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AN INVESTIGATION INTO THE NETWORK STRUCTURES OF ETHYLENE PROPYLENE TERPOLYMER ELASTOMERS.

SUBMITTED FOR THE DEGREE OF Ph.D.

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The work described in this Thesis was carried out between October 1967 and September 1970 and was Supervised by J.E.STUCKEY.

SUMMARY

A series of ethylene propylene terpolymer vulcanizates, prepared by varying termonomer type, cure system, cure time and cure temperature, are characterized by determining the number and type of cross-links present. The termonomers used represent the types currently available in commercial quantities. Characterization is carried out by measuring the C_1 constant of the Mooney Rivlin Saunders equation before and after treatment with the chemical probes propane-2-thiol/piperidine and n-hexane thiol/piperidine, thus making it possible to calculate the relative proportions of mono-sulphidic, di-sulphidic and poly- sulphidic cross-links. The cure systems used included both sulphur and peroxide formulations. Specific physical properties are determined for each network and an attempt is made to correlate observed changes in these with variations in network structure. A survey of the economics of each formulation based on a calculated efficiency parameter for each cure system is included.

Values of C_1 are calculated from compression modulus data after the reliability of the technique when used with ethylene propylene terpolymers had been established. This is carried out by comparing values from both compression and extension stress strain measurements for natural rubber vulcanizates and by assessing the effects of sample dimensions and the degree of swelling. The technique of compression modulus is much more widely applicable than previously thought.

The basic structure of an ethylene propylene terpolymer network appears to be independent of the type of cure

system used (sulphur based systems only), the proportions of constituent cross-links being nearly constant.

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1. INTRODUCTION

1.1. E.P.D.M.'s

The virtues of a completely saturated elastomer chain had long been recognised. Such a polymer would have inherent resistance to ozone, oxygen and heat. Butyl rubber was an approach to this type of structure, being a homopolymer of iso-butylene containing about two percent of 1.4 polymerized isoprene. The resultant polymer had a low degree of unsaturation, whilst later, production of the ethylene propylene copolymers introduced completely saturated elastomers. Difficulty with the vulcanization of both these elastomers was encountered. The conventional sulphur based cure systems required some degree of unsaturation to work effectively. Therefore, butyl rubber needed a higher loading of curative whilst the completely saturated polymers required a peroxide, or to be irradiated, to effect cure. This initiated a search for a polymer with a saturated main chain which could be cured by conventional means. The resultant polymer, the ethylene propylene terpolymer (E.P.D.M.) will be discussed later.

1.1.1. E.P.D.M. - Historical.

The use of the ethylene propylene copolymers as rubbers was pioneered by the Montecatini Company of Italy in the mid 1950's. Despite their completely saturated nature, crosslinking was facilitated by peroxides or by irradiation. Later, the Du Pont Corporation in the U.S.A. produced a similar range of products, which came to be known as the ethylene propylene rubbers (E.P.R., or as designated by A.S.T.M. - E.P.M.). The search for a sulphur vulcanizable E.P.M. led to the development of the ethylene propylene terpolymer (E.P.T., or E.P.D.M.).

By 1959, several pilot plants, notably those of Du Pont, Enjay and Uniroyal, were producing these polymers. Large ranges of E.P.D.M.'s including several oil extended grades, were becoming commercially available by the early 1960's.

1.1.2. An introduction to E.P.D.M.

The ethylene propylene terpolymers are synthetic elastomers prepared from ethylene, propylene and a small proportion of a non-conjugated diene, using a solution polymerization process and a Ziegler/Natta type catalyst. The ratios of ethylene, propylene and diene are usually 16:8:1, although the amounts of ethylene and propylene are sometimes varied, the proportion of ethylene lying between 70 and 30 percent.

The presence of the diene ensures pendant unsaturation after polymerization, thus facilitating normal sulphur vulcanization. The polymer also contains a small proportion of stabilizer. Current commercial dienes are: (see figure 1)

dicyclopentadiene
1:4 hexadiene
ethylidene norbornene

Many other termonomers have been used or tried, but few have been successful. Two shown in figure 1, methylene norbornene and 1:5 cyclo-octadiene, have both appeared in commercial polymers, others, which have never reached this stage, are listed below:

4 vinyl cyclo hexane[1]
divinyl benzene[2]
trans 1:2 divinyl cyclobutene[3]
methyltetrahydroindene[4]
1:5 hexadiene[5]
1:4 pentadiene[6]

The essential requirement of a termonomer is that 1:4 addition be precluded since this would leave residual unsaturation in the main chain; only 1:2 addition will leave a completely saturated main chain with pendant unsaturation. Groupings alpha to the unsaturation play an important part in the vulcanization reaction. Each termonomer has different groupings, e.g. 1:4 hexadiene has an alpha-methyl and an alpha-methylene, whilst dicyclopentadiene has an alpha-methylene and an alpha-tertiary carbon atom. These will doubtless affect the vulcanization reaction of their respective polymers. The amount of diene introduced will control the level of unsaturation and hence the level of crosslinking. Recent developments in the polymerization process have allowed much greater control over the proportion of termonomer introduced. The ethylidene norbornene, claimed to produce the fastest curing polymer, is the most recent termonomer to be introduced commercially, and is already used in the greatest quantities.

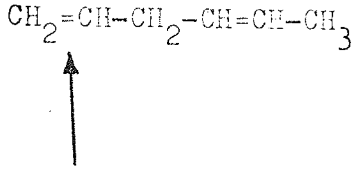
Polymerisation proceeds in solution utilizing a Ziegler - Natta catalyst, which is used for its activity and not for its stereo- specificity. Stereo-regularity causes an increase in crystallinity and a reduction in the elastomeric properties. Two typical catalyst systems, both developed for polymerizing dicyclopentadiene with ethylene and propylene are:

a) a binary system being made up of a compound of a transition metal of group 1VA or VA and an aluminium hydride being soluble in organic solvents.[8]

b) also soluble, consists of an alkyl aluminium sesqui chloride and a vanadium oxitri-chloride capable of homopolymerizing ethylene but not propylene.[9]

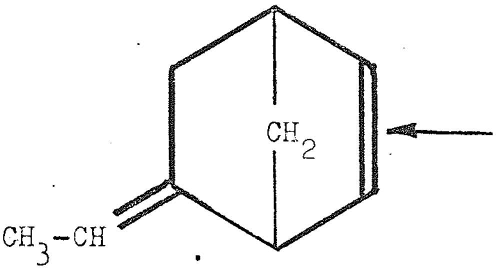
FIGURE 1

TERMONOMER SPECIES

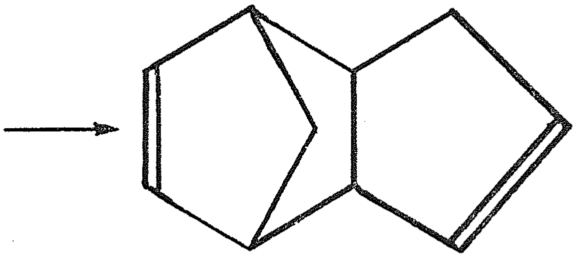


$CH_2=CH-CH_2-CH=CH-CH_3$

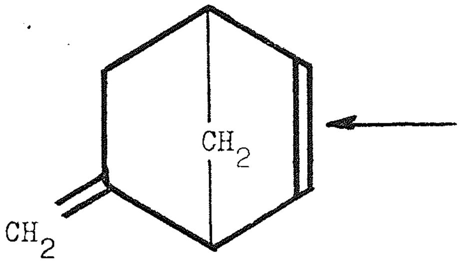
1:4 Hexadiene



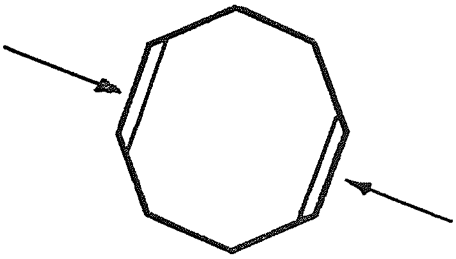
Ethylidene Norbornene



Dicyclopentadiene



Methylene Norbornene



Cyclo-octa 1:5 diene

→ Indicates polymerizable double bond

Typical catalyst and co-catalyst species are listed in Table 1:

Table 1

Ziegler type catalyst systems

Catalysts: groups 1 - 111	Co-catalysts: groups 1V - V111
Alkyls AlR_3, NaR	Halides $CrCl_3$, $TiCl_4$, WCl_6
Hydrides $LiAlH_4$	Oxyhalides $VOCl_3$
Mixed Alkyls/Halides AlR_2Cl	Alkoxides $Zr(OR)_4$
Alkoxide $A1(CH_3)_2(OCH_3)$	Mixed Alkyls/Halides TiR_2Cl_2

Apart from those properties of this elastomer which are inherent from its chemical structure, the E.P.D.M.'s are outstanding for their ability to accept large quantities of both oil and filler. Hence, from a commercial point of view, what is basically an expensive raw material can produce a viable product.

1.1.3. E.P.D.M. - Technology.

Since their comparatively recent conception, the E.P.D.M. elastomers have captured a large portion of the synthetic rubber market due to their inherent chemical properties and their ease of application. Already, their combination of processing ease and vulcanizate properties is bringing these elastomers into the category of general purpose elastomers. The disadvantage of a comparatively high price is offset by their ability to accept large quantities of fillers and extenders. Formulations containing 400 parts of carbon black and 200 parts of oil are in common use, although such loadings do inevitably cause a reduction in the physical properties of the vulcanizate. As has been mentioned, some producers market grades which are oil extended to varying degrees, e.g. 50 parts oil (Du Pont) and 100 parts oil (Uniroyal). The oils used are generally naphthenic or paraffinic.

The external mixing characteristics of these polymers are generally good using mainly cold mill rolls and a tight nip. The higher molecular weight grades tend to be "nervy" unless some processing aid is used. Internal mixing is usually preferred, the polymer, oil and filler being added at the same time. "Upside down" mixing has been used where high loadings of black and oil are required. In this case the oil and black are added before the polymer. Hot mixing in an internal mixer

(176 - 205°C) in the presence of a chemical promoter prior to the addition of the curatives is reported to improve the physical properties of the final vulcanizate. Vast quantities of these polymers are used for extrusion which normally takes place with a cold screw, warm barrel (65°C) and hot head and die (80 - 120°C). For complex or thin sections it is preferable to use a grade having a higher molecular weight or ethylene content, which will provide a higher green strength.

Provided that only moderately filled stocks are used, E.P.D.M. compounds can be calendered over a wide range of temperatures. Conditions are easily adjusted for skimming and frictioning of these polymers. As expected, the E.P.D.M. type polymers are subject to the same viscosity limitations as other general purpose rubbers, but even so they flow well during compression, transfer and injection moulding. Rapid removal from moulds is permitted by the excellent hot tear strength shown by these polymers. Injection moulding is normally reserved for the high tonnage applications such as footwear, automotive parts, etc., due to the high capital expense.

Cure systems used with these elastomers are as varied as those used for natural rubber. In general, higher levels of curatives are utilized to help overcome the inherently slow cure. Perhaps the most effective cure systems used are those where sulphur is assisted by a thiuram activated by a thiazole. Peroxides are often used in conjunction with sulphur but sulphur donor systems are usually avoided due to their very long cure cycles.

Recently, several accelerators have been developed for use specifically with these polymers.

lastomers lends itself well to the newer vulcanization techniques. High energy radiation has been used to cure high ethylene polymers and large volume automotive extrusions are continuously vulcanized by liquid curing media (L.C.M.). Compounds can exhibit short cure cycles if hot salt baths (eutectic mixtures) are used, provided that the polymer has a high unsaturation level and is free of moisture and other volatiles. A high green strength is also an advantage. Sponges based on E.P. type rubbers are easily produced by the conventional means utilizing conventional blowing agents.

Blends of E.P.D.M. are now becoming more important as initial problems of co-cure are overcome.

1.1.4. Commercial and Comparative.

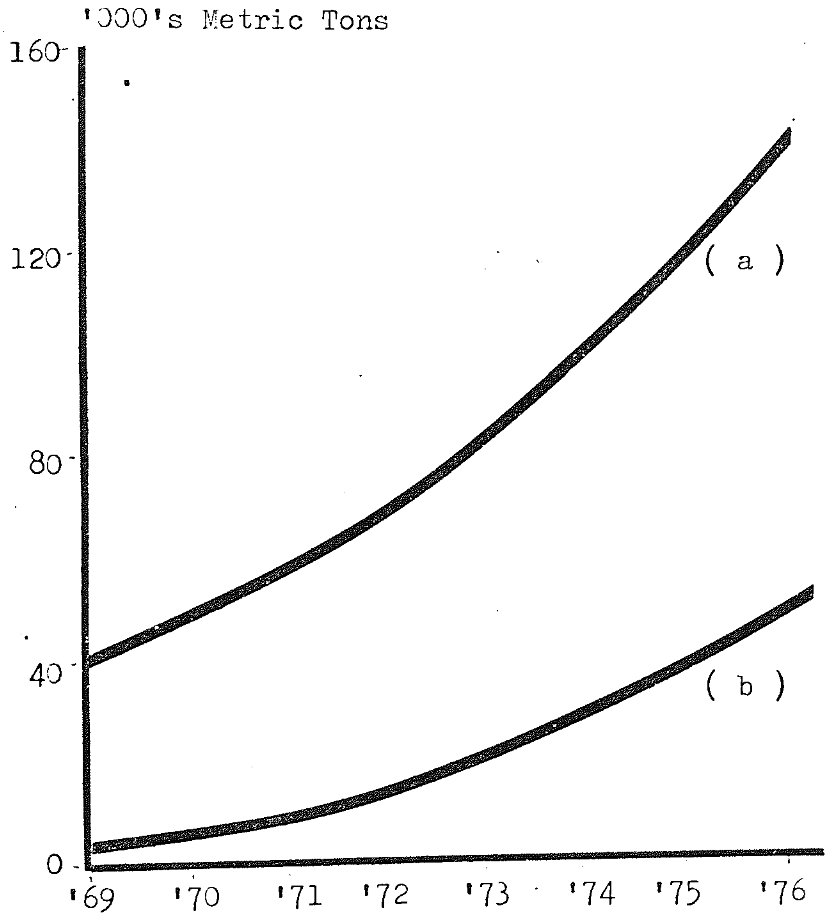
Severe restrictions on the production of E.P. type rubbers, levied by the original patent holders (Montecatini, Dunlop) have limited use in the U.K., since all such polymers have had to be imported. However, the patents lapse in 1972 and it has been predicted that by 1974 the U.K. will be the largest user of E.P. type elastomers in the Western European Trade Area.

Thus, figures quoted in this section will be mainly for the U.S.A. and the rest of the Western European area.

Graph 1 depicts the present and expected sales of all E.P.D.M. in the Western European Trade Area and compares this with sales of one brand of E.P.D.M. on the American domestic market. Producers of E.P.D.M.'s in this area are listed in Table 2.

GRAPH 1.

Potential Sales of E.P.D.M. in '000 Metric Tons



(a) W.Europe (excluding tyre casings).

(b) One major brand on the U.S. domestic market

TABLE 2

Producers of E.P.D.M. in the Western European Trade Area

Company	Present capacity tons / annum	Future capacity tons / annum	Date
International Synthetic Rubber Company Limited	15,000	30,000	1970/2
Dutch State Mines	14,000	26,000	1970/2
Huls Hoescht	- 0 -	25,000	1971/2
Esso Sp.A (France)	- 0 -	10,000	1972
Montecatini Sp.A	6,000	18,000	1970/2

America is the largest single market for E.P.D.M. elastomers. It has recently been estimated that each car now leaving the U.S. factories contains three pounds of E.P.D.M. in non-tyre products. An analysis of this American E.P.D.M. usage is shown in Graph 2. The polymer cannot yet be used in the manufacture of tyres because of its low building tack and its poor tensile adhesion. The small quantity indicated in Graph 2 as being used for this purpose represents side wall compositions and experimental tyre production. It is anticipated that the present problems will soon be overcome and that the tonnage of E.P.D.M.'s used for tyre production will increase four fold between 1973 and 1975. At present there are only six manufacturers of E.P.D.M. in the Western World, these, together with their trade names and country of origin, are shown in Table 3

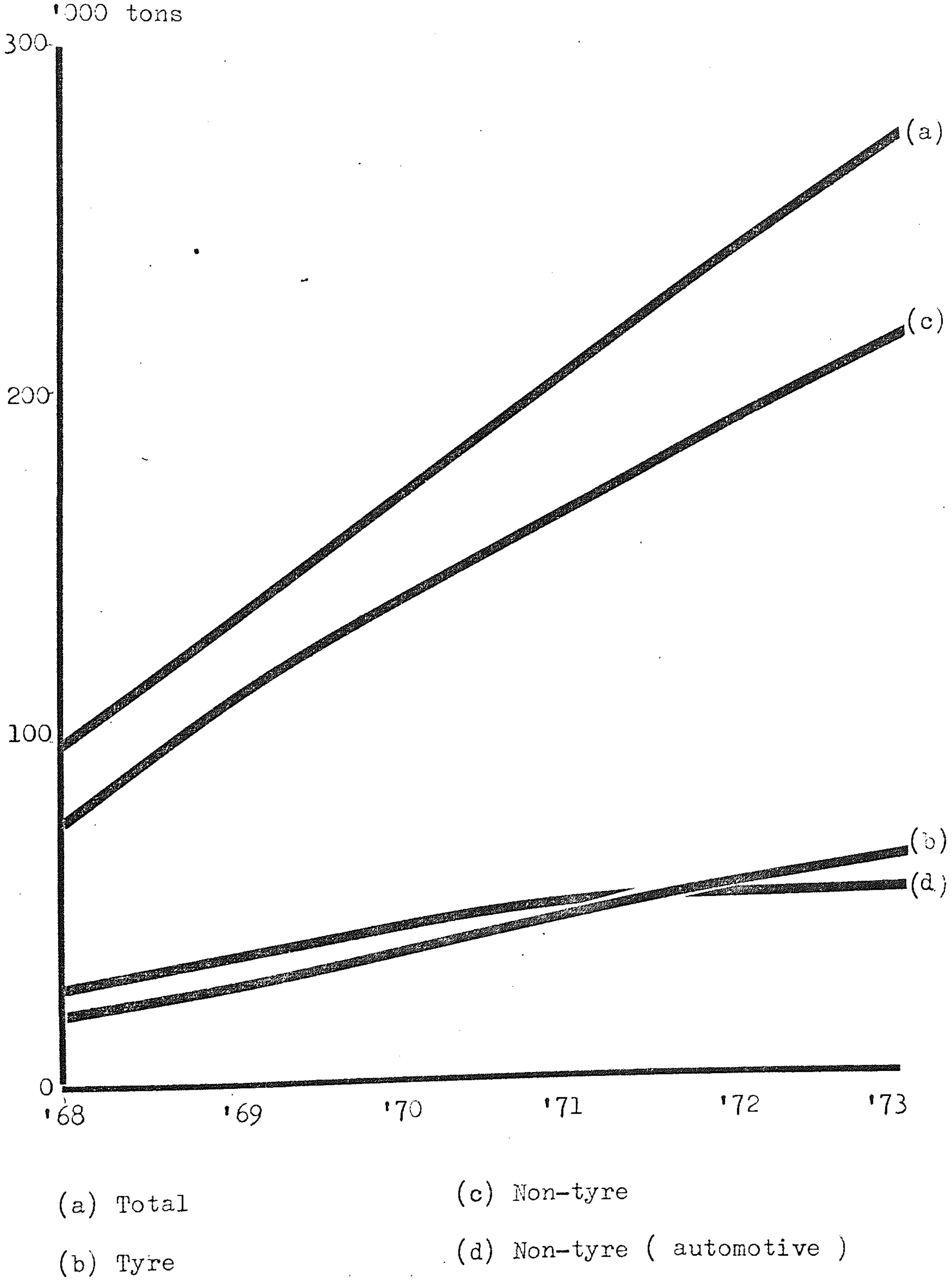
Graph 3 shows the approximate location, together with present and future capacities, of plants producing E.P.D.M.'s throughout the world (excluding the Communist Block).

Much of the information contained in sections 1.1.4. and 1.1.5. was obtained by private communication with one of the major producers of E.P.D.M. rubbers.

A comparison of the properties of E.P.D.M. and other elastomers is shown in Table 4. The fairly low specific gravity of the polymer is useful in production of lighter materials. Its excellent resistance to both heat and ozone stems from its completely saturated backbone chains. Like the E.P.M. rubbers, it has excellent electrical properties. It is resistant to steam, acids and bases but should not be used in prolonged contact with oils. Its ability to absorb

GRAPH 2.

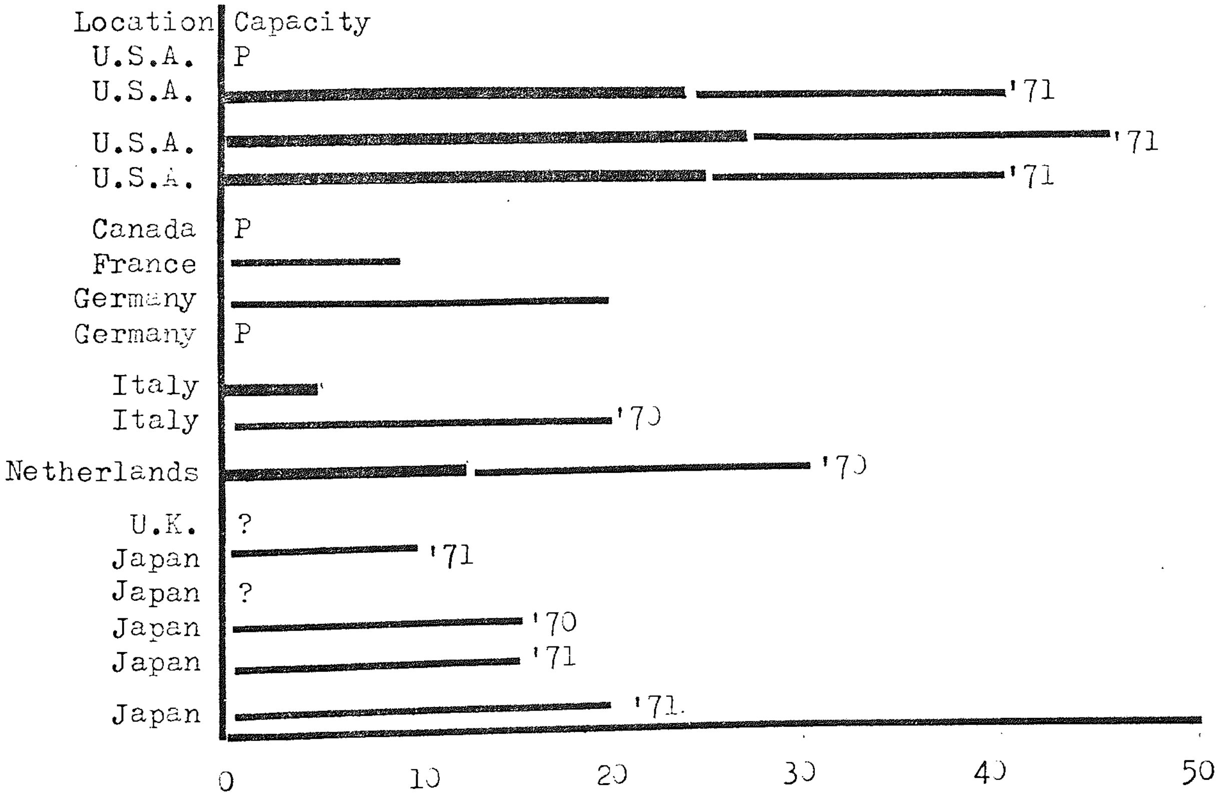
Breakdown of E.P.D.M. Usage for the U.S. Domestic Market



GRAPH 3.

Location and Present and Future Capacities of Plants Producing E.P.D.M.'s (Excluding the Communist Block)

P	Pilot plant
▬	Existing capacity
▬	Planned capacity
'70	Year of expected completion (where known)



'000 Tons

TABLE 3

Trade Names of E.P.D.M.'s produced in the Western World.

Company	Country	Trade Name
Copolymer Rubber and Chemical Co.	U.S.A.	EPSYN
E.I. Du Pont du Nemours and Co. Ltd.	U.S.A.	NORDEL
Enjay Chemical Corporation	U.S.A.	VISTALON
Montecatini Petrochemica Sp.A.	Italy	DUTRAL TER
Dutch State Mines	Netherlands	KELTAN
Uniroyal Inc.	U.S.A.	ROYALENE

TABLE 4

Comparison of properties of elastomers.

E : Excellent

G : Good

F : Fair

P : Poor

	E.P.D.M.	S.B.R.	BUTYL	NEOPRENE	N.R.
S.G.	0.865	0.94	0.92	1.23	0.9
Resistance to heat	E	F/G	E	G	F/P
O_3 and weathering	E	P	G	G	F
Cold	E	F/G	P	F	E
Acids and Bases	G/E	G	E	F	F/G
Oils	Not suitable for severe exposure			G	P
Abrasion	G	G	F	E	E
Tearing	G	F	G	G	G
Steam	E	G	E	P	G
Comp. set	G	E	F	G	E
Flame	Require special compounding			G	P
Dynamic props.	G/E	G	P	G	G
Colour stability	E	G/E	G/E	P	F/G
Electrical properties	E	G	E	P	F/P

large quantities of oil and black assists its abrasion resistance, although special compounding is required to obtain a suitable degree of flame resistance. Its compression set, colour stability and dynamic properties are good.

The prices (July 1970) of common synthetic elastomers are presented in Table 5. Although cheaper than most synthetic elastomers, E.P.D.M.'s are 50% more expensive than natural rubber and S.B.R. However, the oil extended range of E.P.D.M.'s can compete favourably in the general purpose range.

1.1.5. Applications.

A convenient classification of end uses for elastomers is automotive and non automotive which is basically tyre and non tyre. This is because over half of all the rubber used is in the production of tyres. E.P.D.M.'s have made very little ingress into this field but many attempts have been made, and are being made, with varying degrees of success.[10] Blends of E.P.D.M. and butyl have been tried for whole tyre production[11] whilst side walls made of E.P.D.M. are used on many tyres in the U.S.A.[12] A further use of these polymers in the tyre industry is as coatings for wire beads, although this is virtually limited to tyres produced from E.P.D.M. butyl or blends.[13]

E.P.M.'s are also used in this context for coating rayon cords.[14] The excellent ozone and heat resistance of E.P.D.M.'s are utilized in non tyre aspects of the automotive industry. Typical E.P.D.M. components used in the modern car include solid and sponge door gaskets, heater and radiator hose, bumper facings, weather strip, brake components, cable

TABLE V

Current prices (July 1970) of synthetic rubbers quoted in U.S. dollars per pound

		U.S.A.	U.K.
E.P.D.M.	Slow curing	0.30	0.30
	Fast curing	0.30	0.30
	Oil extended	0.20	0.21
E.P.M.		0.27	0.24
Butyl		0.40	0.39
Chloroprene		0.40	0.39
Nitrile		0.50	0.43
S.B.R.		0.18	0.22
Natural Rubber	SMR1	0.19	0.22
	SMR 5	0.18	0.21

insulation, O-rings, distributor covers and various other mouldings. Non automotive uses include exhaust hoses, door and general construction gaskets, sheeting, cable insulation (E.P.M.), C-belts, calendered sheet, heavy paper rolls, conveyors for hot minerals, gaskets for washing machines, refrigerators, etc. It is also being used to line the main fuel chambers of both solid and liquid fuel rockets. Small quantities of E.P.D.M.'s have already been used to improve the ozone resistance of other elastomers by blending.[14]

1.2. THEORY

1.2.1. Introduction

Rubber networks may be represented as in Figure 2 which shows a schematic diagram of the typical features. The characterization of such a network involves measurement of cross-link density by physical means, the use of chemical probes to react with specific types of cross-link, and the use of model compounds.

Rubber-like substances are capable of undergoing large deformations and exhibit almost spontaneous recovery to near their initial dimensions when the deforming force is removed. The molecular requirements necessary are summarized below. Long molecules, existing in the unstressed state in a large number of random configurations, are essential. Under stress these molecules will straighten out and become more ordered, but when the deformation is removed, they will return to the random state. Low inter-molecular forces, i.e. the absence of polar groupings and crystallization forces, together with a suitable glass transition (Tg), ensure that the polymer will have the freedom to rapidly take up the random configurations.

Permanence of structure is attained by a comparatively small number of cross-links, which prevent slippage of the chains.

1.2.2. Stress Strain Behaviour.

The stress strain behaviour of rubber like substances has been described by Mooney[15a], Rivlin[16] and Saunders[17], by the empirical relationship shown in equation 1 :

$$f = 2A_o(\lambda - \lambda^{-2})(C_1 + \lambda^{-1}C_2) \quad . \quad . \quad (1)$$

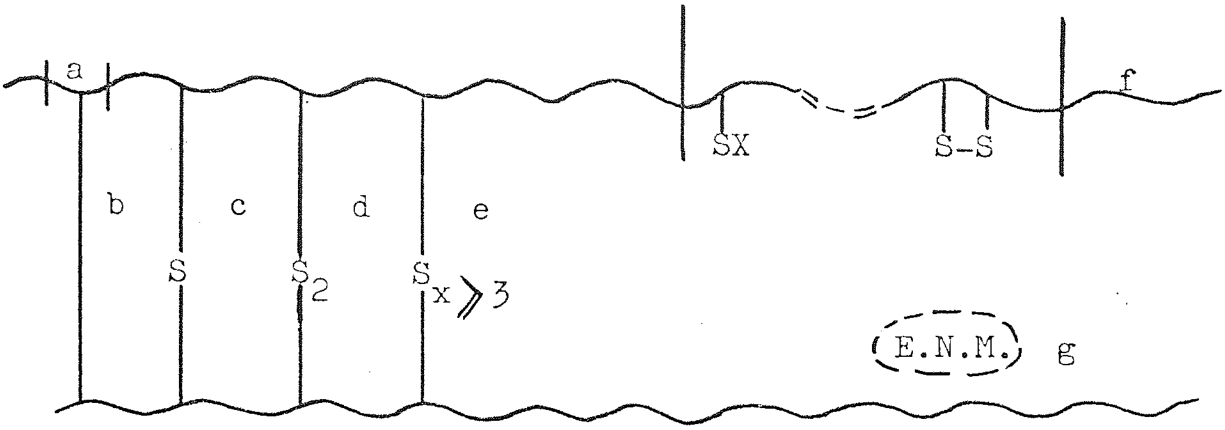
where f is the deforming force producing an extension ratio λ on a specimen with cross sectional area A_o. C_1 and C_2 are two parameters, normally known as the elastic parameters, required to complete the relationship. By analogy with similar expressions derived from a statistical thermo dynamic approach to elasticity theory (see Appendix VII), C_1 can be related to $M_{c.phys}$, the physically manifested number average molecular weight of the inter cross-link network chains (equation 2) :

$$C_1 = \frac{P\,R\,T}{2\,M_{c.phys}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This will not necessarily be identical to the number average molecular weight between chemical cross-links ($M_{c.chem}$) due to the presence of chain ends and entanglements. P is the density of the rubber hydrocarbon, R is the gas constant and T the absolute temperature. Statistical derivations assume that the network comprises of infinitely long chains connected only by tetrafunctional cross-links (figure 2). Hence the relationship between the cross-link density and $(2\,M_{c.phys})^{-1}$,

FIGURE 2

Features of a typical rubber network.



a) cross-linking site (termonomer)

b) carbon-carbon cross-links (peroxide vulcanization)

c) mono-sulphide cross-link

d) di-sulphide cross-link

e) poly-sulphide cross-link (three or more sulphur atoms)

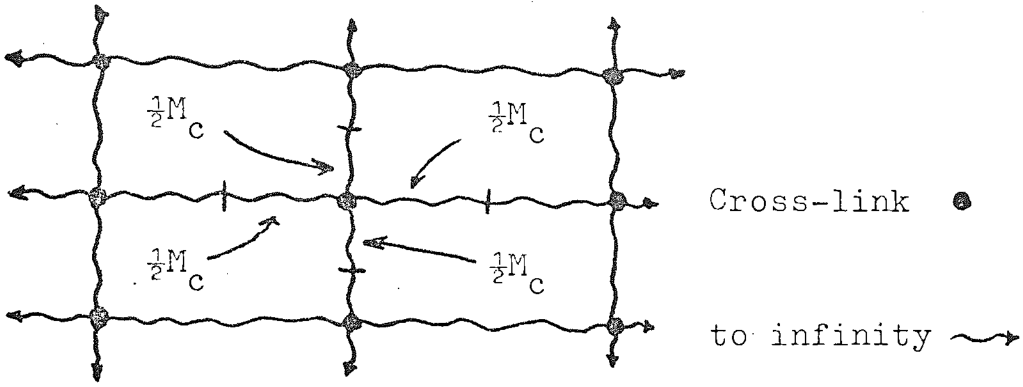
f) main chain modifications, e.g. cyclic sulphides, pendant accelerator fragments, conjugated unsaturation etc.

g) extra network material, any material added at the polymerisation or compounding stage, or formed during the vulcanization, which is not chemically bound to the network.

see figure 3:

FIGURE 3

Ideal network structure.



In reality, no chains extend to infinity and chain ends affect the behaviour of the network, as do purely physical entanglements. An outstanding contribution by Mullins[18] enabled a calculation of $M_{c.chem} / M_n$ dynes cm^{-2} for natural rubber where M_n is the number average molecular weight of the rubber immediately before vulcanization.

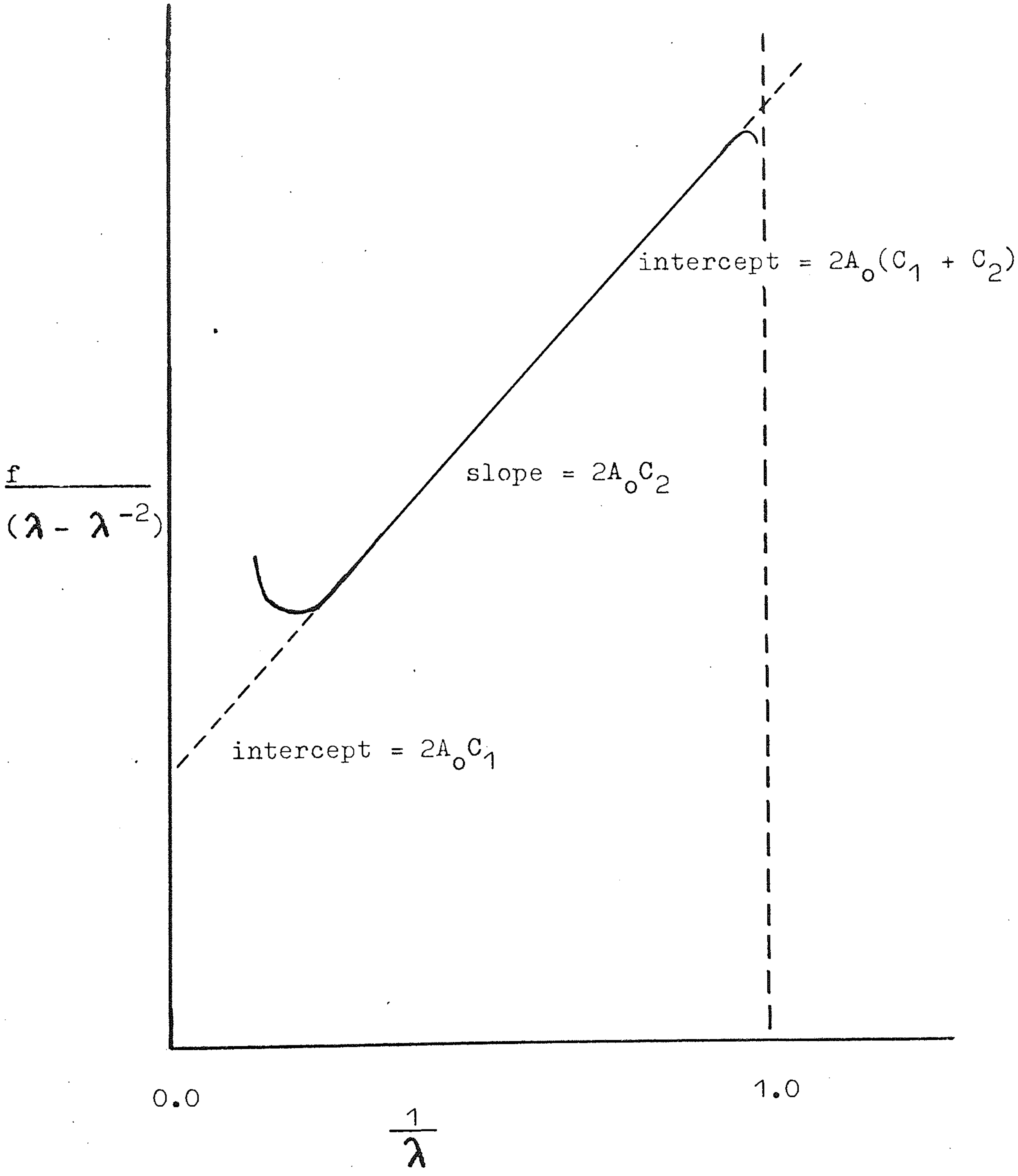
1.2.3. C_1 by extension stress strain.

Values of C_1 may be obtained from simple stress strain measurements using a technique pioneered by Greensmith.[19] A series of values of deforming force (f) and extension ratios (λ) are determined experimentally. The resultant plot of $f/(\lambda - \lambda^{-2})$ against $1/\lambda$ is depicted schematically in graph 4. The slope is given by $2A_oC_2$ whilst the intercepts at $1/\lambda = 1$ and $1/\lambda = 0$ are $2A_o(C_1 + C_2)$ and $2A_oC_1$ respectively. The portions of non-linearity or "upturn" are due to the limits of elasticity theory being surpassed. The technique can also be used with samples swollen to equilibrium when the governing equation becomes: (equation 4)

$$f = 2A_oV_r^{-\frac{1}{3}} (\lambda - \lambda^{-2}) \quad (C_1 + C_2\lambda^{-1}) \; . \; . \; . \; . \; . \; . \quad (4)$$

GRAPH 4

Plot of $f/(\lambda - \lambda^{-2})$ against $1/\lambda$ to determine C_1 for extension stress strain technique.



where V_r is the volume fraction of rubber in the swollen network.

1.2.4. C_1 by compression of swollen samples.

At high degrees of swelling it has been shown that the C_2 constant of equation 4 becomes effectively zero, reducing the expression to: (equation 5)

$$f = 2A_oC_1V_r^{-\frac{1}{3}}(\lambda - \lambda^{-2}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The required V_r values have been quoted as 0.25 or less.[20,21] Further approximations, the first (equation 6) being valid for small deformations, the second (equation 7) experimental, result in a much simplified expression for C_1 (equation 8).

$$\lambda - \lambda^{-2} = 3\Delta h/h_s \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$h_s = h_oV_r^{-\frac{1}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$C_1 = f/\Delta h\ (h_o/6A_o) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where h_o, h_s and Δh represent the initial height, the swollen height and the deformation of the sample. In this simple expression, the term $f/\Delta h$ is obtained from the slope of the plot of experimental compression stress strain values of f and corresponding values of Δh. The term $h_o/6A_o$ is determined solely by the original dimensions of the sample. Later refinements of the approximation to $(\lambda - \lambda^{-2})$ produced a modified expression (equation 9).[22]

$$C_1 = \frac{f}{\Delta h} \cdot \frac{h_o}{A_o 6} \cdot \frac{1}{1 + V_r^{-\frac{1}{3}}\Delta h\, h_o^{-1}} \quad . \quad . \quad (9)$$

Workers at the Royal Aircraft Establishment have used results relying on a single load and deformation measurement. The exact expression contains no approximation to the $(\lambda - \lambda^{-2})$ term, but has introduced a new measurement, h_d, the height of the swollen, deformed sample (equation 10)[23,24]

$$C_1 = \frac{f\ h_o h_d^2}{2A_o(h_d^3 - h_s^{\ 3})} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

A further exact expression was derived by Melley and Stuckey[25] (equation 11).

$$C_1 = \frac{fV_r^{\frac{1}{3}}}{2A_o} \left[\frac{3\ h_s \Delta h^2 - 3\ h_s^2 \Delta h\ - \Delta h^3}{h_s^3\ -\ 2h_s^2\ \Delta h + h_s \Delta h^2} \right]^{-1} \quad . \quad . \qquad (11)$$

Experimental techniques vary mainly in the size of sample tested. Cluff et al[20] and the "single point" exponents[23,24] used samples 0.75 inches diameter, 0.5 inches thick and 0.5 inches diameter, 0.25 inches thick respectively (compression set buttons being convenient). Smith, after developing the reticulometer[21], used much smaller samples, 0.4 cm^2 by 0.2 cm thick, these having the advantage of reaching an equilibrium swell value in a much shorter time. An assessment of the validity of these equations is discussed in section 1.3. The effect of sample dimensions and V_r will be investigated together with that of the mathematical approximations; and the technique of compression modulus compared with that of extension stress strain.[25] The compression technique is preferable with the E.P.D.M. elastomers since their rapid relaxation rate and poor gum strength do not lend themselves to the extension method.[26]

1.2.5. Use of the Flory Rehner Equation.

This equation (equation 12)[27,28], later modified by Flory[29] (equation 13) relates the M_c value of a swollen vulcanizate to its V_r value and the polymer solvent interaction parameter. (χ).

$$-(\ln(1-V_r) + V_r + \chi V_r^2) = \rho V_o M_c^{-1} V_r^{\frac{1}{3}} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$-(\ln(1-V_r) + V_r + \chi V_r^2) = \rho V_o M_c^{-1} (V_r^{\frac{1}{3}} - V_r/2) \quad . \quad . \quad (13)$$

where V_o is the molar volume of the solvent.

Thus, knowing χ, M_c may be calculated from V_r only. However, insufficient data has been assembled to assess the variation of χ with changes in the network to make this a universal technique. The results of this work show changes in χ value after the network has been treated with chemical probes. Other workers have already shown that a small change in χ results in quite large changes in M_c[30] and that values of χ for samples of natural rubber cured with C.B.S. change with the state of cure.[31]

1.2.6. Chemical Probes.

A chemical probe may be defined as a reagent which will react quantitatively with a specific type of cross-link, and which can be introduced homogeneously into, and be removed from a network without causing any undesirable side reactions. These requirements were specified as early as 1948 by Bloomfield.[32] Commonly used chemical probes are:

a) aqueous sodium sulphite
b) methyl iodide
c) tri phenyl phosphine
d) ^{35}S
e) lithium aluminium hydride
f) tri alkyl phosphites
g) sodium di-n-butyl phosphite
h) propane-2-thiol /piperidine)"thiol amine" reagent

i) n-hexane thiol/piperidine)
) "thiol amine" reagents
j) xylene thiol/piperidine)

a) aqueous sodium sulphite[33,34] reacts with dialkyl polysulphides by removing the interterminal sulphur atoms. Unfortunately the aqueous medium precludes it from widespread use with rubbers.

b) methyl iodide, first used by Meyer and Hohenemser[35] and later developed by Selker and Kemp[36], destroys all sulphur cross-links under suitable conditions, leaving only carbon-carbon cross-links intact. It is easily swollen into and removed from the network.

c) tri phenyl phosphine, developed as a probe by Moore and Trego[37], is used in solution in dry benzene. The action of the probe is to remove sulphur atoms from poly-sulphidic chains to produce di-sulphides and in cases where there is an alkenyl terminal group, to produce mono-sulphides. This probe is normally used in conjunction with total combined sulphur determinations for the determination of the E and E' parameters. The E parameter introduced by Moore and Trego[38] is defined as in equation 14.

$$E = \frac{\text{g. atoms of network combined sulphur/ g.network}}{\text{g.molecules of chemical cross-links/ g.network}} \quad . \quad . \quad (14)$$

The E' parameter is defined by the same expression but using values measured after the network has been treated with tri phenyl phosphine. By inspection, it becomes obvious that the expression $E - E'$ is a measure of the average number of sulphur atoms per poly-sulphidic cross-link, whilst $E' - 1$ gives a value of the amount of sulphur combined as main chain modification.

d) radioactive ^{35}S can be used for semiquantitive estimation of poly-sulphidic linkages by making use of the sulphur interchange reaction[39]. Since this probe, in nature and technique, is different from the more conventional types, its many other uses will not be discussed here. They are listed in the review by Saville and Watson[40].

e) lithium aluminium hydride in tetrahydrofuran will react with di and poly sulphidic cross-links, converting internal sulphur atoms to hydrogen sulphide and terminal ones to bound thiol groups. This work pioneered by Studebaker and Nabors[41,42], entailed the estimation of bound thiol groups and measurement of the volume of gas evolved. The probe is suspect in that many side reactions take place with certain main chain modifications and pendant accelerator groupings.

f) tri alkyl phosphites, the esters of tervalent phosphorous acid, are chemically closely related with tri phenyl phosphine, and desulphurate poly-sulphidic linkages to disulphides[43] with ease. They will also cleave simple disulphides in a simple reaction.[44]

g) sodium di-n-butyl phosphite, now discredited due to intense side reactions, has been used to cleave poly and di sulphide cross-links.[38]

h,i,j) the 'thiol amine' probes utilise the nucleophilic attack by a thiolate ion upon a poly-sulphidic linkage. The extent of the reaction of the ion, formed by the interaction of a mercaptan and a base (normally piperidine), depends upon the reaction conditions, i.e. the nucleophilicity of the ion, time and temperature. A solution of propane-2-thiol and piperidine[40] in n-heptane will cleave, under the prescribed conditions, 98% of poly-sulphidic linkages but only 2% of the di-sulphidic linkages, whereas n-hexane thiol[40] or xylene thiol[45,46] in piperidine will cleave all poly and di-sulphidic cross-links. The probes to be used for this work are the two thiol amine reagents propane-2-thiol/piperidine in n-heptane and n-hexane thiol/piperidine. Further information on probes and other methods of characterization can be found in the review by Saville and Watson[40] and the relevant chapters in certain well known texts.[47,48,49]

1.3. Purpose of Work.

1.3.1. Network Structures.

A series of networks as described in section 1.2. using polymers containing different diene species will be prepared by using various cure systems and by varying the vulcanization temperatures and times. These networks will then be characterized in terms of the total number and the relative proportions of mono-sulphidic, di-sulphidic and poly-sulphidic cross-links, by the use of the chemical probes propane-2-thiol/piperidine and n-hexane thiol/piperidine.

1.3.2. Correlation with Physical Properties.

In an attempt to correlate the physical properties of the different vulcanizates with their chemical structures, a number of selected properties will be measured. These include:

a) hardness
b) modulus at 100% extension
c) elongation at break
d) ultimate tensile strength
e) compression set

Since all vulcanizates are unfilled, the physical properties will be very inferior and of no practical significance.

1.3.3. Experimental Techniques.

The techniques envisaged for this work have been used previously, but mainly with natural rubber. Thus, their applicability to E.P.D.M. vulcanizates will be investigated and suitable conditions determined. The technique used to obtain cross-link density (compression modulus determination) will be investigated in some depth in order to ascertain its validity i.e. comparison of the values of C_1 obtained from compression and extension stress strain data using natural rubber vulcanizates. The effect of sample dimensions, the degree of swelling and mathematical approximations will also be investigated.

1.3.4. Efficiency and Economics.

An attempt will be made to define an efficiency parameter with which to assess the various cure systems used. This parameter will be compared with the economic considerations of the individual formulations.

1.4. Previous Work.

No work at the time of commencement had been published on the characterization of E.P.D.M. networks. A few of the more progressive reports are mentioned below. Dunn[50] looked at the effect of sulphur on the peroxide cure of ethylene propylene rubbers, and its relation to their physical properties. The work involved the use of stress relaxation techniques although V_r determinations were made to estimate the proportion of poly-sulphidic cross-links and total cross-link density, the chemical probe propan-2-thiol being used to differentiate between them. Laud and Stuckey[51,52] used stress relaxation to study the thermal and thermal oxidative ageing of E.P.D.M. vulcanizates; use of two thiol amine reagents was integrated to look at the relaxation properties of specific cross-links. Two papers describing the work on the reaction mechanisms and structures obtained from several E.P.D.M. (Nordel) vulcanizates were presented by Saegebarth[45] and Frensdorff.[46] Infra red examination was used to study the removal of unsaturation from the rubber during vulcanization and the mechanisms were likened to those of natural rubber and S.B.R. These workers only differentiated between mono-sulphides and cross-links containing two or more sulphur atoms, using xylyl mercaptan/piperidine reagent. An excellent correlation between entanglements and chemical cross-links in E.P.D.M. vulcanizates was made by Baldwin, Borzel and Makowski[53] of the Enjay Corporation. By using a peroxide cure system they obtained an equation whereby the chemical network chain density $M_{c.chem}$ could be determined (equation 15).

$$\nu_t = \nu_c(1 - 2P/M\nu_c) + (\nu_e^o + b\,\nu_t)\,(1 - 2P/(M_c\nu + P))^2 \,. \quad (15)$$

where $\nu = \dfrac{P}{M_c}$.

and the subscripts t and c refer to the total and chemical values respectively.

M is the number average molecular weight of the elastomer directly before vulcanizing and ν_e^o and b are constants for that particular polymer. Unfortunately, the constants ν_e^o and b were evaluated for a specific E.N.B. polymer and hence only figures for this material can be converted to $M_{c.chem}$.

Recently several papers on this topic have emerged from Japan. One by Kujimato and Nakade[54] looked at the effect of the diene monomer on the rate and structure of cross-linking in E.P.D.M.'s. Using a range of commercial termonomers, the structures were determined with the aid of lithium aluminium hydride and tri phenyl phosphine whilst the rates were studied by following the usage of unsaturation by an infra red technique. In a contempary paper, Imoto et al[55] looked at the nature of sulphur existing in the vulcanized network. They used, extraction, HCl treatment and lithium aluminium hydride techniques to resolve the network. In a further paper[56] this team looked at the oxidative degradation of E.P.D.M.'s utilizing stress relaxation and oxygen absorption techniques.

Levine and Haines[57] have now perfected an infra red method for determining ethylidene norbornene in E.P.D.M.'s.

The conclusions of the above workers will be discussed with the results of this work in a later section.

2. EXPERIMENTAL

The cumbersome nomenclature in certain equations was used to conform with that of the computer program.

2.1. Vulcanizate Preparation.

2.1.1. Formulations.

The E.P.D.M. formulations are shown in Table 6. A.B.C. and V were used to study the effect of variation of the vulcanizing system for a given termonomer (Enjay 3509 - methylene norbornene). A and B are analogous to the conventional high sulphur and sulphur donor systems used with natural rubber, C is a simple peroxide cure system and V is based on a new accelerator Vocol,[58] developed for use with these polymers. Formulations B,N,E and R were used to look at the effect of different termonomers using a single vulcanization system. The termonomers used were: methylene norbornene, ethylidene norbornene, dicyclo pentadiene and 1:4 hexadiene.

Formulations based on natural rubber (used in the comparison of techniques for determining C_1) are shown in Table 7. These simple formulations, differing only in peroxide loading, were used to produce a range of cross-link densities. Formulation 3 was used to determine the effect of sample dimensions on compression modulus results.

2.1.2. Polymers Used.

The natural rubber used throughout this work was technically specified as Natural Rubber R.S.S.1 (yellow circle).

The E.P.D.M. elastomers were Royalene 301T (Uniroyal Ltd.), Nordel 1040 (Du Pont Ltd.) and Vistalon 479 (Enjay Corp. Ltd.). Technical specifications of these polymers are listed in Table 8. All polymers contained a small proportion (0.2/0.35 weight percent) of stabilizer added at the polymerization stage, a typical substance being a butyrated hydroxy toluene.

2.1.3. Vulcanizing Ingredients.

Tetramethyl thiuram disulphide (T.M.T.D.), mercaptobenzthiazole (M.B.T.), dimorpholinodisulphide (D.M.D.S.) and zinc di-n-butyl dithiophosphite were donated by Monsanto Chemicals Ltd. who use the trade names Thiurad, Thiotax, Sulfasan R, and Vocol respectively. The T.M.T.D. was recrystallized from chloroform (m.p.t. 148 - 149°C) and the M.B.T. recrystallized from benzene after decolorisation with animal charcoal (m.p.t. 180°C). The D.M.D.S. and Vocol were used as supplied. Di-cumyl peroxide (Dicup R) was provided by Hercules Powder Co. Ltd. Titration with iodine and thiosulphate showed it to be 99% pure; because of its instability it was stored at -20°C until required.

2.1.4. Compounding.

The natural rubber peroxide formulations were compounded on a water cooled 12 inch laboratory two roll mill. The polymer was cut into small pieces, banded on the mill using a tight nip and the peroxide added. The stocks were milled to a Wallace plasticity of 18.5. Each stock received eight endwise passes immediately prior to vulcanization to ensure good dispersion.

TABLE 6

E.P.D.M. Formulation.

	A	B	C	V	N	E	R
Enjay 3509[a]	100	100	100	100	-	-	-
Nordel 1040[b]	-	-	-	-	100	-	-
Enjay 479[c]	-	-	-	-	-	100	-
Royalene 301T[d]	-	-	-	-	-	-	100
Zinc Oxide	5	5	5	5	5	5	5
Stearic Acid	1	1	1	1	1	1	1
Sulphur	2.0	-	-	2.0	-	-	-
T.M.T.D.	1.5	2.0	-	0.75	2.0	2.0	2.0
M.B.T.	0.5	-	-	1.5	-	-	-
D.M.D.S.	-	2.0	-	-	2.0	2.0	2.0
Dicumyl Peroxide	-	-	2.5	-	-	-	-
Vocol	-	-	-	3.0	-	-	-

a : methylene norbornene (M.N.B.)

b : 1:4 hexadiene

c : ethylidene norbornene (E.N.B.)

d : dicyclopentadiene (D.C.P.D.)

TABLE 7

Natural Rubber Formulations.

	1	2	3	4
Natural Rubber	100	100	100	100
Dicumyl Peroxide	1	2	3	4

TABLE 8

Technical Specification of E.P.D.M.

Polymer	Termonomer	E/P Ratio	ML4@100	I_2 No.	wt.% unsat	S.G.	Cure Rate
Royalene 301T	D.C.P.D.	65/35	60	10	3.0	0.865	slow
Nordel 1040	1:4 Hexadiene	59/41	75	10	3.2	0.85	slow
Enjay 3509	M.N.B.	60/40	57-67	8-10	2-3	0.86	fast
Enjay 479	E.N.B.	60/40	62	12	4	0.86	fast

Two kilogram batches of the E.P.D.M. polymers were masticated on the mill using a tight nip for five minutes and the zinc oxide and stearic acid added until dispersed. The remaining ingredients were then incorporated, the sulphur, when used, being the last to be added. In all cases mixing times were kept as short as possible, each batch was weighed after mixing to ensure that there had been no loss of material. The Nordel proved to be easier to handle on the mill than the other polymers.

2.1.5. Storage.

Compounded stocks and vulcanized sheets were stored in sealed polythene bags at - 20°C.

Prior to vulcanization the stocks were allowed to reach room temperature and then remilled on a cold mill to ensure redispersion of the ingredients. Stored vulcanized sheets were allowed to reattain ambient temperature and wiped with a clean dry cloth before experimental samples were taken from them.

The inhibition of maturation reactions in the vulcanized sheet by the cold storage process was assessed by determining the modulus at 100% extension of samples removed at weekly intervals. There was no detectable change over a period of eight weeks.

2.1.6. Vulcanization.

The natural rubber formulations (1-4), used for the correlation of the two techniques for determining C_1, were vulcanized in frame plate moulds preheated to the vulcanizing temperature ($140 \pm \frac{1}{2}$°C). The moulds, measuring 30.5 cm square were sprayed with a mould release agent, as were the 0.24 cm spacers. They were then loaded and returned to the steam heated presses for the vulcanization time of 120 mins ± 30 secs, after which time they were quenched, opened and the sheet removed. Samples used for the investigation of the effect of dimensions on compression modulus results were prepared in a stepped mould. This mould, being 15.25 cm square, had a cavity varying from 0.18 cm to 0.29 cm in three increments producing specimens of nominal thicknesses 0.18 cm, 0.25 cm and 0.29 cm. This sheet was cured in a steam heated press at 140 ± $\frac{1}{2}$°C for 6 hours.

The E.P.D.M. formulations A,B,C, and V were each vulcanized at 150°C, 170°C, 200°C and 240°C for 15 mins, 30 mins, 60 mins, 120 mins, and 240 mins, giving a total of twenty vulcanizates per formulation. Formulations N, E and R were vulcanized at 150°C and 170°C for each of the above times. Vulcanization was carried out in preheated frame sheet moulds (30.5 cm square) using a spacer 0.2 cm thick. Release agent was not used as it was found to produce staining. Cures at 150°C and 170°C took place in a steam heated press with temperature control of ± $\frac{1}{2}$°C. The higher cure temperatures required an electrical induction press which had a temperature control of ± 2°C. Long cure times were measured to ± 30 secs, whilst the shorter ones were measured to ± 10 secs. After the requisite times the moulds were quenched in cold water and the dried sheets stored at -20°C. When vulcanizing at higher temperatures, porosity became a problem and most vulcanizates exhibited the effect to some degree at 240°C. Visible degradation occurred around the edges of the sheets at 240°C after 240 min.

This took the form of surface discoloration and embrittlement and in extreme cases it made the removal of the vulcanizate from the mould difficult.

2.1.7. Continuous Measurement of Cure.

Samples of the compounded stock were vulcanized on the model L.S.D. Monsanto Rheometer fitted with micro dies[59] at temperatures of 150°C, 170°C and 200°C. In every case the rotor amplitude was 3°, a torque range of 100 inch pounds was selected and a preheat period of 30 secs. allowed before the commencement of recording. Since the upper temperature limit of the Monsanto Rheometer is 200°C, the cures at 240°C were followed using the Wallace Shawbury Curometer. The purpose of these cures was to estimate the time required to attain 80%, 90% and total cross-linking.

Plate 1 shows a general view of the Monsanto Rheometer and plate 2 a close up of the micro die and rotor. The Wallace Shawbury is shown in plate 3. Both instruments have been fully described in the literature.[60,61]

2.2. Sample Preparation.

2.2.1. Cutting Procedure.

To avoid the edge effects caused by the lower temperature associated with the edge of the press plattens, samples were always taken from the central portions of the very large test sheets (30.5 cm square).

For the C_1-tension determination, strips (0.46 cm x 15 cm) were punched from the sheets using a specially made cutter.

The test specimens for compression modulus determinations (nominally 0.5 cm square), however, were cut from the sheets using a surgical scalpel. This method was preferred because it avoided the concave edges produced by the punching operation.[62]

2.2.2. Sample Measurement.

All measurements of length were made using a vernier microscope reading to 0.001 cm. Weights were determined with an analytical balance with a sensitivity of ± 0.0001g.

For C_1 tension determination, A_o (the average cross-sectional area) was required. This was calculated from the weight, length and density of the sample. Density determination is discussed in section 2.3.4.

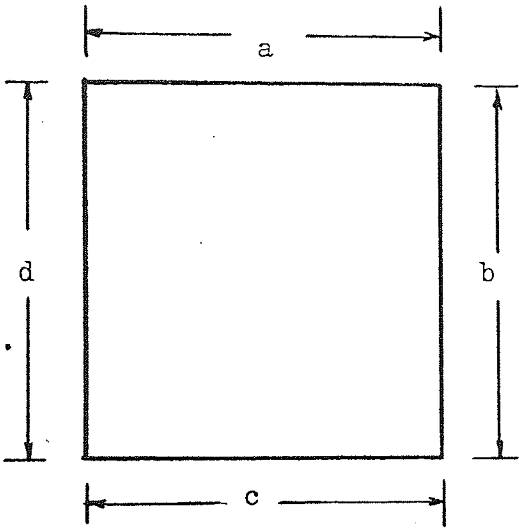
The values required for compression modulus determination were A_o, h_o (the initial height of the sample) and the sample weight (wtr). Wtr was determined as above, and h_o was obtained by averaging four readings of the height. A_o was computed from the values of length of the four sides of the specimen as shown in figure 4.

2.2.3. Physical Test Specimens.

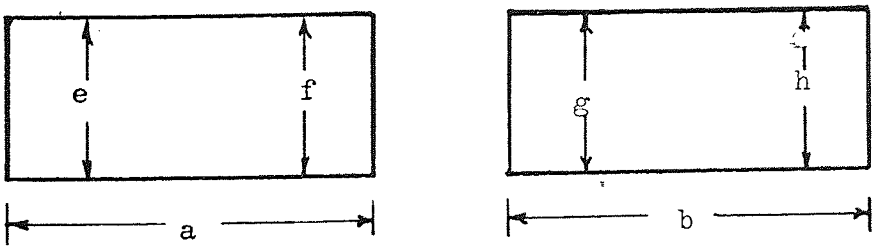
Samples for the determination of ultimate tensile strength, modulus at 100% extension and elongation at break were punched using a British Standard dumbell cutter (B.S. 903A4). The thickness and width of each test sample were obtained by averaging three values of each. Hardness tests were carried out on surplus material. Compression set samples were cut from the sheet using a 0.5 inch diameter cork borer.

FIGURE 4

Dimensions of a compression modulus sample.



$$A_o = \frac{(a + c)}{2} \cdot \frac{(b + d)}{2}$$



$$h_o = \frac{(e + f + g + h)}{4}$$

Measurements of height were made using a thickness gauge reading to 0.001 inches.

2.3. Swelling.

2.3.1. Experimental Techniques.

Compression modulus samples were weighed (wtr) and then completely immersed in solvent contained in weighing bottles with tightly fitting polythene caps.

These were placed in a thermostatically controlled water bath at $25 \pm \frac{1}{2}$ °C for a period in excess of the determined equilibrium swelling time, (2.3.3.), usually overnight. The swollen sample was blotted lightly to remove excess solvent before weighing in a tared bottle (wts). Deswelling took place in a vacuum oven at 50°C until a constant weight (wtd) was reached. Incremental swelling[63] was considered to have so little effect as to be ignored. The sophisticated technique for determining the swollen weight (wts) proposed by Ellis and Welding[64] was not used since the reproducibility of the results indicated a suitably low error.

The volume fraction of rubber hydrocarbon in the swollen network, V_r, was calculated according to the expression:

$$V_r = \frac{\text{Volume of rubber in the swollen sample}}{\text{Volume of rubber in the swollen sample + volume of swelling solvent.}}$$

$$= \frac{(wtr/\ denr)}{(wtr/\ denr) + (wts - wtr)\ /\ dens} \quad . \quad . \quad . \quad . \qquad (16)$$

Where denr and dens are the densities of the rubber network and the solvent respectively. A more accurate expression was obtained by using the deswollen weight, wtd, thus accounting for solvent removable material. This was used throughout this work.

$$V_r = \frac{(wtd/denr)}{(wtd/denr) + (wts - wtd) / dens} \quad . \quad . \qquad (17)$$

Extra network material (e.n.m.) was obtained using equation 18:

$$e.n.m. = wtr - wtd \; . \quad . \quad . \quad . \quad . \qquad (18)$$

2.3.2. Choice of Solvents.

The solvent selected had to produce a suitable value of V_r and have a reasonably short equilibrium swell time. As n-heptane was required in the probe work it was an obvious choice. A series of specimens of formulation B were swollen in various solvents in order to determine V_r. From these experimentally determined values, together with their respective equilibrium swelling times, n-heptane was chosen for the work with E.P.D.M.'s. The solvents investigated are listed below:

n-heptane
benzene
toluene
carbon tetrachloride
methyl ethyl ketone
tetra hydrofuran
decahydronaphthalene

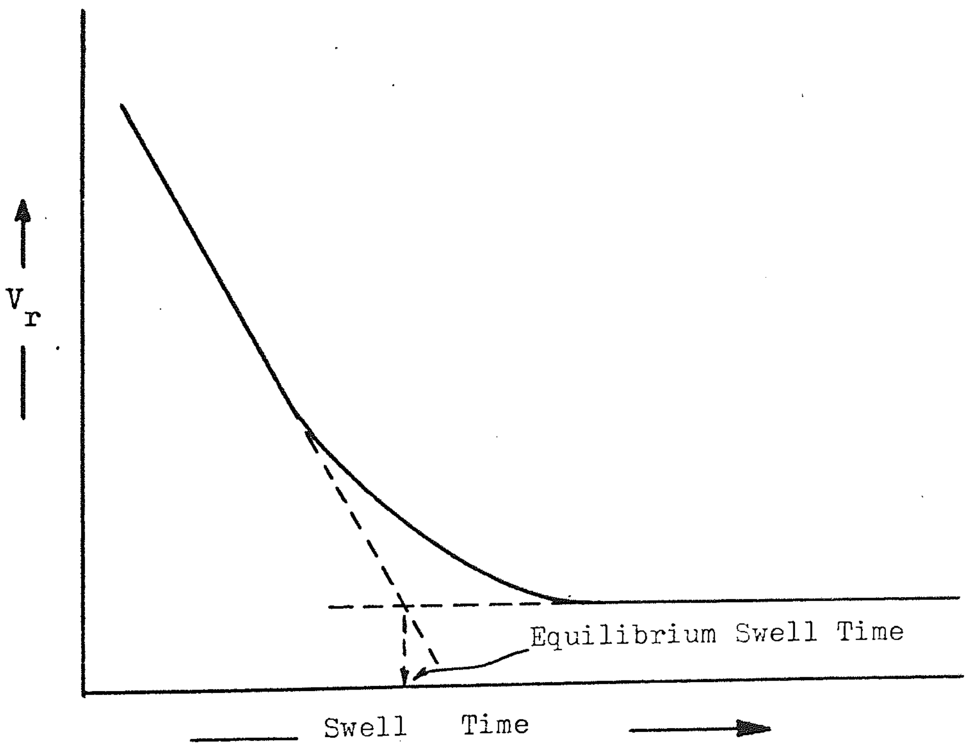
Benzene was used with natural rubber in order to conform with previous work.

2.3.3. Equilibrium Swelling Time.

Equilibrium swelling times were obtained by measuring the V_r values of a number of specimens which had been allowed to swell in the chosen solvent at 25°C for a series of times. The intersection of the extrapolated linear portions of the V_r vs. time curves (see figure 5) was taken as the minimum time required under these conditions to reach swelling equilibrium.

FIGURE 5

Determination of Equilibrium Swelling Time.



2.3.4. Determination of Physical Constants.

The densities of elastomer vulcanizates were determined using Archimedes Principle. The water bath in which measurements were taken was maintained at 25°C. The densities of the solvents were obtained using specific gravity bottles. Values of V_o (the molar volume) for each solvent were calculated from the experimentally determined density and the molecular weight.

2.4. Tension Stress Strain.

The apparatus and method described below were devised at the Natural Rubber Producers Research Association (N.R.P.R.A.) by Dr. H.W. Greensmith.[19]

2.4.1. Apparatus.

The apparatus shown in plates 4 and 5 was built to specifications provided by N.R.P.R.A. The function of the equipment was to determine the loads (f) required to maintain a series of fixed extension ratios (λ) upon the test sample. This was carried out by clamping the sample between two grips, the upper one being movable, the lower one being fixed and in circuit with a small neon light, making it possible to determine a zero or null position. The upper clamp could be moved to a number of fixed points or stations which corresponded to integral steps of $1/\lambda$ of 0.05 over the range $\lambda = 1.05$ to 5. Fixed points covering grip separation of 9.950 cm to 10.000 cm were available for determining the initial length (l_o) of the specimen. A weight pan was attached to the lower grip for counterbalancing the tension in the test piece.

For correlation with compression modulus results, determinations should be carried out at 25°C, however, as the laboratory temperature was noted, the expression quoted by Bristow and Porter[65] was used (equation 19) to convert the result to a value at 25°C.

$$C_{1(25^{\circ}C)} = \frac{C_{1(T^{\circ}C)} \times 298}{273 + T} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (19)$$

2.4.3. Sample Preparation.

The sample prepared as described earlier (2.2.1.) was cut to a length of 12 cm and from the surplus a 1 cm length was retained.

2.4.4. Test Sequence.

Calibration of the instrument was carried out by setting the right hand (graduated) chain dial to zero and placing the 1 cm length of sample on to the weight pan. The null point was then found using the left hand chain dial. The small length of rubber was removed. The grips were removed from their clamps and the test specimen fixed in them. A jig (plate 6) was used to ensure the correct alignment of the sample in the grips. This produced an l_o value of approximately 10.00 cm. To avoid sample deformation the screws were tightened only with the fingers. The exact length of rubber between the clamps was determined by extending the sample over the range 9.950 cm. to 10.000 cm. A strict time schedule was observed; successive extensions were made at sixty second intervals, the loads being read only after the extension had been maintained for 55 seconds.

Before the main determination was carried out, the sample was relaxed for a period of fifteen minutes. It was then extended over the range $\lambda = 1.05$ to 5. A set time sequence was again followed, in this case successive extensions were made at intervals of two minutes, the loads producing the null points being taken one minute fifty seconds after each extension.

All determinations were carried out in triplicate. The strict timing of the tests minimised relaxation effects.

2.4.5. Treatment of Data.

l_o was determined from a plot of clamp separation against the load required to produce the null point. The curve was extrapolated to zero load to produce the value of l_o (figure 6).

C_1 was calculated by the graphical method already described (1.4.3.) i.e. from a plot of $f/(\lambda - \lambda^{-2})$ against $1/\lambda$. Values of $(\lambda - \lambda^{-2})$ and $(1/\lambda)$ were obtained from the tables prepared by A.J. Lovett[66]. These tables, together with the various clamp separations, are presented in appendix I.

2.5. Compression Modulus.

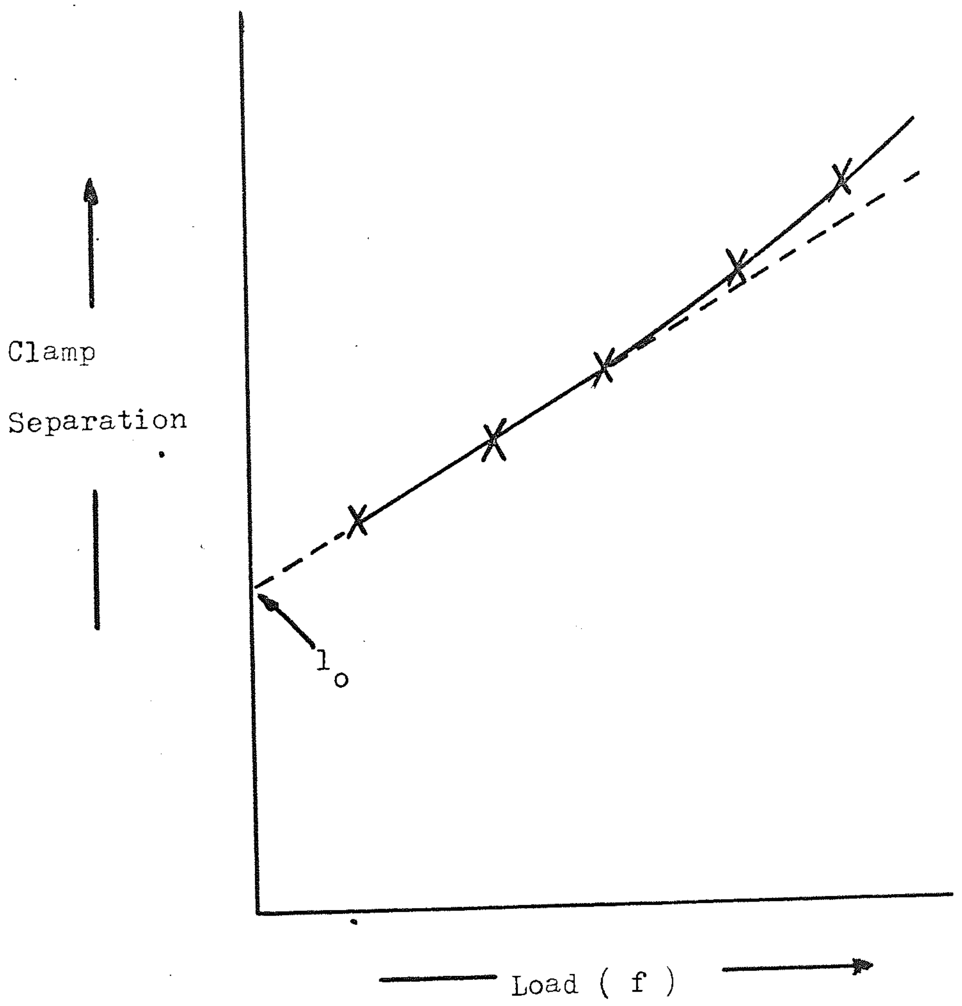
The technique to be used was based on the micro method described by D.A. Smith.[21] Tension techniques were unsuitable for reasons already mentioned and the micro compression method represented a much more convenient and rapid determination.

2.5.1. Apparatus.

The apparatus marketed under the name "Wallace Smith Reticulometer" was produced by W.H. Wallace of Croydon.

FIGURE 6.

l_o determination for C_1 tension experiments.



Plates 7 and 8 show a general view and detail of the compression head and solvent pot respectively. A line diagram of the more important features is shown as figure 7. It comprised a Wallace rubber micro hardness tester[67] with a wedge factor of 6:1 modified in the following respects:

a) the I.R.H.D. dial guage was replaced by a dial micrometer graduated in 0.01 mm dimensions.

b) a jacketed reticulometer test cup was substituted for the flat base of the test bed and a flat circular stainless steel disc (1.9 cm diameter) took the place of the indenter.

c) a larger weight pan was fitted.

A source of thermostatted water at the test temperature was required, together with a means of circulating it through the reticulometer pot.

2.5.2. Experimental Conditions.

The pot was filled with solvent before testing and allowed to equilibrate to the test temperature (25°C). Loss of solvent by evaporation was overcome by periodic addition of fresh solvent also at 25°C.

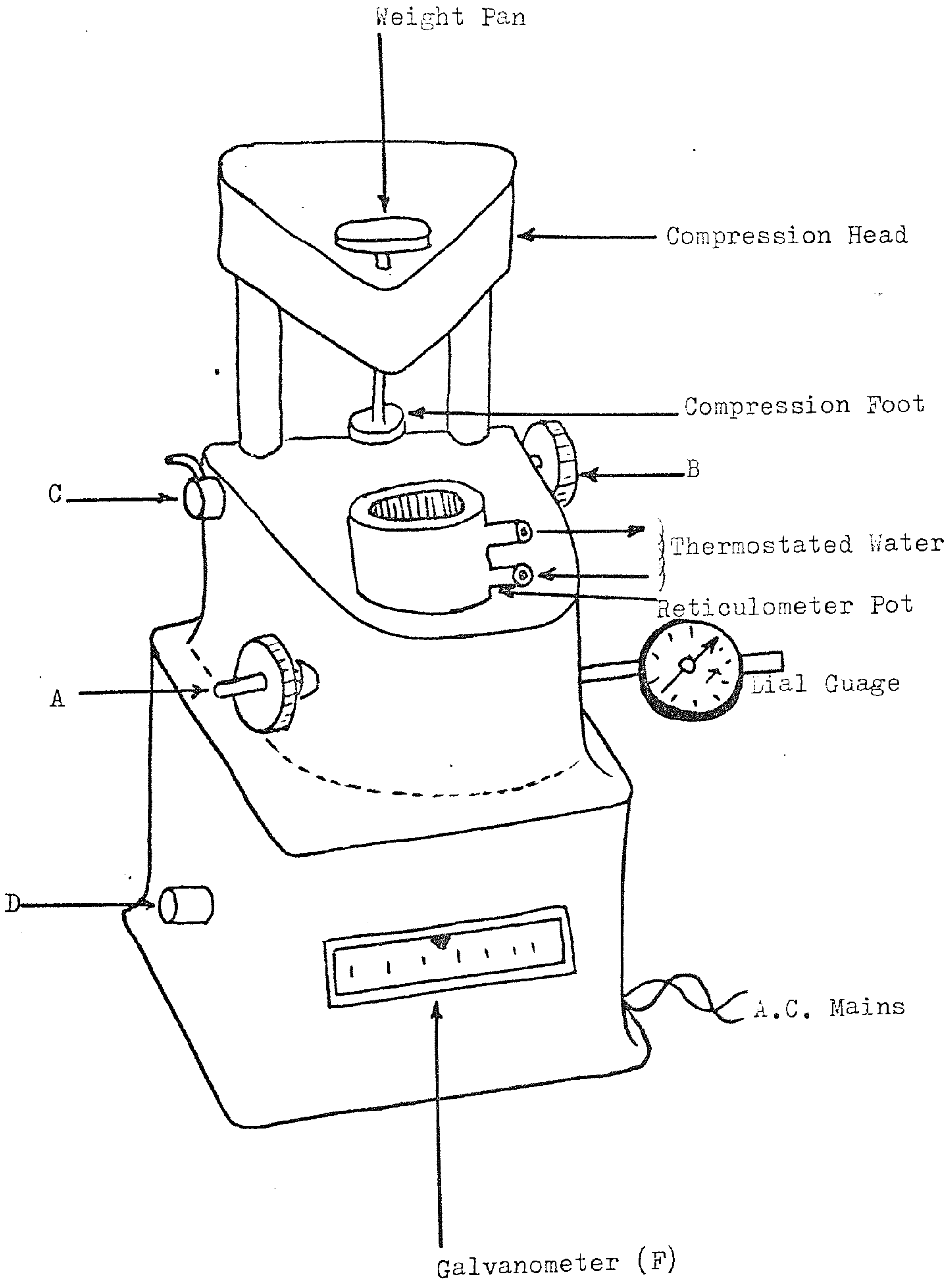
2.5.3. Sample Preparation.

This has been described in sections 2.2.1. and 2.2.2. Throughout the test sequence samples were kept in individual labelled bottles.

2.5.4. Test Sequence.

FIGURE 7.

Line Diagram of the Important Features of the Reticulometer.



After determining the swollen weight (wts) the sample was placed centrally in the reticulometer pot. Using wheel B the compression head was lowered until immersed, at which point the dial guage was set to zero (wheel A) as was the centre reading galvanometer (F) using wheel D. The head was lowered until the foot just made contact with the sample, when it was locked in position with the lever C. The sample was prestressed by the addition of a load in excess of the proposed experimental range for a period of twenty seconds. After a relaxation period of five minutes, a dead load weight was added to the weight pan for sixty seconds and the first experimental load was then placed on the pan causing a deflection on the galvanometer F. The wheel A was turned, raising the pot, until the galvanometer returned to zero. The stop watch was then started, the load removed and the reading on the dial guage noted before it was returned to zero by means of wheel A. After twenty seconds the dead load was returned to the pan and the cycle repeated for each experimental load. A typical series of load values is presented in figure 8.

FIGURE 8.

Typical loads for Compression Modulus Determinations.

Excess Load : 500 g

Dead Load : 25 g

Experimental Loads : 50 g, 100 g, 150 g, 200 g, 250 g, 300 g,
300 g, 250 g, 200 g, 150 g, 100 g, 50 g.

The number of experimental loads used in a determination varies greatly. Smith, in his early work, used 30[21] but with his more refined approximation used only 12[22]; Cluff et al[20] used 10 whilst Thomas et al[23,24] used only one. At Aston, various workers have used between 10[68] and 80[69] depending on experimental conditions. For this work most determinations were carried out using 8 readings.

All determination were carried out in triplicate.

2.5.5. Treatment of Data.

Data for this technique were in the form of a series of loads (f) and the corresponding changes in sample height (Δh). These could be analysed by any or all of the methods indicated in section 1.2.4. A plot of load (f) against Δh, or a function of Δh, produced a straight line, the slope of which was proportional to the C_1 constant.

2.6. Standardization of Compression Modulus Conditions.

Several points regarding the general applicability of the micro compression technique have been raised[70,25] Those listed below were investigated before commencing the characterization studies:

a) Effect of V_r on values of C_1 obtained.
b) Effect of sample dimensions on values of C_1 obtained.
c) Maintenance of sample shape during compression.

2.6.1. Effect of V_r on values of C_1 obtained.

Formulation 3 (natural rubber - dicumyl peroxide) was chosen for this work. It was cured at 140 ±½°C for six hours and ten minutes. Triplicate sets of samples (0.4 cm square) were immersed in each of the following solvents at 25°C:

Benzene
decahydronaphthalene
tetrahydrofuran
n-heptane
toluene
methylethylketone

The solvent in which the sample was swollen was used in the reticulometer pot during the compression modulus determination. A series of values of C_1 and V_r were thus obtained. Previous figures for the upper limiting value of V_r were 0.2 or less[21] and 0.25[71], however, V_r values of up to 0.33 have been used with success.[22,25] These are reported in sections 3.2.2. and 3.3.

2.6.2. Effect of Sample Dimensions on Values of C_1 Determined.

A sample of formulation 3 was vulcanized for 6 hours 10 minutes at $140\pm\frac{1}{2}^{\circ}C$ in a stepped mould which produced a moulding of three different sections; 0.18 cm, 0.25 cm, and 0.29 cm. This extended cure time was that required to reach the plateau level as determined in the Monsanto Rheometer. Twelve samples were cut from each section, comprising of four different cross-sectional areas in triplicate. This resulted in twelve combinations of A_o and h_o. These samples were swollen at $25^{\circ}C$ in benzene for a period in excess of the equilibrium swelling time. C_1 was then determined by compression modulus. Three C_1 tension samples were cut from the surplus and C_1 determined by this technique (section 2.4.)

The results gave a series of values of C_1 corresponding to a combination of A_o and h_o, and are presented in section 3.2.3.

2.6.3. Sample Deformation.

It was essential that the specimen maintained its rectangular section throughout the test and that no "barrelling" occurred, since this would make the calculation of the load bearing cross-sectional area difficult. Using the larger test pieces[22,24] this point could be checked visually, a point made by Moore[72], however, the use of the reticulometer precluded a visual check.

samples in the reticulometer. A simple apparatus (plate 9) was devised with a balance arm capable of compressing a sample between microscope slides, whilst allowing continuous visible checks to be made. The whole apparatus was immersed in a bath of solvent.

2.6.4. Extent of Compression.

Much discussion has taken place regarding the percentage compression which should be used. This depended to some extent on the mathematical approximations used in analysing the data. Use of the simple expression of Cluff et al[20] required a maximum compression of 5%,[22] though use of a more exact approximation increased this value to 15%.[21] Thomas et al[23,24] when examining E.P.M.'s stated that compression should not be below 4%, but values as low as 2% have been used without noting the gross errors that he suggested (section 3.2.3.).

2.7. Comparison of the Tension and Compression Techniques.

Formulations 1 - 4 were milled to a Wallace plasticity number of 20±2 (molecular weight range 177,500 to 197,000) prior to vulcanizing at 140±½°C for two hours as previously described. From each sheet were taken three C_1 tension samples and three compression modulus samples. The values of C_1 were then determined in the manners previously described. Values of C_1 tension for formulation 4 could not be obtained since the samples proved to be too brittle for clamping. The results are presented in section 3.3.

2.8. Use of the propane-2-thiol/Piperidine Reagent.

The probe solution consisted of a solution of propane-2-thiol and piperidine in n-heptane. The n-heptane used was the same laboratory grade as that used for swelling. The propane-2-thiol, obtained from B.D.H. Ltd., was checked for purity by gas chromatographic means. Due to its unpleasant odour and ease of oxidation it was purchased in small quantities and hence the use of G.L.C. became a standard procedure. (All samples were above 95% purity, many of them assaying 99%) They were stored at -20°C. Piperidine (Robinson Bros. Ltd.) was distilled under nitrogen at reduced pressure in two litre portions as required, and stored under an atmosphere of "white spot" nitrogen in the dark.

2.8.2. Sample Preparation.

Samples were prepared as described in sections 2.2.1. and 2.2.2. i.e. as for compression modulus.

2.8.3. Preparation and Use of the Probe Solution.

The solution was prepared in a vessel so designed that an atmosphere of nitrogen could be maintained in it. A three necked, round bottomed flask fitted with two gas taps and a stopper was used for this purpose. The vessel was well flushed out with "white spot" nitrogen and 300 ml of n-heptane introduced. To the solvent were added 12.84 ml of the piperidine and 12.21 ml of the propane-2-thiol before the flask was sealed under nitrogen. The vessel used for probe treatment (figure 9) was well flushed out with "white spot" nitrogen before the test samples were introduced. It was then half filled with probe solution and sealed under nitrogen. During the requisite reaction time it was shaken occasionally. All tests involving probe solutions were conducted in a fume cupboard. After the

reaction time had elapsed, the samples were returned to their labelled bottles and the probe removed by heating at 50°C for 48 hours in a vacuum oven. Some workers[74] recommend that on removal from the probe solution the samples be washed with 30-40 pet.ether before being placed in the vacuum oven, however, Campbell[75] states that this is purely a matter of choice.
An alternative technique,[74] developed by Russell (N.R.P.R.A.), involved the preswelling of the samples before introducing them into the probe.

2.8.4. Probe Reaction Time.

The probe reacts by the mechanism depicted in fig 10, by cleaving poly-sulphidic linkages. There is, however, a slower reaction between the probe and di-sulphide links (fig. 11). The extent of the slower reaction may be limited by careful choice of reaction time. With natural rubber vulcanizates, for example, a reaction time of two hours at 25°C will cleave 98% of poly-sulphidic links but only 2% of di-sulphidic[76]. The optimum reaction time for E.P.D.M.'s was determined by reacting a series of samples for various times with the probe solution. The V_r values of these samples were then determined in the normal way and plotted against reaction time (fig. 12).
The optimum reaction time was taken as the intercept of the straight portions of the curve, relating to the fast and slow reactions. The results are presented in section 3.2.4.

FIGURE 9.

Vessel for propane-2-thiol/Piperidine Reactions.

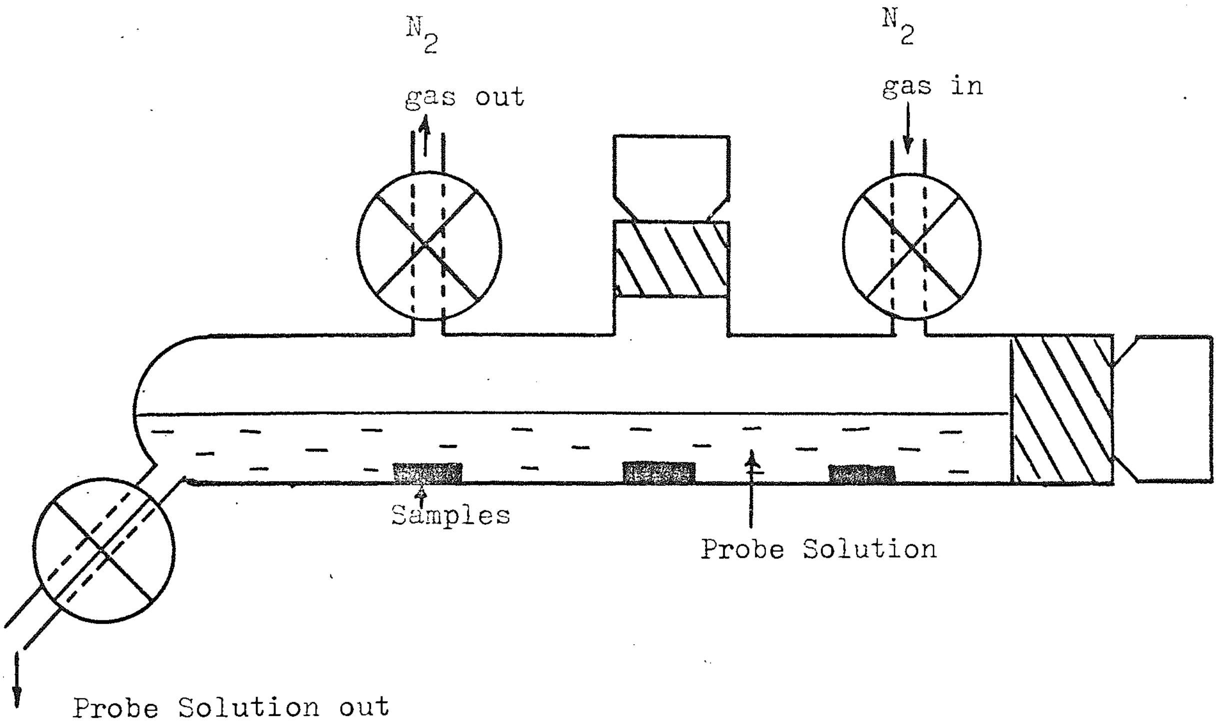


FIGURE 10.

Reaction Mechanism for Propan-2-thiol/Piperidine with Polysulphide Cross-links.

Pr^i :: $(CH_3)_2CH-$

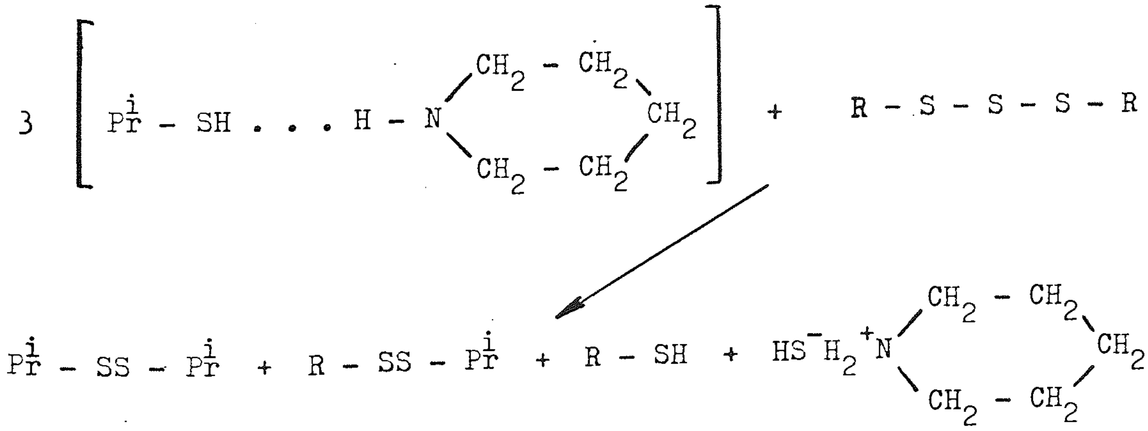
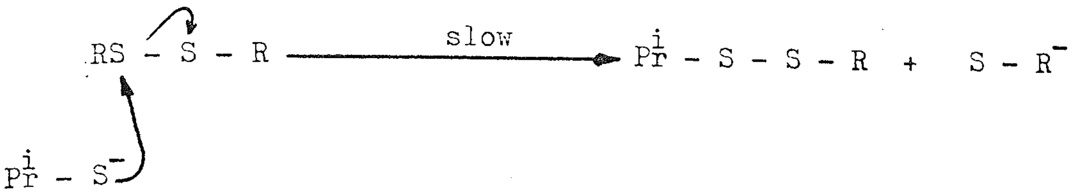


FIGURE 11.

Mechanism for the Slow Reaction Between Propane-2-thiol/Piperidine and Di-sulphide Cross-links.

$Pr^i :: (CH_3)_2\ CH-$

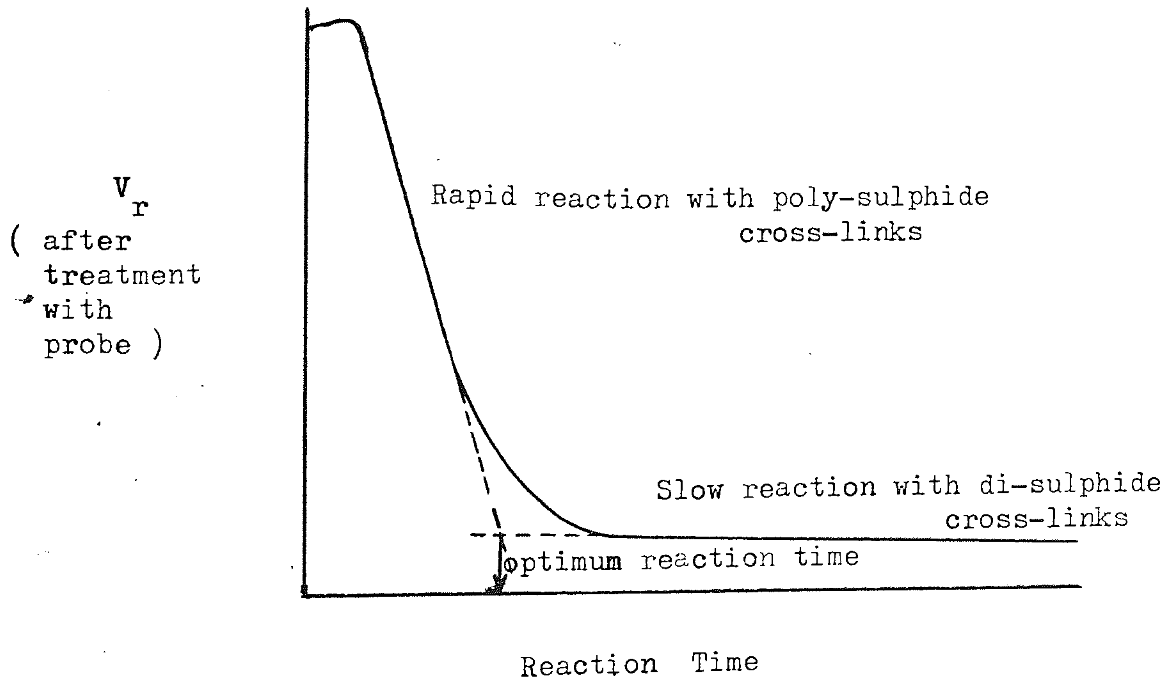


$$RS - S - R \xrightarrow{slow} Pr^i - S - S - R + S - R^-$$

$Pr^i - S^-$

FIGURE 12.

Determination of the Optimum Reaction time for Propane-2-thiol/ Piperidine Probe.



2.8.5. Post Treatment.

After treatment with, and removal of the chemical probe solution, the samples were swollen to equilibrium in n-heptane and their C_1 values determined by compression modulus, (Section 2.5.4.)

2.8.6. Destruction of the Probe Solution.

Two methods were available for the destruction of used chemical probe solution. The first involved addition to an acidified solution of aqueous potassium dichromate; the second, addition to an ammoniacal solution of copper sulphate. The latter was preferred as the reaction products were comparatively odourless.

Excess probe solution was kept for no longer than five days, after which time it was destroyed.

2.9. Use of the n-hexane Thiol/Piperidine Probe.

2.9.1. Reagents Used.

The probe solution consisted of a mixture of n-hexane thiol and piperidine. The piperidine used has been described in section 2.8.1. The n-hexane thiol was purchased as required from Eastman Chemicals Ltd. and assayed before use by G.L.C. All samples were found to be of at least 98% purity.

2.9.2. Sample Preparation.

Preparation of samples has been discussed previously in sections 2.2.1. and 2.2.2.

2.9.3. Preparation and Use of the Probe Solution.

The vessel used (figure 13) consisted of an H-tube, one arm of which terminated in a vacuum tap and cone, the other with a socket and suitable stopper. 10.0 ml of piperidine was introduced with the samples into arm A, and 2.1 ml of n-hexane thiol into arm B. The stopper was then replaced and the vessel evacuated. The reagents were degassed twice by freezing with liquid nitrogen before being mixed. The degassing was repeated once after mixing and the vessel sealed under vacuum (0.1 to 0.01 Torr), before being placed in a water bath (25°C) for the predetermined reaction time. After that time had elapsed the samples were placed in individual bottles and all traces of the thiol and piperidine removed by heating for twenty-four hours in a vacuum oven at 50°C.

2.9.4. Probe Reaction Time.

Both di- and poly-sulphidic cross-links were cleaved by the reagent. The reaction was chemically similar to that of the propane-2-thiol /piperidine probe. The increased reactivity was caused by an increase in the nucleophilicity of the alkane thiol ion, which in turn was due to a change in the electron donating nature of the alkyl grouping (figure 14). The optimum reaction time was determined in the manner already described for the propane-2-thiol/piperidine probe (section 2.8.4.).

2.9.5. Post Treatment.

As for the propane-2-thiol/piperidine probed samples (section 2.8.5.).

FIGURE 13

Vessel for the n-hexane thiol/piperidine treatment.

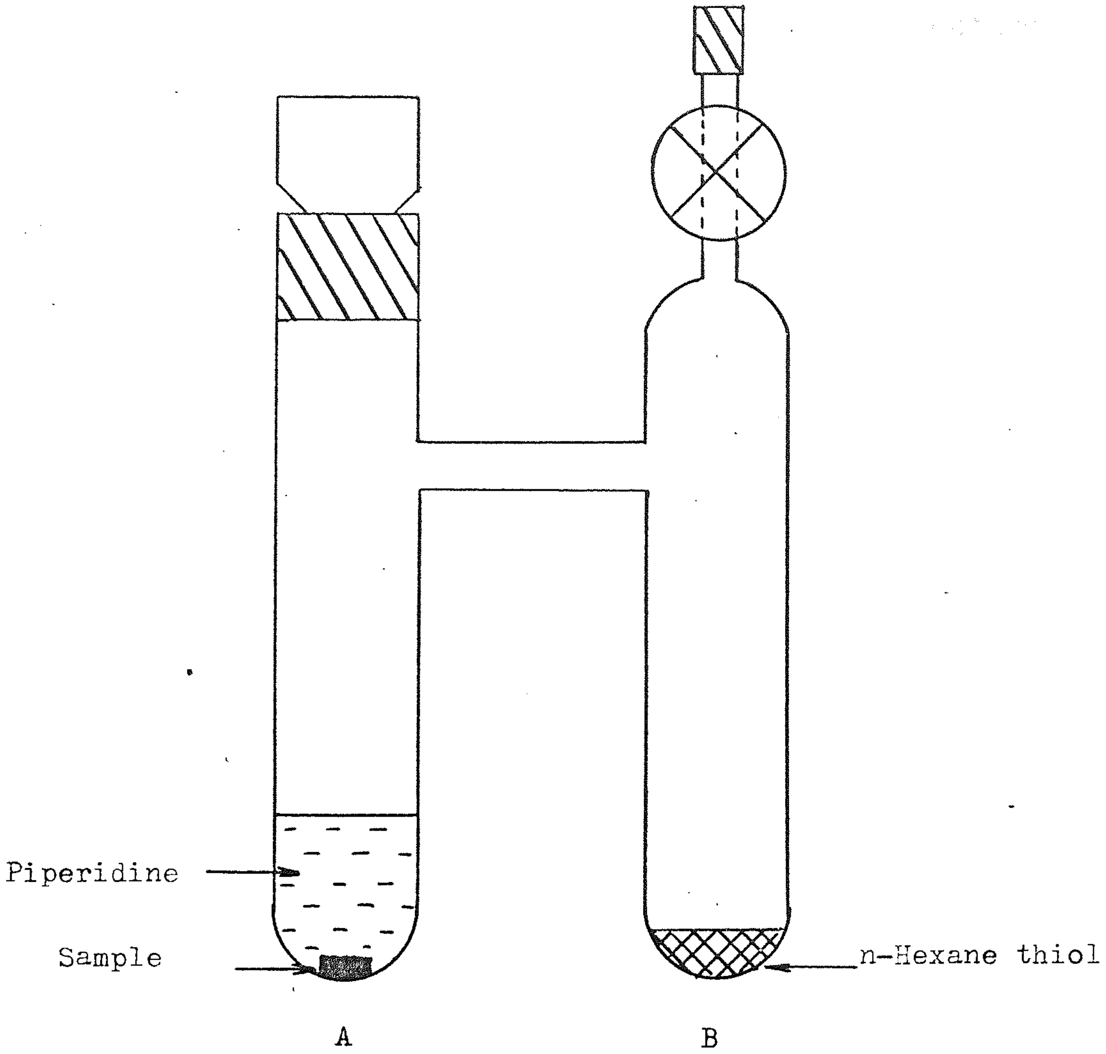
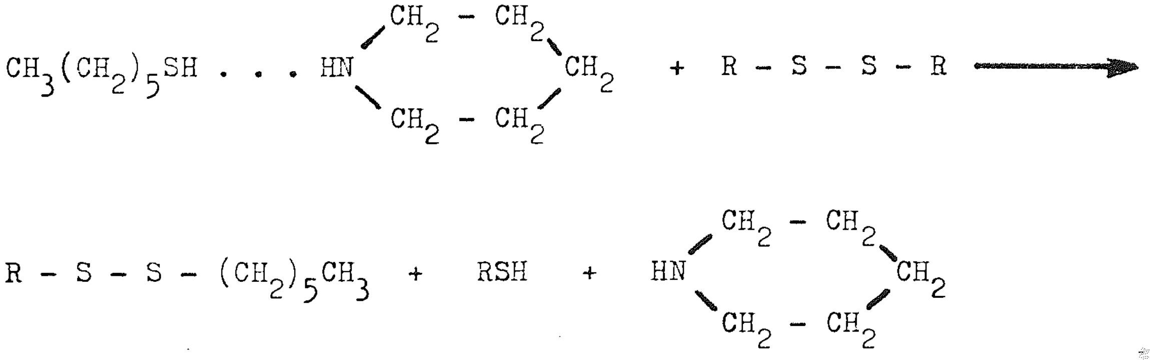


FIGURE 14

Reaction mechanism between n-hexane thiol/piperidine and $-S_{x \geqslant 2}-$ cross-links.



2.9.6. Destruction of Probe Solution.

As for propane-2-thiol/piperidine probe solution (section 2.8.6.).

2.10 Physical Tests.

2.10.1. Ultimate Tensile Strength, Elongation at Break and Modulus at 100% Extension.

All these determinations were made on a single test piece using a Tensometer type 'E' instrument. The preparation of the specimens has been described earlier (section 2.2.3.). The results represent the average values obtained from six individual tests. In cases where restricted elongation prohibited modulus at 100% extension being measured, modulus at 50% extension was used. Figure 15 shows a typical stress strain curve and indicates the analytical technique used.

2.10.2. Hardness.

Hardness in I.R.H.D. was measured using a Wallace Hardness tester (standard foot test). Five readings of hardness were taken for each vulcanizate, the final result representing an average of them.

2.10.3. Compression Set.

Sample preparation has been described in section 2.2.3. Using the British Standard (B.S. 903 pt. 18) constant deflection method, samples were compressed to 60% of their initial height (h_0) for 24 hours at 70°C. After they had been relaxed for one hour their height (h_c) was measured. Compression set was calculated from equation 20. The determinations were carried out in triplicate and the average taken.

$$\text{Compression Set} = \frac{h_o - h_c}{h_c} \times 100\% \quad . \quad . \quad . \quad . \qquad (20)$$

FIGURE 15

Typical Stress-strain Curve and Analytical Technique.

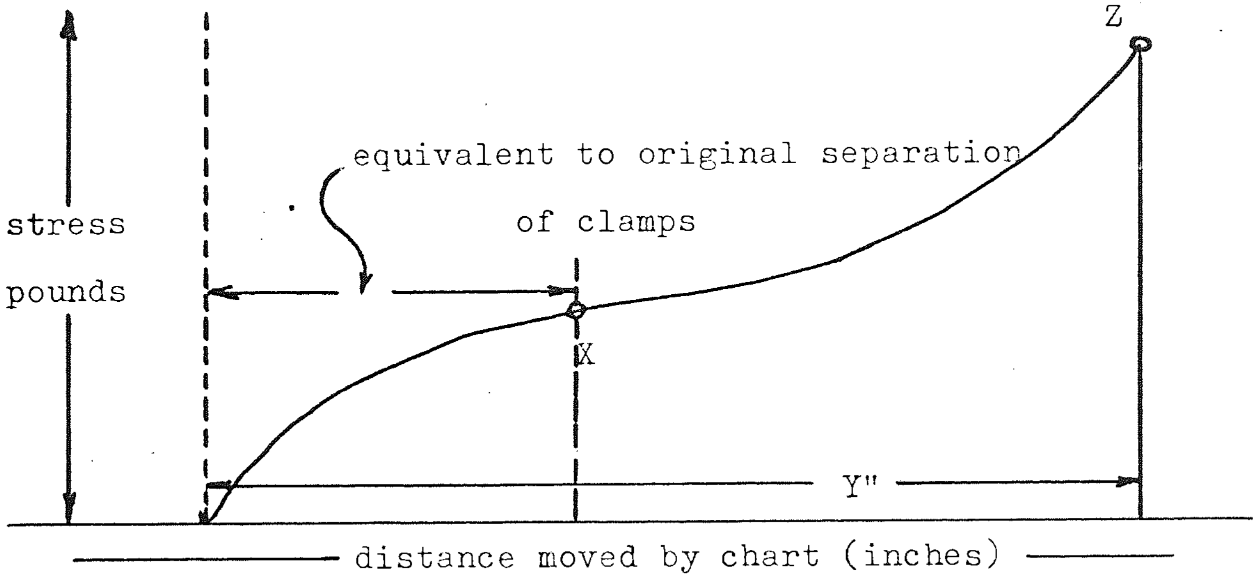


chart speed = crosshead speed.

$$\text{Ultimate Tensile Strength} = \frac{Z}{10} \times \text{full scale deflection}/A_o \text{ p.s.i.}$$

% Elongation at Break = (Y/original separation of clamps) x 100%

$$\text{Modulus at 100\% extension} = \frac{X}{10} \times \text{full scale deflection}/A_o \text{ p.s.i.}$$

3. RESULTS.

3.1. Use of Computer.

The time required for hand calculations would have been so excessive that it was decided to utilise the computer. A number of programs were written over the period of research, the one finally used being written in Algol 60[77] and run on an I.C.L. 1900 series computer. From the experimental data the program calculated C_1 by the various methods available. Graph plotting was eliminated by the use of the method of least squares. $M_{c.phys}$, and cross-link density (C.L.D.) were derived from the calculated value of C_1. The program, together with the specimen data and print out, is presented in appendix 2.

3.2. Standardization of Techniques.

3.2.1. Equilibrium Swelling Time and V_r.

Benzene was the solvent chosen for the work with natural rubber in order that the results obtained could be compared with those of previous workers.[21] Using samples of the size described in 2.2.1., equilibrium swelling of natural rubber in benzene was attained in about two hours. The solvent chosen for the characterization work with E.P.D.M. was n-heptane, since it was to be used for the probe work, had a suitable V_r value (0.24) and swelling time (5 hours), and was readily available.

3.2.2. Effect of V_r on results of Compression Technique.

Using a variety of solvents, a series of values of V_r and C_1

was obtained for a single natural rubber network. The solvents used and the resultant values of C_1 and V_r are presented in Table 9. The results are depicted in Graph 5. Solvents numbered 1 - 5 having V_r values in the range 0.22 to 0.33 produced values of C_1 in the order 2.76 ± 0.4, an error of ± 14%. The error was much greater than either the average experimental error found for C_1 determination (±3.8%) or the variation between C_1 tension values and C_1 compression values (see section 3.3.).

From the results it appeared that the value of V_r would affect the results which made solvent choice an important factor, however, a change in V_r caused by changes in cross-link density did not have the same effect (3.2.3.). The high values of V_r and C_1 obtained with methyl ethyl ketone (no. 6) were due to the fact that the solvent was polar in nature and thus somewhat incompatible with the base polymer.

The choice of solvent which would yield a value of V_r giving the correct value of C_1 was difficult to make. The value of C_1 (extension) for the vulcanizate was $2.35 \pm 0.5\%$ $g.cm^{-2} \times 10^{-3}$, and one solution was therefore to select the solvent which gave this result in compression.

Neither technique was absolute so in the absence of any new technique the problem remained unsolved. For this work it was decided to use comparison with C_1 tension to estimate the suitability of any solvent.

3.2.3. Effect of Sample Dimensions on Compression Modulus Determinations.

C_1 was calculated for specimens of varying dimensions prepared

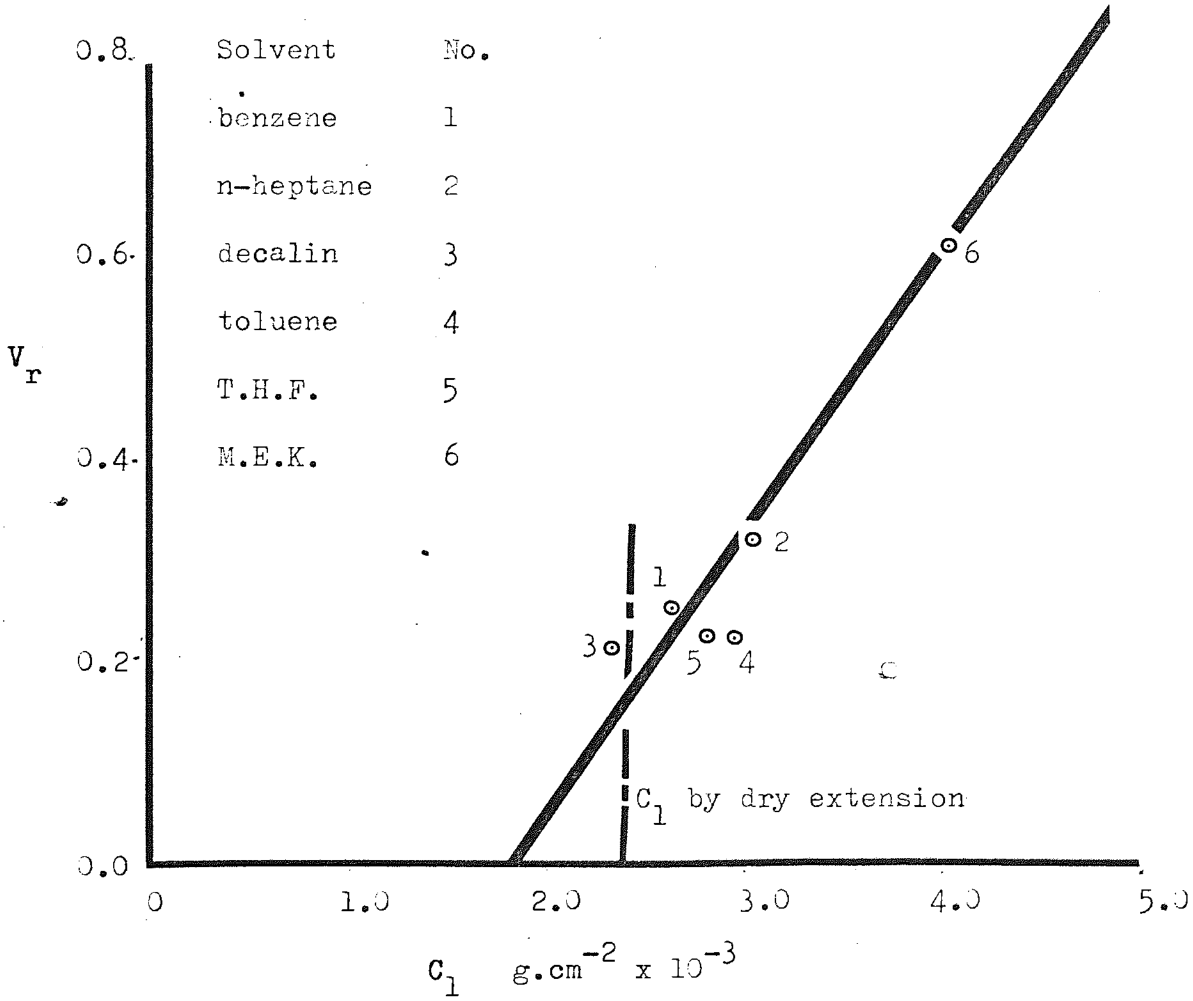
TABLE 9

Effect of V_r on C_1 as determined by Compression Modulus.

Solvent	No.	V_r	C_1 g.cm^{-2} x 10^{-3}
benzene	1	0.235	2.63
n-heptane	2	0.332	3.10
decalin	3	0.223	2.31
toluene	4	0.234	2.95
T.H.F.	5	0.234	2.80
M.E.K.	6	0.616	4.01

GRAPH 5.

V_r against C_1 as determined by Compression Modulus



as previously described (2.6.2.). Values of A_o used were approximately 0.13 cm^2, 0.23 cm^2, 0.42 cm^2 and 0.62 cm^2 and of h_o, 0.18 cm, 0.25 cm and 0.29 cm. The V_r value for all these samples was found to be 0.245 ± 3%. A summary of the values of C_1 (including those by stress strain) is presented in Table 10. The variation of C_1, with sample dimensions, is depicted in graphs 6 and 7. C_1 was found to be 2.56 ± 6%, the variation between individual sets being ± 6.4%. Thus it can be concluded that dimensions of the specimen did not effect the estimate of C_1 obtained using the compression modulus technique. C_1 obtained by dry tension was 2.35 ± 0.5% (max) which indicated that the compression technique produced results higher by 8.5%, which was approximately equal to the variations found by Loan[71] and Smith.[21] The extent of compression was dictated by the cross-link density of the material, the maximum and minimum used being 20% and 2%.

3.2.4. Determination of Optimum Reaction Times for the Chemical Probes.

The results are in the form of a series of V_r values obtained for samples after treatment with the probes for various times (t) (2.8.4. and 2.9.4.). The data for the propane-2-thiol/piperidine probe and the n-hexane thiol/piperidine probe is presented in graphs 8 and 9.

The optimum times for the probes, when used with E.P.D.M. vulcanizates were 5 hours thirty five minutes for the propane 2-thiol/piperidine reagent and forty eight hours for the n-hexane thiol/piperidine probe, the latter was the same time as that required for natural rubber. The reaction times were for the conditions described in sections 2.8.3. and 2.9.3.

TABLE 10

Values of C_1 Measured by Compression Modulus for Samples of Varying Dimensions.

A_o cm^2 / h_o cm	0.13	0.23	0.42	0.62
0.18	2.41	2.71	2.64	2.48
0.25	2.69	-	2.40	2.48
0.29	2.53	2.61	2.64	2.53

C_1 measured in g.cm^{-2} x 10^{-3}

C_1 (dry tension) : 2.35 ± 0.5% g.cm^{-2} x 10^{-3}

3.3. Comparison of C_1 by various techniques.

By use of the techniques of compression modulus and dry extension stress strain, the C_1 constants for a series of natural rubber vulcanizates (formulations 1 - 4) were determined. Table 11 shows the peroxide loading, experimentally determined densities, V_r values and values of C_1 obtained by each technique.

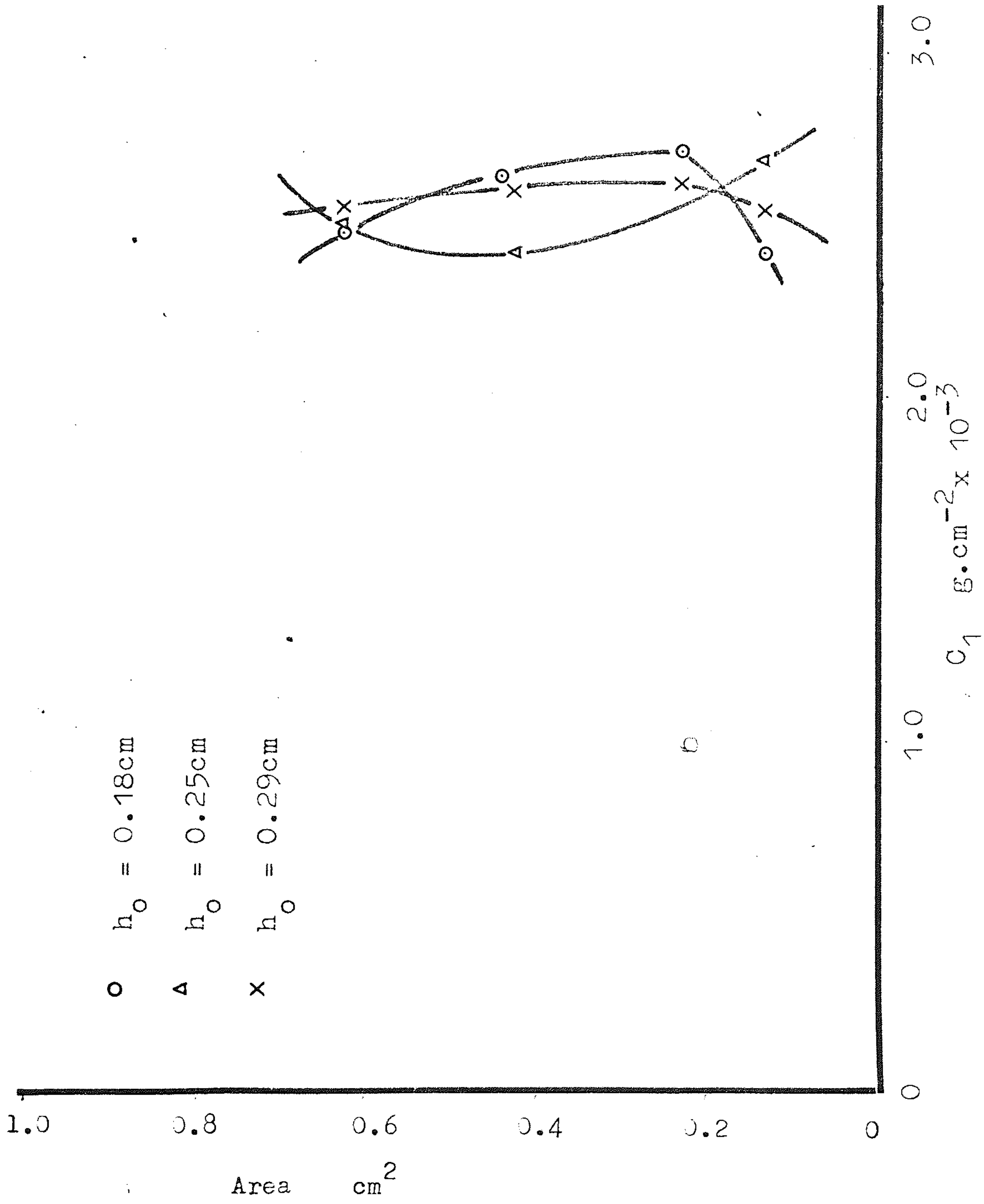
The C_1 tension values were corrected to 25°C[65] and the C_1 compression modulus figure was calculated by the Kay Moore Thomas[24] equation. Each of the experimental results represented the mean of a triplicate set. Average errors are presented at the foot of each column. These figures are shown diagramatically in graph 10 where C_1 tension was plotted against C_1 compression. The results calculated from the compression modulus data by all of the treatments mentioned earlier are presented in Table 12. Although the difference in numerical values increased with increasing C_1 value, the percentage variation decreased.

GRAPH 6.

Effect of Sample Area on Compression Modulus Results.

Sample Area against C_1 from Compression Modulus

(h_o being constant)

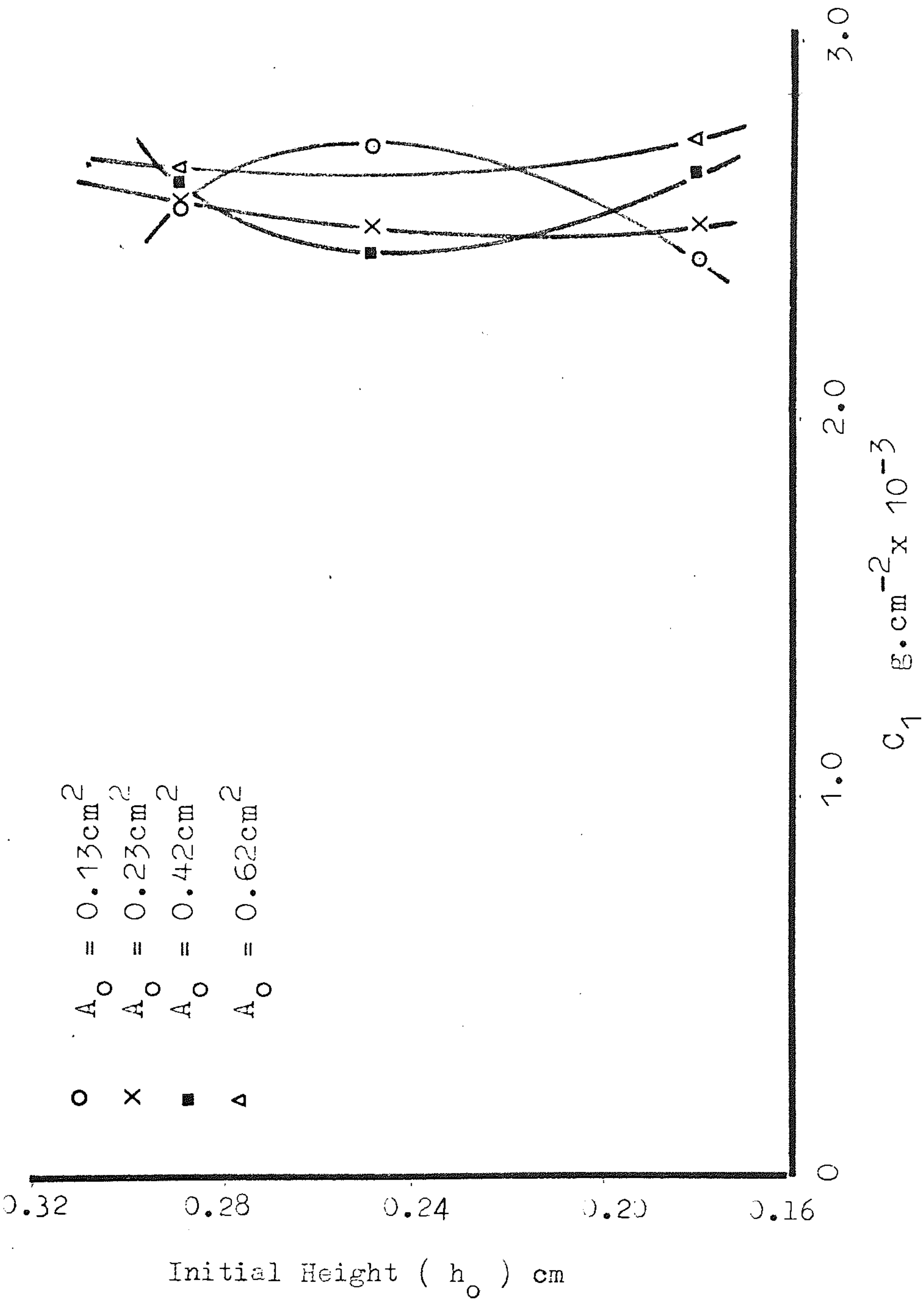


GRAPH 7.

Effect of Initial Height of Sample on Compression Modulus Results

Initial height of Sample (h_o) against C_1 from Compression Modulus

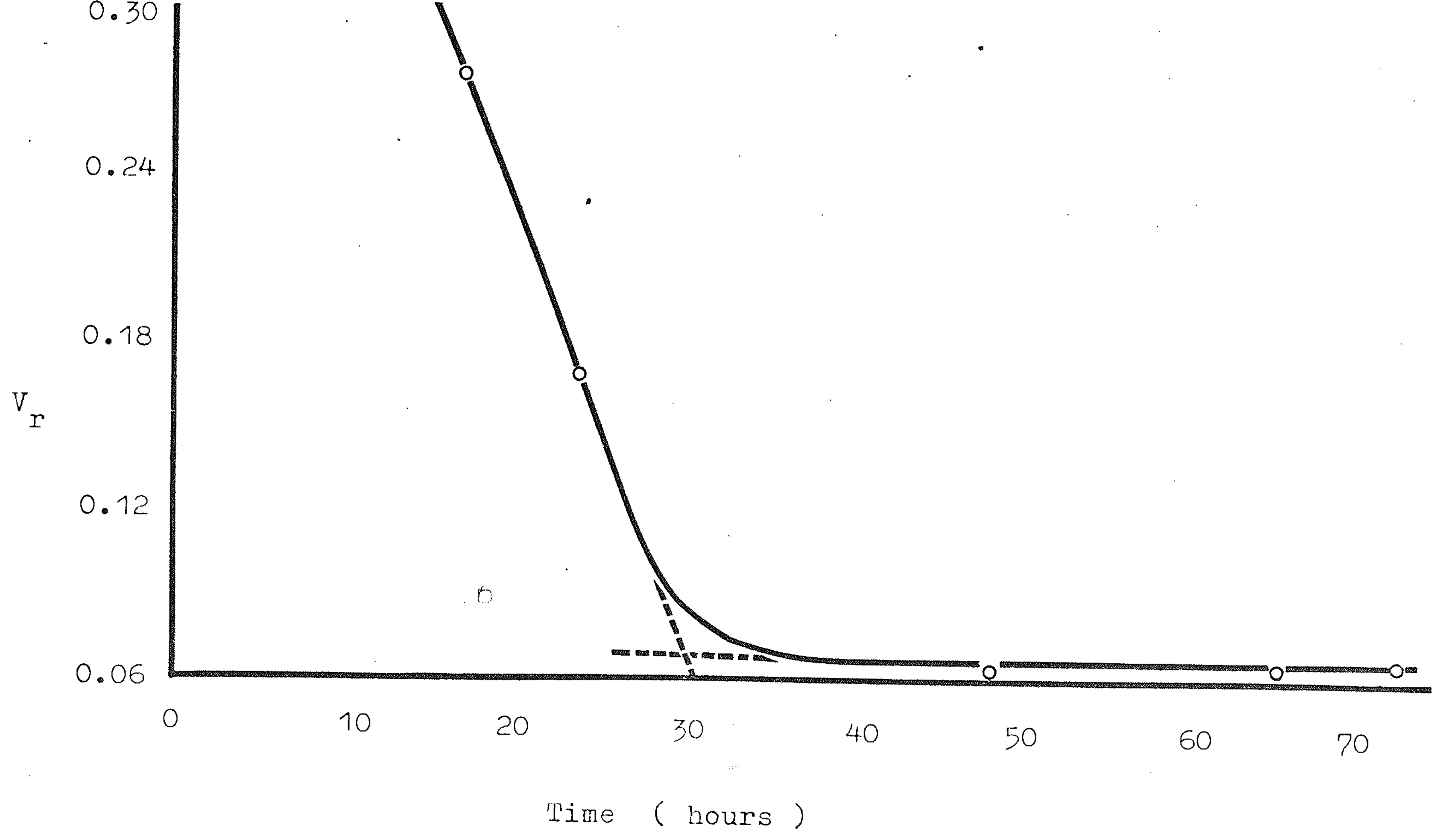
(A_o. the cross sectional area of the sample, being constant)



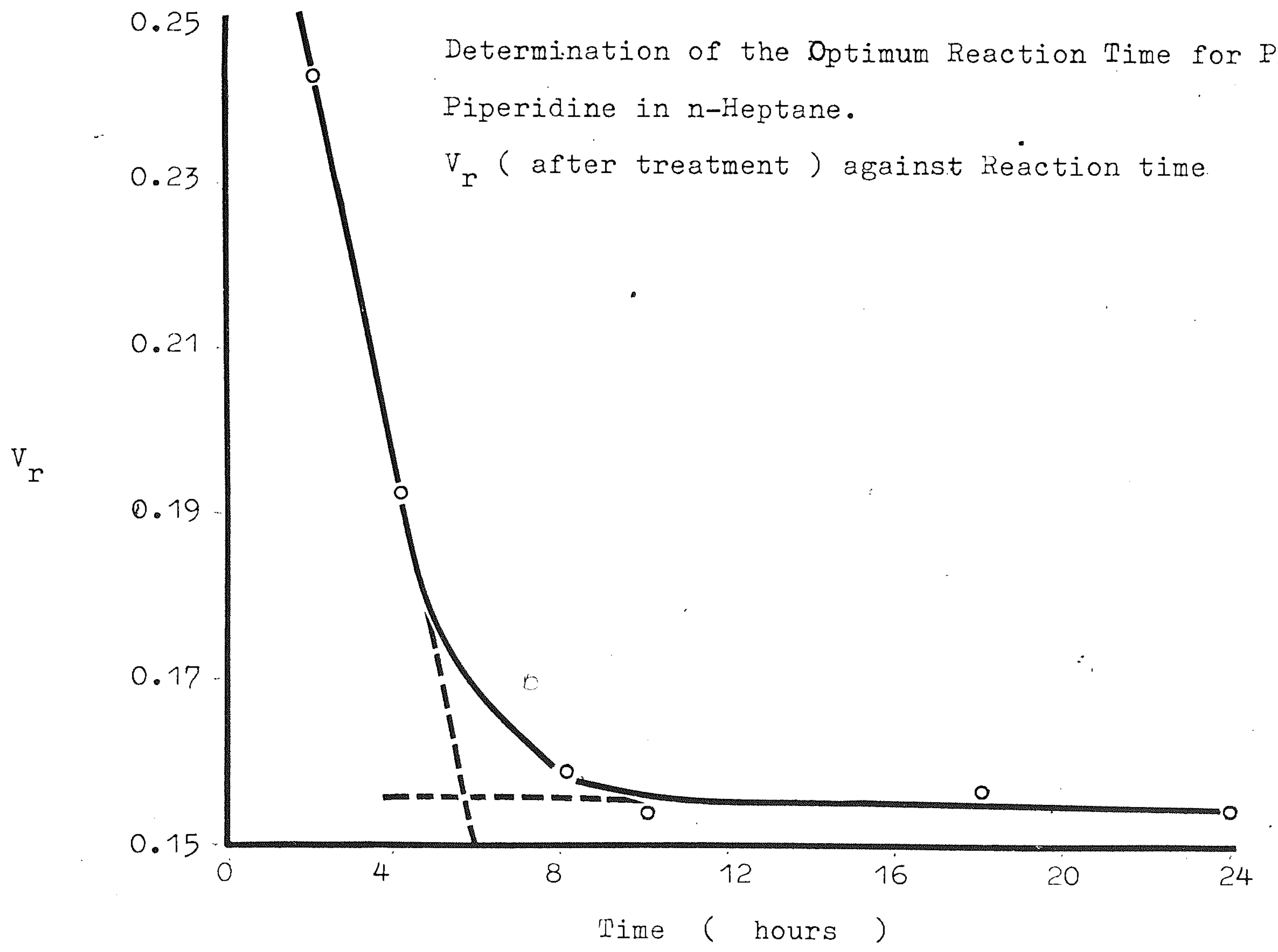
GRAPH 8.

Determination of Optimum Reaction Time for n-Hexane thiol/Piperidine.

V_r (measured after reaction) against Reaction time



GRAPH 9.



Determination of the Optimum Reaction Time for Propane-2-thiol/ Piperidine in n-Heptane.

V_r (after treatment) against Reaction time

At lower values of C_1 variation of 15% was found, this decreased to 6% at higher values i.e. within the experimental error of the compression technique.

From this survey it was concluded that the compression modulus method was suitable for the characterization work, and further, that the best mathematical treatments were those of Kay, Moore and Thomas[23,24] and Melley and Stuckey.[25] The effects caused by the various mathematical approximations, however, were small. Assuming the value obtained by the exact method was correct then the Cluff, Gladding and Pariser equation produced figures high by an average of 3.2% whilst the Smith Khan Khadim method resulted in values high by an average of 0.6%. Both these values were well within the average experimental error for the determination (±3.8%). Generally speaking, the compression modulus technique was much more rapid than the tension method and also less laborious. The reproducibility of the technique was suitable.

3.4. Compression Results for E.P.D.M. Vulcanizates.

These took the form of many hundreds of sets of weights, dimensions and compression modulus data. After being systematically punched they were processed in the computer which calculated V_r and the weight of solvent removable material (E.N.M) and then C_1, $M_{c.phys}$ and the cross-link density (C.L.D.) for each of the mathematical treatments mentioned earlier. In addition the slope and intercept of the experimental plots were calculated where relevant. All determinations were carried out in triplicate and the final result expressed as the average of these three values. As the major aim of this work was the characterization of network structures, the individual result chosen to express this was

TABLE 11

Comparison of the Values of C_1 as Measured by Extension and Compression Techniques.

Formulation	Peroxide loading p.p.h.r.	denr. g/cc 25°C	25°C V_r benzene	C_1 * extension $g.cm^{-2} x 10^{-3}$	C_1 ** compression $g.cm^{-2} x 10^{-3}$
1	1	0.917	0.173	0.98	1.05
2	2	0.920	0.228	1.79	1.97
3	3	0.920	0.261	2.46	2.60
4	4	0.921	0.310	-	3.59
maximum % error in triplicate set			±1.75	±1.6	±3.8

* Corrected to 25°C

** Kay, Moore and Thomas method.

TABLE 12.

C_1 (Compression Modulus) Calculated by the Various Treatments.

Treatment	Formulation			
	1	2	3	4
Cluff Gladding Pariser[29]	1.10	2.03	2.65	3.72
Smith Khan-Khadim[31]	1.06	1.98	2.60	3.65
Melley Stuckey[34]	1.05	1.97	2.60	3.59
Kay Moore Thomas[33]	1.05	1.97	2.60	3.59
Dry Extension*	0.98	1.79	2.46	-

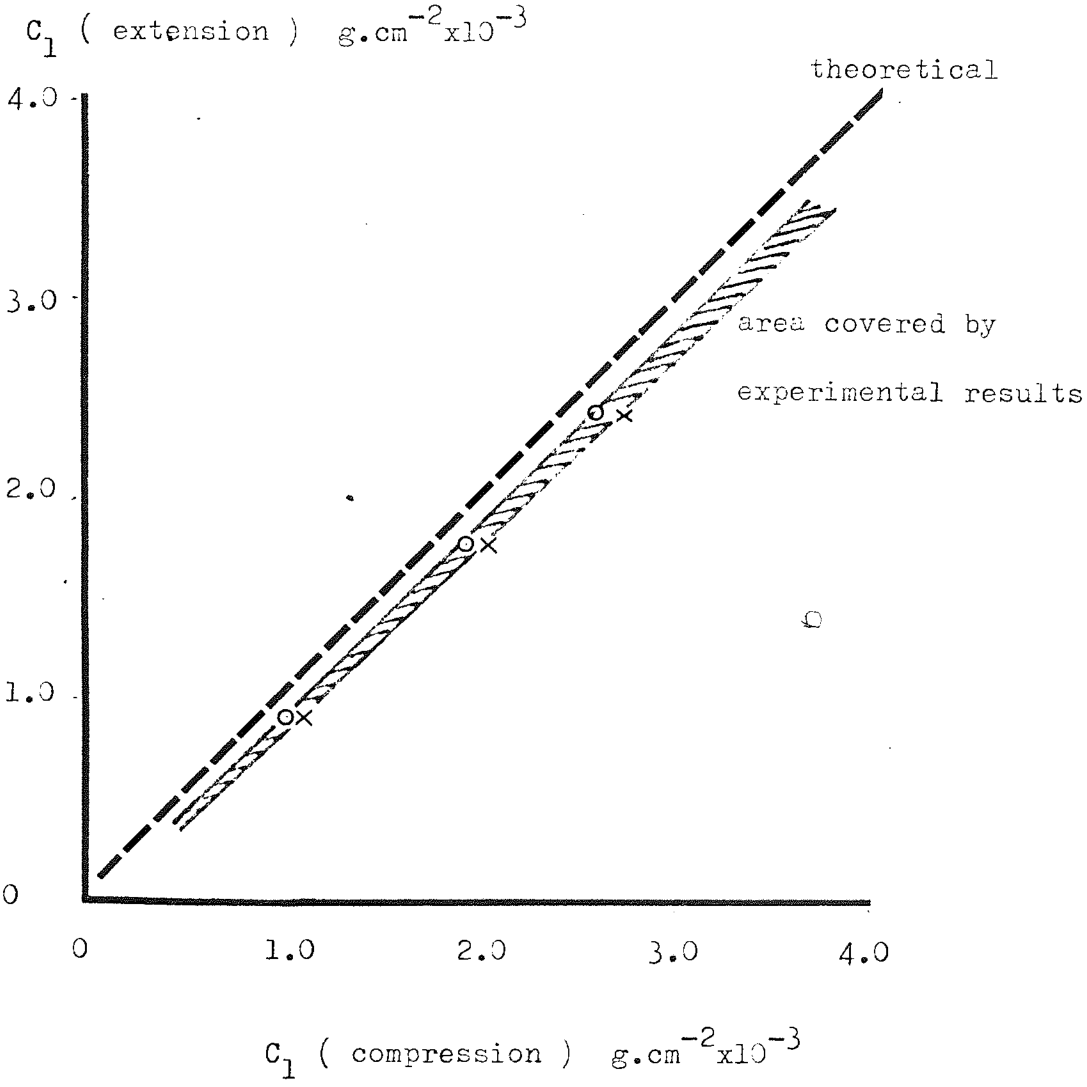
C_1 quoted in $g.cm^{-2} \times 10^{-3}$

* corrected to 25°C.

GRAPH 10.

Comparison of C_1 Values as Determined by the Extension and Compression Techniques

C_1 (extension) against C_1 (compression)



that of cross-link density (C.L.D.). Table 13 presents the values of C.L.D. obtained for formulation A before and after treatment with propane-2-thiol and n-hexane thiol probe reagents. Similar tables containing the results for the other E.P.D.M. formulations are presented in Appendix 3. The mathematical treatment used, for convenience, was that of Kay, Moore and Thomas.

3.5. Calculation of Results.

Using the values of cross-link density tabulated in the previous section the total cross-link density (C.L.D.) and the relative figures for mono-sulphidic cross-links ($C.L.D._m$), di-sulphidic cross-links ($C.L.D._d$) and poly-sulphidic cross-links ($C.L.D._p$) were calculated in the following manner.

The value of cross-link density before probe treatment was taken as a measure of the total number of cross-links present. The equivalent value obtained after treatment with propane-2-thiol/piperidine probe represented a measure of the sum of both mono-sulphidic and di-sulphides. The proportion of poly-sulphides present was obtained from the difference between these two.

After treatment with n-hexane thiol/piperidine the C.L.D. was a measure of the mono sulphide links present, and the difference between the two probed values produced a value of di-sulphidic linkages. This analysis was carried out on all results, the resulting figures for formulation A are presented in Table 14 whilst those for the other E.P.D.M. formulations are presented in Appendix 4. These results are shown in graphs 11 to 28. Graphs 29 to 32 compare the total cross-link densities at each

TABLE 13

Cross-link Density Values Obtained with Formulation A

Treatment Cure Characteristics		Cross-link Densities g.moles. cross-links/g. network x 10^5		
cure T°C	cure t min.	before probe treatment	propane-2-thiol treatment	n-heptane thiol treatment
150	15	5.77	2.26	*
	30	9.09	5.91	0.59
	60	11.45	8.34	2.55
	120	12.11	11.10	5.45
	240	13.38	15.44	8.23
170	15	10.62	9.46	2.56
	30	11.72	10.77	5.11
	60	12.12	13.06	8.30
	120	11.73	14.58	10.15
	240	11.40	13.02	11.37
200	15	9.44	10.55	8.01
	30	9.33	10.07	8.45
	60	9.12	10.82	8.12
	160	9.28	8.99	8.22
	240	8.73	8.75	7.93
240	15	6.54	6.61	6.61
	30	7.06	6.22	6.51
	60	6.62	5.89	6.32
	120	6.15	6.58	6.10
	240	5.69	6.06	5.48

* sample destroyed by treatment

TABLE 14

Cross-link densities associated with Specific Cross-link types: formulation A

Cure Characteristics		Cross-link Density (g.moles crosslinks/g. network x 10^5)			
T°C	t(min)	Total	Mono-S	Di-S	Poly-S
150	15	5.769	-	2.262	3.507
	30	9.092	0.587	5.302	3.183
	60	11.446	2.550	5.786	3.110
	120	12.109	5.451	5.648	1.010
	240	13.380	8.233	5.147	*
170	15	10.624	2.563	6.897	1.164
	30	11.719	5.113	5.656	0.950
	60	12.124	8.303	3.821	*
	120	11.725	10.152	1.573	*
	240	11.404	11.371	0.033	*
200	15	9.439	8.007	1.432	*
	30	9.333	8.447	0.886	*
	60	9.122	8.118	1.004	*
	120	9.289	8.223	0.772	*
	240	8.733	7.930	0.803	*
240	15	6.543	6.611	*	*
	30	7.069	6.508	0.561	*
	60	6.619	6.319	0.300	*
	120	6.152	6.099	0.053	*
	240	5.695	5.484	0.211	*

* :: Negative Value.

cure temperature. A survey of the figures in Table 13 (and those in Appendix 3) indicated that a few results for the number of poly-sulphidic cross-links would be negative numbers. Formation of cross-links during or after the probe reaction could have accounted for these results. Such a reaction was thought possible by workers at N.R.P.R.A.[74] who believed that cross-links could be introduced by reaction between pendant thiol groups and any remaining unsaturation, or as the result of oxidative attack during or after the probe reaction. Further to this an increase in V_r was noted by Moore and Trego[38] after treating an E.P.M. with probe solutions. This has also been noted by others.[78,79]

These results are discussed in section 4.

The units of C.L.D. and time in graphs 12 to 33 are g. moles of cross-links/g. network x 10^5 and hours respectively.

3.6. Physical Test Results.

The results of the hardness ultimate tensile strength modulus at 100% extension elongation at break and compression set tests carried out on vulcanizates of formulation A are presented in Table 15. The corresponding values for formulations B,C,V,N,E and R are presented in Appendix 5.

These results will be discussed in section 4.6.

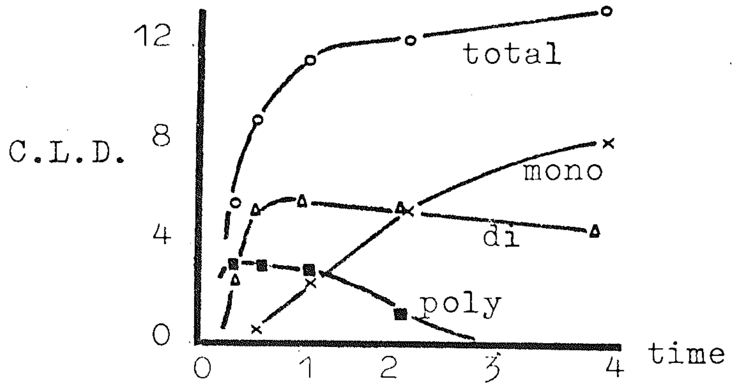
3.7. Comparison with Rheographs.

Monsanto Rheographs were obtained for each formulation at all temperatures apart from 240°C (when Shawbury Cureometer traces were recorded). There was excellent agreement between the

GRAPH 11.

Network structure of Formulation A

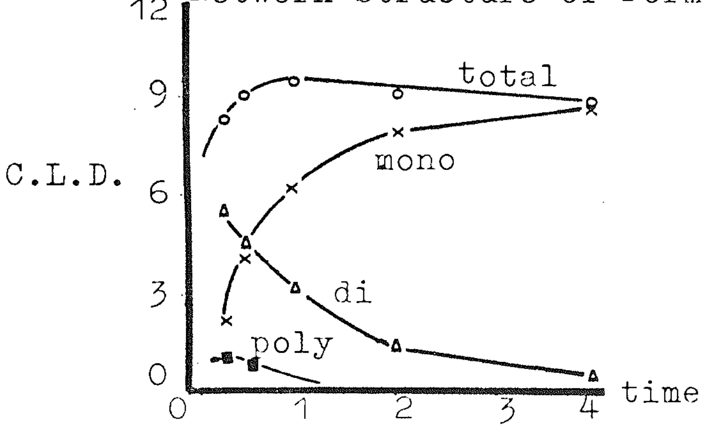
(150°C)



GRAPH 12.

Network structure of Formulation A

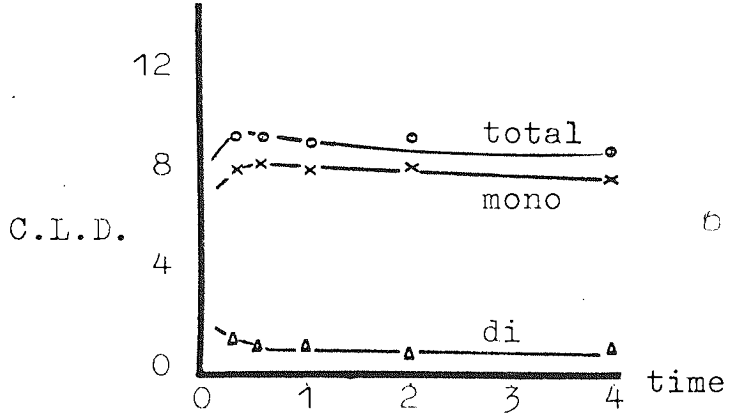
(170°C)



GRAPH 13.

Network structure of Formulation A

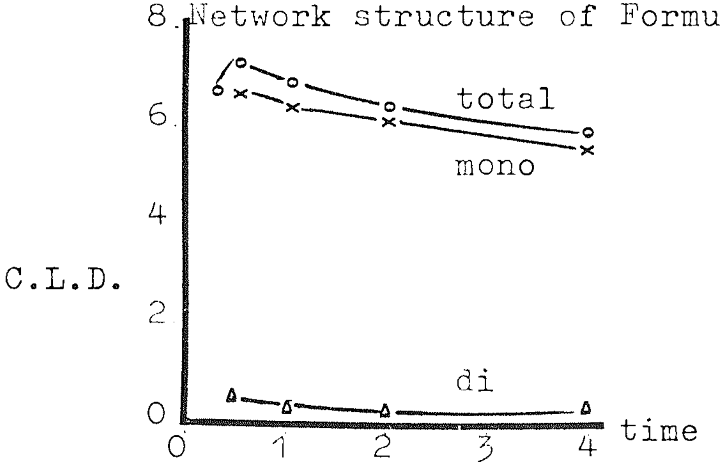
(200°C)



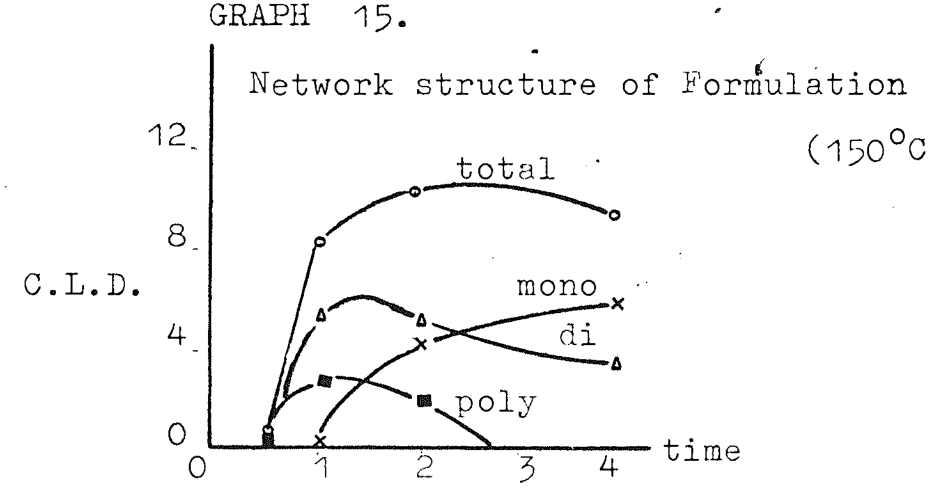
GRAPH 14.

Network structure of Formulation A

(240°C)

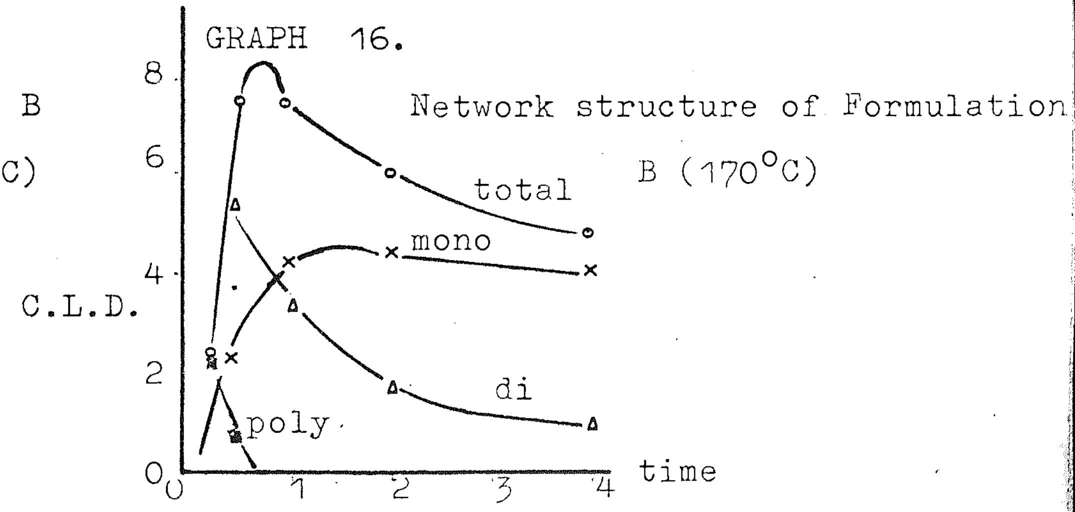


GRAPH 15.



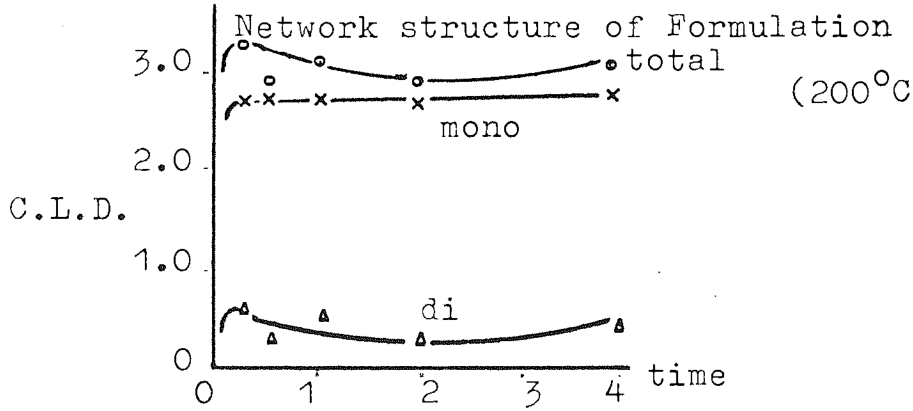
Network structure of Formulation B (150°C)

GRAPH 16.



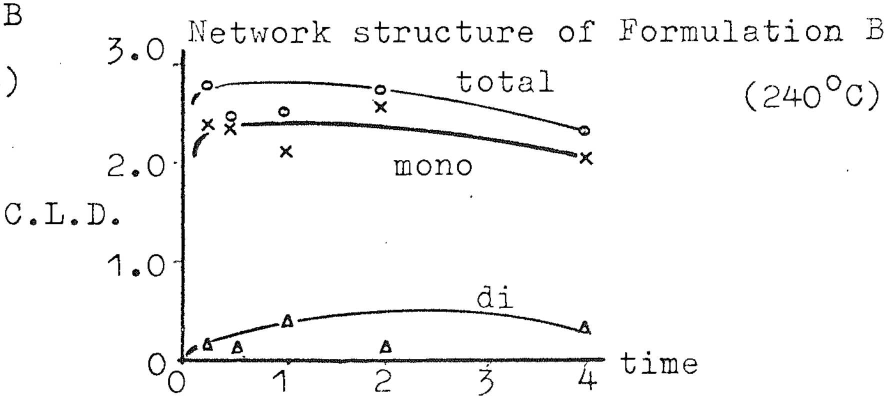
Network structure of Formulation B (170°C)

GRAPH 17.



Network structure of Formulation B (200°C)

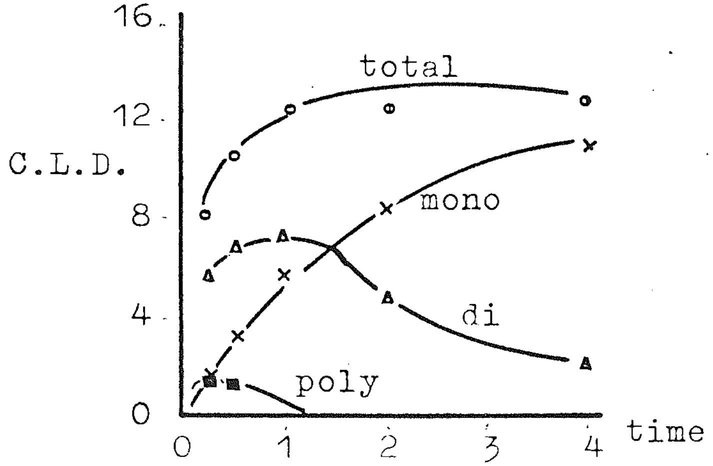
GRAPH 18.



Network structure of Formulation B (240°C)

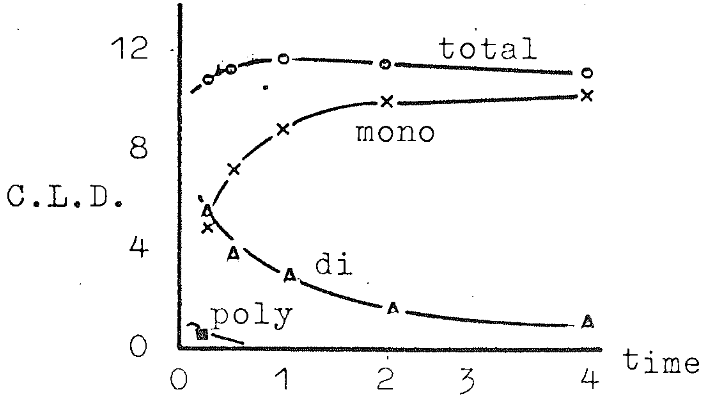
GRAPH 19.

Network structure of Formulation V (150°C)



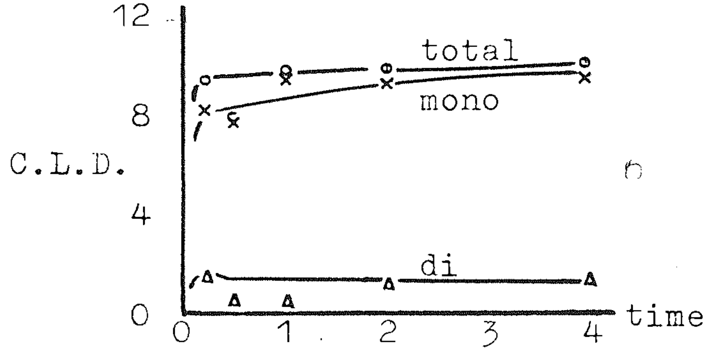
GRAPH 20.

Network structure of Formulation V (170°C)



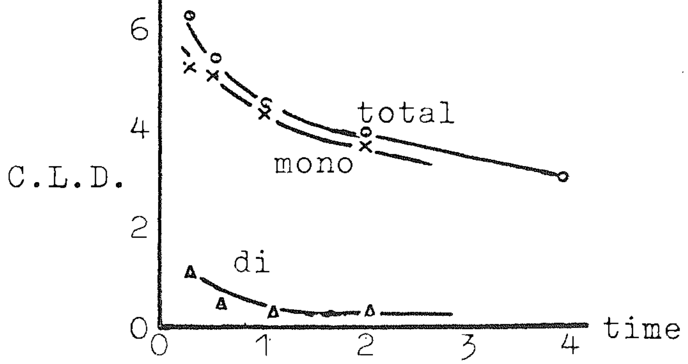
GRAPH 21.

Network structure of Formulation V (200°C)



GRAPH 22.

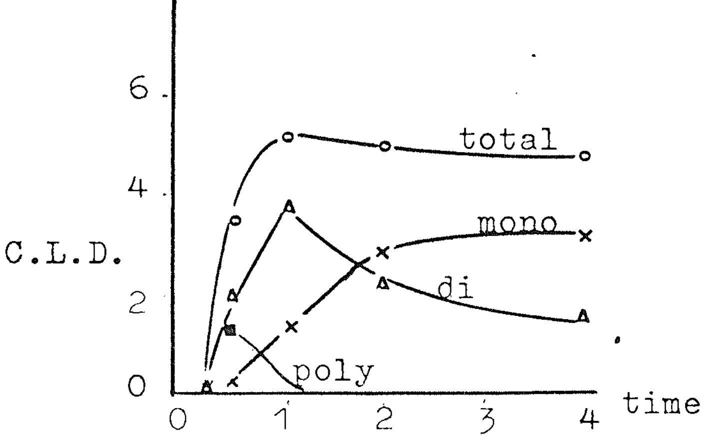
Network structure of Formulation V (240°C)



GRAPH 23.

Network structure of Formulation R

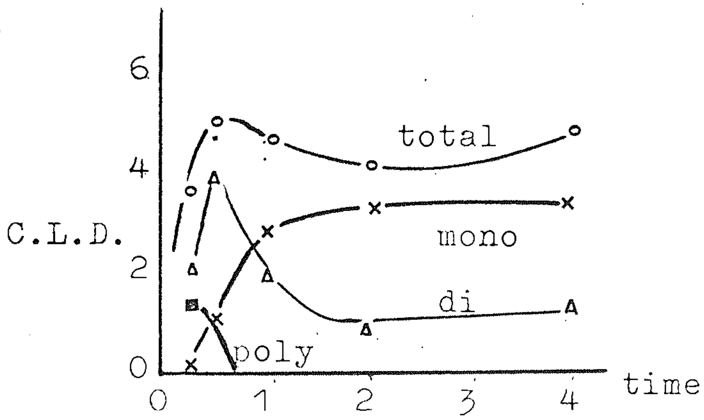
(150°C)



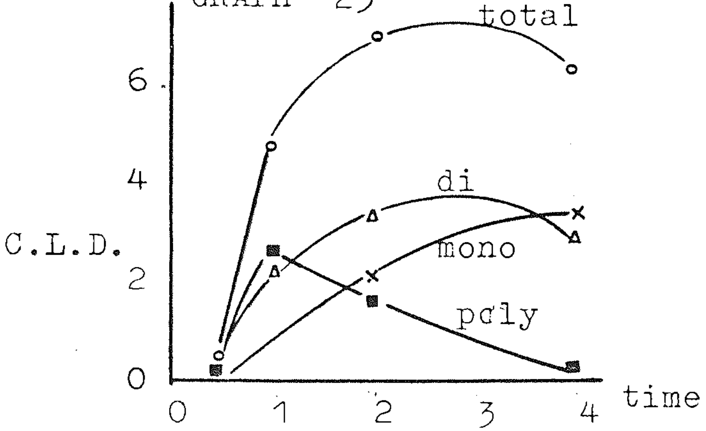
GRAPH 24.

Network structure of Formulation R

(170°C)



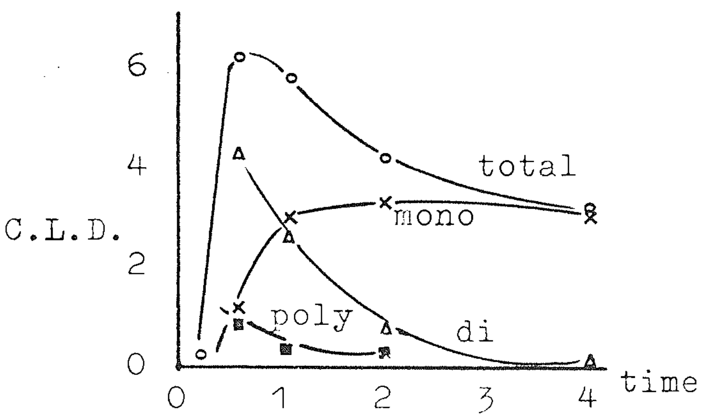
GRAPH 25



Network structure of Formulation N

(150°C)

GRAPH 26

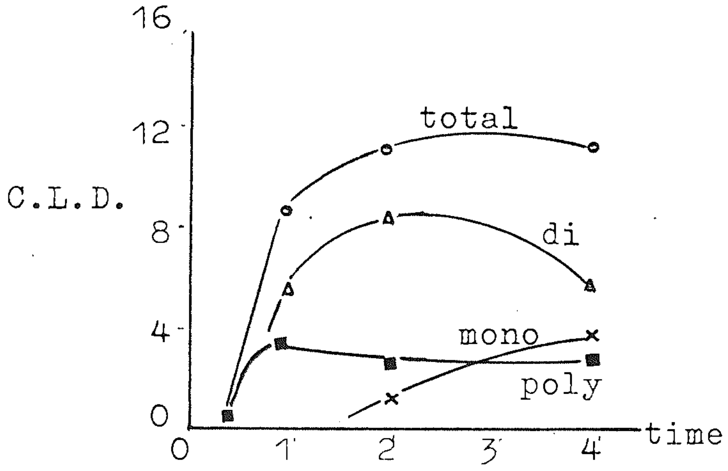


Network structure of Formulation N

(170°C)

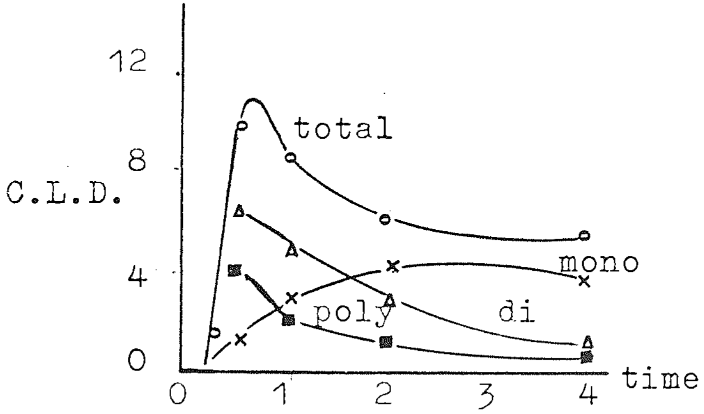
GRAPH 27.

Network structure of Formulation E (150°C)



GRAPH 28

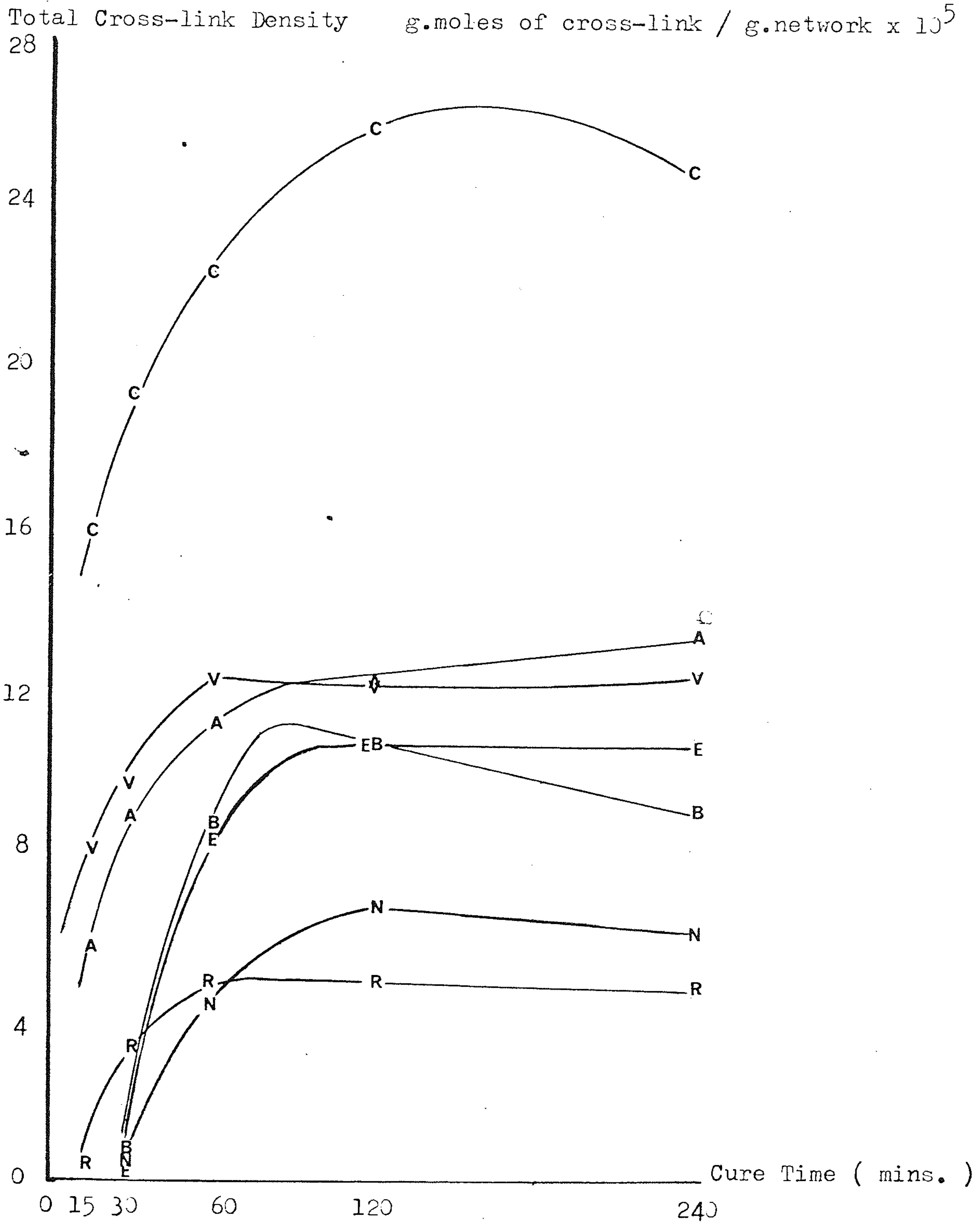
Network structure of Formulation E (170°C)



GRAPH 29.

Summary of the Total Cross-link Densities for all Formulations studied at 150°C

Total Cross-link Density against cure time

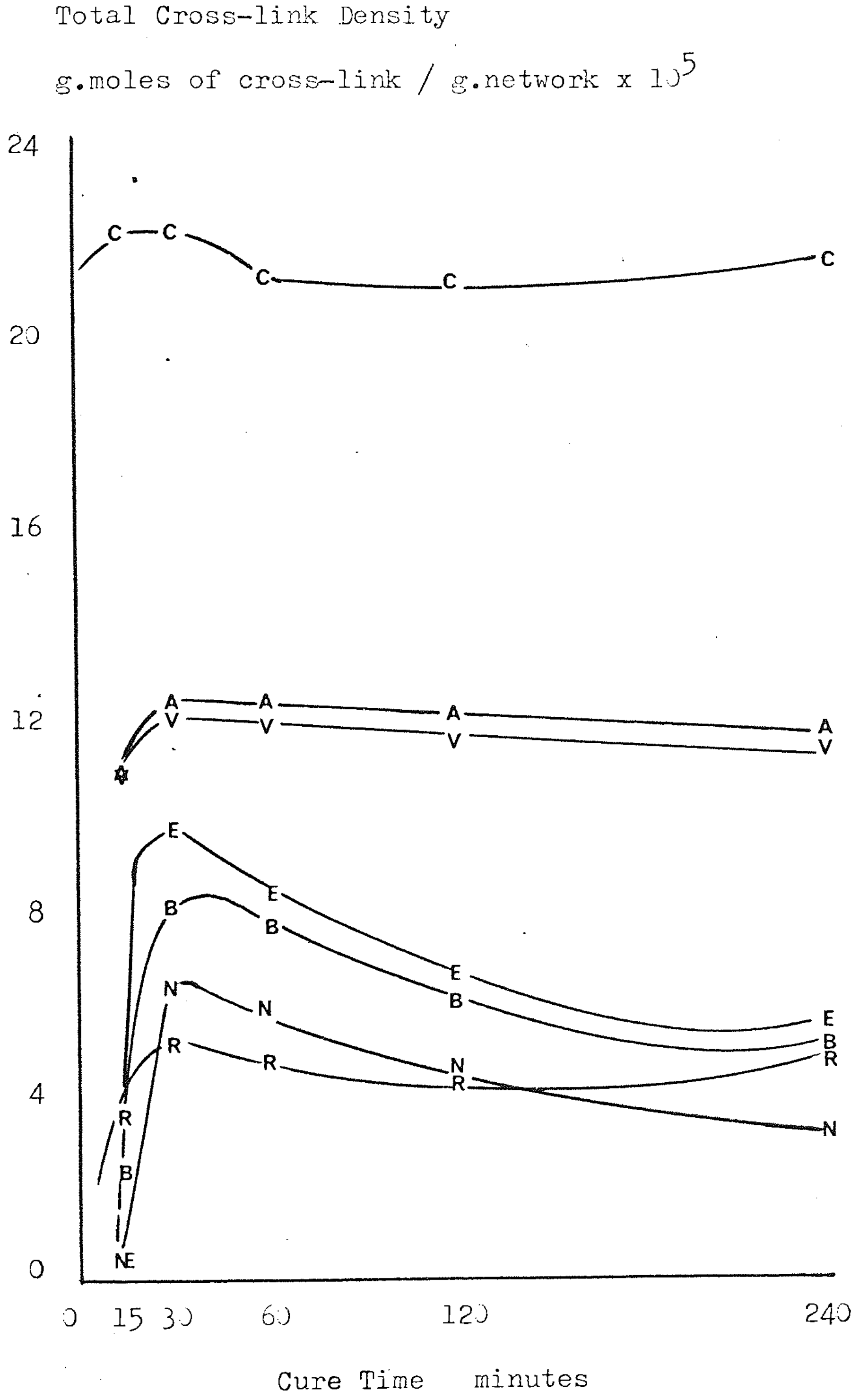


GRAPH 30

Summary of the Total Cross-link Densities for all

Formulations studied at 170°C

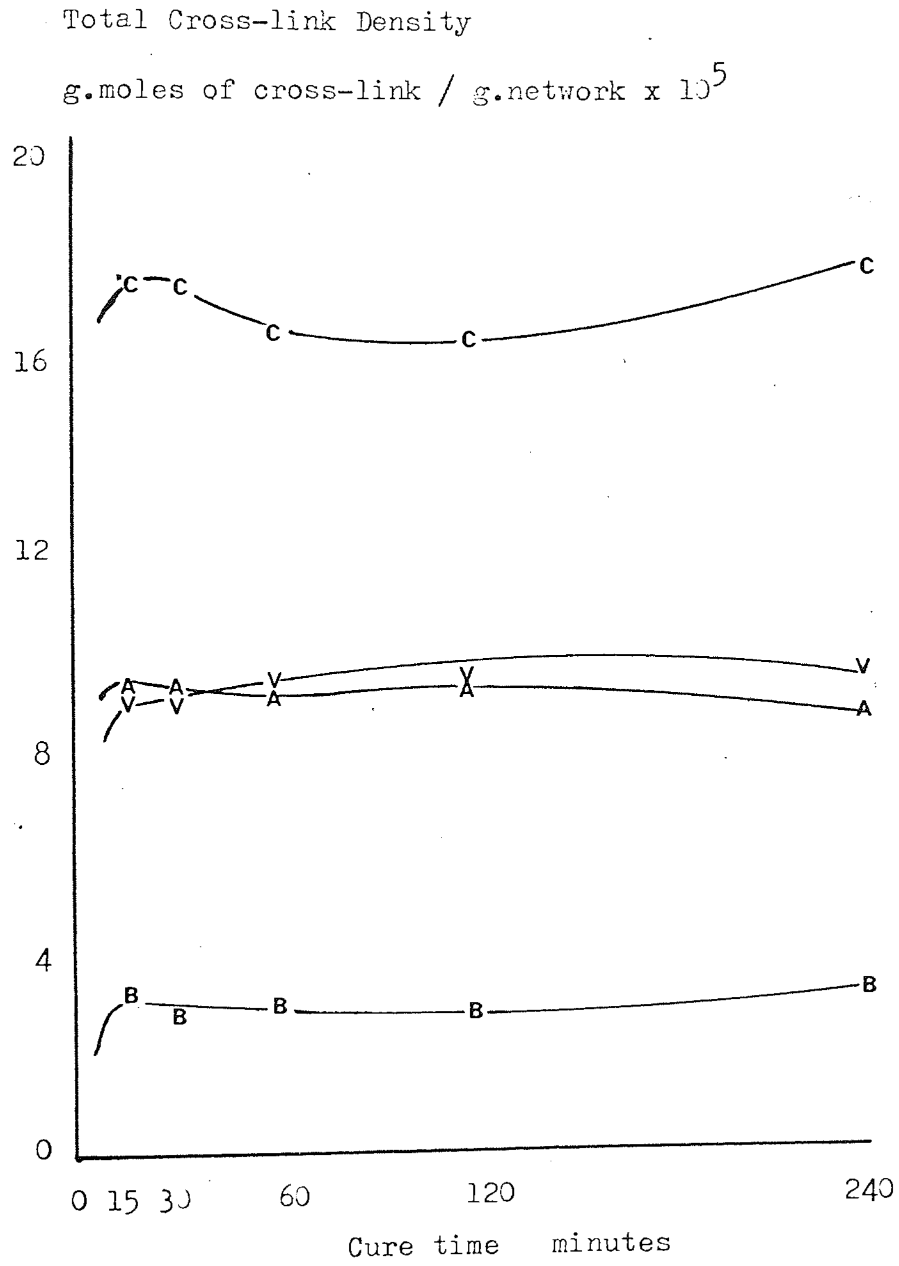
Total cross-link density against cure time



GRAPH 31.

Summary of the Total Cross-link Densities for those Formulations studied at 200°C

Total Cross-link Density against Cure Time



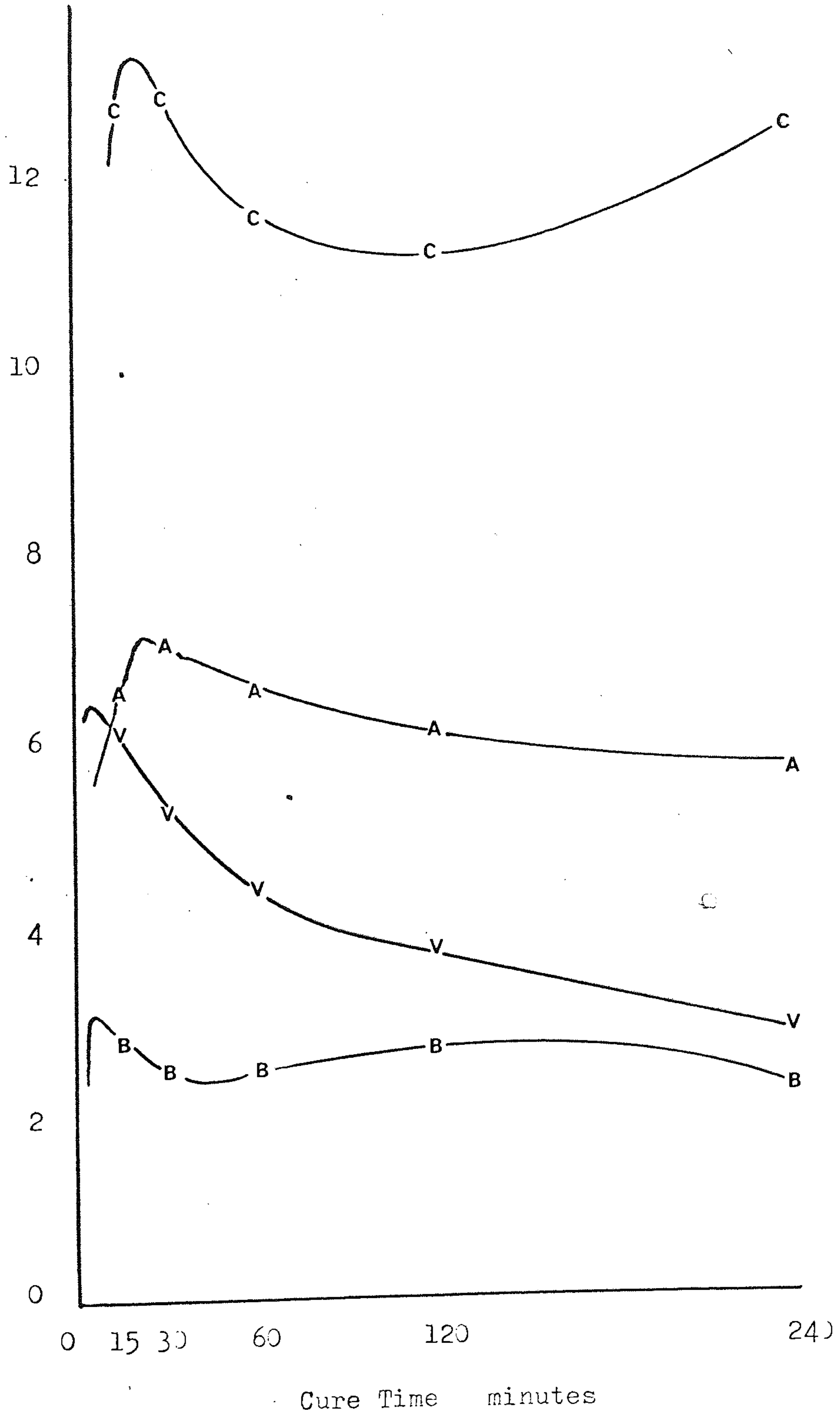
GRAPH 32.

Summary of the Total Cross-link Densities for those Formulations studied at 240°C

Total Cross-link Density against Cure Time

Total Cross-link Density

g.moles of cross-link / g.network x 10^5



Cure Time minutes

TABLE 15.

Physical Properties as Determined for Formulation A.

Cure Characteristics		Physical Property				
Temperature °C	Time min.	Hardness I.R.H.D.	Modulus (100%) p.s.i.	Elongation at break %	U.T.S. p.s.i.	Compression Set %
150	15	59	139.6	543	319.2	14.6
	30	59	149	380	297.0	10.3
	60	61	164.8	262	266.8	7.9
	120	62	180.8	240	289.3	4.5
	240	64	179.1	212	267.6	5.5
170	15	63	155.9	233	229.3	8.7
	30	63	170.0	260	281.1	7.2
	60	64	164.4	290	289.4	5.5
	120	62	163.7	242	251.3	5.7
	240	61	157.9	223	230.6	7.0
200	15	58	*111.8	86	138.9	6.2
	30	58	*101.6	79.2	122.3	3.5
	60	58	*109.3	86.7	138.5	5.4
	120	57	*100.0	80	123.0	4.0
	240	55	*101.3	95.8	136.9	5.2
240	15	53	*102.7	118	146.5	4.8
	30	55	*106.2	105	150.0	4.7
	60	51	* 94.7	109.2	132.0	3.3
	120	56	* 99.4	111	138.9	4.3
	240	56	*101.6	126	135.2	5.6

* :: 50% Modulus

rheographs and the curves depicting total cross-link density in many cases, e.g. graph 33 (formulation A cured at 150°C). Graph 34 (formulation B cured at 150°C) is representative of those where agreement was fair. A kinetic analysis was performed on all rheographs using the technique described by Coran[87]. The results of this analysis have been presented in table 16B.

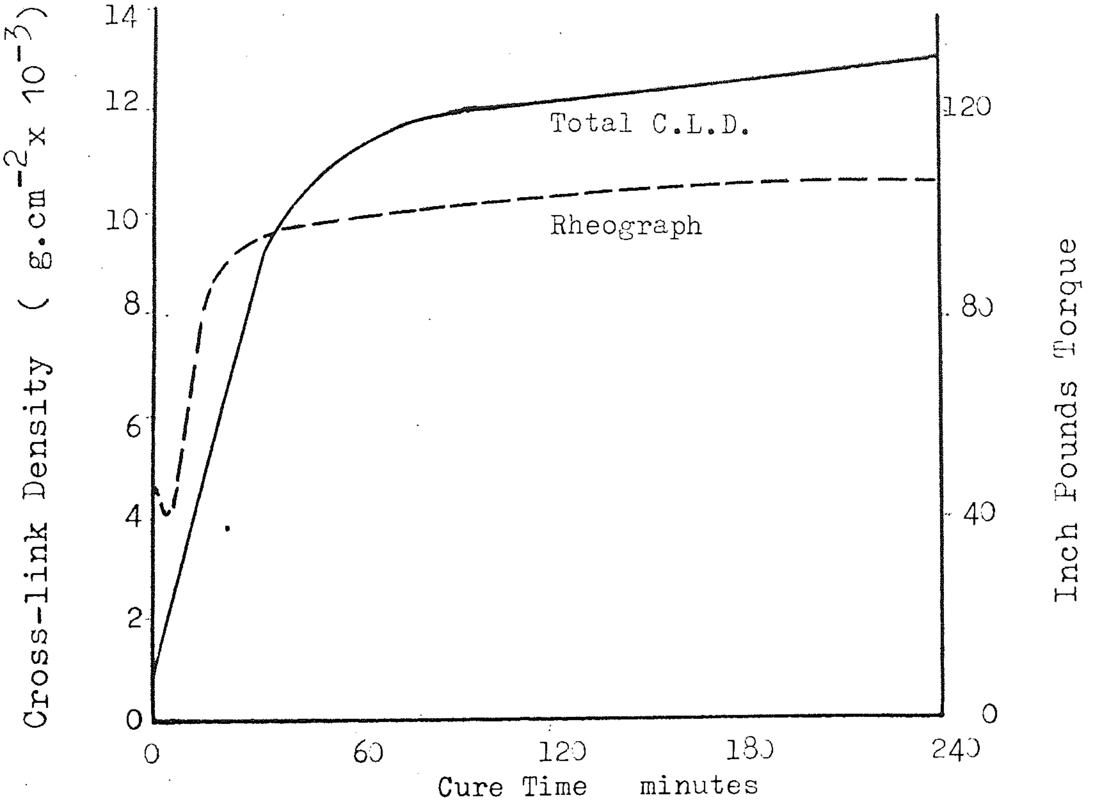
3.8. Errors.

Using an analytical balance, weighings were carried out to the nearest 1/10th mg. (± 0.0001 g). Dimensions of specimens were measured with the aid of a vernier microscope to ± 0.0005 cm. Vulcanization and probe reaction times were measured with a stop clock to an accuracy of ± 30 seconds. A stop watch (± 1 second) was used for the techniques of C_1 determination. Overall experimental errors are stated below. For swelling determinations the error was ± 1.75%. This figure was for unprobed samples; after treatment with a chemical probe there was more scatter in the V_r results and the error could increase to ± 3%. The dry tension technique for C_1 produced results with an experimental error of ± 1.9% (max) whilst compression modulus gave values of ± 3.6%. These figures represented the average error recorded over a range of cross-link densities, in both cases the error decreased with increasing cross-link density, as did the variation between the two techniques.

Experimental errors noted in the physical test determinations were larger than those recorded above, the maximum being ± 1.0% for hardness, ± 3.7% for modulus, ± 16.7% for elongation at break, ± 18.5% for ultimate tensile strength and ± 5.0% for compression set. These errors are exaggerated because of the very low level of physical properties associated with non reinforced E.P.D.M.'s.

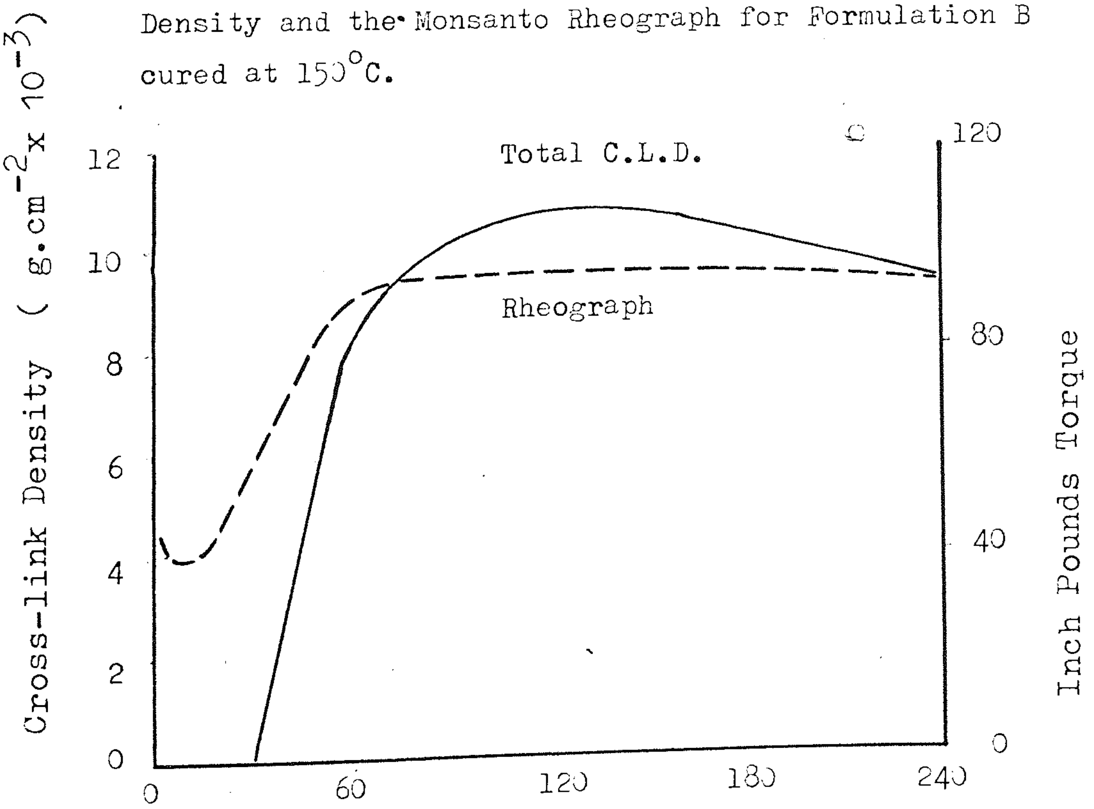
GRAPH 33.

Comparison between the Curve depicting Total Cross-link Density and the Monsanto Rheograph for Formulation A cured at 150°C.



GRAPH 34.

Comparison between the curve depicting Total Cross-link Density and the Monsanto Rheograph for Formulation B cured at 150°C.



4. DISCUSSION OF RESULTS.

4.1. Structure of E.P.D.M. Networks.

4.1.1. Structures in General.

The cross-link structures obtained from the E.P.D.M. vulcanizates investigated were, in general, as expected. The predominance of thermally stable cross-links had been previously reported from stress relaxation data[51,52] and was later confirmed by the more sophisticated technique of cross-link mensuration[45,46]. A few general conclusions regarding the structures investigated in this work are presented below, whilst more detailed comments are contained in the following sections (4.1.2. to 4.1.7.).

a). Polysulphide links: although this cross-link type is no doubt a precurser to the shorter di- and mono-sulphidic links it seldom appears in any abundance in the E.P.D.M. network. When the elevated temperatures (200 and 240°C) are used, no poly-sulphide links could be found. However one must assume that at the shortest cure time investigated (15 minutes), all of this cross-link type must have undergone shortening reactions. At the lower temperatures one half of the vulcanizates had lost their poly-sulphidic content before one hour of cure had elapsed. Most of the other networks retained a proportion of these linkages, however small, up to and presumably beyond a cure time of four hours.

b). Di-sulphide links: these links often reached concentrations of over fifty percent in the early stages of cure, then decreasing as they desulphurated to the predominate mono-sulphide link. In formulations A.B and V at low temperatures (150°C) this level (i.e. fifty percent or more) was in fact retained for at least one hour of cure whilst at 170°C the period was 75 minutes, (30 minutes in the case of formulation B). With different termonomers various effects were noted. Formulations R and B were similar whilst formulation N at 150°C never reached a di-sulphide content greater than fifty percent. Formulation E on the other hand maintains this level for over two hours at 150°C. At 170°C both formulations N and B reach this level after 30 and 60 minutes respectively.

Tables showing the proportions of cross-link types expressed as a percentage of the total cross-link density are presented as table 16 (formulation A) and Appendix VI (formulations B, V, N, E and R).

4.1.2. Cure Systems.

a). Sulphur based systems.

The seemingly constant proportions of thermally stable monosulphidic links found in sulphur cured compounds are indicative of the similarities in the network structures of E.P.D.M.'s. The overall conclusion which can be drawn relating to the effect of cure system on structure is that network structures appear to be independant of cure system. This would indicate that, providing all cures were taken to optimum, the basic structures would follow a set pattern.

As the cure system appears to have little effect on the structure, other aspects which are dependant upon the cure system become very important. Certain of these , termonomer type and concentration, cost, cure time and temperature, are discussed in the following sections, others are discussed below.

The structure at optimum cure is independant of the cure system so that rate of attainment of this optimum becomes of interest. The values of the first order reaction rate constants (k') (table 16b) for those systems with various cure systems and the same termonomer indicate that the fastest system is formulation V, whilst the slowest is formulation B . Since the optimum cross-link density values follow the same order and time to optimum cure varies such that formulations V and B are similar and formulation A much greater, it becomes obvious that rate of introduction of cross-links need not be the only important factor. In fact there are certain applications (high temperature injection moulding, L.C.M. curing etc.) where the induction period becomes of prime importance. Again it can be seen from table 16b that the induction periods (t_i') for formulations A and V (1.5 and 3.2 minutes respectively) are much shorter than that for formulation B (13.75 minutes). Optimum cure will also be affected by the rate of change of the proportions of the constituent cross-link types; which themselves will be dependent upon the cure system and also on the termonomer type (section 4.1.3.). The order of rate of loss of poly-sulphides during cure at 150°C is:

formulation V $>$ formulation B $>$ formulation A

There are available now many accelerators which are known to produce faster cures in E.P.D.M. polymers. The only accelerator specifically recommended for use with these polymers which has been investigated in this work is Vocol (a di-thiophosphate). This did produce higher levels of cross-linking but at the lower temperatures there was little difference between it and the conventional accelerated sulphur system (formulation A). Other accelerators which are known to produce good fast cures in E.P.D.M.'s are listed below:

Tellurac : (tellurium diethyldithiocarbamate) Vanderbilt
CUPS : (copper salt of M.B.T.) American Cyanamid
Copper DD : (copper di methyldithiocarbamate) Robinson Bros.
Royalac 133 : (ferric dimethyldithiocarbamate) Uniroyal
Royalac 141 : (undisclosed) Uniroyal

It is of interest to note that these materials are salts of metals other than zinc and this may be the reason, or one of the reasons for their success.

A second factor which must be considered in relation to the cure system is that of level or degree of cross-linking. The financial aspects of cure systems and degree of cross-linking have been discussed fully in section 4.2.2. The data obtained from kinetic analysis of the Monsanto rheographs shows that the maximum rheometer modulus obtained (which can be related with modulus at 300% extension). is greatest for formulation A and smallest for formulation B at 150°C, whilst the maximum cross-link density figures show formulations A and V in reversed positions. The time required to reach maximum cross-link densities indicate no trends worthy of note, a fact which is also true for the t_{100} and t_{90} values obtained from analysis of the rheographs. The t_{60} values ,however, do indicate a trend which suggests that formulation B is the slowest to reach level of modulus development , formulation V being the fastest.

A further point which has been shown to affect the level of cure is the proportion of available sulphur in the cure system. This value has been proved to be directly proportional to the optimum total cross-link density (section 2.3.).

The thermal stability (resistance to reversion) of the networks produced for this work was on the whole good when compared to that associated with the general purpose elastomers. The system utilising Vocol was in general the best from this view point with the exception of the cure at 240°C. In this case formulation V exhibited an almost catastrophic reversion.

Other remarks of a more general technological nature which relate to the cure systems have been included in section 4.2.1.

If we consider the overall balance of vulcanizate characteristics based on structure and structural characteristics, rate of cure, induction periods, scorch times and cost etc. then we can deduce the following points:-

a) at 150°C formulation V offers the best overall range of properties and formulation B the worst. However, formulation A would be cheaper than formulation V and hence this would become the overiding factor.

b) as the temperature increases to 170°C the characteristics offered by formulations A and V become virtually identical and thus the choice would be governed by economic considerations. This status also applies for those vulcanizates produced at even higher temperatures.

b). Peroxide cured networks.

The major variation between sulphur and peroxide cure systems is that peroxide cure produces a much higher cross-link density, nearly twice that produced by a sulphur based system. This is easily explained since the sulphur is limited to an unsaturation point for cross-link formation whereas the peroxide one is not. This means that there is a limiting cross-link density for sulphur systems beyond which they may not pass whilst the peroxide system is not limited in any way. It is of interest to note that the peroxide system showed reversion and a general lowering of cross-link density with increasing cure temperature and time. The use of peroxides by themselves is not common in industry as in most cases where a peroxide is used, one tends to find the use of a co-agent as well. Typical co-agents are sulphur, di-ethylene glycol and triethanolamine. The action of these substances would be either to aid the initial decomposition of the peroxide, or to react with the radical formed by the abstraction of a hydrogen atom from the main chain to form the cross-link precursor.

TABLE 16.

Proportions of Constituent Cross-links in Vulcanizates prepared from Formulation A.

Cure T °C	Cure t min.	Total C.L.D.	% mono-sulphide	% di-sulphide	% poly-sulphide
150	15	5.796	-	39.2	60.8
	30	9.092	6.45	58.55	35.0
	60	11.446	22.3	50.5	27.2
	120	12.109	45.0	46.6	8.4
	240	13.380	61.5	38.5	-
170	15	10.624	24.12	64.92	10.96
	30	11.719	43.63	48.26	8.11
	60	12.124	68.48	31.52	-
	120	11.725	86.58	13.42	-
	240	11.404	96.98	3.02	-
200	15	9.439	84.83	15.17	-
	30	9.333	90.51	9.49	-
	60	9.122	88.99	11.01	-
	120	9.289	88.52	11.48	-
	240	8.733	90.80	9.20	-
240	15	6.543	-	-	-
	30	7.069	92.06	7.94	-
	60	6.619	95.47	4.53	-
	120	6.152	99.14	0.86	-
	240	5.695	96.29	3.71	-

TABLE 16b.

Data obtained from the kinetic analysis of the Monsanto Rheographs.

Definitions:

R_{max}	maximum modulus as recorded on the rheometer (units: inch-pounds torque)
scorch	time required for the compound to exhibit an increase in modulus of two scale units from its minimum value (units: minutes)
t'_i	induction time noted prior to the commencement of the initial vulcanization reaction (units: minutes)
t''_i	induction time noted prior to the commencement of the second slow vulcanization reaction (units: minutes)
k'	rate of the initial (fast) vulcanization reaction (units: $minutes^{-1}$)
k"	rate of the second (slow) vulcanization reaction (units: $minutes^{-1}$)
t_{60}	time required to complete 60% of the vulcanization reaction as shown by rheometer modulus development (units: minutes)
t_{90}	time required to complete 90% of the vulcanization reaction as shown by rheometer modulus development (units: minutes)
t_{100}	time required to complete the vulcanization reaction as shown by rheometer modulus development (units: minutes)

TABLE 16b (cont.)

temperature / form. / parameter	150°C				170°C				200°C			
	A	B	C	V	A	B	C	V	A	B	C	V
K_{max} "lbs.	69.0	56.0	86.0	64.5	68.0	54.0	77.0	63.0	60.0	40.5	77.0	40.5
Scorch min.	3.5	10.75	1.75	1.6	1.8	5.0	0.5	0.75	1.1	3.15	0.2	0.88
t'_i min.	3.2	13.75	1.75	1.5	1.6	7.1	0.6	1.0	0.9	3.57	0.33	0.75
t''_i min.	12.0	-	8.0	5.0	5.7	15.2	3.25	6.75	4.8	-	-	2.5
k' min^{-1}	0.13	0.07	0.15	0.26	0.37	0.31	0.62	0.35	0.30	2.0	2.63	0.86
k" min^{-1}	0.02	-	0.07	0.06	0.10	0.17	0.48	0.03	0.02	-	-	0.09
t_{60} min.	11.5	36.4	9.62	7.5	4.0	11.6	2.2	3.0	4.5	4.75	0.78	2.0
t_{90} min.	62.0	72.0	28.75	30.0	14.5	15.4	5.0	20.75	12.5	5.25	1.3	13.0
t_{100} min.	200	100	70.0	70.0	60.0	24.0	10.0	114	27.5	6.75	2.5	4.8

TABLE 16b (cont.)

temperature / form. / parameter	150°C			170°C		
	N	E	R	N	E	R
π_{max} " lbs.	40.5	56.0	39.5	40.5	54.0	37.0
Scorch min.	19.5	6.0	17.5	7.0	4.6	7.5
t_i' min.	20.75	11.8	11.0	9.2	8.3	7.1
t_i'' min.	49.5	-	54.5	-	-	25.0
k' $min.^{-1}$	0.07	0.06	0.06	0.37	0.41	0.23
k" $min.^{-1}$	0.05	-	0.02	-	-	0.18
t_{60} min.	37.5	30.5	32.0	13.45	12.0	12.8
t_{90} min.	56.0	54.0	57.0	17.75	15.6	20.3
t_{100} min	100	110	108	26.25	22.5	30.0

4.1.3. Structure and Termonomer Type.

The polymers investigated in this work contained those termonomer types currently in commercial use. Polymers were chosen in order that the only real difference was in termonomer type. The effect of termonomer content was not investigated as the polymers all had similar unsaturation levels. As can be seen from Table 8 the range of iodine numbers of the polymers investigated was only from 8 to 12, representing a weight percent unsaturation of between 3 and 4. Polymers with iodine numbers of up to 24 are now available and are recommended for fast cures, high temperature cures and for blends with unsaturated polymers.

Graphs 29 and 30 compare the total cross-link densities of the polymers containing the various termonomers when cured at 150°C and 170°C. The values of cross-link densities obtained covered a wide range although there is a tendency for the range to narrow at higher temperatures when competing reactions become more prevalent. The wide range of optimum cross-link densities obtained with the various termonomers is evidence of the difference in reactivity of the pendant unsaturation groupings. As was mentioned earlier, one of the requisites of a termonomer species was that it contained two non-conjugated unsaturation sites of differing reactivity. The importance of the differing reactivity was evidenced by the abortive attempts to utilise cyclo-octa-1:5-diene which resulted in complete gelation since both double bonds were of equal reactivity. From the figures obtained at 150°C the order of decreasing optimum cross-link density is:-

$$\text{MNB} \rangle \text{ENB} \rangle \text{1:4 hexadiene} \rangle \text{DCPD}$$

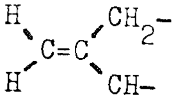
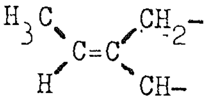
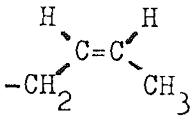
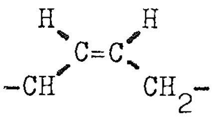
and at 170°C is:-

$$\text{ENB} \rangle \text{MNB} \rangle \text{1:4 hexadiene} \rangle \text{DCPD}$$

Table 16a shows the order at 150°C with the unsaturation point and its alpha-groupings.

TABLE 16a.

Termonomer reactivity at 150°C

Termonomer	MNB	ENB	1:4 hexadiene	DCPD
Decreasing Optimum C.L.D.	⟶			
Unsaturation Site				

Unfortunately, despite the fact that we have four types of alpha grouping and four values of optimum cross-link density, the possible use of simultaneous equations to derive an expression for reactivity of any polymerised termonomer is ruled out by the number of permutations in which these alpha groups may be situated about the double bond. In addition, variations in stabilisers, shortstops and molecular weight modifiers from manufacturer to manufacturer would all effect the resultsobtained. A further point worthy of note is that the three terpolymers which produced the highest cross-link densities also exhibited reversion whilst the dicyclopentadiene did not. Another point in favour of this termonomer was that as the cure temperature increased the optimum cross-link density was unaffected, whilst the polymers produced from the other species showed definite reductions in this value. The rates at which the cross-links were introduced followed the same order as for the optimum cross-link densities. The major variance here is that the reactionwith the DCPD appears to start off at a much earlier stage than do those for the others. Perhaps the process of building an elastomer networkis not far removed from, to be analogous to crystal growth, where the slower the reaction the more perfect the product.

Finally, the rate at which the poly-sulphidic links were converted to mono-sulphidic ones varied between the termonomers. Reference to graphs 15,23,25,and 27 show that at 150°C the rate at which poly-sulphidic cross-links are lost is in the order of termonomers:-

DCPD $\rangle$ MNB $\rangle$ 1:4 hexadiene $\rangle$ ENB

This indicates that the termonomer species have some effect on the stability of the initially formed poly-sulphidic links. As the cure temperature increases these differences become smaller and smaller.

4.1.4. Structure and Cure Time (at constant temperature).

A change in cure time at any given temperature will result in two major changes in the network, namely

i) a change in the total cross-link density

ii) a change in the proportions of the constituent cross-link types

The reasons for and nature of these changes will be discussed in this section.

As the network is built up there are two competing processes occurring. These are the introduction or formation of cross-links and thermal degradation due to cross-link and/or main chain scission. Since there is a limit to the number of cross-links which can be introduced then there will obviously be a maximum value in the plot of cross-link density against time. The position of this maximum could be expected to vary with the type of termonomer, the ammount of available sulphur in the cure system and to some extent on the cure system itself. The effect of the termonomer on the time required to produce a given degree of cure, i.e. the rate at which it can be used to introduce cross-links is:-

MNB 〉 ENB 〉 DCPD 〉 1:4 hexadiene

fastest slowest

The rate in general is found to be to be roughly proportional to the total concentration of available sulphur in the cure system. Reversion processes are very slow at the lower temperatures and again the rate of these tends to be somewhat dependant upon ter-monomer type, the order being

MNB 〉 1:4 hexadiene 〉 ENB = DCPD at 150°C

and ENB 〉 MNB 〉 1:4 hexadiene 〉 DCPD at 170°C

The effect of cure system on reversion would indicate that formulation B is least stable whilst formulations A and V are comparable and stable at temperatures upto 200°C. The comments listed above relating to the formation of a network will also apply to the peroxide cure system, except that in the case of such a cure the rate of attainment of the maxima in the cross-link density curve will depend solely upon the half life of the peroxide at the cure temperature. The effect of a change in cure time upon the total cross-link density is more difficult to define as it will depend upon the relative times and consequently could either cause an increase or a decrease.

When considering the effect of cure time on the proportions of the constituent cross-links it is as well to consider the method by which the network is built. When a cross-link is first introduced to the network it will be poly-sulphidic in nature. At a later stage in the vulcanization these initial cross-links will undergo a succession of de-sulphurating reactions until they ultimately contain only one sulphur atom. As we have defined our cross-link types as poly-sulphidic (those with three or more sulphur atoms), di-sulphidic (those with two sulphur atoms) and mono-sulphidic (those with one sulphur atom only) then we can consider network development as being the resultant of three simultaneous rections. These are:-

a) introduction of poly-sulphidic linkages,

b) desulphuration of poly-sulphide links to di-sulphides,

c) desulphuration of di-sulphide links to mono-sulphides.

The initial introduction of polysulphide links would, if no further reaction was possible, follow a curve identical to that describing total cross-link density. As reactions 'b' and 'c' take place, however, the proportion of poly-sulphidic links passes through a maximum value and declines, the species ultimately becoming "extinct". Using similar reasoning one can see that the proportion of di-sulphidic links will also pass through a maxima and decrease whilst the stable mono-sulphide links continue to increase. This build up is depicted well in graph 11. The build up of the network by the process described above will be dependant upon cure time, cure temperature and the extra network materials (accelerator complexes, intermediates etc.). The rate of build up of mono-sulphidic links is fastest for formulation V at 150°C but at higher temperatures there is little to choose between formulations V and A. Formulation B is the slowest throughout the temperature range. When relating this rate to the termonomer type it interesting to note that at 150°C the build up with 1:4 hexadiene and DCPD are roughly equivalent and faster than the others, whilst these positions are reversed at 170°C. Formulation V shows the shortest time to peak poly-sulphide and disulphide content although again at higher temperatures the difference becomes less. As with total cross-link density, it is very difficult to make an assessment of the changes that could be expected as the result of a change in cure time, without knowing both the initial and the final time

4.1.5. Structure and Cure Temperature.

There are many similarities between the effects of cure temperature and cure time. In most cases an increase in cure temperature will cause the same effects as an increase in cure time. The one major variation of importance is that an increase in cure temperature will cause a decrease in the optimum total cross-link density obtainable. In fact as we go from a cure time at 150°C to one at 240°C for formulation A the optimum cross-link density is halved. This fact is general for all of the cure systems studied as is shown clearly in graphs 29 to 32. A further point worthy of note is that as with other chemical reactions a change in temperature causes a change in the rate if the reaction. Thus, an increase in vulcanization temperature causes an increase in both rate of introduction of cross-links and in the rate of conversion of polysulphides to mono-sulphidic links. Coupled with this we also observe an increase in the rate of reversion, presumably being caused by the thermal degradation of the main chain and/or cross-links. The effect of temperature on rate can be most easily observed with peroxide cure systems since any increase in temperature will reduce the half life of the peroxide in the system, thus releasing radicals for cross-linking at an earlier stage and more rapidly.

With the increasing useof high temperature cure media in the industry, the high temperature cure behaviour of E.P.D.M. type polymers is becoming more important. This work has not elucidated the situation to any degree since the shortest curetime investigated i.e. fifteen minutes , is far to long toobe of any commercial interest. Cure times of less than one minute at 220°C are now common in salt baths and fluid beds. Obviously the compounds used for such cures are specifically designed for them, the major difference being in the cure system chosen. It seems relatively safe to assume that the processes which have taken place in the systems investigated in a matter of minutes will take place in a matter of seconds in a specially designed compound for high temperature curing.

4.1.6. Time Temperature Interdependance.

It is somewhat difficult to use the results as presented for prediction of vulcanizing conditions. As a result of this a contour graph was prepared which presented a summary of the characterization of one cure system. As the graph itself was large and complex, only a description of the method of construction and a simplified version of the plot will be presented. The graph was based upon the interdependance of time (t) and temperature (T):

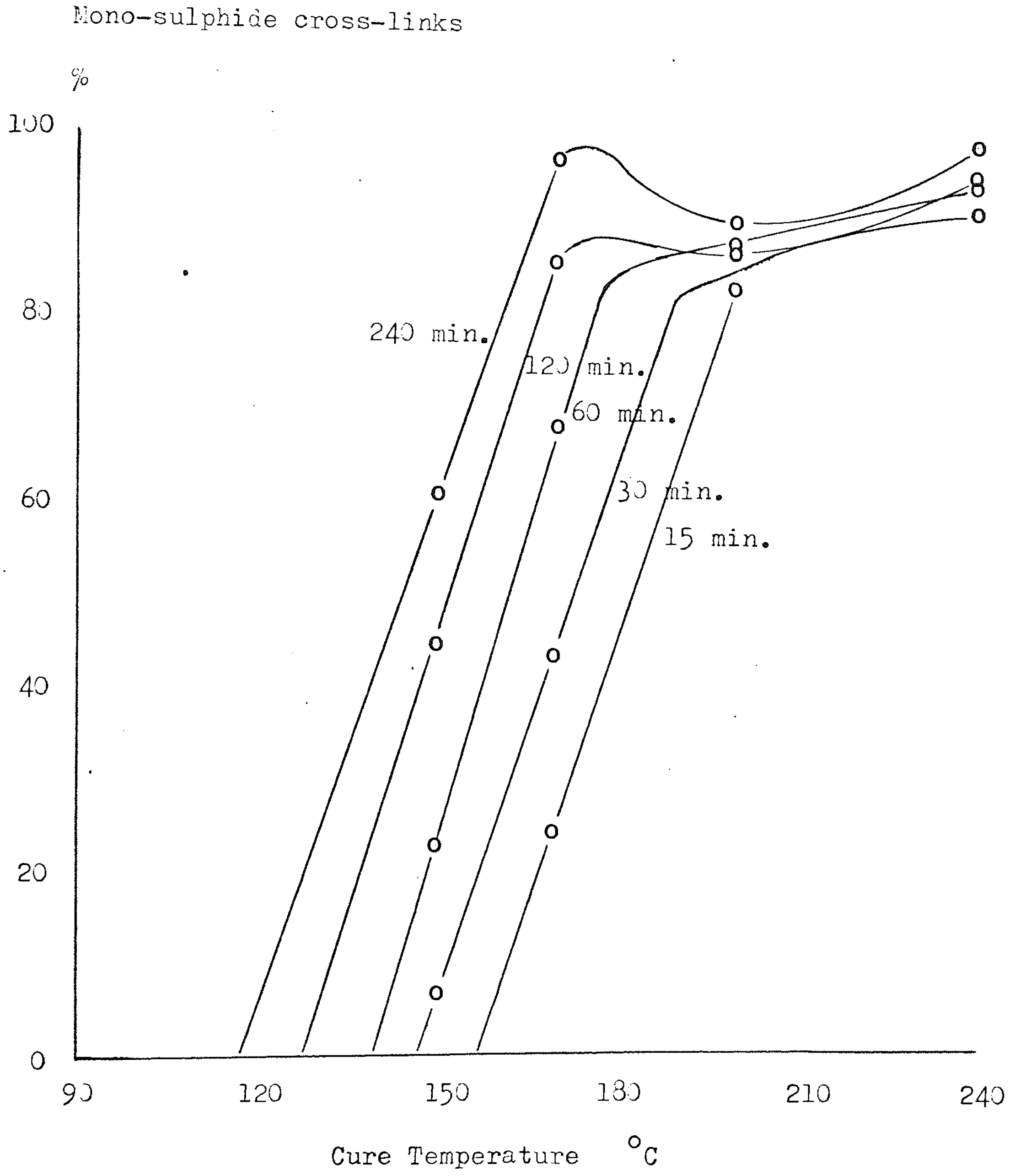
The various stages of the construction of the graph are outlined below:

(the results used are those obtained for formulation A)

- a) A plot of percentage of mono-sulphide linkages against cure temperature for a given cure time was prepared. This produced a family of curves (one per cure time) which were straight lines and roughly parallel (graph 35).
- b) By reading values of time at a given percentage of mono-sulphide links a time/temperature graph was prepared showing curves for a given percentage of mono-sulphide linkages. Again a family of curves was obtained, which was almost exponential in form (graph 36). The temperature scale went only to 210°C since at most temperatures over 200°C the proportion of mono-sulphide cross-links was high, even at short cure times. This series of curves can be used to obtain an estimate of mono-sulphide links given the cure temperature and time (or vice versa).
- c) Stage 'a' was repeated using the values of di-sulphide content. Here a family of parabola type curves was obtained which indicated the build up and subsequent decline of this cross-link (graph 37). The full lines indicated the region covered by experimental results, the broken lines indicated their probable course.
- d) A repeat of stage 'b' using graph 37 to produce the values of percentage di-sulphide loading and time produced the the time temperature plot relating to di-sulphide linkages (graph 38). Again the dotted portions of the curve were supposition and the time scale was extended to cover the probable extent of these curves.
- e) The two time temperature graphs (36 and 38) were then superimposed on top of each other using the larger axis; those used for the original plot measuring fifteen inches by twenty five inches.

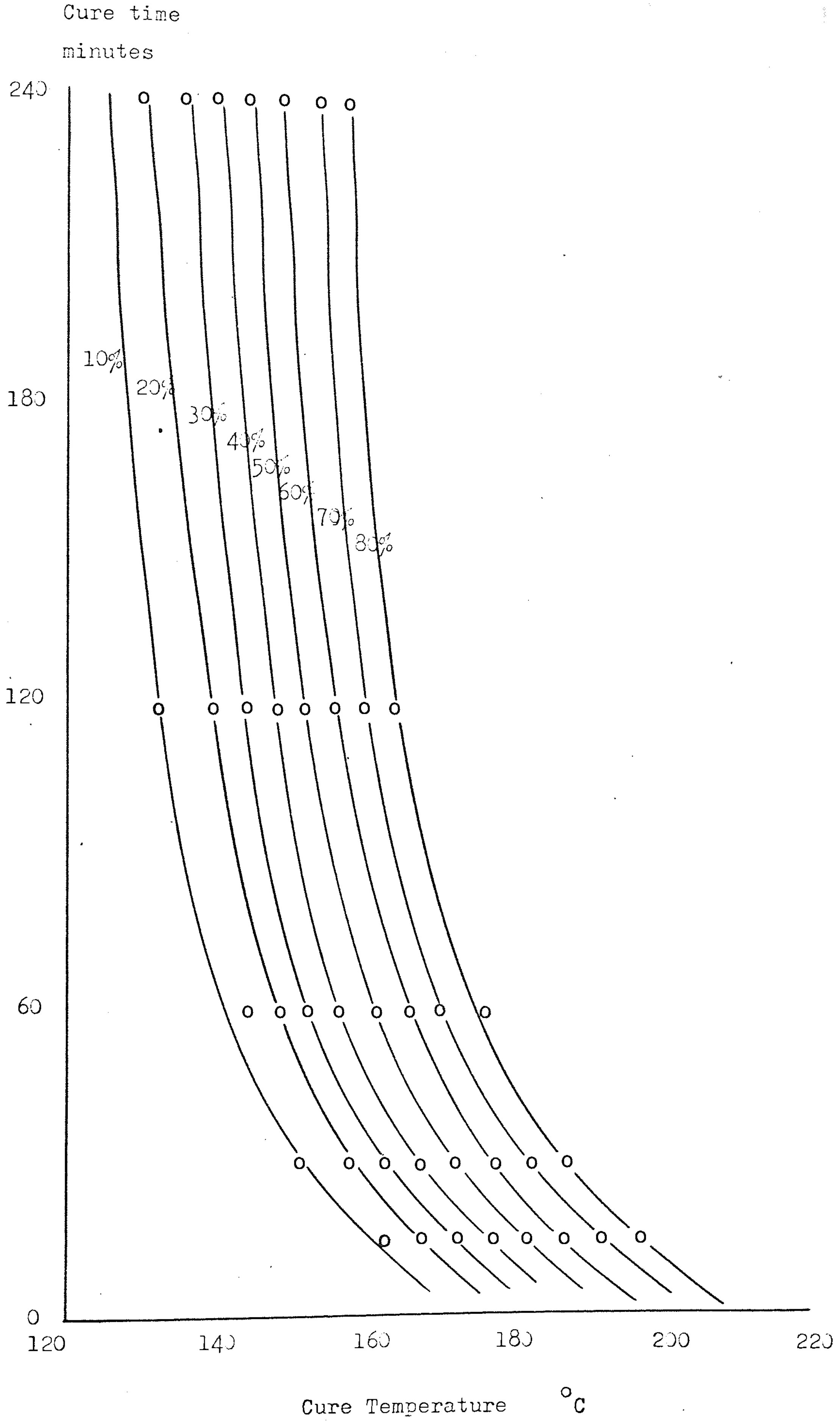
GRAPH 35.

Plot of percentage mono-sulphide cross-links against cure temperature for formulation A.



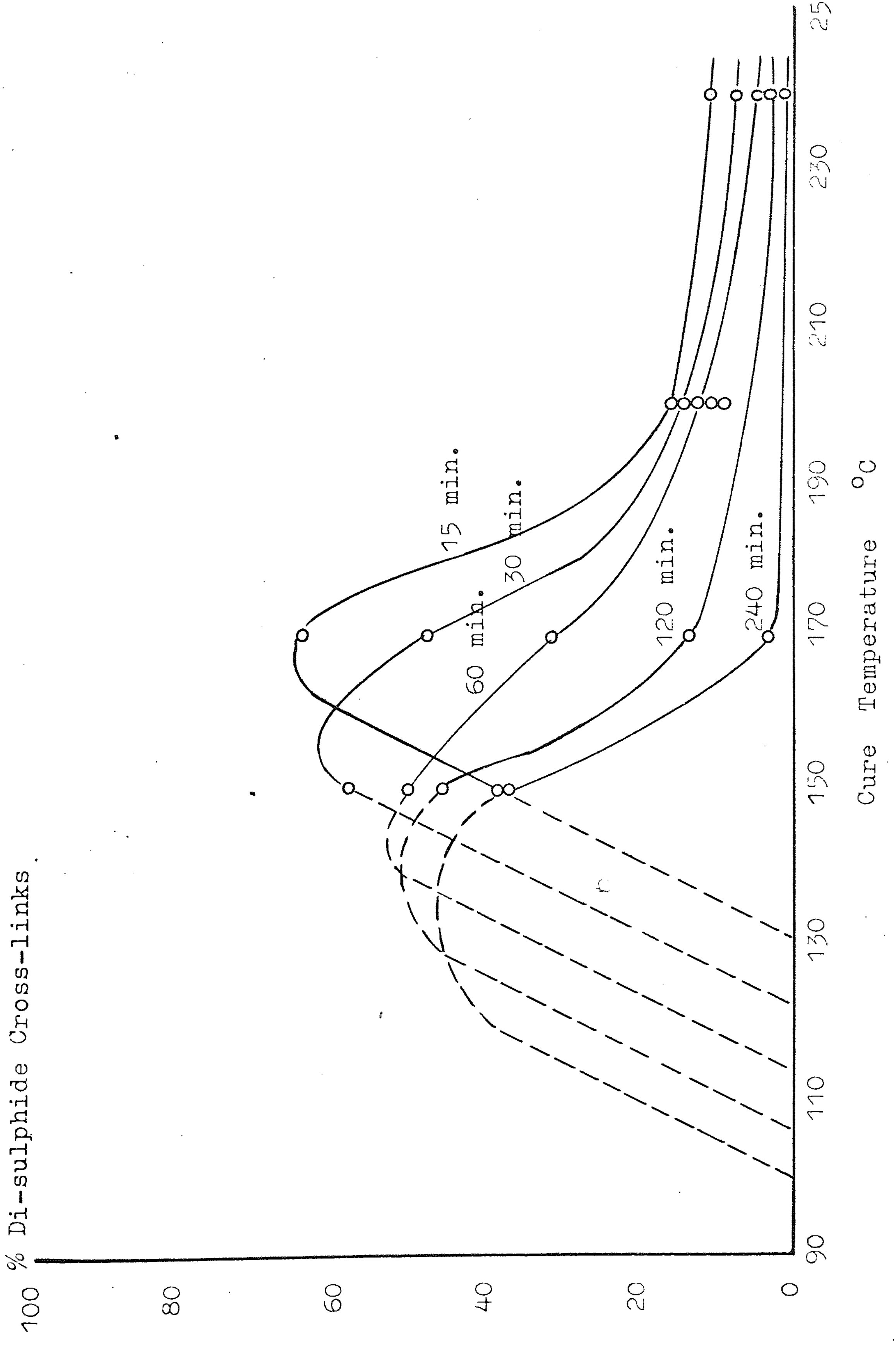
GRAPH 36

Time/Temperature contour graph for mono-sulphide cross-links in vulcanizates of Formulation A



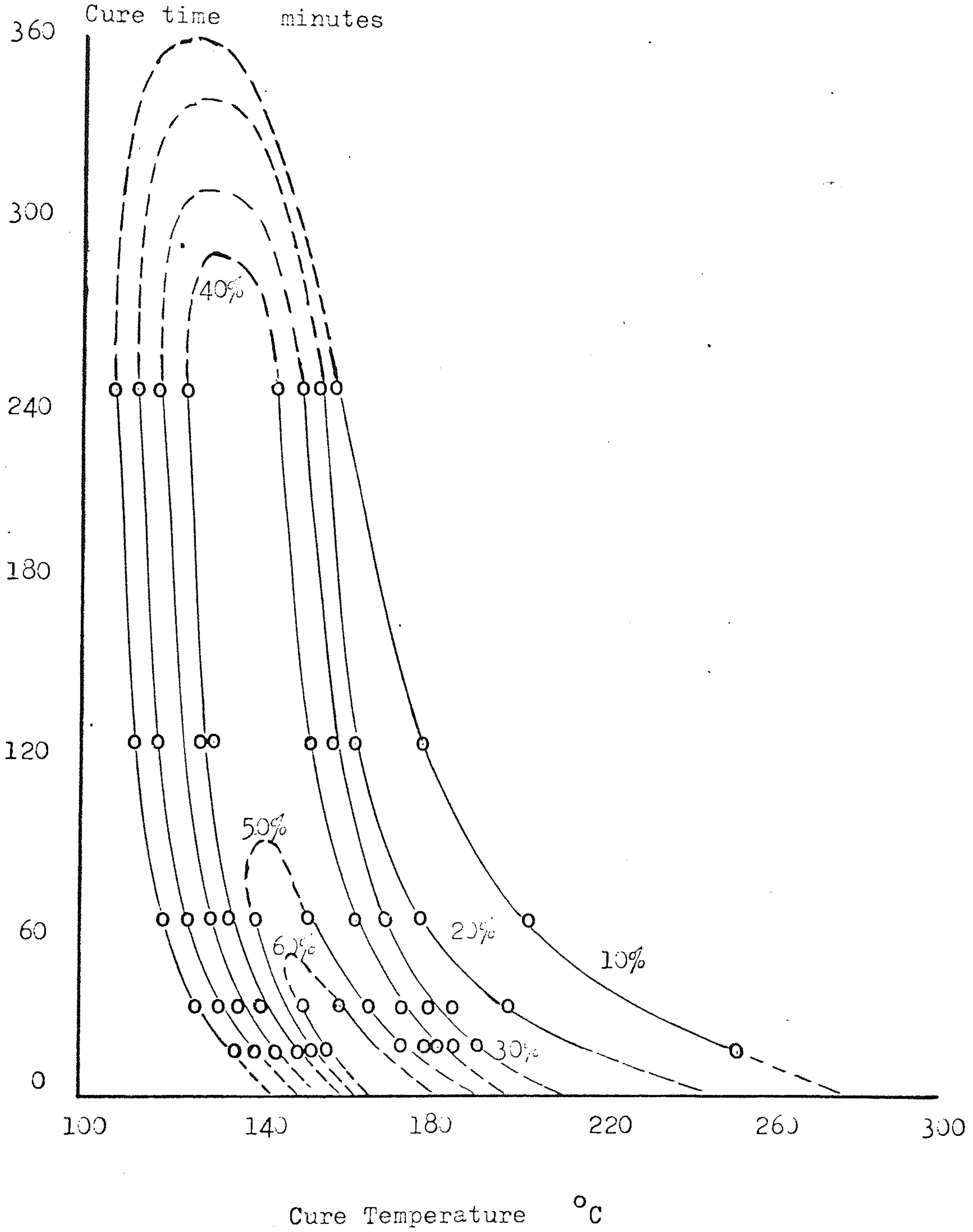
GRAPH 37.

Plot of percentage di-sulphide cross-links against cure temperature for Formulation A



GRAPH 38.

Time/Temperature contour graph for di-sulphide cross-links in vulcanizates of Formulation A.



- f) Light shading of the portion of the graph to the left of the maxima of the di-sulphide contours marked those portions of the time temperature plot where poly-sulphides were found (graph 39); the unshaded areas being those where poly-sulphides were rare.
- g) From the rheographs the times required to obtain 80%, 90% and 100% of cure (t_{80}, t_{90}, and t_{100}) were obtained. These were then plotted on the time temperature graph to show at which conditions the cure became technologically viable. Should there be pronounced reversion then two values of t_{90} and even t_{80} may be required at each temperature thus setting an upper and lower limit to cure time.
- h) From the total cross-link density curves, the times required to attain the maximum cross-link density at each temperature were noted (t_{max}). These can be plotted on the time temperature plot.
- i) Finally, the total cross-link density values at the various cure times were added to the plot using a second vertical axis. The value of the maximum cross-link density obtainable at each temperature was plotted against that temperature.

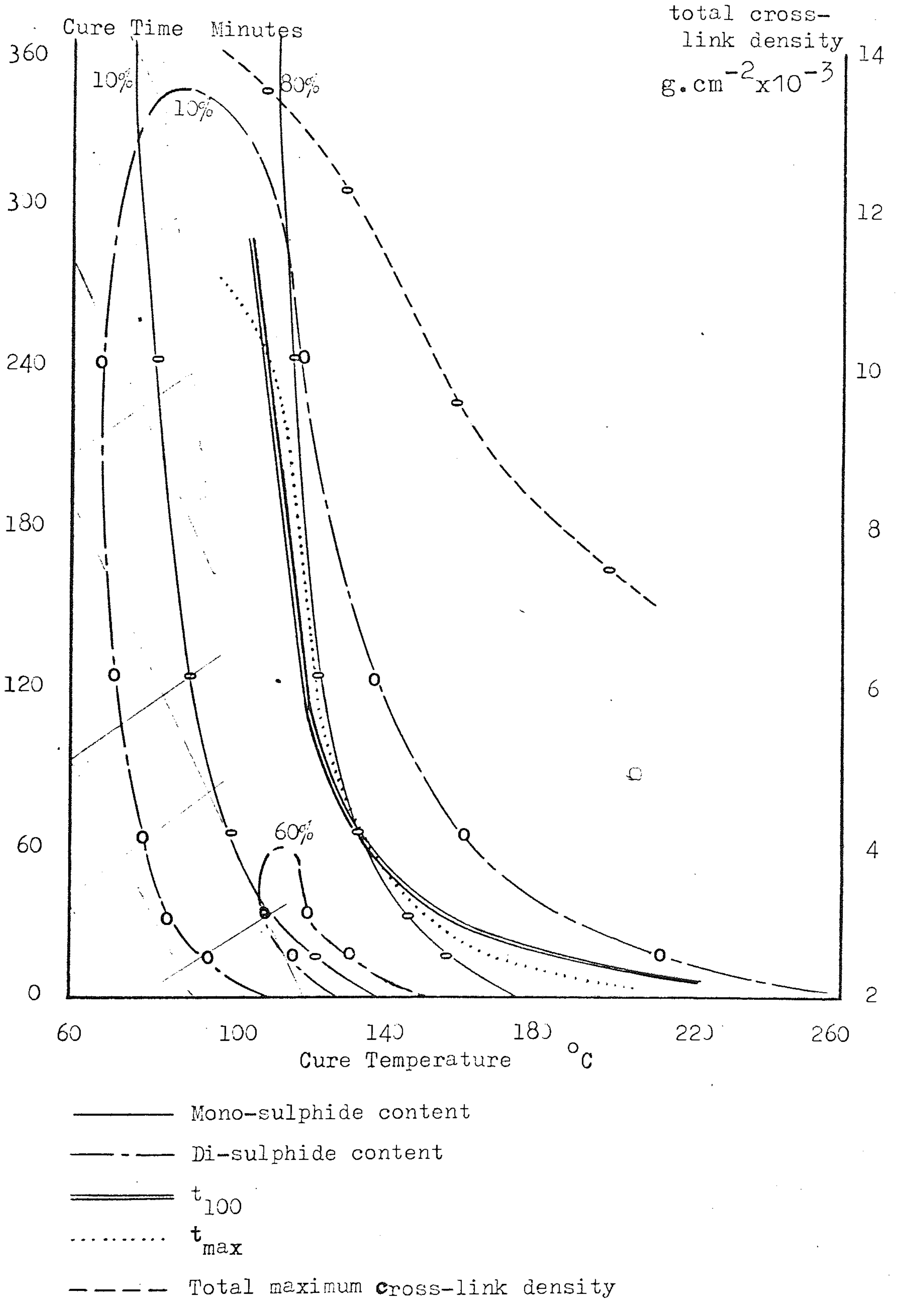
The resultant graph is depicted in graph 39 which shows the outline of a contour graph and comprised only:

1) limits of mono-sulphide contours (10% and 80%)
2) limits of di-sulphide contours (10% and 60%)
3) time to 100% cure (t_{100}) from rheographs
4) time to maximum cross-link density (t_{max}).
5) maximum obtained cross-link density.

The contour graph could be used to predict, under prescribed cure conditions, not only the cross-link density obtained but the cross-link composition produced, and whether or not the cure was technologically viable. Alternatively, for a given cross-lin

GRAPH 39.

Contour Graph showing the network structures obtained with Formulation A over the whole time and temperature ranges.



composition and density, a range of suitable curing conditions i.e. temperature and time, could be selected. A plot of this type was only applicable to a given formulation but once performed, comprehensively described the possible variations of network structure, and how they could be obtained.

4.1.7. Structure and Physical Properties.

In order to leave the networks free from extraneous materials and to avoid the use of chemicals which would or could in some way interfere with the cure media the investigations described in this work were conducted on gum vulcanizates. The poor physical properties developed by unfilled E.P.D.M. vulcanizates are accepted, and hence great difficulty was found in observing strict trends in the measured properties. In general few comments can be made relating the observed structures and the measured properties. At the lower temperatures the physical properties followed those trends that would have been expected of them. At higher temperatures, where the network structures produced were a relatively constant mixture of mono-sulphidic and di- sulphidic linkages almost all semblance of any correlation had disappeared. Hardness and modulus follow the total cross-link density at the low temperatures whilst tensile strength and elongation tended to follow the disappearing poly and di-sulphidic linkages. Compression set as expected followed the mono- sulphidic link concentration.

A further generalisation which can be observed as a result of this work is that the tensile strength and elongation reach a maximum fairly early in the cure whilst compression set and modulus "peak" at a later stage.

4.2. Other Conclusions Regarding E.P.D.M.'s.

4.2.1. Technological Aspects.

The compounds examined for this work would be of little use in industry due to their poor physical properties and excessive prices (economic aspects will be discussed in the following section). It is, however, possible to discuss a few general points which arose during this investigation and to embelish this by drawing upon the literature.

a) The polymers used for this work were easy to process on a mill, although specialised techniques had to be used. Excessive mill times were avoided and as long as tight nips were used , few problems were encountered. The Nordel (1:4 hexadiene) and Royalene (DCPD) polymers handled better than the others. This fact is probably more indicative of the polymerisation techniques than the termonomer used. It is difficult to generalise when discussing the processability of E.PD.M.'s since this work was conducted on polymers of similar characteristics. It is known[83] that with polymers of differing ethylene content new difficulties ~~neccessating~~ necessitating other techniques are noted. Oil extension also effects processing ease as does molecular weight and molecular weight distribution. The use of internal mixers is known to produce some problems with this class of polymer but provided care is taken these are easily overcome. Certain types of E.PD.M. are notorious for crumbing in these mixers if left by themselves and thus early addition of fillers and extenders is necessitated. In cases where high filler and oil loadings are used "upside down mixing" is preferred in order to improve dispersion and to decrease mixer cycles. Injection moulding and extrusion of E.P.D.M. compounds are relatively easy providing that care is taken in compounding. Grades are now available with low mooney viscosities which were developed specifically for these fabrication techniques. E.P.D.M. sheeting prepared on calenders is now used as pond liners and again provided that careful compounding is used there are few problems in fabrication although the inherent slow cure and general low temperatures of sheet curing equip-ment do tend to slow down lines.

b) The moulding characteristics of these polymers were good although a little difficulty was encountered at higher temperatures where some visible degradation took place around the edges of the samples. Flash extruded easily into the channels and voids were not encountered . In some cases at higher temperatures, localized porosity occurred, but not in sufficient amounts to make the cutting of samples difficult. Although this could not be tolerated in production it only occurred ~~ocured~~ after extended cure times which would be commercially impracticable. No sticking to moulds was encountered and this is again evidence of the non-tacky nature of these polymers. This fact indicated that there is no need to use a mould release agent and in any case the use of such a material produced staining on the sample surfaces.

c) No quantitative tests to assess tack were carried out but the Royalene and Nordel polymers were marginally better than the Enjay materials, although this level was negligable when compared with the tack of a general purpose elastomer. The various cure systems had no appreciable effect on the tack.

d) Colour is often unimportant since in most cases the polymer would be filled with carbon black. They are, however, currently finding applications in white compounds and this problem should be considered. Of the compounds investigated the "whitest", as expected , was the peroxide cured system. The sulphur based vulcanizates exhibited varying degrees of discoloration, moving from A, which was quite lightly discoloured, to V which was badly discoloured. The degree of discoloration increased with increasing cure temperature. The problem in the samples investigated could be over-come by the judicious addition of titanium dioxide. In industrial compounding of light coloured compounds efforts are made to restrict the choice of cureatives to those which are non-staining and non-discolouring. Unfortunately, most of the faster accelerators for these elastomers (section 4.1.2.) tend to be staining and /or discolouring, thus in consequence titanium dioxide loadings of up to 30 p.h.r. are common.

e) Only vulcanizates produced from formulation V exhibited a lasting and unpleasant odour, which could have been detrimental in service. The characteristic odour of dicumyl peroxide and of peroxides in general can be overcome by the use of blends of peroxides[80]. The problem of odour and taste can become very important when the final end product comes into contact with food stuffs or drinking water, since the taste and / or odour are easily transferred.The odour is easily removed by the addition of a reodourant whilst the problem of taste necessitates the reformulating of the mix.

f) At normal processing temperatures (150 - 200°C) the cure of E.P.D.M.'s offered no problems apart from their inherent slowness. Scorch seldom worries the compounder, neither does rate of cure , both being varied between "safe" limits by careful choice of accelerators, polymer and filler. Cross link density again could be varied by choice of compounding ingredients. Under normal conditions reversion was a factor which did not need to be considered , because, due to the hot tear strength of these polymers they are often removed from the mould after only fourty to fifty percent of the cross-linking has occurred. The stability of the E.P.D.M.'s make them aptly suited to the newer high temperature vulcanization techniques such as salt baths, fluid beds, C.V. tubes and with suitable compounding micro-wave ovens.

g) Bloom was, quite surprisingly, not noticed on any of the vulcanizates prepared for this work. In general press cured E.P.D.M. is quite prone to blooming. Current thought on this problem is that there is a thre-shold limit for each accelerator below which it will not bloom. In general these limits are in the order of 3.0 phr for the thiazoles and most sulphenamides, 2.0 phr for some of the higher molecular weight dithiocarbamates and 0.8 phr for the thiurams and the bulk of the di-thiocarbamates.

4.2.2. Economics.

Although the various merits of the cure systems and polymers have been discussed, the economic aspects, which are of prime importance, must be considered. A comparison was therefore made between the cost per unit weight of the vulcanizates and the cost per cross-link formed. By obtaining the current prices (July 1970) of ingredients, of accelerators from Monsanto Chemical Limited, of polymers from Uniroyal Chemical Division Limited, and of other ingredients from R.A.P.R.A. (Rubber and Plastics Research

Association of Great Britain), a simple costing was performed. Table 17 shows the cost in pence per kilogram of vulcanizates (excluding processing costs which were assumed to be constant). The second column expresses the figure as a percentage of an arbitrary average price of 60 pence per kilogram for ease of comparison. In order to differentiate between the simple cost per kilogram of vulcanizate and the cost per cross-link, the price per gram was compared with the cross-link density to produce a relative figure for the price of one gram molecule of cross-link. This was also expressed as a percentage of an arbitrary value of 800 pence per gram molecule of cross-link. The cross-link density figures used were the maxima obtained at 150°C cure. Perhaps the most interesting fact which arose from these figures was that although formulation C had the highest cost per kilogram, it had the lowest relative cost per gram molecule of cross-link, the latter figure being more important when a tight cure was required. Although formulation V was recommended for use with E.P.D.M.'s it was more expensive on both counts than the standard formulation A. Formulations N and R were both reasonably priced when concerned with the bulk price of the formulation, but both produced very expensive cross-links, being three times and nearly five times as expensive as formulation C.

In vulcanizates B,N,E and R the same compounding ingredients but different termonomer type E.P.D.M.'s were used. As the polymers were equally priced the costing based on pence per kilogram was the same, but due to the different termonomer activation there was a very large difference in the cost per gram molecule of cross-link, 628 to 1,390.

TABLE 17

Prices of Formulations

Costing Formulation	cost/kg d/kg*	expressed as % of 60d/kg*	cost/g.mole of cross-link d/g mole*	expressed as % of 800d/g.mole*
1	47.2	79	1021.6	128
2	52.0	87	602.6	75
3	57.2	96	502.4	63
4	62.0	103	393.18	49
A	64.3	107	476.3	60
B	69.4	116	641.4	80
C	76.0	127	293.4	37
V	66.5	111	531.9	67
N	69.4	116	1035.8	129
E	69.4	116	628.6	78
R	69.4	116	1388.1	173

* old pence

4.2.3. Efficiency of Vulcanization.

The number of cross-links introduced by a sulphur based system was limited by the number of cross-linking sites available. By assuming that one cross-link required two points of unsaturation, and calculating the theoretical number of double bonds present, relative efficiency parameters (Q) were calculated for each cure system. The theoretical number of double bonds was calculated as weight of polymer containing one gram molecule of termonomer and compared with the figure for the weight of vulcanizate containing one gram molecule of cross-link (calculated from the value of the maximum cross-link density attained). The result (Q) was expressed as a percentage. Table 18 presents the Q values for formulations A,B,C, and V when cured at 150°C.

TABLE 18

Efficiency Rating of Formulations A,B,C, and V.

Cure system	A	B	C	V
Q %	94.3	76.4	182.9	88.3

The main point indicated was that formulation C had a Q value of 182.9%, suggesting that it was not limited to points of unsaturation as cross-linking sites. The empirical statement "that total cross-link density is related to the proportion of sulphur" can now be ratified. The weight percentage of sulphur present in each of the cure systems A,B, and V was compared with the respective Q values. Table 19 presents these results, and they have been plotted as graph 40. As can be seen there was a linear relationship between the total concentration of available sulphur and the efficiency of vulcanization.

TABLE 19

Efficiency of Cure and Concentration of Available Sulphur.

Formulation	A	B	V
Sulphur wt %	25.4	11.14	22.1
Q	94.3	76.4	88.3

It was obvious from the total cross-link density curves that the maximum value decreasedwith increasing cure temperature. The Q values of all the E.P.D.M. formulations have been calculated to show this effect. These are presented in table 20 and graph 41.

TABLE 20

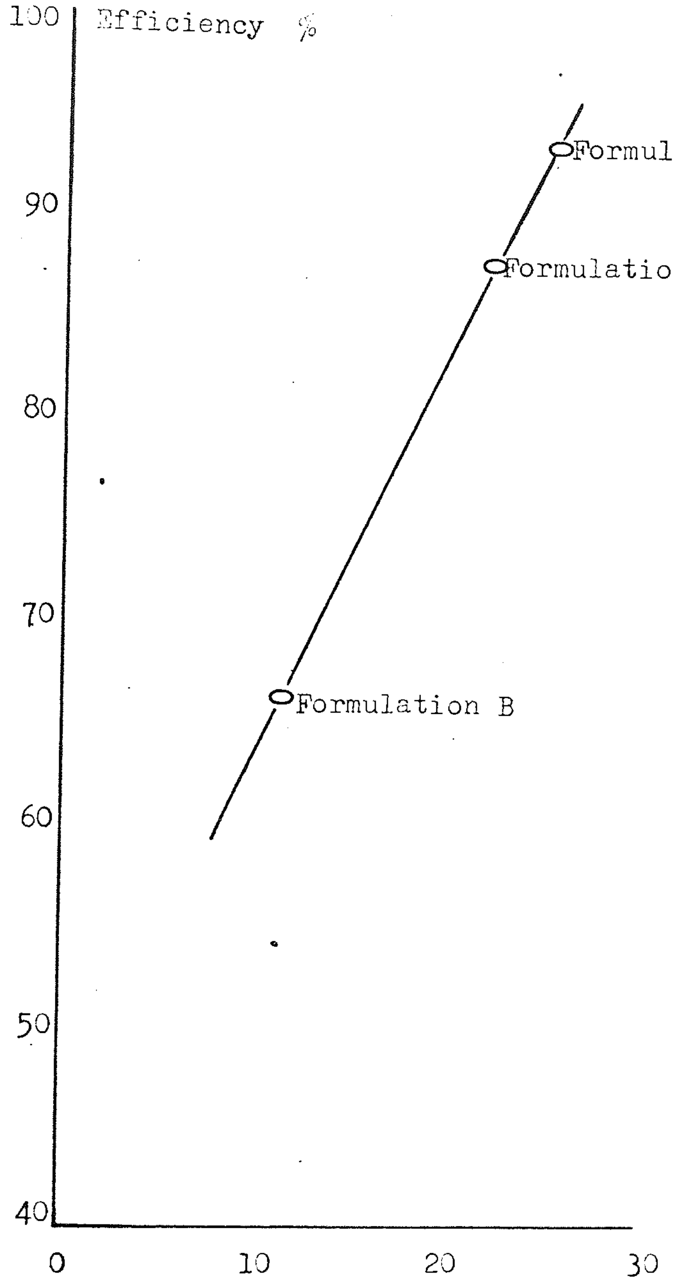
Efficiency of Cure at Various Temperatures.

Temp °C / Formulation	150	170	200	240
A	94.3	79	68	51
B	76.4	56	22	19
C	182.9	156	123	91
V	88.3	80.5	67.5	44
N	33.6	32.0	-	-
E	66.2	55.5	-	-
R	44.0	44.0	-	-

As can be seen, formulation R had a constant value of Q whilst all the others showed a definite decrease in Q at varying rates. Formulations A, V and C showed an almost linear decrease in Q over the range studied.

GRAPH 40.

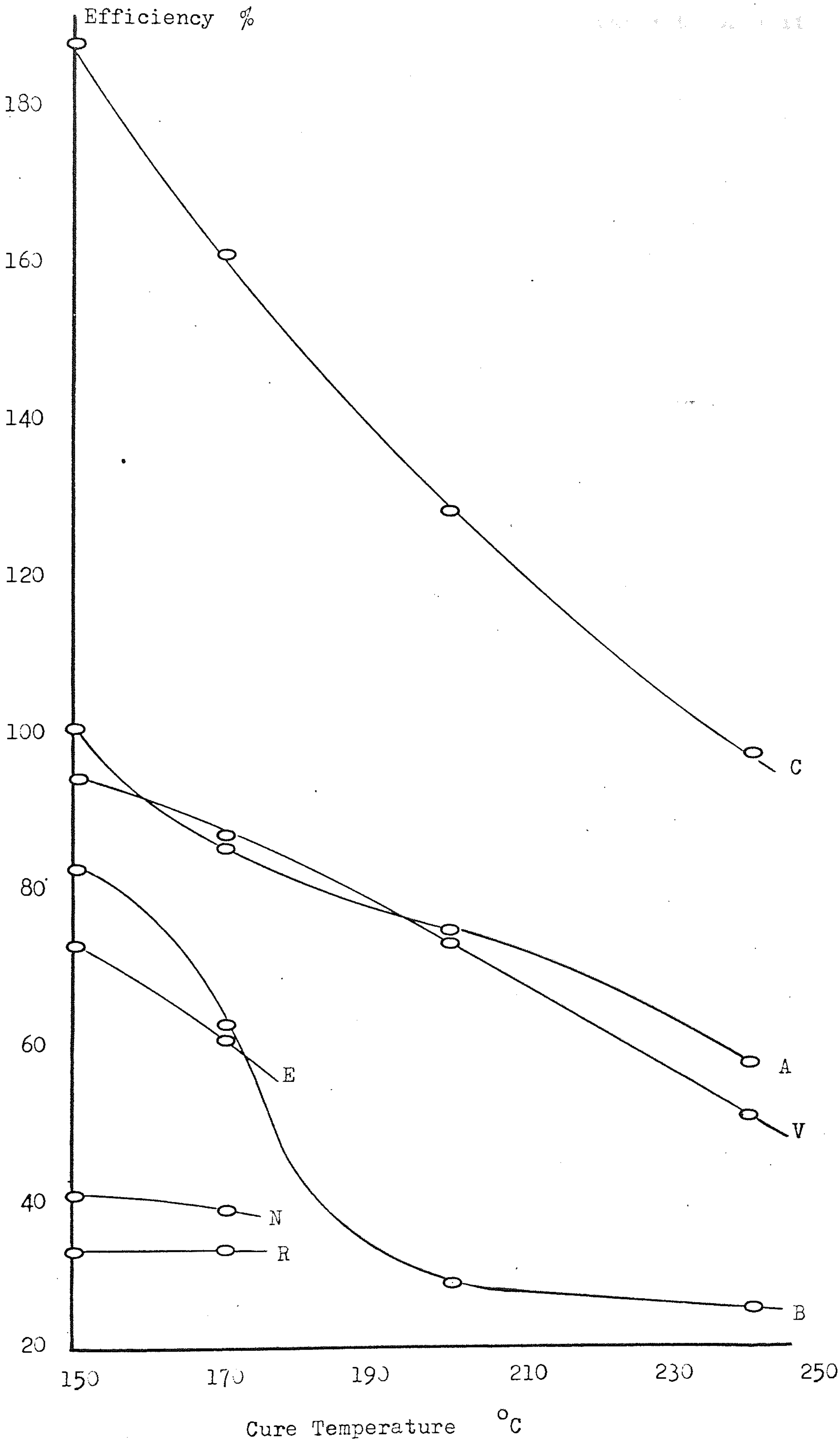
Graph of the Efficiency parameter (Q) expressed as a percent against the total available concentration of sulphur in the cure system, also expressed as a percent



Total available sulphur in the cure system expressed as a %

GRAPH 41.

Plot of the Efficiency parameter (Q) expressed as a percent against the Cure temperature.



Although cross-link density figures indicate a reversed order, the higher efficiency noted with formulation R when compared to formulation N, is easily explained. On considering the molecular weights of DCPD and 1:4 hexadiene (132 compared to 82) it becomes obvious that for equivalent weight percent loadings their will be more molecules of 1:4 hexadiene than DCPD.

4.3. Conclusions With Respect To Techniques Used.

4.3.1. Swelling

In general, technique of equilibrium swelling is a simple, rapid and accurate method of determining the cross-link density of a vulcanizate providing the polymer solvent interaction parameter for the polymer/solvent pair is known. In this work the stress strain behaviour of the vulcanizates was observed when samples were in the swollen state in order that the effect of the C_2 parameter of the M.R.S. equation becomes zero, thus simplifying the calculations. Choice of solvents for the swelling procedure was of some importance since this affected the value of volume swelling (V_r) obtained, which in turn had an effect on the calculated value of C_1 and hence on the determined value of cross-link density. Although earlier workers limited the maximum values of V_r to 0.20[21] and 0.25[71] values of up to 0.33 were used in this work without any detrimental effects. Perhaps the most critical procedure in the swelling technique is that of weighing the swollen sample. In order to minimise the loss of solvent during this operation Ellis and Welding[63,64] devised a sophisticated technique wherin the swollen sample was weighed in an atmosphere of solvent vapour. The findings described in this work indicated that provided adequate care is taken and the weighing is performed speedily, the use of a tared stoppered weighing bottle could produce accurate results.

The solvent chosen for use with E.P.D.M. in this work was n-heptane since not only did it produce a V_r value in the required order but it was also to be used in the probe work.

4.3.2. C_1 by the Tension Technique.

The tension stress strain technique is recognised as a well established and accurate technique for obtaining values of C_1

for network evaluation. Although normally used for dry specimens it can be adapted for use with samples swollen to equilibrium. It has the advantage of producing values of C_2 as well, although at present little additional information can be obtained from these values. The strict time sequence is essential in order to maintain accuracy by removing relaxation effects. In consequence it can only be used with polymers possessing suitable relaxation rates (low) and green strengths (high). In general it is found to be laborious and the calculations would have presented some difficulty to the amateur programmer since the areas of " λ upturn" were variable. However, the computer was used to calculate values of $(\lambda - \lambda^{-2})$ and λ^{-1} over a suitable range[66].

4.3.3. C_1 by the Compression Modulus Technique.

This technique, used for the bulk of the determinations mentioned in this work produced results which in evaluations compared favourably with those obtained when utilising the tension technique. As neither technique is absolute it is difficult to compare results from other than a relative stand point. Careful choice of solvent (4.3.1.) and use of the exact mathematical expression (4.3.4.) increase the accuracy of the technique and widen the range of experimental conditions over which the technique is applicable. The use of the micro-method described by Smith[21] decreases the time required to swell the samples. Use of the smaller samples has produced a number of critisims from other workers[70], the main one being the danger of anisotropic swelling producing false values of C_1 and that a similar error caused by gross edge effects and barrelling of the samples during the determination. The effect of each of the above has been evaluated and found to be negligible. The technique itself requires rigorous timing in order to reduce relaxation effects but is somewhat less tedious than the extension method. The most laborious part of the technique is that of calculating the C_1 parameter from the experimentally determined load (f) and deflection (Δ h) values. This task was considerably shortened by the utilization of a computer (4.3.5.).

4.3.4. Mathematics.

As has been indicated earlier in this work the calculation of cross-link density is dependent upon the relationship between the C_1 parameter and the $M_{c.chem}$ or $M_{c.phys}$. The C_1 parameter itself is obtained from the experimental results taken during the compression modulus determinations performed on swollen samples. The experimental values of load and deflection are then evaluated in such a manner that when some function of $f / (\lambda - \lambda^{-2})$ is plotted against some function of $1/\lambda$ the slope of the graph will be some simple function of C_1. The major problem in this mathematical analysis is that of obtaining the values of the function of $(\lambda - \lambda^{-2})$. As further refinements were made to the original Cluff et al[20] equation (equation 8) by Smith et al[22], (equation 9) , Thomas et al[24] (equation 10). and by Melley et al (equation 11), the only difference apart from a loss of simplicity is a decrease in the degree of approximation occuring in the mathematical analysis. The degree of approximation varies with the cross-link densities although at these levels of cross-linking it is numerically smaller. Both the approaches of Thomas et al[24] and Melley et al[25] are mathematically exact and at normal ranges of cross-link densities produce the same results, which are closer to those results obtained when using the Tension method than any of the other approaches. Throughout this work results obtained from the compression modulus techniques have been compared to those of the dry stress strain technique in order to evaluate their credibility. For the bulk of the work the results produced by the Thomas et al equation were used, simply because of their ease of abstraction from the computer throw-out. However, it should be pointed out that there is no evidence that the results obtained by either method are absolute. Thus in reality the results presented in this work should be treated as relative, and not as absolute, until some new fundamental technique for evaluating cross-link densities can be found. The ranges of experimental conditions over which the various mathematical approximations can be used depends upon the degree of the approximation itself, but also, as is evidenced when considering the two exact derivations, upon those parameters chosen to be measured. Thus even an exact derivation will be limited in use to that range of experimental conditions in which the parameter can be accurately determined.

4.3.5. Use of the Computer.

Despite the simplicity of the original expressions formulated by Cluff et al[20] the evaluation of ten or more sets of data by hand became a laborious task. Use of the more complex expression derived Melley et al[25] resulted in a laborious time consuming process to evaluate one data sequence. By use of the computer the time required to analyse a complete set of data by all known mathematical approaches was reduced from three hours to a fraction of a second. Careful programing resulted in a single program which eliminated the need to produce a graph in order to obtain the slope and intercept of the plots of a function of ($\lambda - \lambda^{-2}$) against $1/\lambda$. Using the method of least squares the equation of the best straight line is calculated thus providing values of both slope and intercept. The calculations in a work of this size make it essential to utilize the computer to its fullest extent in order that sufficient time is available to complete the experimental work.

4.3.6. Chemical Probes.

Both chemical probes used in obtaining the results noted in previous sections were of the "thiol/amine" type, namely the propane-2-thiol/piperidine and the n-hexane thiol/piperidine, and were found to be easy to use, requiring little exotic apparatus. However, due to the unpleasant nature of both probe solutions, extreme care was essential in the preparation, use and disposal of these materials. Due to the relative ease of oxidation of these materials it became essential to store the thiols in a refridgerator and to check the quality of each new batch on arrival and periodically during storage. The piperidine used was distilled in an inert atmosphere and any subsequent storage was in a sealed vessel under an inert atmosphere and in the dark. The solutions, once made up, were used immediately where ever possible, but in any case no solution was kept longer than five days. With regard to the disposal of the prepared probe solutions, the method preferred of those investigated was that of addition to ammoniacal copper sulphate solution. The main reason for this choice was the comparative odourless products when compared to those products formed during other disposal techniques.

Initially reaction conditions for the use of the probe solutions with E.P.D.M. vulcanizates had to be determined and as a starting point the techniques used by N.R.P.R.A.[40] were adopted and the reaction time adjusted to suit this polymer. It was found that for the propane-2-thiol/piperidine in n-heptane the optimum reaction time was five and one half hours (asopposed to that of two hours for natural rubber) whilst in the case of the n-hexane thiol/piperidine a similar time to that required by natural rubber, namely forty eight hours, was found to be suitable. In the use of n-hexane thiol/ piperidine the reactions were conducted in vacuo but at a lower pressure than suggested by N.R.P.R.A. and without noting any ill effects. The resistance of the polymer to oxidative attack may be the prime factor for this. Several experiments using propane-2-thiol/piperidine, conducted on samples of vulcanizates cured for either long times and/or at high temperatures indicated an increase in cross-link density. After a series of extensive experiments to check these results it was obvious that the effect was genuine and appeared to be exhibited under conditions where the cross-link being "probed" for was expected to be absent. In such a case the probe solution would become effectively redundant. It is possible that under these conditions oxidation of the probe on a small scale could result in a cross-linking reaction but to date no plausable explanation has been forwarded to deal with this phenomena.

4.4. Discussion regarding the work of Previous Workers.

The conclusions regarding techniques, drawn from this work have already been discussed in light of conclusions drawn by other workers in previous sections. Thus this section will be confined to the major aim of the work, namely the elucidation of the network structures of E.P.D.M. vulcanizates.

The work of Laud and Stuckey [51, 52], which was in fact the precursor to this project was conducted on the same base polymer (Enjay 3509), using the same formulations and ingredients. The only variation was that Laud included a small proportion of carbon black (15 phr of FEF black) in order to give his vulcanizates sufficient strength for the analytical technique of stress relaxation. The important facts evolving from this work were the high levels of the stable mono-sulphide links observed and the rapid rate of conversion of polysulphidic links formed initially with the sulphur donor system.

Frensdorf [46] and Saegabarth [45] both presented work from the same source. They investigated vulcanizates of 1:4 hexadiene polymers swollen in cyclo-hexane, and followed the compression technique described by Cluff et al [20], limiting the extent of compression to 5%. Investigations into the effect of solvent choice showed that for a good solvent (cyclo-hexane) the measured value of χ was constant whereas for a poor solvent (T.H.F.) the χ value varied and was in fact a function of V_r. Their work utilized a thiol-amine probe based on xylyl-thiol. They varied mercaptan, base and solvent, only to get the same result, thus proving that the probe solution was breaking all cross-links with more than one sulphur atom. Although they experimented with filled vulcanizates they found it impossible to obtain meaningful results. They too assumed that during sulphur vulcanization 50% of the unsaturation would be consumed and from experimentation, working from this premise, figures of 40 – 45 elastically effective cross-links per hundred initial unsaturation sites were obtained for a cure system similar to formulation A (TMTM : 1.5 ; MBT : 0.5 ; Sulphur : 3.0). This is equivalent to a Q value of between 80% and 90%.

This figure is very much higher than the figures obtained in this work for 1:4 hexadiene polymer but there are certain facts which make a comparison dangerous:-

a) no mention is made of the complete range of polymer characteristics

b) the cure system contains 1.0 phr more sulphur

c) the cure system utilises a more effective accelerator c.f. TMTM (tetra methyl thiuram monosulphide)

It is of interest to note that these workers believe that it is possible that the number of attacks at unsaturated sites involving allylic rearrangements may outnumber those involving simple saturation. Optimum Cross-link density was attained in 20 - 40 minutes at $160^{\circ}C$, which when bearing in mind the formulation variations mentioned above would appear to agree with the results obtained from this work. These workers also noted the tendency for modulus and ultimate tensile strength to follow the total concentration of cross-links and for compression set and ageing characteristics to follow the concentration of the shorter mono-sulphidic linkages, a fact deducted from this work as well. Frensdorf, however, did not differentiate between polysulphidic $(-S_3-)$ and disulphides $(-S_2-)$ and thus any sulphur linkage comprising of two or more sulphur atoms was considered as being poly-sulphidic in nature. When commenting upon the effect of cure time (at $160^{\circ}C$) these workers state that an increase in cure time causes an increase in cross-link density and in the proportion of monosulphidic linkages. However, since as in this work reversion was noted, it would be safer not to generalise on the effect of cure time. When comparing various cure systems (conventional sulphur, specialized sulphur, sulphur donor) these authors note that with respect to the time to optimum cross-link density the order is:-

$$\text{Specialized} \ \rangle \ \text{S - donor} \ \rangle \ \text{conv. S}$$

and the level of cross-linking is the same. It is interesting to note that the percentage of mono-sulphidide links (after two hours of cure) also follow this order. In this work the order of conventional sulphur and sulphur donor systems (A & B) are reversed, this being undoubtabley due to the additional sulphur used by Frensdorf et al in his conventional sulphur system. Nordel (1:4 hexadiene termonomer) produced the highest percentage of mono-sulphidic cross-links, with the exception of the ROYALENE D.C.P.D. compound. When considering the effect of the concentration of sulphur it was noted that as the level increased so did the cross-link density and also the concentration of mono-sulphidic links (160°C for 60 minutes). As cure temperature was increased it was noted that the time to optimum cure was halved for each 10°C rise (approximately) but that this was accompanied by an overall drop in cross-link density. The proportions of mono-sulphidic links remained consistent indicating that the activation energy for conversion of poly-sulphides to mono-sulphides at each temperature is the same. All of these have been substantiated by this work. Frensdorf spent much time in analysis of Monsanto Rheographs of each formulation and noted that the plot obtained from the kinetic analysis of his Rheographs indicated that the vulcanization comprised of two reactions, the first, a fast one (k_1) the rate of which was dependent upon the cure system, the second one (k_2) being slower and having a constant rate value, suggesting it be for a reaction involving a common intermediate. Although some Rheographs produced for this work could be shown to indicate two reactions there was no noticable similarity or conclusion that could be made regarding them (see Table 16B).

As can be seen, where k_2 values are obtained no constructive information can be obtained from them. It is of interest to note that k_1 values for these formulations using the sulphur donor system (B,N,E and R), at 150°C do show some similarity although this is beginning to disappear at 170°C

The workers at the Royal Aircraft Establishment (24) confined their evaluations to E.P.M.'s and apart from the single point technique, which has been discussed, perhaps the most interesting fact to come from this work is the linear variation of χ with C_1 (and V_r).

Baldwin (53) and his co-workers spent much effort in producing an equation equivalent to the Mullins equation, i.e. one taking into consideration entanglements and chain ends. However, the equation is suitable for use with one polymer only and hence was of little use in this work.

Klingbeil, Philis and Tokita (84) have indicated that E.N.B. is more effective than D.C.P.D. or 1:4 hexadiene in sulphur cures. They measured the utilization of unsaturation in such cures and noted that E.N.B. utilizes 50% of its unsaturation whilst 1:4 hexadiene uses only 20-25%. Thus these figures correlate well with those presented in this work. These authors also predict an optimum sulphur level and note the similarity in efficiency between 1:4-hexadiene and D.C.P.D.

Angier and Lauria (85) compared the physical properties of filled Vistalon 3509 with various cure systems. The results have been summarised in Figure 16D and compared with those obtained from this work. However, these comparisons mean very little due to the nature of the unfilled vulcanizates studied.

Imoto and co-workers,[55,56] investigated a series of cure system Types, some at various loadings. Their analysis of structure consisted of measuring combined sulphur via the schematic shown in figure 16E

Figure 16D

Comparison of physical properties of filled Vistolan 3509 with various cure systems. (cured for 30 minutes).

(S: sulphur SD: sulphur donor P: peroxide)

Property	Angier & Lauria		R.E.M.
	ORDER	RANGE	ORDER
Hardness Shore A	S>SD>P	76 - 74	P>S>SD
M200	S>P>SD	1900 -940	S>SD>P
U.T.S.	S>SD>P	2400 -1140	S>SD>P
E/B	SD>P>S	460 - 300	SD>S>P
Mooney Scorch	S>SD	8 - 17	P>S>SD

Figure 16E

Schematic Analytical Pattern

TOTAL S*_______(FREE S
(RETAINED S*_______(ZnS
(COMBINED S*_______(MONO S
(POLY S*

Values denoted * were measured, the remainder were obtained by difference.

They obtained cross-link densities from swelling data and differentiated between mono and poly sulphides by the use of Lithium Aluminium hydride. They noted that when sulphur is used as a coagent it finishes up bonded to the polymer. They found that most of the combined sulphur is present as mono-sulphide links. As expected, these workers noted that in a pure sulphur donor system the proportion of mono sulphide linkages far exceeds the proportion of poly-sulphide links, but what was not so predictable was that with a sulphur/TMTD cure a faster rate of change from poly to mono was recorded. These workers also produced evidence to show that the rate of formation of zinc sulphide is equivalent to the cure rate. These results, in general, are very similar to those trends pointed out from this work.

Another notable Japanese contribution is that of Kujimoto and Nakade (54). They used equilibrium swelling in toluene of samples containing various cure systems and cured at 160°C. After assuming a χ value of 0.49 they used the Flory-Rehner equation to provide values of cross-link density. Cross-link types were identified by the use of Lithium Aluminium Hydride (polysulphide) and use of Triphenylphosphine gave figures for combined sulphur and average length of poly-sulphidic chains. Much use was also made of infra-red techniques. The system based upon Royalene 301 utilizing a cure system based upon TMTD/MBT/Sulphur and cured at 160°C produced a structure which was generally very similar to that produced with Formulation R of this work, however, a much higher cross-link density was recorded by Kujimoto et al.

Dudek and Bueche[86] investigated the χ values and noted that for an E.P.D.M. (53% ethylene) χ was a function of the cross-link density in heptane and benzene. They measured χ and cross-link density in fourteen solvents, using only swelling and compression modulus, limiting their deformation to 5%. They noted that plots of χ versus V_r in n-heptane were both linear and horizontal whilst for benzene the equivalent curve was only linear. Their investigations indicated that there was a chain entanglement contribution with E.P.M.'s and this of course will lead to a large C_2 value.

Loan in his excellent chapter in the S.C.I. Monograph on Techniques of Polymer Science[71] evaluates the compression modulus technique utilising natural rubber, S.B.R. and polyurethane. He notes that although C_1 is only slightly dependent upon V_r, C_2 is dependent in a linear fashion and in fact becomes zero at V_r = 0.25. Treloar has shown that:-

$$\frac{f\ v_r^{\frac{1}{3}}}{2A_o(\lambda - \lambda^{-1})} = C_1$$

is followed quite closely during compressive deformations. The work carried out for this contribution utilised V_r values of up to 0.33 without the gross errors one would expect when considering the work of Loan and the large C_2 values suggested by Dudek and Bueche. Loan also investigated peroxide cures of E.P.M's and noted that secondary hydrogen abstraction would lead to cross-linking whilst tertiary hydrogen abstraction would lead to scission. Loan also notes that the use of a peroxide would lead to cross-linking with an efficiency greater than or equal to one, a fact confirmed by the work described herein.

4.5. Summary of Conclusions

4.5.1. Concerning Vulcanizates of E.P.D.M.'s.

The most important facts which arose from this work with regard to structures of E.P.D.M.'s were:

1) The network structures based on sulphur cross-links were all very similar regardless of the cure system used. They contained a preponderance of thermally stable mono-sulphidic cross-links. At extended cure times the di and poly-sulphide virtually disappeared.

2) A much higher level of cross-linking was attainable with peroxide cured vulcanizates.

3) The nature of the termonomer affected both the rate and degree of the cross-linking reaction, and was in the order:

MNB $>$ ENB $>$ 1:4 hexadiene $>$ DCPD (rate)

and

MNB $>$ ENB $>$ DCPD $>$ 1:4 hexadiene (level)

respectively.

4) An increase in the cure temperature caused an overall drop in the maximum obtainable cross-link densities.

5) A simple accelerated sulphur cure system proved to be both the most efficient and the cheapest, although other advantages were obtained by the use of a more expensive system, i.e. Vocol gave an improvement in the rate of cure and a much safer scorch time and such systems exhibited less reversion.

4.5.2. Concerning Techniques Used.

Swelling was asimple yet accurate technique which, when used with small specimens, could be quite rapid. If accurate values of χ were known estimates of M_c could be obtained, however it should not be used after probe work without an independant determination of χ. Compression modulus was a rapid and simple technique for the determination of the C_1 parameter. Choice of solvent was important since this effected the values of V_r and subsequently of C_1 and M_c obtained. V_r values of less than 0.33 were preferable in order to avoid gross errors. The micro method of D.A.Smith[21] was used as the smaller samples reached equilibrium swelling in a much shorter time. Sample dimensions were found to have little effect on the results obtained provided that equilibrium swelling was attained.Results were taken over larger ranges of both V_r and percent compression than had been previously used. V_r values of up to 0.33 and compression values of between 0 and 20 percent were used. Although the use of the more sophisticated mathematical approximations produced results ever closer to those produced by the stress-strain technique, the percentage change in the numerical result was less than experimental error for the compression modulus technique and thus these approximations were of academic interest only. The use of the thiol/amine reagents as chemical probes was found to be simple and effective, and invaluable in the characterization of the E.P.D.M. networks. Their unpleasant nature required that care was taken in their storage and use. From the results of this workit appeared that the reagent propane-2-thiol/piperidine was capable, under certain circumstances, of producing a situation whereby cross-links could be formed. Much cross-checking by methods such as critical path analysis and the use of real and apparent values of cross-link density etc., however, all produced the answer that there was in fact a real increase in the cross-link density. It was of interest to note that this phenomena was only observed when the proportion of poly-sulphidic cross-links was so small that it could not be measured. The overall range for the increase in cross-link density was 11%.

5. SUGGESTIONS FOR FURTHER WORK

One obvious point which should receive further attention is that of converting the $M_{c.phys}$ values to $M_{c.chem}$. Although this can be done for the Enjay 479 polymer[53] the values of the constants in the final correlation equation must be determined for each polymer used. This involves the comparison of the calculated and measured number of cross-links obtained with a peroxide cure.

The results of this work are not of major technological importance since the networks were not filled. A further suggestion, therefore, is to repeat the characterizations carried out using filled stocks, using the techniques already pioneered by Porter[81] and Russell[82]

On comparing the results of the characterizations and the somewhat empirical work on efficiency, it would be of interest to compare with those formulations already studied an unaccelerated sulphur cure system and a cure system based on a mixture of a peroxide and sulphur.

The characterization work could be usefully continued by looking at the E and E' parameters as defined by Moore and Trego[3] in order to assess accurately the quantity and nature of any main chain modifications present in E.P.D.M. vulcanizates, together with obtaining additional information on the exact nature of the poly-sulphide linkages.

Finally, and a little more basically, an examination of the effects of other termonomers, their level in the polymers, the ratio of the ethylene and propylene and the loading and nature of stabilizers on the structure of E.P.D.M. networks would yield much useful information.

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APPENDIX I

Containing the values of clamp separation and $1/\lambda$ and $(\lambda - \lambda^{-2})$ for test specimens whose initial length is in the region 0.950 to 10.000, for the C_1 dry extension technique.

CLAMP SEPARATION

Station	Separation (cm)	Used for
A	9.906	l_o determination
B	10.000	
C	10.104	
D	10.204	
E	10.306	
F	10.414	
1	10.536	main C_1 determination
2	11.112	
3	11.772	
4	12.500	
5	13.334	
6	14.290	
7	15.394	
8	16.676	
9	18.188	
10	20.006	

VALUES OF ($\lambda - \lambda^{-2}$)

Station l_o (cm)	1	2	3	4	5	6	7	8	9	10
9.950	0.1670	0.3150	0.4687	0.6227	0.7833	0.9514	1.1294	1.3200	1.5287	1.7633
9.955	0.1656	0.3136	0.4674	0.6214	0.7820	0.9502	1.1282	1.3188	1.5274	1.7620
9.960	0.1642	0.3123	0.4661	0.6201	0.7808	0.9489	1.1220	1.3176	1.5262	1.7603
9.965	0.1628	0.3109	0.4448	0.6189	0.7796	0.9477	1.1258	1.3164	1.5250	1.7595
9.970	0.1613	0.3095	0.4635	0.6176	0.7783	0.9465	1.1246	1.3152	1.5238	1.7583
9.975	0.1599	0.3082	0.4621	0.6163	0.7771	0.9453	1.1234	1.3140	1.5226	1.7570
9.980	0.1585	0.3068	0.4608	0.6151	0.7759	0.9441	1.1222	1.3128	1.5214	1.7558
9.985	0.1570	0.3054	0.4595	0.6138	0.7746	0.9424	1.1210	1.3116	1.5201	1.7545
9.990	0.1556	0.3021	0.4582	0.6125	0.7734	0.9417	1.1198	1.3104	1.5189	1.7533
9.995	0.1542	0.3027	0.4567	0.6113	0.7722	0.9405	1.1196	1.3092	1.5177	1.7520
10.000	0.1528	0.3013	0.4556	0.6100	0.7710	0.9393	1.1174	1.3080	1.5165	1.7503

VALUES OF $1/\lambda$

Station l_o(cm)	1	2	3	4	5	6	7	8	9	10
9.950	0.944	0.895	0.842	0.796	0.746	0.696	0.646	0.597	0.547	0.497
9.955	0.945	0.896	0.846	0.796	0.747	0.697	0.647	0.597	0.547	0.498
9.960	0.945	0.896	0.846	0.797	0.747	0.697	0.647	0.597	0.548	0.498
9.965	0.946	0.897	0.847	0.797	0.747	0.697	0.647	0.598	0.548	0.498
9.970	0.946	0.897	0.847	0.798	0.748	0.698	0.648	0.598	0.548	0.498
9.975	0.947	0.898	0.847	0.798	0.748	0.698	0.648	0.598	0.548	0.499
9.980	0.947	0.898	0.848	0.798	0.749	0.698	0.648	0.598	0.549	0.499
9.985	0.948	0.899	0.848	0.799	0.749	0.699	0.649	0.599	0.549	0.499
9.990	0.948	0.899	0.849	0.799	0.749	0.699	0.649	0.599	0.549	0.499
9.995	0.949	0.899	0.849	0.799	0.749	0.699	0.649	0.599	0.550	0.500
10.000	0.949	0.900	0.849	0.800	0.750	0.700	0.650	0.600	0.550	0.500

APPENDIX II

Containing the computer program used to analyse the results. The program is written in Algol 60 and is in dialect suitable for use with I.C.L. 1900 series machines. The program is preceded by a list of identifiers and followed by specimen data presentation and print-out.

Identifiers Used.

COMP	change in height on compression (Δ h)
LOAD	load (f) required to cause Δ h
WTR	weight of sample
WTS	weight of swollen sample
WTD	weight of deswollen sample
ENM	weight of solvent removable extra network material
DENS	density of solvent
DENR	density of vulcanizate
VOLS	volume of solvent in swollen sample
VOLR	volume of rubber in swollen sample
VR	volume swelling ratio
A	dimensions of the test specimen
B	
C	
D	
E	
F	
G	
H	
AO	cross-sectional area of the unswollen sample
HO	height of the unswollen sample
HS	height of the undeformed swollen sample
HD	height of the deformed swollen sample
CICGP	C_1 by the Cluff et al. mathematical treatment
CISK	C_1 by the Smith KhanKhadim mathematical treatment
HSP	value of Δ h in the single point method
LDSP	value of f in the single point method
CIKMT	C_1 from the mathematical approach of Kay, Moore and Thomas

CIREM	C_1 as derived from the mathematical treatment of Melley and Stuckey
KI	χ via the Cluff et al. mathematics
VO	molar volume of the solvent
MCPHYS	$M_{c,phys}$ as calculated with the mathematics of Cluff et al.
TEMP	test temperature
CLD	cross-link density after Cluff et al.
M	slope of the experimental plot as defined by Cluff et al.
MS	slope of the plot after Smith-KhanKhadim
GP	intercept of the plot after Cluff et al
GS	intercept of the plot after Smith-KhanKhadim
SN	sample number
MCSK	$M_{c,phys}$ after Smith-KhanKhadim
KISK	χ " " "
CLDS	cross-link density " " "
MR	slope of plot after Melley and Stuckey
GR	intercept of plot " " " "
MCR	$M_{c,phys}$ " " " "
KIR	χ " " " "
CLDR	cross-link density " " " "
MCKMT	$M_{c,phys}$ after Kay,Moore and Thomas
KIKMT	χ " " " " "
CLDKMT	cross-link density " " " " "
FORM)) COND)	identifiers for convenience of labelling data sequences

NO	number of samples investigated in any data sequence
N	number of readings taken in the compression modulus determination
I)) J)	Control integers used in cycle commands of the program.

PROGRAM: ZOREMI/1

```
TRACE 2

BEGIN COMMENT THIS PROGRAM CALCULATES THE C1 PARAMETER
      FOR ELASTOMER NETWORKS FROM COMPRESSION MODULUS
      DATA USING THE THEORETICAL TREATMENTS OF CLUFF ET
      AL, SMITH/KHANKHADIM, MELLEY AND KAY ET AL;
      INTEGER  J,I,N,NO;
      REAL WTR,WTS,WTD,ENM,DENS,DENR,VOLS,VOLR,VR,A,B,C,
      D,E,F,G,H,AO,HO,HS,HD,CICGP,CISK,HSP,LDSP,CIKMT,
      CIREM,KI,VC,MCPHYS,TEMP,CLD,M,MS,GP,GS,SN,MCSK,
      KISK,CLDS,MR,GR,MCR,KIR,CLDR,MCKMT,KIKMT,CLDKMT,
      FORM,COND;
      INTEGER ARRAY REF [1:50] ;
      REAL PROCEDURE  SIGMA(X,I,N);INTEGER I,N ;REAL X;
      BEGIN REAL SUM; SUM:=0; FOR I:=1 STEP 1 UNTIL N
            DO SUM:=SUM+X; SIGMA:=SUM;
      END OF SIGMA;
      PROCEDURE  LSQ(Y,X,M,G,I,N);
      REAL Y,M,X,G; INTEGER  I,N;
      BEGIN REAL DENOM; ARRAY  A,B[1:N] ;
            FOR I:=1 STEP 1UNTIL N  DO
            BEGIN  A[I]:=  X↑2; B[I] := X*Y;
            END;
            DENOM:= N*SIGMA(A[I],I,N) -SIGMA(X,I,N)↑2;
            G:=(SIGMA(Y,I,N)*SIGMA(A[I],I,N) - SIGMA(X,
            I,N)*SIGMA(B[I],I,N))/DENOM;
            M:=(N*SIGMA(B[I],I,N)-SIGMA(X,I,N)*SIGMA(Y,I,N))/DENOM;

      END OF LSQ;
      FORM:=READ;PRINT(FORM,2,2);COND:=READ;PRINT(COND,
      3,1);NO:=READ;PRINT(NO,2,0);
      FOR J:=1 STEP 1 UNTIL NO DO
```

```
BEGIN N:=READ;NEWLINE(3);PRINT(N,2,0);SN:=READ;
          PRINT(SN,3,1);
          BEGIN ARRAY COMP,LOAD [1:N] ;
                    FOR I:=1 STEP 1 UNTIL N DO
                    BEGIN COMP[I]:=READ;NEWLINE(1);PRINT
                              (COMP [I ],1,8);LOAD[I]:=READ;
                              PRINT(LOAD[I],3,1);
                    END;
                    LSQ(LOAD[I],COMP[I],M,GP,I,N);
                    NEWLINE(1); PRINT(M,8,2);PRINT(GP,3,2);
                    NEWLINE(1);
                    TEMP:=READ;PRINT(TEMP,3,1);DENR:=READ;
                    PRINT(DENR,1,5);VO:=READ;PRINT(VO,3,4);
                    DENS:=READ;PRINT(DENS,1,4);WTR:=READ;
                    PRINT(WTR,1,4);WTS:=READ;PRINT(WTS,1,4);
                    WTD:=READ;PRINT(WTD,1,4);
                    VOLR:=WTD/DENR;
                    VOLS:=(WTS-WTD)/DENS;
                    VR:=VOLR/(VOLR+VOLS);
                    ENM:=WTR -WTD;
                    NEWLINE(1);PRINT(VR,1,4);PRINT(ENM,2,4);
                    NEWLINE(1);
                    A:=READ;PRINT(A,1,3);B:=READ;PRINT(B,1,3);
                    C:=READ;PRINT(C,1,3);D:=READ;PRINT(D,1,3);
                    E:=READ;PRINT(E,1,3);F:=READ;PRINT(F,1,3);
                    G:=READ;PRINT(G,1,3);H:=READ;PRINT(H,1,3);
                    AO:=(A+C)/2*(B+D)/2; HO:=(E+F+G+H)/4;
                    CICGP:=M*981*HO/(6*AO);
                    MCPHYS:=DENR*8.314&7*TEMP/(2*CICGP);
                    KI:=(((-DENR*VO*(VR↑ (1/3)-VR/2))/MCPHYS)
                    -VR-LN(1-VR))/VR↑ 2;
                    CLD:=1/(2*MCPHYS); NEWLINE(1);
```

```
PRINT(CLD,1,8);
LSQ(LOAD[I],(COMP[I]*(HO+VR↑(1/3)*COMP[I]
)),MS,GS,I,N);
NEWLINE(1);PRINT(MS,6,2);PRINT(GS,1,5);
CISK:=MS*981*(HO↑2)/(6*AO);
MCSK:=DENR*8.314&7*TEMP/(2*CISK);
KISK:=(((-DENR*VO*(VR↑(1/3)-VR/2))/MCSK
)-VR-LN(1-VR))/VR↑2;
CLDS:=1/(2*MCSK);NEWLINE(1);
PRINT(CISK,8,1);
PRINT(MCSK,5,2);PRINT(KISK,1,5);
PRINT(CLDS,1,8);
HS:=HO/(VR↑(1/3));
LSQ(LOAD[I],(HS*((3*HS*(COMP[I]↑2)-3*
(HS↑2)*COMP[I]-(COMP[I]↑3))/((HS↑3)-
2*(HS↑2)*COMP[I]+(COMP[I]↑2)*HS))),MR,
GR,I,N);
NEWLINE(1);PRINT(MR,8,2);PRINT(GR,8,8);
CIREM:=MR*981*HO/(2*AO);
MCR:=DENR*8.314&7*TEMP/(2*CIREM);
KIR:=(((-DENR*VO*(VR↑(1/3)-VR/2))/
MCR)-VR-LN(1-VR))/VR↑2;
CLDR:=1/(2*MCR);
NEWLINE(1);
PRINT(CIREM,8,1);PRINT(MCR,5,2);
PRINT(KIR,1,5);PRINT(CLDR,1,8);
NEWLINE(1);
HSP:=READ;PRINT(HSP,1,6);LDSP:=READ;
PRINT(LDSP,3,1);
HD:=HS-HSP;
CIKMT:=(981*LDSP*HO*(HD↑2))/(2*AO*(
HS↑3 -HD↑3));
```

```
                  MCKMT:=DENR*8.314&7*TEMP/(2*CIKMT);
                  KIKMT:=(((-DENR*VO*(VR↑(1/3)-VR/2))
                  /MCKMT)-VR-LN(1-VR))/VR↑2;
                  CLDKMT:=1/(2*MCKMT);
                  NEWLINE(1);
                  PRINT(CIKMT,8,1);PRINT(MCKMT,5,2);
                  PRINT(KIKMT,1,5);PRINT(CLDKMT,1,8);
            END,
      END;
END OF PROGRAM;
```

Form of Print Out From Computer.

The analysed results from the computer will take the form:-

```
FORM   COND   NO



*N   SN
 COMP(1)   LOAD(1)
 COMP(2)   LOAD(2)
       .        .
       .        .
       .        .
 COMP(N)   LOAD(N)
 M   GP
 TEMP   DENR   VO   DENS   WTR   WTS   WTD
 VR   ENM
 A   B   C   D   E   F   G   H
 CICGP   MCPHYS   KI   CLD
 MS   GS
 CISK   MCSK   KISK   CLDS
 MR   GR
 CIREM   MCR   KIR   CLDR
 HSP   LDSP
*CIKMT   MCKMT   KIKMT   CLDKMT
```

The section between the *'s will be repeated NO times, once for every set of data fed in.

Presentation of Data

Data is fed into the computer in the following order:-

FORM COND

NO (integer controlling number of sets of results to be analysed)

*N (integer controlling number of compression modulus points per sample)

COMP(1) LOAD(1)

COMP(2) LOAD(2)

. .

. .

. .

COMP(N) LOAD(N)

TEMP DENR VO DENS

WTR WTS WTD

A B C D E F G H

*HSP LDSP

The section between the two *'s is repeated NO times: each repeat containing data for different samples.

APPENDIX III

Containing tables showing cross-link density (C.L.D.) figures for formulations B,V,C,N,E and R; before and after treatment with the chemical probes propane-2-thiol /piperidine and n-hexane thiol/piperidine.

FORMULATION B.

treatment cure characteristics		cross-link density g.mole cross-links / g. network x 10^5		
temp. (°C)	time(min)	before probe treatment	propane-2-thiol/ piperidine	n-hexane thiol/ piperidine
150	15	*	*	*
	30	0.64	*	*
	60	8.67	6.24	0.57
	120	10.82	9.20	3.90
	240	9.10	9.48	5.74
170	15	2.38	2.87	*
	30	7.79	7.72	2.35
	60	7.41	8.14	4.17
	120	5.82	6.32	4.24
	240	4.75	4.81	3.96
200	15	3.15	3.53	2.63
	30	2.78	3.02	2.59
	60	2.92	3.03	2.51
	120	2.77	2.95	2.54
	240	3.02	3.16	2.67
240	15	2.77	2.64	2.38
	30	2.49	2.67	2.38
	60	2.49	2.50	2.07
	120	2.70	2.86	2.59
	240	2.25	2.21	1.96

* sample destroyed by treatment

FORMULATION V.

treatment / cure characteristics		cross-link density g.mole cross-links / g. network x 10^5		
temp. (°C)	time(min)	before probe treatment	propane-2-thiol/ piperidine	n-hexane thiol/ piperidine
150	15	8.24	7.03	1.28
	30	10.69	9.77	2.93
	60	12.30	12.32	5.29
	120	12.10	12.94	7.78
	240	12.39	13.81	10.73
170	15	10.69	10.39	4.73
	30	11.11	12.02	7.20
	60	11.39	12.01	8.80
	120	11.09	11.86	9.71
	240	10.99	12.20	10.26
200	15	9.17	9.56	7.94
	30	8.94	9.69	8.88
	60	9.37	9.81	9.29
	120	9.24	8.65	8.67
	240	9.59	9.39	8.88
240	15	6.13	7.61	5.12
	30	5.21	5.99	4.93
	60	4.40	6.57	4.36
	120	3.79	4.32	3.46
	240	2.95	3.81	3.11

FORMULATION C.

cure temp. °C / cure time min.	150	170	200	240
15	14.62	21.96	17.28	12.85
30	19.47	21.91	17.11	12.90
60	22.27	20.99	16.37	11.63
120	25.88	20.69	16.50	11.36
240	24.78	21.42	17.66	12.77

FORMULATION R.

treatment / cure characteristics		cross-link density g.mole cross-links / g. network x 10^5		
temp. (°C)	time(min)	before probe treatment	propane-2-thiol/ piperidine	n-hexane thiol/ piperidine
150	15	0.21	0.05	*
	30	3.33	2.12	0.27
	60	4.90	4.95	1.21
	120	4.88	5.96	2.78
	240	4.73	5.27	3.16
170	15	3.56	2.18	0.07
	30	4.96	5.26	1.09
	60	4.57	5.58	2.58
	120	4.17	4.98	3.25
	240	4.75	5.21	5.21

* sample destroyed by treatment

FORMULATIONS N AND E.

treatment / cure characteristics		cross-link density g.mole cross-links / g. network x 10^5		
temp (°C)	time(min)	before probe treatment	propane-2-thiol/ piperidine	n-hexane thiol/ piperidine
FORMULATION N.				
150	15	*	*	*
	30	0.05	*	*
	60	4.50	2.02	*
	120	6.70	5.21	2.05
	240	6.11	5.95	3.16
170	15	0.08	*	*
	30	6.11	5.26	1.06
	60	5.68	5.42	2.99
	120	4.25	4.02	3.35
	240	3.13	3.22	3.10
FORMULATION E				
150	15	*	*	*
	30	0.28	*	*
	60	8.36	5.17	*
	120	10.82	8.74	0.75
	240	10.66	8.45	3.24
170	15	0.89	*	*
	30	9.49	6.31	0.43
	60	8.07	6.65	2.43
	120	6.49	5.97	3.71
	240	5.28	4.91	3.71

* sample destroyed by treatment

APPENDIX IV.

Containing analysed results of network characterization for formulations B,V,N,E and R.

All values of cross-link density are quoted in gram moles of cross-links / gram network x 10^5.

FORMULATION B.

Cure Characteristics		Cross-link density			
temp °C	time min.	total	mono-sulphide	di-sulphide	poly-sulphide
150	15	-	-	-	-
	30	0.642	-	-	100%
	60	8.674	0.573	5.672	2.429
	120	10.824	3.987	5.215	1.622
	240	9.104	5.743	3.313	*
170	15	2.386	-	-	100%
	30	7.787	2.352	5.366	0.07
	60	7.411	4.165	3.246	*
	120	5.817	4.242	1.575	*
	240	4.750	3.957	0.793	*
200	15	3.145	2.629	0.516	*
	30	2.778	2.592	0.186	*
	60	2.915	2.510	0.405	*
	120	2.769	2.542	0.270	*
	240	3.022	2.670	0.352	*
240	15	2.679	2.388	0.251	0.13
	30	2.492	2.332	0.160	*
	60	2.495	2.074	0.421	*
	120	2.704	2.598	0.106	*
	240	2.251	1.955	0.296	0.39

* negative value

FORMULATION V.

Cure Characteristics		Cross-link Density			
temp °C	time min	total	mono-sulphide	di-sulphide	poly-sulphide
150	15	8.242	1.285	5.744	1.213
	30	10.697	2.928	6.845	0.924
	60	12.295	5.290	7.005	*
	120	12.101	7.775	4.326	*
	240	12.390	10.729	1.661	*
170	15	10.670	4.733	5.658	0.279
	30	11.110	7.197	3.913	*
	60	11.394	8.801	2.593	*
	120	11.087	9.709	1.387	*
	240	10.998	10.262	0.736	*
200	15	9.169	7.943	1.226	*
	30	8.936	8.884	0.052	*
	60	9.372	9.289	0.083	*
	120	9.238	8.665	0.575	0.586
	240	9.587	8.879	0.708	0.190
240	15	6.129	5.126	1.003	*
	30	5.215	4.926	0.292	*
	60	4.402	4.363	0.039	*
	120	3.790	3.458	0.332	*
	240	2.954	3.109	*	*

* negative value

FORMULATIONS R AND N.

Cure Characteristics		Cross-link Density			
temp °C	time min	total	mono-sulphide	di-sulphide	poly-sulphide

FORMULATION R.

150	15	0.210	-	0.045	0.165
	30	3.327	0.270	1.849	1.208
	60	4.903	1.215	3.688	*
	120	4.880	2.781	2.099	*
	240	4.728	3.165	1.563	*
170	15	3.558	0.073	2.109	1.376
	30	4.964	1.098	3.866	*
	60	4.565	2.588	1.977	*
	120	4.171	3.254	0.917	*
	240	4.746	3.427	1.319	*

FORMULATION N.

150	15	-	-	-	-
	30	0.050	-	-	0.050
	60	4.503	-	2.024	2.477
	120	6.704	2.048	3.165	1.491
	240	6.105	3.156	2.796	0.153
170	15	0.078	-	-	0.078
	30	6.112	1.069	4.192	0.851
	60	5.681	2.999	2.428	0.254
	120	4.250	3.352	0.669	0.229
	240	3.134	3.105	0.029	*

* negative value

FORMULATION E.

Cure Characteristics		Cross-link Density			
temp °C	time min	total	mono-sulphide	di-sulphide	poly-sulphide
150	15	-	-	-	-
	30	0.284	-	-	0.284
	60	8.369	-	5.178	3.191
	120	10.825	0.752	7.988	2.085
	240	10.659	3.240	5.206	2.213
170	15	0.887	-	-	0.887
	30	9.487	0.435	5.873	3.179
	60	8.075	2.434	4.218	1.423
	120	6.498	3.713	2.258	0.527
	240	5.287	3.875	1.040	0.372

APPENDIX V.

Containing the results of the physical tests (hardness, ultimate tensile strength, modulus at 100% elongation, elongation at break and compression set) for formulations B,C,V,N,E and R.

FORMULATION B.

Cure characteristics		Physical Property				
		hardness	100% modulus	elong. @break	U.T.S.	comp. set
temp(°C)	time(min)	I.R.H.D.	p.s.i.	%	p.s.i.	%
150	15	37	100.5	351	66.2	30.1
	30	53	126.2	1565	491.0	23.2
	60	64	136.7	346	240.2	9.3
	120	65	149.8	260	224.9	5.7
	240	66	154.9	296	242.6	5.2
170	15	40	126.0	872	444.2	32.4
	30	64	144.6	274	216.2	4.9
	60	64	132.9	307	224.8	7.4
	120	62	138.7	372	228.3	8.9
	240	62	142.6	352	206.4	8.5
200	15	55	130.3	587	262.8	8.6
	30	54	127.7	535	241.3	7.2
	60	51	98.5	407	186.7	10.6
	120	51	120.3	491	186.4	8.9
	240	53	114.1	356	137.5	7.9
240	15	44	115.1	243	146.1	13.5
	30	41	113.8	265	143.5	17.2
	60	42	106.9	210	129.3	16.5
	120	51	108.2	148	113.3	13.1
	240	42	111.9	276	145.9	16.1

FORMULATION C.

Cure Characteristics		Physical Property				
temp °C	time min	hardness I.R.H.D.	100% modulus p.s.i.	Elong. @break %	U.T.S. p.s.i.	comp. set %
150	15	65	104.6	151	190.6	2.8
	30	66	120.2	80	152.7	0
	60	67	126.8	73	166.7	1.2
	120	67	140.2	71	181.8	1.6
	240	65	154.2	67	178.5	1.0
170	15	65	136.1	88	187.9	2.4
	30	66	131.4	86.5	181.8	3.5
	60	66	135.3	80.9	180.6	3.0
	120	67	126.4	80.8	163.5	1.1
	240	65	140.2	86.7	193.9	1.4
200	15	63	104.5	68.3	129.2	2.0
	30	61	105.9	79.2	145.2	10.0
	60	61	113.6	90	159.9	1.0
	120	61	116.3	107.5	179.0	1.4
	240	61	110.9	87.5	148.4	1.0
240	15	57	101.8	73.3	129.1	2.4
	30	60	97.0	76.7	125.8	2.1
	60	58	99.3	76.7	124.1	2.6
	120	52	95.7	55	100.3	1.9
	240	59	93.8	67.5	106.7	2.9

FORMULATION V.

Cure Characteristics		Physical Property				
temp °C	time min	hardness I.R.H.D.	100% modulus p.s.i.	elong. @break %	U.T.S. p.s.i.	comp. set %
150	15	62	154.9	154.9	300.0	10.9
	30	64	153.3	283.0	256.1	9.8
	60	66	163.5	255.0	273.9	7.8
	120	65	173.9	240.0	281.2	7.2
	240	63	176.2	208.0	257.5	4.3
170	15	62	173.0	237.0	277.9	7.0
	30	62	184.2	227.0	282.7	4.4
	60	62	173.9	207.0	251.0	3.0
	120	62	164.2	202.0	227.0	3.2
	240	59	175.0	240.0	283.3	3.8
200	15	58	176.4	186.0	219.9	3.8
	30	60	149.1	153.0	177.8	4.5
	60	59	141.1	189.0	188.6	3.1
	120	58	137.5	210.0	193.6	4.1
	240	58	132.9	152.0	172.5	4.0
240	15	55	*96.6	98.8	127.8	7.6
	30	55	128.9	120.0	133.5	4.3
	60	55	123.8	158.0	140.1	3.3
	120	53	110.3	148.0	121.5	7.3
	240	49	111.3	136.0	118.5	9.3

* 50% modulus

FORMULATIONS E AND N.

Cure Characteristics		Physical Property				
temp °C	time min	hardness I.R.H.D.	100% modulus p.s.i.	elong. @break %	U.T.S. p.s.i.	comp. set %

FORMULATION E.

temp °C	time min	hardness I.R.H.D.	100% modulus p.s.i.	elong. @break %	U.T.S. p.s.i.	comp. set %
150	15	33	100	1600+	685.7	32.7
	30	44	119.1	1600+	372.0	26.0
	60	55	151.1	345	250.6	7.4
	120	56	155.8	326	275.1	6.2
	240	56	156.4	277	239.2	7.0
170	15	46	113.0	772	201.8	24.5
	30	53	140.0	300	221.1	6.7
	60	53	136.7	282	199.7	8.4
	120	52	122.4	328	189.3	10.5
	240	51	120.6	355	185.0	11.0

FORMULATION N.

temp °C	time min	hardness I.R.H.D.	100% modulus p.s.i.	elong. @break %	U.T.S. p.s.i.	comp. set %
150	15	very soft	very small	very large	very small	30.1
	30	42	73.3	1600+	160	23.8
	60	48	108.3	570	243.7	11.8
	120	49	116.6	348	187.9	7.0
	240	48	114.6	368	189.8	6.9
170	15	35	73.2	1600+	178.9	31.9
	30	49	119.1	440	218.7	8.2
	60	47	107.1	468	201.1	6.8
	120	47	109.7	553	207.7	5.9
	240	45	95.2	745	235.7	6.3

FORMULATION R

Cure Characteristics		Physical Property				
temp °C	time min	hardness I.R.H.D.	100% modulus p.s.i.	elong. @break %	U.T.S. p.s.i.	comp. set %
150	15	35	89.3	1600+	294.6	36.1
	30	49	132.4	1234	1164.2	17.1
	60	51	146.9	825	602.1	13.6
	120	52	159.6	553	499.1	12.8
	240	50	160.1	324	380.3	22.2
170	15	50	137.6	1363	1233.2	17.7
	30	52	144.1	68.3	454.3	10.0
	60	52	134.9	872	581.9	19.6
	120	48	132.7	832	503.3	15.8
	240	43	134.9	538	312.1	16.1

APPENDIX VI.

Containing characterization results in which the values of concentration of component cross-links have been expressed as percentages of total cross-link density. Formulations B,V,N,E and R.

FORMULATION B.

Cure Characteristic		total	%	%	%
temp(^{o}C)	time(min)	C.L.D.	$-S_1-$	$-S_2-$	$-S_x \geqslant 3-$
150	15	-	-	-	-
	30	0.642	-	-	100
	60	8.674	6.6	65.5	27.9
	120	10.824	36.8	48.2	15.0
	240	9.104	63.0	37.0	-
170	15	2.386	-	-	100
	30	7.787	30.1	69.0	0.9
	60	7.411	56.0	44.0	-
	120	5.817	73.0	27.0	-
	240	4.750	83.5	16.5	-
200	15	3.145	83.6	16.4	-
	30	2.778	93.3	6.7	-
	60	2.915	86.0	14.0	-
	120	2.769	92.0	8.0	-
	240	3.022	81.5	19.5	-
240	15	2.769	86.0	14.0	-
	30	2.492	94.0	6.0	-
	60	2.495	83.5	16.5	-
	120	2.704	87.0	12.0	-
	240	2.251	87.0	13.0	-

FORMULATION V.

Cure Characteristics		total	%	%	%
temp(°C)	time(min)	C.L.D.	$-S_1-$	$-S_2-$	$-S_{x\geq 3}-$
150	15	8.242	15.6	69.7	14.7
	30	10.697	27.4	64.0	8.6
	60	12.295	43.0	57.0	-
	120	12.101	64.3	35.7	-
	240	12.390	86.8	13.2	-
170	15	10.670	44.4	53.0	2.6
	30	11.110	64.8	35.2	-
	60	11.394	77.2	22.8	-
	120	11.087	87.6	12.4	-
	240	10.998	93.7	6.7	-
200	15	9.169	86.6	13.4	-
	30	8.936	99.4	0.6	-
	60	9.372	99.1	0.9	-
	120	9.238	93.8	6.2	-
	240	9.587	92.6	7.4	-
240	15	6.129	83.6	16.4	-
	30	5.218	94.4	5.6	-
	60	4.402	99.1	0.9	-
	120	3.790	91.1	8.9	-
	240	2.954	-	-	-

FORMULATIONS N AND E.

Cure Characteristic		total	%	%	%
temp(°C)	time(min)	C.L.D.	$-S_1-$	$-S_2-$	$-S_{x\geq 3}-$
FORMULATION N.					
150	15	-	-	-	-
	30	0.050	-	-	100
	60	4.503	-	45.0	55.0
	120	6.704	30.5	47.2	22.2
	240	6.105	51.7	45.8	2.5
170	15	0.078	-	-	100
	30	6.112	17.5	68.6	13.9
	60	5.681	52.8	42.7	4.5
	120	4.250	78.6	15.7	5.4
	240	3.134	99.1	0.9	-
FORMULATION E.					
150	15	-	-	-	-
	30	0.284	-	-	100
	60	8.368	-	61.9	38.1
	120	10.825	6.9	73.8	19.3
	240	10.659	30.4	48.8	20.8
170	15	0.887	-	-	100
	30	9.487	4.6	61.9	33.5
	60	8.075	30.1	52.2	17.6
	120	6.498	57.1	34.7	8.1
	240	5.287	73.3	19.7	7.0

FORMULATION R.

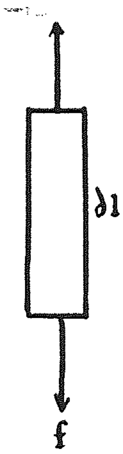
Cure Characteristic		total	%	%	%
temp(°C)	time(min)	C.L.D.	$-S_1-$	$-S_2-$	$-S_{x \gg 3}-$
150	15	0.210	-	21.4	78.6
	30	3.327	8.1	55.6	36.3
	60	4.903	24.8	75.2	-
	120	4.880	57.0	43.0	-
	240	4.728	66.9	33.1	-
170	15	3.558	2.1	59.3	38.7
	30	4.964	22.1	77.9	-
	60	4.565	56.7	43.3	-
	120	4.171	78.0	22.0	-
	240	4.746	72.0	27.8	0.2

Appendix VII.

Kinetic Theory of Rubber-like Elasticity

One of the major characteristics of rubber is that it can undergo vast changes in shape with insignificant changes in volume, for example stretching to 200% extension is accomplished by a volume change of 0.1%. Hence in theory it is possible to consider such changes as occuring at constant volume. Thus if we work from the first and second laws of Classical Thermodynamics we can consider the change as a variation in the free energy of the rubber to account for the work done. This can be expressed in a mathematical form as :-

$$\underset{\text{work}}{\partial W} = \underset{\text{energy}}{\partial E} - \underset{\text{entropy}}{T \partial S}$$



the work term can also be expressed as :-

$$\partial W = f dl$$

which as we are considering only change at constant volume (V), can be expressed in detail as :-

$$f = \left(\frac{\partial E}{\partial l}\right)_{V,T} - \left(T\frac{\partial S}{\partial l}\right)_{V,T}$$

(T :: Temperature)

The first term, for a gum rubber, is small compared to the second term; a situation similar to that found in gases. This dependance upon entropy changes allows the kinetic theory of Rubber-like Elasticity to be postulated. Let us begin with the Maxwell relation:

$$\left(\frac{\partial f}{\partial T}\right)_{l} = -\left(\frac{\partial S}{\partial l}\right)_{T}$$

which expresses the force neccessary to maintain constant length during a change in temperature. Hence the term $(\partial E / \partial l)_{V,T}$ can be obtained by difference.

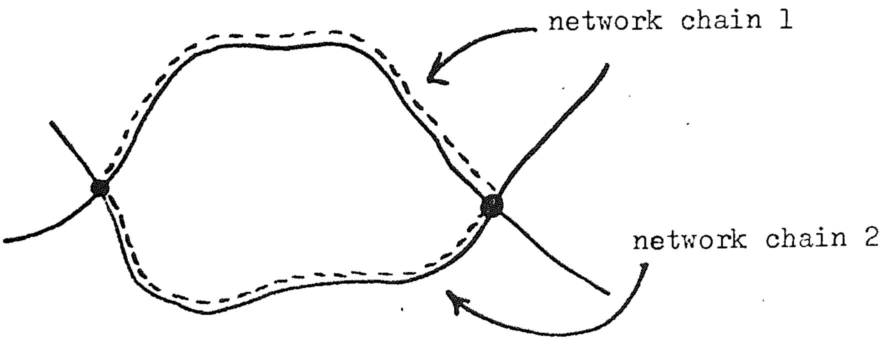
In reality some account of volume change must be made and the t $(\partial f / \partial T)$ is the best replaced by that of $(\partial f / \partial T)_{l,V}$.

Thus for an"ideal" rubber the equation to be used would become:-

$$f = -\left(T\left(\frac{\partial S}{\partial l}\right)_{V,T} \right)$$

i.e. we have calculated a value of f in terms of a function of l. Physical deformation of a rubber results in its heating up, because of reaction entropy, a reaction analogous to the pumping of a gas. It is however, more difficult to calculate S as a function of volume for the system being considered than it is for an ideal gas.

At this point we will define the network chain, and this is that part of the rubber molecule main chain which joins together two cross-links.'



Let us consider single chain properties. These are:-

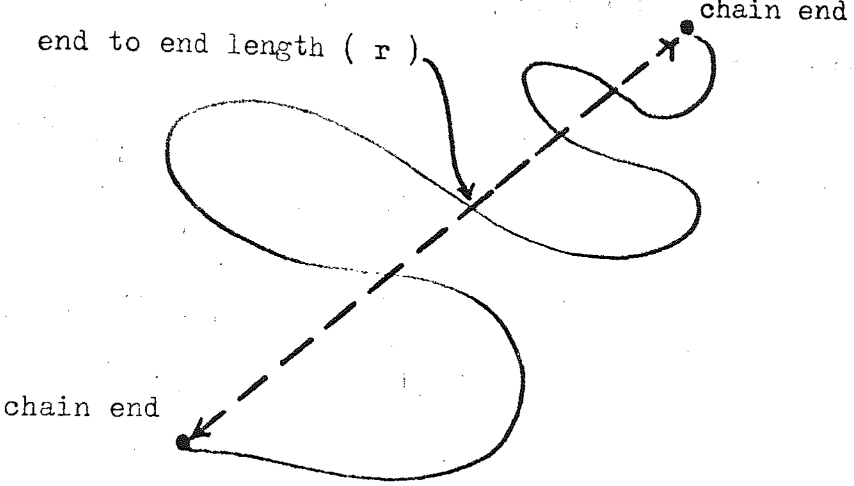
1) it possesses two ends

2) between these ends is an area of chemical material which is very flexible - flexibility arises from rotation about single bonds. Thus when the network is deformed there is a large degree of distortion of any chain, but this is effected not by distortion of the bond angles but by changes in the conformation of the molecule. If we consider our chain as a series of links then the major defects are:-

a) there is no volume filling

b) there are no correlations between successive links

Let the chain consist of n links each of length l'. The end to end length of the chain can be represented by r (see figure below)



We are interested in the work that has to be done to pull the ends apart as a function of r. This work will have two components:-

1) free energy
2) entropy

if no change in the internal energy is assumed, then, because of Brownian movement of chains, we have work needed since there must be an entropy change. In order to approach this we can use the method of statistical mechanics to calculate the number of possible configurations. This is a well known problem, namely that of Random Flight.

$$S = k \log(\text{ number of possible configurations })$$

where k is the Boltzman constant.

The number of configurations is greater when $r=0$, i.e. when the chain ends are touching. The number decreases to 1 when $r = nl'$ and hence the entropy will vary from nl' to infinity.

The result obtained from this treatment is of the form

$$S = C - Kb^{2}r^{2}$$

Where b is a measure of the breadth of the distribution and is given by

$${}^{2} \qquad \frac{3}{}$$

This distribution can be termed Gaussian if:-

a) n is large

b) r is much less than nl'

The second assumption is much harder to justify. The constant b can be related to the R.M.S. value of the end to end distances:

$$b^2 = \frac{3}{2\,\bar{r}^2}$$

where $\bar{r}$ is the mean length of the chain in the free condition.

Thus we can now write:-

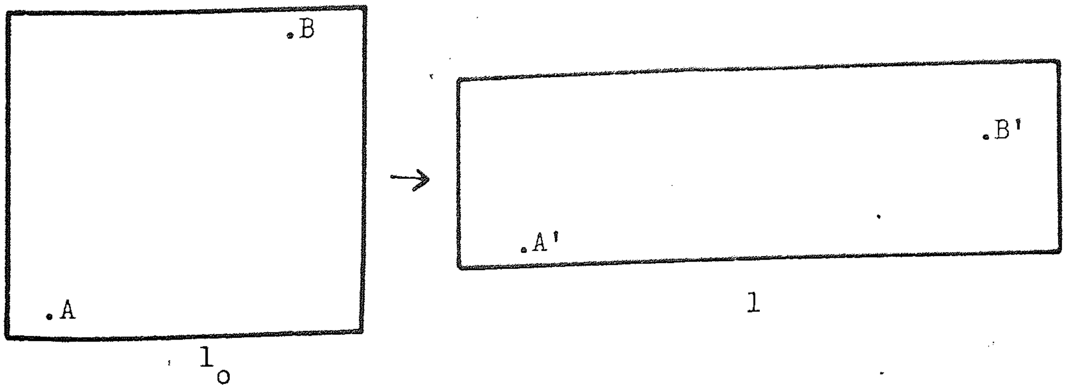
$$f = - T \frac{\partial S}{\partial r}$$

$$= + T\, 2\, k\, b^2\, r$$

This model solution is known as the Entropic spring and applies only when no energy is going to the internal energy.

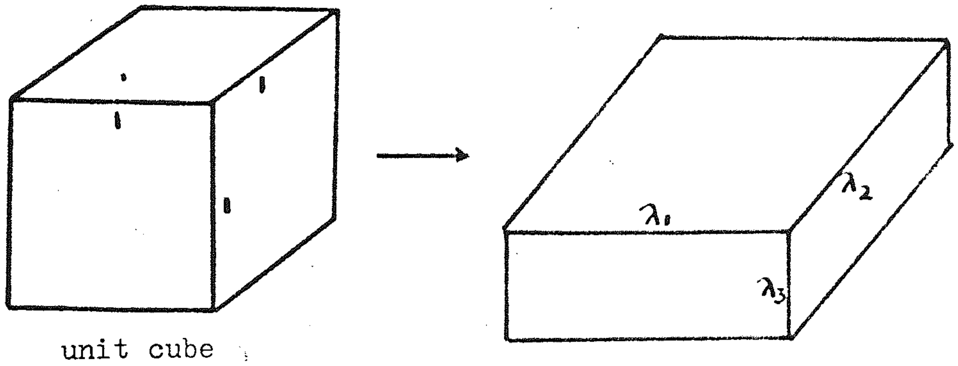
When considering a network comprising of a finite number of chains one has to first find the entropy of individual chains and then integrate to get the entropy of the whole sample. In order to do this we must assume that the point of cross-linking is at a fixed point. This assumption can be justified by the use of a more sophisticated model provided that the distribution of the curve is Gaussian.

Let us now consider a sample which undergoes a deformation thus:-



the cross-links at points A and B, move on extension to points A' and B', the movement being governed by an affine relationship (i.e. that they move in the same way as the body points in the continuum, and again this is justified if the distribution is Gaussian).

A further assumption is that the total entropy change being equal to the sum of the changes of each of the individual chains. This assumption is questioned by some. If the deformation can be represented by:-



then since there is no volume change

$$\lambda_1 \lambda_2 \lambda_3 = 1$$

thus

$$\Delta S = -\tfrac{1}{2} N k \left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right)$$

where N is the number of network chains per unit volume. (3 is included in order that $\Delta S = 0$ when λ_1, λ_2 and λ_3 all equal 1, i.e. no change).

$\bar{r}^2$ is the summation of r^2 for a number of free chains

$\bar{r}_i^2$ is the summation of r^2 before deformation

If this ratio can be assumed to be 1'(chemically this might not neccessarily be true because cross-linking reactions will take a finite time). However, much work has to be carried out to justify this assumption. The work δW is that required to go from the cube to the new form i.e.

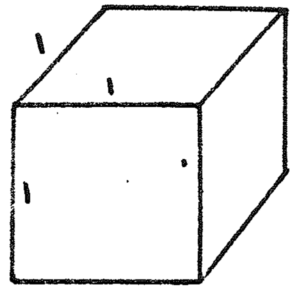
$$W = -T\Delta S = \tfrac{1}{2} N k T(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)$$

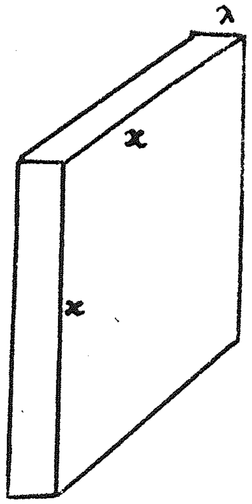
At this point it is of interest to note some of the assumptions that were not required, for example:-

1) no limitations on the size of λ_1, λ_2 and λ_3,

2) no restriction on the chemistry of the chains.

When we come to experimental measurements for the theory we must consider the case of stretching a square sample:-





Since square dimensions become $1/\lambda^{\frac{1}{2}}$ which is derived from $\lambda x^2 = 1$ (since there is no change in volume), then

$$W = \tfrac{1}{2} N k T(\lambda^2 + 2/\lambda - 3)$$

and

$$\partial w = \tfrac{1}{2} N k T(2\lambda - 2/\lambda^2)\,\partial\lambda$$

now as

$$\partial w = F\,\partial\lambda$$

then

$$F = N k T(\lambda - 1/\lambda^2)$$

N.B. this expression can be used for a force in any direction - not neccessarily an extension.

F is the force per unit area of unstrained section.

$$F = f / A_o$$

thus

$$f = A_o N k T(\lambda - 1/\lambda^2)$$

From the definition of N, namely the number of network chains per unit volume (making no allowance for chain ends or physical entanglements caused by the cross-linking reaction) we can state that N / P is the number of active network chains per unit weight, thus

$$N \ M_c / P = N_o = \text{number of active chains per gram molecule}$$

Now

$$k = R / N_o$$

so that

$$N \ k \ T = P \ R \ T / M_c$$

Where M_c is the number average molecular weight of the network chains. R is the gas constant and P is the density.

Thus

$$f = P R T (\lambda - 1/\lambda^2) / M_c$$

Analysis takes into account chain ends but not physical entanglements etc.

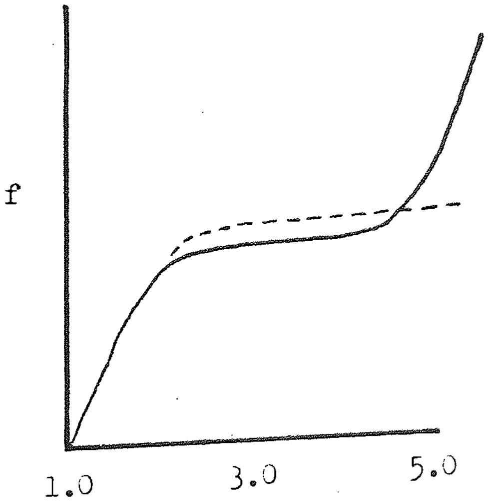
$$G = N k T \approx P R T / M_c$$

or

$$P R T (1 - 2M_c / M) / M_c$$

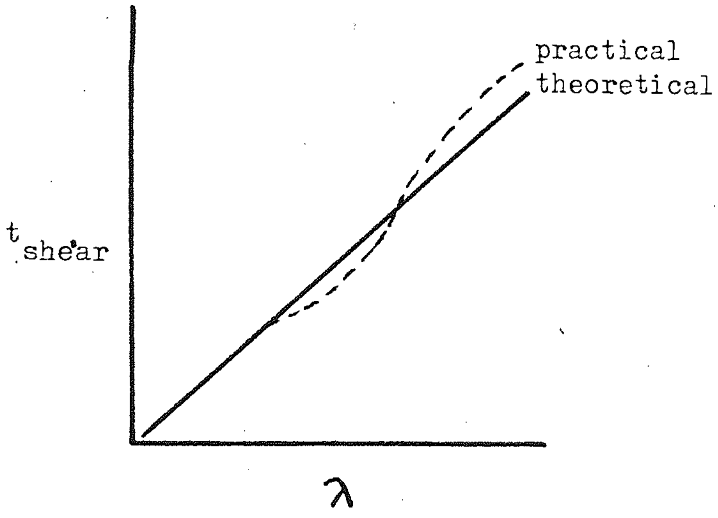
Where M is the molecular weight of chains before cross-linking.

With a peroxide gum stock vulcanizate in extension a curve as below is obtained:-



by determining the slope at the origin in order to evaluate a value of N (the variable parameter) one can plot a theoretical curve (depicted by ----). The theoretical curve is a fair fit to the experimental curve but there is an obvious discrepency at higher values of λ.

A similar effect is found in shear, but in this case N is not a variable parameter. (see diagram below)



In general it can be noted that:-

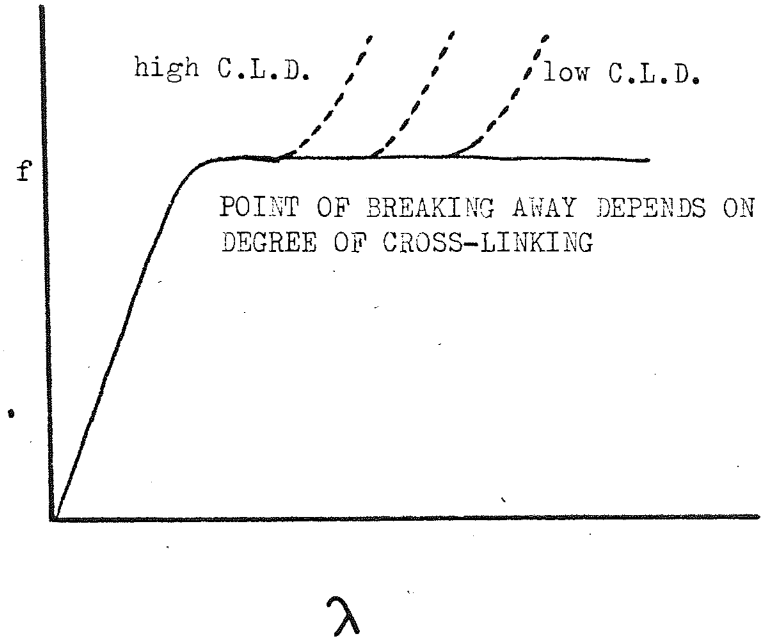
1) the fit at the origin is good,
2) shape of curve is very similar,
3) deviates at higher values of λ , normally an increase,
4) tends to be a little low at intermediate values of λ .

Point 3, which is true for rubbers at high extensions, is normally referredto as being outside the limits of elasticity. In fact it could be a crystallization effect. If so it should be alleviated by increasing the test temperature or by conducting the tests on samples swollen to equilibrium. Secondly, with reference to the Gaussian statistical equation:-

$$S = C - k b^2 r^2$$

then if r is not very much smaller than nl' the statistics will not apply. When r becomes closer to nl' (i.e. on extension) higher terms of r^2 become involved and the Gaussian statistics do not apply.

Calculations involving non-Gaussian distributions of r^2 (very difficult) will give better agrement with the point of breaking away from the theoretical curve:- (see diagram below)



This effect is called the "finite chain extension effect".

Mooney and Rivlin, in their work, used the approach of a physicist or engineer, namely that of considering the properties of a "lump of stuff " . A more general form of the equation

$$W = NkT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)$$

should be

$$W = NkT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + C_2(1/\lambda_1^2 + 1/\lambda_2^2 + 1/\lambda_3^2 - 3)$$

Rivlin emphasised that the material must be homogeneous and that the λ terms must be square terms because deformations are possible in all directions. Thus the simplest expression becomes

$$W = fn(I_1, I_2)$$

where

$$I_1 = (\lambda_1^2 + \lambda_2^2 + \lambda_3^2)$$

and

$$I_2 = (1/\lambda_1^2 + 1/\lambda_2^2 + 1/\lambda_3^2)$$

or to be more specific

$$W = C_1 (I_1 - 3) + C_2 (I_2 - 3)$$

where

$$C_1 = \tfrac{1}{2} N k T$$

By using the approach of virtual work we can get

$$f = 2 (\lambda - 1/\lambda^2)(\partial W / \partial I_1 + 1/\lambda (\partial W / \partial I_2))$$

and since

$$\partial W / \partial I_1 = C_1$$

and

$$\partial W / \partial I_2 = C_2$$

the Mooney-Rivlin relationship becomes

$$f = 2 (\lambda - 1/\lambda^2)(C_1 + 1/\lambda . C_2)$$

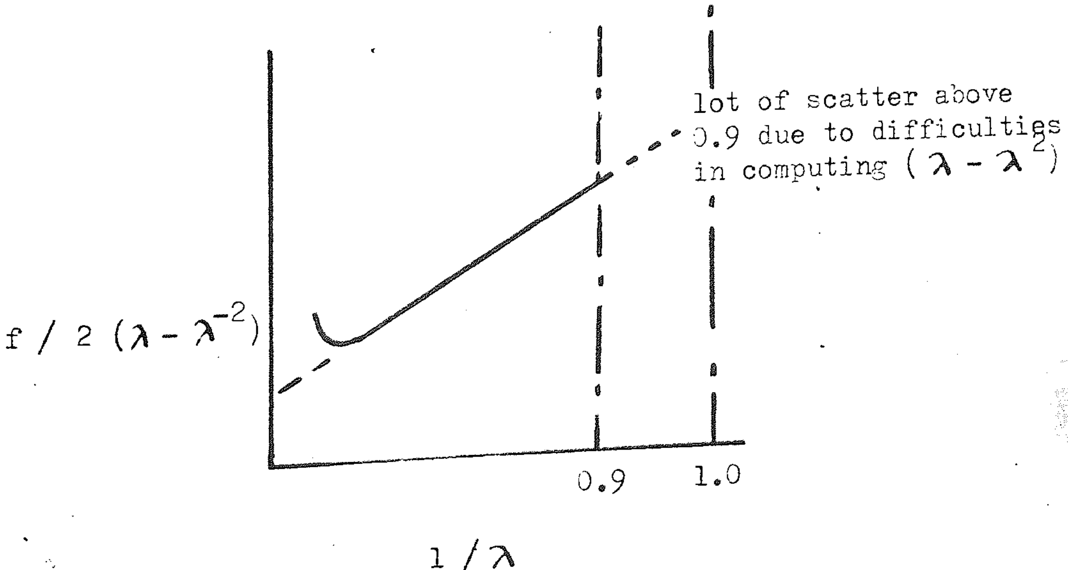
or

$$f / 2 (\lambda - 1/\lambda^2) = \partial W / \partial I_1 + 1/\lambda . \partial W / \partial I_2$$

$$= \tfrac{1}{2} N k T \text{ (according to kinetic theory)}$$

$$= C_1 + 1/\lambda . C_2 \text{ (according to Mooney-Rivlin)}$$

Experimental results show

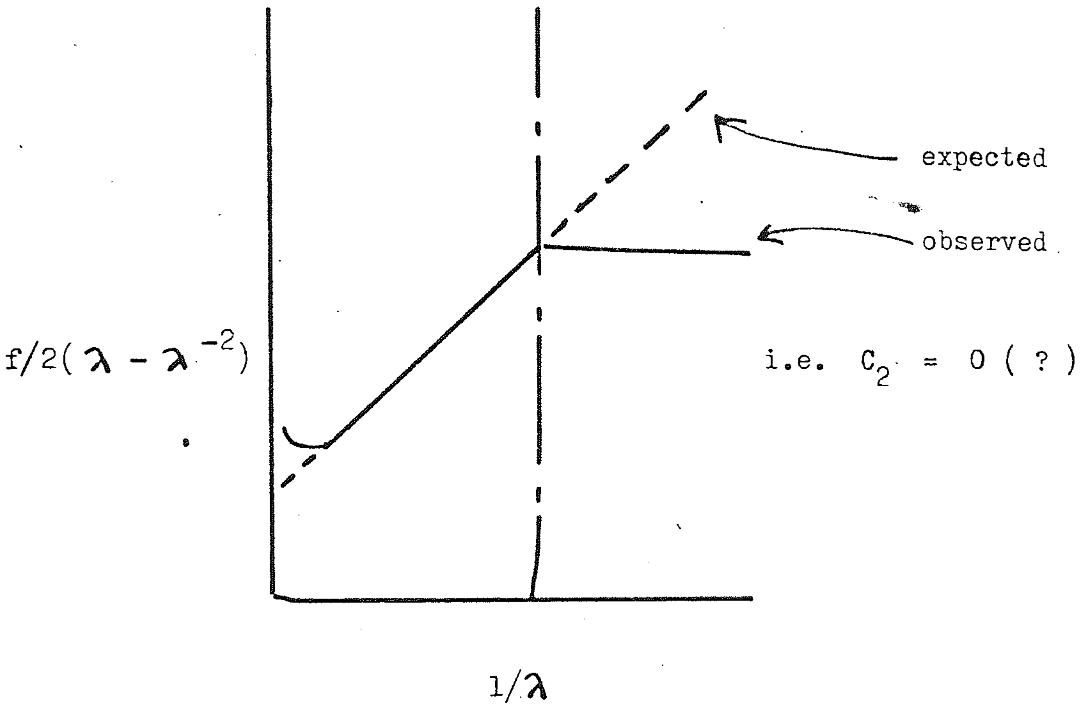


which suggests the validity of the Mooney-Rivlin relationship.

Extrapolation to $1/\lambda = 0$ provides a value of C_1

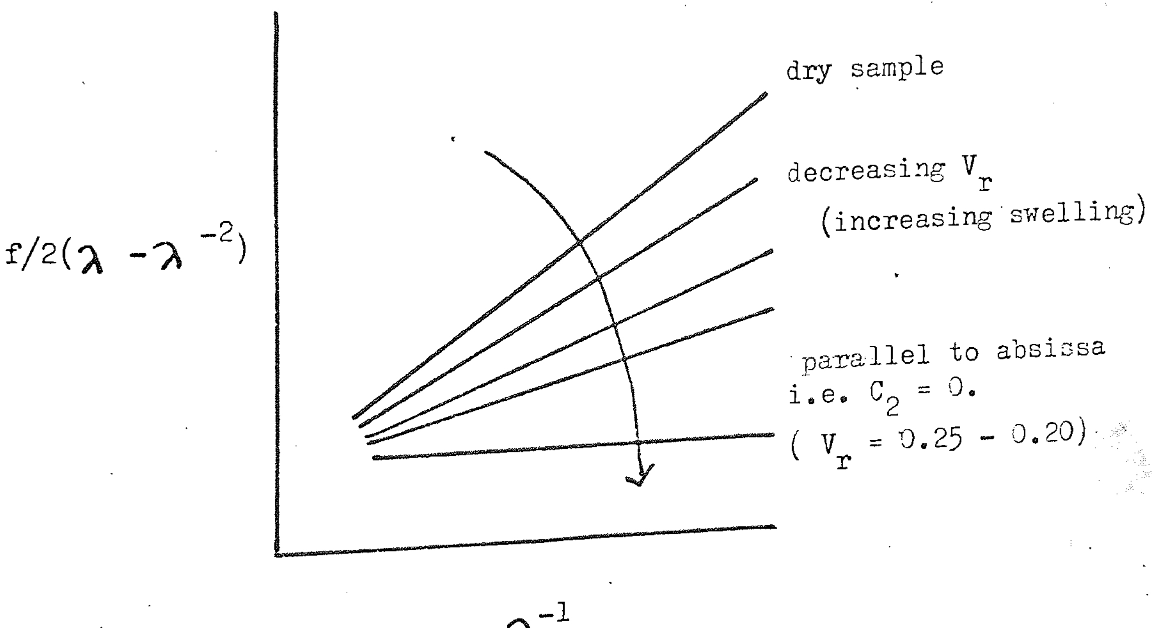
Extrapolation to $1/\lambda = 1$ provides a value of $C_1 + C_2$

For values of $1/\lambda$ greater than 1, i.e. in compression we get:-



therefore f is independant of $1/\lambda$ above $1/\lambda = 1$.

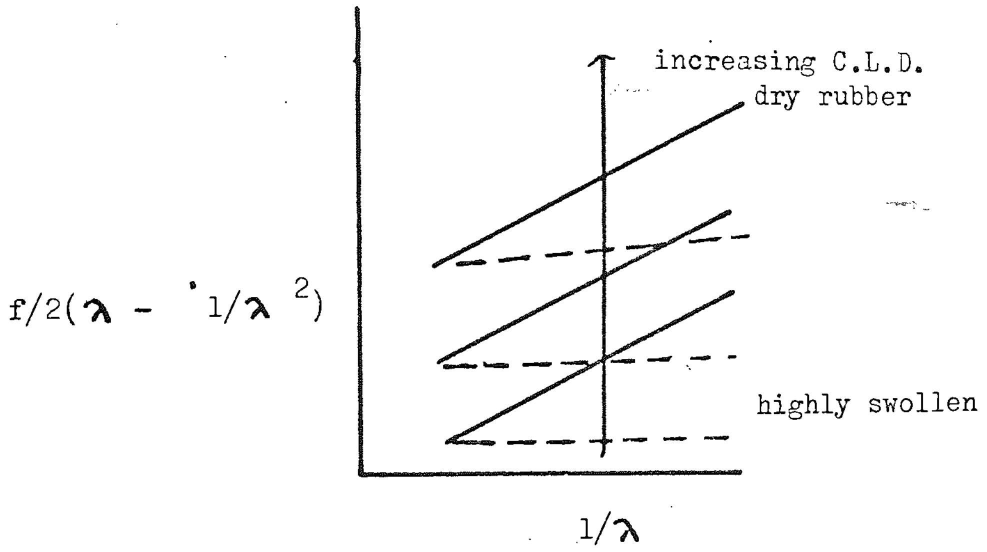
To get an idea of the molecular significance of C_2 we must consider swollen samples. The effect of decreasing V_r upon the slope (C_2) of the curve can be seen in the figure below:-



i.e. obey's the kinetic theory.

When V_r is in the region 0.25 to 0.2 relations are followed more closely and the departures noted earlier fade out on increase in swelling.

It has been noticed that for samples of increasing cross-link density C_2 is constant whilst values of C_1 increase, i.e.:-



i.e. C_2 is constant whilst C_1 increases.

This suggests that C_1 is as predicted by the kinetic theory, i.e.

$$C_1 = \tfrac{1}{2} N k T$$

The molecular significance of C_2 remains an enigma. In the case of equilibrium swelling we assume that the elastomer is a liquid being amorphous and exhibiting Brownian motion. Of the various approaches used here the most useful from a practical point of view is that of Flory-Huggins. Their explanation produced an expression relating the free energy change to the network characteristics via the values of volume swelling (V_r) , degree of polymerization (x) and the polymer solvent interaction parameter (χ).

$$\Delta G = R T (LN(1 - V_r) + (1 - 1/x)V_r + \chi V_r^2)$$

When the degree of polymerization is high 1/x is small and(1 - 1/x)

$$\Delta G = RT\left(LN(1-V_r) + V_r + \chi V_r^2 \right)$$

for all values of χ less than 0.5 G is negative at all values of V_r and hence mixing will go ahead in all proportions. If χ is greater than 0.5 then there will be a limit to the mixing. Thus if a suitable solvent is found for the polymer a relationship can be produced to evaluate M_c if V_r and χ are known:-

$$-\left(LN(1-V_r) + V_r + \chi V_r^2\right) = \frac{2V_0 C_1 . V_r^{\frac{1}{3}}}{RT}$$

Flory later modified this to:-

$$-\left(LN(1-V_r) + V_r + \chi V_r^2\right) = \frac{V_0}{M_c} . \left(V_r^{\frac{1}{3}} - V_r/2\right)$$

which takes into account the elastic component of the free energy. In order to have produced this equation Flory assumed that the system comprised of a number of components i.e. chains, cross-links, etc. Thus

entropy of system = entropy of components

and

entropy of deformed system = entropy of deformed components

thus

difference = entropy of deformation

$$S = \tfrac{1}{2} N k \left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right)$$

or as Flory formulated

$$S = \tfrac{1}{2} N k \left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 - LN \lambda_1 \lambda_2 \lambda_3 \right)$$

The final term is not important in dry rubbers but is important in swollen samples since λ_1, λ_2 and λ_3 all increase at the same time.

PHOTOGRAPHS

PLATE 1.

General view of the Monsanto Oscillating Disc Rheometer

(Model LSD)

PLATE 2.

Detail from the Monsanto Rheometer showing the two piece Micro Dies and Rotor.

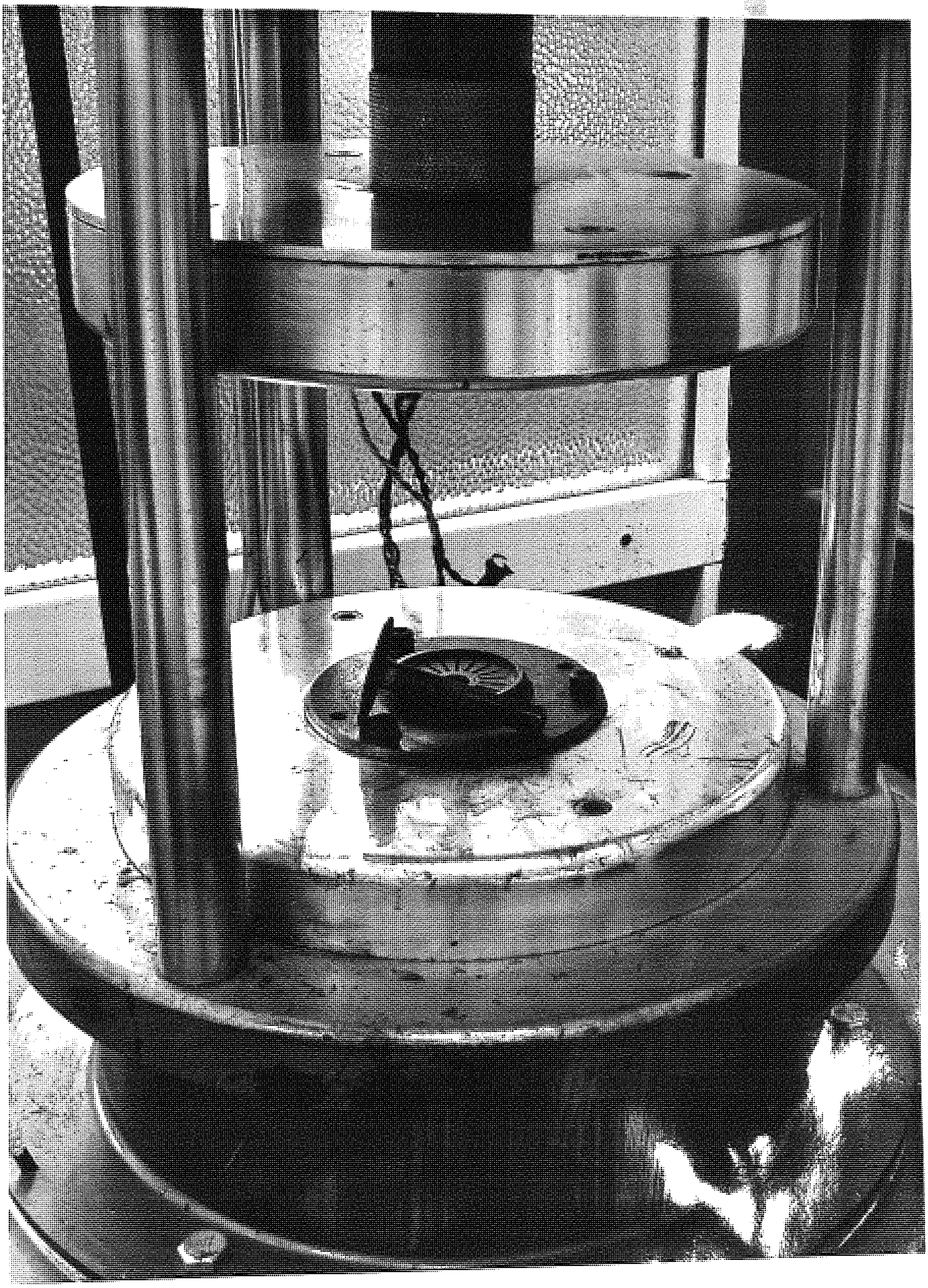


PLATE 3.

General view of the Shawbury Curometer Mk.II.

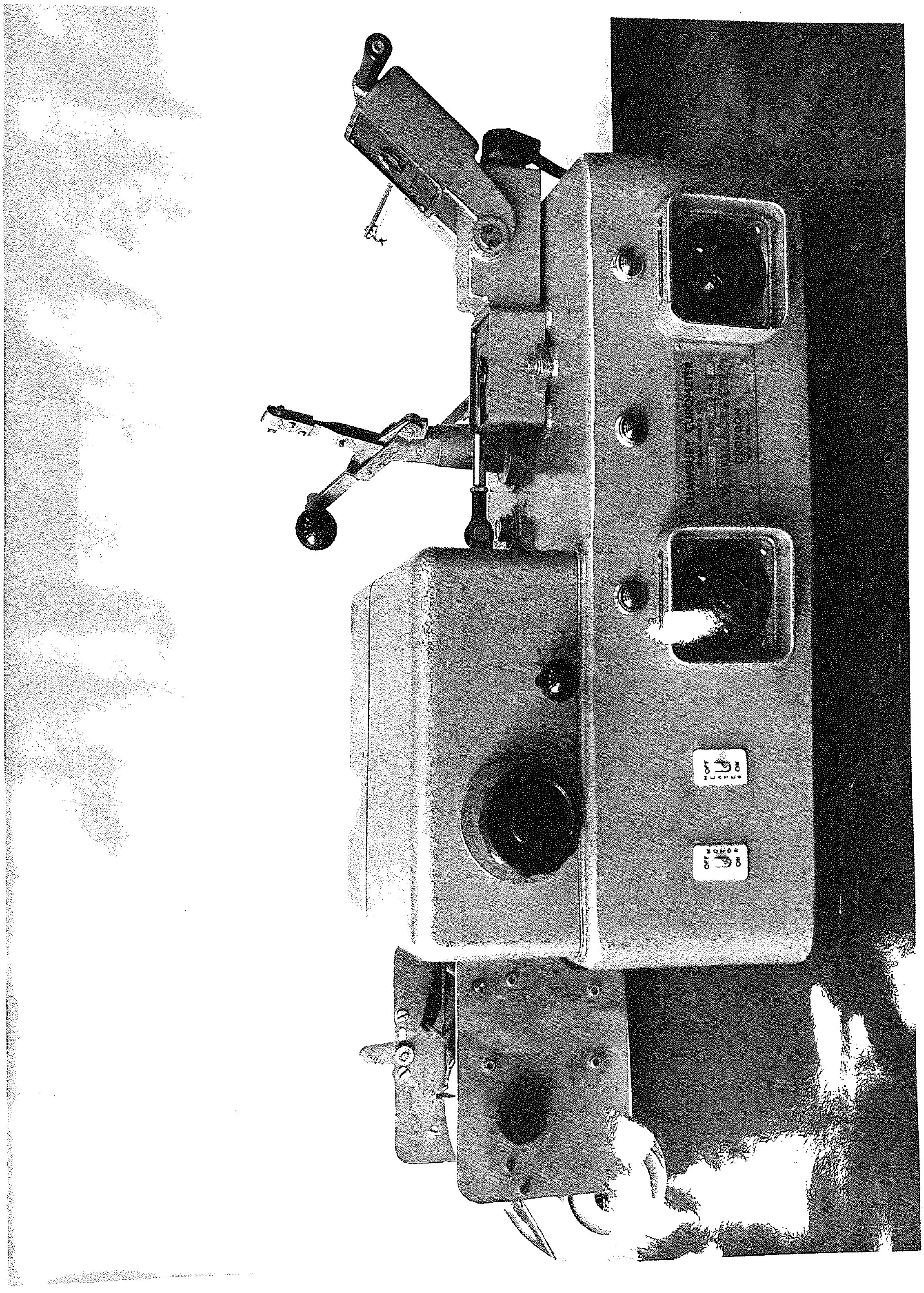


PLATE 4.

General view of the Greensmith apparatus for determining the C_1 parameter by extension stress-strain.

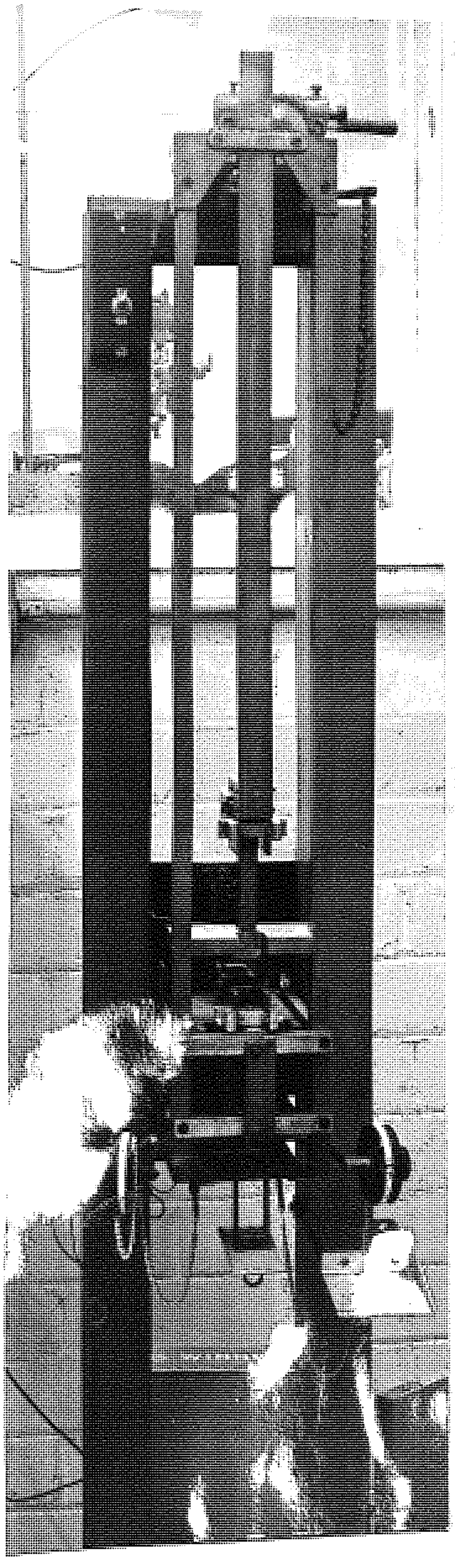


PLATE 5.

Detail from the Greensmith apparatus showing the clamping and balance systems.

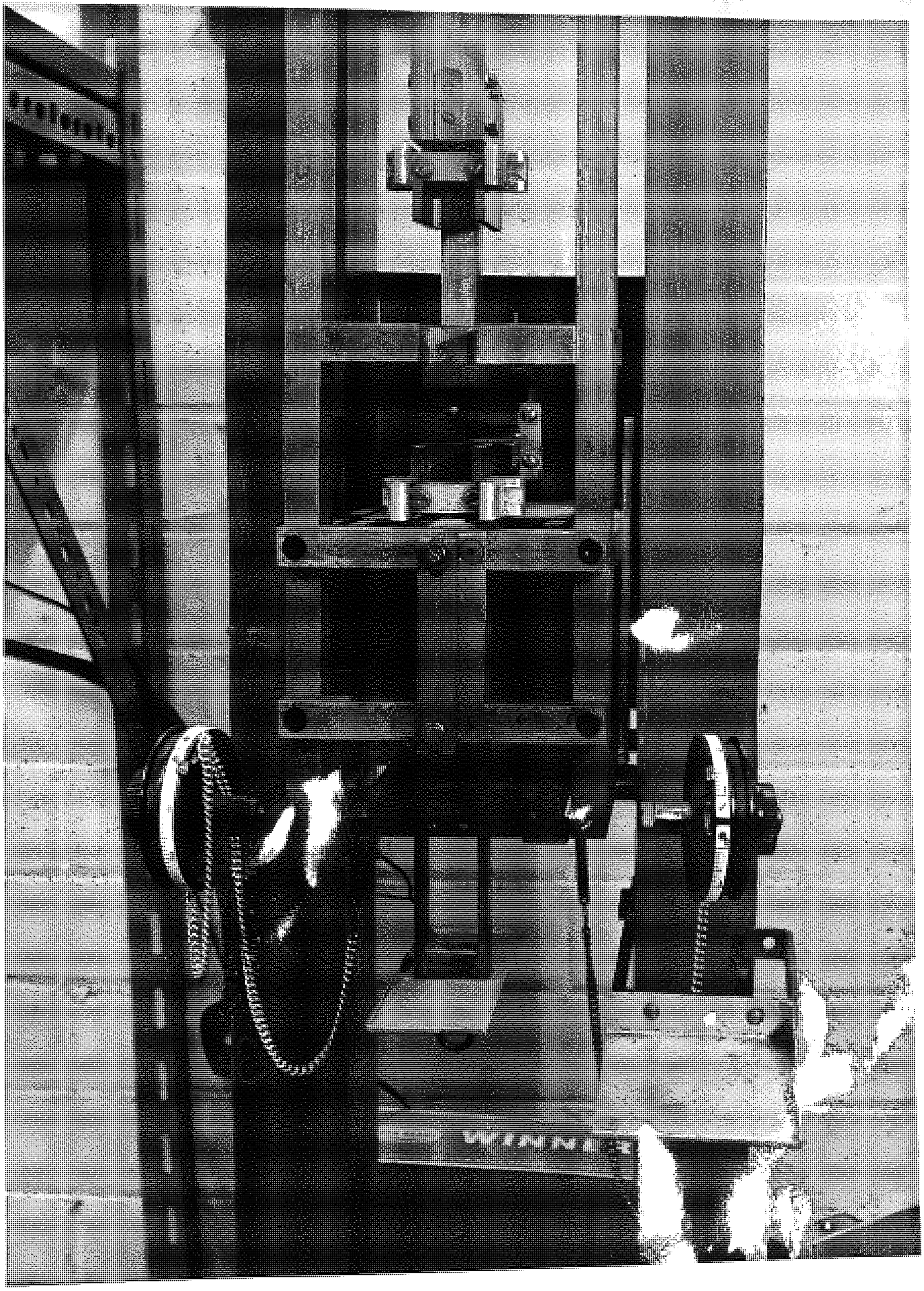


PLATE 6.

Jig used to load the C_1 dry extension test piece into the clamps.

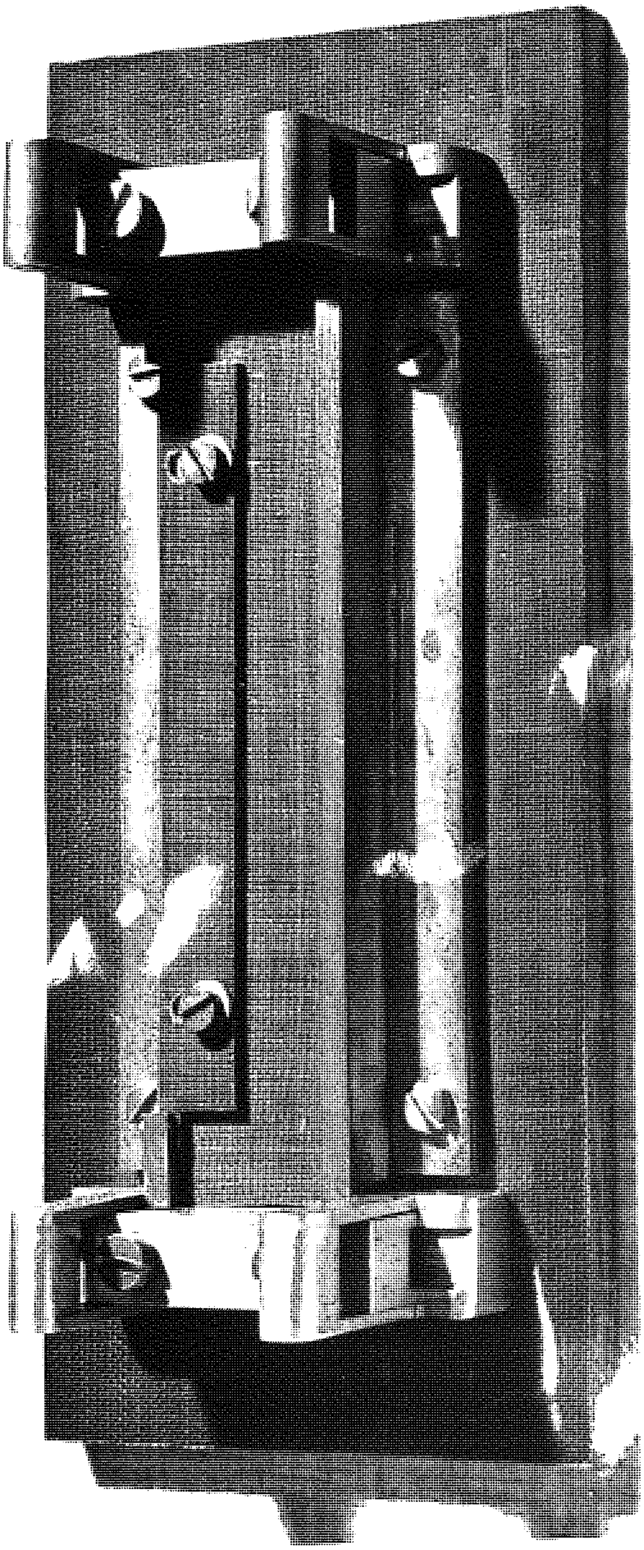


PLATE 7.

General view of the Wallace-Smith Reticulometer.

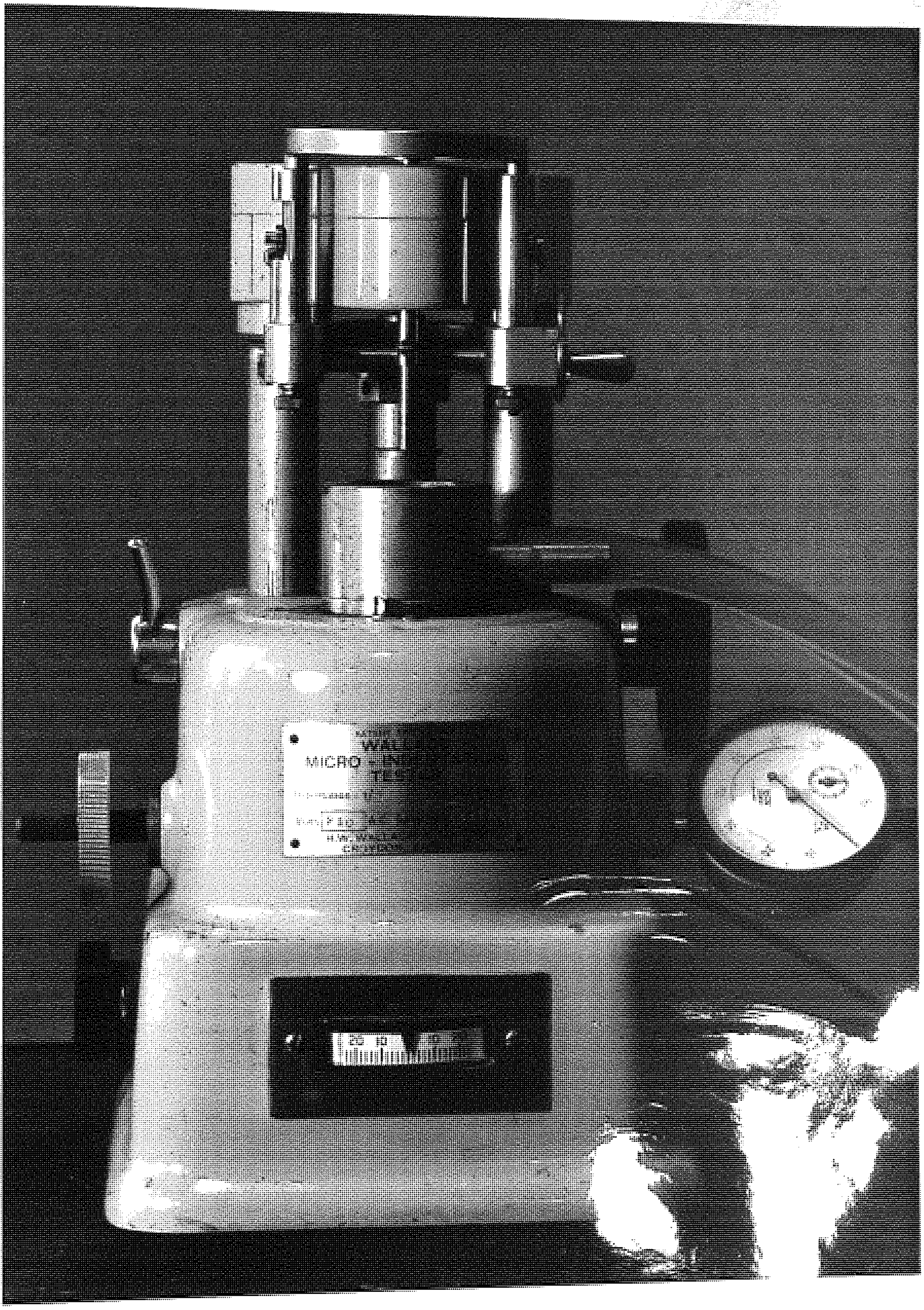


PLATE 8.

Detail from the Wallace-Smith Reticulometer showing the reticulometer pot and compression head.

PLATE 9.

Apparatus used to observe the behaviour of a swollen sample under a compressive force whilst immersed in solvent.