatograms produced by H.P.L.C. analysis of extract of newly cured hydroxyterminated polybutadiene. The regular peaks observed after extraction of uncured HTPB are not observed and no obvious peaks are observed in the 284 nm region. This indicates no interference with results from antioxidants should occur. The chromatograms showing extracts of the cured sample after oven ageing at 60°C are shown in appendix 1.

Figures 28 to 32 show graphs of percent of expected level of various peaks detected by H.P.L.C. during the oven ageing of deep tube mould samples (for method see section 2.7). The value of percent of expected level indicates the amount of certain peaks present in the extract compared to the amount expected to be present by the known amount initially added. It can be seen in most cases that all the added antioxidant is not recovered. This could be due to either; the functioning of the antioxidant in stabilising the polymer, incomplete extraction of the antioxidant during preparation for H.P.L.C. analysis, or reaction of the antioxidant during curing.

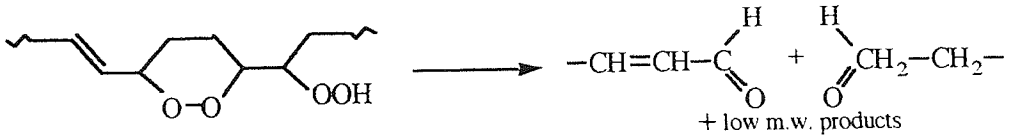
Figure 33 shows the chromatograms produced from the H.P.L.C analysis of IPPD-NO· prepared in earlier work [31].

5.3 Discussion

5.3.1 Infra-red Analysis of the Thermal Ageing of Thin Layer Cured Binder Samples

Infra-red analysis has been used a number of times to follow the changes in structure occurring in polybutadiene during oxidation. It was found that the products of oxidation were similar at both low and high (above 100°C) temperatures [71] the main difference being the stationary level of peroxides. These were seen to decompose during thermal analysis at 90°C thus were at a

very low level in the higher temperature samples. In this work a thin layer sample was oxidised at 80°C after curing for 7 days at 60°C. During this curing time the sample containing no antioxidant (fig. 1) was heavily oxidised and further ageing at 80°C caused no change in the spectra. The spectra showed the expected peaks for the products of oxidised polybutadiene. Both the formation of a strong hydroxyl peak in the region of 3400 cm^{-1} and the carbonyl peak at 1720 cm^{-1} are associated with the oxidation of polybutadiene [71, 73]. The carbonyl peak is broad due to the formation of a variety of C=O species [73], these include α,β-unsaturated aldehyde and saturated aldehyde formed from cyclic peroxides via reaction 91 absorbing at 1727 and 1700 cm^{-1} respectively. Also a range of carboxylic acids; the saturated acids absorbing at 1760 cm^{-1}, associated acid species in the region 1724-1700 cm^{-1} and α-β unsaturated carbonyls at 1694-1689 cm^{-1}.



91

As in other studies the resolution of the region below 1500 cm^{-1} became poor due to oxidation. It is suggested this is due to the formation of water during the oxidation, possibly via reaction 92.

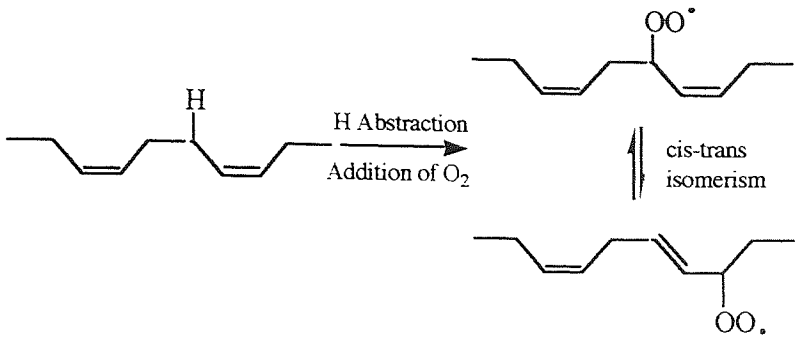
$$2ROOH \longrightarrow RO^{\bullet} + RO_2^{\bullet} + H_2O \qquad 92$$

During this study it may be expected that any water formed would rapidly evaporate, the production of a large number of varied oxidation products would also cause a large number of peaks in this fingerprint region making it difficult to decipher.

For samples containing antioxidants (figs. 2 to 14) it was possible to follow the oxidation of the samples during ageing by the formation of the -OH and -C=O absorptions. An exception was the sample containing 0.2% DLTP which was heavily oxidised during curing, i.e. before ageing. This is expected as

analysis of thin layers thermally aged (fig. 4-6) showed a rapid increase in cross-link density. This, as discussed in chapter 4, is due to initial pro-oxidant species produced by the sulfur containing DLTP causing rapid early oxidation, the antioxidant features developing too late to prevent the oxidation of the unstable polybutadiene. The shape of the curves produced by these analyses showed a period where oxidation was being inhibited by the presence of the antioxidant, but once the antioxidant activity was removed rapid uninhibited oxidation occurred.

During oxidation of polybutadiene cross-linking occurs which is associated with the removal of unsaturation [76, 77, 80, 81, 83]. It has been seen [76] that the three types of unsaturation present in polybutadiene react at different rates, the least stable vinyl 1,2 bond reacting fastest and the most stable trans slowest. Attempts to follow the removal of these structures by infra-red was relatively unsuccessful. In all cases (fig. 2 to 14) the peak corresponding to the double bond at 1640 cm^{-1} shows no real decrease even after increases in the -OH and -C=O absorbencies indicate oxidation has occurred. Visual examination of the samples also indicated cross-linking had occurred as the samples became brittle. Concurrent analysis of peaks corresponding to C-H bonds associated with the different types of unsaturation [156] did show changes in the levels of double bonds. But since these absorbencies occurred in the region from 1000 to 600 cm^{-1} oxidation products of the polybutadiene can interfere with their measurement. These peaks do show decreases during the oxidation but the results are not very clear or reproducible. In the cases of the cis and trans double bonds the situation will be complicated by oxidative cis trans isomerism which has been seen to occur [74] via reaction 93.



93

Also these peaks will decrease due to the initial stage of oxidation, hydrogen abstraction which will further complicate the results. Thus drawing conclusions about the reactivity of the different double bonds is impossible from these results.

5.3.1.1 Comparison of Antioxidant Performance in Thin Layer Binder Samples by Infra-red Spectroscopy.

As was discussed in the last section the increases in peaks associated with -OH and -C=O groups clearly indicated the onset of oxidation in thin layer binder samples containing antioxidants. In the cases of samples containing Calco 2246 (figs. 2 & 3) and IPPD (fig. 5) prepared by stirring it is clear IPPD is at least twice as efficient as Calco 2246 under these conditions. This was also observed in the analysis of increase in cross-link density for thin layer dish samples at 80°C (fig. 4-5), which are similar conditions to those used for the infra-red analysis. In deep tube samples the two antioxidants performed equally as well and the difference in performance is suggested to be due to the very high level of oxygen causing the formation of pro-oxidant dienones in the case of Calco 2246.

In the cases of the samples containing mixed antioxidant systems, the samples containing 3:1 IPPD:Calco 2246 (fig. 8 & 9) prepared by stirring performed in a similar way as the sample containing the single antioxidants although the results are not as reproducible as the single antioxidants. This concurs with the results from the analysis of the tube samples (fig. 4-15 & 4-23)

indicating no synergistic effect is occurring. The two other mixed samples contain the hetero synergistic mix of Calco 2246 and the sulfur containing DLTP but with 1:1 (fig. 14) and 3:1 (fig. 13) ratios. In the tube samples both of these combinations produced synergistic effects when compared to Calco 2246 alone. As thin layers, prepared for analysis by infra-red, only the sample containing a 3:1 Calco 2246:DLTP (fig. 16) ratio showed synergism, delaying the onset of oxidation by three times that of the Calco 2246 alone. Conversely the 1:1 ratio under the conditions used for infra-red analysis showed a pro-oxidant effect. This must be due to the rapid diffusion of oxygen possible in this sample when compared to that of the tube sample. In the case of the tube sample the lower level of chain breaker antioxidant is able to cope with the initial pro-oxidant species developed by DLTP. In the thin layer samples the high level of oxygen must cause the propagation of more chains thus reacting with more of the Calco 2246, reducing the effectiveness of the mixed system as too low a level of CB-D remains to be effective. This also probably occurs at the surface of the tube samples but as the antioxidants are mobile they will be able to diffuse from the bulk into the areas where they are most required.

During analysis of the deep tube samples an anomaly was observed in the results of samples containing 3:1 IPPD:2246 (fig. 4-23). In this case one sample performed much more efficiently than others. During the preparation of this sample an ultrasound bath had been used to help mix the antioxidants, but attempts to reproduce this effect with other samples was unsuccessful. However samples containing the two antioxidants alone and in the 3:1 combination were also prepared using ultrasound for analysis by infra-red (0.2 % Calco 2246 fig. 4, 0.2 % IPPD figs. 6 & 7, 0.2 % 3:1 IPPD:Calco 2246 figs. 10 & 11). When the increases in -OH and -C=O peaks for these samples are compared to the increase for samples prepared by stirring (fig. 15 and 17 to 19) clearly the ultrasound is having a beneficial effect on the antioxidant efficiency, in the case of 3:1 IPPD:2246 potentially doubling the antioxidant effectiveness. This effect occurred whether ultrasound was performed before addition (figs. 4, 7 & 11) or

after addition (figs. 6 & 10) of the cross-linking agent. An explanation could be production of efficient reaction products from the antioxidant as it is known that ultrasound can produce free radicals [180, 181] thus antioxidant transformations to dimers, trimers and oligomers could be formed.

It is known that ultrasound can have powerful effects on chemical reactions [180]. The usual explanation for this effect is the inducement of cavitation in the solvent. Cavitation is caused when the ultrasonic sound waves 'pull' apart the solvent to produce small bubbles. These bubbles can subsequently collapse producing high pressures (1000 atm.) and temperatures (5000 K). Depending on the conditions they may also remain stable for a period where such extremes are not observed but the extra life allows more time for them to affect the reaction. These high temperatures and pressures have been shown to produce free radicals [180] and to also cause degradation of polymers via a free radical route [181]. In most of these cases the reactions were performed in solvent systems using high power sonic probes, the cavitation occurring in the solvent [181]. In this work only a relatively low powered cleaning sonic bath was used with the glass beaker containing the polybutadiene samples standing in water to transmit the ultrasonic waves. Under these conditions it would be unlikely that cavitation would occur in the polybutadiene sample and it is much more likely the effect of the ultrasound is to cause vibration of the molecules causing increase in temperature and a mixing effect. The temperature was seen to increase during the ultrasound to a maximum of approximately 70°C after about 90 minutes, but samples containing IPPD were often warmed to 60°C to aid solubility during stirring.

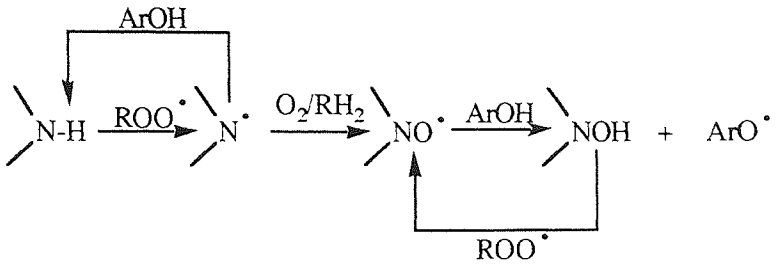
At various times during the ultrasound treatment of samples (which underwent ultrasound before addition of the cross-linking agent) small amounts were removed and H.P.L.C was performed on the extracts (see section 2.7 for method). If the antioxidant was being transformed it may be expected the detected level of the original antioxidant would steadily drop as the period of

ultrasound increased. Analysis of the peaks produced by the H.P.L.C. of these samples (figs. 24, 25 & 26) showed no steady decrease but do show variation in the levels of the main antioxidant and smaller peaks. This may indicate cycling regenerative reactions occurring as comparison of the overall levels of the antioxidants extracted from ultrasound treated samples were similar to those found for the stirred samples. Analysis of the chromatograms showed no new peaks formed compared to those seen in the standards which may have been expected if new transformations were occurring. But all cases when the ageing of the samples prepared by stirring (figs. 3, 5 & 8) was compared to the ageing of the samples prepared by ultrasound for 120 min. in the results from infra-red show the ultrasound treated samples to be more effective (fig. 19).

The H.P.L.C. and corresponding ageing results suggest that the effect of ultrasound is one of both mixing and alteration to the antioxidants. The fact that the performance of low solubility IPPD is improved by ultrasound could be explained by mixing (see fig. 17). However mixing would be expected to have little influence on the samples containing only Calco 2246, as the antioxidant is readily soluble in polybutadiene, but the efficiency of Calco 2246 can be doubled by use of ultrasound (see fig. 15). This indicates some interaction is also occurring. The exact effect of these interactions are still unclear and further work is required to investigate the effects.

What is clear is that the method of preparation can have a major effect on the antioxidants' efficiency. Where similar preparation methods are used (i.e. either stirring or ultrasound) for the single antioxidants (Calco 2246 or IPPD) reproducible stabilisation is observed (see figs. 15 and 17). But this is not the case when the two antioxidants are mixed in a ratio of 3:1 (fig. 18), here the results are much more varied when prepared by either method. This inconsistency is also observed in samples prepared in tube moulds where results showed the mix to be both very efficient and similar to the single antioxidants depending on the sample (see fig. 4-23). This indicates that in certain

circumstances the antioxidants are acting separately, producing results similar to single antioxidants. But it is also possible for a synergistic system to form greatly increasing the efficiency of the stabilisers. The normal mechanism suggested for this type of stabilisation is the phenol acting as a reservoir for the regeneration of the amine that performs the major stabilisation (scheme 2).



Scheme 5-2 Mechanism of regeneration of amine species by phenols

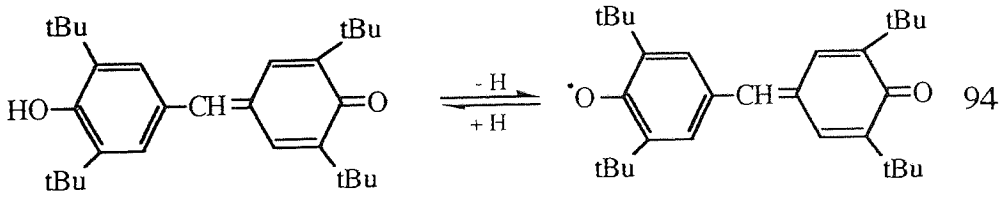
The use of infra-red spectroscopy to analyse thermally aged thin layer samples produced results which predicted the excellent effectiveness of the 3:1 Calco 2246:DLTP samples. This suggests this would be an effective method to reduce the time for predicting antioxidants efficiency.

5.3.2 H.P.L.C. Analysis of Extracts From Tube Moulds.

To attempt to gain more information about the fate of the antioxidants the extract from selected samples prepared in tube moulds were analysed using H.P.L.C. (for method see section 2.7). The samples analysed were similar to those analysed by infra-red spectroscopy discussed in the last section. During these analyses it was hoped to see peaks appear which would relate to antioxidant transformation products. In fact in all cases no peaks, that were not seen in the antioxidants initially, formed during the analysis (for 3D and 284 nm chromatographs see appendix 1). This could be due to the transformation products not being extracted during the preparation or not being detected by the H.P.L.C. method, or because they were not formed or formed at very low levels.

Other work [171] has suggested that during functioning of Calco 2246 the main transformation products formed are the dimers and trimers. There was no evidence from H.P.L.C. analysis in this work of the formation of these species. Analysis of the peaks observed in the chromatograms (original Calco 2246 at 33 min and peak A at 35 min), which were both present in the standard, shows cycling in the measured amounts present (fig. 28). It must be noted that the results plotted are of the percent of sample expected when compared to the standard amount added. Therefore, although the percentage expected of original values are similar, the actual peak areas are very different, the peak for Calco 2246 being at least 20 times larger (see table 2-9 and chromatograms in appendix 1).

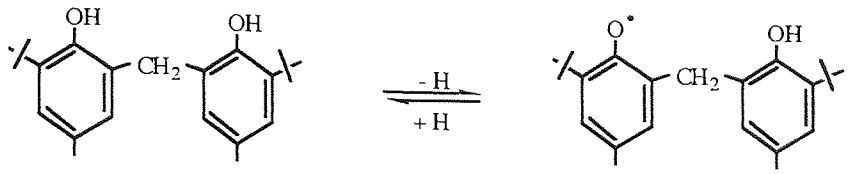
Similar cycling of antioxidant and transformation products has been observed in other systems containing antioxidant, notably in the case of galvinoxyl during the stabilisation of polymer during processing [182]. In this case the galvinoxyl acts as a hydrogen acceptor (CB-A) forming the corresponding hydrogalvinoxyl that can then act as a hydrogen donor (CB-D) (reaction 94)



94

In the deep tube samples conditions would have existed where a mix of alkyl and peroxide radicals were present. Therefore it may have been postulated that a similar redox couple could form with Calco 2246 (reaction 95). However that peak A is so much smaller than the Calco 2246 suggests that this is unlikely as it would be expected that the phenoxyl radical would have a similar U.V. spectrum. This would include a similar extinction coefficient as the original Calco 2246 due to the presence of the benzene ring. Also this is not a very

sterically hindered phenoxyl so may not be expected to have a long half life thus would be unlikely to be detected.



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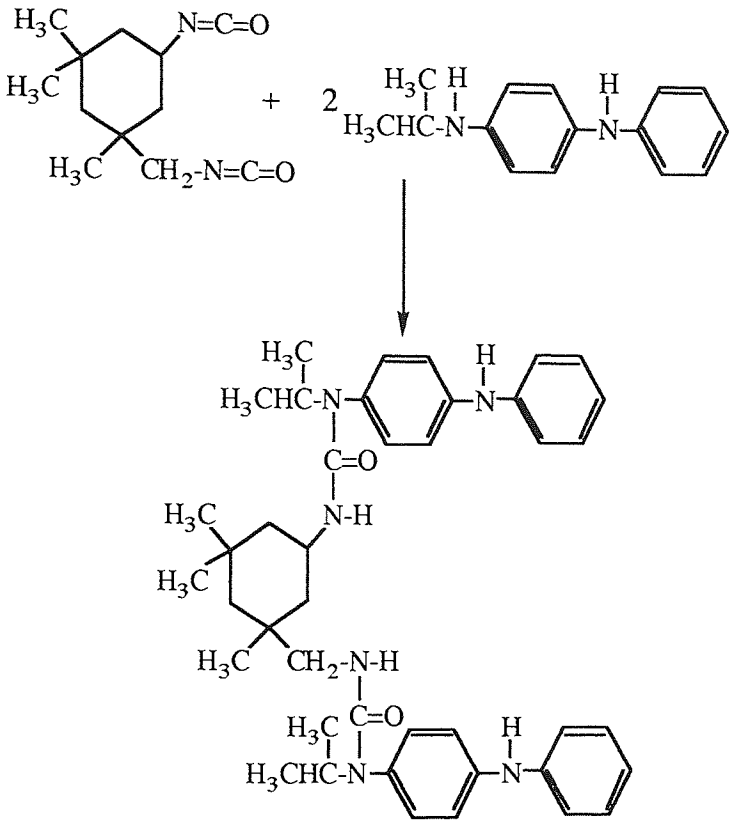
Similar cycling is also observed in samples containing Calco 2246 mixed with IPPD (figs. 30 A & 31 A) and if this variation was due to experimental error both peaks would be expected to decrease or increase simultaneously (as in fig. 24). This shows that the effect is real, but the other product involved is unknown. It should be noted that during this time the cross-link density of the binder increased, indicating oxidation of the polybutadiene was occurring. Clearly during this time a substantial level of the original Calco 2246 was still present. This means that the Calco 2246 is unable to react quickly enough to terminate the oxidative chains, i.e. the readily oxidised polybutadiene reacts more quickly with itself than the antioxidant. Therefore a less hindered phenol, which would react faster, is required to terminate the autoxidation. This would help to explain the effectiveness of γ-tocopherol which is less hindered than Calco 2246.

As expected when samples containing IPPD are analysed (see figs. 29, 30 B, and 31 B) no IPPD is observed after the initial 7 days curing time. This is due to a reaction between the IPPD and the cross-linking agent as shown in chapter 3 (reaction 96).



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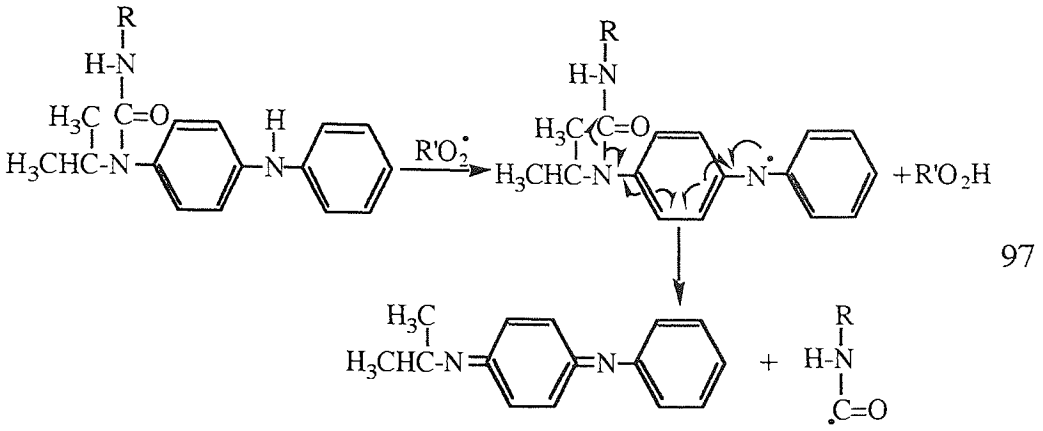
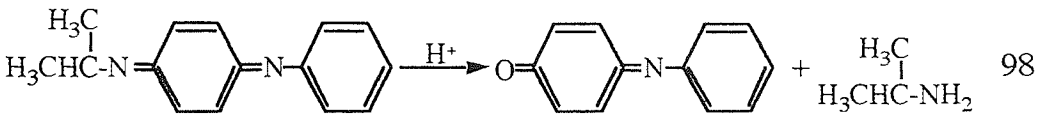
This reaction still leaves the most active N-H group available to act as an antioxidant. The other peaks that were present in the IPPD standard are also virtually absent after the curing period, but during the oxidation a number of these peaks reappear, indicating they are transformation products. One of the impurities often found in commercial samples of N-alkyl-N'-aryl-1,4-phenylene diamines [105] is N-phenyl-1,4-phenylene diamine. This will also react with the cross-linking agent and thus if present in the standard would be removed during curing.

It is known that the main transformation product from 1,4-phenylene diamines is the benzoquinone diimide [111, 112]. In this case the reaction to produce this product could not proceed as normal as the second N-H group that is usually lost is not present. Therefore to produce the benzoquinone diimide either the phenol or the added cross-linker would have to be lost. That the products from the transformations appear at similar times to species present in the standards initially indicates it is the cross-linker that is lost allowing the formation of the expected benzoquinone diimide (reaction 97). In the case of

IPPD the formed quinone diimide is easily hydrolysed and produces N-phenyl-1,4-benzoquinone monoimide and an amine (reaction 98).





It is possible that these transformation products would be present in the commercially available IPPD, these could then be lost during curing. The fact that an N-H is still present on the IPPD bound to the curing agent means the formation of benzoquinone diimide is still possible, and once this has formed the other transformation products could be formed. The formation of these transformation products shows that IPPD is still able to function as an antioxidant as expected but its efficiency is not as high as may be predicted. It is known [105] that benzoquinone diamines have radical scavenging abilities and during their action can become incorporated into unsaturated polymer chains. It would therefore be expected that the presence of such species would be important in the stabilisation of the deep mould samples. The concentration of benzoquinone diimide would be expected to increase in as the initial bound IPPD reacts then decreases as the benzoquinone diimide became bound to the polymer and degraded by hydrolysis to the N-phenyl-1,4-benzoquinone monoimide and amine. This could account for the peaks observed in the H.P.L.C. analysis but the actual assignment of these peaks is not possible without further study. Other products that are suggested to form during

stabilisation by amines are the nitroxyls [113-115]. H.P.L.C. analysis of nitroxyl prepared in earlier work (fig. 33) [31] shows that this would not be expected to be detected if present so is not one of the products shown during the ageing. Other work [112] has suggested that the role of nitroxyls is minimal in stabilisation and results of analysis of the efficiency of the nitroxyl in these systems [31] seem to agree with this.

As was shown in section 5.3.1 the effectiveness of samples containing a mix of 3:1 IPPD:Calco 2246 can vary greatly depending on its preparation. This was also observed for deep tube samples analysed by increasing cross-link density. H.P.L.C. analysis was performed on two deep tube samples, which, although both prepared using ultrasound, performed very differently in use. H.P.L.C. results from the sample prepared on the 12/10/94, which performed similarly to the single antioxidants alone, showed similar levels of abstracted antioxidants as was shown by the individual antioxidants (compare fig. 30 A with fig. 28 and fig. 30 B with fig. 29). In the other sample analysed by H.P.L.C., prepared on 28/7/93, which performed very well, different initial levels of both Calco 2246 and peaks D and E were detected (compare fig. 31 A with fig. 28 and fig. 31 B with fig. 28). In this case much lower levels of Calco 2246 (20% compared to 50%) and much higher levels of peak D (40% compared to 15%) and peak E (25% compared to 5%) are initially abstracted. The excellent performance of the sample prepared on the 28/7/93 indicated a synergistic mechanism was occurring. If the mechanism was as shown in scheme 5-2 then this would be consistent with the results of the H.P.L.C. analysis, the Calco 2246 being sacrificed for the amine. This would have occurred during curing when the sample was liquid and the antioxidants could move freely. The initiation of this mechanism is not known and further investigation is required to gain a greater understanding.

The chromatographic analysis of a sample containing the synergistic mixture of 3:1 Calco 2246:DLTP only showed peaks associated with the Calco

2246. Analysis of the extract with time did not show the same cycling of the two peaks as in the other samples containing Calco 2246 (compare fig. 32 with fig. 28 & figs. 31 & 30 A). Also the level of the Calco 2246 peak does not vary as much as in the other samples and may be within experimental error. This is due to the different mechanism of action of the antioxidant. The main antioxidant action is performed by the products of the DLTP which acts as a catalytic peroxide decomposer [131]. The main role of the Calco 2246 is therefore to remove the initial prooxidant species produced by the initial transformations of DLTP (see scheme 1-10).

5.4 Overview of Results.

From the results of this work clearly a more efficient stabiliser system than the currently used Calco 2246 is possible.

A concern over the reduction of the efficiency of antioxidants by their reaction with the cross-linking agent IPDI was shown to be unfounded in the case of the phenolic type of antioxidants. These were shown not to react with the cross-linking agent either when mixed in an inert solvent or when added in increasing levels to the binder preparation (figs. 3-5 to 3-14). The high levels of the antioxidant Calco 2246 detected in tube aged samples by H.P.L.C. reinforced these findings. This was not the case with the more nucleophilic amine antioxidant IPPD. This reacted with the cross-linker and the reaction appeared to proceed more rapidly than the corresponding reaction between the hydroxyterminated polybutadiene and the cross-linker (see fig. 3-17). This was obviously of concern as it detrimentally affected the cross-linking reaction at antioxidant concentrations as low as 1.0 % (see fig. 3-29) and would be expected to have affected the performance of the antioxidant.

In earlier work it was shown that IPPD performed similarly to Calco 2246 when used to stabilise 5 mm thick films (see fig. 3-51) and similar results were observed in this work for deep tube samples (see fig. 4-2). Where the two

antioxidants differ in performance is in situations where there are high levels of oxygen are present. Dynamic thermal analysis in an oxygen rich atmosphere indicated that IPPD performed considerably better than Calco 2246, or any of the other phenolic antioxidants, in both cured and uncured samples (see figs. 3-48 & 3-46 respectively). This difference was also observed during the analysis of thin layers of binder by either; increase in cross-link density (fig. 4-5), or by infra-red spectroscopy (fig. 5-19). These results were explained by the potential formation of prooxidant peroxydienones by phenolic antioxidants in high temperature oxygen rich atmospheres [163, 164]. The greater efficiency of Calco 2246 over most of the other phenolic antioxidants is explained by its reluctance to form the peroxydienone [171].

It is clear from these results that the conditions at the surface of the binder samples were different from those deeper in the samples as represented by the tube samples. Earlier work [31] showed that below the tube sample surface (approx. 5 mm) the level of peroxides present was low, also that in samples aged with no oxygen present no increase in cross-linking occurred. Thus the cross-linking had to be initiated by the oxidation of the sample surface. In samples containing certain antioxidants, such as DLTP and Irgafos 168 (see figs. 4-4 and 4-6), a heavily cross-linked 'skin' formed on the samples due to the antioxidants poor stabilisation ability. Under this 'skin' the cross-link density increased very slowly, much slower than that of samples containing more efficient antioxidants such as Calco 2246 (see fig. 4-4). This difference could be explained by either the prevention of the diffusion of oxygen into the sample by the 'skin', or the skin being fully oxidised making it unable to initiate new radical chains. That in other samples cross-linking occurs in the lower layers, where obviously a low level of peroxide is present [31], suggests oxygen is not required to cause cross-links. Alkyl radicals formed from the abstraction of hydrogen are able to cause cross-linking by their attack on unsaturation [82] (reaction 99).

$$R^{\bullet} + RCH{=}CHR' \longrightarrow RO\text{-}RCH\text{-}C^{\bullet}HR' \qquad 99$$

It has been suggested that the intermolecular attack is at least one quarter as common as hydrogen abstraction [82]. Therefore in the case of 'skin' formation, it is the fact that the heavily cross-linked surface no longer initiates radical chains, rather than the decrease in oxygen diffusion prevents the lower layer cross-linking. The fact the oxygen cannot diffuse through the surface will prevent initiation at just below the surface.

In samples containing the more efficient antioxidants, such as Calco 2246 and IPPD, the increase in cross-link density at the surface was lower than samples with less efficient or no antioxidant (see figs. 4-5 & 4-6). This allowed the continuation of initiation at the surface by oxygen and therefore causes propagation of the radical chains, via alkyl radicals, into the sample. Thus an increase in cross-link density in the lower layers occurs.

To prevent both the formation of the 'skin', which would crack under dynamic stress, and the increase in cross-link density in the lower layers, the complete removal of the surface peroxide species is required. It would also be beneficial if the antioxidant contained a certain amount of CB-A activity to terminate any alkyl radicals which propagate into the deeper layers of the samples. Calco 2246 is not a good enough CB-D antioxidant to terminate all the formed peroxides and therefore a low level are able to propagate and cause the cross-linking. The addition of the catalytic peroxide decomposer DLTP strongly increases the removal of the peroxides at the sample surface thus decreasing propagation and cross-linking. The DLTP requires the presence of a certain level of CB-D antioxidant as during its initial stages of action prooxidant species are produced [127], which is why samples containing DLTP alone form a 'skin'. The CB-D antioxidant stabilises these initial prooxidant species, giving time for the catalytic peroxide decomposer species to form. These then very efficiently remove the peroxides formed in the surface. This produces the strongly synergistic 3:1 Calco 2246:DLTP system that performs well both in thin layers (see fig. 16) and in deep tube samples (see fig. 4-24).

The excellent performance of γ-tocopherol has been seen in other work using elastomers [165]. In this work it has been shown to be more effective than any other single antioxidant and is as powerful as the synergistic system discussed above (see fig. 4-26). γ-Tocopherol is a less hindered phenol than Calco 2246 (for structures see table 2-3) so is likely to be more reactive therefore able to terminate alkylperoxy radicals more quickly. Also it is known to produce a number of novel transformation products which have further antioxidant activity [175] (see chapter 4 for more details). This makes it a very powerful antioxidant for the unstable polybutadiene.

It was also shown that the method of sample preparation can have a strong effect on an antioxidants performance. The use of ultrasound was shown to increase the stability of a number of samples containing the phenol Calco 2246, the amine IPPD and a mixture of the two (see section 5.3.1.1). This was attributed to either increased antioxidant mixing on a molecular level or the formation of novel species from the antioxidants or a combination of the two. The most interesting results were found for samples containing a 3:1 mix of IPPD and Calco 2246. With these samples both in tube moulds (fig. 4-23) and in thin layers (fig. 18) results varied from performing similarly to the single antioxidant to being the most efficient system observed (i.e. no increase in cross-link density after 200 days at 60°C). This suggests that under certain conditions a synergism can be created between the two CB-D antioxidants. The actual trigger for this synergism is at present unknown.

Therefore improvement of the binders ageing performance can be achieved by the single phenolic antioxidant γ-tocopherol or by the heterosynergistic mix of 3:1 Calco 2246:DLTP. The performance may be improved further if the full potential of the homosynergistic mix of 3:1 IPPD:Calco 2246 can be harnessed.

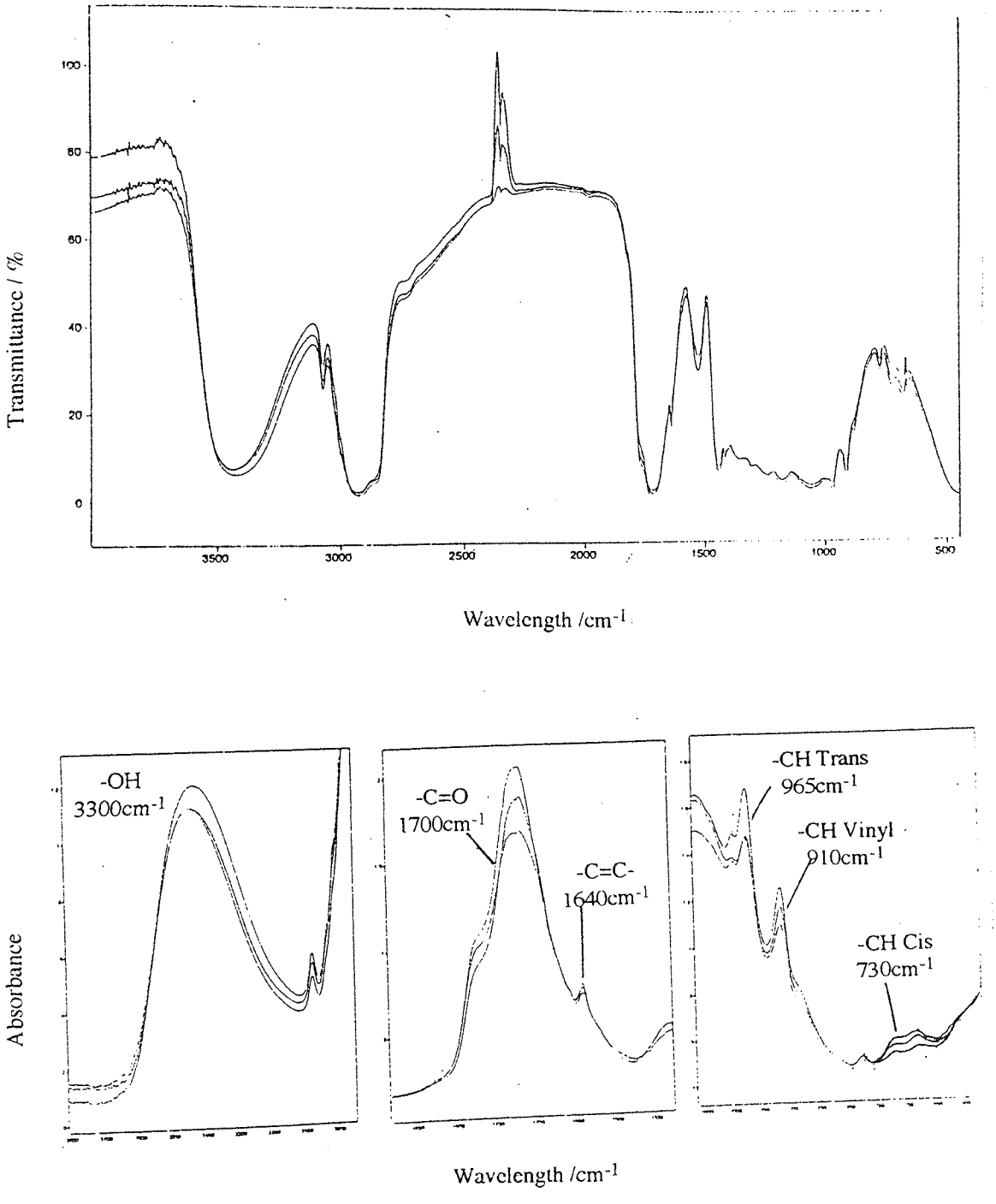


Figure 5-1 Associated infra-red spectra showing the oxidation at 80°C, with time, of a thin layer of cured binder. (Graphs were not produced as sample was fully oxidised during 7 days curing)

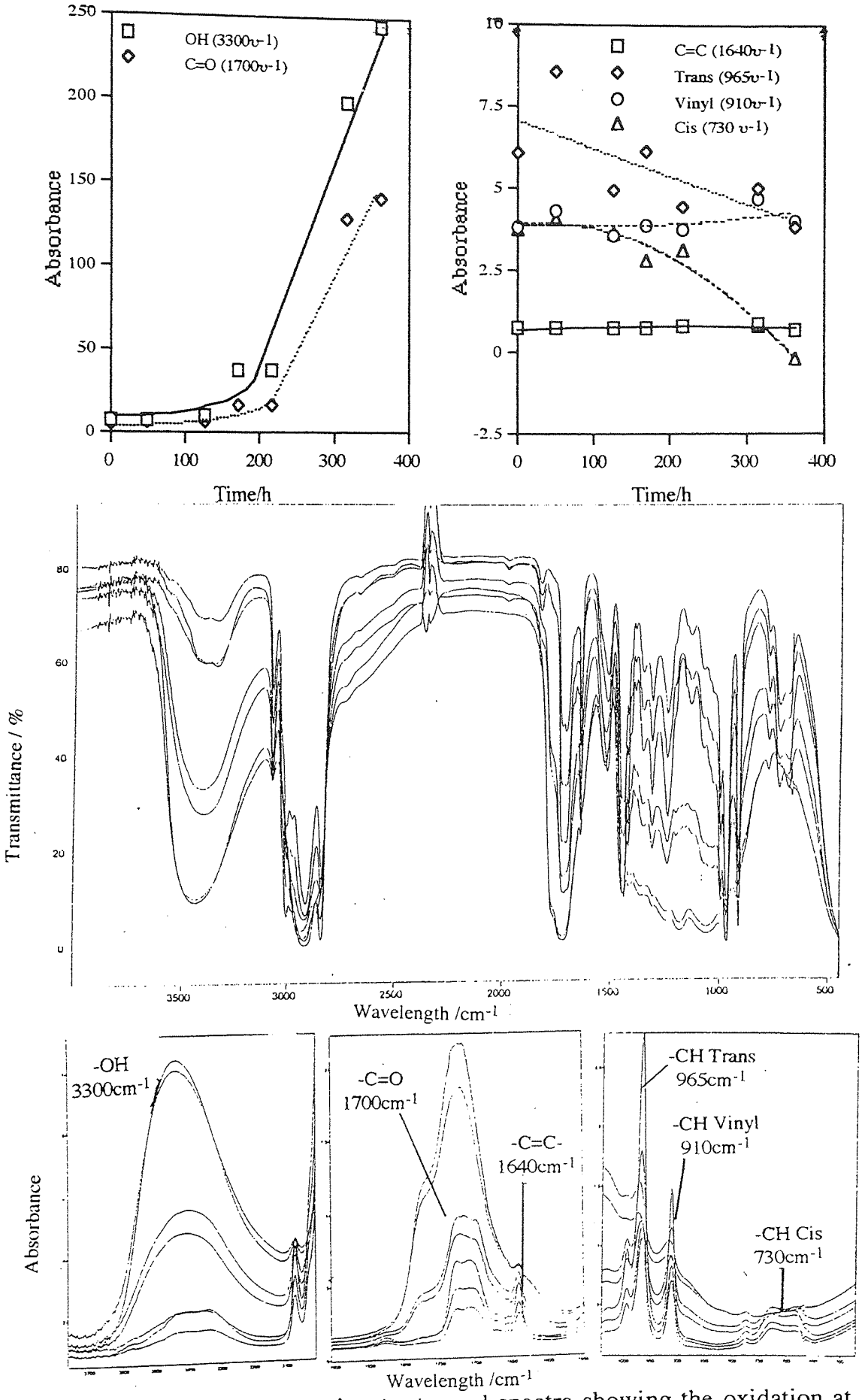


Figure 5-2 Graphs and associated infra-red spectra showing the oxidation at 80°C, with time, of a thin layer of cured binder containing Calco 2246 (0.2% w/w) prepared by stirring (i). Numbers on graphs indicate absorption wavelength of IR peaks in cm^{-1}.

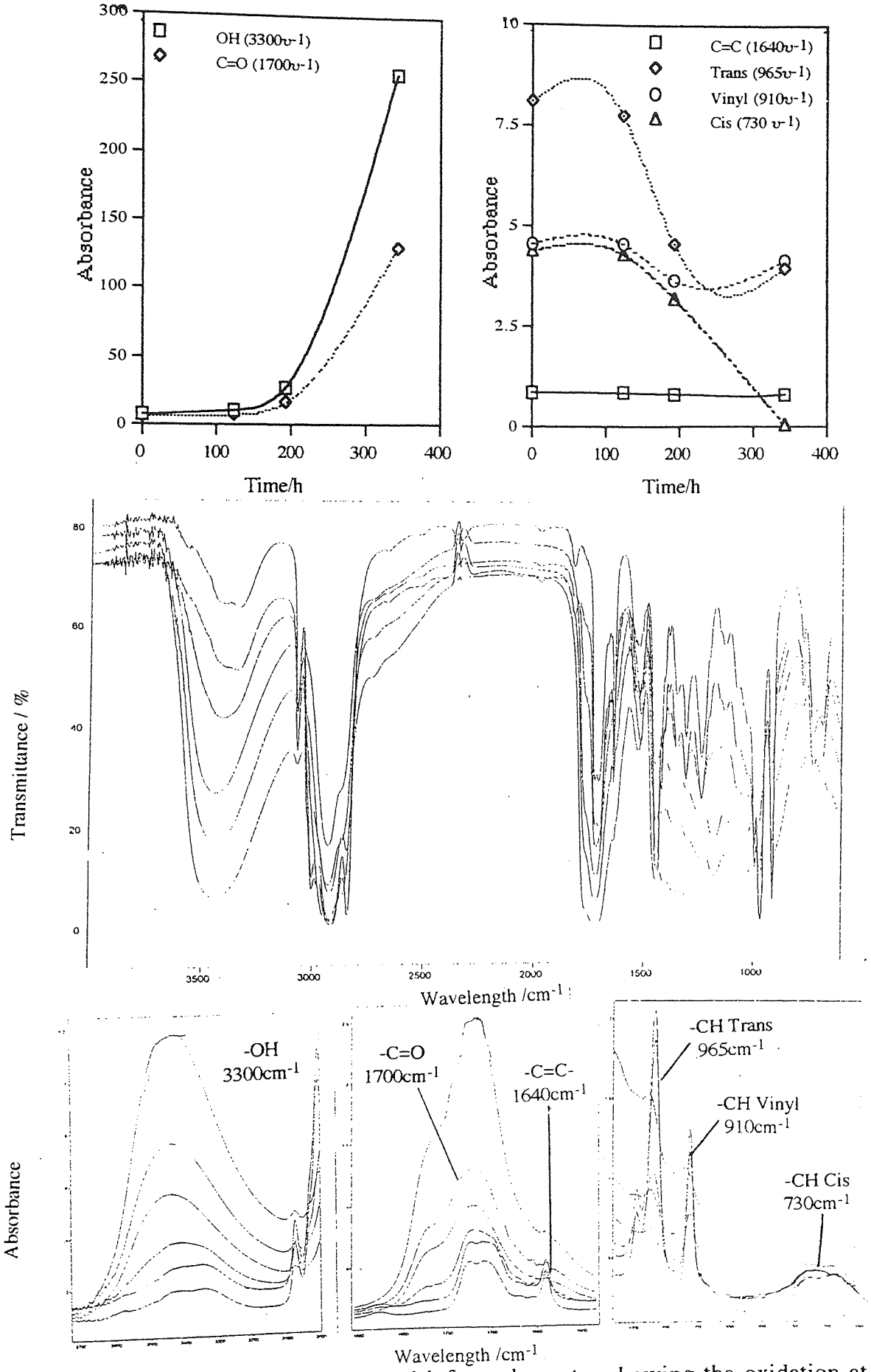


Figure 5-3 Graphs and associated infra-red spectra showing the oxidation at 80°C, with time, of a thin layer of cured binder containing Calco 2246 (0.2% w/w) prepared by stirring (ii). Numbers on graphs indicate absorption wavelength of IR peaks in cm^{-1}.

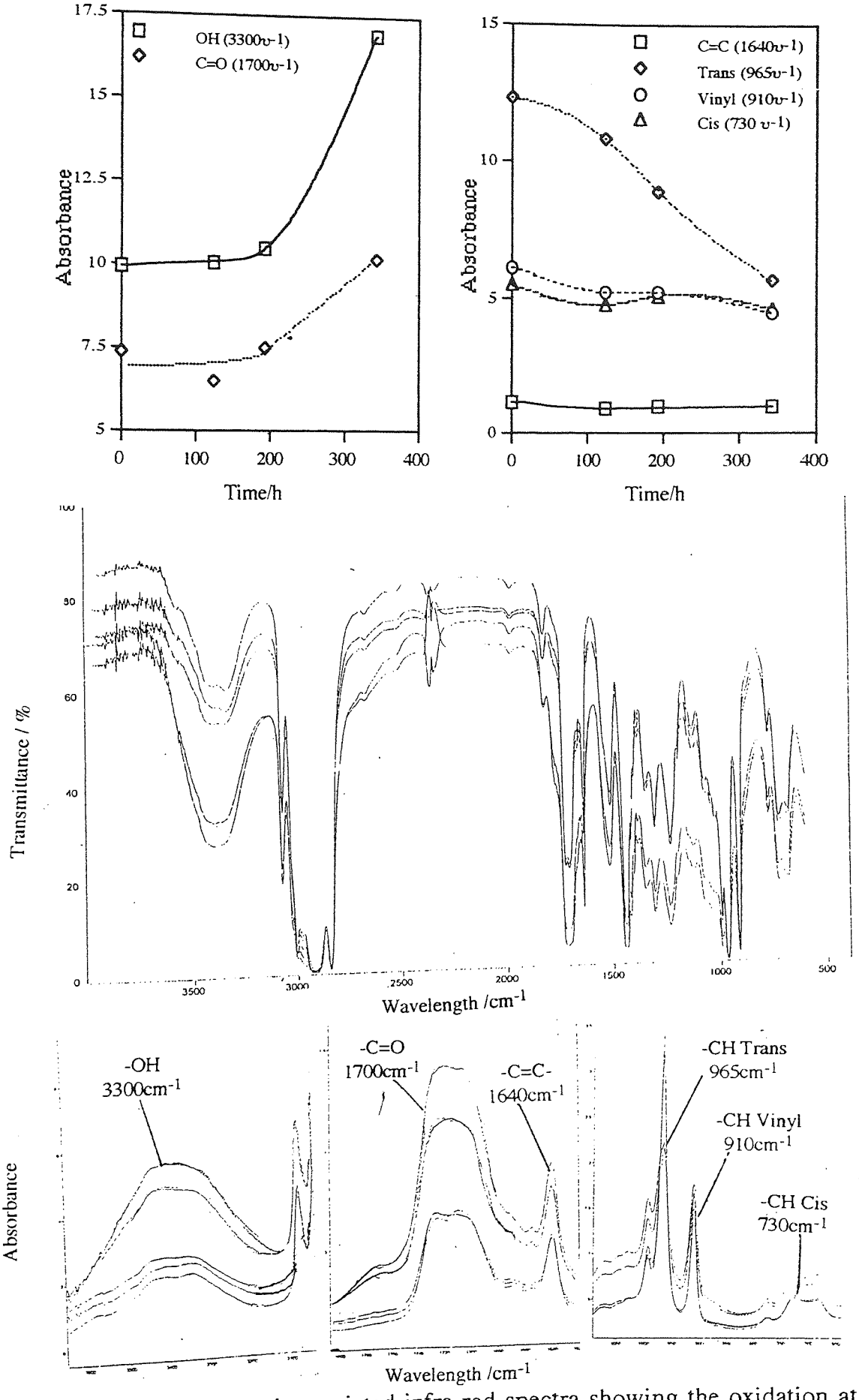


Figure 5-4 Graphs and associated infra-red spectra showing the oxidation at 80°C, with time, of a thin layer of cured binder containing Calco 2246 (0.2% w/w) prepared by ultrasound. Numbers on graphs indicate absorption wavelength of IR peaks in cm^{-1}.

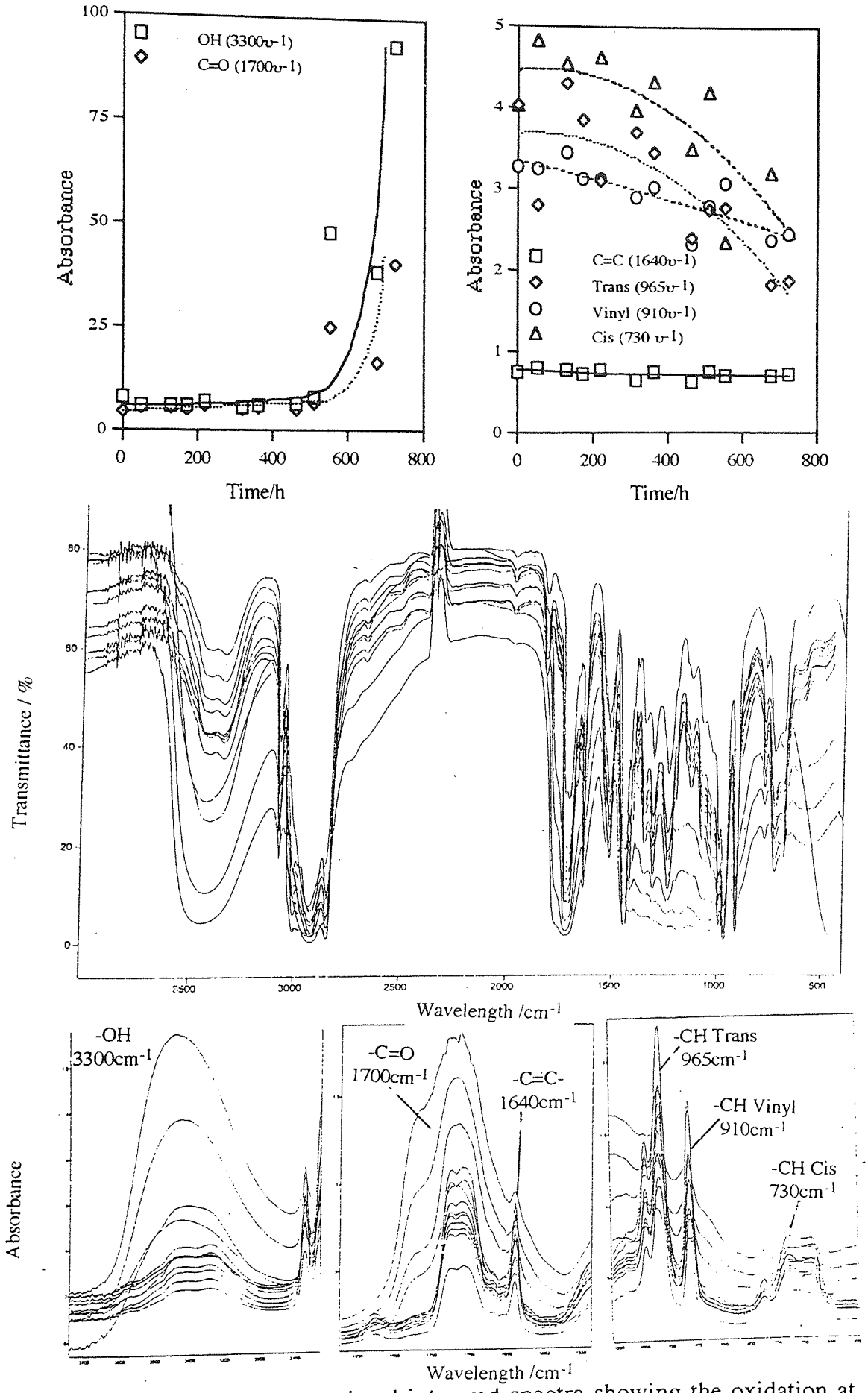


Figure 5-5 Graphs and associated infra-red spectra showing the oxidation at 80°C, with time, of a thin layer of cured binder containing IPPD (0.2% w/w) prepared by stirring. Numbers on graphs indicate absorption wavelength of IR peaks in cm^{-1}.

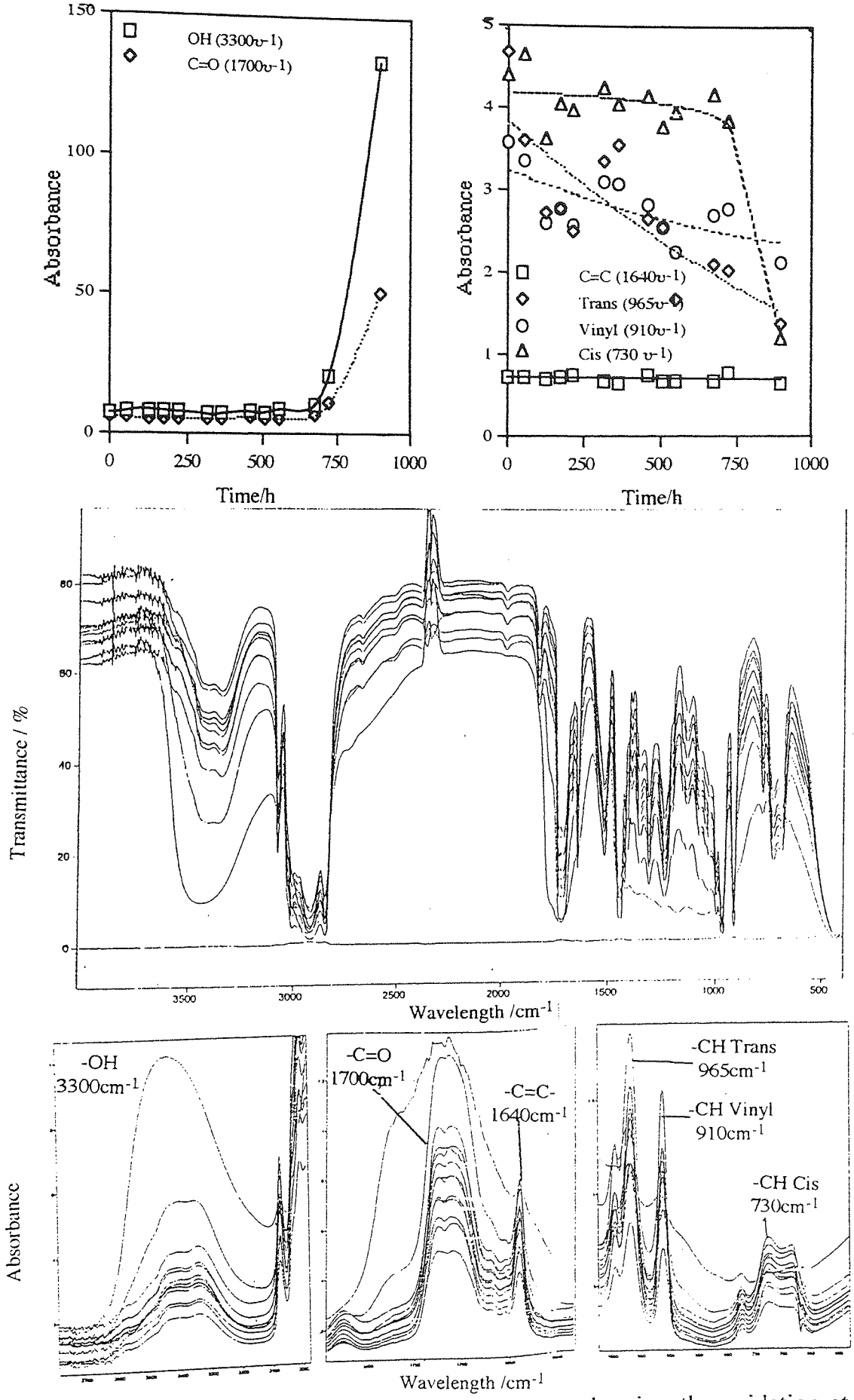


Figure 5-6 Graphs and associated infra-red spectra showing the oxidation at 80°C, with time, of a thin layer of cured binder containing IPPD (0.2% w/w) prepared by ultrasound (i). Numbers on graphs indicate absorption wavelength of IR peaks in cm^{-1}.

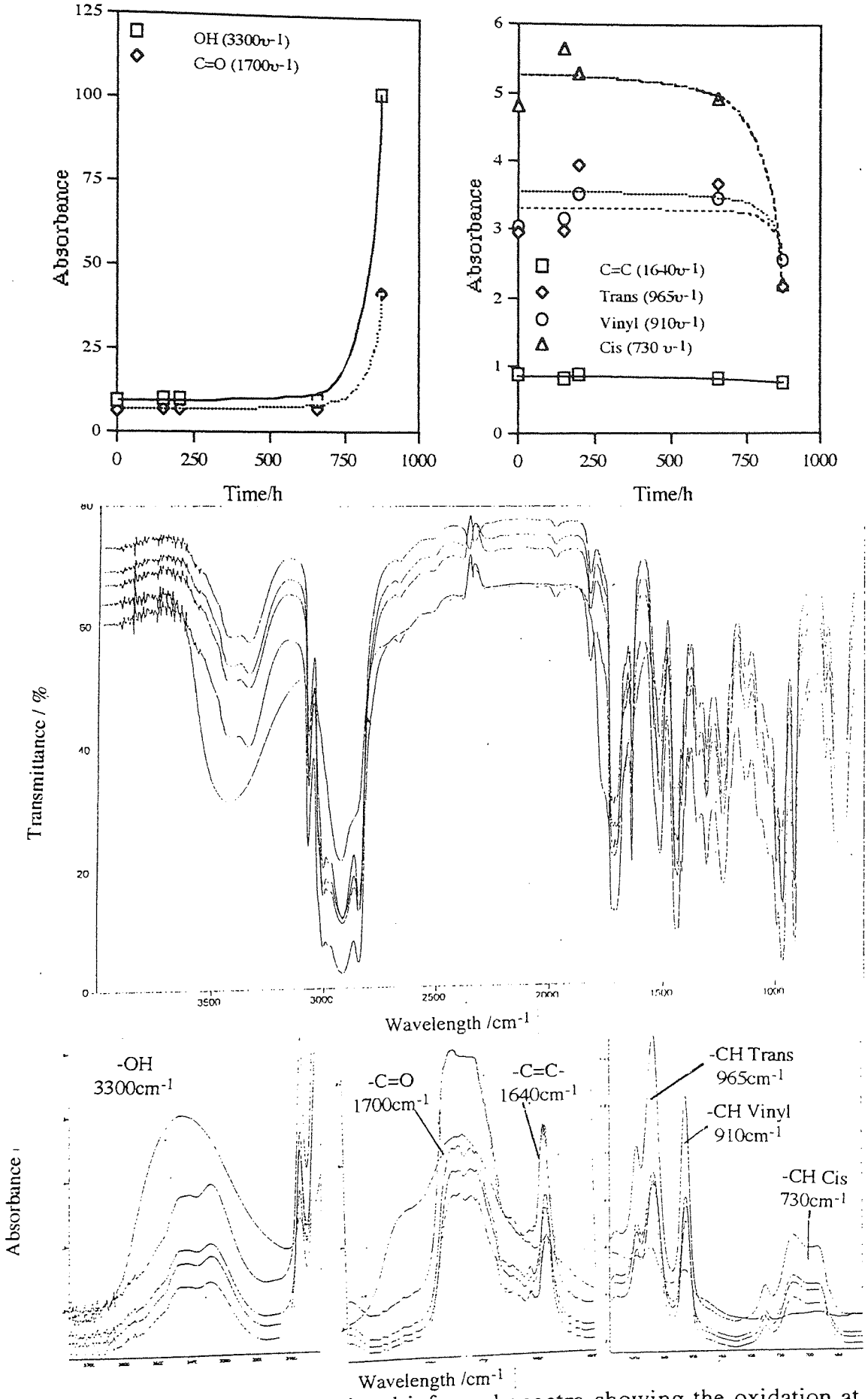


Figure 5-7 Graphs and associated infra-red spectra showing the oxidation at 80°C, with time, of a thin layer of cured binder containing IPPD (0.2% w/w) prepared by ultrasound (ii). Numbers on graphs indicate absorption wavelength of IR peaks in cm^{-1}.

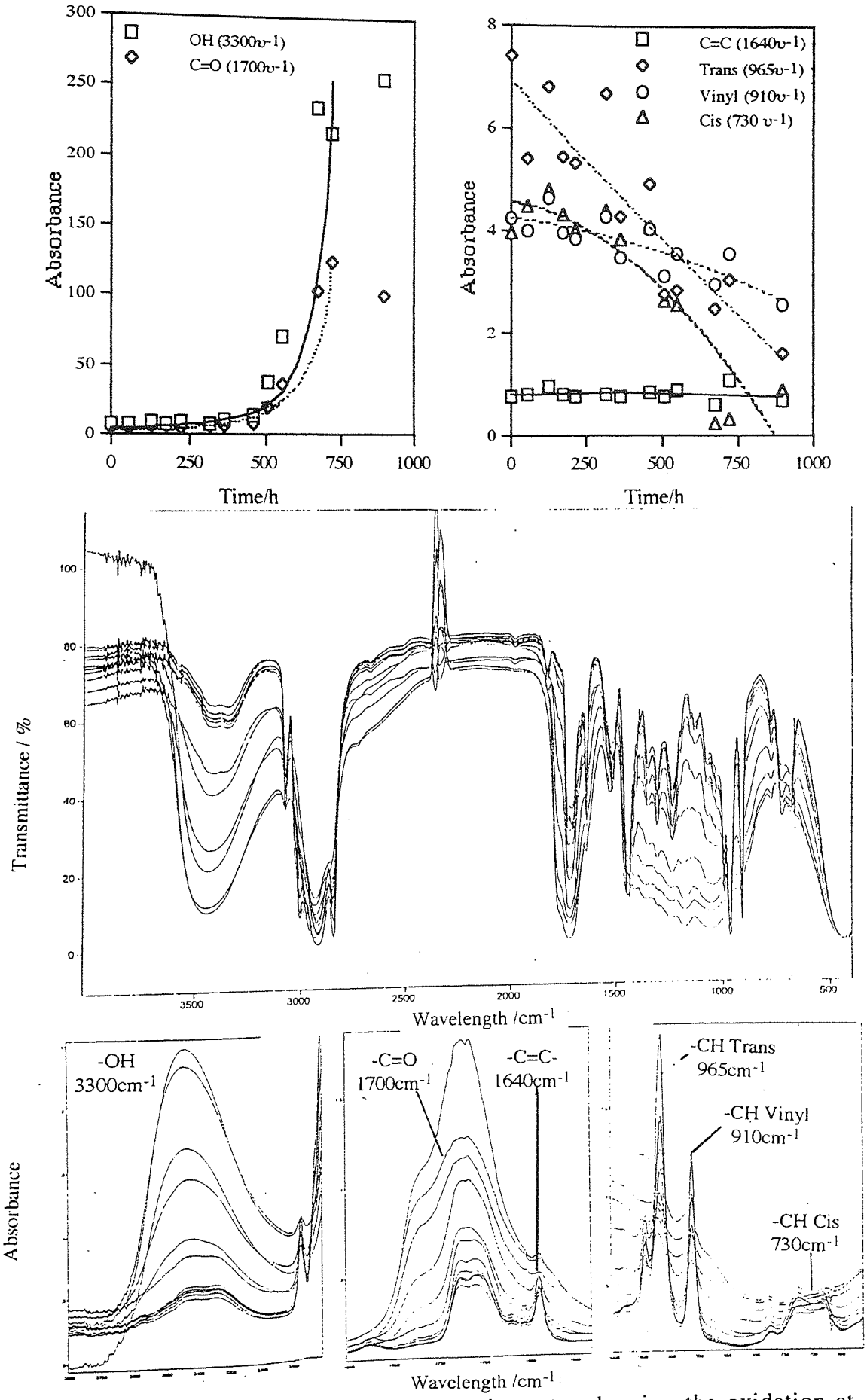


Figure 5-8 Graphs and associated infra-red spectra showing the oxidation at 80°C, with time, of a thin layer of cured binder containing 3:1 IPPD:Calco 2246 (0.2% w/w) prepared by stirring (i). Numbers on graphs indicate absorption wavelength of IR peaks in cm^{-1}.

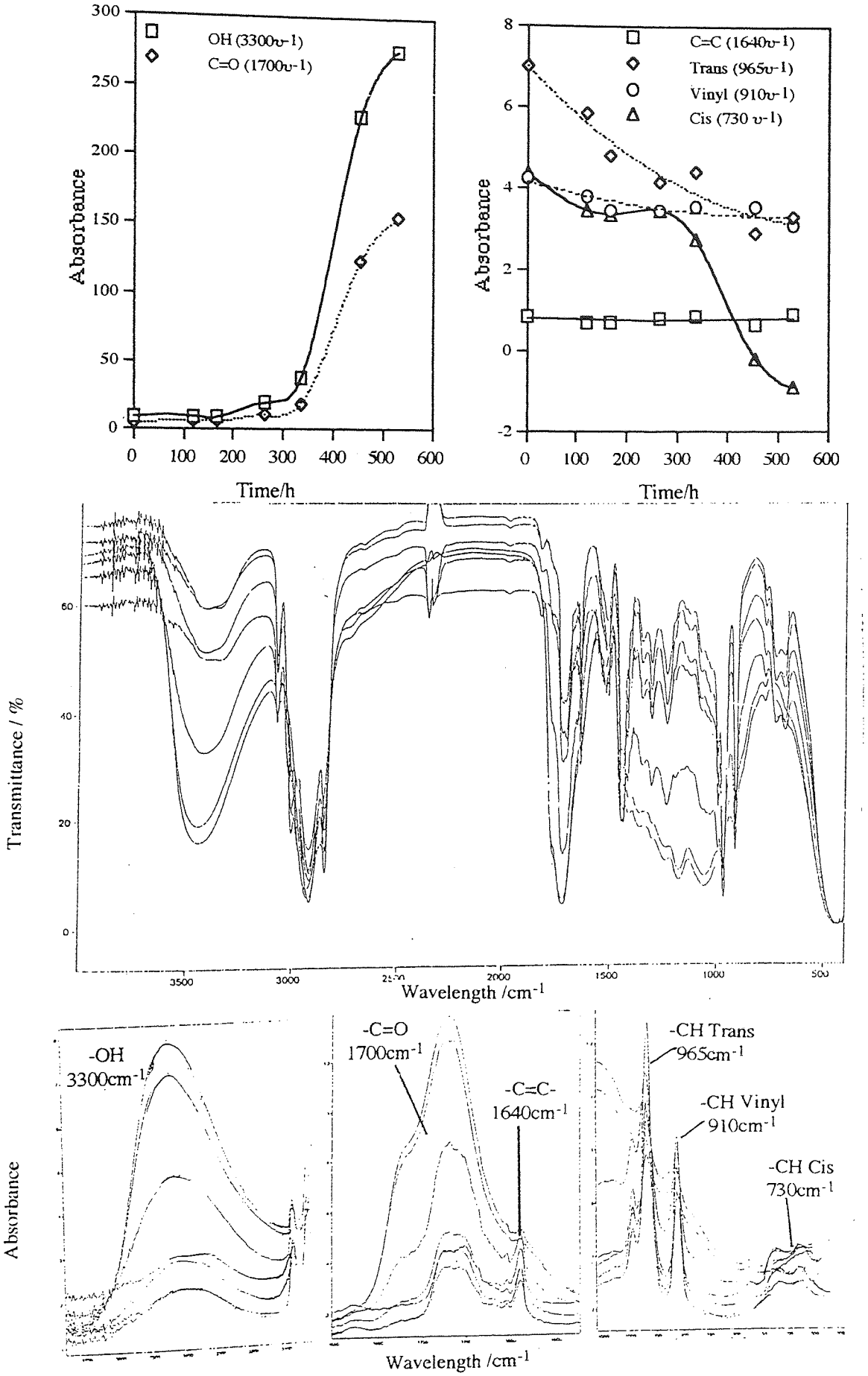


Figure 5-9 Graphs and associated infra-red spectra showing the oxidation at 80°C, with time, of a thin layer of cured binder containing 3:1 IPPD:Calco 2246 (0.2% w/w) prepared by stirring (ii). Numbers on graphs indicate absorption wavelength of IR peaks in cm^{-1}.

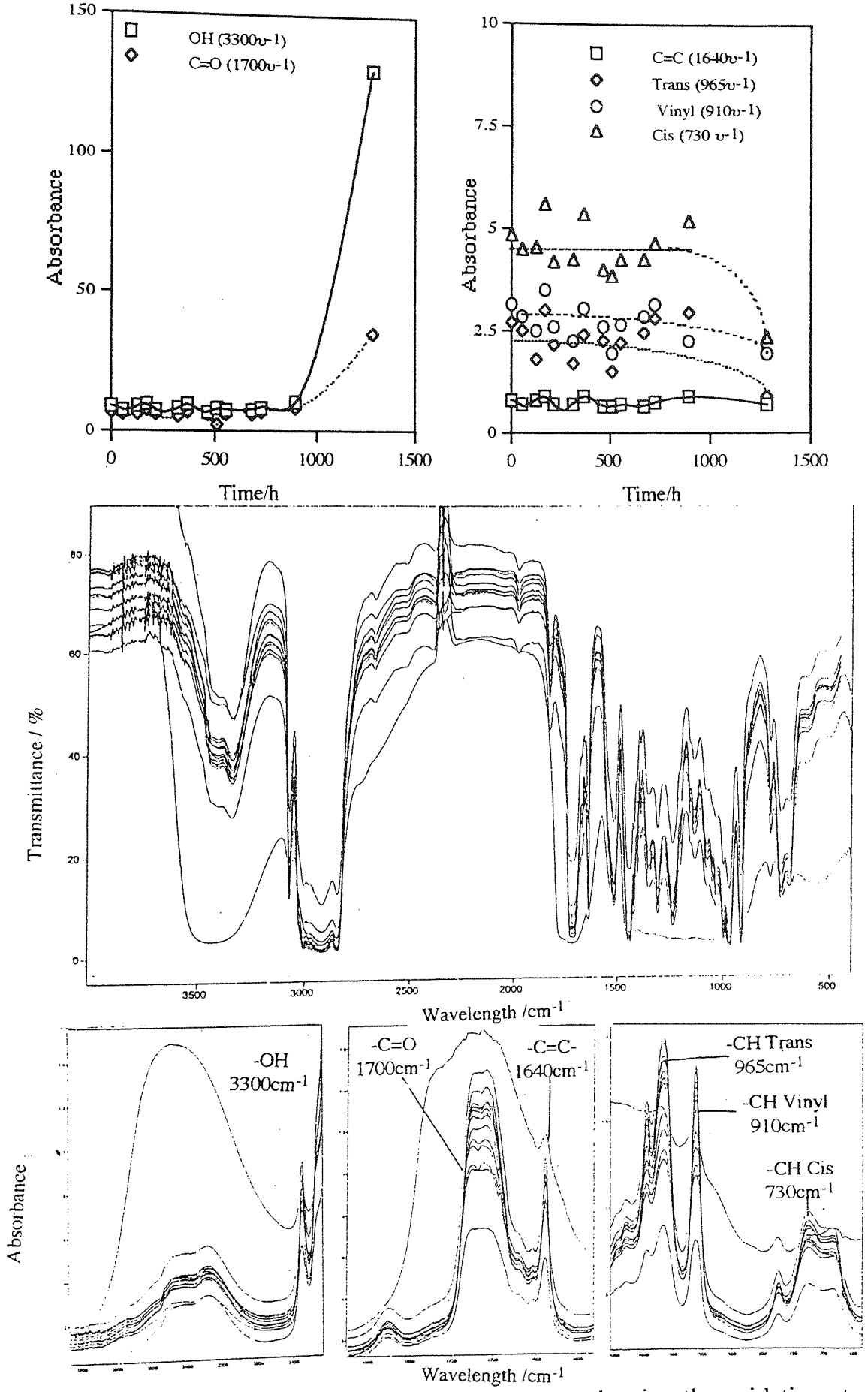


Figure 5-10 Graphs and associated infra-red spectra showing the oxidation at 80°C, with time of a thin layer of cured binder containing 3:1 IPPD:Calco 2246 (0.2% w/w) prepared by ultrasound (i). Numbers on graphs indicate absorption wavelength of IR peaks in cm^{-1}.

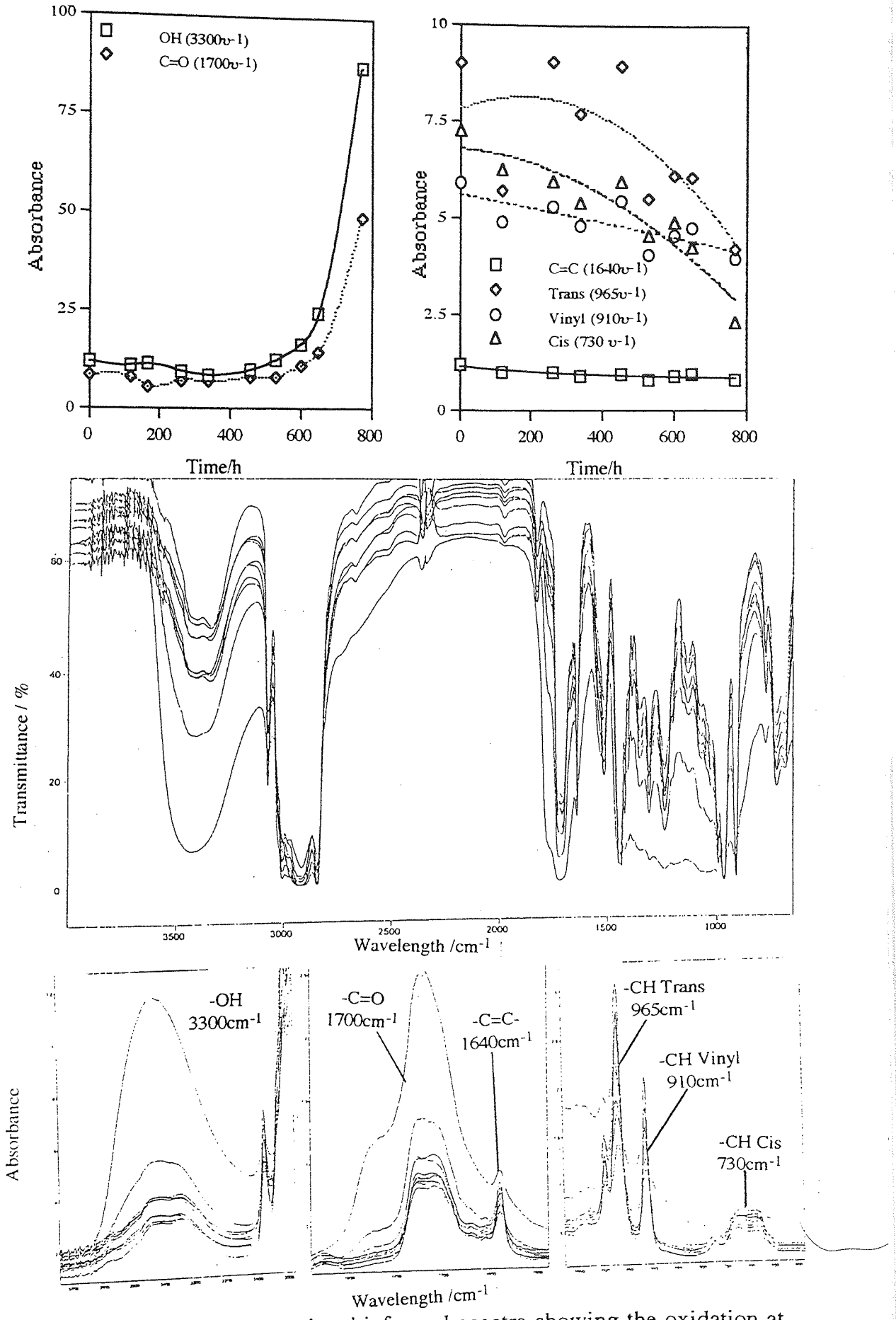


Figure 5-11 Graphs and associated infra-red spectra showing the oxidation at 80°C, with time, of a thin layer of cured binder containing 3:1 IPPD:Calco 2246 (0.2% w/w) prepared by ultrasound (ii). Numbers on graphs indicate absorption wavelength of IR peaks in cm^{-1}.

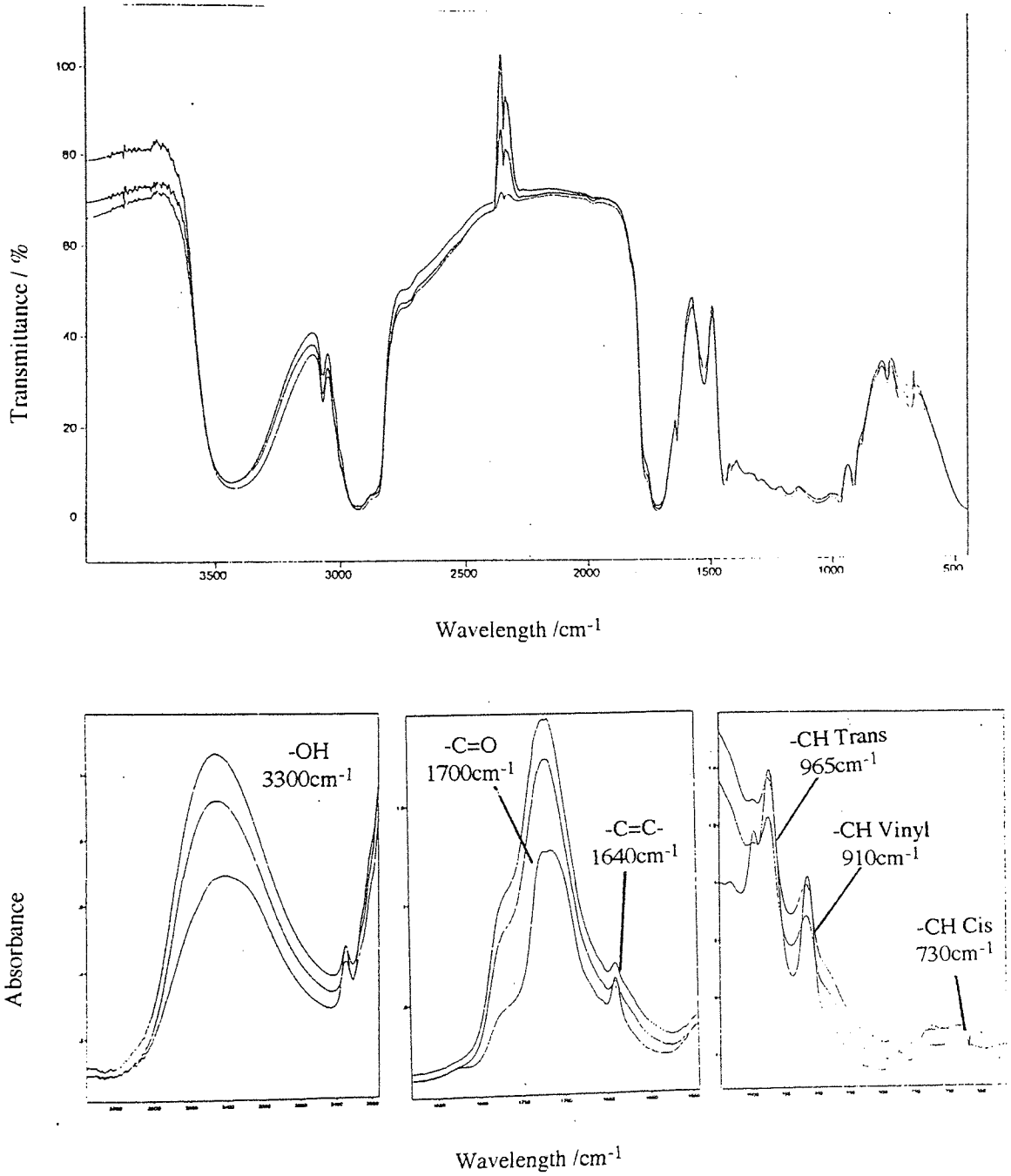


Figure 5-12 Associated infra-red spectra showing the oxidation at 80°C, with time, of a thin layer of cured binder containing DLTP (0.2% w/w) (Graphs were not produced as sample was fully oxidised during 7 days curing).

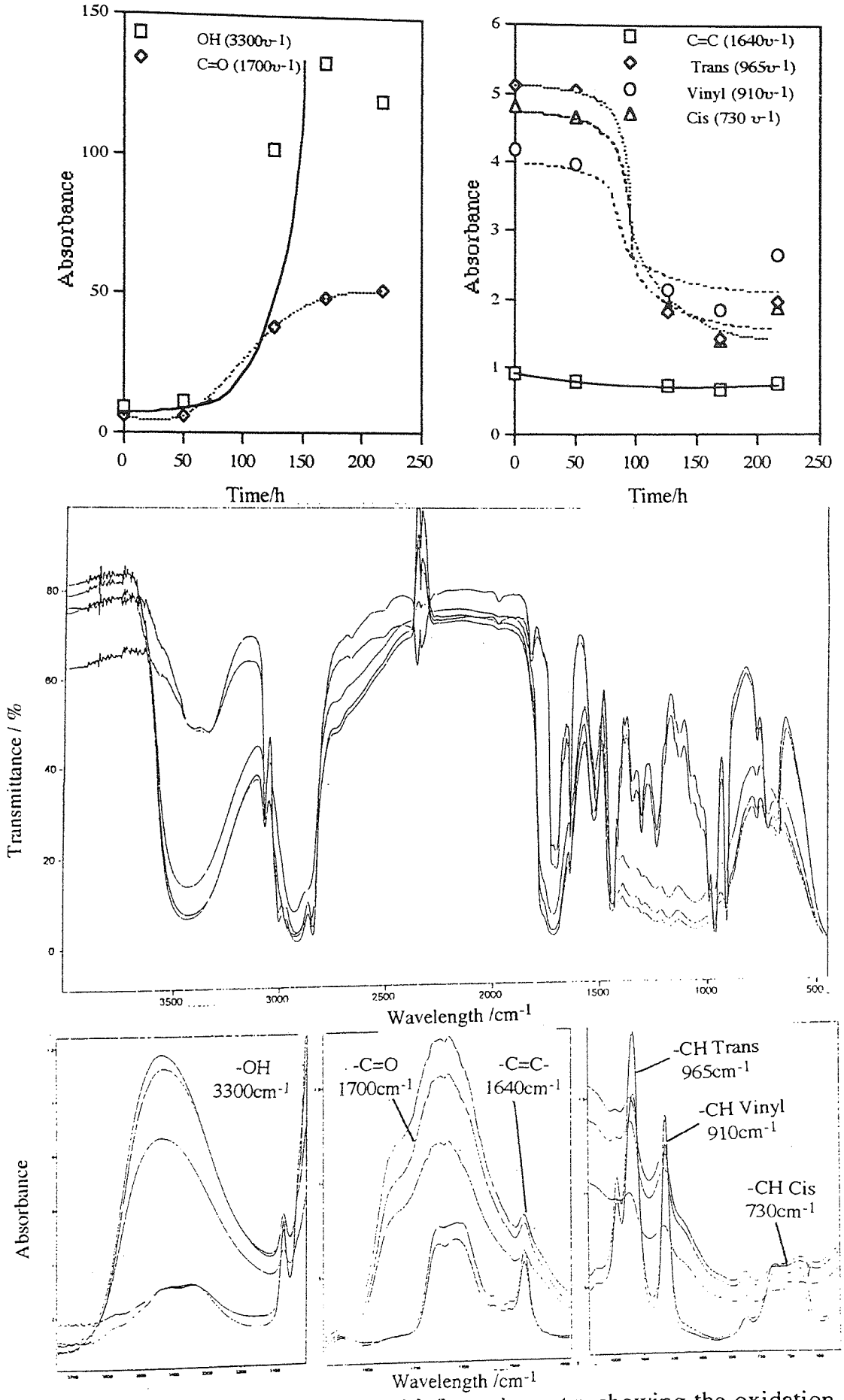


Figure 5-13 Graphs and associated infra-red spectra showing the oxidation at 80°C, with time, of a thin layer of cured binder containing 1:1 Calco 2246:DLTP (0.2% w/w) prepared by stirring. Numbers on graphs indicate absorption wavelength of IR peaks in cm^{-1}.

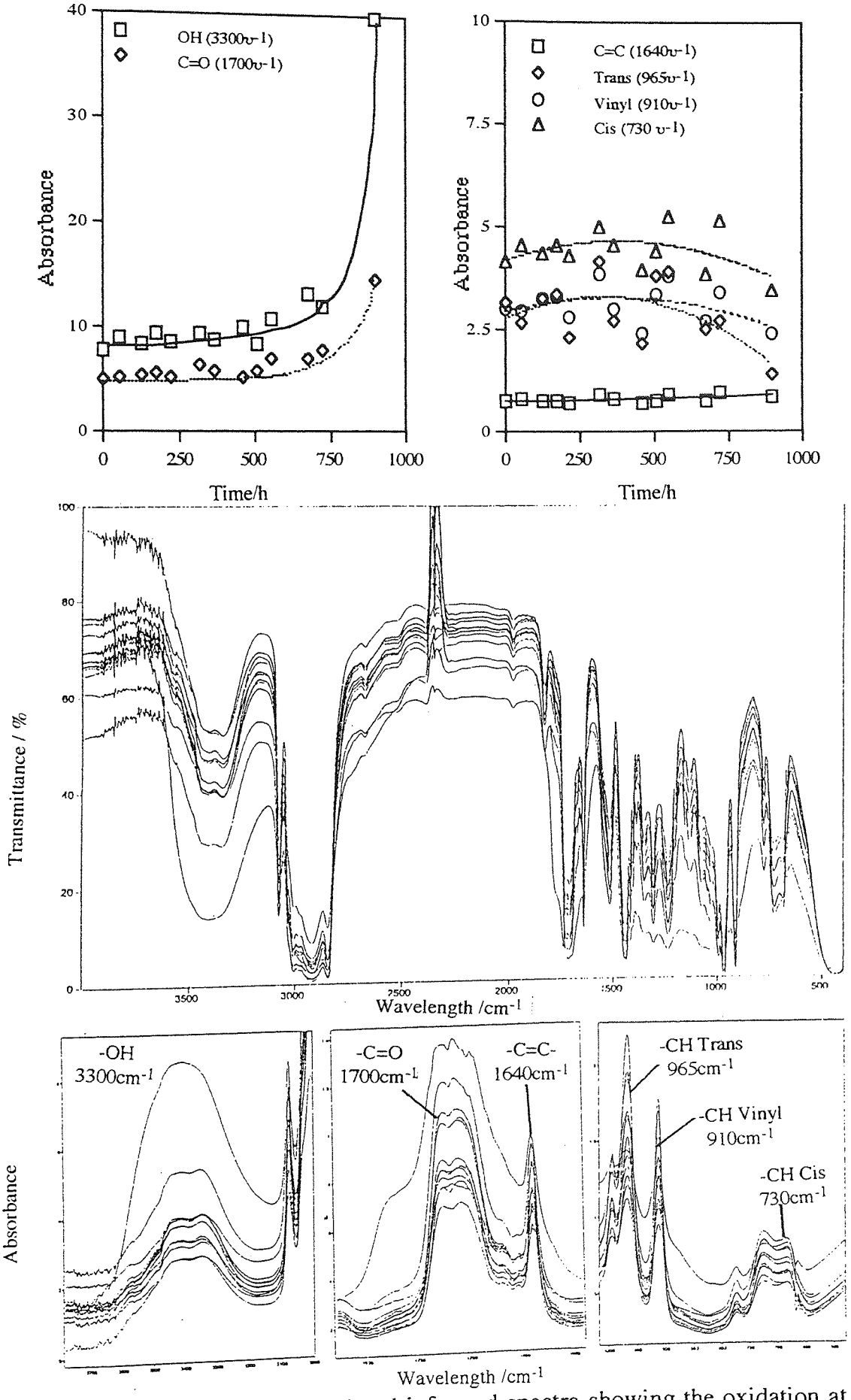


Figure 5-14 Graphs and associated infra-red spectra showing the oxidation at 80°C, with time, of a thin layer of cured binder containing 3:1 Calco 2246:DLTP (0.2% w/w) prepared by stirring. Numbers on graphs indicate absorption wavelength of IR peaks in cm^{-1}.

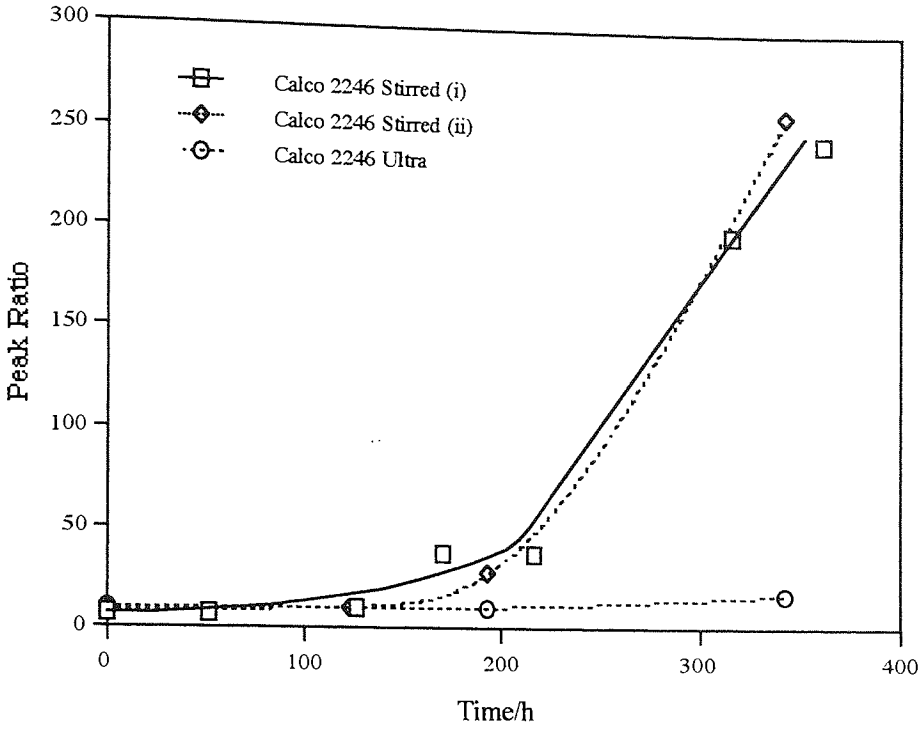


Figure 5-15 Graph comparing increase in OH concentration during the oxidation at 80°C, with time, of thin layer of cured binder samples containing Calco 2246 (0.2% w/w) (Ultra indicates sample prepared by ultrasound (i) & (ii) indicate repeat samples)

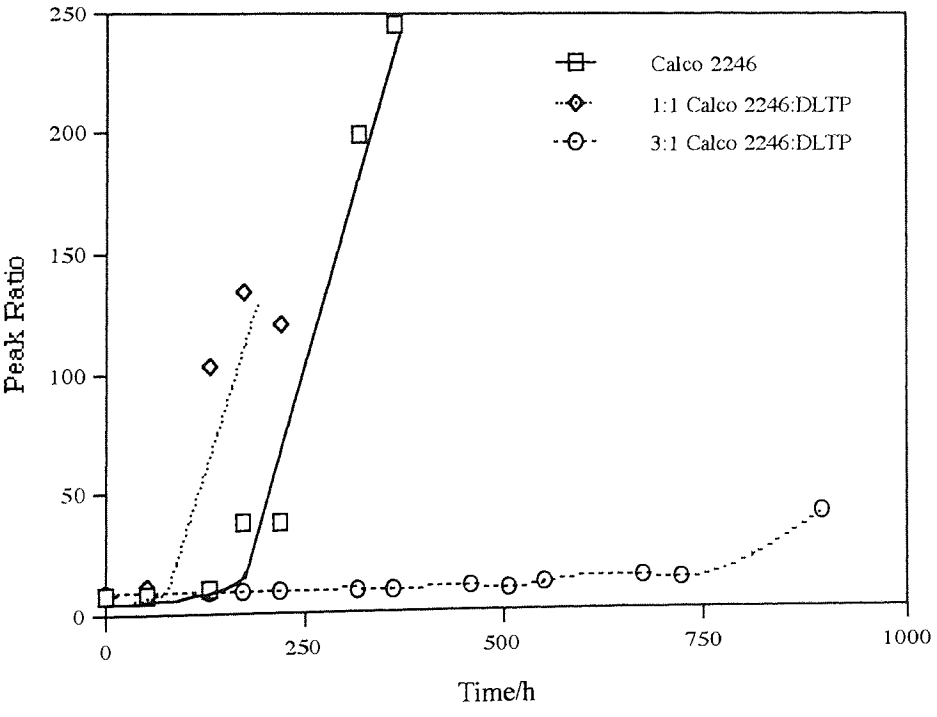


Figure 5-16 Graph comparing increase in OH concentration during the oxidation at 80°C, with time, of thin layer of cured binder samples containing either Calco 2246, 1:1 Calco 2246:DLTP or 3:1 Calco 2246:DLTP (0.2% w/w).

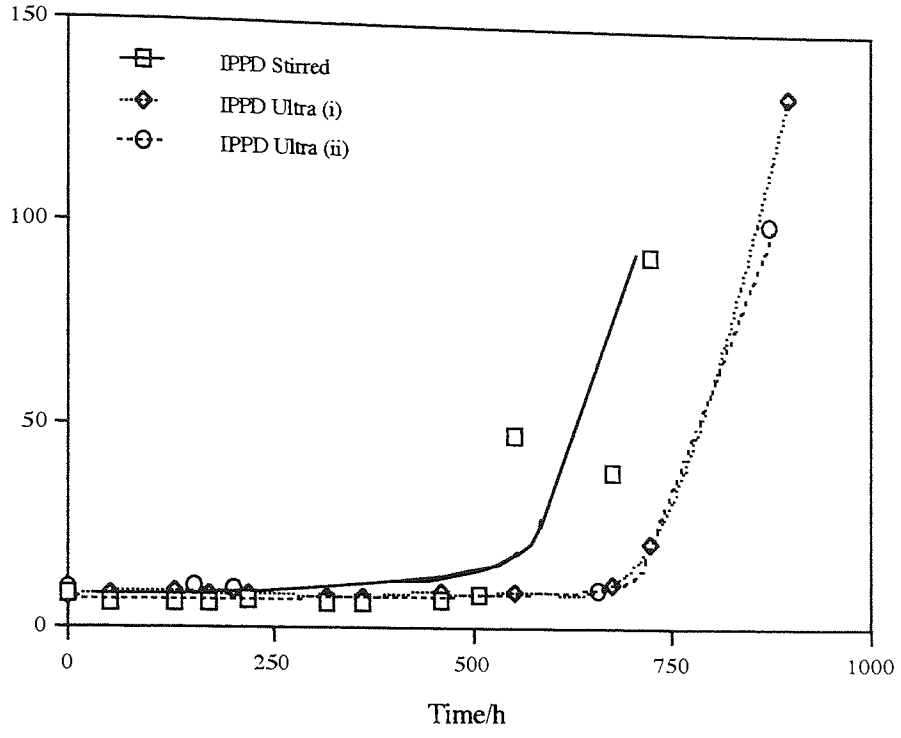


Figure 5-17 Graph comparing increase in OH concentration during the oxidation at 80°C, with time, of thin layer of cured binder samples containing IPPD (0.2% w/w). (Ultra indicates sample prepared by ultrasound (i) & (ii) indicate repeat samples)

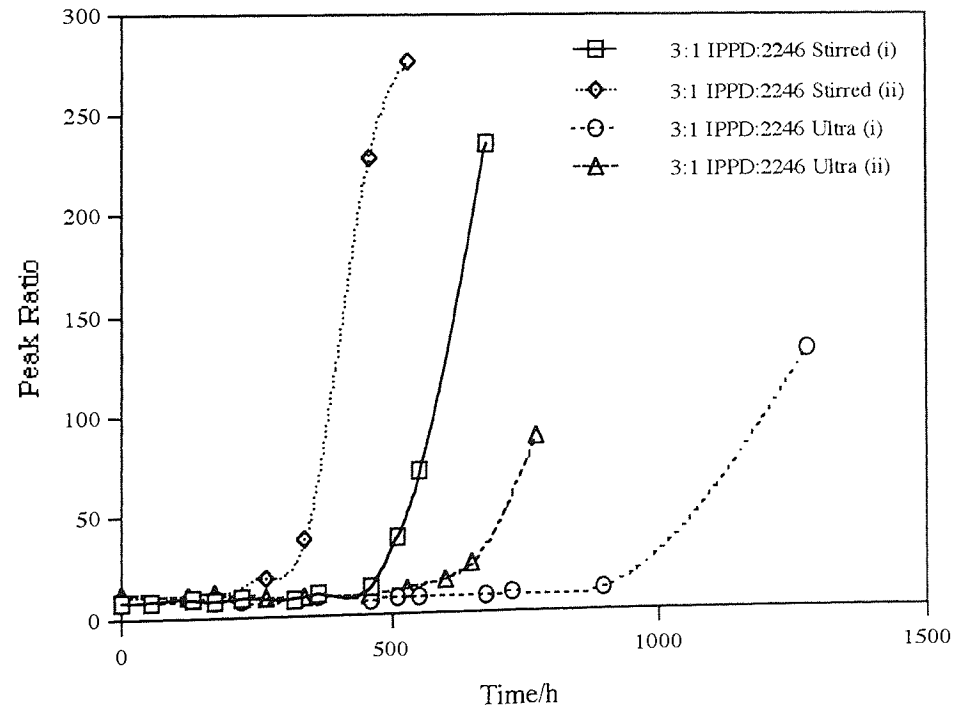


Figure 5-18 Graph comparing increase in OH concentration during the oxidation at 80°C, with time, of thin layer of cured binder samples containing 3:1 IPPD:Calco 2246 (0.2% w/w). (Ultra indicates sample prepared by ultrasound (i) & (ii) indicate repeat samples)

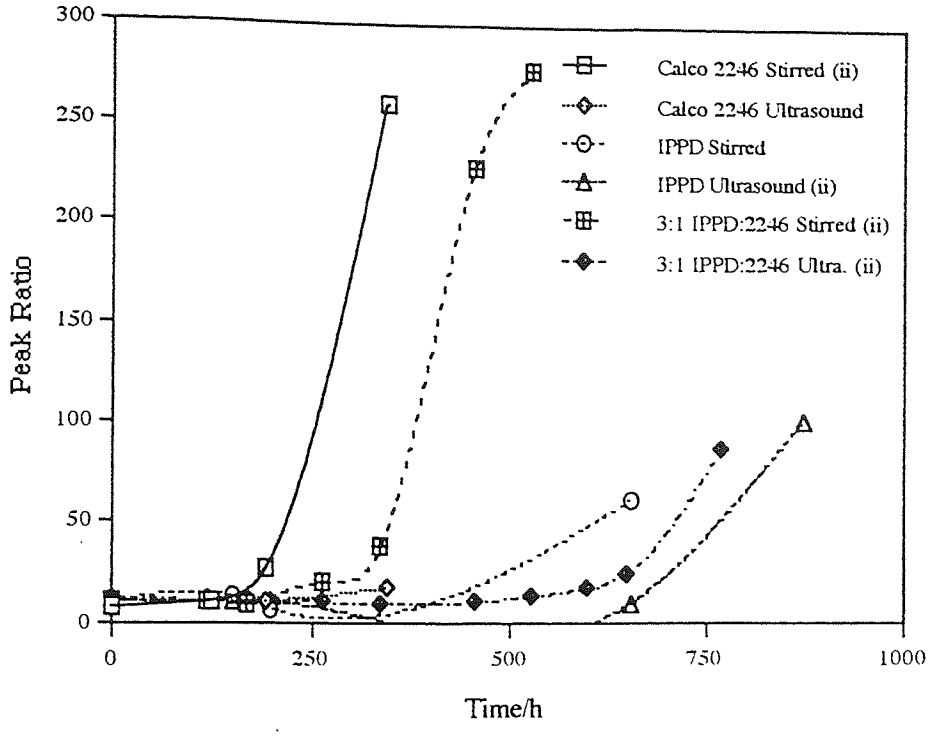


Figure 5-19 Graph comparing increase in OH concentration during the oxidation at 80°C, with time, of thin layer of cured binder samples prepared by using either stirring or ultrasound (ultrasound applied for 120 min.) (Ultra indicates sample prepared by ultrasound (i) & (ii) indicate repeat samples)

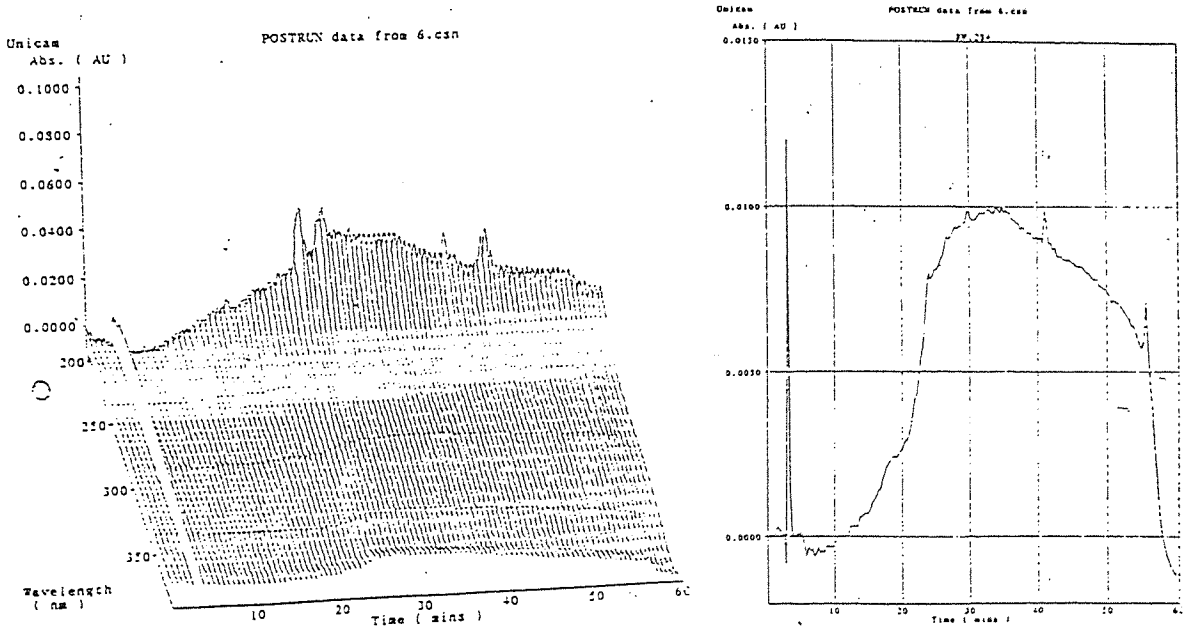


Figure 5-20 Three dimensional and 284 nm wavelength H.P.L.C chromatograms for injection of AcN solvent only.

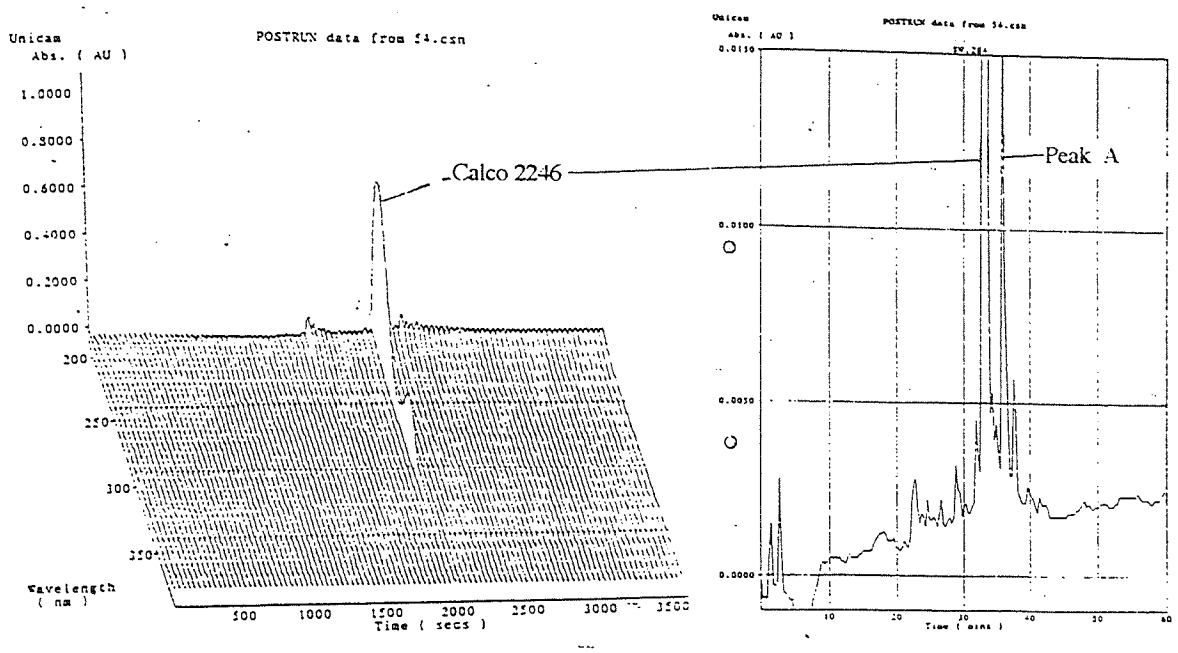


Figure 5-21 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of Calco 2246 standard.

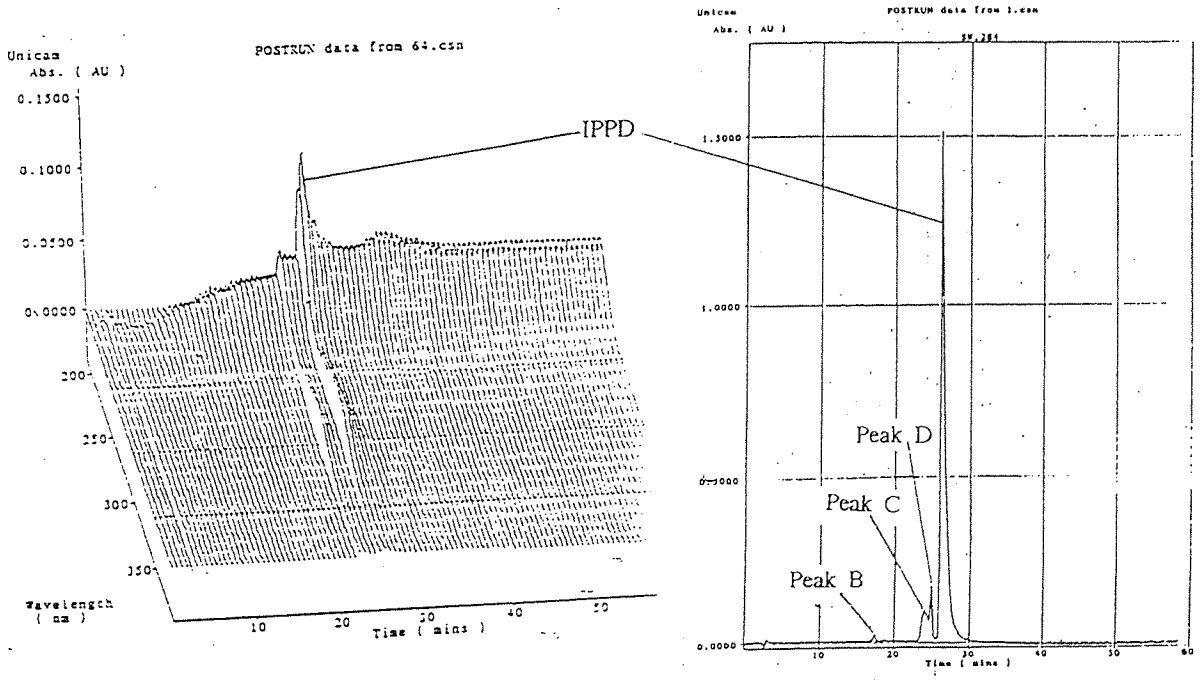


Figure 5-22 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of IPPD standard.

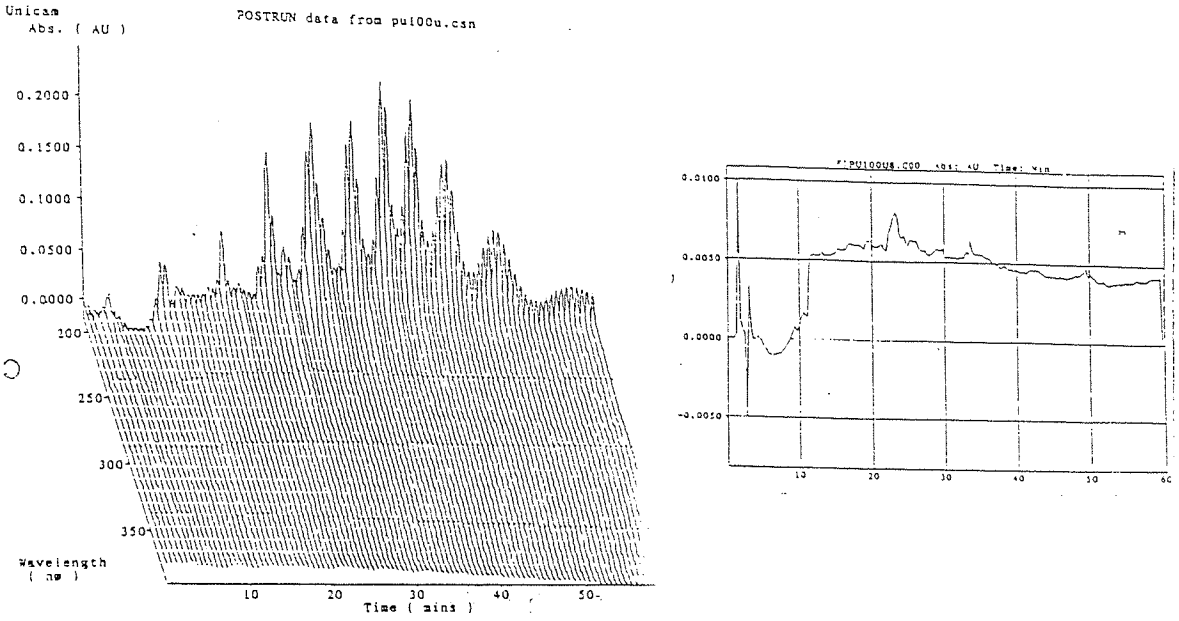


Figure 5-23 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of AcN extract of uncured HTPB.

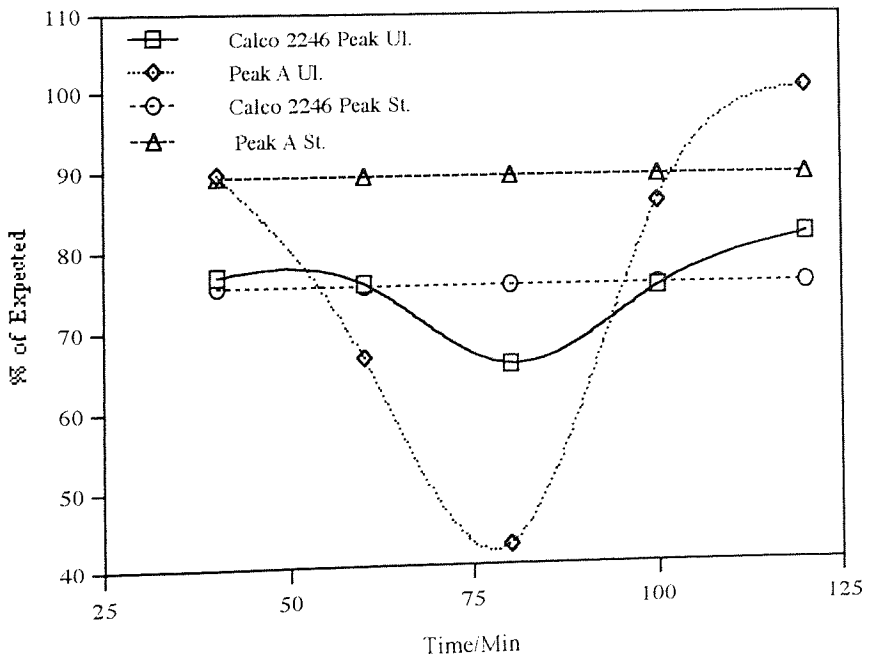
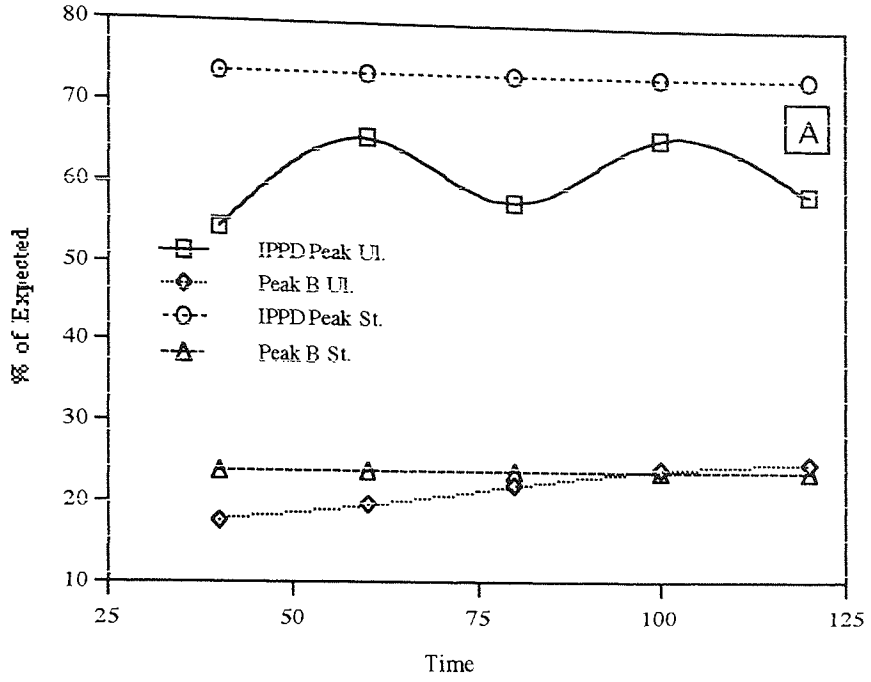


Figure 5-24 Graph showing the variation in percent of expected level of antioxidant extracted versus time of ultrasound for Calco 2246 (0.2% w/w) in uncured HTPB. (Ul. = Sample underwent ultrasound, St. = samples was stirred for which only 1 sample was analysed)



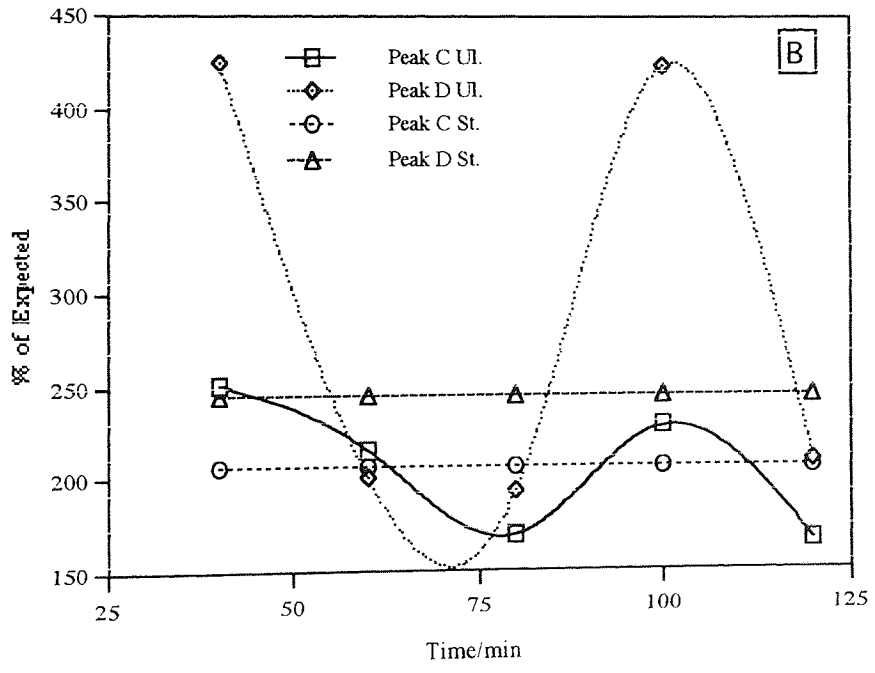
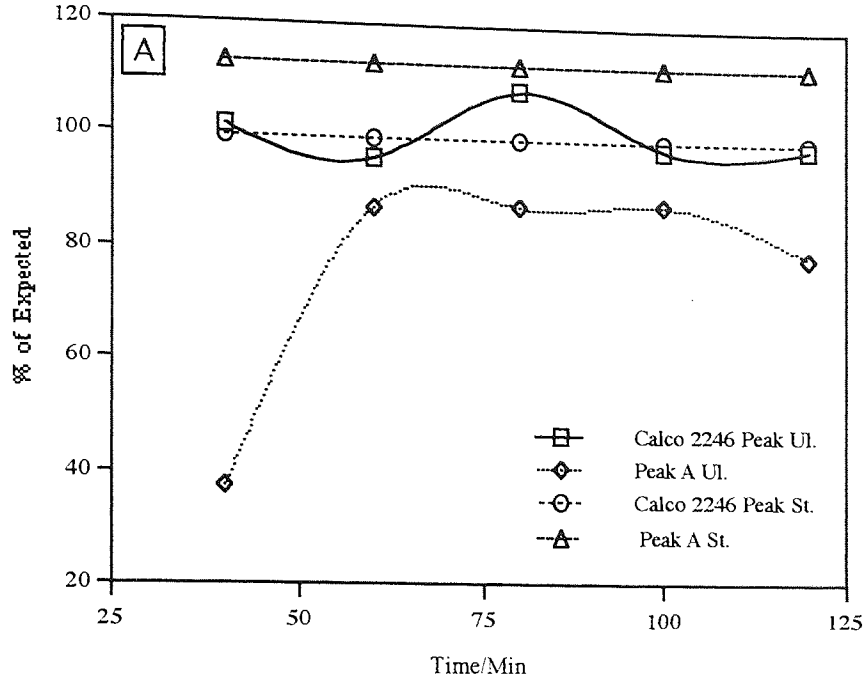


Figure 5-25 A & B Graphs showing the variation percent of expected level of antioxidant extracted versus time of ultrasound for IPPD (0.2% w/w) in uncured HTPB. (Ul. = Sample underwent ultrasound, St. = samples was stirred for which only 1 sample was analysed)



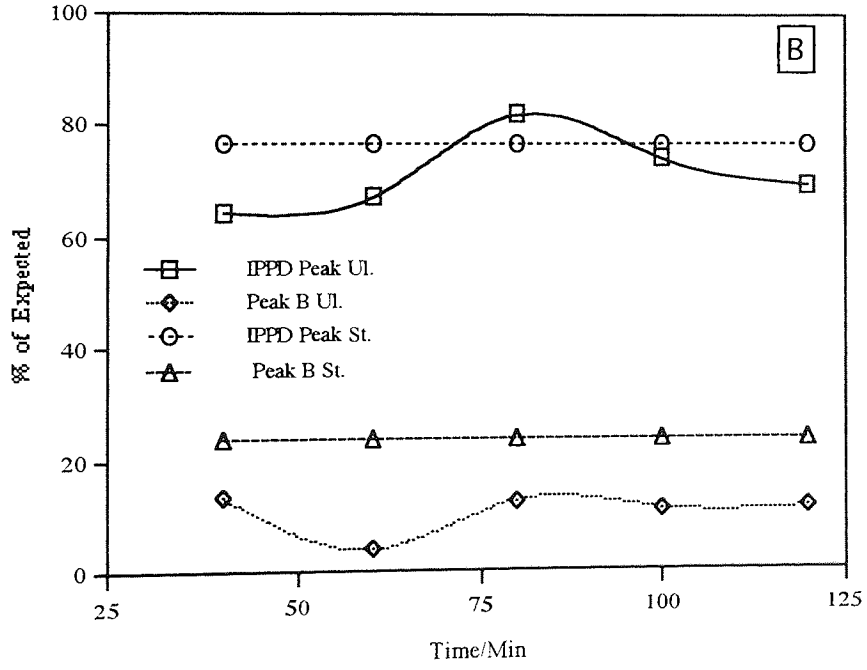


Figure 5-26 A & B For caption see next page

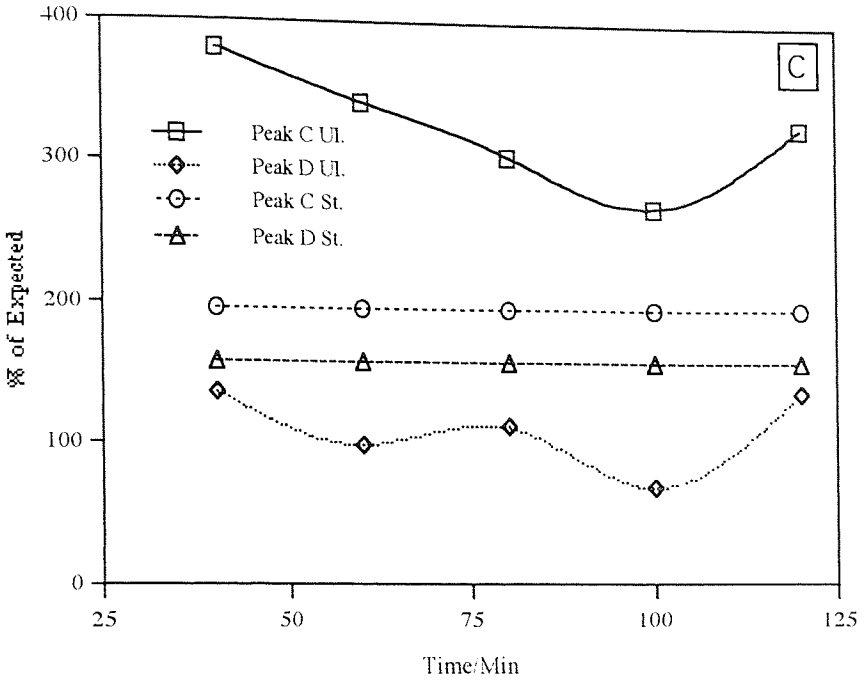


Figure 5-26 A, B & C Graphs showing the variation in percent of expected level of antioxidant extracted versus time of ultrasound for 3:1 IPPD:2246 (0.2% w/w) in uncured HTPB. (Ul. = Sample underwent ultrasound, St. = samples was stirred for which only 1 sample was analysed)

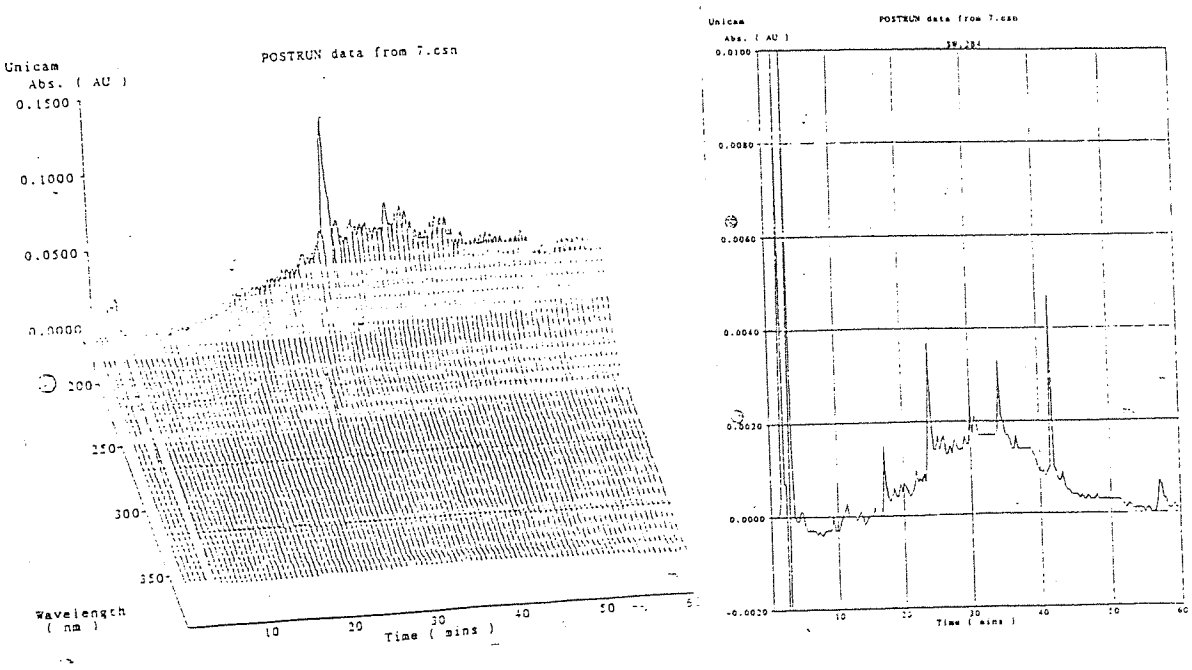


Figure 5-27 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract of cured HTPB.

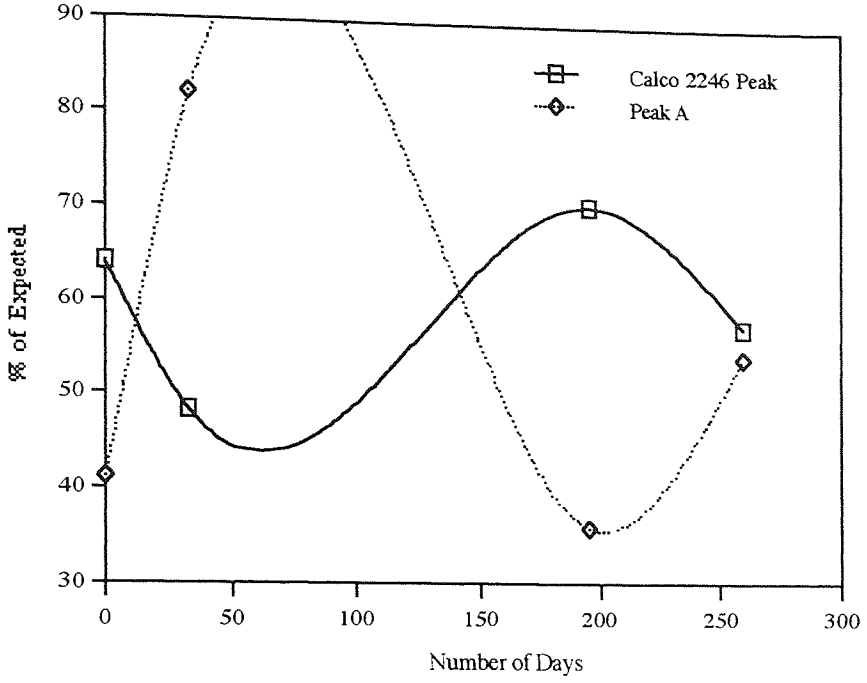


Figure 5-28 Graph showing the variation in % of added level versus time of oven ageing for peaks in binder samples containing Calco 2246 (0.2% w/w)

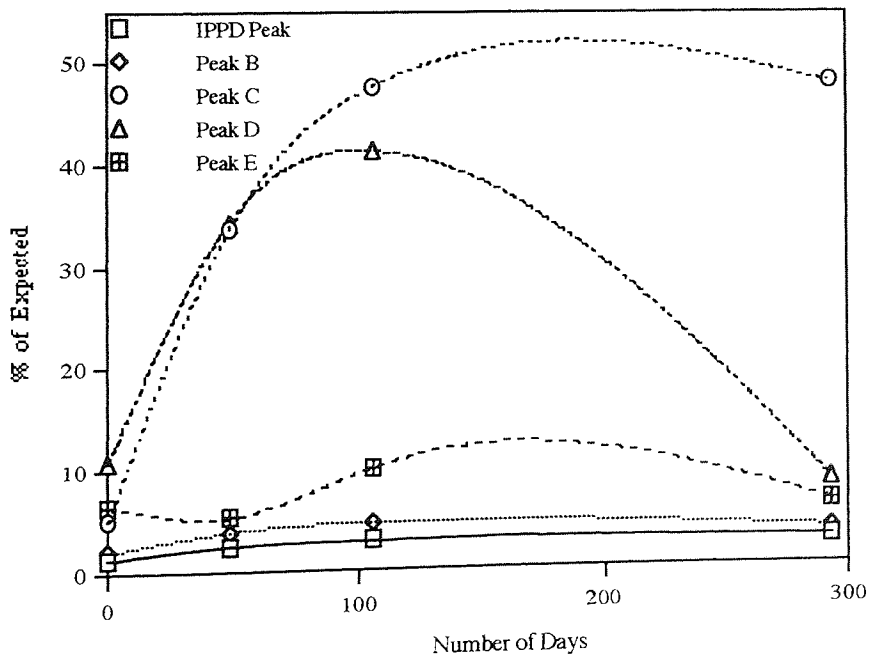
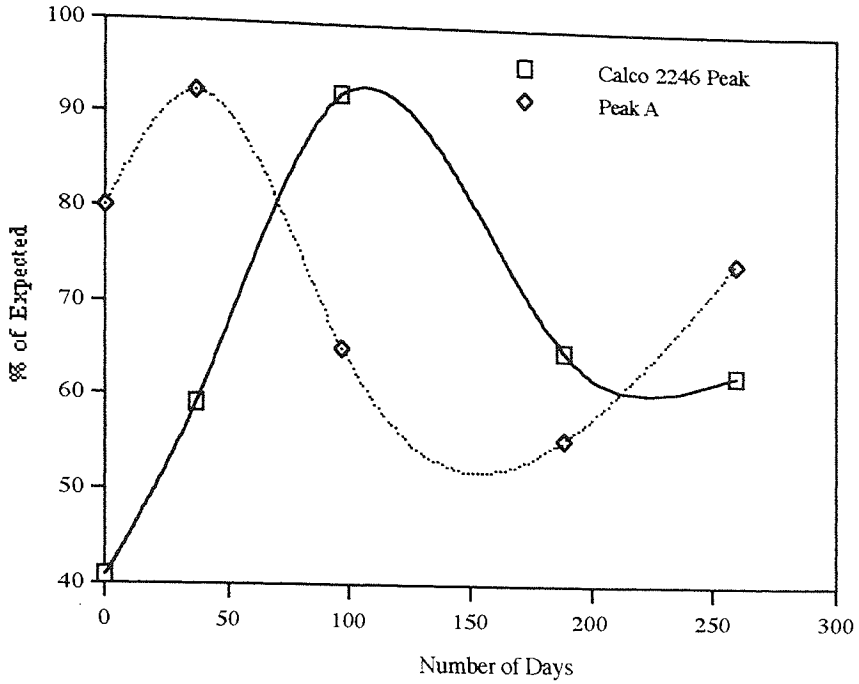


Figure 5-29 Graph showing the variation in % of added level versus time of oven ageing for peaks in binder samples containing IPPD (0.2% w/w)



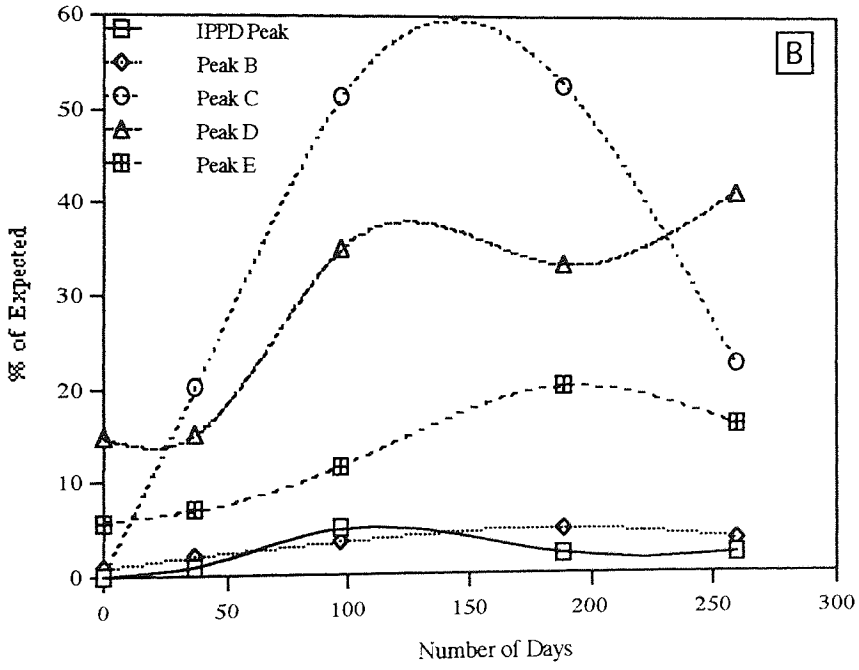
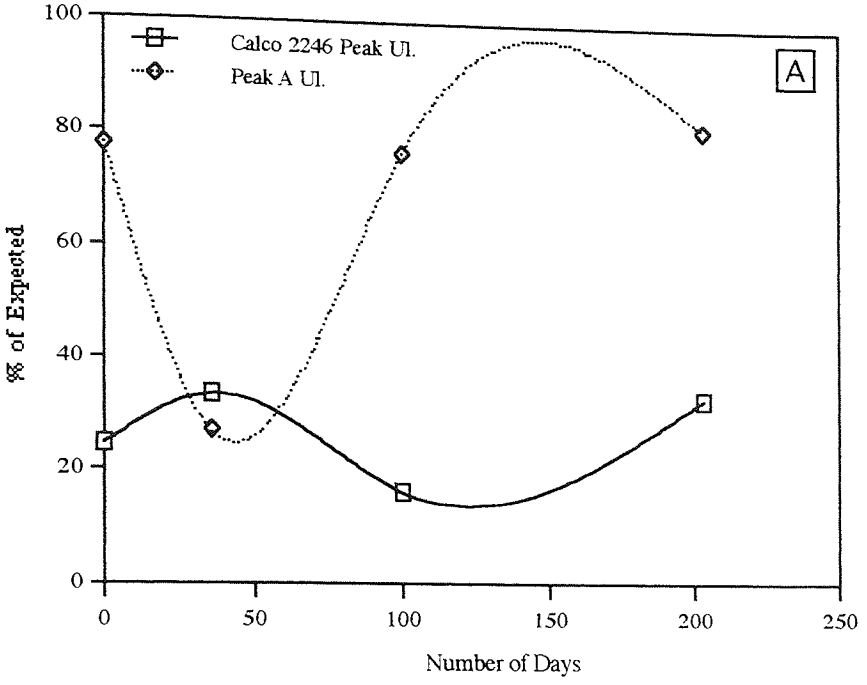


Figure 5-30 A & B Graphs showing the variation in % of added level versus time of oven ageing for peaks in binder samples containing 3:1 IPPD:2246 (0.2% w/w) prepared using ultrasound on 12/10/94. (Sample which showed poor stabilisation)



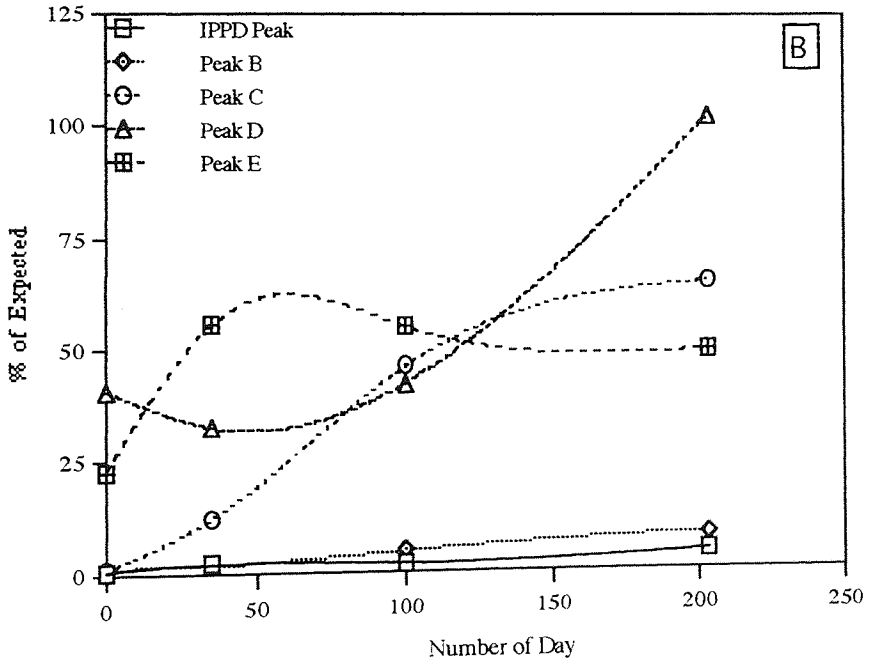


Figure 5-31 A & B Graphs showing the variation in % of added level versus time of oven ageing for peaks in binder samples containing 3:1 IPPD:2246 (0.2% w/w) prepared using ultrasound on 28/7/93. (Sample which showed excellent stabilisation)

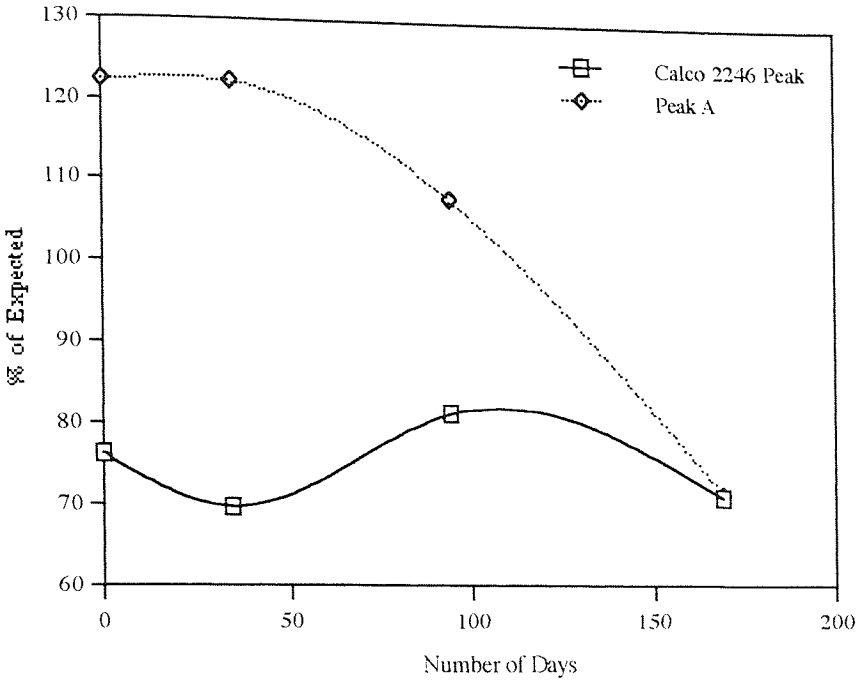


Figure 5-32 Graph showing the variation in % of added level versus time of oven ageing for peaks in binder samples containing 3:1 2246:DLTP (0.2% w/w).

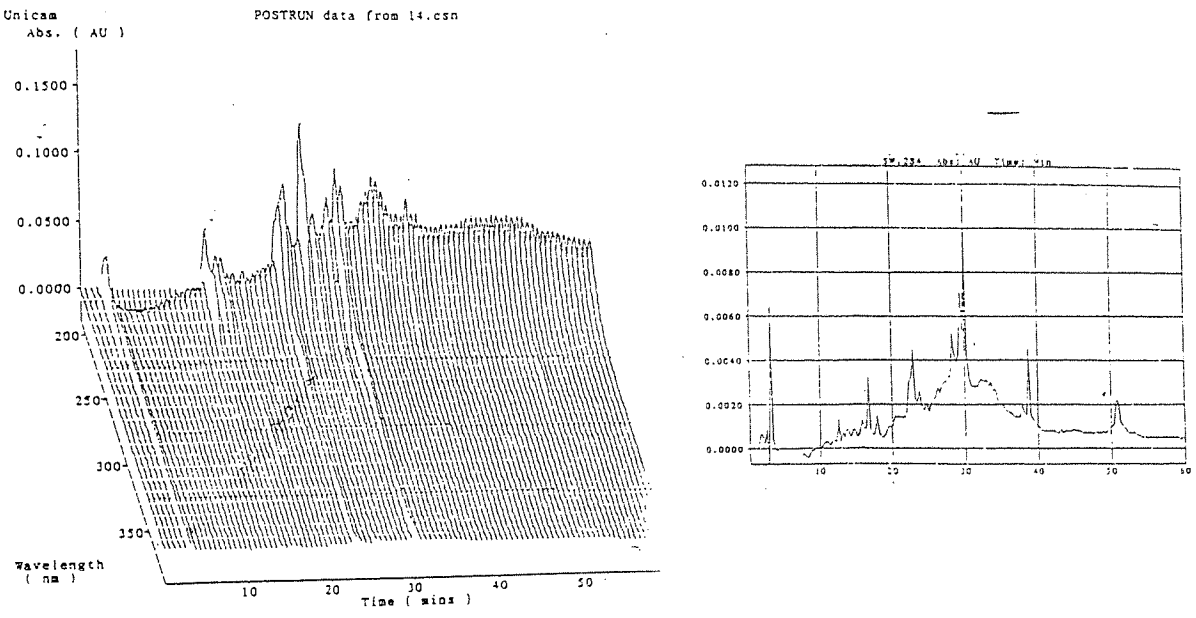


Figure 5-33 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of IPPD-NO$^{\cdot}$.

CHAPTER SIX

6 CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK.

6.1 Conclusions

1. Synergistic antioxidant combinations which perform more efficiently than the current commercial antioxidant Calco 2246 can be prepared. Of these the most promising was the heterosynergistic mix of the chain breaking donor antioxidant Calco 2246 with the peroxide decomposer DLTP in a 3:1 ratio. The DLTP acted as the main antioxidant with Calco 2246 removing prooxidant species produced during early stages DLTP activity.

2. γ-Tocopherol alone was found to be as effective as the synergistic combinations and more effective than any other single antioxidant including α-tocopherol. This is due to its lower steric hindrance and novel transformation products.

3. Phenolic antioxidants did not react with the cross-linking agent during the curing reaction. Conversely the more nucleophilic amine IPPD did react and at a higher rate than the reaction between the cross-linking agent and hydroxyterminated polybutadiene, potentially affecting both the cross-link density and the action of the antioxidant. Therefore the use of amines should be avoided. Autosynergistic antioxidants containing amines and sulfur containing antioxidants can also react with the cross-linking agent but not to the same extent as IPPD.

4. The effectiveness of an antioxidant can be altered depending on the method of sample preparation. The use of ultrasound was shown to double the effectiveness of the phenol Calco 2246 and increase by $1/3^{rd}$ the effectiveness of IPPD. The effect of ultrasound on samples containing a 3:1 mix of the two antioxidants is variable but may be able to cause an exceptionally efficient homosynergistic mechanism to form. The mechanism by which this extra

performance is achieved is unclear but more efficient mixing or transformation of the antioxidant is possible.

5. In the case of polybutadiene samples stabilised by some single moiety antioxidants, but not all, a relationship between the results from dynamic thermal analysis and oven ageing results was found. Conversely for potentially synergistic antioxidant mixes no relationship existed. Therefore the use of thermal analysis as a rapid method to predict antioxidant effectiveness would not be recommended. A potentially more universal method of accelerated testing is the analysis of thin layer samples by infra red spectroscopy.

6.2 Suggestions for Further Work

It will always be possible to test a wider range of antioxidants and mixes of antioxidants.

This work indicates that analysis of further antioxidants should be concentrated on mixes of unhindered phenolic antioxidants with sulfur containing peroxide decomposers such as DLTP. The readily oxidisable polybutadiene substrate requires the use of a higher level of phenolic than sulfur containing antioxidant to prevent early initiation of oxidation by the prooxidant species produced by the sulfur containing compounds.

The phenol that should first be investigated in combination with DLTP is the very effective γ-tocopherol. It may be that the mix of γ-tocopherol with DLTP may show no improvement over γ-tocopherol alone which was very efficient. In the mix between Calco 2246 and DLTP the DLTP performs the majority of the stabilisation, but with γ-tocopherol both will be able to perform as main antioxidants potentially improving overall performance. It would be also an advantage to use the infra-red analysis of thin layer to reduce the time required for these analyses.

Further investigation into the effect of ultrasound on stabilisation efficiency is likely to show benefits. It was shown in this work that the use of ultrasound could improve the efficiency of a number of antioxidants and potentially trigger the formation of a very efficient homosynergistic mechanism. The actual mechanism by which ultrasound causes the enhancement of antioxidants is still unclear. Investigation into whether the effect is universal to antioxidant systems such as γ-tocopherol and γ-tocopherol:DLTP would be very interesting. If similar performance improvements as were seen for the samples analysed in this work were seen in these already efficient samples the ageing resistance of the binder could be improved by a further 100 %.

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APPENDIX 1

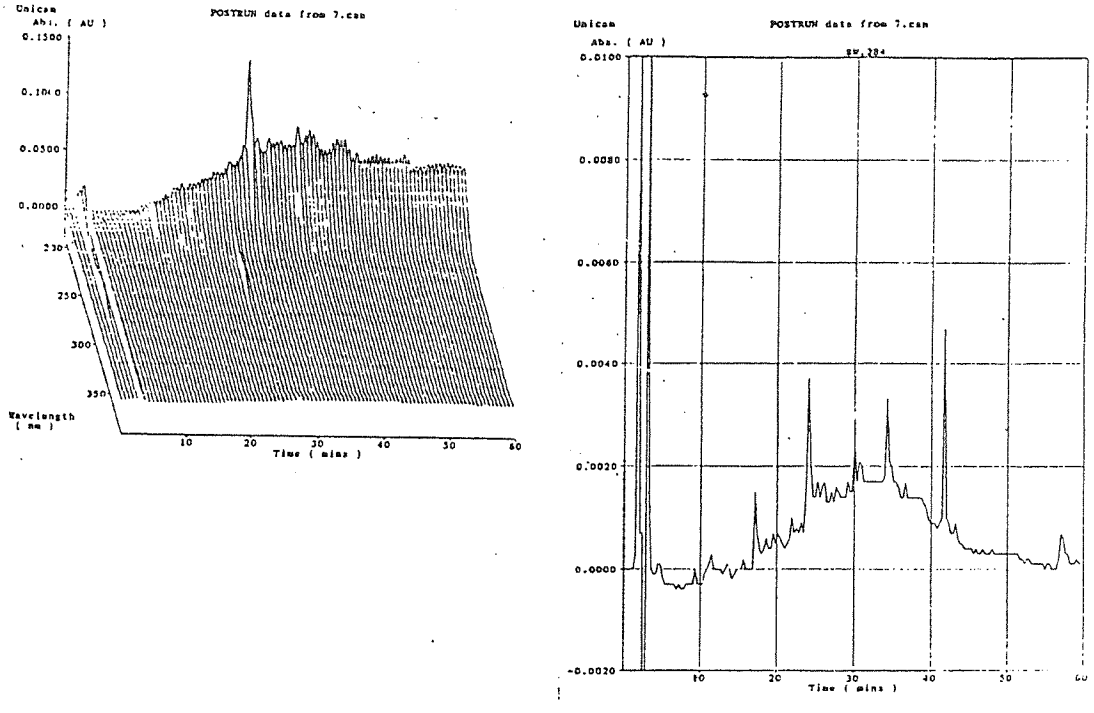

Figure A1-1 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured pure HTPB prepared on 5/10/94 aged for 7 days at 60°C.

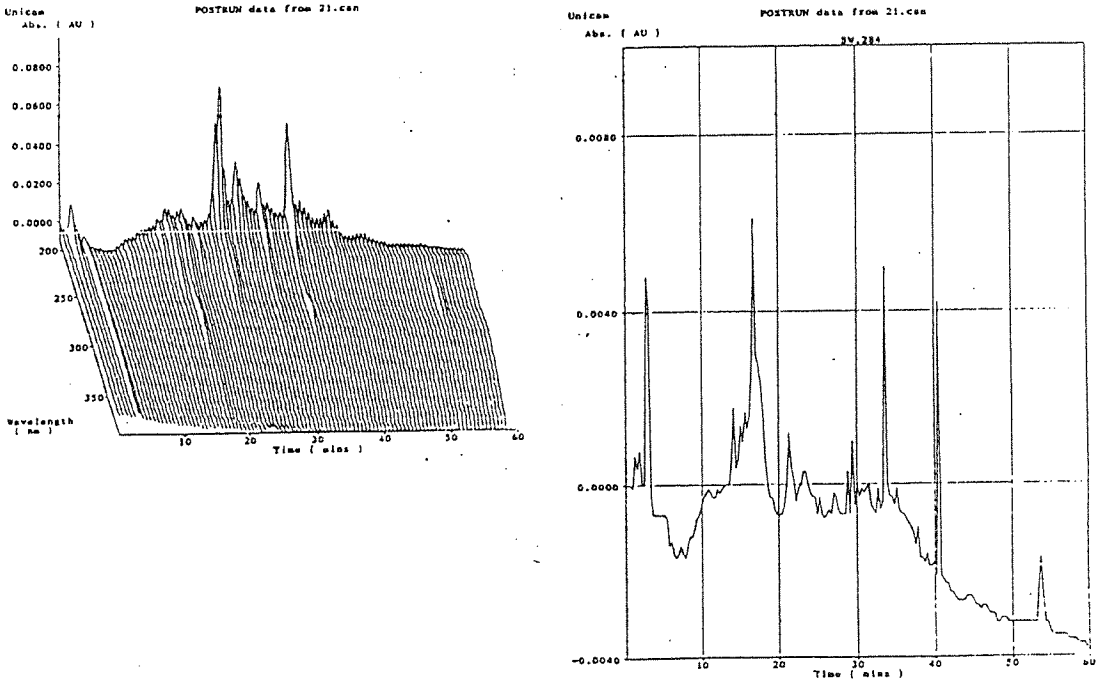

Figure A1-2 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured pure HTPB prepared on 5/10/94 aged for 41 days at 60°C.

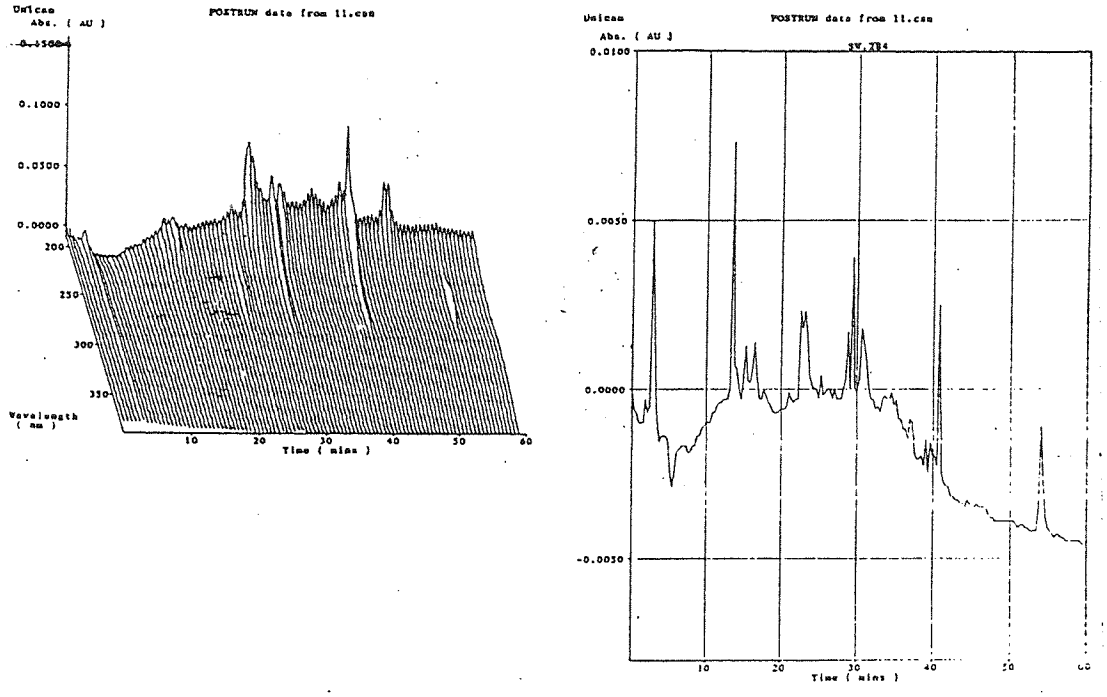

Figure A1-3 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured pure HTPB prepared on 5/10/94 aged for 111 days at 60°C.

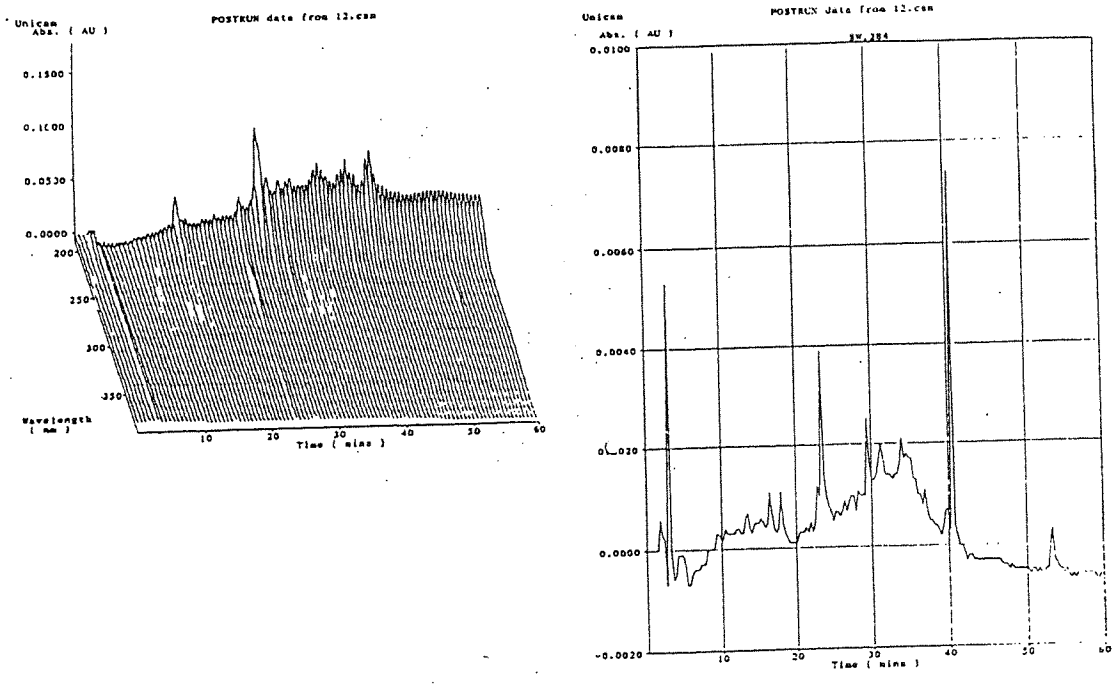

Figure A1-4 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured pure HTPB prepared on 5/10/94 aged for 203 days at 60°C.

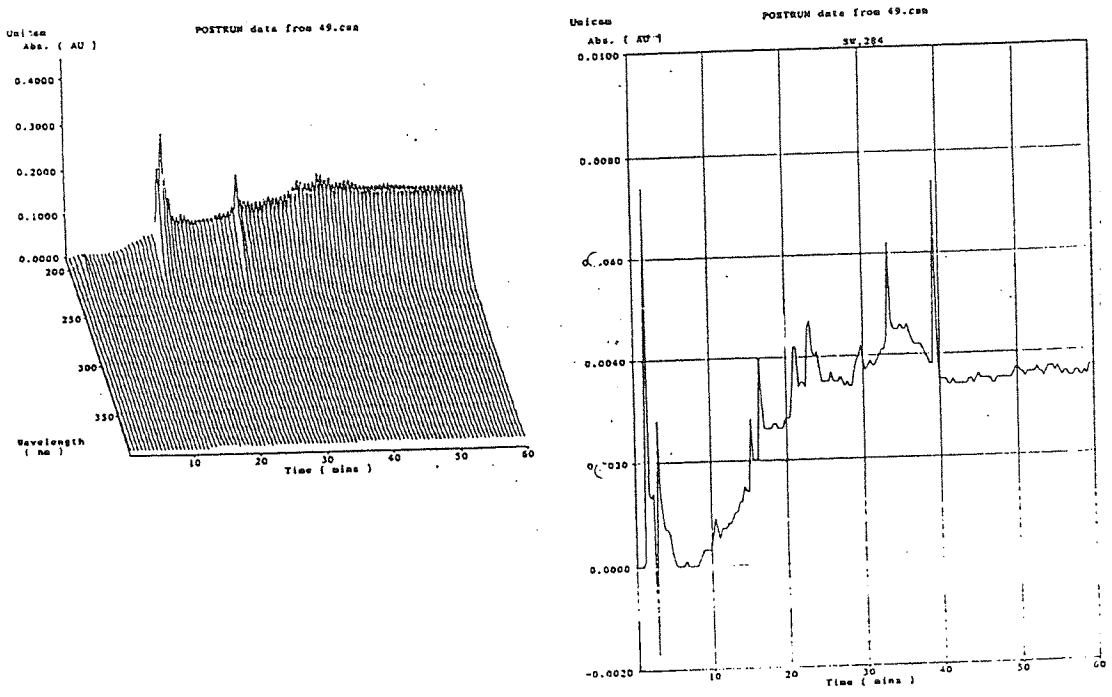

Figure A1-5 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured pure HTPB prepared on 5/10/94 aged for 267 days at 60°C.

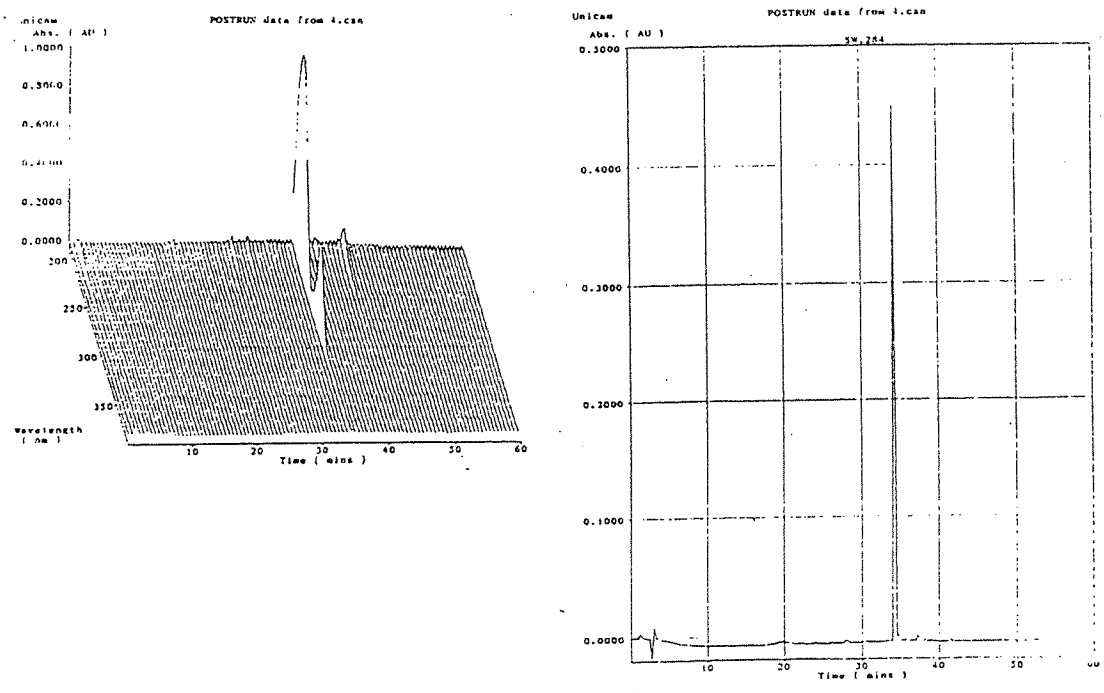

Figure A1-6 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% Calco 2246 prepared on 5/10/94 aged for 7 days at 60°C.

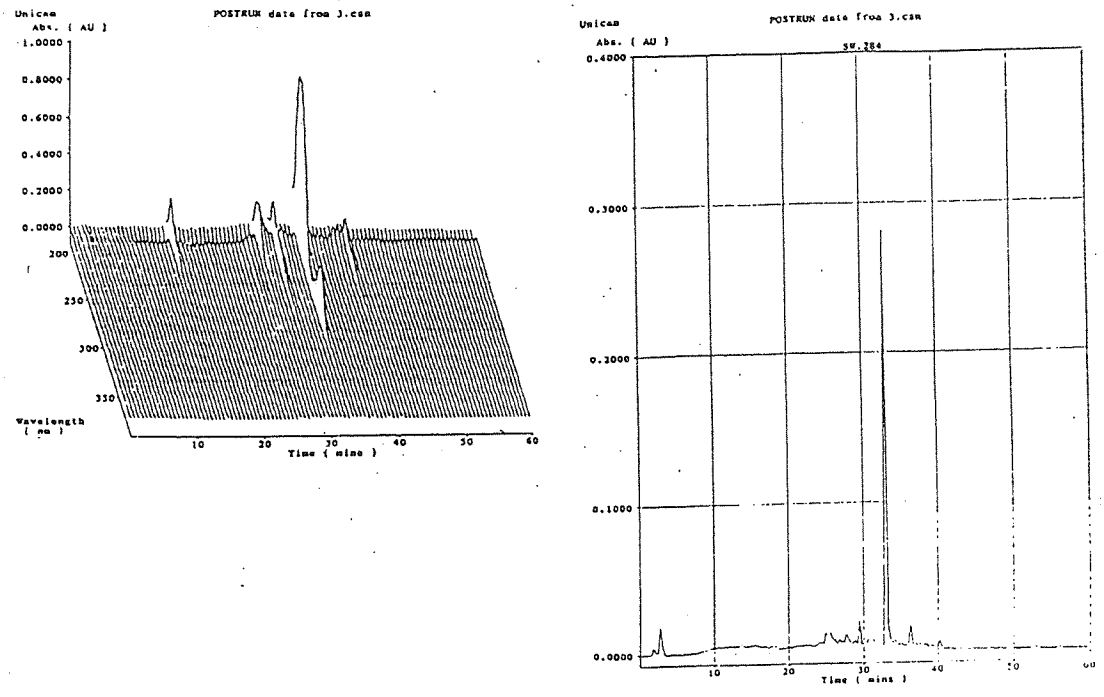

Figure A1-7 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% Calco 2246 prepared on 5/10/94 aged for 41 days at 60°C.

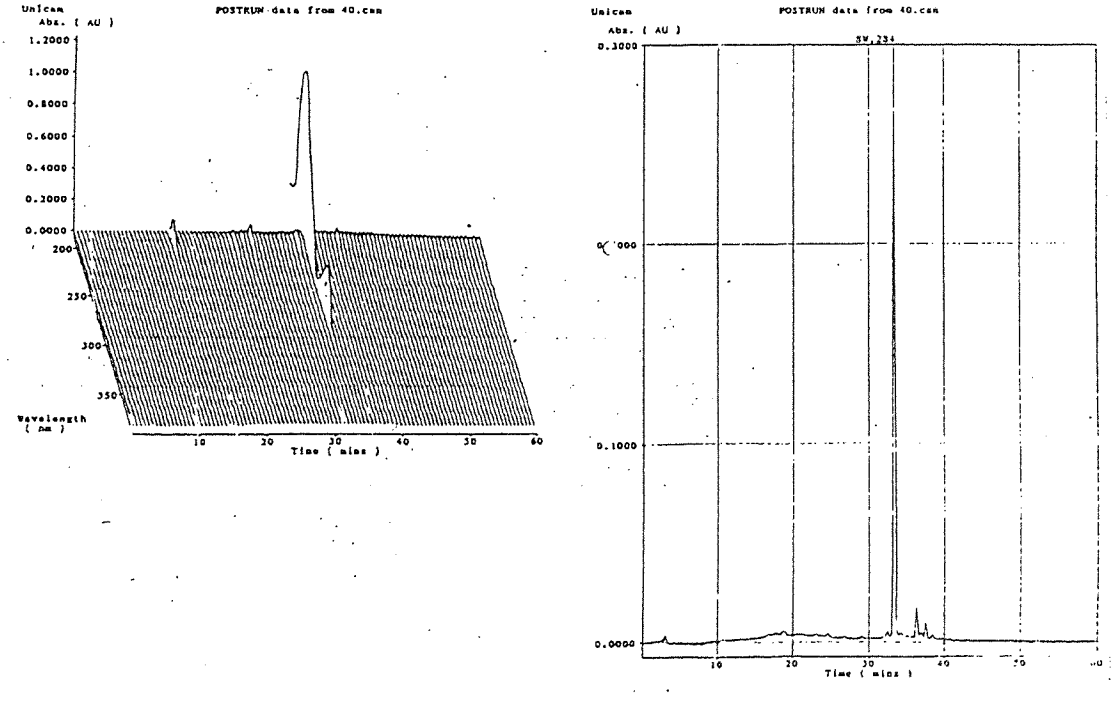

Figure A1-8 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% Calco 2246 prepared on 5/10/94 aged for 203 days at 60°C.

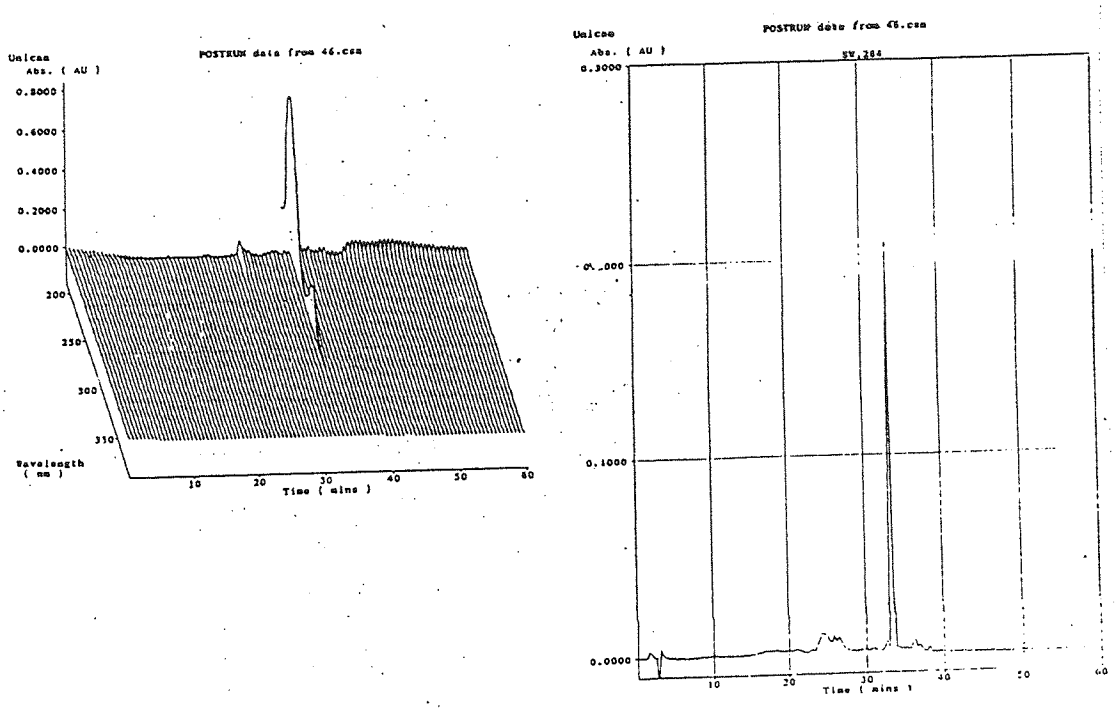

Figure A1-9 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% Calco 2246 prepared on 5/10/94 aged for 267 days at 60°C.

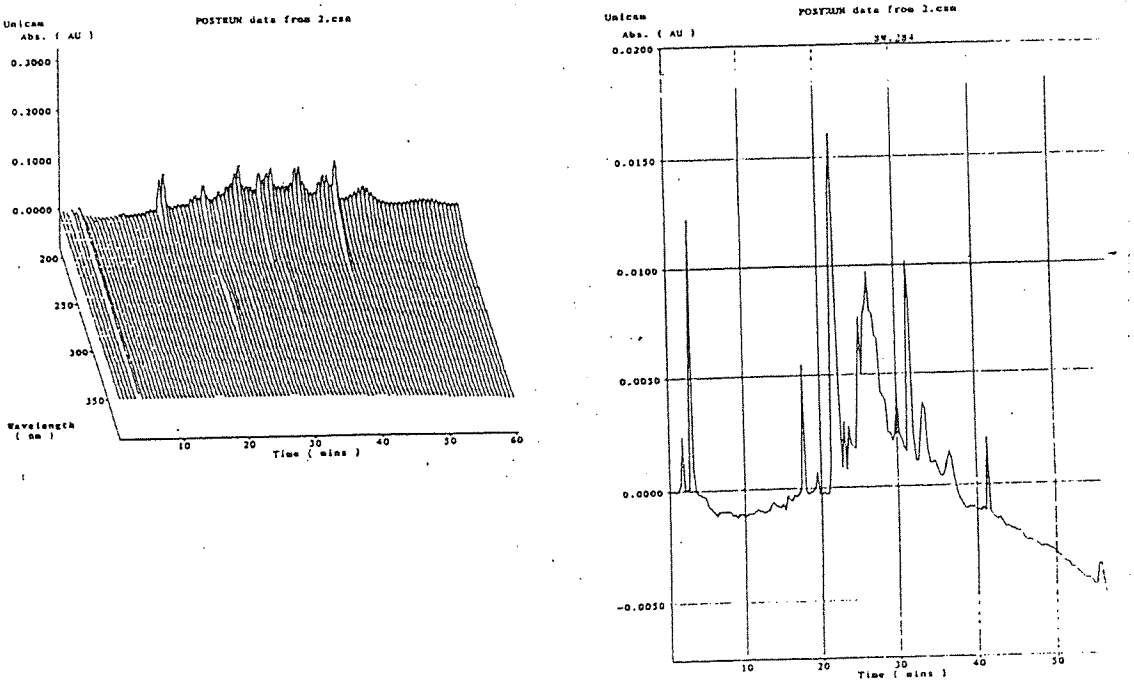

Figure A1-10 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% IPPD prepared on 7/12/94 aged for 7 days at 60°C.

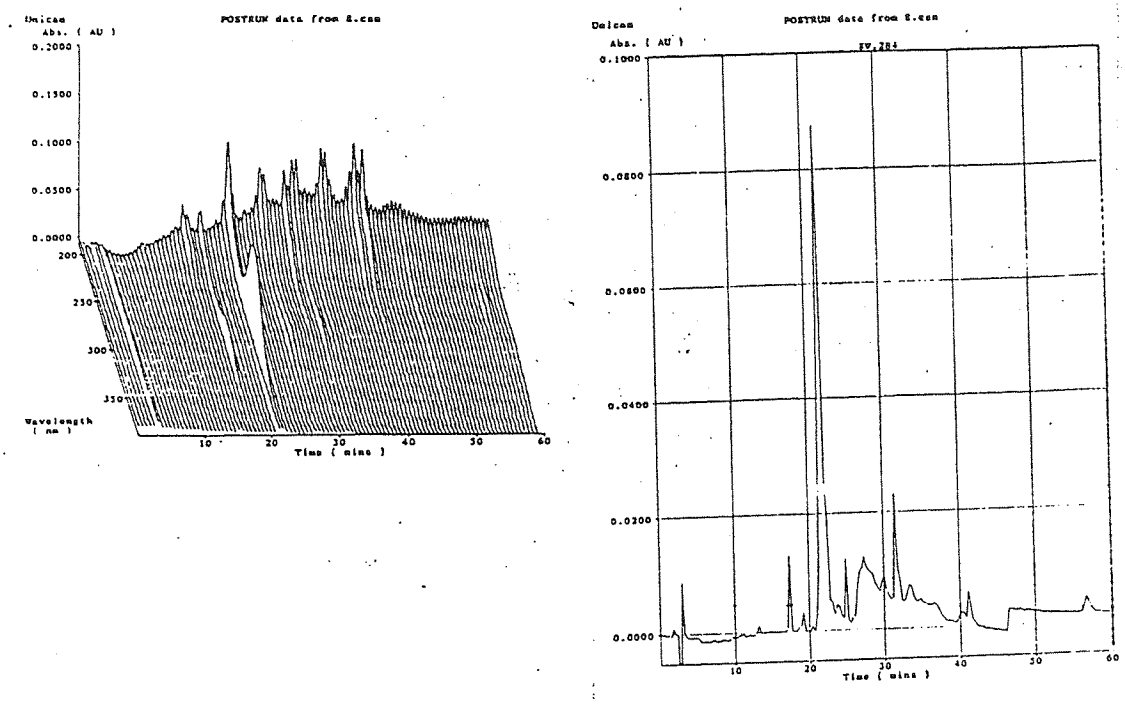

Figure A1-11 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% IPPD prepared on 7/12/94 aged for 44 days at 60°C.

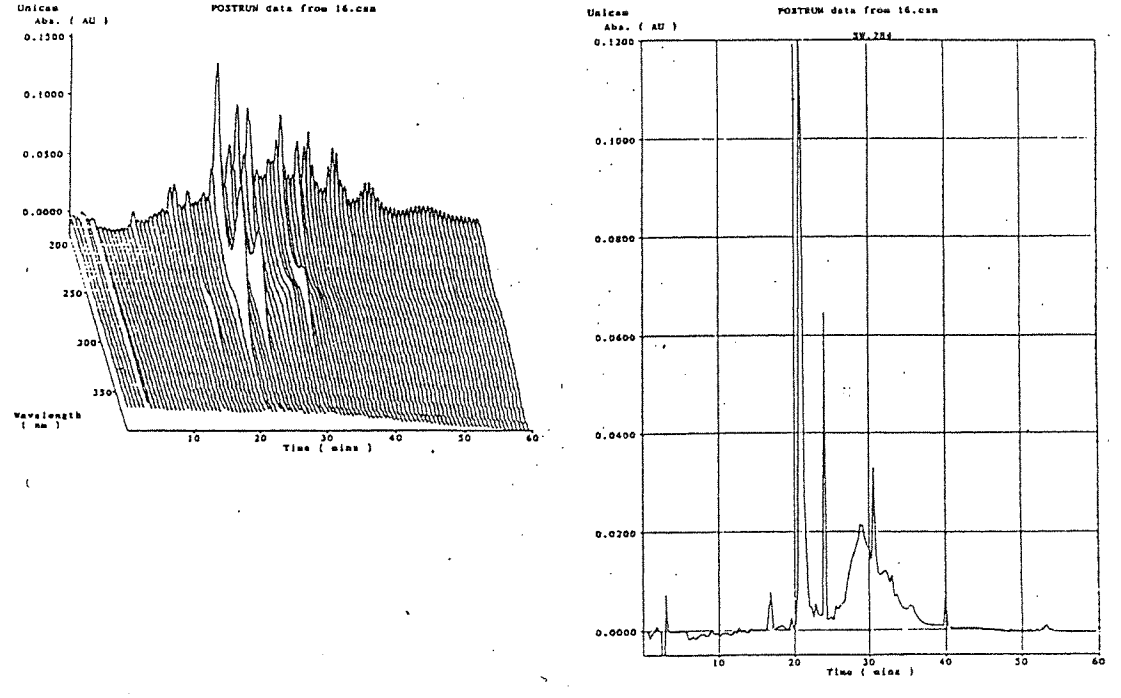

Figure A1-12 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% IPPD prepared on 7/12/94 aged for 105 days at 60°C.

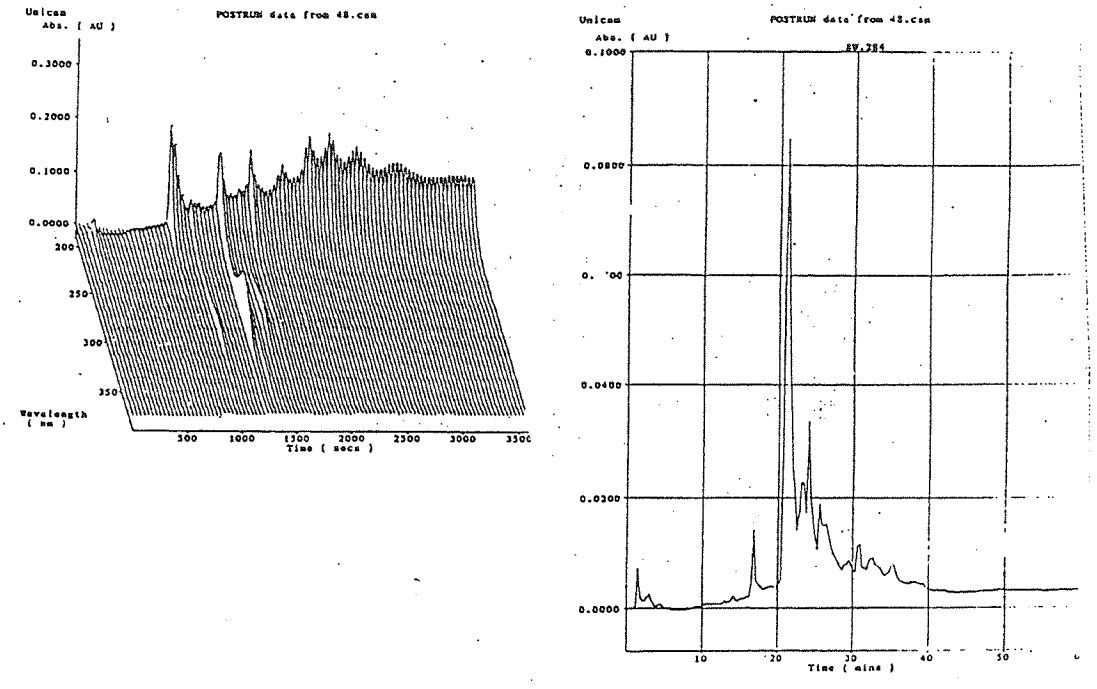

Figure A1-13 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% IPPD prepared on 7/12/94 aged for 204 days at 60°C.

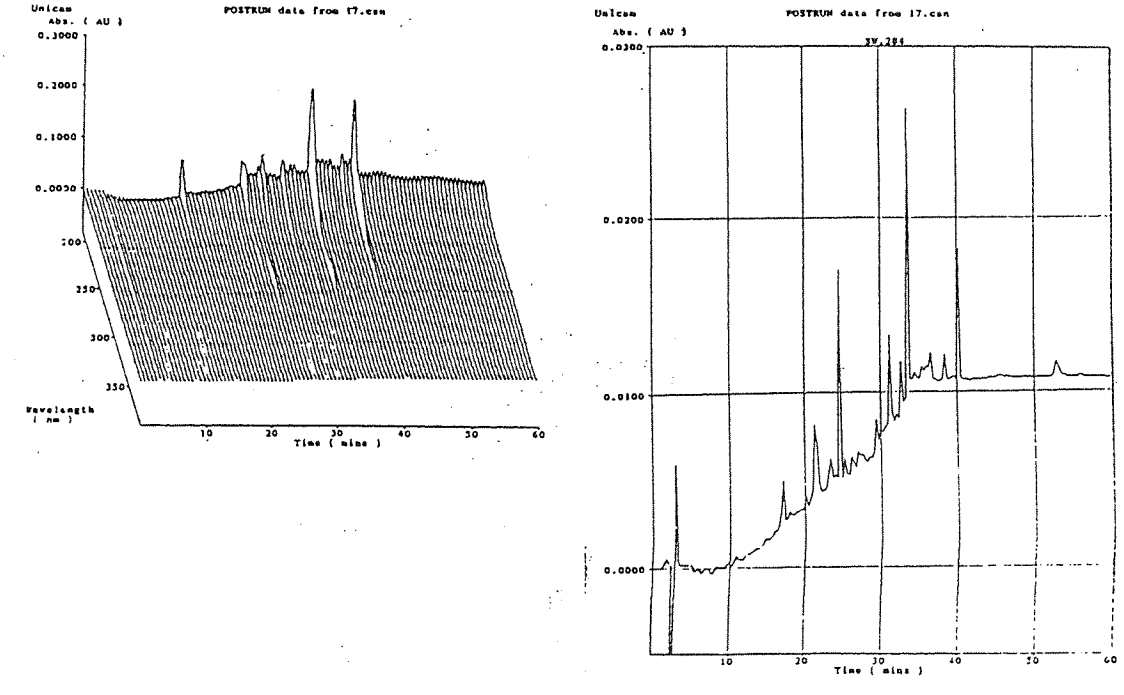

Figure A1-14 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% 3:1 IPPD:2246 prepared on 12/10/94 which showed poor stabilisation aged for 7 days at 60°C.

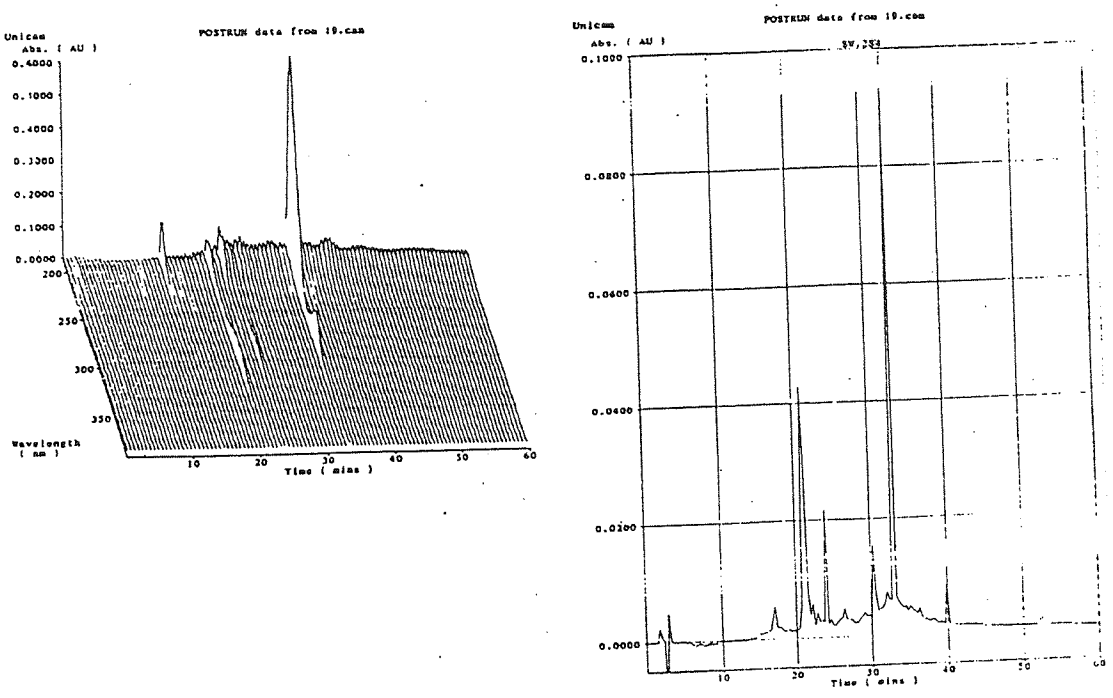

Figure A1-15 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% 3:1 IPPD:2246 prepared on 12/10/94 which showed poor stabilisation aged for 44 days at 60°C.

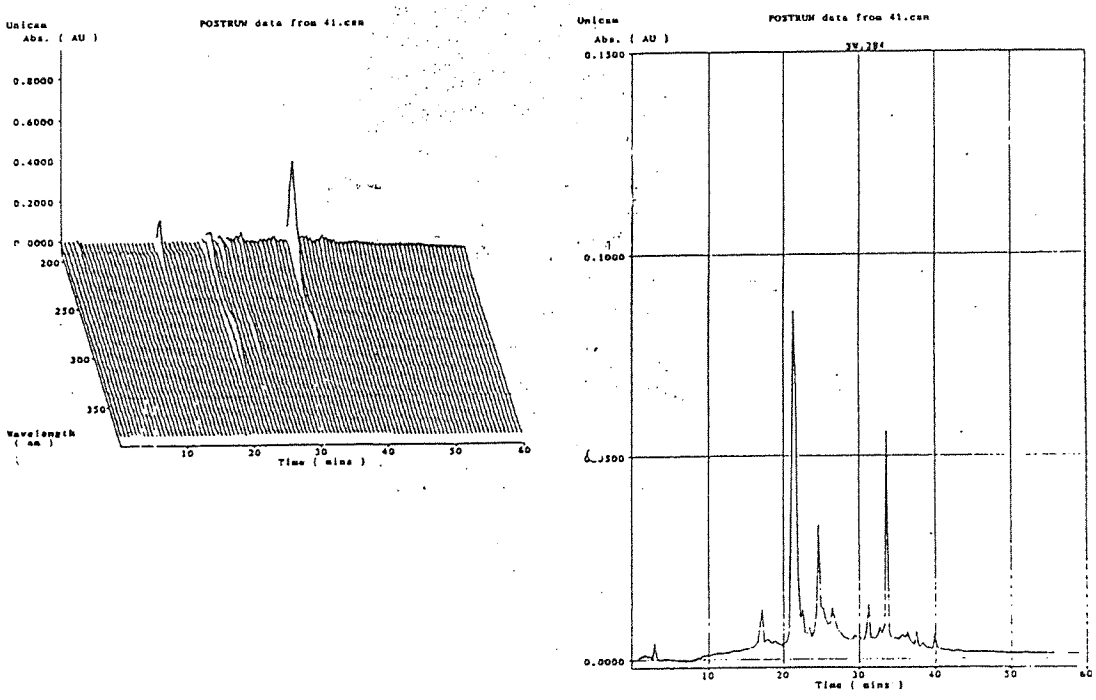

Figure A1-16 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% 3:1 IPPD:2246 prepared on 12/10/94 which showed poor stabilisation aged for 104 days at 60°C.

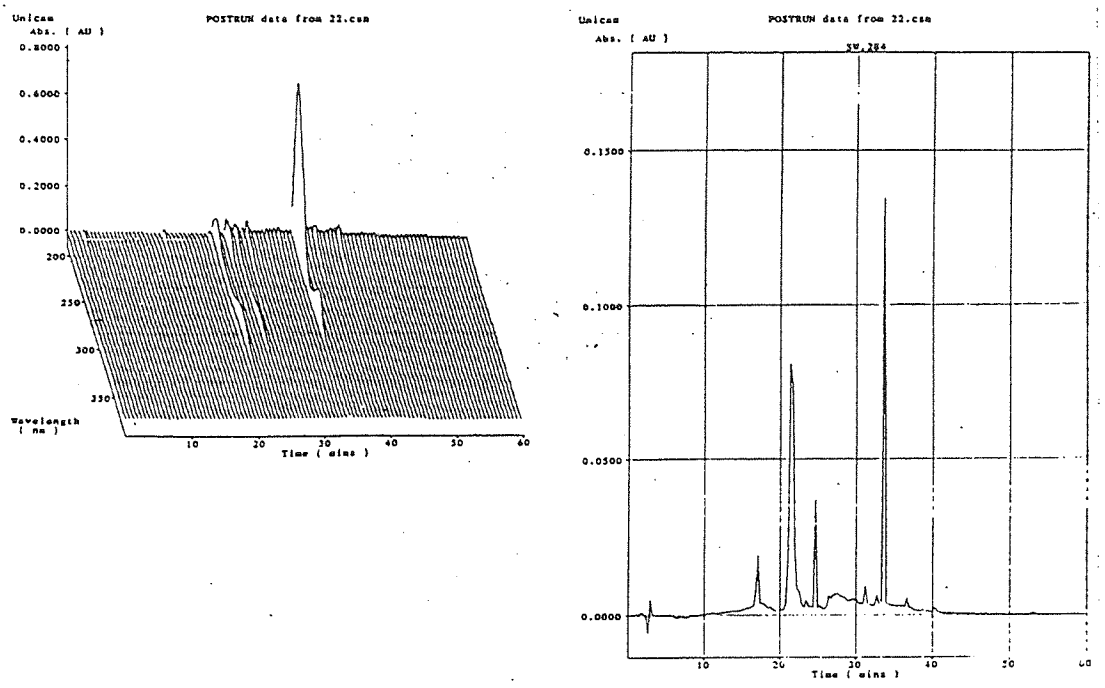

Figure A1-17 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% 3:1 IPPD:2246 prepared on 12/10/94 which showed poor stabilisation aged for 196 days at 60°C.

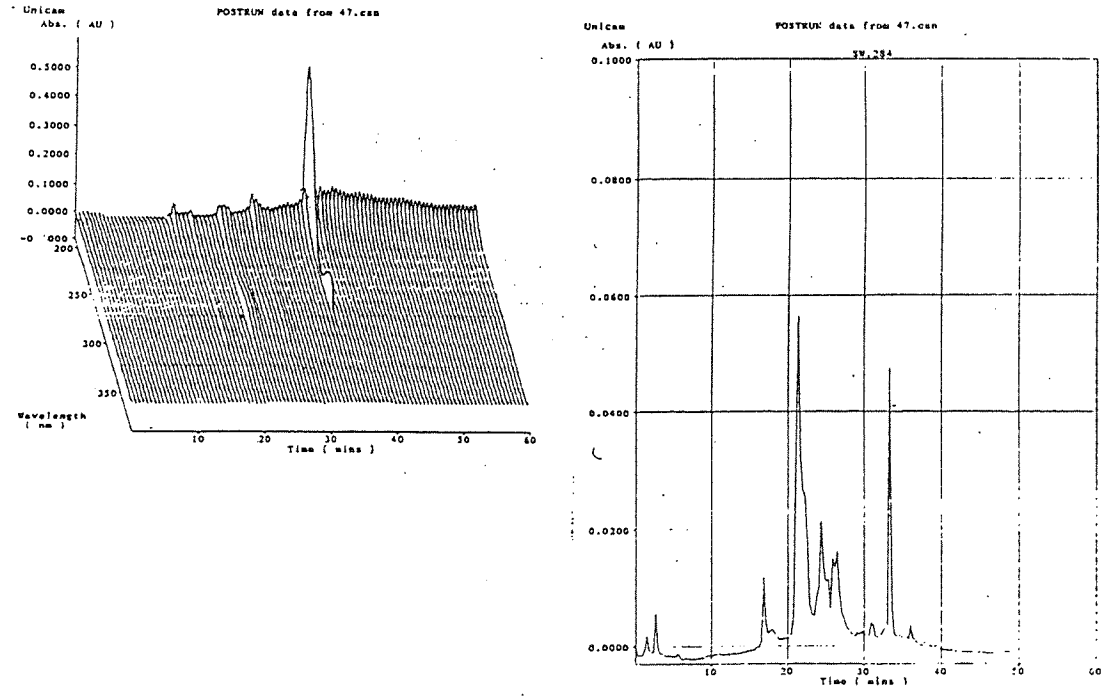

Figure A1-18 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% 3:1 IPPD:2246 prepared on 12/10/94 which showed poor stabilisation aged for 266 days at 60°C.

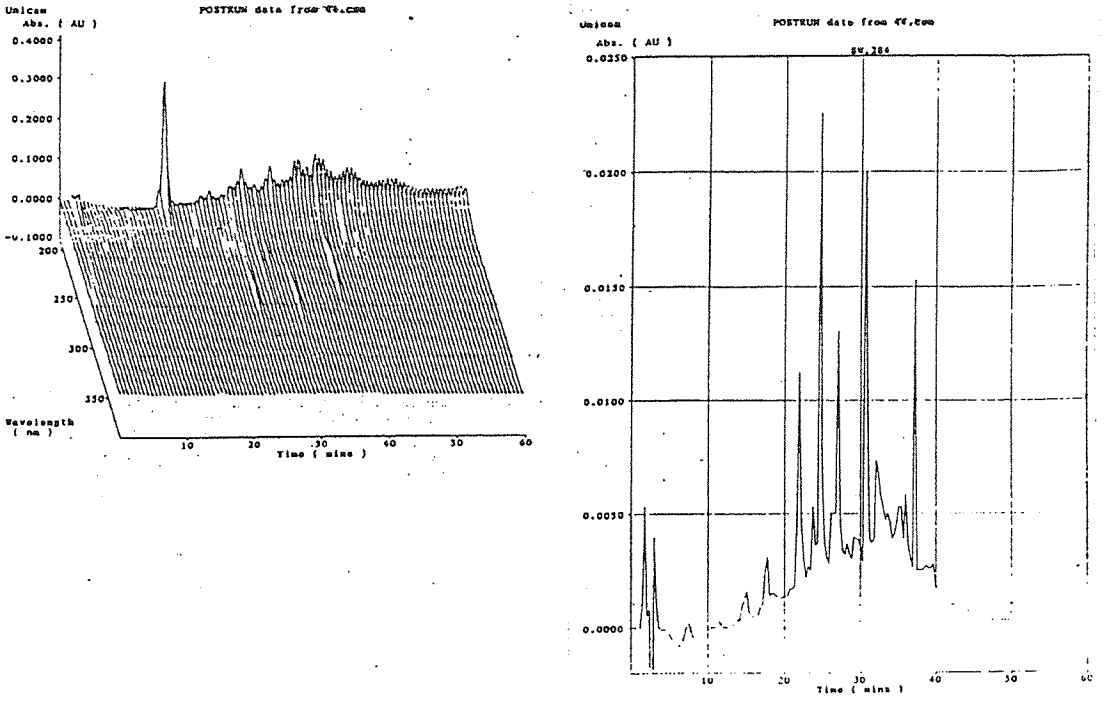

Figure A1-19 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% 3:1 IPPD:2246 prepared on 28/7/93 which showed excellent stabilisation aged for 7 days at 60°C.

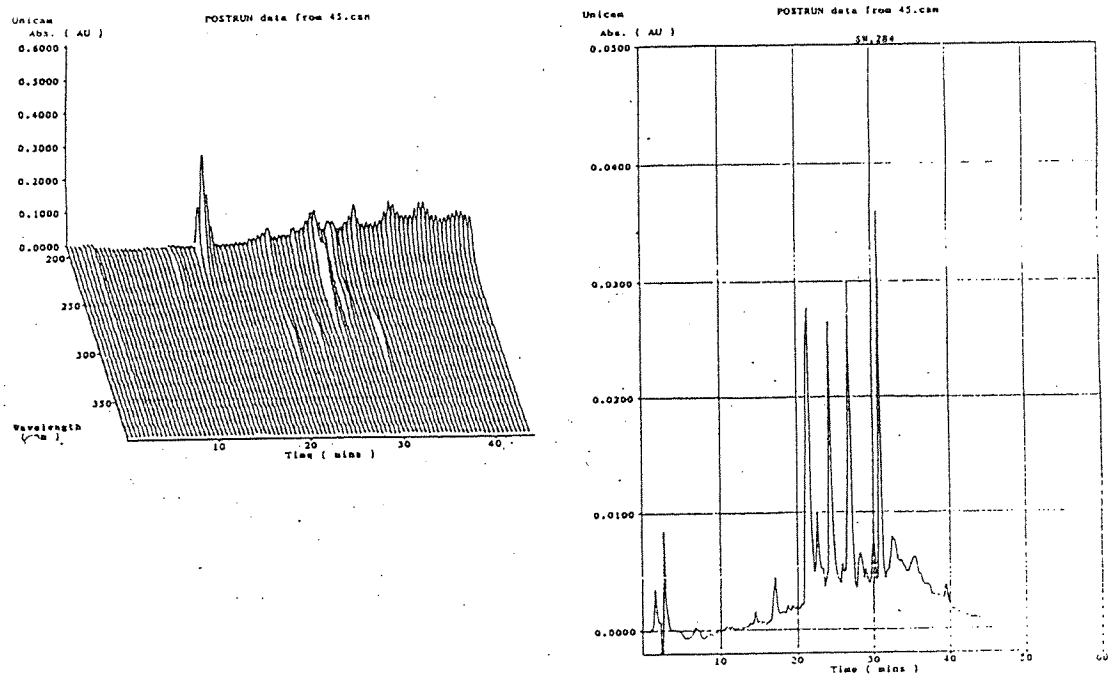

Figure A1-20 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% 3:1 IPPD:2246 prepared on 28/7/93 which showed excellent stabilisation aged for 42 days at 60°C.

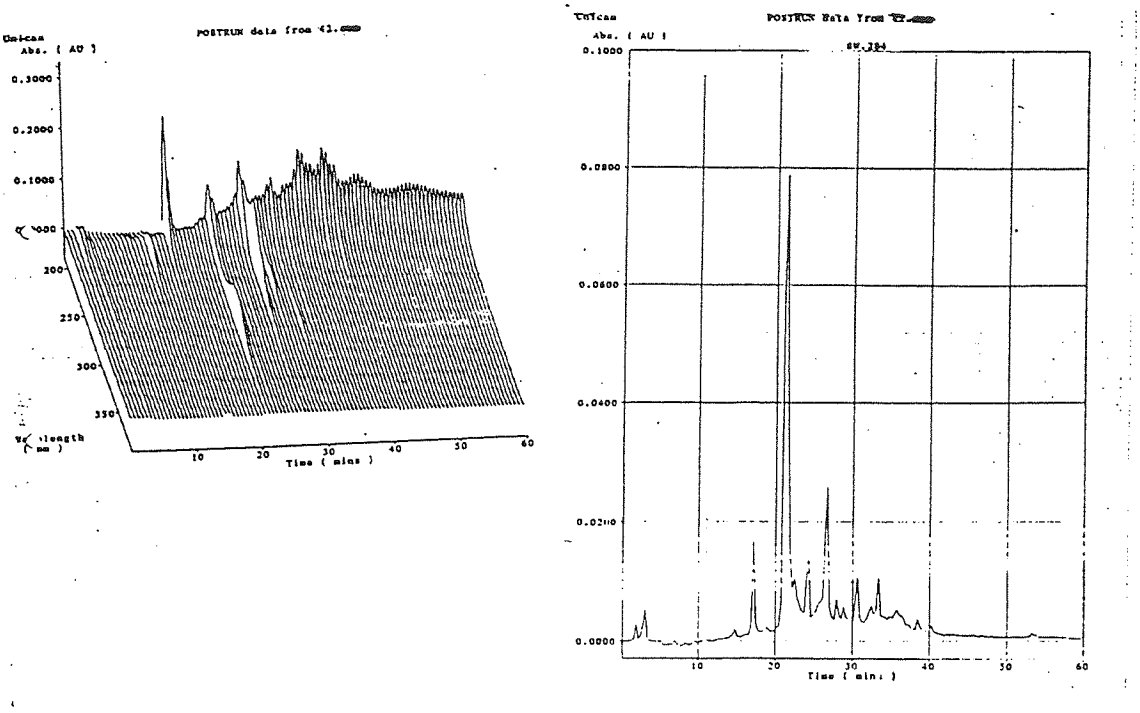

Figure A1-21 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% 3:1 IPPD:2246 prepared on 28/7/93 which showed excellent stabilisation aged for 101 days at 60°C.

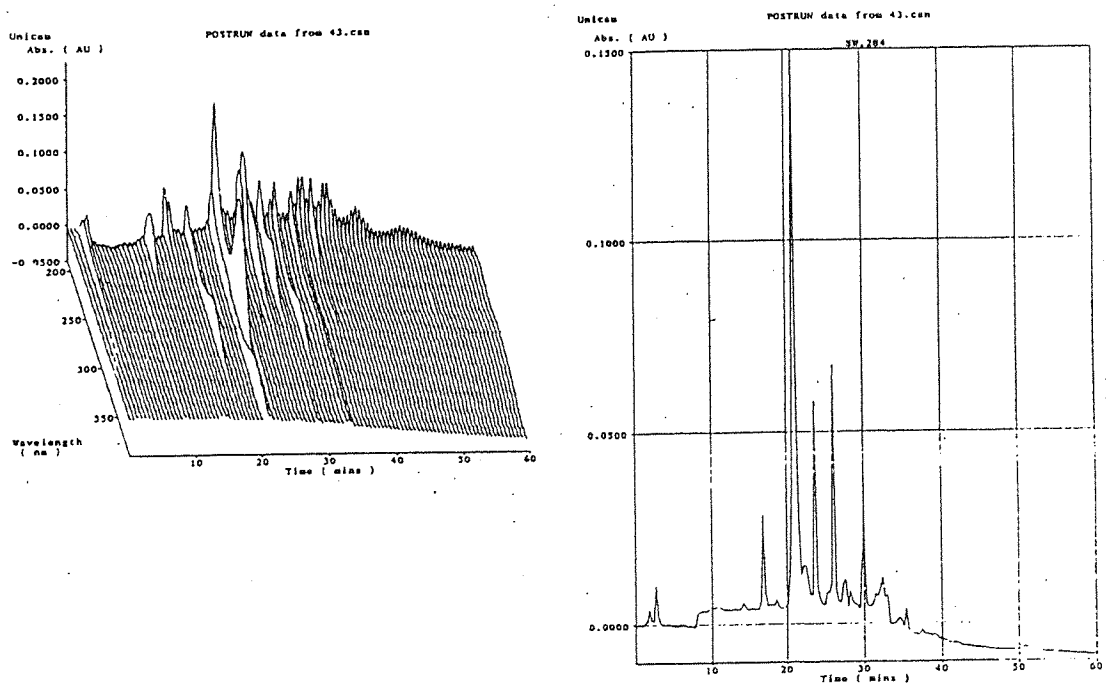

Figure A1-22 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% 3:1 IPPD:2246 prepared on 28/7/93 which showed excellent stabilisation aged for 210 days at 60°C.

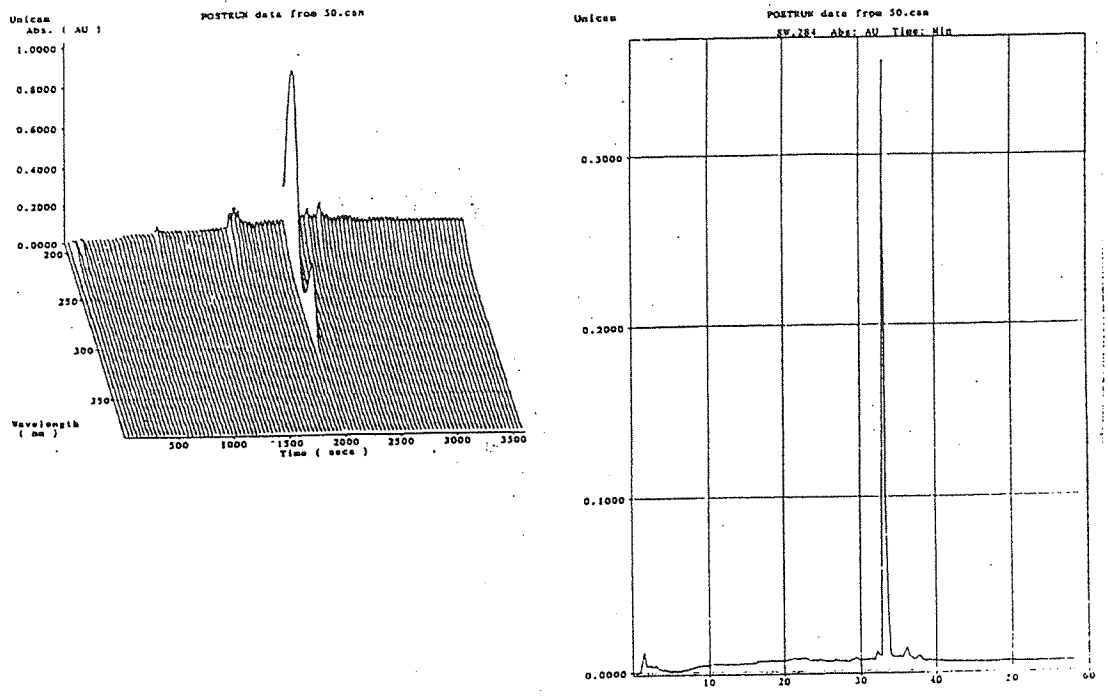

Figure A1-23 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% 3:1 Calco 2246:DLTP prepared on 27/9/94 aged for 7 days at 60°C.

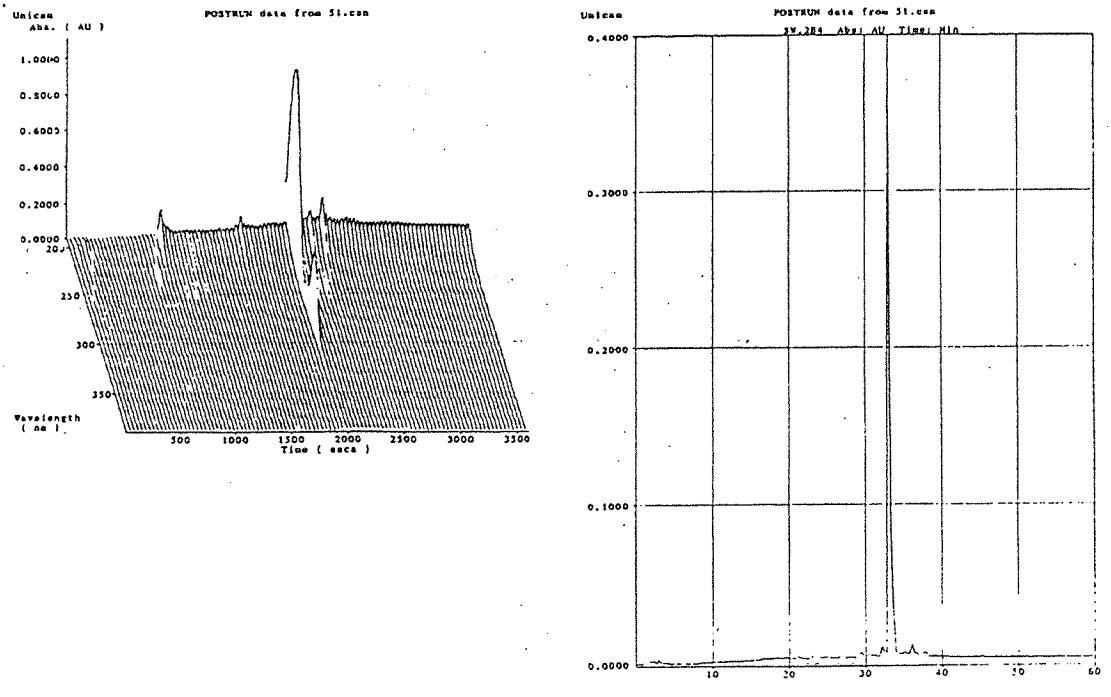

Figure A1-24 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% 3:1 Calco 2246:DLTP prepared on 27/9/94 aged for 41 days at 60°C.

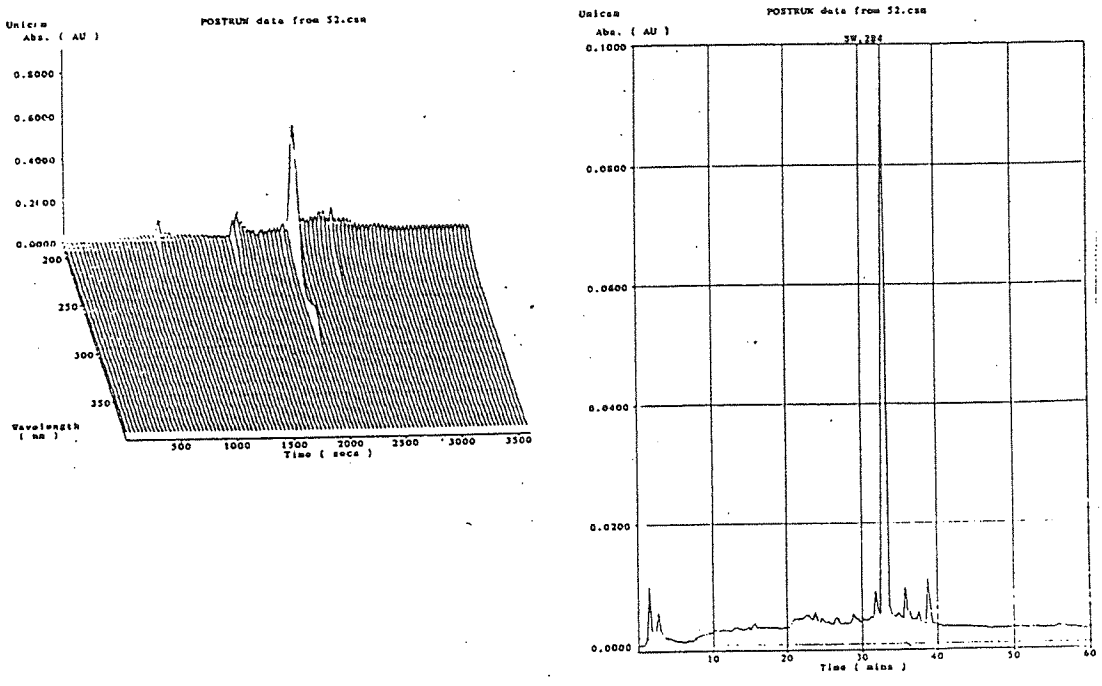

Figure A1-25 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% 3:1 Calco 2246:DLTP prepared on 27/9/94 aged for 101 days at 60°C.

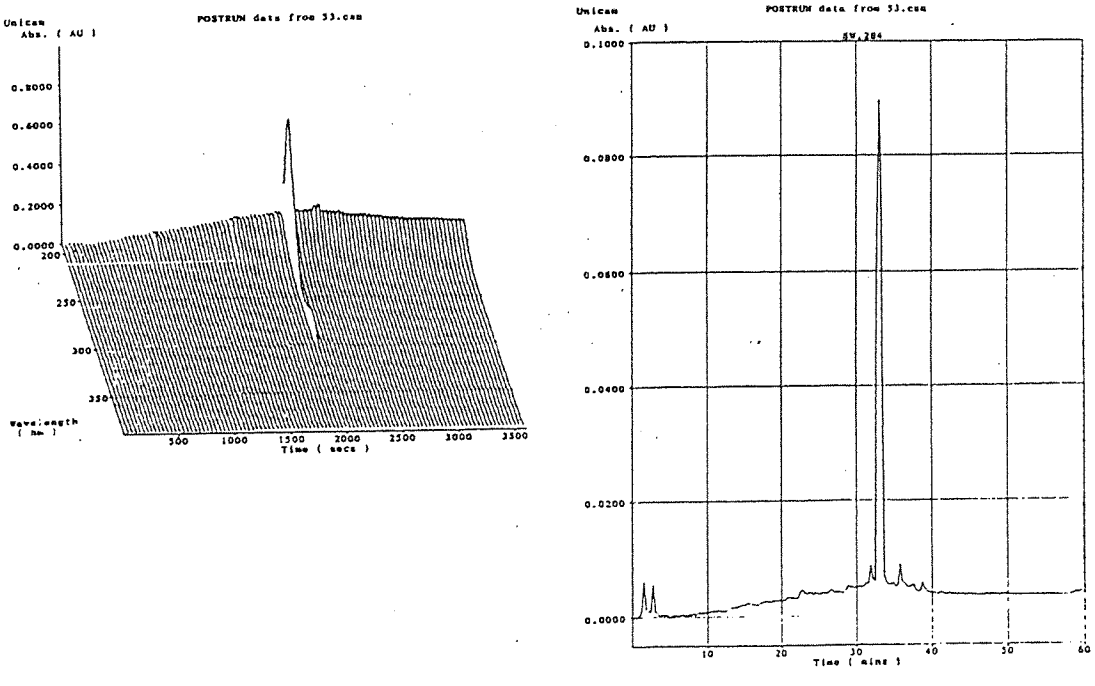

Figure A1-26 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% 3:1 Calco 2246:DLTP prepared on 27/9/94 aged for 176 days at 60°C.

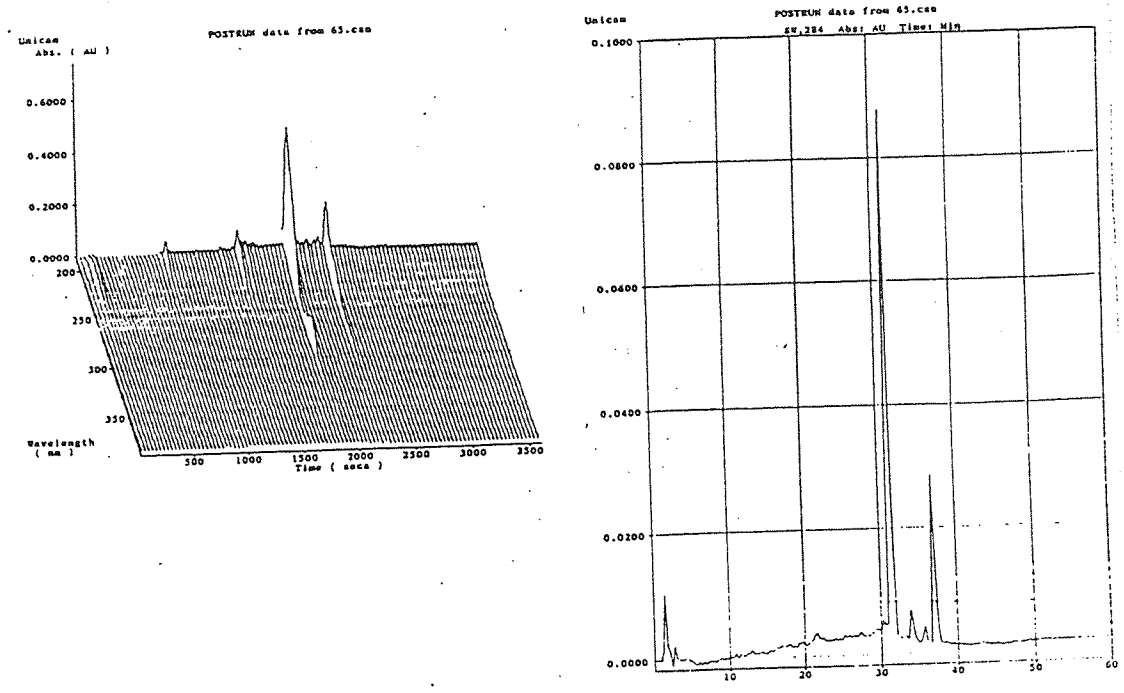

Figure A1-27 Three dimensional and 284 nm wavelength H.P.L.C chromatograms of extract from cured HTPB containing 0.2% 3:1 Calco 2246:DLTP prepared on 27/9/94 aged for 247 days at 60°C.