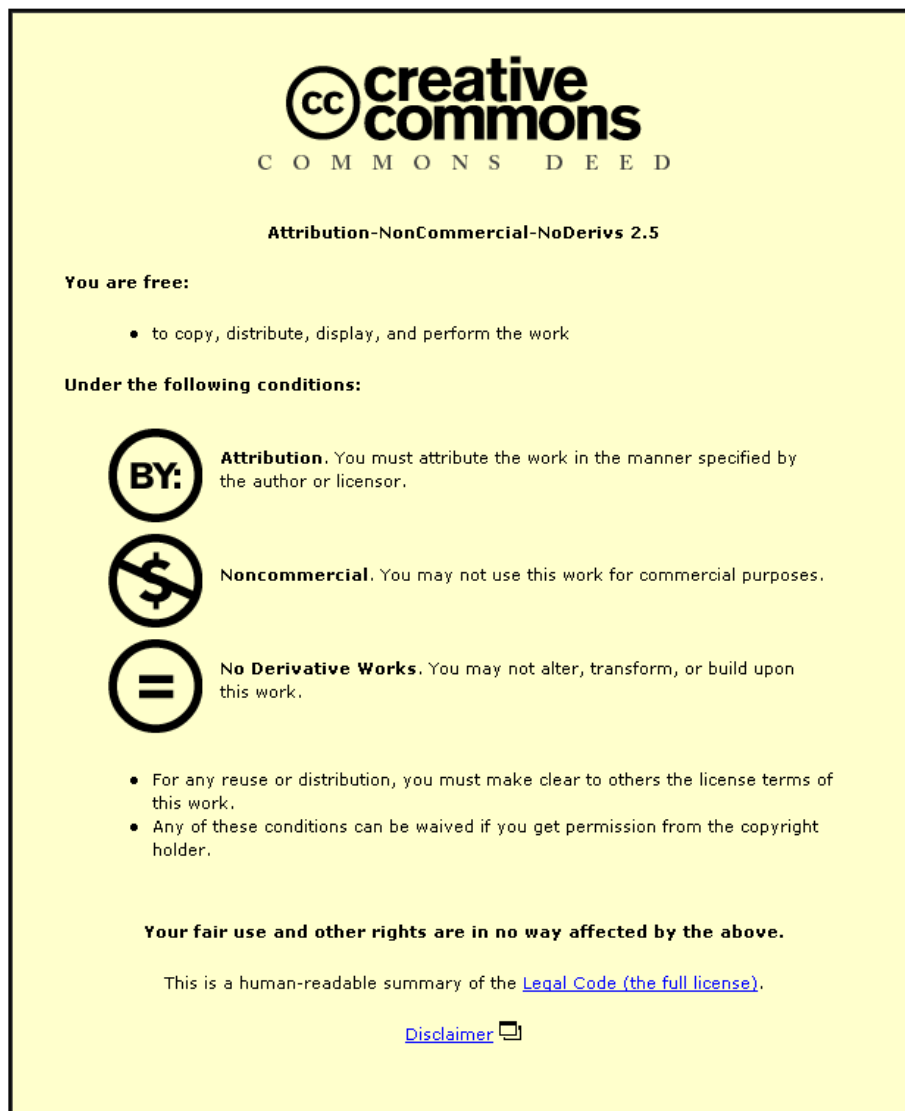


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THE MODES OF ACTION OF LUBRICANTS
IN ELASTOMERS AND ELASTOMER COMPOUNDS

by

MOHAMAD O. NUWAYRI

A Doctoral Thesis submitted in partial fulfilment
of the requirements for the award of
the degree of
Doctor of Philosophy
of the
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Supervisor: P.K. Freakley
Institute of Polymer Technology

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Dedicated to my parents and my wife, Georgina
for their support and encouragement.

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ABSTRACT

To modify the rheological behaviour of rubber compounds, in order to improve their processing behaviour, lubricants based on fatty acid derivatives are added at the mixing stage. This research has been directed towards identifying the modes of action of commercially available lubricants in a number of elastomers and elastomer compounds, with the objective of providing a rational basis for the further development of lubricants. The primary tool for rheological measurement was an advanced biconical rotor rheometer (Negretti TMS Rheometer); and a capillary rheometer was used to provide an independent verification of results. Conceptual and mathematical models have been proposed which provide a rational explanation and simulation of lubricant action. The conceptual model takes account of elastomer morphology, relative solubility parameters of elastomer and lubricant and chemical reactions between the lubricant and elastomer in order to explain internal lubrication, chain extension/cross-linking, solvation and external lubrication. The mathematical model simulates the primary lubricant actions of internal lubrication and chain extension/cross-linking.

ABBREVIATIONS AND NOMENCLATURE

NR	-	Natural Rubber
CSM	-	Chlorosulphonated Polyethylene
EPDM	-	Ethylene propylene terpolymer
ISAF	-	Intermediate super abrasion furnace
SRF-HM	-	Semi-reinforcing furnace
HAF	-	High abrasion furnace
η	-	Viscosity
η_a	-	Apparent viscosity
τ	-	Shear stress
$\dot{\gamma}$	-	Shear rate
ω	-	Angular velocity (radius/second)
t	-	Thickness of the gap between the rotor and the walls of the testing cavity
R	-	Radius of rotor or capillary
r	-	Radius less than R
α	-	The cone angle of the biconical rotor
T	-	Torque
T_c	-	Torque due to rotor's surface
T_e	-	Torque at edge of the rotor
Y	-	Thickness of the rotor's edge
ΔP	-	The pressure difference between the two ends of a capillary tube
L	-	Capillary lengths
L_w	-	Shear stress at wall of capillary tube
γ_w	-	Shear rate at wall of capillary tube
Q	-	Volumetric flow rate
ΔF	-	Free energy change
ΔH	-	The enthalpy
ΔS	-	The entropy
δ	-	Solubility parameter
C_c	-	Concentration at which chain extension/cross-linking starts to occur
C_R	-	Concentration at which external lubrication starts to occur

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CHAPTER 1

INTRODUCTION

Processing aids have been used for many years in the rubber industry to solve problems encountered in mixing, calendering, extrusion, building operations and moulding. One group of materials that falls under the processing aids category is lubricants. A lubricant can be defined as any material that is added to the rubber compound to modify its rheological properties in order to improve its processing behaviour. The rubber industry requires that additives such as lubricants should have minimal effect on the cure characteristics and the final physical properties of the product. The tyre industry in particular has strict requirements that interply adhesion and cord reinforcement should not be affected by the migration of lubricants to the rubber surface. Being of chemical nature, lubricants are prone to affect the various chemical reactions leading to the final physical properties of the product. This implies that lubricants should be added in small concentrations to rubber compounds in order to minimise any adverse effect on the final physical properties of the compound that could result from its presence.

The present state of understanding of lubricant action is very limited and directed towards particular applications. In order to be able to satisfy the different requirements presented by the various rubber companies, the modes of action of lubricants on elastomers and elastomer compounds should be understood. Having identified the various functions that can be accomplished by a lubricant, a certain

requirement in a particular process can then be obtained by specifying the right lubricant.

The aim of this study is to provide a basis for the rational development of new materials.

In view of the foregoing, the objectives of this study are:

- i) To identify the different modes of action of lubricants in elastomers and elastomer compounds.
- ii) To examine the various factors that affect the modes of action of lubricants.
- iii) To develop a conceptual model that will explain the various modes of action of lubricants on the rheological properties of elastomers and elastomer compounds.
- iv) To examine the effect of commercially available lubricants on rubber compounds used in the rubber industry.
- v) To develop a phenomenological mathematical model that will describe the dependence of the apparent viscosity of a rubber compound on lubricant concentration.

Chapter 2 of this study reviews rheological behaviour of polymers and the effect of additives on it. The different mechanisms of lubricant action proposed in earlier publications are also presented. Chapter 3 presents the theory underlying the various measurement techniques used. In chapter 4, the equipment development and operation methods are presented, as well as the mixing and sample preparation techniques. Chapter 5 deals with the preliminary experimental results from which a conceptual and a mathematical model

are developed in chapter 6. Chapter 7 presents the results of experiments developed to validate the conceptual model proposed in chapter 6. In chapter 8, the various conclusions about the two models, the lubricants used and the measuring techniques are presented. Also, recommendations for further work are suggested.

CHAPTER 2

LITERATURE SURVEY

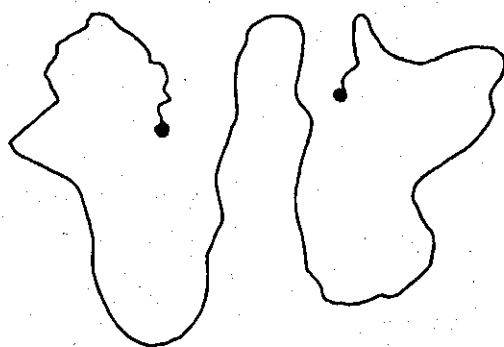
2.1. RHEOLOGICAL BEHAVIOUR OF POLYMERS

Today the concept that polymers consist of very long chains of covalently bonded atoms is almost universally accepted[1]. It is also recognized that regardless of whether a polymer is natural or synthetic, it consists of a backbone of multitudinous covalently bonded atoms. The difference between the physical properties of the different polymers depends to a large extent on the regularity of polymer structure and the relative strength of the intermolecular secondary valance bonds. The latter may be strong hydrogen bonds, moderately strong dipole-dipole forces, or London forces.

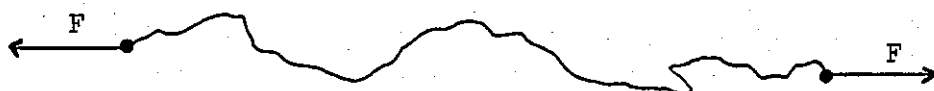
A polymer chain in isolation will take up a wide variety of stereoscopic conformations, governed by three factors[2]:

- a) The statistics of random processes.
- b) A preference for certain sequences of bond arrangement because of steric and energetic restraints within the molecule.
- c) The exclusion of some hypothetical conformations which would require parts of the chain to occupy the same volume in space.

If tensile forces are applied at the ends of a polymer chain, it will assume a somewhat oriented conformation, but when the tensile forces are removed, the chain will recoil to one of its more stable conformations[3] (see Figure 2.1.). Unvulcanised rubber, in its



(a)



(b)

Figure 2.1 : a) Random elastomer chain
b) Oriented elastomer chain.

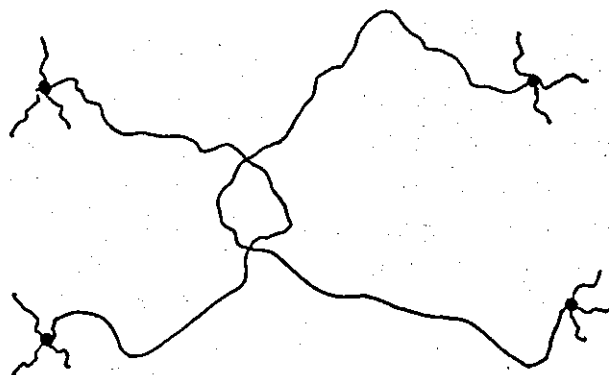


Figure 2.2 : Elastomer chain entanglement.

simplest morphology, is made up of such polymeric chains. The ability of the chains to move past each other when a tensile force is applied gives it its viscous properties; and their ability to recoil when the stress is removed gives it its elastic properties.

Viscosity, is the measure of the resistance of the liquid to flow and is more exactly defined as the ratio of the shearing stress $[\tau]$ to the rate of shearing $[\dot{\gamma}]$

$$\eta = \frac{\tau}{\dot{\gamma}} \quad \dots (2.1.)$$

For a Newtonian liquid, the viscosity is a constant regardless of the rate of shearing $(\dot{\gamma})$. This is not the case in most real liquids and especially not with polymers. One only has to imagine the different conformations taken by the polymeric chains at different levels of stress to know that the resistance of a polymer to flow when the chain is in its random conformation (see Figure 2.1.[a]) is different from its resistance to flow when the chain is in its oriented conformation (see Figure 2.1.[b]). This is the problem encountered in the simplest case, where the Eyring activation theory[4] is applicable.

Eyring states that the activated moving units in a flowing liquid are either the molecules of the liquid, or the chain segments of the molecules if the material is a high polymer. However, there are both theoretical and experimental reasons for believing that, at least in many cases, there are coherent masses, containing many molecules of the liquids, which move and rotate essentially as coherent units[5]. In organic liquids of low molecular weight, such units are suggested by

the X-ray evidence of cybotaxis[6]. Glasses are generally supposed to contain regions of higher and lower order in atomic arrangements[7]. Mooney[8] revised the Eyring theory to bring it into harmony with the large size of the rheological units in elastomers. In the revised theory the macroscopic viscosity is assumed to result from the friction of the rheological units as they slide over each other. The frictional force is treated as a consequence of temporary molecular attachments across the boundaries of the units. Mooney[5] suggested that the existence of the rheological units was due to entanglement or thixotropic attachments. These units would move and rotate as elastic solid bodies. The diameters for a series of different elastomers tested in his paper lay in the range from 1 to 35 microns.

The concept of chain entanglement first arose more than fifty-five years ago. In 1932, Busse[9] distinguished between the weak Van der Waals forces occurring over most of the molecule's length which offered almost no resistance to motion, and a few widely-separated strong interactions which served, for short times at least, to bind the structure into a three-dimensional network.

Treloar[10] pointed out that such physical coupling or entanglement might indeed be expected, given the long flexible nature of individual molecules and random, interpenetrating arrangements in the solid. Regions where molecules were looped through one another (see Figure 2.2.) might offer high resistance to deformation for a time. but the loops would eventually slip or be removed and reformed by random thermal motion.

Graessley[11] discounted the past theories attempting to explain the nature of entanglements in flexible non-polar polymers in topological terms, eg. loops, kinks, etc... No matter what the explanation of the entanglement phenomenon is; its existence is widely accepted.

2.2. ELASTOMER COMPOUND RHEOLOGY: FILLERS AND PROCESS OILS

Fillers, process oils and other additives should be compounded with raw rubber in order to obtain a rubber compound with useful physical properties. The addition of fillers and process oils to an elastomer has a major influence on its rheological properties.

2.2.1. Filler:

Carbon black is the preferred rubber filler and is used for the majority of situations where reinforcement is required. For the reinforcement of white or light coloured mixes, silicon and other white fillers can be used. The nature of the interaction of elastomers with particular fillers is complex and can be divided in two categories; chemical interaction and physical interaction.

The chemical interaction comes in two forms: adsorption and free radical association. It has long been known that rubber can be adsorbed from solutions onto carbon black and activated carbon[12]. In addition, Watson[13], has shown that when carbon black compounds are masticated, the black surface acts as a free radical acceptor.

The physical interaction was obvious when experimental studies of the influence of fillers on the viscosity of the rubber compound showed extraordinary behaviour that does not obviously follow from any hydrodynamic theory. For small particles (Diameter $< 1000 \text{ \AA}$), the viscosity is strongly dependent upon particle size. The smaller the size of particles, the larger the viscosity at any volume loading. The reason for the enhanced contribution to the viscosity of the very small carbon black particles has been the subject of considerable discussion through the years. One view which has gained attention and some acceptance is that given by Medalia[14] and Kraus[15]. They suggested that the carbon black consists of complex primary aggregates of fused small particles[16] and the effective volume of the black includes not only the black volume itself but that the polymer occluded onto the internal void volume associated with the primary aggregate. This makes carbon black a special case, by adding a physical interaction to its chemical interaction with the polymer.

Generally, filler-reinforced polymers exhibit an increase in viscosity, an apparent decrease in elastic memory and the development of thixotropy. Filled polymers exhibit unusual viscosity - shear rate dependence. At low volume loadings, the behaviour is similar to that of pure polymers, but at moderate and high volume loadings, yield values are observed. Thus the viscosity is very large at low shear rates and decreases rapidly with increasing shear rate. As for the effect of fillers on the viscoelastic properties of polymers, it has long been realized by rubber technologists that fillers, especially carbon black "deaden" rubber and other polymers and give improved extrusion characteristics such as decreased extrudate distortion and

extrudate swell. The elastic recovery in rubber compounds measured in a Mooney viscometer decreases with black loading.

Extensive studies on fillers were presented by Vinogradov et al[17] and by Nakajima[18].

2.2.2. Process Oils

Process oils are the second major additive in rubber compounds after fillers. At levels of 5-20 Phr, process oils are considered as processing aids and at higher levels they are considered as extenders. Process oils are divided into three major categories: aromatic, paraffinic and naphthenic.

The typical oil molecule contains unsaturated rings (aromatic), saturated rings (naphthenic) and side chains which impart paraffinic characteristics.

In aromatic oils, the predominant ring structure is aromatic while in naphthenic oil there is a predominance of saturated rings containing no double bonds. In paraffinic oils, saturated naphthenic rings predominate but there are fewer rings per molecule and there are larger numbers of hydrocarbon chains attached to the rings than in naphthenic oils. The aromatic molecules are important since they probably affect rubber properties more than any other constituent. Saturated materials are basically inert and impart good colour and stability[23].

When used as processing aids, the process oils reduce the overall viscosity of the compound to a workable level, reduce process power consumption, help control heat generation and facilitate dispersion of pigments. The influence of viscous aromatic, naphthenic and other oils on rheological behaviour of rubber and rubber compounds has been considered by Kraus and Gruver[19], Collins and Oetzel[20], Derringer[21] and Nakajima and Harrell[22].

2.3. RHEOLOGICAL FACTORS WHICH LIMIT PROCESS PERFORMANCE

The common and important subjects concerning the rubber industry are:

- 1) To design compounds which are trouble-free in mixing and downstream operations.
- 2) To achieve consistency in the rheological properties of the mixed compound.
- 3) To reduce costs by achieving a higher unit-production rate.

The mixing of rubber with other ingredients can present two major problems. These are melt fracture (or crumbing) and temperature rise.

With some compounds and mixing conditions there is a tendency for the rubber to undergo melt fracture where the rubber breaks up into crumbs and becomes coated with particulate additives, such as fillers, which act as effective partitioning agents. When this occurs, effective mixing ceases and is very difficult to recover, although an oil addition will sometimes remedy the situation by wetting the loose

filler and providing a nucleus from which viscous flow can recommence[24]. Crumbing of a batch is a phenomenon which is usually encountered with narrow molecular-weight distribution rubbers of low green strength[25].

Temperature rise due to shear heating while mixing can become a problem since rubber in general is a poor heat conductor. In some cases, such as internal mixing, the rubber can rise to temperatures high enough to start up the vulcanisation process in localized areas of the compound, even though the overall temperature is still quite low, thus altering its rheological properties. The same problem can also be encountered in down stream process operations like extrusion.

Practical extrusion dies are normally short in comparison with their aperture size and are often required to impart a complex shape to the extrudate. An abrupt lead-in taper to a die, or a design giving a nonuniform exit velocity distribution, will severely limit the output rate which can be achieved before the onset of melt fracture[26]. This in appearance can range from a slight, but unacceptable roughness on the surface of an extrudate to an extreme distortion.

Many other problems are encountered during the different processes that make the final product. Process machine designers and factory process engineers, compounders and raw material suppliers, including producers of rubbers, fillers, oils and other materials, are continually making efforts more or less towards the objectives mentioned at the beginning of this sub-section.

Consistency in the rheological properties of the mixed compounds might help us to avoid some problems encountered in the down stream process operations. It may be achieved by single sourcing the raw rubber and other ingredients; or by having a proper understanding of the effect of different ingredients in the rheological properties of the compound. The latter gives us the ability to design a compound to the particular process's rheological property requirements.

2.4. PROCESS AIDS

Any ingredient added to a rubber compound designed to improve the handling characteristics of the compound during any of the processing steps can be included in the process aid category. It is obvious that this class of materials covers quite a long and interesting list of products. The various processing steps which may benefit from the use of process aids are:

- 1) Mixing: In mills or Internal mixers.
- 2) Calendering.
- 3) Extrusion.
- 4) Building Operations.
- 5) Moulding: Compression, transfer, injection.
- 6) Release from molds.

The first step in the compounding sequence is mixing. Most elastomers are not easily fabricated and must usually be plasticized or softened to enable easy incorporation of compounding ingredients. An elastomer can be softened by mechanical breakdown, chemical

breakdown or by addition of a physical softener i.e. lubricant. Some polymers, most notably natural rubber, show significant decrease in viscosity under shear forces such as those encountered during mill mixing[27] while others such as CSM (chlorosulphonated polyethylene) undergo only minor changes. Chemical breakdown can be achieved by adding chemical peptizers to the rubber.

Chemical peptizers fit the definition of a processing aid and would be used during the initial compounding operation. These are generally radical acceptors or oxidation catalysts which effectively remove the free radicals formed during milling or mixing of the polymer, thus, preventing recombination and resulting in the softening of the polymer.

Physical softening of polymers can be achieved by adding lubricants at the mixing stage. The major lubricants currently in use are metallic stearate, stearic acid, natural and synthetic waxes, low molecular weight polyethylene, amorphous polypropylene, powdered fluorocarbons, fatty acids and fatty acid derivatives and a large number of proprietary products whose compositions are not disclosed. We can also say that process oils are lubricants to some extent. We will look at lubricants more closely in the next section (Section 2.5.).

Other process aids are made of resins[28]. Resins have been separated from softeners and extenders because, although they may be used as softeners and/or extenders, they can often be used in other

applications. They can act as cure agents and tackifiers to improve the building operations of the final product.

Silicones are well known in the rubber industry for their use as release agents in molding operations. Due to their incompatibility with most organic materials, they form an excellent barrier between a rubber part and the surface of a mold. In addition, because of their excellent heat resistance, they minimize build-up and fouling of molds. They are used in small concentration levels of 0.1 to 0.5 Phr.

2.5. MECHANISMS PROPOSED FOR LUBRICANT ACTION

Many types of lubricants have been used over the years to overcome the basic problem in processing rubber compounds, namely, the shaping or molding of a high viscosity rubber compound with maximum output and minimum time or energy input. The products mentioned in Section 2.4. are only an example of the types of lubricants that we can encounter.

O'Connor and Slinger[23] classified lubricants as either external lubricants or internal lubricants. External lubricants function to eliminate friction between the polymer and the metal surface of processing and molding equipment. Internal lubricants are added to affect the flow characteristics of polymers, to improve knitting of the compound and to reduce excessive heat build-up in process and to improve the wetting properties of the compounding ingredients with the polymer system. Many products perform both functions simultaneously in a specific compound. In this research, lubricants are defined as

any material that is added to the rubber compound to modify its rheological properties.

The theory behind lubricants and their correct application is still one of the ill-defined areas of rubber technology. The old adage "Try it; you will like it!" is often the only significant positive performance data which can be offered. The main objective of a lubricant manufacturer is to produce a material, which, when added to a rubber compound at relatively low loading levels (0.5 to 10 Phr) will improve processability without adversely affecting the physical properties of the final product. Most of the products mentioned earlier, as well as affecting the flow properties of the rubber compound, are known to affect properties such as hardness, tackiness, ageing, compression set, etc... The most effective product will be the one that will work at very low concentrations where the side effects are minimal and can be neglected. Such products are mainly mixtures of fatty acid derivatives.

In a recently published paper, LeBlanc and Lloyd[29] considered the mechanisms by which such lubricants can influence rubber processing and proposed three models depending upon the compatibility of the lubricant with the compound.

Model 1: The lubricant has low compatibility

Such a product was thought to bloom at the rubber/metal interface and behave as an External lubricant, thus inducing slippage in processing equipment.

Model 2: The lubricant has medium compatibility

Providing its concentration was kept below a certain limit, the material was thought to act as an Internal lubricant, favouring slippage between the flow units (Section 3.1.) of the compound. If the limit of concentration is exceeded, then an external lubrication action (Model 1) is added which may become dominant.

Model 3: The lubricant has high compatibility

Such materials were thought to modify the rheological properties of rubber compounds in a completely different manner. As no blooming was observed by LeBlanc and Lloyd, they developed the concept of Bulk viscosity Modifiers. Such materials with high compatibility with the rubber compound were thought to act via two proposed mechanisms.

Model 3a: Through intermacromolecular action, to produce a reduction in the magnitude of entanglement between polymer molecules.

Model 3b: Through intramacromolecular action, diffusing between the polymer molecules and consequently softening it by swelling.

So, Lloyd and LeBlanc's definition of a Bulk Viscosity Modifier is that it is a rheological chemical which modifies the processing behaviour of rubber compounds through action at the macromolecular level, rather than by a change in slippage at the rubber-metal interface of the processing equipment used.

In their paper they compared the effects of a light oil (CIRCOLIGHT RPO) and a material of polymeric origin, having the capability to cross-link (BVMO01) as a bulk viscosity modifier. Both products were added at levels 2, 3 and 5 phr to a natural rubber tread compound in the internal mixer. The physical properties of the final product showed minor losses, generally within test reproducibility, except at the highest level of additives (5 phr) for which the 300% modulus was decreased by around 8% versus the control. Hardness and compression set were essentially unaffected, while the resilience was slightly decreased with BVMO01.

Using the capillary rheometer (Section 3.3.), they plotted the variation in the apparent viscosity (Eq. 2.2.) versus rheochemical level for the light oil and the BVMO01.

$$\eta_a = \frac{\tau}{\dot{\gamma}} \quad \text{..... (2.2.)}$$

where τ = Shear stress at the wall of the capillary

$\dot{\gamma}$ = Shear rate at the wall of the capillary

η_a = The apparent viscosity at the wall of the capillary.

At low levels, both the bulk viscosity modifier and the oil produced almost the same decrease in apparent viscosity (around .3%).

As the level increased, the BVM gave a continuous decrease in apparent viscosity with concentration (around 13% viscosity drop with 5 phr), whereas the oil plateaued out when the additive concentration exceeded 3 phr.

The light oil, below a critical concentration, remained essentially dispersed within the rubber compound and produced mainly internal lubrication. Above this critical concentration, the oil exuded at the rubber-metal interface and acted as an external lubricant.

CHAPTER 3

MEASUREMENT TECHNIQUES AND SUPPORTING THEORY

3.1. INTRODUCTION

The underlying theory and calculations for the different measuring techniques used in this research are summarized in this chapter.

3.2. FLOW IN A BICONICAL ROTOR RHEOMETER

In a rheological instrument of the rotational type, such as the biconical rotor rheometer, a sample can be maintained in a state of continuous shear until a steady or quasisteady state is attained. In 1936 M. Mooney[30] developed the earliest rotational rheological instrument suitable for rubbers. In his design the outer cylinder, or stator, is in the form of a split block, which opens up for easy insertion of the sample. The inner cylinder, or rotor, is mounted on a hollow shaft which is driven by weights. Another rotational instrument, in which the rotor is a flat disk and the stator a shallow cup enclosing the disk, was developed by M. Mooney[31] for routine control tests.

A variation of the disk viscometer was introduced by Piper and Scott[32], who substituted a biconical rotor for the flat disk (Figure 3.1.).

The biconical form has the advantage that the rate of shear in the sample is approximately uniform over the face of the rotor, which is

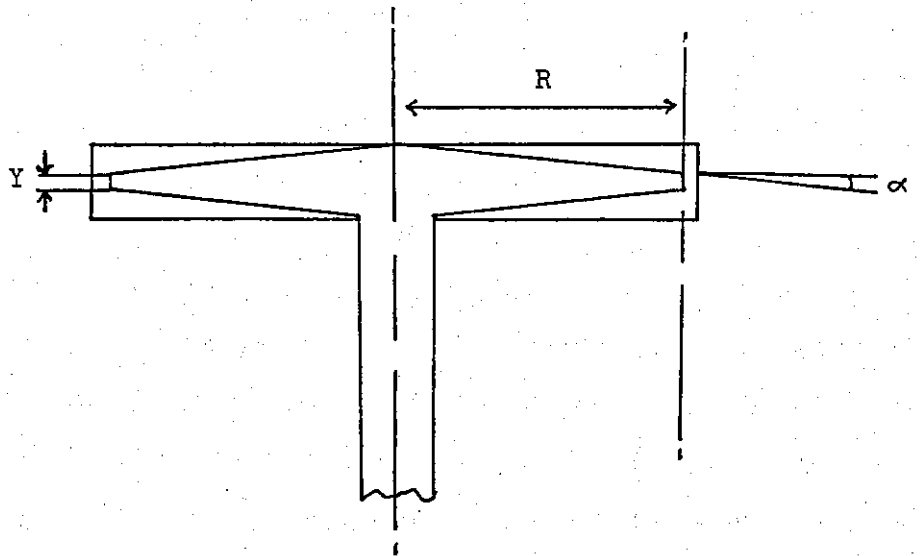


Figure 3.1 : Modified Mooney viscometer with biconical rotor.

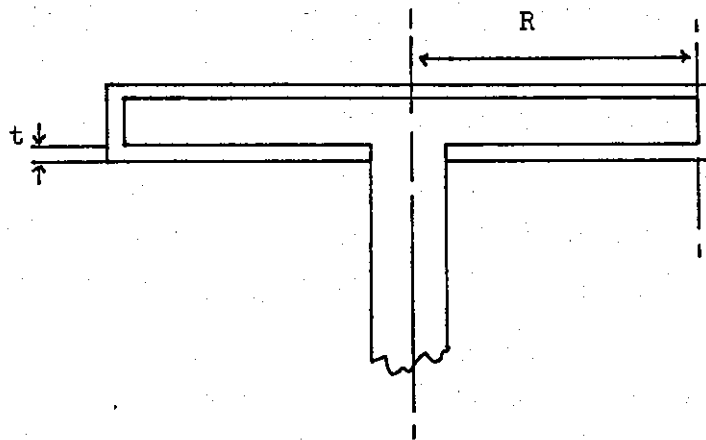


Figure 3.2 : Mooney viscometer.

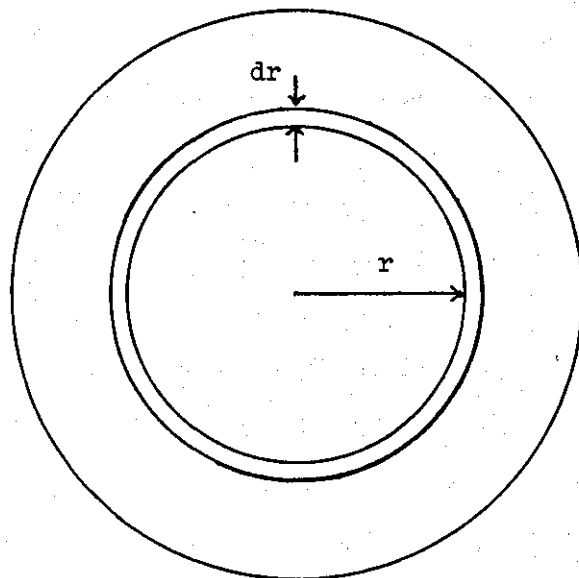


Figure 3.3 : Annular section of rotor.

not the case with the disk rotor. Hence, the biconical rotor permits a calculation of the true viscosity at a known, single rate of shear, except for edge effects; while the flat disk rotor gives only an average viscosity over a range of shear rates.

With the disk viscometer, better known as Mooney Viscometer (Figure 3.2.), the shear rate on the surface of the disk at any radius r is given by:

$$\dot{\gamma}(r) = Wr/t \quad \dots (3.1.)$$

where W is the angular velocity of the rotor in radians/seconds.

r is any radius less than the radius of the disk rotor (R)

t is the thickness of the gap between the rotor and the walls of the cavity

$\dot{\gamma}$ is the shear rate in 1/seconds.

To get a uniform shear rate between $r = 0$ and $r = R$, it is necessary for $r/t = \text{constant}$. This is achieved by using the biconical rotor for which $r/t \approx \alpha$, where α is the cone angle in radians (Figure 3.1.), provided that $\alpha < 6^\circ$. The shear rate is then:

$$\dot{\gamma} = W/\alpha \quad \dots (3.2.)$$

The total torque on the rotor (T) is the sum of the torque due to the double surface of the cone ($2 \times T_c$), and the Couette flow at the edges (T_e). The torque on the rotor due to flow over and under the conical surfaces can be evaluated by considering a typical circular element of width dr at radius r (Figure 3.3.).

The torque applied by this section is:

$$\frac{dT_c}{r} = (2\pi r \cdot dr) \tau \quad \dots (3.3)$$

$$\text{i.e. } dT_c = (2\pi r^2 dr) \tau \quad \dots (3.4)$$

where τ is the shear stress

Integrating between $r = 0$ and $r = R$ we get

$$T_c = \frac{2}{3} \pi R^3 \tau \quad \dots (3.5)$$

The torque due to the region of Couette flow, assuming a Newtonian behaviour at the corners, can be approximated to:

$$T_e = 2\pi R^2 Y \tau \quad \dots (3.6.)$$

where Y is the thickness of the rotor at the edge (Figure 3.3.).

The total torque will then be equal to:

$$T = 2T_c + T_e = \frac{4}{3} \pi R^3 \tau \left(R + \frac{3Y}{2} \right) \quad \dots (3.7.)$$

The errors resulting from the assumptions made here can be minimized by reducing the edge thickness of the rotor as far as possible.

Equation 3.1 serves to derive the shear rate from the measurable angular velocity and equation 3.7. can be written in the following form:

$$\tau = \frac{3}{4} \frac{T}{\pi R^3 \left(R + \frac{3Y}{2} \right)} \quad \dots (3.8.)$$

This will give the shear stress(τ) from the measurable torque applied on the rotor(T).

Another assumption was made during these calculations, that the material inside the cavity is completely attached to the metal surfaces. That is to say, that no slippage will occur on the metal surfaces when a torque is applied. The slippage of rubber compounds on hot metal surfaces is known to occur. Mooney and Black[33] made slip measurements using extrusion measurements with dies of different lengths and diameters. Decker and Roth[34] made measurements with the Mooney viscometer using a standard serrated rotor and a smooth rotor. Lower torque readings with the smooth rotor, when observed, can be attributed to surface slip. The likelihood of slippage depends on both the kind of rubber and the kind of metal on the surface of the rotors[35].

When slippage occurs in a biconical rotor rheometer, the angular velocity W resulting from a given torque is the sum of the viscous shear component W_r and the angular slip component W_s .

$$\text{ie. } W_v = W - W_s \quad \dots (3.9.)$$

Using equation 3.2, the shear rate will be:

$$\dot{\gamma} = \frac{W - W_s}{\alpha} \quad \dots (3.10.)$$

Transposing the angular slip velocity to a linear velocity presents problems since the latter quantity is dependent on the radius. However, it can be argued that the peripheral region of the rotor will make the greatest contribution to slippage[36], giving the approximate

relation:

$$V_m = W_m R \quad \dots (3.11.)$$

The slip velocity is often found to be related to shear stress by the empirical equation

$$V_m = K \tilde{\tau}^m \quad \dots (3.12.)$$

It is thought that slippage is due to a boundary layer providing lubrication between the rubber and the metal surface. Moore and Turner[37] report that angular velocities differing by a factor of 180 have been observed between grooved and polished rotors operating at similar shear stresses.

3.3. FLOW IN A CAPILLARY RHEOMETER

The capillary rheometer (Figure 3.4.) is one of the oldest and most widely used experimental methods for measuring the viscosity of fluids. It was used by Marzetti[38], the pioneer of rheological testing in the field of rubber technology, and has been widely used in recent years, eg. [39][40].

The basic idea of the instrument is to relate the pressure loss for extrusion through a small diameter tube of a certain length and diameter to the shear stress at the capillary wall; and the extrusion rate to a wall shear rate. However, in deriving the expressions for shear stress and shear rate, the following assumptions are made:

- 1) The flow must be steady
- 2) There are no radial and tangential components of flow velocity

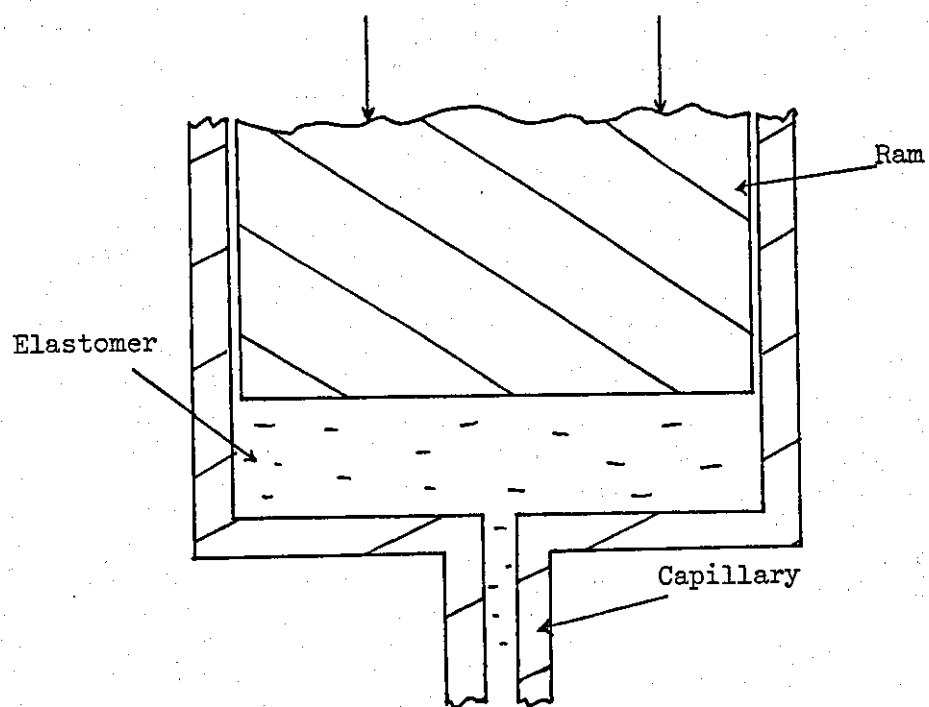


Figure 3.4 : Capillary rheometer.

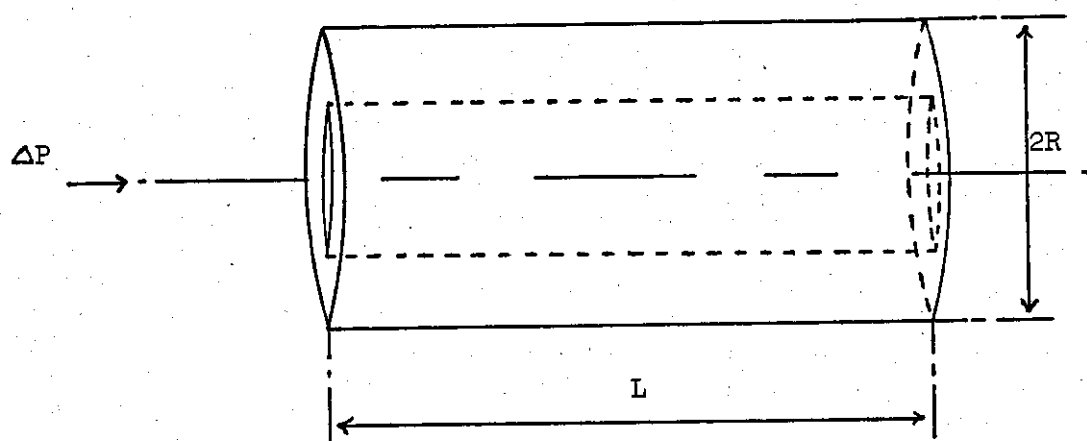


Figure 3.5 : Capillary tube.

- 3) The axial velocity is a function of the distance from the axis alone
- 4) There is no slippage at the wall (ie. velocity at the wall = 0)
- 5) The fluid is incompressible
- 6) There are no external forces
- 7) Isothermal conditions prevail throughout
- 8) Viscosity does not change appreciably with the change in pressure down the tube.

Consider a fluid in laminar flow in a tube of radius, R , and length, L , with a pressure difference, ΔP , between the ends of the capillary (Figure 3.5.). For steady flow, the viscous force tending to retard the flow will be exactly balanced by the force resulting from the pressure difference between the two ends.

ie. for a circular column of radius r we will have:

$$(2\pi r L)\tau = \pi r^2 \Delta P$$

$$\therefore \tau = \frac{\Delta P r}{2L} \quad \dots (3.13.)$$

The shear stress at the centre of the capillary is zero and becomes a maximum at the wall. The shear rate also varies with the radius, and the mode of variation depends on the velocity distribution which, in turn, is determined by the nature of the fluid.

Since both the shear stress and shear rate vary with the radius, it is essential that the flow curve be constructed by using shear stresses and shear rates for the same point in the capillary. The most convenient location is the wall of the capillary. The shear

stress at the capillary wall is:

$$\tau_w = \Delta P R / 2L \quad \dots (3.14.)$$

The shear rate at the wall is a more difficult quantity to determine from the experimental data. For a Newtonian fluid, the shear rate at the capillary wall is given by:

$$\dot{\gamma}_w = \frac{4 Q}{\pi R^3} \quad \dots (3.15.)$$

where Q is the volumetric flow of fluid.

To obtain the true rate of shear at the capillary wall using only the assumptions listed above we have to correct that obtained for a Newtonian fluid by a factor derived by Rabinowitsch[41]. The wall shear rate for a pseudoplastic material is:

$$\dot{\gamma}_w = \frac{3n + 1}{n} \frac{Q}{\pi R^3} \quad \dots (3.16.)$$

where n is the slope of a log-log plot of τ_w vs $4Q/\pi R^3$

The transition from the reservoir or barrel of the rheometer to the capillary results in a region of convergent flow being formed which must be eliminated or accounted for, to enable the pressure drop ΔP resulting from the fully developed laminar flow in the capillary to be determined. There is also a transition region at the capillary exit which must be taken into account. It is customary to treat the "end-effects" in terms of effective capillary length $(L + \epsilon R)$, which is greater than the actual capillary length. The effective shear stress at the wall can be calculated from equation 3.10:

$$\tau_w = \frac{\Delta P R}{2(L + \epsilon R)} \quad \dots (3.17.)$$

The simplest method available for making the end corrections is to use two dies of similar radius but of different lengths. under similar conditions of volumetric flow rate and temperature. The shear stress at the wall of the first die will be:

$$\tau_w = \frac{\Delta P_1 R}{2(L_1 + \epsilon R)} \quad \dots (3.18.)$$

and for the second die:

$$\tau_w = \frac{\Delta P_2 R}{2(L_2 + \epsilon R)} \quad \dots (3.19.)$$

If we eliminate ϵ using those two equations we get

$$\tau_w = \frac{(\Delta P_1 - \Delta P_2) R}{2(L_1 - L_2)} \quad \dots (3.20.)$$

However, this two-point method does not give any indication of the compliance of the material to the general assumptions for capillary flow. The technique due to Bagley[42] is more reliable and useful in this respect, since a number of dies of similar radius but of different lengths are used. If the general assumptions are valid, plotting ΔP vs L/R gives a straight line with ϵ as intercept. However, if significant wall slip, thixotropy, or viscous dissipation effects are present, the ΔP vs. L/R plot will not conform to a straight line, indicating that the capillary rheometer is unsuitable for the material.

3.4. GEL PERMEATION CHROMATOGRAPHY

Gel permeation chromatography (GPC) is a special form of liquid chromatography. Elution is carried out on a rigid porous support, and separation is based on molecular size and shape. The smaller the

hydrodynamic volume the steeper a particle penetrates into the support. Consequently, the largest particles are eluted first.

The method was originally used to separate biopolymers in aqueous solution on cross-linked dextrane gels. The introduction of solvent-resistant support materials made it possible to fractionate synthetic polymers. Suitable products are now available to carry out separations of components in any molecular weight range. However, most of the work is presently done on systems in the molecular weight range of a few thousands to a million.

GPC is a recently developed method of fractionation(1950). It has the major advantages of providing good fractionation in a relatively short time; the data on the fractions can be collected automatically. Because of these advantages, it is now the most widely used method for the separation and isolation of high-molecular-weight fractions and for determining polymer molecular weight distributions. A vastly simplified model of the separation mechanism is that smaller polymer molecules can enter freely into all the pores of the column packing while very large molecules can enter none of these pores. Molecules of intermediate size have access to varying amounts of the available pore volume. Early work on GPC showed that synthetic polymers which were soluble in organic solvents were not so readily fractionated by GPC.

In 1962, Moore[43] reported on two major improvements on GPC: A method for producing cross-linked gels with a wide range of pore sizes, and the use of a differential refractometer for continuous

detection; many workers soon reported on extensive applications of the technique.

3.5. SOLUBILITY PARAMETERS

Probably the most useful theory of solubility is that proposed by Hildebrand[45]. This is based on the thermodynamically sound principle that the free energy change upon dissolution of a polymer in a solvent must be negative. The free energy change can be calculated from the equation:

$$\Delta F = \Delta H - T\Delta S \quad \dots (3.21.)$$

where ΔH is the enthalpy, ΔS is the entropy and T is the temperature.

A polymer molecule, because of its size and shape, does not have much freedom of translation past its neighbouring molecules; it is also so thoroughly entangled with its neighbours that the freedom of rotation and even of segmental motion is inhibited. When small solvent molecules are mixed with large polymer molecules, the latter accept a great increase in entropy. They are now more free to move about as a whole (depending on viscosity), but in addition their configurational entropy is greatly increased because the newly obtained freedom of rotation about carbon-to-carbon bonds allows a molecule to contort into many different shapes. The ΔS term in the above equation is therefore relatively large, and since the term is negative, the product of temperature time entropy tends to make the

free energy (ΔF) negative. The restricting factor therefore is the ΔH term which measures the heat of mixing.

In a mixing process, the molecules of each component are separated by the interposition of a molecule from the second component. Hildebrand reasoned that the energy of this separation (to an infinite distance) could be measured by the heat of vapourization. If the energy to separate the molecules of component A is sufficiently different from the energy required to separate the molecules of component B, each species of molecule will prefer its like neighbours and will refuse to mix with the molecules of the other component. On the other hand, if the energies required to separate these two species are relatively similar, the molecules of component A will tolerate the proximity of B molecules and vice-versa. Hildebrand, therefore, proposed that the square root of the energy, in calories per cc, required to separate the molecules of a given substance be designated as solubility parameter, " δ ".

If the solubility parameters of two substances were identical, then they would be miscible in all proportions. Because the entropy term in the free energy equation has a finite negative value, there would be an allowable difference in solubility parameters which would still permit mixing. When this theory was used to predict the solubility of polymers in a variety of solvents, it was only partially successful. It was apparent that other intermolecular forces were at work which could not be calculated by this simple procedure. Hydrogen bonding, probably the strongest type of intermolecular force in a nonelectrolyte, was the clue for making the solubility parameter

theory unsuccessful. No satisfactory method for calculating hydrogen bond interactions was available. The early application of this principle depended on the qualitative arrangement of solvents into three hydrogen bonded classes: Alcohols, acids and amines (strongly hydrogen bonded); esters, ketones and ethers (moderately hydrogen bonded); and hydrocarbons (poorly hydrogen bonded). In spite of the crudity of this procedure, the prediction of solubility based on solubility parameters within each class is 90% successful.

Because the energy of vapourization of polymers cannot be obtained without decomposition, the solubility parameter is most easily obtained by testing in solvents with different " δ " values. This procedure led to the second pragmatic extension of Hildebrand's concept. Namely, the determination of a solubility parameter range rather than a single value. By this procedure the actual values of ΔH and ΔS do not need to be known. The point at which ΔF becomes positive is determined by experimental observation of insolubility.

CHAPTER 4

EXPERIMENTAL

4.1. INTRODUCTION

The basic means chosen for the characterisation of lubricant action was the apparent viscosity versus lubricant concentration relationship at constant shear stress (Sections 4.2.1.1. and 4.2.1.5.). All the other experimental methods were directed towards explaining or validating the observed apparent viscosity versus concentration relationships.

Measurements for the influence of lubricants on the processability of a rubber compound depend to a large extent on the particular testing equipment considered. Each instrument has a different geometry that can impart a different stress history on different elements of the rubber compound tested. A capillary rheometer (Section 3.3.), although it can achieve the high shear rates encountered in some processing equipment, it has the disadvantage of subjecting the rubber compound sample to a range of shear stresses along the radius of its capillary. The shear stress profile encountered in the capillary can complicate the interpretation of the experimental observations. Also, the Mooney viscometer, which uses a disk shaped rotor (Section 3.2.), has the same disadvantage of subjecting the rubber compound sample to a range of shear stresses. The Negretti TMS biconical rotor rheometer (Section 4.2.1.) was selected as the main testing instrument for the investigation.

4.2. EQUIPMENT DEVELOPMENT AND OPERATIONAL METHODS

4.2.1. The Negretti TMS Rheometer

The Negretti TMS biconical rotor rheometer (Figure 4.1.) has the following features which made it particularly appropriate for the investigation.

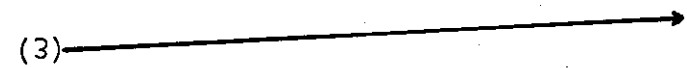
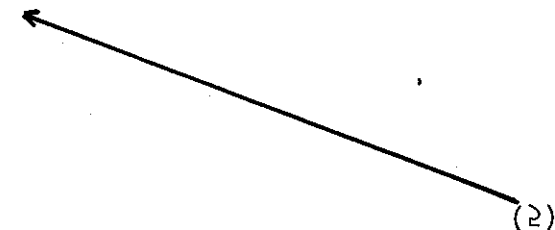
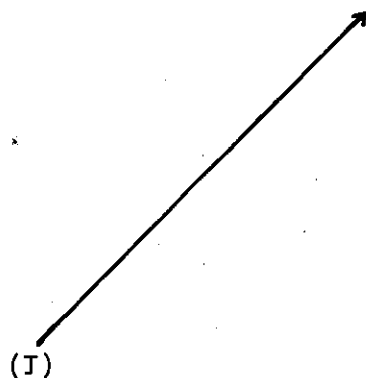
4.2.1.1. The Biconical Rotors

A biconical rotor rheometer (Section 3.2.), has the advantage of imparting an approximately constant shear stress throughout the test sample.

During the research both smooth and grooved rotors were used with the TMS rheometer. The two rotors had similar dimensions (Figure 4.2.) and were made from the same metal (EN8). Substituting the dimensions given in Figure 4.3. into equation 3.2. (Section 3.2.), the shear rate ($\dot{\gamma}$ 1/sec) was found to be equal to the rotor speed (rev/min). From equation 3.8. (Section 3.2.), the relation between the shear stress (τ KPa) and the measured torque (T N.m) was calculated (Appendix A) and found to be:

$$\tau \text{ (KPa)} = 17.87 \times T \text{ (N.m)} \quad \dots (4.1.)$$

The smooth rotor was used in conjunction with the grooved rotor to detect the occurrence of wall slip at the rubber metal interface (Section 3.2.). The grooves on the surface of the grooved rotor (Figure 4.2.) were assumed to inhibit the development of the thin



2) The neglected MPCOT

4) B&W

3) Rubber gis

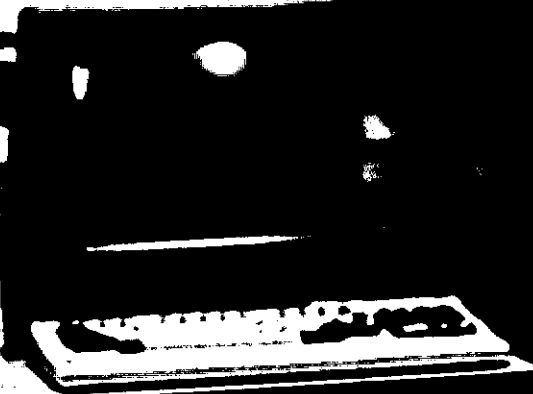
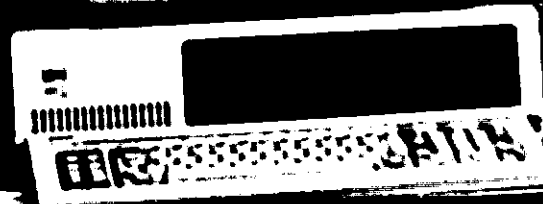
5) ADU terminal for the MPCOT

1) The IBM PC

FIGURE 1-1: The neglected LMS Rheometer.



TMS Rheometer



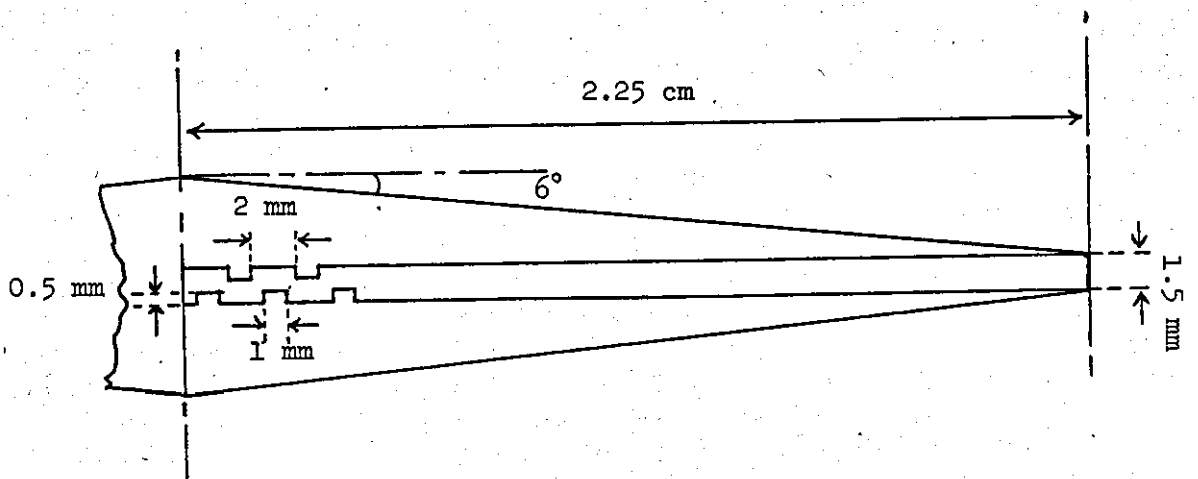


Figure 4.2 : Dimensions for TMS rheometer rotor.

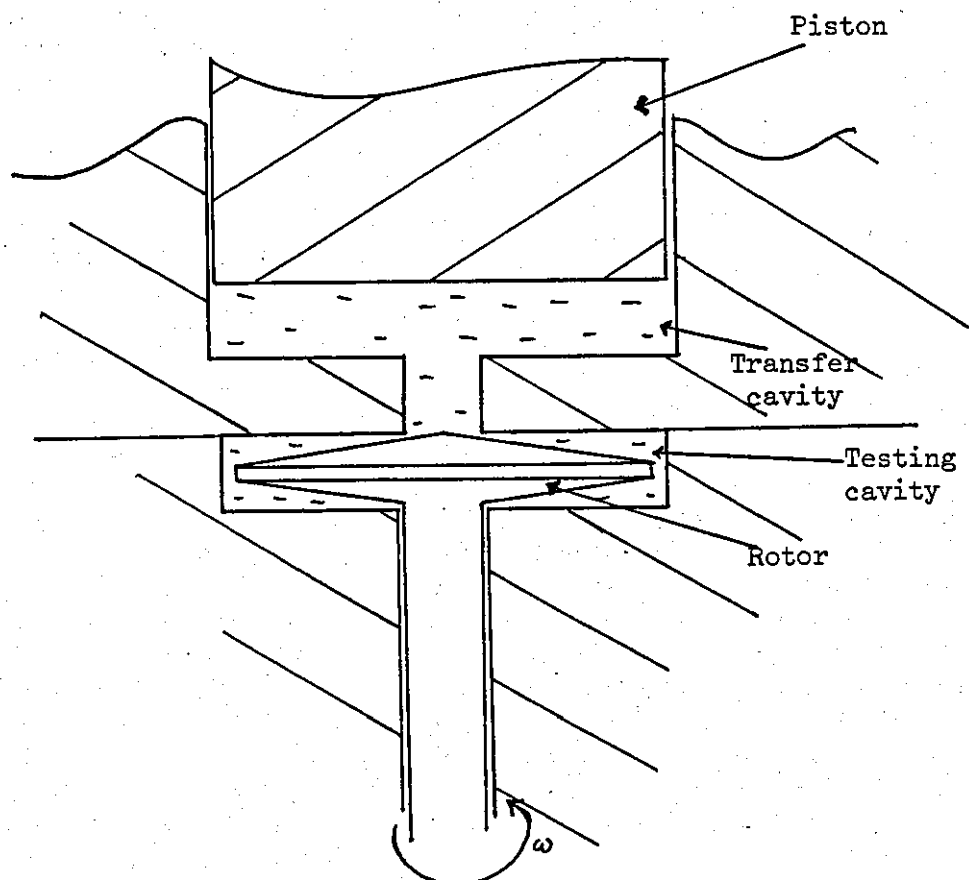


Figure 4.3 : Diagram for TMS biconical rotor rheometer.

lubricating film at the rubber metal surface that might occur in the presence of an external lubricant.

4.2.1.2. The Transfer Cavity Filling

The Negretti TMS rheometer uses a transfer cavity filling method (Figure 4.3.). Using this arrangement the sample which is placed in the transfer cavity can be heated up to a uniform, predetermined mixed temperature before being injected into the test cavity. This has the following advantages over the compression molding filling method used in the Mooney viscometer (Section 3.2.):

- 1) The rubber in contact with the rotor has a freshly generated surface, compared with the compression molded surface of the sample in a Mooney viscometer. The effects of surface oxidation and contamination of the sample to be tested can be eliminated.
- 2) The closed cavity and transfer cylinder arrangement permits a precise control of hydrostatic pressure, which can be altered by changing the air pressure controlling the ram. With the Mooney viscometer the amount of sample put in the cavity influences the pressure.
- 3) Having the test cavity shot prior to filling gives a "flashless" molding of the test sample. With the compression molding technique used with the Mooney viscometer, "Open Flash" is bound to occur if we are to be sure that the testing cavity was filled. The flashless molding ensures that the clearance between the cavity and rotor is constant from test to test.

4.2.1.3. The Negretti MPC 84:

The Negretti TMS rheometer is controlled by a programmable controller, the Negretti MPC 84 (Figure 4.1.). The MPC 84 controller is a flexible process control system which can be configured to control complex systems with up to eight control loops and sixteen simultaneous sequence programs. Continuous control schemes can be programmed using the Negretti developed interpretive language "SENZTROL". In our case, the MPC 84 was configured to control the following functions:

- 1) The temperatures of the ram, upper die and lower die (Figure 4.1.).
- 2) The opening and closing of the dies.
- 3) The raising and lowering of the ram.
- 4) A switch for changing the pneumatic pressure applied to the ram between two adjustable valves.
- 5) The opening and closing of the safety window (Figure 4.1.).
- 6) The speed of the stopper motor driving the rotor (to any value between 0.1 rev/min and 100 rev/min, ie. from 0.1 to 100 1/sec shear rate).

The sampling period of each sequence program can be adjusted to any value between 0.1 sec and 25 sec, to give priority to important tasks. The sampling time of a control block can be adjusted between 0.5 sec and 25 sec, making the MPC 84 a very slow controller. Another disadvantage of the MPC 84 is that its Random Access Memory (RAM) is only 16K for Database and sequence editing and is, therefore very limited for the storage of the collected data.

4.2.1.4. The IBM PC Interface

In order to overcome the limitations of the MPC 84, the controller was connected via an interface to an IBM Personal Computer "XT". The results obtained from the TMS rheometer were transferred to the IBM PC where they were collected and stored in a file on a floppy disk.

4.2.1.5. The Software:

Using the TMS rheometer in conjunction with the MPC 84 and the IBM PC, an experimental routine was needed in order to observe the effect of increasing amounts of lubricants on the rheological properties of an elastomer compound. This could be done via three different routes:

- 1) A set of shear rates ($\dot{\gamma}$) could be applied on the elastomer sample and their corresponding shear stresses ($\bar{\tau}$) measured. Dividing the shear stress by the shear rate would give the apparent viscosity (η_a) (Eq. 3.1.) of the test sample.
- 1i) A set of shear stresses ($\bar{\tau}$) could be applied on the test sample and their corresponding shear rates ($\dot{\gamma}$) measured. The apparent viscosity (η_a) could then be calculated using equation 3.1.
- 1ii) The test sample could be stressed to a certain level and after stopping the rotor, the time it takes for the shear stress value to drop to $\chi\%$ of its original value could then be measured. (Stress Relaxation).

It is essential, for comparison purposes, that the stress history of each of the elastomer samples containing different levels of lubricants is the same. In the first case, levels of shear rates

applied on elastomer samples with different rheological properties will generate different levels of shear stresses from sample to sample. This will make each sample's stress history different from the rest. This will also occur with the same sample when tested with smooth and grooved rotors. If wall slip is occurring on the surface of the smooth rotor, the shear stress measured will be much lower than that measured with the grooved rotor (which is supposed to inhibit wall slip). For this reason, it was found more logical to apply a set of shear stresses and measure their corresponding shear rates to provide apparent viscosities that can be compared from sample to sample.

Using the Negretti TMS rheometer with the MPC 84 and the IBM PC, a set of three interactive programs was developed to control the rheometer to do the three types of experimental routines described earlier.

Program 1

The program named "TESTER" (Appendix B) was developed to apply a predetermined set of shear rates on an elastomer sample and collect a set of corresponding shear stresses. From the IBM PC, TESTER uses one of the sequences (Appendix C) in the MPC 84 controller and operates as follows:

When called TESTER shows the following menu:

- A) Create a new file
- B) Run the newly created file
- C) Run an old existing file
- D) Run the newly created file on the same sample

- E) Run an old existing file on the same sample
- F) Printout a result file
- G) Escape

i) Setting the test conditions:

Option 'A' on the menu opens a sequential file on a floppy disk in which all the details of the new experiment would be stored. The program starts by asking for the reference name of the new file. Then, it asks for the temperature required for the experiment and the time needed to preheat the sample. Then, it asks for the number of steps required to be programmed. Finally, it asks for the details of those steps to be entered. Each step consists of a shear rate and the time for which it would be applied.

ii) The filling procedure:

To start the filling of the test cavity (Fig 4.4) with the test sample, options 'B' or 'C' in the menu could be chosen. In all cases the filling procedure is standard except for the sample's temperature and preheat time which could be altered from one experiment to another.

If option 'B' is pressed, the test conditions entered into the sequential file created using option 'A' will be loaded onto the MCP84 controller. This in turn will control the temperatures of the ram and the upper and lower dies (Fig 4.1) to the required value. When this is done, the IBM PC will produce a message on its VDU asking the operator to fill the transfer cavity with the test sample, to depress the rotor to activate a switch to ensure that the rotor is in its

correct position before the filling procedure is started and finally to stay away from the safety window and press the space bar. When that is done, the following steps will be carried out:

- The protective window will shut
- The dies will close-up
- The ram will be positioned on the test sample
- The preheat timing will start
- At the end of the preheat time, the hydrostatic pressure in the ram will switch to 85 psi
- The rotor speed will be set to 0.5 rev/min clockwise
- The stepper motor will be switched on
- After 30 seconds, the motor will be switched off
- The pressure applied by the ram will switch back to 45 psi
- After allowing 10 seconds for the air entrapped in the testing cavity to escape, the rotor speed will be set to 0.5 rev/min anticlockwise
- The stepper motor will be switched on again
- After 30 seconds, the motor will be switched off
- After 10 seconds, the rotor speed will be set to 0.5 rev/min clockwise
- The pressure applied by the ram will switch to 85 psi
- The stepper motor will be switched on
- The torque applied by the rotor will be measured after intervals of 20 seconds.
- The latest torque value will be checked against the previous one

- If the latest value is smaller or equal to the previous one, the motor will be switched off
- The hydrostatic pressure in the ram will switch back to 45 psi, thus completing the filling routine.

iii) The testing procedure

Ten seconds after the filling procedure is completed, the testing procedure can be carried out. The pre-programmed shear rates can be implemented one after the other for pre-programmed times. The first eighteen results will be collected at intervals of 0.1 sec. The rest of the results will be collected at various time intervals depending on the sampling speed of the controller. The results are obtained in shear stress values (kPa) and recorded, together with the time on a sequential file on a floppy disk. At the end of the experiment the result will be closed and the menu displayed.

iv) Printout of results

To printout the results stored on a floppy disk, option "F" from the menu should be pressed. The program will ask whether the operator wanted the results displayed on the monitor or not. Three different printout formats are available:

- 1) To printout the last ten shear stresses obtained for each shear rate applied. These can be averaged to give the shear rate versus shear stress relationship.
- 2) To printout selectively some of the results of each shear rate.
- 3) To printout the whole result file.

Program 2

The program named "SLIPPER" (Appendix D) has basically the same structure as TESTER. It was developed in order to apply a predetermined set of shear stresses on an elastomer sample and to collect a set of corresponding shear rates.

SLIPPER has the same filling procedure as TESTER. When running, the pre-programmed shear stresses will be transferred from the IBM PC to the MPC 84 where they will be used as set values for one of the MPC 84 inbuilt three term PID control loops. The output is controlled from the change of error to give an incremental proportional action, with an integral action added to gain zero error steady-state, plus a derivative term from the change of input rate to give stability. In order to control the whole range of rotor speeds available (see Section 4.2.1.3.), two sets of proportional, integral and derivative gain terms were needed. The output from the control loop will then be implemented on the stepper motor to give the right shear rate needed to create the preset shear stresses.

Having the control loop set to its fastest sampling speed of 0.5 secs, another 0.5 sec was needed to implement the output term on the TMS making the overall sampling time of the order of 1 sec. This is a very slow sampling time and the response time to attain equilibrium was found to be of the order of two minutes, depending on the level of shear stress required and on the elastomer compound. The results obtained were collected as shear rates (1/sec) with their corresponding offsets from the setpoint (shear stress error). This was found to help the operator to check whether the required shear

stress is reached and whether we have control or not. Having stored the results on a floppy disk, they can be retrieved and printed out later on. The printout routine in SLIPPER is similar to that in TESTER where the results can be printed out in three formats. The results are printed out as shear rates with their corresponding shear stress errors.

Program 3

SLIPPER had to receive minor alterations in order to give the time at which each result was taken. This is essential in order to allow a stress relaxation experiment to be carried out.

For this type of experiments, two steps are needed to be programmed into the routine. the first step stresses the test sample to a predetermined value. The second step stops the stepper motor and measures the decline in shear stress with time. The results obtained are collected and can be printed out later on as shear stress versus and time of measurement.

4.2.2. The Davenport Capillary Rheometer

4.2.2.1. Instrument's Details

The Davenport capillary rheometer was used in conjunction with two dies of similar diameters (2mm) and different lengths (10mm and 20 mm). The diameter of the barrel (Figure 4.4.) is 19mm. The pressure in the barrel is measured using a pressure transducer and the data is collected on a chart recorder. The speed of the ram can be varied manually.

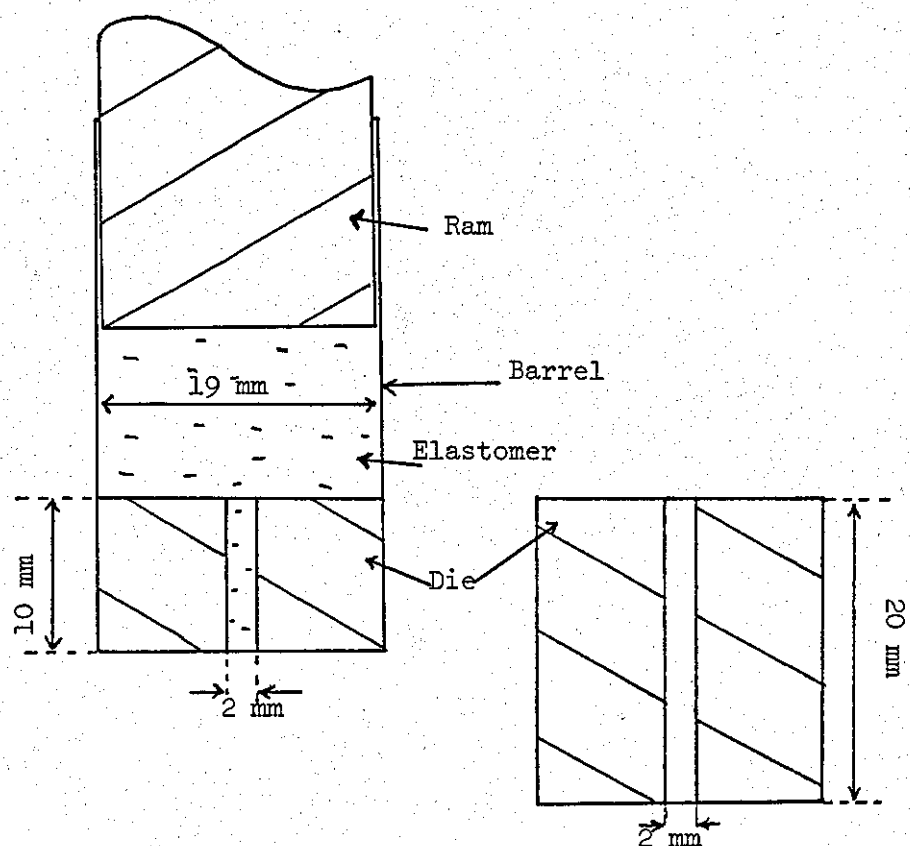


Figure 4.4 : Dimensions of Davenport capillary rheometer.

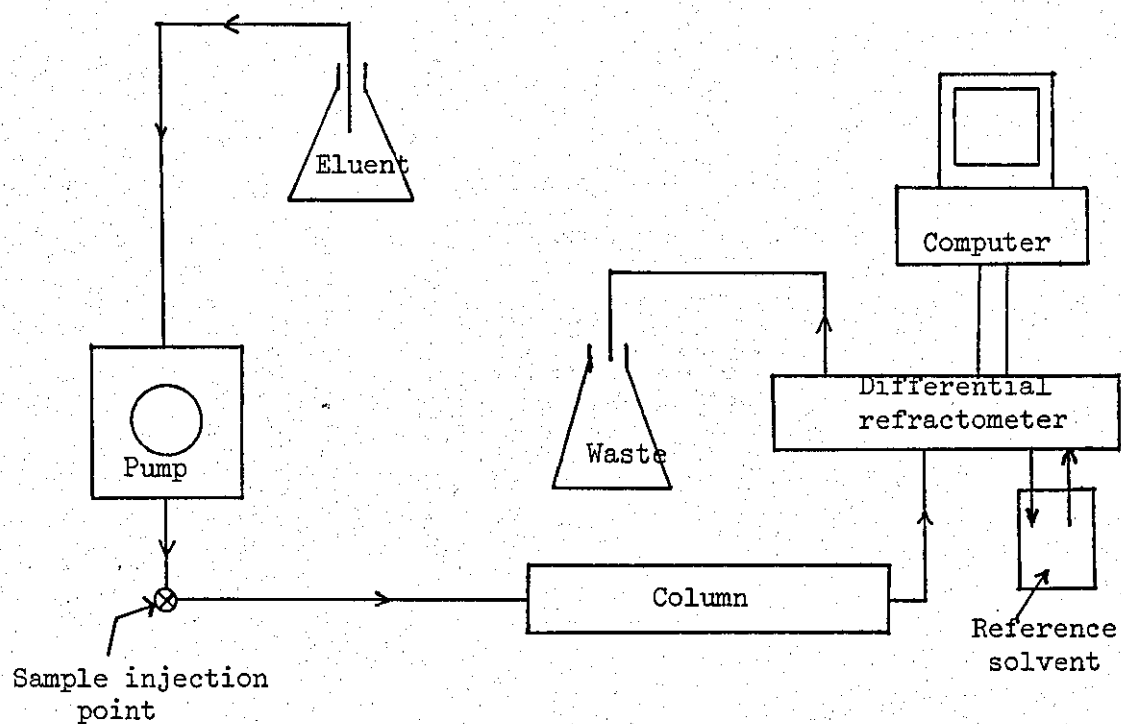


Figure 4.5 : Diagram of Gel Permeation Chromatography equipment.

4.2.2.2. Testing Procedures

The elastomer compound should be placed into the barrel of the rheometer and heated up to the required temperature for five minutes. Then, a set of ram speeds can be applied on the sample and the resulting pressure in the barrel recorded. Finally, the same procedure should be repeated with the second die using the same set of ram speeds.

The ram speed was translated into flow rates (Q mm³/sec) using the following equation:

$$Q = V \times \pi \times R^2 \quad \dots (4.2.)$$

where V is the ram speed (mm/sec)

R is the radius of the barrel (mm)

Equation 3.20. of Section 3.3. which allows for the correction due to the transition regions at the entry and exit of the capillary, was used to calculate the shear stress at the capillary wall (τ_w KPa). The Rabinowitsch correction (Eq. 3.16.) was then implemented in order to calculate the true shear rates at the capillary wall ($\dot{\gamma}_w$ 1/sec). (Appendix E, for sample calculation).

4.2.3. The Gel Permeation Chromatography Equipment

Gel permeation chromatography (GPC) equipment, supplied by Polymer Labs Ltd., was used in this study to monitor the change in the molecular weight distribution of the elastomer due to the presence of the lubricant. The equipment set-up is illustrated in Figure 4.5. The pump is a Knauer HPLC PUMP 64 and the column is a PL gel (Polymer

Laboratories) column containing highly cross-linked Poly (styrene/divinylbenzene) macroporous particles of particle size equal to 5 μ m. Its internal diameter is 7.5mm and length 30cm. The detection equipment is a Knauer Differential Refractometer and results are collected by a BBC microcomputer (64K).

To run the experiment, the operator has to dissolve the sample in tetrahydrofuran (THF) (~ 1mg of elastomer in 5ml of THF). After complete dissolution, a small sample should be injected through the injection point (Figure 4.5.) into the column. At the same instant a button on the microcomputer should be pressed to start the timing and data collection mechanisms. This has to be done very accurately in order to obtain an accurate molecular weight distribution, since the molecular weight of a sample is related to the time it takes to travel through the gel column (Section 3.4.). The sample is then washed through the column by the eluant (THF). A change in the refractive index of the eluant due to the presence of a foreign material will then be picked-up by the differential refractometer and the data collected, analysed, stored and plotted by the microcomputer.

4.2.4. The Swelling Test

A swelling test was developed for the purpose of checking on the entanglement and cross-link density changes due to the presence of a lubricant in the elastomer. A relatively weak solvent was chosen to swell the elastomer without dissolving it completely.

The swelling test was carried out on EPDM with different concentrations of lubricants. The solvent used for this purpose was 1-1-2-2-Tetrachloroethane. A small sample of the order of 50mg was immersed for a considerable period of time (~ 48 hours) in the solvent at room temperature. After taking the sample out of the solvent and drying it carefully with a tissue, the percent change in the weight of the sample was measured.

The immersion of the sample for a long period of time in the solvent was done to ensure that the diffusion of the solvent into the sample had reached equilibrium. Other sources of error still exist though. These are:

- i) The sample on which the test is carried out may not represent the state of the bulk elastomer.
- ii) The possibility of sample porosity.
- iii) The time it takes to measure the weight of the swelled sample can be critical. The solvent entrapped into the elastomer will evaporate at room-temperature while the sample is being weighed.

4.2.5. The Solubility Parameter Measurement

It has already been stated in Section 3.5. that the square root of the energy per unit volume required to separate the molecules of a given substance was designated by Hildebrand[44] as the solubility parameter, " δ ".

$$\delta = \left(\frac{\Delta E}{V} \right)^{1/2} = \left(\frac{\Delta H - RT}{M/D} \right)^{1/2} \quad \dots (4.3.)$$

where δ is the solubility parameter

ΔE is the energy of vapourisation

V is the molar volume

ΔH is the latent heat of vapourisation

R is the gas constant

T is the temperature

M is the molecular weight

D is the density.

Because we are dealing with a range of materials that might decompose before their energy of vapourisation was obtained, a practical method for determining the solubility parameter range was proposed in Section 3.5. The solubility parameter range was obtained by testing the compound in different solvents of known solubility parameters (δ). The solubility parameter range of the compound would then be that of the solvents that partially or totally dissolved the compound. The technique was very simple but effective. The accuracy of the solubility parameter range depended on the number of solvents used.

4.3. SAMPLE PREPARATION

In order to study the effect of lubricants on the rheological properties of elastomer compounds, it was necessary to ensure that the differences in behaviour observed during our experiments were due to the lubricant's action and not to different preparation techniques. Factors such as mastication, stress history and uniformity of

dispersion could affect the results and this was taken into consideration during the preparation and mixing of the various samples.

4.3.1. Materials Used:

4.3.1.1. Elastomers:

Natural rubber (SMR 20 & 10) and chlorosulphonated polyethylene (Hypalon 40) were first chosen to be the two main systems in which the effect of the lubricants were to be studied. Natural rubber is non-polar, it has unsaturated bonds, its rheological properties change with mastication, it is prone to oxidation and it is compatible with a large range of process oils and materials. On the other hand, chlorosulphonated polyethylene is polar, it has saturated chain bonds, it is resistant to mastication and oxidation and is poorly compatible with most process oils. Other elastomers were also used when it was realised that those differences were not necessarily the ones that would give the information needed for this study. Ethylene propylene terpolymer (EPDM) and polyisobutylene (Vistanex) of four different average molecular weights (Table 4.1.) were also used.

Grade	Flory Molecular Weight
LM - MS - LC	42600 to 46100
LM - MH - LC	50400 to 55800
MM - L - 80	750000 to 1050000
MM - L - 100	1060000 to 1440000

Table 4.1.: Polyisobutylene grades used in this study
supplied by Exxon Chemicals Ltd.

The molecular weight distribution curves for the two grades of Vistanex LM - MS - LC (Figure 7.28.) and LM - MH - LC (Figure 7.29.) were obtained using the GPC equipment (see Section 4.2.3.).

4.3.1.2. Lubricants

Most of the observations made during this study were made using three commercially available lubricants of fatty acid origin:

- 1) Struktol WB212 (m.p. 50 to 60°C)*: Emulsion, with constant water content, of high molecular fatty acid esters and condensation products, bound to chemically indifferent fillers.
- 2) Struktol WB16 (m.p. 97 to 107°C)*: Mixture of fatty acid soaps, predominantly calcium.
- 3) Struktol A50P (m.p. 100 to 105°C)*: Zinc soaps of unsaturated fatty acids.

* Melting points supplied by Schill and Seilacher (U.K.) Ltd.

Also, some pure fatty acid derivatives were used as lubricants. These were:

- 1) Sodium oleate: $\text{CH}_3 (\text{CH}_2)_7 \text{CH} = \text{CH} (\text{CH}_2)_7 \text{CO}_2 \text{Na}$, m. p. = 235°C
- 2) Zinc Hexanoate: $[\text{CH}_3 (\text{CH}_2)_4 \text{CO}_2]_2 \text{Zn}$, m. p. = 144.9°C
- 3) Zinc Decanoate: $[\text{CH}_3 (\text{CH}_2)_8 \text{CO}_2]_2 \text{Zn}$, m. p. = 136.9°C
- 4) Zinc Stearate: $[\text{CH}_3 (\text{CH}_2)_{16} \text{CO}_2]_2 \text{Zn}$, m. p. = 132.6°C

4.3.2. Mixing Equipment

The following equipment was used for the mixing of the elastomer compounds tested during this study:

- 1) Farrel Bridge BR Banbury internal mixer having two-wing rotors and a mixing chamber volume of 1.57 litres.
- 2) Bridge (300mm x 150mm) two-roll mill.
- 3) Brabender Plastograph having Banbury type two-wing rotors and a mixing chamber volume of ~ 25ml.

4.3.3. Elastomer Compounds

In this study, the effect of lubricants was observed on pure elastomers and on some elastomer compounds.

The elastomer compounds used had the following compositions:

- i) Compound 1: 100 phr natural rubber (SMR 20), 60 phr carbon black ISAF (N220), 10 phr process oil (Dutrek 729), 2 phr Stearic acid, 3 phr zinc oxide, 0.5 phr Nonox ZA, 1 phr paraffin wax.
- ii) Compound 2: 100 phr chlorosulphonated polyethylene (Hypalon 40), 80 phr carbon black SRF-HM (N770) and 20 phr process oil (Dutrek 729).
- iii) Compound 3: 100 phr natural rubber (SMR 10), 60 phr carbon black HAF (N330), 2 phr stearic acid, 0.5 phr Permanax TPPD, 1 phr paraffin wax, 10 phr process oil (Dutrek 729) and 2.5 phr sulphur.

4.3.4. Mixing Techniques and Conditions

4.3.4.1. Raw Elastomer Samples:

For raw elastomer samples, mixing was used to incorporate different levels of lubricants into the raw elastomer. Two techniques were used for this purpose:

- i) The Brabender Plastograph was used at two temperature (100 and 150°C). The rotor speed was set to 55 rev/min. The mixing time was 2 minutes.
- ii) After sheeting the raw elastomer on the two-roll mill different levels of lubricants were incorporated. The temperature was set to 100°C.

4.3.4.2. Elastomer Compound Sample:

The elastomer compound samples were prepared either by mixing the elastomer compound components as a first stage followed by the incorporation of different levels of lubricants or by mixing two batches of the elastomer compound, one of them containing the highest level of lubricants, then, intermixing the two batches to give samples of different lubricant concentrations.

The basic elastomer compounds were mixed in the following way:

- 1) Compound 1 was mixed in the Banbury internal mixer. The rotor speed was 45 rev/min, the temperature was set to 40°C and the fill factor was 0.7. The mixing procedure is described in Table 4.2.

Material	Addition Time (min)
SMR 20 and Zinc Oxide	0
Half the carbon black, Stearic acid, Nonox ZA and the paraffin wax	2
Rest of carbon black and process oil	4
(Batch dumped)	6

Table 4.2. Mixing Procedure for Compound 1

- ii) Compound 2 was also mixed in the Banbury internal mixer. The rotor speed was 60 rev/min, the temperature was 60°C and the fill factor was 0.7. The mixing procedure is described in Table 4.3.

Material	Addition Time
Carbon black and process oil	0
Hypalon 40	1
(Batch dumped)	4

Table 4.3. Mixing Procedure for Compound 2

- iii) Compound 3 was prepared in the internal mixer. The rotor speed was 45 rev/min, the temperature was controlled at 40°C and the fill factor was 0.7. The mixing procedure is described in Table 4.4.

Material	Addition Time
SMR 10 and Zinc Oxide	0
Half the carbon black, Stearic acid, Permonax TPPD and paraffin wax	2
The rest of the carbon black, process oil and sulphur	4

Table 4.4. Mixing Procedure for Compound 3

4.3.5. Sample Conditioning

After mixing, the samples were usually left for at least 24 hours before testing for rheological properties in the TMS rheometer. This was found to be essential for the consistency and relevance of the results. Experiments carried out on polyisobutylene after mixing and before the elapse of the relaxation period gave a large scatter in the results obtained.

4.4. TMS RHEOMETER EXPERIMENT DETAILS AND CONDITIONS

4.4.1. Shear Rate Controlled TMS Rheometer Experiments

The software "TESTER" (Section 4.2.1.5.) was used frequently during this research in order to obtain a shear rate versus shear stress relationship. A set of preprogrammed shear rates was applied on a sample which was first preheated for a standard 4 minute period to the required temperature and injected into the testing cavity.

A typical plot of the shear stress versus time relationship when a higher level of constant shear rate was applied on an elastomer compound sample was found to have the features presented in Figure 4.6.

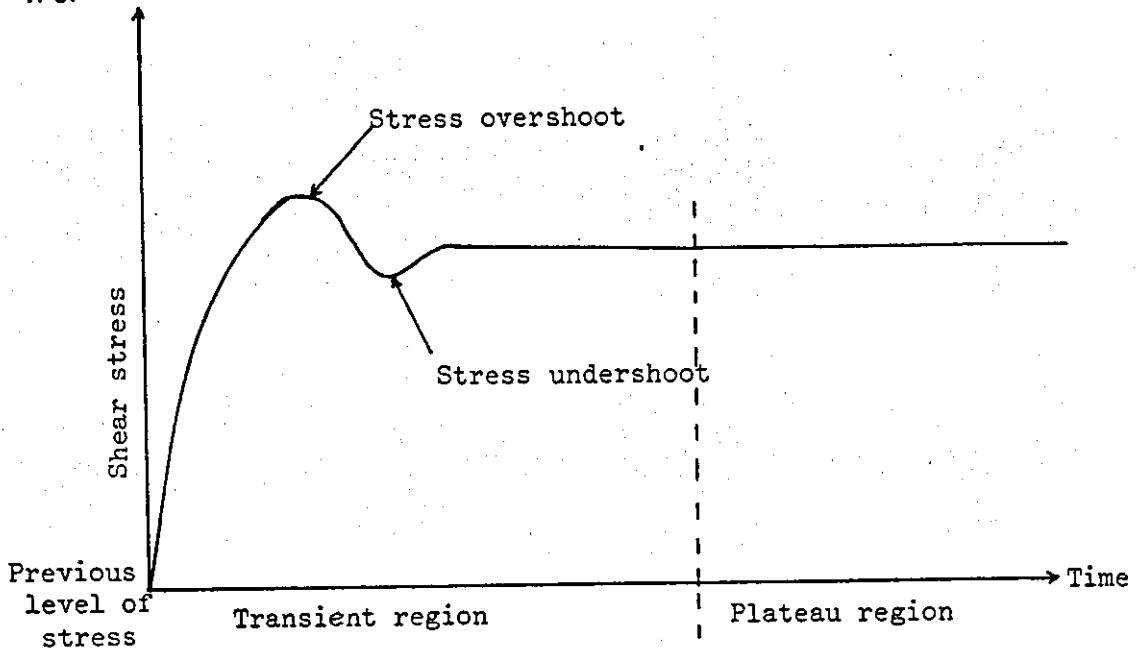


Figure 4.6: Shear stress observed when a higher level of shear rate is applied by the TMS rheometer.

Figure 4.6. Shear stress observed when a higher level of shear rate is applied by the TMS Rheometer

In the transient region, a stress overshoot was sometimes observed depending on the level of change in the applied shear rate and on the type of elastomer compound used. A stress undershoot was more difficult to observe and in some cases did not occur. In the plateau region of the curve, a levelling in the measured shear stress was sometimes obtained. It was noted that at high levels of shear rates (> 10 1/sec depending on the elastomer compound), the plateau in Figure 4.6. tended to have a negative slope. The measured shear stress was decreasing with time due mainly to two reasons:

- i) Shear heating: This would be noticeable if no adequate means of dispensing of it were available.
- ii) Mastication: This would occur to different degrees depending on the elastomer.

Each shear rate level was applied for a period of time long enough to reach the plateau stage. The corresponding shear stress was obtained from the average of the last ten shear stress measurements obtained at each applied shear rate.

4.4.2. Shear Stress Controlled TMS Rheometer Experiments

The software "SLIPPER" (Section 4.2.1.5.) was used during this research where a set of constant shear stresses can be applied on the tested sample. The advantages of this technique were discussed in Section 4.2.1.5.

In order to apply a set of shear stresses on a sample without exceeding the mechanical limits of the TMS rheometer ($0.1 \text{ 1/sec} < \text{Shear rate} < 100 \text{ 1/sec}$), TESTER was used to do a preliminary experiment in order to get an idea about the shear rate versus shear stress relationship in that particular sample.

After preheating the sample to the required temperature for a standard 4 minute period, the sample was injected into the testing cavity and each shear stress was applied on it for 2 minutes. The corresponding shear rates were obtained from the average of the last ten results collected.

CHAPTER 5

EXPERIMENTAL RESULTS PART 1:

DETERMINATION OF LUBRICANT ACTION

5.1. INITIAL EVALUATION OF LUBRICANT ACTION

With the intention of characterising the effects of commercially available lubricants on compounds typical of those used in the rubber industry, three commercially available lubricants (Struktol WB16, WB212 and A50P) were incorporated in a natural rubber compound, at different levels of lubricant concentrations. The first set of results was obtained on the natural rubber compound, (compound 1 (Section 4.3.3.)) after mixing in the manner described in Section 4.3.4.2. and having incorporated different levels of Struktol WB16 (0, 0.25, 0.75, 1.5 and 4 phr lubricant) on the two-roll mill at 100°C. The software used for the experiment was TESTER (Section 4.4.1.). A set of shear rates (0.4, 1, 2, 4, 10, 20, 40 and 100 1/sec) was applied on the sample. The smooth rotor was used for the experiment and the temperature of the experiment was set at 100°C.

Having obtained the shear stress versus shear rate relationship of each of the five lubricant concentration mixes, the apparent viscosity (Eq. 2.2.) versus lubricant concentration at constant shear rates curves were then plotted in Figure 5.1. The curves show the apparent viscosity of the natural rubber compound decreasing exponentially from its original value with lubricant concentrations of 0.25 and 0.75 phr. An unexpected increase in the apparent viscosity was then observed at

FIGURE 5.1: Apparent viscosity versus lubricant concentration for STRUKTOL WB16 In compounded Natural Rubber (Section 5.1)

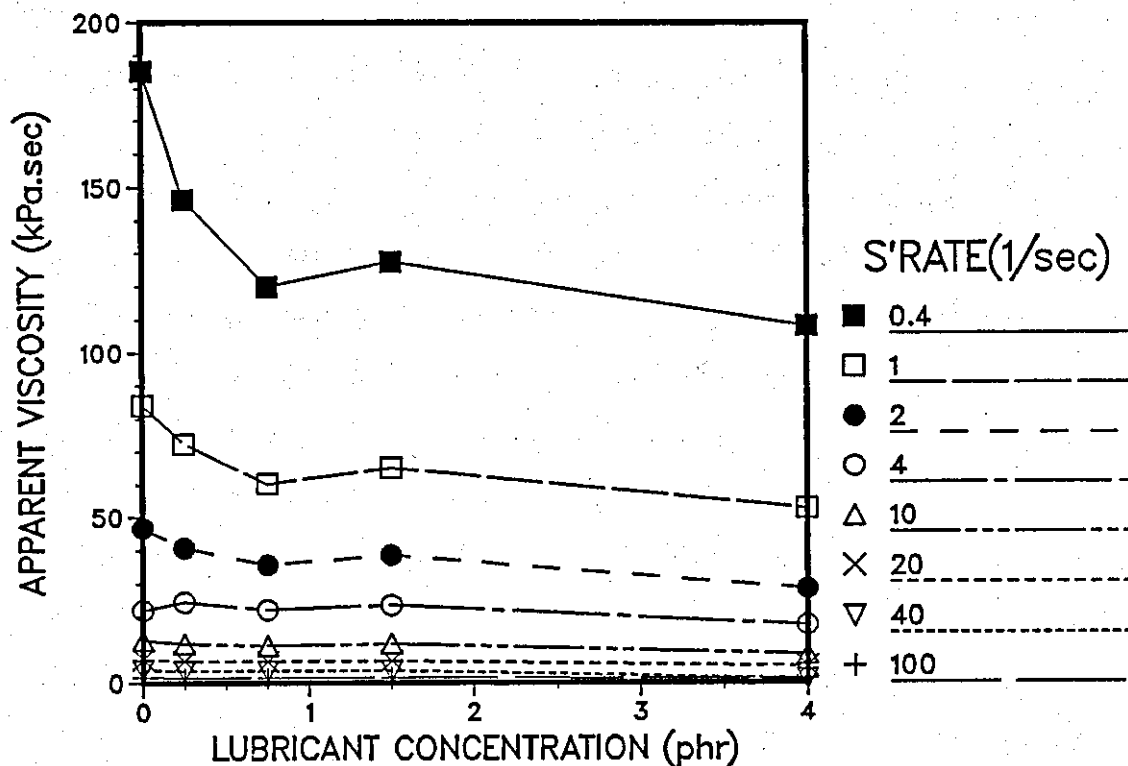
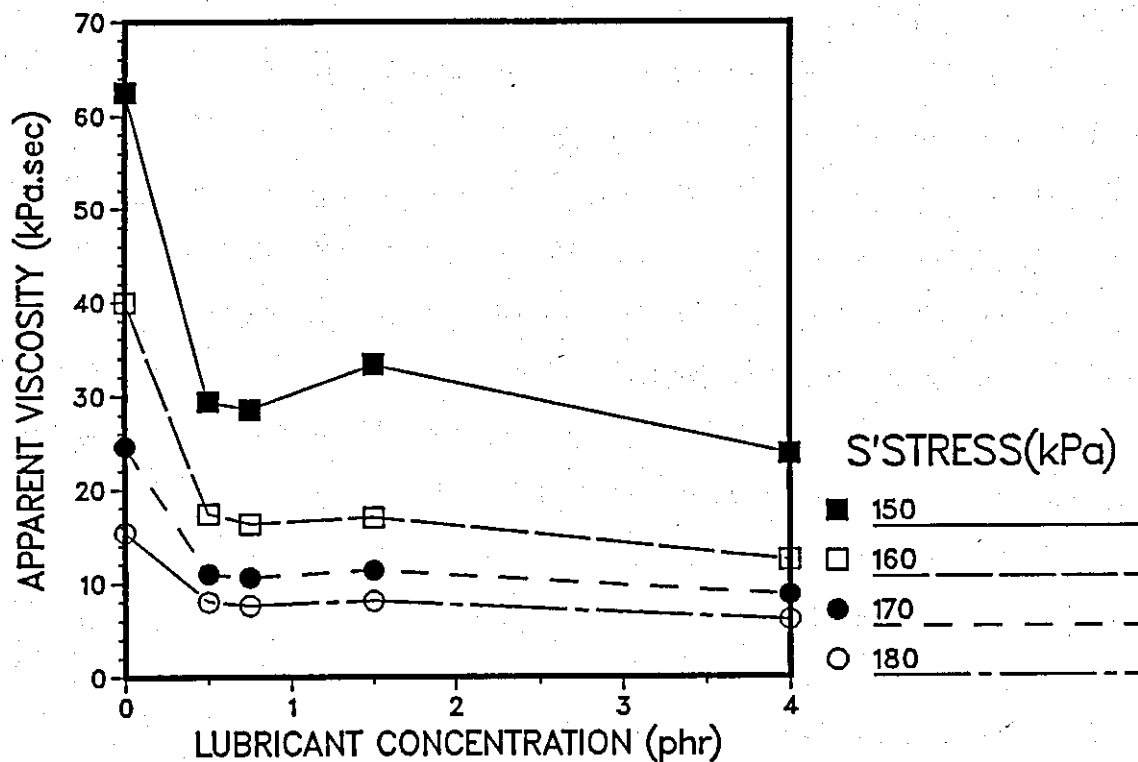


FIGURE 5.2: Apparent viscosity versus lubricant concentration for STRUKTOL WB16 In compounded Natural Rubber (Section 5.2).



1.5 phr lubricant, followed by a further decrease at 4 phr. This was consistently observed in most of the shear rate levels looked at.

It was considered that the results at 1.5 phr lubricant could be due to inconsistency in mixing on rheological measurement. Replicated measurements showed that any inconsistency lays with the mixing treatment.

5.2. EXAMINATION OF THE INFLUENCE OF MIXING TECHNIQUES ON EXPERIMENTAL RESULTS

Being satisfied that the results observed in Figure 5.1. were not due to some measuring inconsistency, another sample was prepared using a different mixing technique from the previous one. In this case, two batches of the natural rubber compound, (compound 1 (Section 4.3.3.)), were prepared in the manner described in Section 4.3.4.2. The second batch was mixed with 4 phr lubricant, Struktol WB16, added in the final stage of mixing. The two batches were then intermixed in the Banbury internal mixer for one and a half minutes to give batches with different lubricant concentrations (0, 0.5, 0.75, 1.5 and 4 phr lubricant). The blending conditions in the Banbury mixer were the same as those used for mixing the natural rubber compound (Section 4.3.4.2.(1)). This was done in order to make sure that the mixing technique was not responsible for the trends observed in Figure 5.1.

The apparent viscosity versus lubricant concentration relationship at constant shear stress values plotted in Figure 5.2. was obtained from the TMS rheometer at 100°C with the SLIPPER software (Section

4.4.2.) and the smooth rotor. In order to check the accuracy of the readings, a set of seven experiments was carried out on the sample containing 0.5 phr lubricant. The percent error was then calculated (Appendix F) showing that the error in the reported viscosities was of the order of $\pm 11\%$.

The plots in Figure 5.2. show the same trends as those observed in the previous experiment. At 0.5 and 0.75 phr lubricant the apparent viscosity was decreasing with increasing lubricant concentrations, but at 1.5 phr lubricant an increase in the apparent viscosity was observed, followed by another decrease at 4 phr lubricant.

Having established that the unexpected apparent viscosity increase at 1.5 phr lubricant concentration was not due to a measurement inconsistency or to some factor related to the mixing technique or to whether we used constant shear rate or constant shear stress for our measurements, it became apparent that the lubricant Struktol WB16 was responsible for the increase in the apparent viscosity at 1.5 phr lubricant, even though the mechanism was not yet understood.

The other features of the results plotted in Figure 5.2. can be seen more clearly by plotting the percent decrease in the apparent viscosity due to the addition of Struktol WB16 (Figure 5.3.). The percent decrease in apparent viscosity was calculated using the following equation:

$$\% \text{ decrease} = \frac{\eta_a(\text{at } 0 \text{ phr lubricant}) - \eta_a(\text{at } x \text{ phr lubricant})}{\eta_a(0 \text{ phr lubricant})} \dots (5.1.)$$

FIGURE 5.3: %Decrease in apparent viscosity versus lubricant concentration for STRUKTOL WB16 In compounded Natural Rubber (Section 5.2)

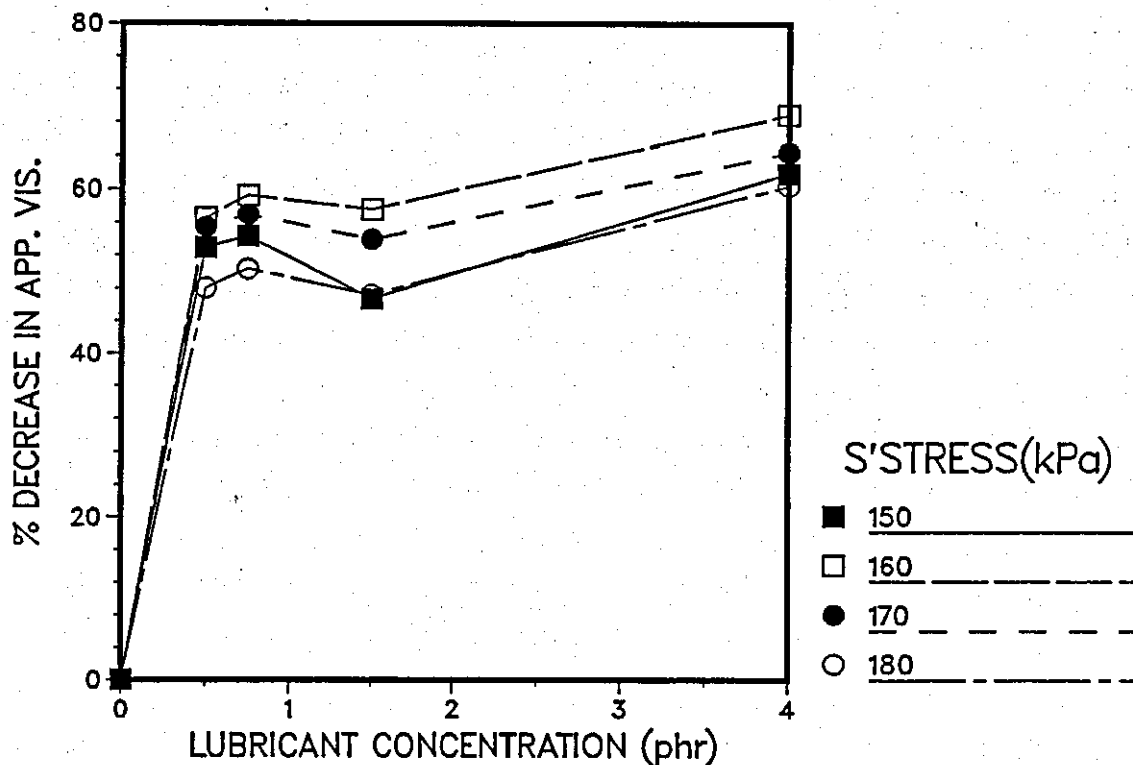
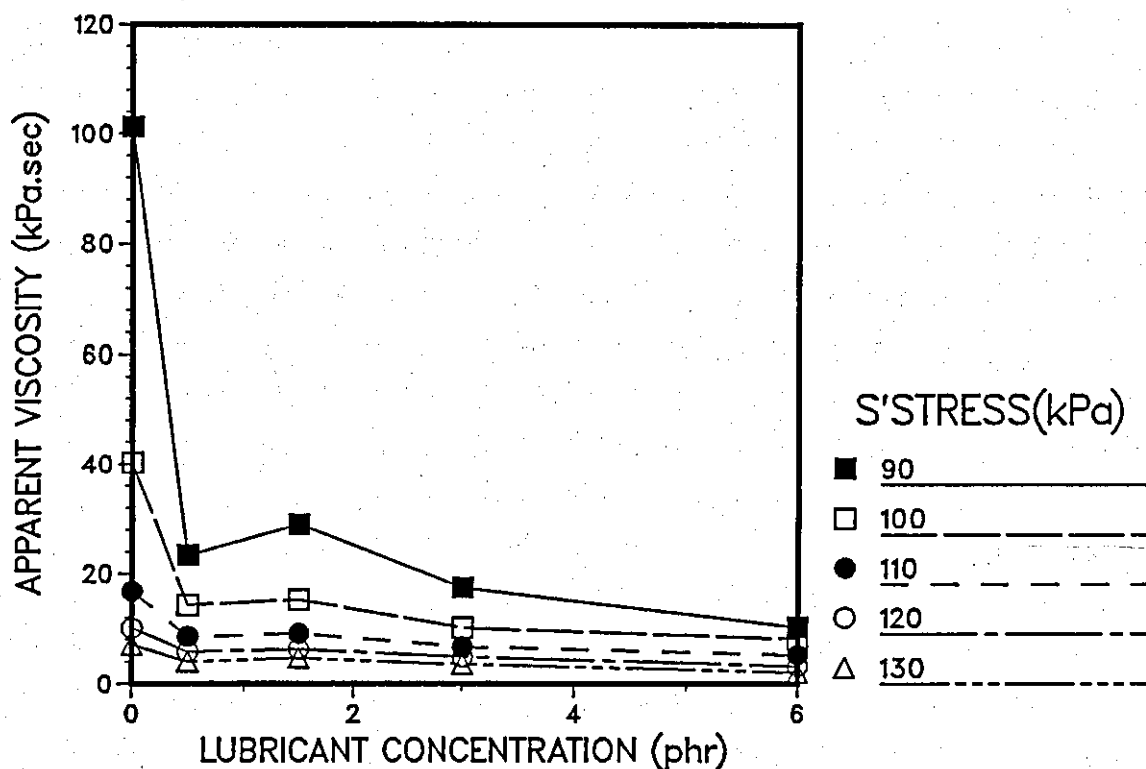


FIGURE 5.4: Apparent viscosity versus lubricant concentration for STRUKTOL WB212 In compounded Natural Rubber (Section 5.3)



The plots in Figure 5.3. show a large decrease in the apparent viscosity ($\sim 50\%$) with a very small amount of lubricant (0.5 phr) followed by a smaller decrease with later additions.

The results obtained from equation 5.1. when plotted against lubricant concentration would be useful to show the type of response resulting from the addition of a lubricant to an elastomer compound, but it would not be a good way of representing the data due to the loss in accuracy resulting from the propagating error in equation 5.1. The error was found to be about 23%. (Appendix H).

5.3. EVALUATION OF THE ACTION OF ALTERNATIVE LUBRICANTS

Having established in the previous section that the lubricant Struktol WB16 was responsible for the increase in the apparent viscosity of the two differently mixed natural rubber compounds (Sections 5.1. and 5.2.) at 1.5 phr lubricant concentration, two natural rubber compounds, (compound 1 (Section 4.3.3.)), mixed in the manner described in Section 4.3.4.2.(1), were prepared by incorporating Struktol WB212 and A50P on the two-roll mill at 100°C. The apparent viscosity versus lubricant concentration relationships for the two samples plotted in Figures 5.4. and 5.5. for Struktol WB212 and A50P respectively were obtained from the TMS rheometer at 100°C with the SLIPPER software (Section 4.4.2.) and the smooth rotor.

Figure 5.4., obtained for the natural rubber compound containing different levels of Struktol WB212 (0, 0.5, 1.5, 3 and 6 phr), shows a similar trend to Figures 5.1. and 5.2., obtained for the same natural

rubber compound containing WB16. The plots showed a large decrease in the apparent viscosity of the elastomer compound with the addition of only 0.5 phr lubricant. At 1.5 phr lubricant, the apparent viscosity of the elastomer compound appeared to increase on its previous value. This was followed by another decrease with 3 phr and 6 phr lubricant. On the other hand, Figure 5.5., obtained for the natural rubber compound containing different levels of Struktol A50P (0, 0.5, 1.5, 4 and 7 phr), shows a smooth exponential decay in the apparent viscosity with increasing lubricant concentration. No increase in the apparent viscosity was observed at any of the tested lubricant concentrations. This could be due either to the fact that such an increase did not occur or that the increase in apparent viscosity was not detected. The reasons for not detecting an increase in the apparent viscosity could be because:

- i) The increase occurred at a lubricant concentration that was not investigated.
- ii) The increase was too weak and contributed only in reducing the rate of decrease in apparent viscosity with respect to lubricant concentration.

The other trend of Figures 5.4. and 5.5. is that at low lubricant concentrations (0.5 phr) a large decrease in the apparent viscosity (~ 50%) was observed.

At the end of the experiments carried out on the natural rubber compound, (compound 1 (Section 4.3.3.)), the adhesion between the rubber and the metal surface of the smooth rotor appeared to be complete and undisturbed, indicating an absence of wall slip.

FIGURE 5.5: Apparent viscosity versus lubricant concentration for STRUKTOL A50P In compounded Natural Rubber (Section 5.3)

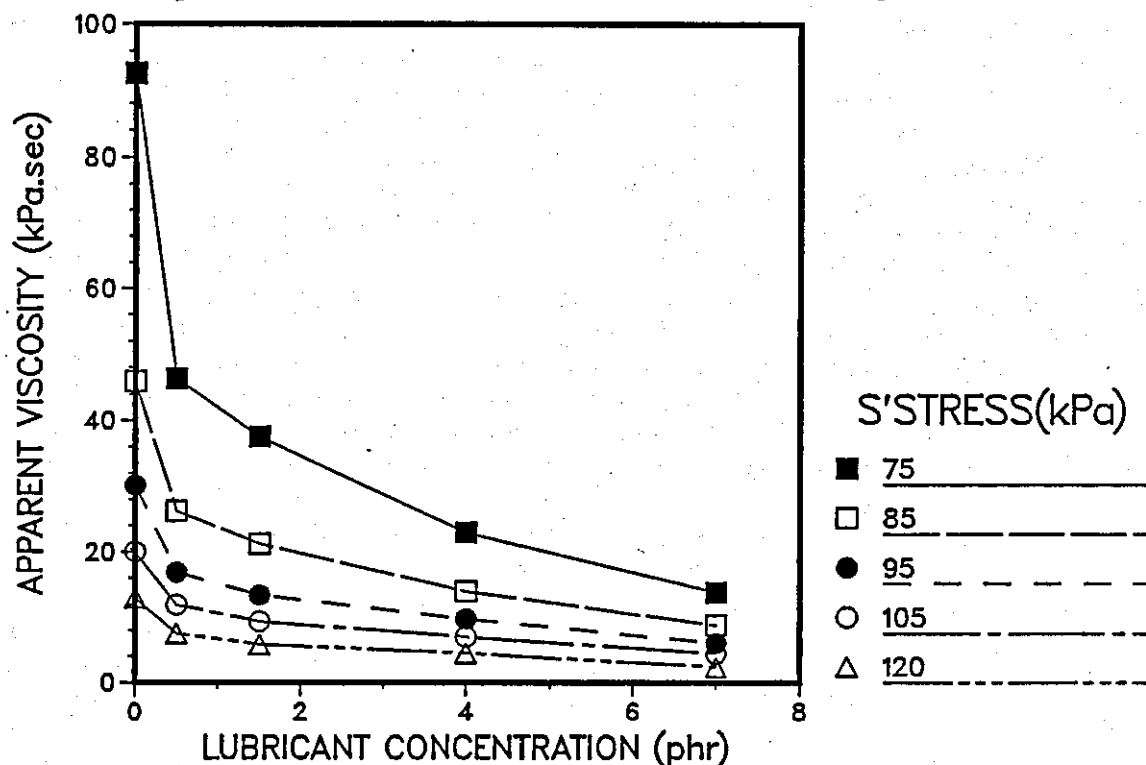
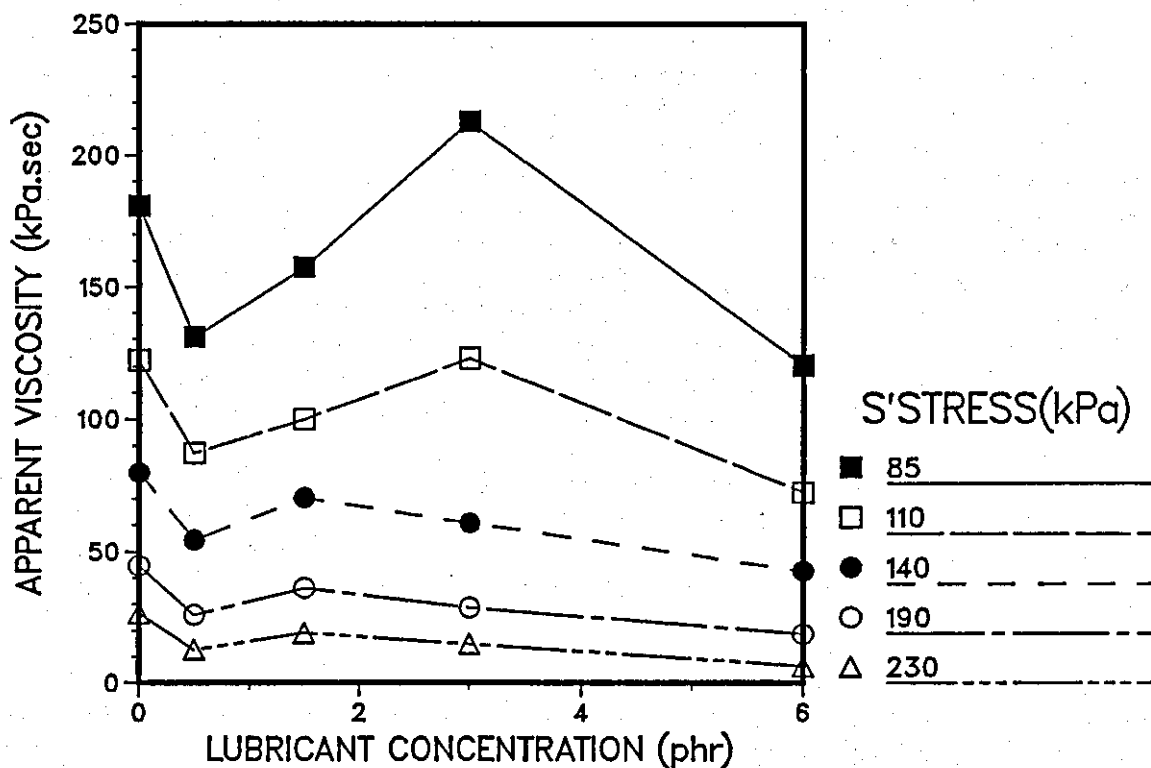


FIGURE 5.6: Apparent viscosity versus lubricant concentration for STRUKTOL WB212 In compounded CSM (Section 5.4).



5.4. EVALUATION OF LUBRICANT ACTION IN A DIFFERENT RUBBER COMPOUND

All the observations made in Sections 5.1, 5.2. and 5.3. were obtained from experiments carried out on the same natural rubber compound with different levels of various lubricants. Chlorosulphonated polyethylene (Hypalon 40) was chosen as our second elastomer to be tested because it has opposite physical and chemical properties to natural rubber (Section 4.3.1.1.).

A simple Hypalon 40 compound, (compound 2 (Section 4.3.3.)), was mixed in the manner described in Section 4.3.4.2. (ii). The apparent viscosity versus lubricant concentration relationship plotted in Figure 5.6. was obtained from the TMS rheometer at 100°C with the SLIPPER software (Section 4.4.2.) and the grooved rotor. The plots indicate that a similar mechanism as that observed with the natural rubber compound was occurring. An initial decrease in the apparent viscosity of the elastomer compound was followed by an increase, followed then by another more gradual decrease.

5.5. EVALUATION OF LUBRICANT ACTION IN THE ABSENCE OF ALL FILLERS AND ADDITIVES

In order to eliminate the possibility of an unexpected interaction between the lubricant and components of the rubber compound other than the elastomer (eg. Fillers and process oils) that may be the cause of the unexpected increase in the apparent viscosity of the CSM compound (compound 2 (Section 4.4.2.), at 1.5 phr Struktol WB212), raw CSM (Hypalon 40) was compounded with different levels of the same

lubricant (0, 0.5, 1.5, 3 and 6 phr) using the two-roll mill at 100°C (Section 4.3.5.1.).

The apparent viscosity versus lubricant concentration relationship plotted in Figure 5.7. was obtained from the TMS rheometer at 100°C with the SLIPPER software (Section 4.4.2.) and the grooved rotor. The plots show that the increase in the apparent viscosity was still existent, but with a slight shift to a higher lubricant concentration (3 phr lubricant instead of 1.5 phr with the compounded Hypalon 40 Figure 5.6). An exponential decay was observed with 0.5 and 1.5 phr lubricant followed by a large increase at 3 phr where the apparent viscosity appeared to level up.

This experiment confirmed that the increase in the apparent viscosity is a result of an interaction with the elastomer component of the compounds tested previously. The other ingredients, such as carbon black and process oil, appeared only to affect the region in which this interaction occurred (Section 7.9.). The increase in the apparent viscosity observed in the majority of the cases studied could be due either to an unexpected physical interaction between the lubricant and the elastomer or to a chemical reaction resulting in strengthening the resistance of the elastomer compounds to flow.

5.6. EVALUATION OF LUBRICANT ACTION MECHANISM WITH GEL PERMEATION CHROMATOGRAPHY

To check for a possible chemical reaction between the elastomer molecules and the lubricant molecules, the molecular weight

FIGURE 5.7: Apparent viscosity versus lubricant concentration for STRUKTOL WB212 In raw CSM (Section 5.5).

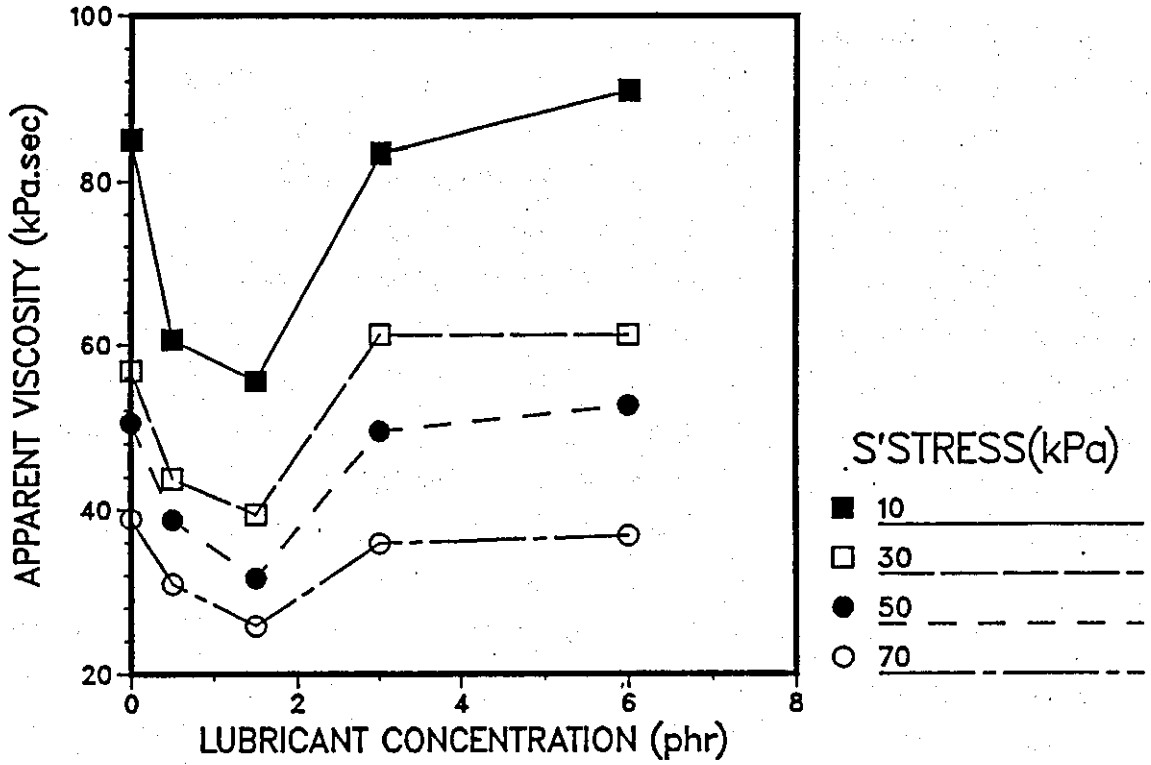
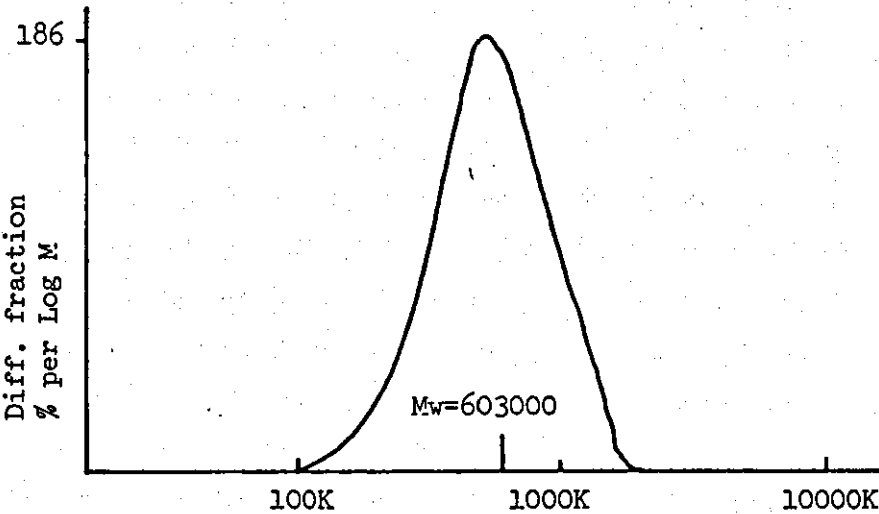


FIGURE 5.8: GPC trace for CSM at 0 phr STRUKTOL WB212 (Section 5.6)



distribution of raw chlorosulphonated polyethylene was measured at a number of lubricant concentrations. After compounding Hypalon 40 with 0, 0.5, 1.5, 3 and 6 phr Struktol WB212 on the two-roll mill at 100°C, small samples were dissolved in tetrahydrofuran (THF) and GPC traces were obtained in the manner described in Section 4.2.3. The traces are shown in Figures 5.8., 5.9., 5.10., 5.11. and 5.12. respectively.

Figures 5.8., 5.9. and 5.10., show similar molecular weight distribution curves. The changes in the calculated average molecular weight shown on the graphs were not significant and could be the results of measurement errors arising from lack of synchronisation of the sample injection into the gel column with the start of the time recording device (Section 4.2.3.). On the other hand, Figures 5.11. and 5.12., obtained for Hypalon 40 containing 3 and 6 phr lubricant respectively, show a change in the shape of the GPC trace. A shoulder followed by a bump on the high molecular weight side of the curve appeared on both traces suggesting an increase in the molecular weight of some of the CSM elastomer molecules, either through chain extension or through cross-linking. This was taken to be a clear indication of a chemical reaction brought about by the presence of the lubricant.

The results obtained with the natural rubber compound and those obtained with the CSM compound and raw elastomer appeared to suggest that the chemical reaction did not occur until a certain lubricant concentration, in this case 3 phr, was reached. This was confirmed by the GPC traces, where an increase was only apparent after a lubricant concentration of 3 phr was attained.

FIGURE 5.9: GPC trace for CSM at 0.5 phr STRUKTOL
WB212 (Section 5.6)

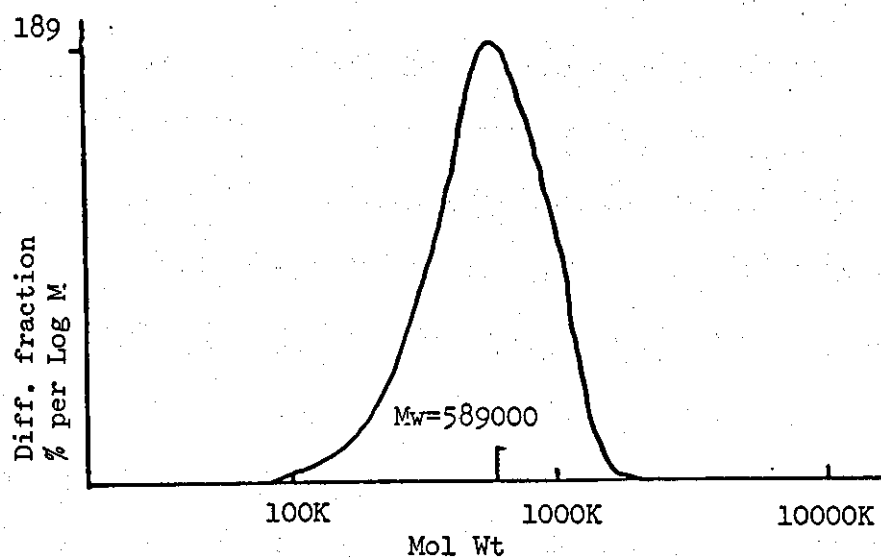


FIGURE 5.10: GPC trace for CSM at 1.5 phr STRUKTOL
WB212 (Section 5.6)

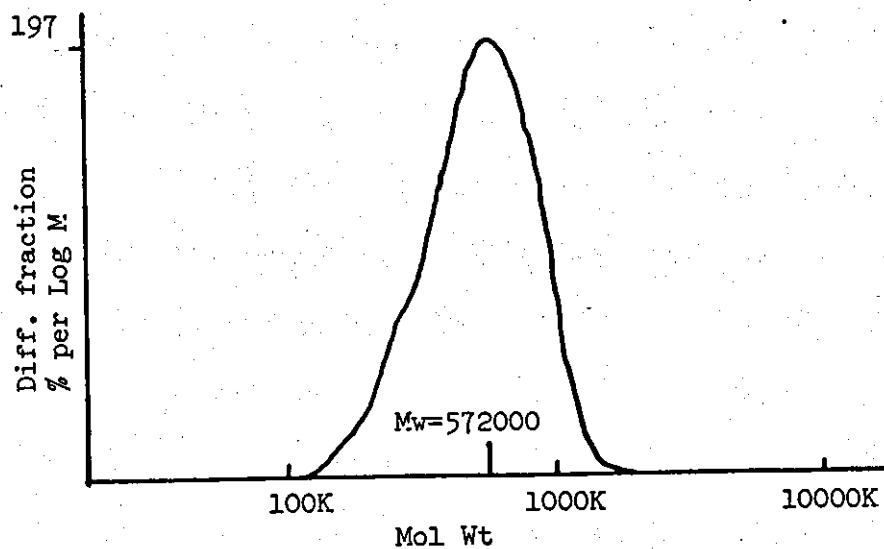


FIGURE 5.11: GPC trace for CSM at 3 phr STRUKTOL
WB212 (Section 5.6)

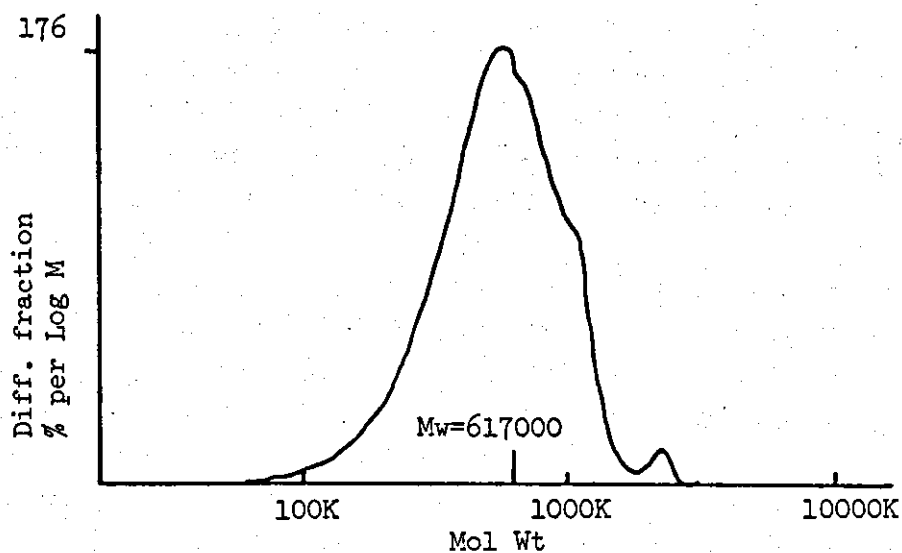
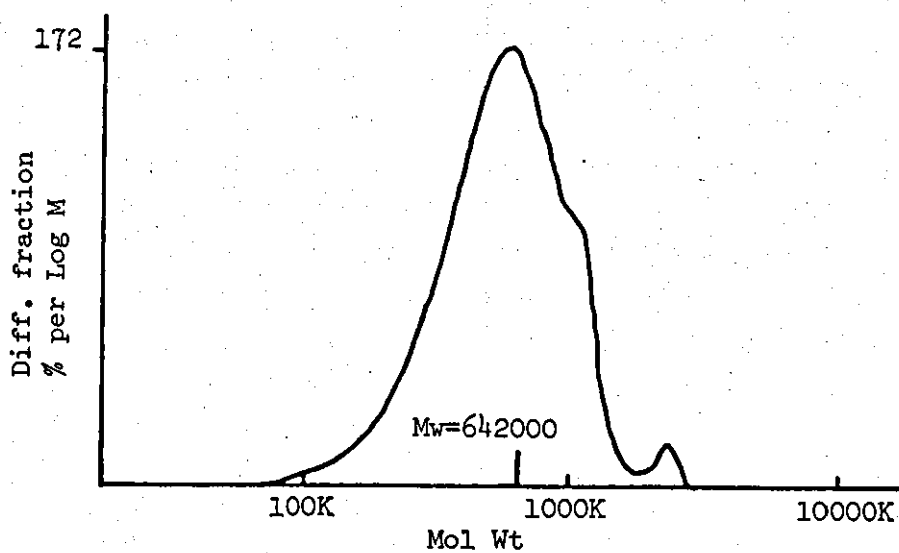


FIGURE 5.12: GPC trace for CSM at 6 phr STRUKTOL
WB212 (Section 5.6)



The sudden increase in the molecular weight of some of the molecular chains of the elastomer resulted in a higher degree of entanglement which presented a higher resistance to flow and thus a higher apparent viscosity.

5.7. VALIDATION OF LUBRICANT ACTION BY CAPILLARY RHEOMETER

MEASUREMENTS

A set of results was obtained for raw EPDM containing different levels of lubricant Struktol WB212 (0, 0.5, 1.5, 3 and 6 phr). The samples were mixed on a Brabender Plastograph for 2 minutes at 100°. The rotor speed was set to 55 rev/min.

The TMS rheometer was used with the smooth rotor at 100°. The software used was SLIPPER (Section 4.4.2.). The apparent viscosity versus lubricant concentration relationship is plotted in Figure 7.14. The plots show an increase in the apparent viscosity with the first additions of lubricant (at 0.5 and 1.5 phr). Later additions (3 and 6 phr lubricant) appeared to reduce the apparent viscosity exponentially.

The same sample was tested using the capillary rheometer (Section 4.2.2.) at 100°C with two dies of similar diameters but of different lengths (Section 4.2.2.). After applying the end correction using the two die technique and the Rabinowitsch correction (Section 3.3.) to the results obtained (Appendix E), the apparent viscosity versus lubricant concentration relationship was plotted in Figure 5.13. Only a limited number of results was obtained before the onset of melt

FIGURE 5.13: Apparent viscosity versus STRUKTOL WB212 concentration in EPDM using capillary rheometer (Section 5.7)

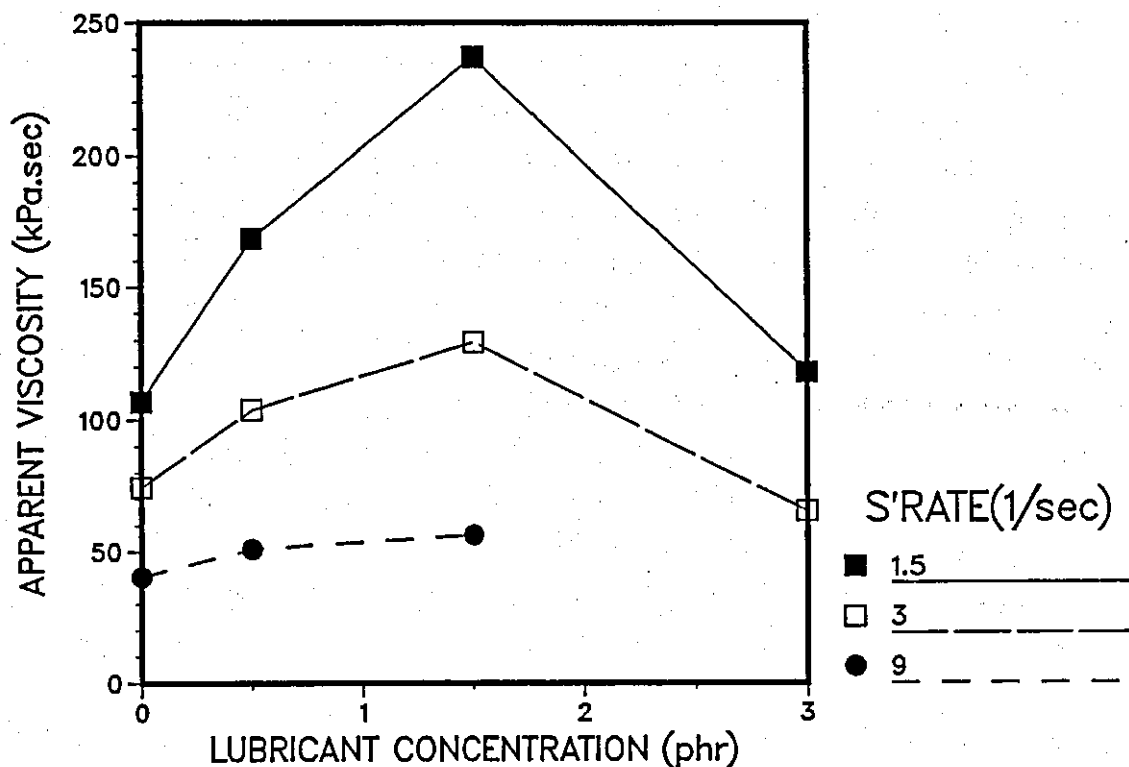
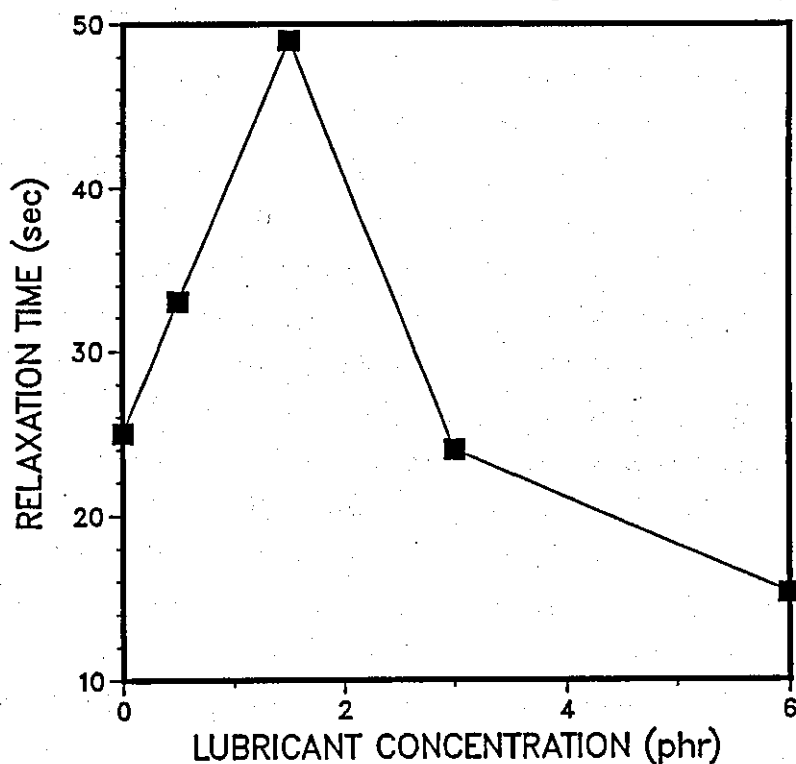


FIGURE 5.14: Stress relaxation for raw EPDM containing various concentrations of STRUKTOL WB212 (Section 5.8)



fracture (Section 2.3.). The plots show the same trends observed in Figure 7.14. An increase in the apparent viscosity at 0.5 and 1.5 phr lubricant was followed by a decrease at 3 phr lubricant.

5.8. STRESS RELAXATION TEST

In order to test the effect of lubricants on the viscoelastic properties of elastomers, a set of results was obtained using the TMS biconical rotor rheometer with the grooved rotor at 100°C. The software used for this purpose was the modified version of SLIPPER (Program 3 Section 4.2.1.5.). A shear stress of 190 kPa.sec was applied for two minutes on raw EPDM containing different levels of Struktol WB212 (0, 0.5, 1.5, 3 and 6 phr) mixed on the two-roll mill at 100°C. After stopping the rotor of the TMS rheometer, the shear stress was measured at different time intervals and stored in a file on a floppy disk. The time it took for the shear stress to drop to 2% of its original value (190 KPa) was collected for each of the test samples at different lubricant concentrations and plotted in Figure 5.14.

The plots show similar trends to those observed in Figure 7.14 from the same compound using the constant shear stress SLIPPER routine (Section 4.4.2.); an initial increase in the apparent viscosity at 0.5 and 1.5 phr lubricant was followed by a decrease with 3 and 6 phr lubricant. Having observed that the dependence of stress relaxation on lubricant concentration follows similar trends to those observed for apparent viscosity, it was decided that no further investigation of stress relaxation would be undertaken.

5.9. DISCUSSION OF LEBLANC AND LLOYD'S MODEL [29]

The results obtained with various elastomer compounds at different levels of various lubricants showed characteristics and trends that could not be explained by the simple model proposed by LeBlanc and Lloyd and described in Section 2.5. The proposed model does not take into consideration the chain extension/cross-linking effect observed with various systems (Section 5.6.). It also can not explain the variations in the apparent viscosity responses observed with the first additions of lubricants at very low concentrations (~ 0.5 phr).

A new model was needed to account for these and other discrepancies in the LeBlanc and Lloyd model.

CHAPTER 6

A THEORY OF LUBRICANT ACTION

6.1. INTRODUCTION

The theory proposed in this section was developed and refined from observations made on rheometry results but it is presented in this section so that the following chapter (Chapter 7) can then deal with the validation of the theory, with reference to a range of experiments.

Earlier, in Section 2.5., an outline of the current theories for the modes of action by which lubricants can influence the elastomer's rheological properties was given. Basically, these described two major modes of action for lubricants; namely external lubrication and internal lubrication. External lubrication occurs when the lubricant exudes to the interface between the metal and the elastomer compound and forms a boundary lubricating film. Internal lubrication is a more complicated mode of action and can involve more than one mechanism. A third mode of action that has to be taken into consideration, as we have seen in the previous chapter, is the chemical reaction between the lubricant and the elastomer molecules, resulting in the adverse effect of increasing the apparent viscosity of the compound.

In this chapter a conceptual model is proposed to aid the understanding of the modes of action of lubricants. Three major factors that can affect the type of response observed from the addition of lubricants to an elastomer compound are considered:

- i) The compatibility of the lubricant with the elastomer compound.
- ii) The morphology of the elastomer compound.
- iii) The chemical reactivity of the lubricant molecules.

Also, a phenomenological mathematical model for simulating the primary action of internal lubrication and the action due to chain extension or cross-linking is proposed.

6.2. A CONCEPTUAL MODEL OF LUBRICANT ACTION

6.2.1. The Effect of the Compatibility of the Lubricant with the Elastomer Compound

The compatibility of the lubricant with the elastomer compound was identified as one of the factors that determined the type of response observed. To illustrate this we look at three situations:

6.2.1.1. The Lubricant is Incompatible with the Elastomer Compound.

During storage the lubricant will diffuse to the surface of the rubber over a period of time to form a thin layer. The situations encountered during rubber processing and rheological testing are not static. Structural alteration of the elastomer compound sample due to flow will help the entrapped molecules to migrate with less obstruction than in a static situation. In the TMS rheometer, the shear flow of the test sample will help the formation of a thin lubricating layer at the rubber/metal interface of the rotor (Figure

6.1.). This will lead to wall slippage by a mechanism named external lubrication.

A second factor that will affect the occurrence of external lubrication is the affinity of the rubber compound to the metal surface of the processing or testing equipment. A rubber compound with high affinity to the metal surface will not allow the development of a lubricating layer at its interface and the incompatible lubricant will stay entrapped in the rubber compound and in certain cases may form an internal layer (Figure 6.2).

A third factor affecting the occurrence of external lubrication is the roughness of the metal's surface. This can be exaggerated by putting grooves on the metal surface (Figure 6.3.). The grooves will serve to maintain a certain degree of contact between the rubber and the metal surface of the testing or processing equipment and will therefore inhibit wall slippage. With the TMS biconical rotor rheometer, if external lubrication occurs, the rotor speed for an applied shear stress using a smooth rotor will be much higher than that obtained for a grooved rotor (~ 180 times higher as reported by Moore and Turner[37]). This can only be true if the grooves on the rotor's surface will maintain some form of contact with the elastomer compound even after the development of a lubricating film.

The fourth factor affecting the occurrence of external lubrication is the concentration of the incompatible lubricant compared to the surface area of the interface between the elastomer compound and the metal. The external lubricant is usually added in very small amounts,

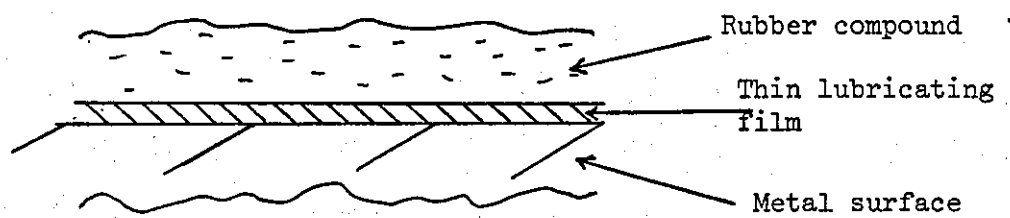


Figure 6.1 : Lubricant exuding to the rubber/ metal interface where a thin lubricating film had developed.

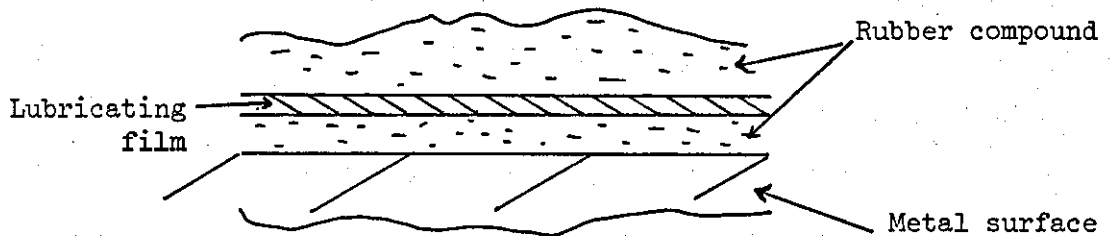


Figure 6.2 : Lubricant prevented from exuding to rubber/metal interface. Thin lubricating film developed between two rubber layers.

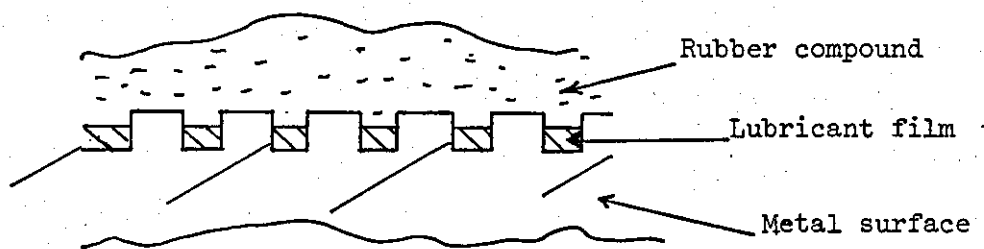


Figure 6.3 : Prevention of wall slippage by the grooves on the metal's surface.

therefore a certain concentration must be exceeded for a continuous lubricating film to occur. Partial external lubrication, where patches or rings of lubricating films (Figure 6.4.) develop at the metal/rubber interface thus lowering the contact area and therefore the flow resistance of the sample, can occur, but will be more difficult to detect than complete lubrication.

6.2.1.2. The Lubricant is Highly Compatible with the Elastomer Compound

Elastomer molecules which consist of a backbone of multitudinous covalently bonded atoms might contain a variety of groups of different polarities and ability to hydrogen bond. A highly compatible lubricant will have very strong attractive forces with at least one of the groups on the elastomer chain. These forces can be:

- i) Hydrogen bonding
- ii) Dipole-dipole attraction
- iii) Van der Waals or London forces.

When the highly compatible lubricant molecules are mixed into the elastomer compound, they will attach themselves to sites on the elastomer chain that will offer the highest attraction (Figure 6.5.).

Flow resistance of elastomers and elastomer compounds can be attributed mainly to secondary valence bonds and molecular chain entanglements (Section 2.1.). A highly compatible molecule of lubricant will ideally have the same attraction characteristics as those presented by the groups on the elastomer chain it is attracted

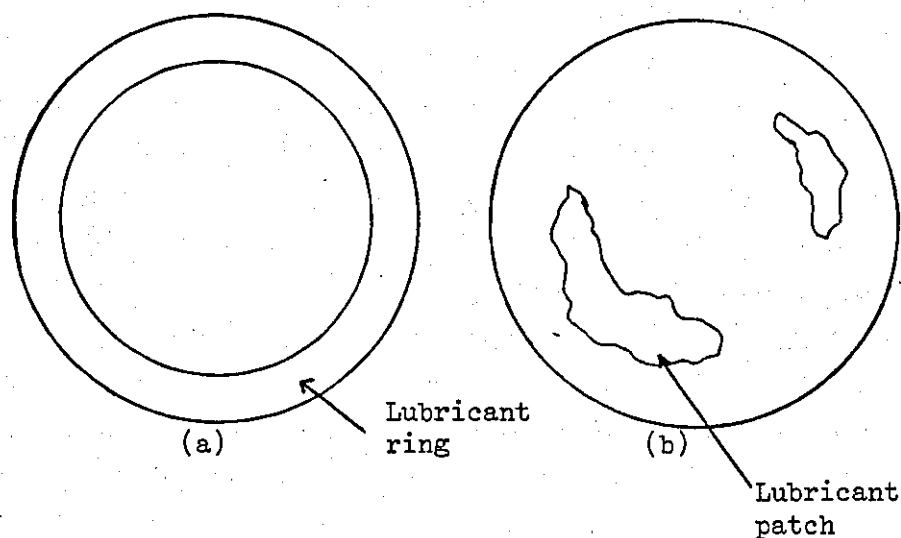


Figure 6.4: Partial external lubrication, where a ring (a) or a patch (b) of lubricant has developed at the rubber/metal interface lowering their contact area.

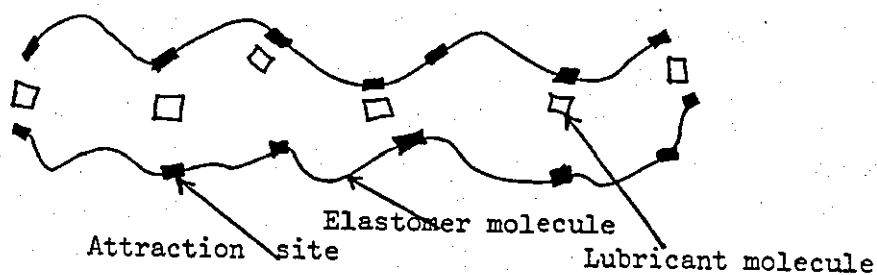


Figure 6.5 : Dissolved lubricant molecules in elastomer.

to and will offer similar attraction forces to neighbouring molecules. At low lubricant concentrations, the effect of such highly compatible lubricant molecules will be barely noticeable. At higher concentrations, the lubricant will start to swell the elastomer compound and a lowering in the apparent viscosity will be observed due to the disentanglement of the elastomer molecules (Section 2.1.) if these were present.

In this case, the lubricant is acting as a solvent rather than as a lubricant changing the structure of the elastomer or elastomer compound through disentanglement. For this reason, this mode of action was termed "Solvation".

6.2.1.3. The Lubricant is of Medium Compatibility with the Elastomer Compound

Most of the practical lubricants seem to fall under this category. This is understandable, since elastomers and elastomer compounds have a range of different types of attraction sites. If a lubricant is compatible with one type of groups on the elastomer molecule it does not follow that it would be compatible with the others. A medium compatibility lubricant will be able to attach itself to an attraction site on the elastomer molecule, but will not have the ability to maintain the same level of attraction generated by the site toward neighbouring molecules. Thus, in this situation, the medium compatibility lubricant molecule is acting as an attraction site mask, reducing the intermolecular attraction forces and the flow resistance of the elastomer or elastomer compound, which results in the reduction

of the apparent viscosity. This mode of action is termed "Internal lubrication".

Internal lubrication is only one of the modes of action that a medium compatibility lubricant can exert. External lubrication (Section 6.2.1.1.) and solvation (Section 6.2.1.2.) can also take place depending on the degree of compatibility of the lubricant with the elastomer or elastomer compound. Two cases within the medium compatibility range are examined to illustrate the type of response obtained with the TMS biconical rotor rheometer (Section 4.2.1.) when a lubricant is added to an elastomer or an elastomer compound:

Case 1: A lubricant of low compatibility.

Being a low compatibility lubricant, only small amounts of it can be dissolved into the test sample. At low lubricant concentrations, the few lubricant molecules that attach themselves to some of the attraction sites on the elastomer molecule will mask its attraction forces very efficiently, reducing its apparent viscosity considerably. If more lubricant is added, an excess amount of unwanted lubricant molecules will start to develop in the test sample without having much effect on the apparent viscosity. After a certain concentration "Cr" of lubricant is attained, there will be enough undissolved lubricant molecules in the test sample to exude to the interface between the rubber and the surface of the smooth rotor; and external lubrication will occur if the conditions for this (Section 6.2.1.1.) are favourable (Figure 6.6.). The existence and position of "Cr" will depend on all the factors that would influence the occurrence of external lubrication.

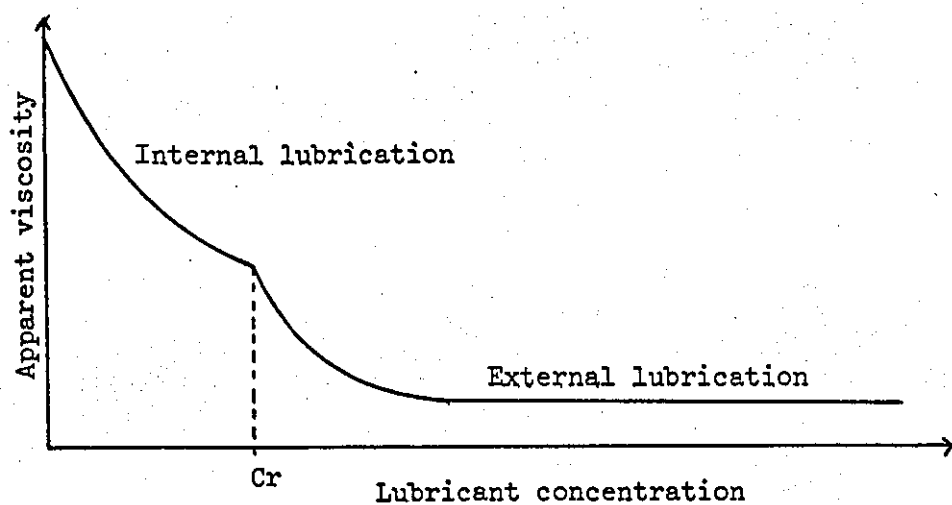


Figure 6.6 : Effect of low compatibility lubricant.

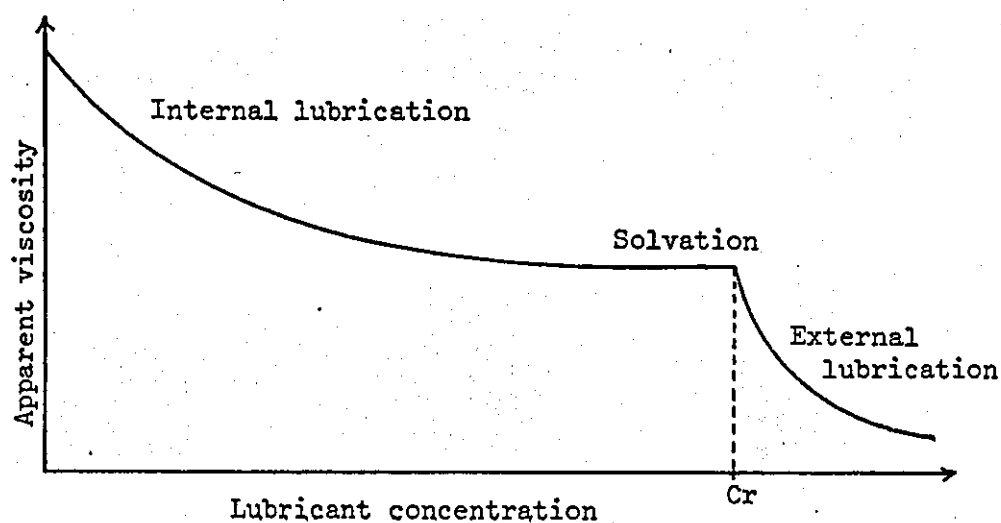


Figure 6.7 : Effect of high compatibility lubricant.

Case 2: A lubricant of high compatibility.

If a high compatibility lubricant is added to the elastomer compound the apparent viscosity will start to drop due to a reduction in the attractive forces in the compound. This drop will not be as steep as in the previous case, since the attractive forces in the elastomer compound are only slightly reduced due to the high compatibility of the lubricant (Section 6.2.1.2.). At higher lubricant concentrations, swelling will occur, accompanied by the disentanglement of the elastomer molecules, i.e. solvation. After a certain lubricant concentration " C_r ", since the lubricant is not fully compatible with the elastomer, external lubrication will occur provided all the conditions for a lubrication film to develop (Section 6.2.1.1.) are favourable (Figure 6.7.).

6.2.2. The Effect of the Morphology of the Elastomer Compound

It was mentioned in Section 2.1., that the type of flow in an elastomer compound will depend to a large extent on its morphology. The existence of chain entanglements[8] is widely accepted. If the structure of a raw elastomer is considered to consist of high entanglement regions surrounded by low entanglement regions (Figure 6.8.) and if a shear stress is applied on the surface of a representative sample unit (Figure 6.9.) of the elastomer the applied shear stress will be translated into shear flow accompanied by axis rotation of the high entanglement unit, which is termed a flow unit (Figure 6.10.). Mooney[8] suggested that in such a case the macroscopic viscosity would be the result of the friction of the flow units as they slid over each other.

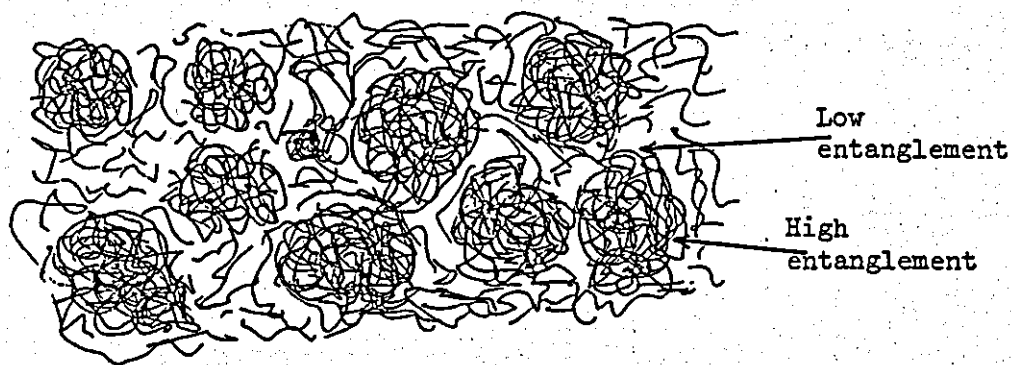


Figure 6.8 : Mophology of elastomers and elastomer compounds.

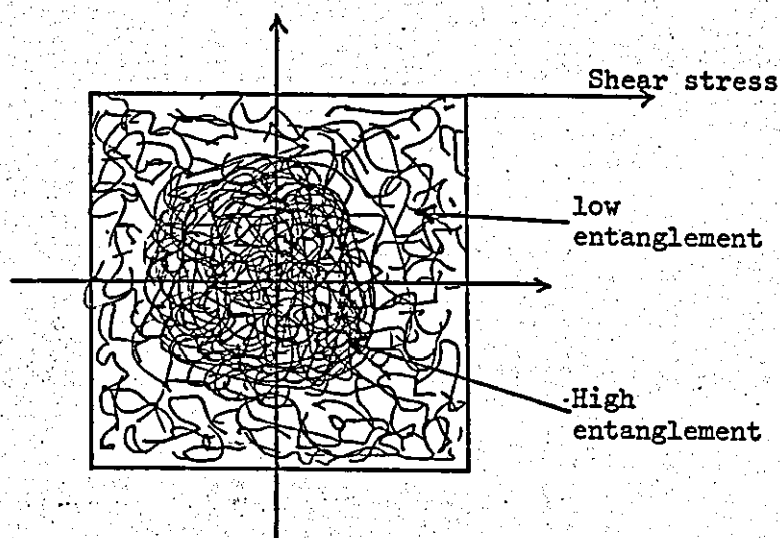


Figure 6.9 : Elastomer/elastomer compound sample unit.

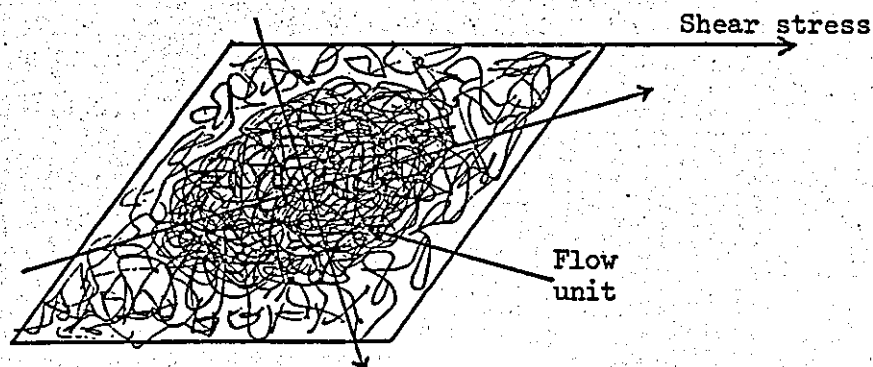


Figure 6.10 : Axis rotation of flow unit due to applied shear stress.

In an elastomer compound containing fillers and process oils (Section 2.2.), the flow units will consist of filler aggregates with strongly attached molecules and the low entanglement region will consist of elastomer molecules swollen by the process oil.

The variation in size and concentration of the flow units will affect the type of response to the addition of lubricants observed in the TMS biconical rotor rheometer measurements. This is illustrated in three cases where the change in the apparent viscosity of an elastomer compound is monitored against the increasing concentration of a medium compatibility lubricant.

6.2.2.1. Low Concentration of Small Flow Units

This case is mainly encountered with low molecular weight, raw elastomers. The small number of flow units will be barely noticeable and the main flow resisting forces will be the friction and attraction forces between the individual elastomer molecules. Thus, a large lubricant concentration will be needed to mask all the attraction sites on the elastomer molecules (Section 6.2.1.2.). The response observed in this case will be a small decrease in the apparent viscosity with increasing lubricant concentration until the stage where the elastomer compound becomes saturated with undissolved lubricant; then, external lubrication will develop if the conditions for a thin lubricating film at the rubber/metal interface were favourable (Section 6.2.1.1.) (Figure 6.11.).

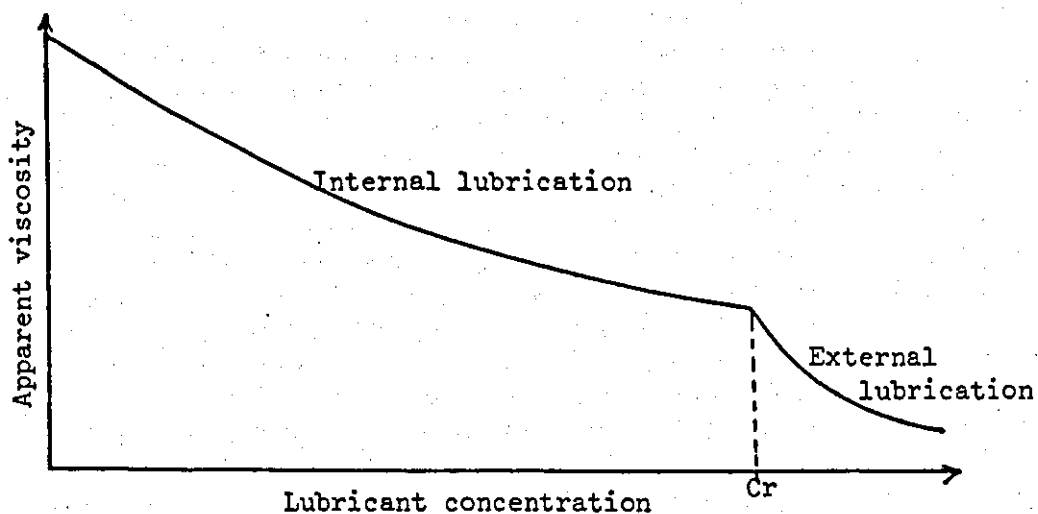


Figure 6.11 : Effect of medium compatibility lubricant on a test sample of low concentration of flow units or high concentration of small flow units.

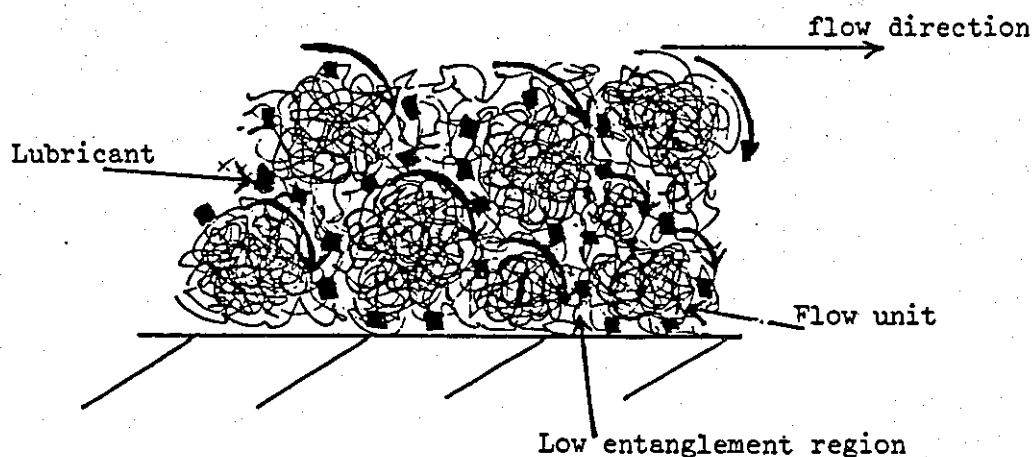


Figure 6.12 : Lubricant molecules facilitating the rotational ability of flow units.

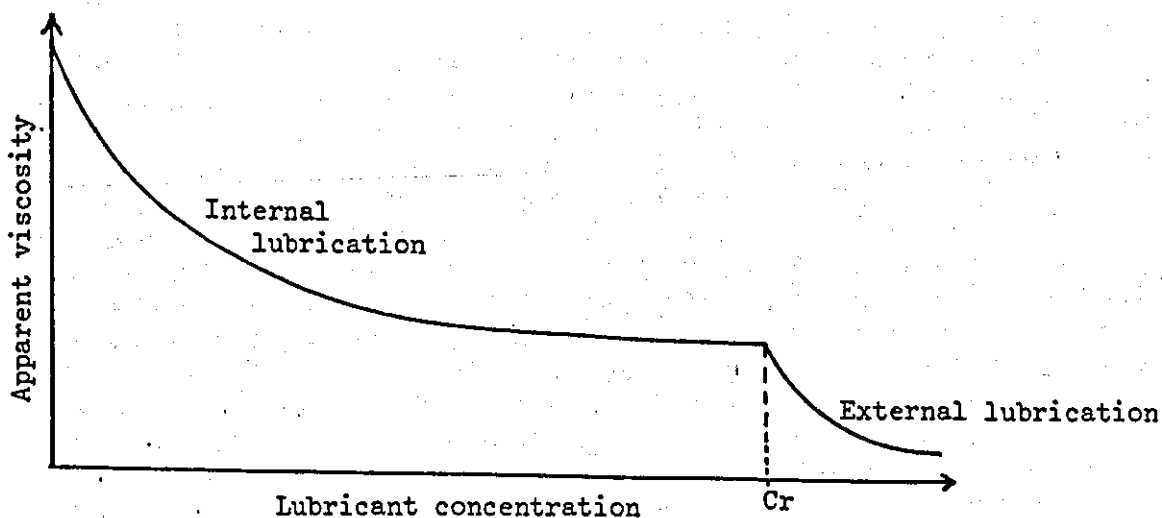


Figure 6.13 : effect of medium compatibility lubricant on a test sample of high concentration of large flow units.

6.2.2.2. High Concentration of Large Flow Units

When lubricant is added to an elastomer compound that has this type of morphology, the lubricant will dissolve mainly in the low entanglement regions where the elastomer molecules will be less tightly packed. Only small amounts of lubricants will be needed to facilitate the rotation of the flow units (Figure 6.12.). The lubricant in this case will be acting on a group of molecules instead of acting on individual elastomer molecules as was the case in Section 6.2.2.1.

The response observed will be a large decrease in the apparent viscosity with relatively small concentrations of the lubricant (Figure 6.13.). With further additions, the lubricant will start to infiltrate into the flow units swelling and disentangling them and thus dividing the flow units into smaller units, altering the morphology of the compound, ie. Solvation (Section 6.2.1.2.). After a certain concentration "Cr" is attained, the lubricant will exude to the rubber/metal interface and external lubrication will occur under favourable conditions (Section 6.2.1.1.) (Figure 6.13.).

6.2.2.3. High Concentration of Small Flow Units

This case differs from the previous one (Section 6.2.2.2.) by having a higher total surface area of flow units. A larger amount of lubricant will be needed to facilitate the rotation of the flow units. Thus, the drop in the apparent viscosity due to the addition of the lubricant will be slower than that observed in the previous case

(Figure 6.11.). At higher lubricant concentrations, external lubrication might occur if conditions were favourable (Section 6.2.1.1.).

6.2.3. Modification of Lubricant Action by Chemical Reaction

The previous sections of this chapter have examined the physical effects of the lubricant molecules in elastomers and elastomer compounds. In addition, a chemical reaction between the lubricant molecules and the elastomer molecules resulting in cross-linking or chain extension has been found to occur (Section 5.6.) with some of the lubricants.

A reactive lubricant will have two concurrent effects when added to a test sample:

- i) A lubricating effect that includes internal lubrication, external lubrication and solvation resulting in the lowering of the apparent viscosity.
- ii) A chemical effect that will result in chain extension or cross-linking which will increase the apparent viscosity in some cases, depending on the morphology of the compound.

For the effect of the chemical reaction to be significant enough to affect the apparent viscosity of the test sample, a certain lubricant concentration " C_c " must be reached. With increasing lubricant concentration the chemical effect will be greater till equilibrium is reached (Figure 6.14). The observed change in the apparent viscosity will be the result of the two opposing actions (Figure 6.15.).

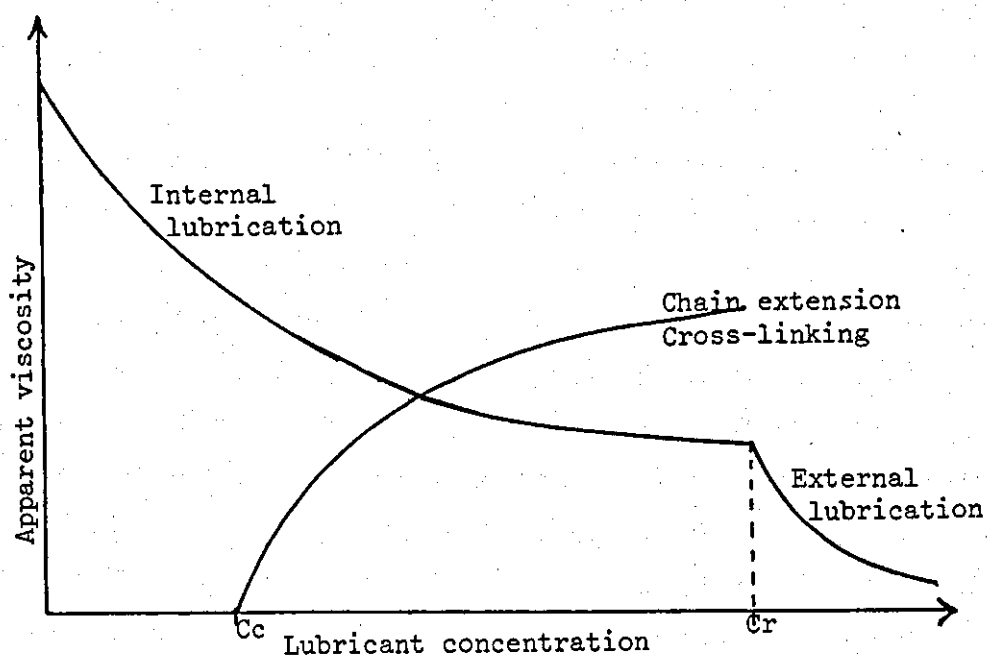


Figure 6.14 : Lubricating and chain extension/ cross-linking effects of lubricants.

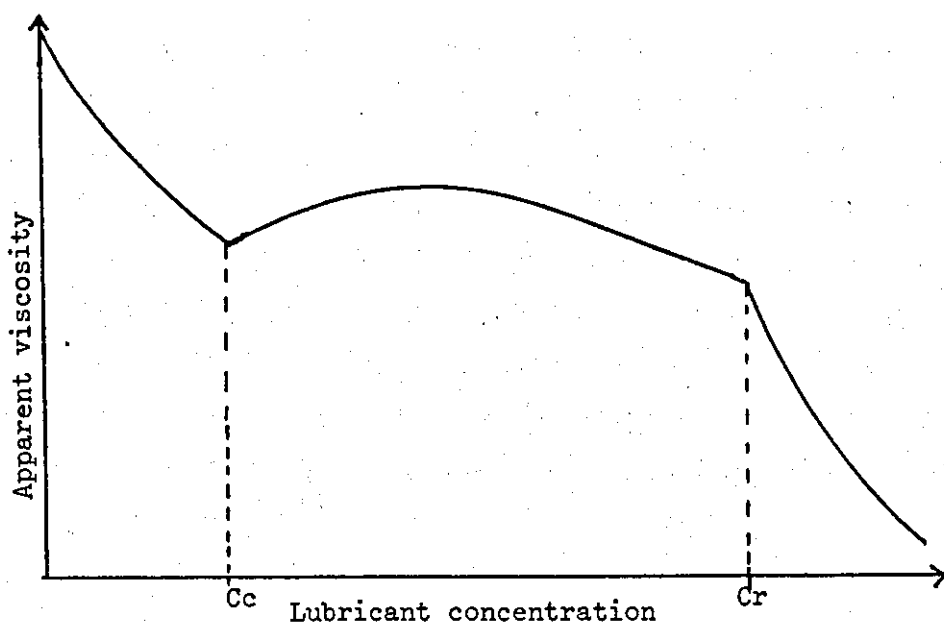


Figure 6.15: Combination of lubricating and chain extension/ cross-linking effects of lubricants on the apparent viscosity of elastomers and elastomer compounds.

6.3. A PHENOMENOLOGICAL MATHEMATICAL MODEL OF LUBRICANT ACTION

A mathematical model is presented in this section to fit the observed apparent viscosity versus lubricant concentration relationship. In this way the lubricating action can be separated from the chain extension/cross-linking action of reactive lubricants (Section 6.2.3.) and evaluated independently. The proposed model does not extend to describe the external lubrication region (lubricant concentration $> C_r$ Figure 6.15.) due to the lack of experimental information and the discontinuity of the curve which would increase the number of parameters used in the model.

The lubricating effect brought about by the presence of the lubricant acting through internal lubrication (Section 6.2.1.3.) or solvation (Section 6.2.1.1.) can be expressed mathematically as a factor reducing the initial apparent viscosity of the test sample. This factor is a function of the lubricant concentration in the test sample and can be expressed as:

$$\eta_m = \eta_1 \cdot f(\text{conc.}) \quad \dots\dots (6.1.)$$

where η_m is the apparent viscosity of the test sample at a certain lubricant concentration.

η_1 is the apparent viscosity of the test sample at zero lubricant concentration.

$f(\text{conc.})$ is a factor function of the lubricant concentration.

The chain extension/cross-linking effect resulting from the chemical reaction between the lubricant molecules and the elastomer molecules in the test sample (Section 5.6.) can be expressed

mathematically by a factor increasing the initial apparent viscosity of the test sample. This factor is also a function of the lubricant concentration in the test sample and would only apply under the constraint that the lubricant concentration should be greater than the concentration where the chain extension/cross-linking effect becomes significant, C_c (Section 6.2.3.). The non-continuous equation will have the following format:

For lubricant concentration $< C_c$:

$$\eta_{\infty} = \eta_1 \quad \dots\dots (6.2.)$$

For lubricant concentration $\geq C_c$

$$\eta_{\infty} = \eta_1 \cdot g(\text{conc.}) \quad \dots\dots (6.3.)$$

where $g(\text{conc.})$ is a factor function of lubricant concentration

In the case where both actions are occurring simultaneously the equation representing the joint effect of lubricants can be written as:

For lubricant concentration $< C_c$

$$\eta_{\infty} = \eta_1 \cdot f(\text{conc.}) \quad \dots\dots (6.1.)$$

For lubricant concentrations $\geq C_c$

$$\eta_{\infty} = \eta_1 \cdot f(\text{conc.}) \cdot g(\text{conc.}) \quad \dots\dots (6.4.)$$

The results obtained throughout this study showed the lubricating effect reducing the apparent viscosity of the test sample in a form that can be described as exponential. The first additions showing the strongest effect followed, at increasing lubricant concentrations, by an accumulation in the excess lubricant to the point where external lubrication occurs and the mathematical model fails (Section 6.2.). To translate these observations into a mathematical equation, the

internal lubricating effect factor $f(\text{conc.})$ Eq.[6.1.] can be expressed as an exponential equation that will have a value of 1 at zero lubricant concentration and a value of B (constant < 1) at infinite lubricant concentration. Applying these conditions on

$$f(\text{conc.}) = a \exp(b \text{Conc.}) + c \quad \dots\dots (6.5.)$$

where a, b and c are constants.

we have: $f(\text{conc.}) = B$ at $\text{Conc.} = \infty$

i.e.

$$B = a \exp(b \cdot \infty) + C$$

If b was positive the exponential term would be infinite and B would also be infinite. Therefore, the constant b should be negative. This means that the exponential term is equal to zero at infinite concentration and the constant c is the equivalent to B.

The second condition is to have $f(\text{conc.}) = 1$ at $\text{conc.} = 0$

i.e.

$$1 = a \exp(b \cdot 0) + B$$

$$\text{i.e. } a = 1 - B$$

Replacing constants a and c by their values and constant b by $(-A)$ where A is a factor that determines the steepness of the exponential curve we get:

$$f(\text{conc.}) = (1 - B) \exp(-A \text{ conc.}) + B \quad \dots\dots (6.6.)$$

Since the factor A represents the steepness of the exponential decay in the apparent viscosity of the test sample, it will be dependent on the compatibility of the lubricant with the elastomer or elastomer compound (Section 6.2.1.) and on the morphology of the test sample (Section 6.2.2.).

The results obtained throughout this study showed that the chain extension/cross-linking effect of the lubricant occurs after a certain lubricant concentration is reached, and tends to diminish with increasing concentration when the reaction reaches equilibrium (Section 6.2.3.) with the result that a decrease in the apparent viscosity reappears at higher concentrations. These observations can be translated into a mathematical equation by replacing the chain extension/cross-linking effect factor $g(\text{conc.})$ (Eq. 6.3.) by an exponential equation of the format:

$$g(\text{conc.}) = a \exp(b \cdot \text{conc.}) + c \quad \dots (6.7.)$$

where a , b and c are constants.

This equation has the constraints that at lubricant concentration equal to C_c the factor should be equal to 1 and at infinite lubricant concentration the factor should be equal to T (constant > 1).

$$\text{ie. } T = a \exp(b \cdot \infty) + c$$

Here too, b should be negative otherwise T would be infinite. This means that the exponential term is equal to zero and $c = T$ at infinite concentrations. The other condition is that: $g(\text{conc.}) = 1$ at $\text{conc.} = C_c$.

$$\text{ie. } 1 = a \exp(b \cdot C_c) + T$$

$$\therefore a = (1 - T) \exp(-b C_c)$$

Replacing the negative constant b by $(-I)$ where I is a positive parameter:

$$a = (1 - T) \exp(I \cdot C_c)$$

Replacing the values of the constants a , b and c into equation 6.7. we get:

$$g(\text{conc.}) = (1 - T) \exp(I \cdot C_c) \exp(-I \cdot \text{conc.}) + T$$

ie. $g(\text{conc.}) = (1 - T) \exp[I(C_c - \text{conc.})] + T \dots (6.8.)$

The factor T in equation 6.8. can be related to the effect that a limited amount of chain extension/cross-linking, due to the presence of the lubricant, has on the morphology and thus on the rheological behaviour of the test sample.

Replacing the values of the two opposing factors f(conc.) (Eq. 6.6.) and g(conc.) (Eq. 6.8.) into equations 6.1. and 6.4. simulating the response of the apparent viscosity of a test sample to additions of lubricant, we get:

For lubricant concentrations $< C_c$

$$\eta_a = \eta_1 \cdot (1 - B) \exp(-A \text{ conc.}) + B \dots (6.9.)$$

For lubricant concentrations $> C_c$

$$\eta_a = \eta_1 \cdot [(1-B) \exp(-A \cdot \text{conc.}) + B] \cdot [(1-T) \exp(I(C_c - \text{conc.})) + T] \dots (6.10.)$$

CHAPTER 7

EXPERIMENTAL RESULTS AND DISCUSSION PART II: EVALUATION AND VALIDATION OF PROPOSED THEORIES

7.1. INTRODUCTION

While the conceptual theories for lubricant action proposed in the previous chapter provide a rational explanation of the mechanisms involved, no direct evidence of their validity has yet been presented. This chapter will be concerned with work undertaken to provide that evidence.

7.2. DISCUSSION OF PRELIMINARY RESULTS (CHAPTER 5)

7.2.1. Lubricant Action on Natural Rubber Compound

The apparent viscosity versus lubricant concentration results obtained for the natural rubber compounds (Sections 5.1., 5.2. and 5.3.) will be interpreted here with reference to the models in the previous chapter.

The trends observed in Figures 5.1. and 5.2. obtained for the natural rubber compound containing different levels of Struktol WB16 indicated the occurrence of internal lubrication (Section 6.2.1.3.) where a small concentration of lubricant is sufficient to facilitate the rotation of a group of entangled elastomer molecules (flow units) thus decreasing the apparent viscosity of the test sample by reducing its resistance to flow. This effect was shown more clearly in Figure

5.3. where a drop of 50% in the apparent viscosity of the NR compound was observed with only 0.5 phr Struktol WB16. Internal lubrication was accompanied by chain extension/cross-linking (Section 6.2.3.) which manifested itself at 1.5 phr by increasing the apparent viscosity of the test sample. At higher lubricant concentrations the reaction leading to chain extension/cross-linking appears to have reached equilibrium and the lubricating effect of Struktol WB16 resumed its action by decreasing the apparent viscosity of the test sample more gradually than at lower concentrations, due to the lack of unoccupied attraction sites offered by the elastomer.

The trends observed in Figure 5.4. for the natural rubber compound containing different levels of Struktol WB212 also showed an initial internal lubrication at 0.5 phr lubricant; decreasing the apparent viscosity by ~ 50% by acting on clusters of elastomer molecules (flow units) facilitating their rotation (Section 6.2.2.2.) and reducing the flow resistance of the test sample. This was followed by a chain extension/cross-linking effect at 1.5 phr lubricant, where the concentration was high enough for such a reaction to occur to a significant degree. At higher lubricant concentrations, the reaction leading to chain extension/cross-linking has reached equilibrium and the lubricant molecules resumed their internal lubricating action which appeared as a gradual decrease in the apparent viscosity at 3 and 6 phr.

The trends observed in Figure 5.5. for the natural rubber compound containing different levels of Struktol A50P did not show any increase in the apparent viscosity of the test sample at any of the tested

concentrations. This could be because either the increase was not detected for the reasons mentioned in Section 5.3. or Struktol A50P was not reactive and its effect was only to lubricate the elastomer's flow. The plots in Figure 5.5. suggest that Struktol A50P was acting through internal lubrication, decreasing the apparent viscosity of the compound by facilitating the rotation of the flow units. This gave a large decrease in the apparent viscosity with only 0.5 phr lubricant followed by a more gradual decrease with further additions.

None of the three lubricants (Struktol WB16, WB212 and A50P) showed any evidence of external lubrication in the natural rubber compound, unless partial external lubrication, where a patch or a ring of lubricating film develops at the metal/rubber interface lowering the contact area and therefore the resistance felt by the rotor (Section 6.2.1.1.), was occurring. Visual observation made at the end of each experiment showed that complete adhesion was present between the rubber and metal surface of the rotor.

7.2.2. Testing for External Lubrication:

The TMS biconical rotor rheometer with the grooved rotor was used at 100°C to determine whether external lubrication was occurring with the natural rubber compound (Compound 1 (Section 4.3.3.)) containing different levels of lubricants Struktol WB16, WB212 and A50P.

7.2.2.1. Preliminary Checking

The batch of natural rubber compound containing 0.25 phr Struktol WB16 compounded on the two-roll mill at 100°C and used in Section 5.1. to obtain the results plotted in Figure 5.1. was tested on the TMS rheometer at 100°C with the grooved rotor using the software TESTER at the same shear rates used with the smooth rotor (Section 5.1.). The results obtained with the grooved and smooth rotors are plotted in Figure 7.1. as apparent viscosity versus log shear rate. The plots show that the results obtained with the grooved rotor at different levels of shear rate were generally lower than those obtained with the smooth rotor. If wall slip was occurring with the smooth rotor and inhibited with the grooved rotor (Section 6.2.1.1.), we would expect the apparent viscosity obtained with the smooth rotor to be lower than that obtained with the grooved one. Figure 7.1. suggests that wall slippage occurred with the grooved rotor and not with the smooth rotor. The test was repeated three times to check for measurement errors.

7.2.2.2. Investigation of the Validity of the External Lubrication Measuring Technique

A possible reason for the unexpected results obtained in Figure 7.1. can be the use of the software TESTER (Section 4.4.1.) which applied a different stress history on each sample (Section 4.2.1.5.).

The batches of natural rubber compound containing different levels of lubricant Struktol WB212 and A50P used in Section 5.3. to obtain

FIGURE 7.1: Apparent viscosity versus Log shear rate for STRUKTOL WB16 In NR using smooth and grooved rotors (Section 7.2.2.1)

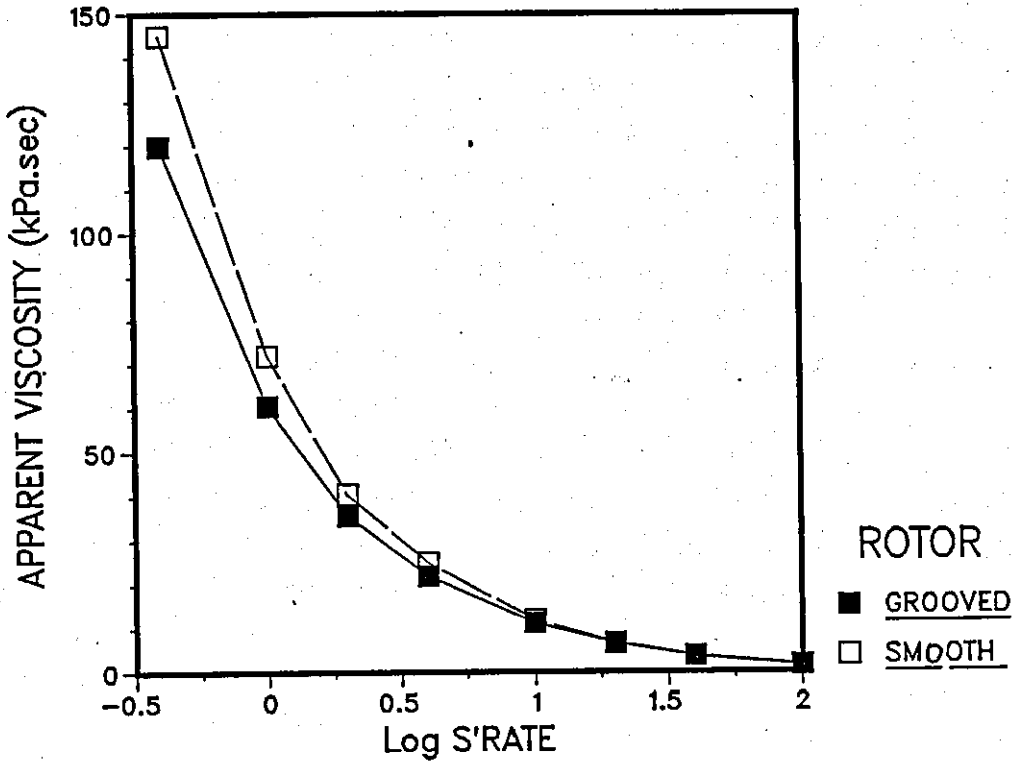
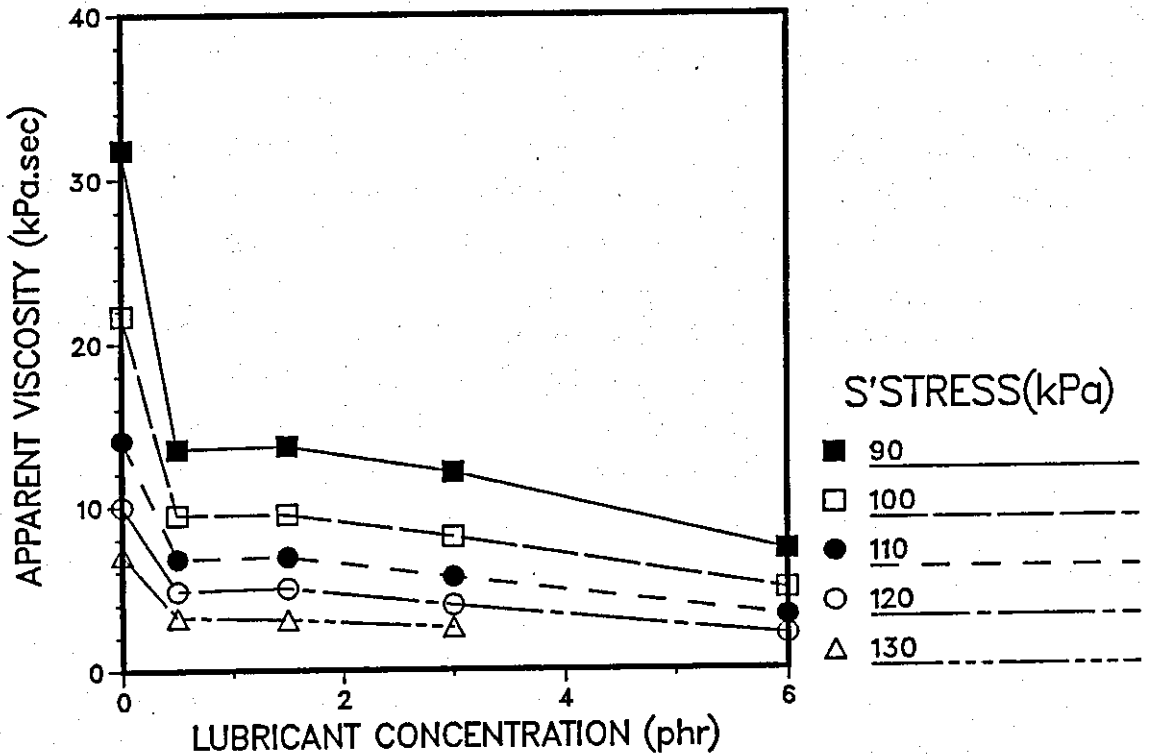


FIGURE 7.2: Apparent viscosity versus lubricant concentration for STRUKTOL WB212 In compounded Natural Rubber (Section 7.2.2.2)



the results shown in Figures 5.4. and 5.5. respectively were tested on the TMS rheometer at 100°C using the grooved rotor and the software SLIPPER (Section 4.4.1.). The results obtained and plotted in Figures 7.2. and 7.3. respectively show generally lower apparent viscosities than those from the smooth rotor with the same stress history (Figures 5.4. and 5.5.). Since it was inconceivable that wall slip was occurring with the grooved rotor and not with the smooth rotor, it was considered that the presence of the grooves on the rotor's surface had affected the observed results in an unexpected manner.

A possible explanation is that the natural rubber compound was flowing into the grooves on the rotor's surface in the manner shown in Figure 7.4. (a) instead of flowing in the expected manner (Figure 7.4. (b)). The consequences are that the natural rubber compound was 'seeing' a smaller rotor, with an imaginary surface lying somewhere between the top and the bottom of the grooves (Figure 7.5.). The position of the new imaginary surface will depend on the depth of the penetration of elastomer flow into the grooves. The change in the position of the new interface will result in a change in the apparent dimensions of the rotor, rendering the thickness "Y" (Figure 7.5. (b)) smaller than expected and the clearance between the cavity's surface and the rotor's surface "t" larger. When the TMS rheometer applies an angular velocity (W) on the test sample, the actual shear rate can be calculated by equation 3.1.:

$$\dot{\gamma}(r) = W r/t \quad \dots (3.1.)$$

In the case of the smooth rotor, all the dimensions are known and equation 3.2. can be safely used to calculate the shear rate applied

FIGURE 7.3: Apparent viscosity versus lubricant concentration for STRUKTOL A50P In compounded Natural Rubber (Section 7.2.2.2)

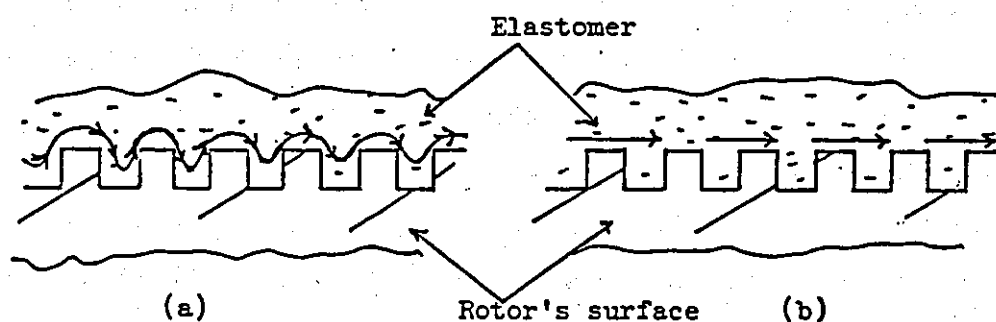
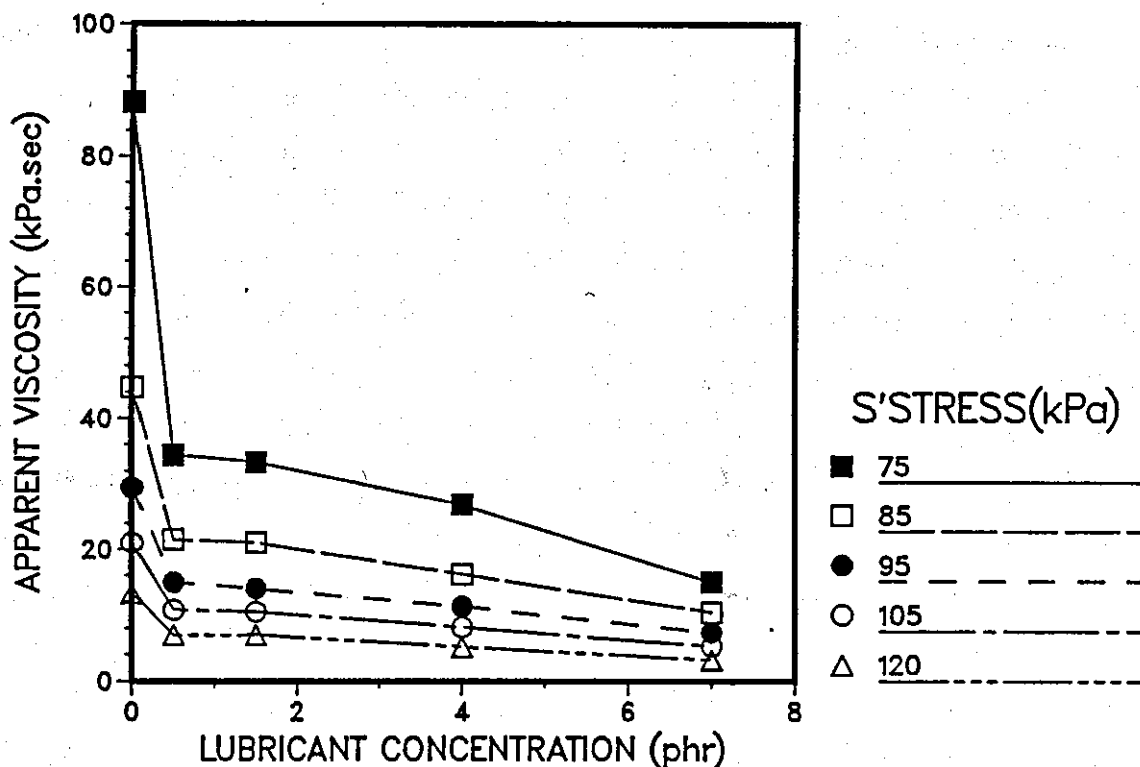


Figure 7.4 : a) Suspected mode of flow of natural rubber compound.
b) Expected mode of flow on grooved rotor's surface.

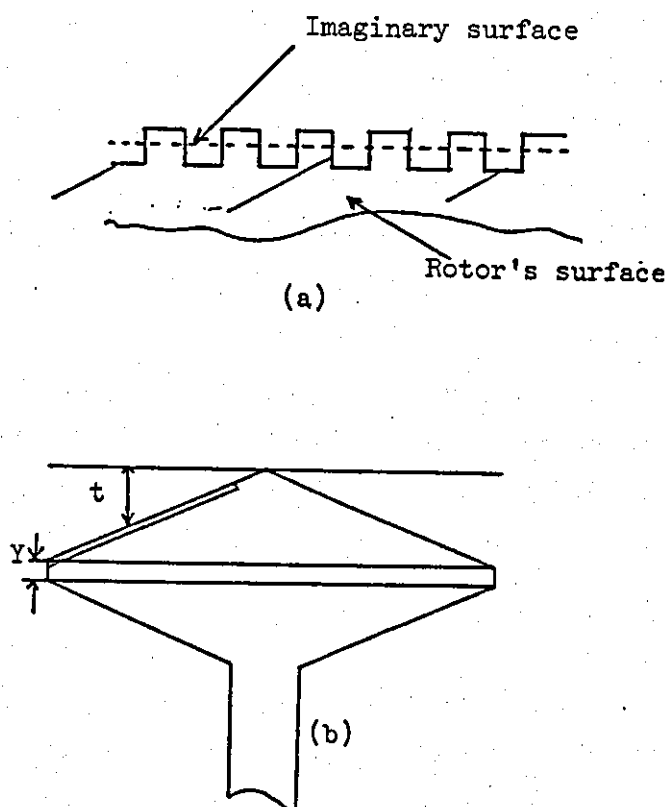


Figure 7.5: a) Imaginary surface.

b) Dimensions affected by the change in the position of the imaginary surface.

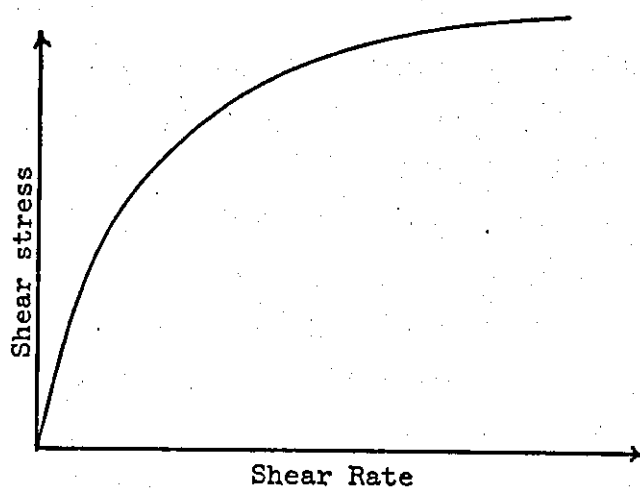


Figure 7.6: Curve representing shear rate versus shear stress relationship for elastomers and elastomer compounds.

by the rotor at a certain angular velocity, but in the case where the grooved rotor is used the clearance "t" is not known and can be greater than the one used for our calculations depending on the position of the imaginary surface (Figure 7.5.(a)). A greater clearance "t" will imply a shear rate smaller than the calculated one.

Due to elastomers being strongly non-Newtonian, a typical shear stress versus shear rate relationship for elastomers and elastomer compounds will have the characteristics shown in Figure 7.6. At low shear rates a small change in the shear rate will result in a large change in the shear stress. This will result in a change in the apparent viscosity of the test sample, which is calculated using the uncorrected dimensions of the rotor. At higher shear rates a small change in the shear rate will not change the shear stress of the test sample to the same degree as at low shear rates and the effect on the apparent viscosity will be insignificant.

This was observed in Figure 7.1. where at low shear rates the apparent viscosity results obtained with the grooved rotor were lower than those obtained with the smooth one and at higher shear rates the apparent viscosities were similar in both cases.

In the case where SLIPPER (Section 4.4.2.) was used, a larger shear rate was needed to achieve the required shear stress since the test sample is effectively thicker with the grooved rotor than that tested with the smooth rotor. This explains why a lower apparent viscosity was obtained with the grooved rotor than with the smooth rotor (Figures 5.4., 5.5., 7.2. and 7.3).

In any case, wall slip, such as the one observed by Moore and Turner[37] where the angular velocity observed with the smooth rotor was 180 times greater than that observed with the grooved one at similar shear stresses, was not observed with the natural rubber compounds containing the lubricants Struktol WB16, WB212 and A50P. Despite the uncertainty of the grooved rotor measurements, it was clear that no external lubrication was occurring with any of the natural rubber compound test samples studied.

7.2.2.3. Investigation of the Effect of the Apparent Viscosity of Natural Rubber on the Performance of the Grooved Rotor

The batches of natural rubber compounds containing different levels of lubricant Struktol WB16 incorporated by intermixing two batches of natural rubber (Compound 1 (Section 4.3.3.)) containing 0 and 4 phr lubricant into different lubricant concentration (0, 0.5, 0.75, 1.5 and 4 phr) samples were tested in Section 5.2. on the TMS rheometer with the smooth rotor to give the results plotted in Figure 5.2.

A set of results was obtained from the same natural rubber batches using the TMS rheometer at 100°C with the grooved rotor. The results obtained and plotted in Figure 7.7. were not significantly different from those obtained with the smooth rotor indicating that the phenomenon observed with the other natural compound mixes was not occurring in this case.

The results obtained with the natural rubber compound where the lubricant had been incorporated on the two-roll mill had an apparent

FIGURE 7.7: Apparent viscosity versus lubricant concentration for STRUKTOL WB16 In Natural Rubber (Section 7.2.2.3)

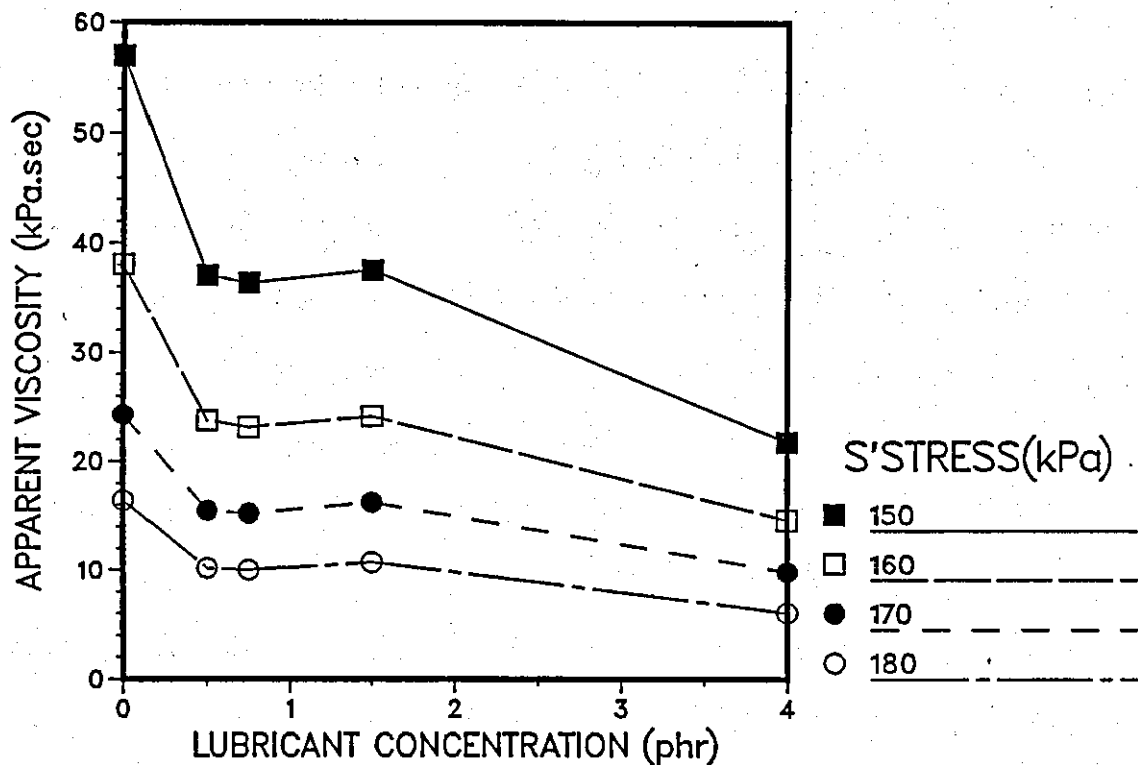
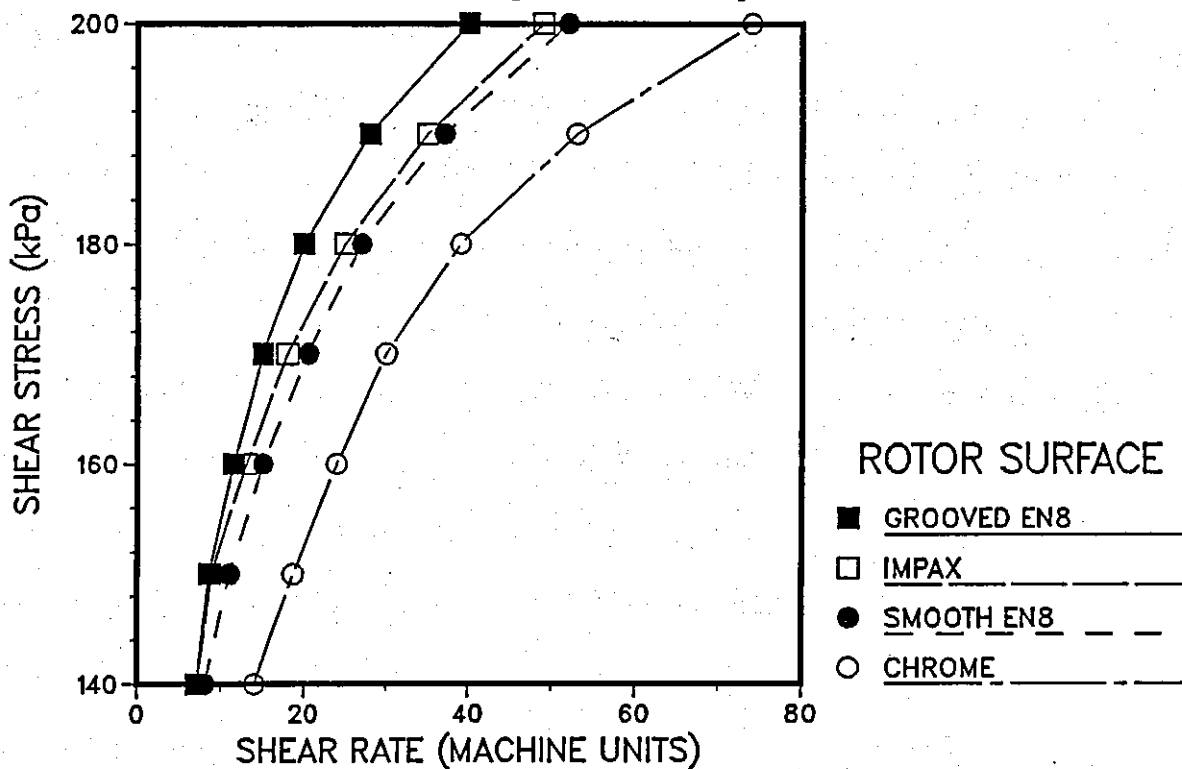


FIGURE 7.8: Shear stress versus shear rate of compounded Natural rubber using different rotors (Section 7.3)



viscosity in the region of ~ 7 KPa.sec at ~ 130 KPa shear stress. the results obtained with the natural rubber compound, having different lubricant concentrations obtained by intermixing in the Banbury internal mixer, had an apparent viscosity of ~ 57 KPa.sec at ~ 150 KPa shear stress, indicating a much more viscous compound. From this observation, it was assumed that the test sample resisted significant flow into the grooves of the rotor making its flow comparable to that on a smooth rotor (Figure 7.4. (b)).

The two Figures 5.2. and 7.7. obtained for the test sample using the smooth and the grooved rotor respectively indicated that no external lubrication was occurring on the smooth rotor's surface and that the mode of action of the lubricant Struktol WB16 was as described in Section 7.1.1.

7.2.3. Lubricant Action on Chlorosulphonated Polyethylene

The results obtained for the chlorosulphonated polyethylene compound (Compound 2 (Section 4.3.3.)) with the TMS rheometer using the smooth rotor and the software SLIPPER at 100°C were plotted in Figure 5.6. (Section 5.4.). The plots show that internal lubrication was occurring with 0.5 phr Struktol WB212, decreasing the apparent viscosity of the test sample (Section 6.2.1.3.). At 1.5 and 3 phr lubricant the concentration had reached a significant level for the chemical reaction leading to chain extension/cross-linking (Section 6.2.3.) to increase the apparent viscosity of the test sample. At higher lubricant concentrations the reaction had reached equilibrium allowing the internal lubricating action of Struktol WB212 to resume

its effect by reducing the apparent viscosity of the test sample at 6 phr lubricant.

The original decrease in the apparent viscosity at 0.5 phr attributed to internal lubrication was not as sharp as the one observed with all the natural rubber compounds studied (Figures 5.1., 5.2., 5.3., 5.4. and 5.5.).

This could be due to one or more of the following possibilities:

- i) The morphology of the chlorosulphonated polyethylene compound is comprises of a high concentration of small flow units (Section 6.2.2.3.) presenting a larger surface area to be lubricated than that presented by the larger flow units of the natural rubber compounds. This will require a higher concentration of lubricants to mask all the attraction sites on the surface of the flow units in order to facilitate their rotation and thus decrease the apparent viscosity of the compound.
- ii) The lubricant Struktol WB212 has a higher compatibility with the chlorosulphonated polyethylene compound than with the natural rubber compound; ie. when a lubricant molecule is attached to one of the sites on one of the CSM molecules it will present higher attraction forces to the neighbouring CSM molecules than when present in the less compatible natural rubber compound (Section 6.2.1.3.). This explains why the lubricant Struktol WB212 was a better lubricant in the natural rubber compound decreasing the attractive forces between the molecules more efficiently.
- iii) The lubricant Struktol WB212 has a low compatibility with the elastomer compound and only a small amount of the added lubricant

was acting on the CSM compound as an internal lubricant, masking a small number of the attraction sites that are compatible with the lubricant.

It was noted during this experiment that in some cases a lubricating film had developed. This was very inconsistent and occurred between two layers of the test sample in the manner described in Section 6.2.1.1. (Figure 6.2.). It was also noted when the CSM compound was being cleared out from the rotor and the testing cavity of the TMS (Figure 4.3.) that the compound had a very high affinity to the metal surfaces of the rotor and testing cavity, manifested by its strong adhesion to those surfaces.

It appears from the foregoing, that the lubricant Struktol WB212 had a low compatibility with the CSM compound; and after saturating the sites available for the lubricant molecules, the excess lubricant was building up, with increasing lubricant concentration, with little effect on the apparent viscosity of the compound. The excess lubricant was prevented from exuding to the rubber/metal interface due to the affinity of the rubber to the metal surface of the rotor.

Results were obtained on the same compound under similar conditions using the TMS rheometer with the grooved rotor to check for any undetected external lubrication at the smooth rotor's surface, but the results were found to be identical to those obtained with the smooth rotor, within experimental error.

The results obtained on raw chlorosulphonated polyethylene (Hypalon 40) containing different levels of lubricant Struktol WB212 incorporated on the two-roll mill at 100°C were presented in Section 5.5. and plotted in Figure 5.7. The plots show that internal lubrication was occurring at 0.5 and 1.5 phr lubricant in the same manner as with the CSM compound. At 3 and 6 phr, the lubricant concentration was high enough for the chemical reaction leading to chain extension/cross-linking to increase the apparent viscosity. Here too, the same observations about the occurrence of an occasional lubricating film between two layers of elastomer and the strong adhesion between the rubber and metal surfaces of the TMS rheometer were made. The only difference between the type of response observed with raw CSM (Figure 5.7.) and that with compounded CSM (Figure 5.6.) was the retarded increase in the apparent viscosity of the compounded CSM which affected the balance in the chemical reaction leading to chain extension/cross-linking. Here too, a set of results was obtained with the TMS rheometer using the grooved rotor and the results were found to be identical to those from the smooth rotor within experimental error.

7.3. INVESTIGATING THE EFFECT OF THE ROTOR MATERIAL

Two batches of the natural rubber compound (Compound 1 (Section 4.3.3.)) were mixed in the manner described in Section 4.3.4.2. The second batch was mixed with 4 phr lubricant, Struktol WB16, added in the final stage of mixing. Samples from the natural compound mixes were tested using a TMS biconical rotor rheometer made available by the Avon Rubber Company Ltd. and equipped with rotors made from a

range of steels. A set of shear stresses was applied at 100°C on the different test samples prepared. The rotors used were: grooved EN8, smooth EN8, smooth IMPAX and smooth chrome plated. The results obtained for the natural rubber compound with 0 phr and 4 phr lubricant were plotted in Figures 7.8. and 7.9. respectively as shear stress (KPa) versus shear rate (machine units).

The plots show a significant difference between the results obtained with different rotors emphasizing the importance of the rubber metal interaction with respect to the observed data. The arrangement of the results obtained with different rotors did not change when 4 phr lubricant was added to the original compound. If slippage was occurring at the surface of any of the rotors due to the presence of the lubricant, an increase in the shear rates would be observed, changing the position of the rotor's curve compared to the others. This could be taken as further evidence that no external lubrication was occurring due to the presence of Struktol WB16.

7.4. MATHEMATICAL MODEL FITTING

A mathematical model was developed (Eq. 6.10.) in Section 6.3. to mimic the response of the apparent viscosity of elastomers and elastomer compounds to the additions of lubricants until the development of external lubrication, where the model fails to apply.

The model has six parameters, the apparent viscosity at 0 phr lubricant being one of them. The other five parameters have to be calculated from the data collected at various lubricant

FIGURE 7.9: Shear stress versus shear rate for compounded Natural Rubber with 4phr STRUKTOL WB16 using different rotors (Section 7.3)

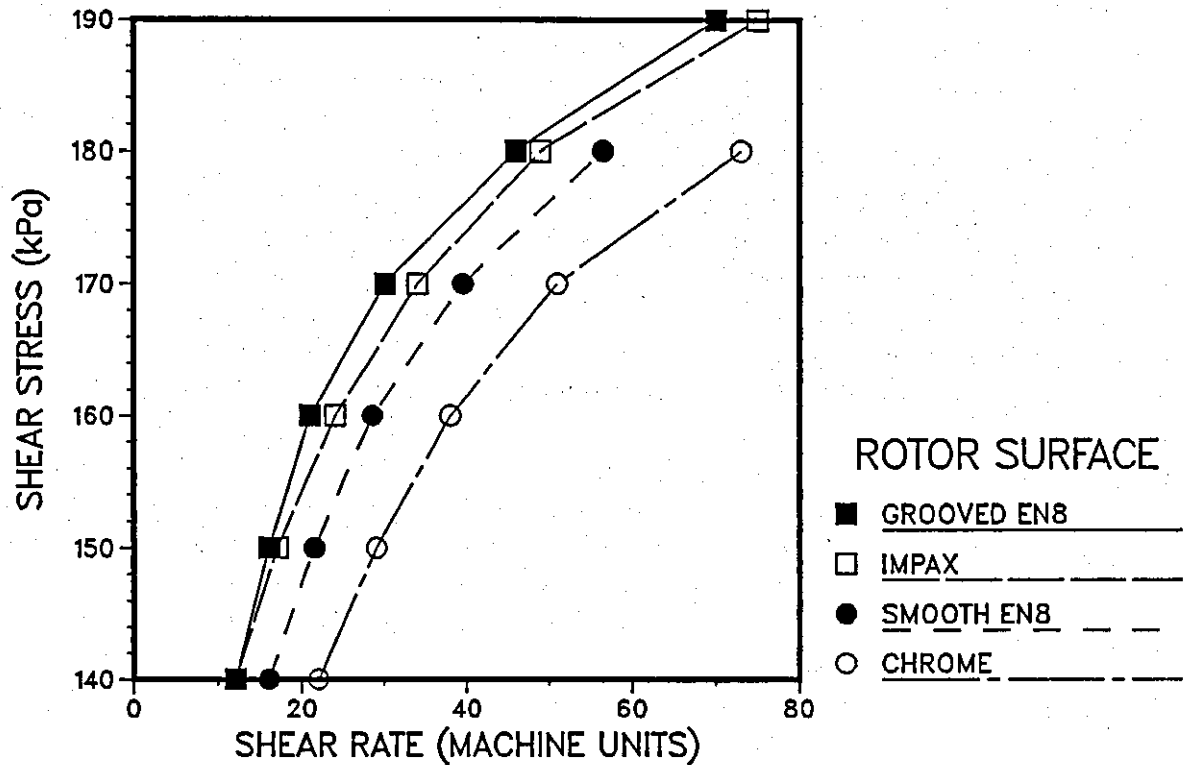
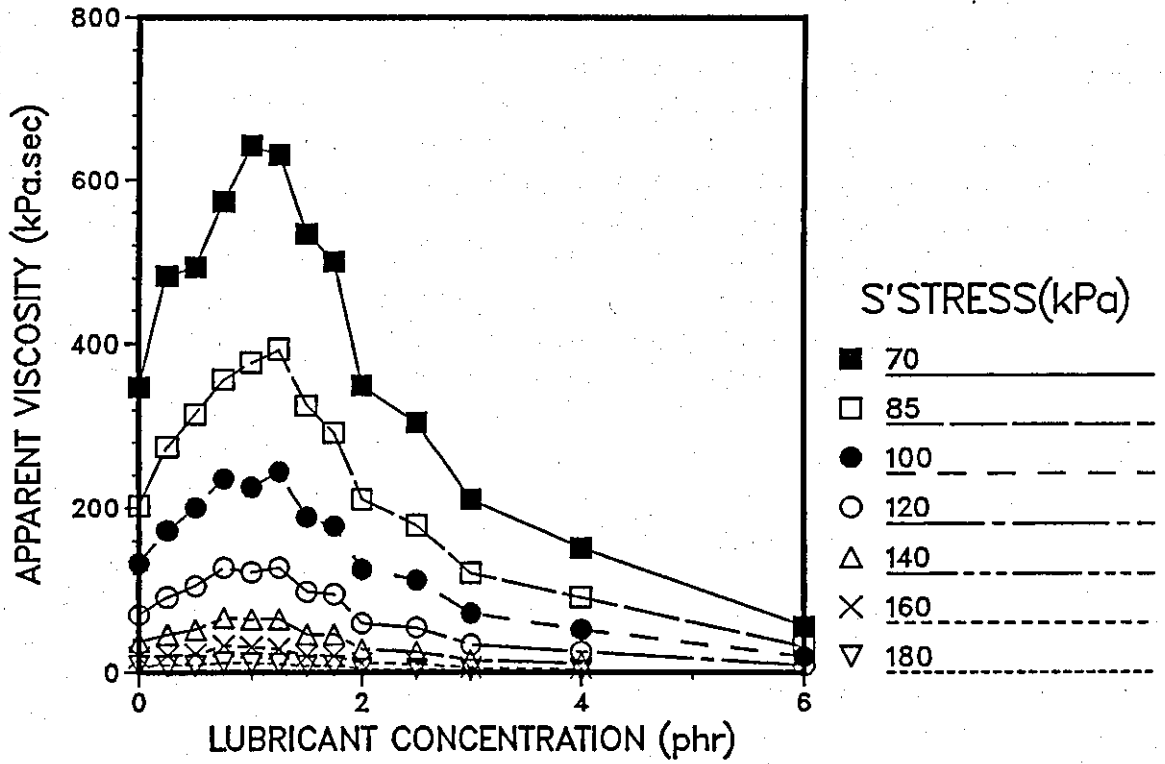


FIGURE 7.10: Apparent viscosity versus lubricant concentration for STRUKTOL WB212 in raw Natural Rubber (Section 7.4)



concentrations. Most of the results obtained throughout this study offer only four data points, at any one shear stress, other than that obtained at 0 phr lubricant. The five parameters of equation 6.10. can not be calculated by using only four data points. A minimum number of five data points is required for this purpose. For this, a set of results was obtained for raw natural rubber (SMR 10) containing thirteen different concentrations of lubricant Struktol WB212 (0, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2., 2.5, 3, 4 and 6 phr) compounded for two minutes in the Brabender Plastograph at a rotor speed of 55rev/min and mixing chamber temperature of 100°C. The results (Figure 7.10.) were obtained on the TMS rheometer with the grooved rotor at 100°C using the software SLIPPER (Section 4.4.2.). The plots show an initial increase in apparent viscosity with the first additions of lubricant Struktol WB212, indicating the occurrence of chain extension/cross-linking. After the reaction had reached an equilibrium level (~ 1.25 phr lubricant), the lubricant started to decrease the apparent viscosity of the elastomer through internal lubrication by masking the attraction sites that resisted flow in the test sample (Section 6.2.1.3.).

In order to calculate the parameters that would best fit the results reported in Figure 7.10. an optimization program was needed (Appendix G). The program developed was made to minimize the least square error criterion[46] expressed as:

$$\text{minimize } ER = \sum_{i=1}^n [W_i E_i (\text{Conc.})]^2 \quad \dots (7.1.)$$

where W_1, W_2, \dots, W_n are termed weights or penalties and have the effect of emphasizing errors of importance in the formulation of the problem.

E_1, E_2, \dots, E_n are the errors at each of the tested lubricant concentrations calculated by:

$$E_i(\text{conc.}) = \frac{\text{Measured } \eta_a - \text{Calculated } \eta_a}{\text{Measured } \eta_a} \dots (7.2.)$$

where η_a is the apparent viscosity of the test sample at a particular lubricant concentration.

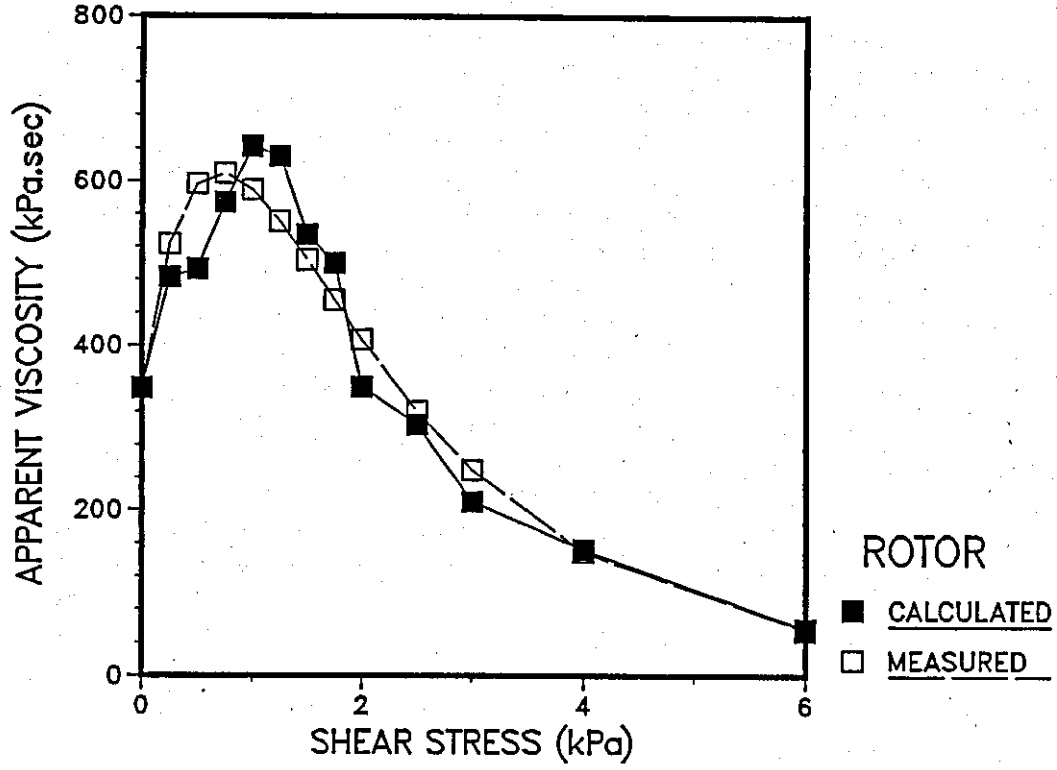
The optimization technique used to minimize the least square error criterion was the pattern search[46]. This technique takes incremental steps after suitable directions have been found by local exploration. If the search progresses well in terms of decrementing the objective function the step size is increased. If it is not progressing, either because the minimum is near or because of difficulties (eg. a narrow valley), the step size is reduced. When the step size is reduced below a set figure the search is ended.

Using the optimization program developed (Appendix G), the five parameters in equation 6.10. were obtained for the raw natural rubber test samples (Figure 7.10.) and reported in Table 7.1.

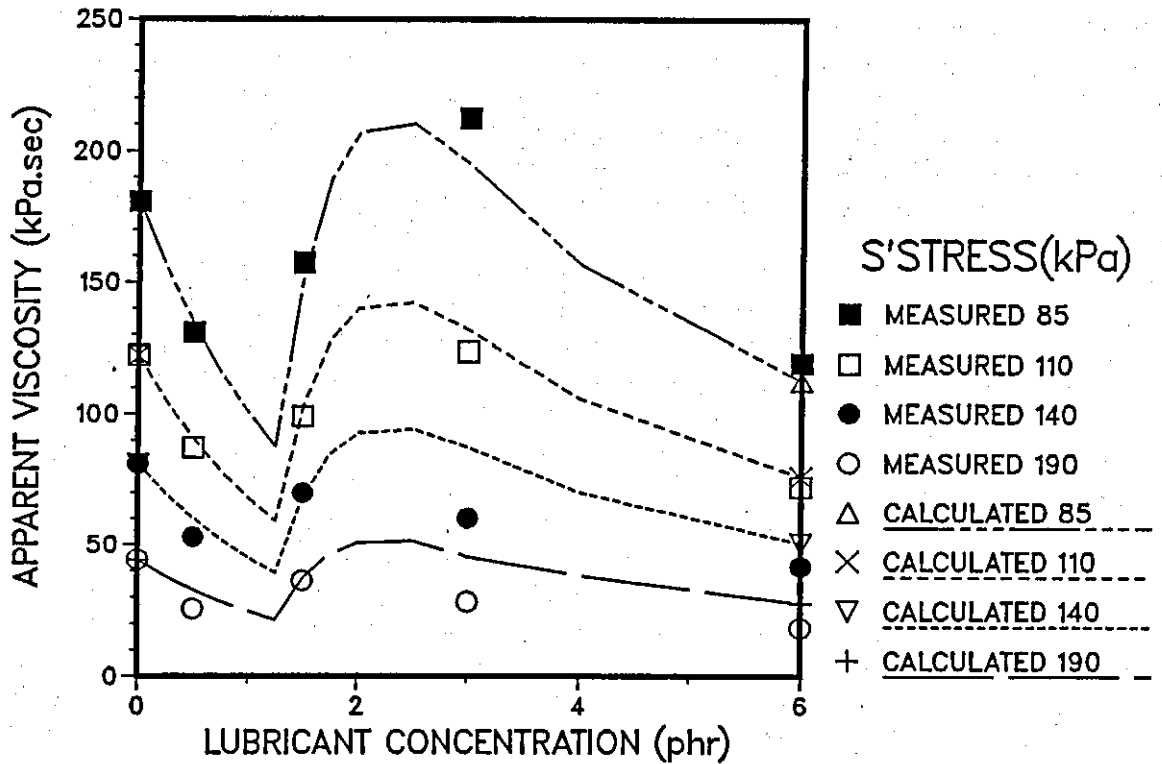
Shear Stress KPa	η_a kPa.sec	A	B	I	T	C _e
70	348.26	0.55	0.006	1.25	3.69	0
100	132.63	0.6	0.01	1.27	3.86	0
120	70.18	0.65	0.012	1.3	3.9	0
140	37.33	0.7	0	1.13	4.24	0

Table 7.1. Mathematical model parameters for raw natural rubber with Struktol WB212

**FIGURE 7.11: Mathematically fitted curve
for STRUKTOL WB212 In raw Natural
Rubber at 70 kPa stress (Section 7.4)**



**FIGURE 7.12: Mathematically fitted curve
for STRUKTOL WB212 In raw CSM
(Section 7.4)**



An example of the calculated curve compared to the measured one is plotted for 70 KPa shear stress in Figure 7.11. The plot shows a reasonable fit over the whole lubricant concentration range. Taking into consideration the calculation errors encountered in the optimization routine, the parameters presented in Table 7.1. appeared to be changing very little with increasing applied shear stress. The small differences observed between the parameters at different shear stresses are insignificant and can be attributed to experimental errors, computational errors and shear heating at higher shear stresses.

Having obtained the parameters for the raw natural rubber elastomer, the type of response observed if chain extension/cross-linking was not occurring can now be examined. Substituting the parameters A, B and η_1 (Table 7.1.) into equation 6.9., the lubricating effect of Struktol WB212 on raw natural rubber without the interference of the chemical reaction can be calculated. The calculated drop in the apparent viscosity at 0.5 phr lubricant, if no reaction was occurring, would be around 25% of the original value (η_1). We can compare this to the results obtained with the compounded natural rubber compound (Figure 5.4.) where a drop of ~ 60% was observed at the same concentration. The presence of fillers and process oils in the natural rubber compound not only affects the equilibrium of the chemical reaction leading to chain extension/cross-linking, but also changes the morphology of the elastomer to make its response to internal lubrication more effective by increasing the concentration and size of the flow units (Section 6.2.2.)

An attempt was made to fit the proposed model on the results obtained for the chlorosulphonated polyethylene compound (Figure 5.6.) where only five results were obtained at various shear stresses. To do this, the twenty results obtained at different shear stresses were fitted with one set of parameters. This did not solve the situation even though the problem was changed to fitting twenty results with six parameters. The fact is that the results obtained at different shear stresses are near multiples of each other, ie. if the results obtained at 110 KPa shear stress were all multiplied by a single value they would fit the results obtained at 85 KPa (Figure 5.6.). This makes the situation an ill-conditioned one, where a large number of solutions can be found for the problem.

In order to simplify the problem for the optimization program (Appendix G), the parameter C_c , which defines the concentration at which chain extension/cross-linking starts to occur, was made constant at 1. The least square error criterion was then minimized to obtain a preliminary set of parameters. The other parameters were then made constant in sequence until a satisfactory set of parameters was obtained. The parameters obtained are not the ones that will give an optimum fit to the results of Figure 5.6., but appear to be adequate, as can be seen from Figure 7.12. The parameters obtained are:

$A = 0.656$, $B = 0.078$, $I = 0.79$, $T = 6.63$ and $C_c = 1.256$.

7.5. THE EFFECT OF ELASTOMER-LUBRICANT COMPATIBILITY ON THE MODES OF ACTION OF LUBRICANTS

In order to study the effect of compatibility on the modes of action of lubricants, ethylene propylene terpolymer (EPDM) samples containing different levels of Struktol WB212, A50P and WB16 were prepared on the Brabender Plastograph. The temperature in the mixing chamber was controlled at 100°C and the rotor speed was set to 55rev/min. The mixing time was two minutes.

7.5.1. Investigation of the Compatibility of EPDM with Lubricants

Five solvents of known solubility parameters (Table 5.) were used to determine the solubility parameter ranges for EPDM and the lubricants Struktol WB212, A50P and WB16 in the manner described in Section 4.2.5.

Solvent	Solubility Parameter δ (Cal/c.c)
Diethyl Ether	7.4
Cyclohexane	8.2
Xylene	8.8
Chloroform	9.3
Acetone	10.0

Table 5. Solvents used for determination of solubility parameter ranges

A lubricant was confirmed as being positively soluble in a solvent of known solubility parameter when partial dissolution was observed. None of the solvents completely dissolved any of the lubricants. This is understandable since Struktol WB212, A50P and WB16 are blends of

different fatty acid derivatives (Section 4.3.1.2.). The results obtained are shown in Figure 7.13.

The rough test used showed some differences between the different lubricants. Struktol WB212 shared only one solvent with EPDM (Chloroform), while Struktol A50P shared two of the solvents that dissolved or swelled EPDM from the opposite ends of the range (Cyclohexane and Chloroform). Struktol WB16, on the other hand, was partially dissolved by all the three solvents that dissolved or swelled EPDM (Chloroform, Xylene and Cyclohexane).

7.5.2. Struktol WB212 with Raw EPDM

A set of results was obtained for EPDM containing different levels of lubricant Struktol WB212 (0, 0.5, 1.5, 3 and 6 phr) using the TMS rheometer at 100°C with the smooth rotor. The results obtained are plotted in Figure 7.14.

The plots show an increase in the apparent viscosity with the first two additions of lubricant (0.5 and 1.5 phr) indicating the occurrence of chain extension/cross-linking (Section 6.2.3.). After the reaction had reached equilibrium level, the lubricant resumed its lubricating action by decreasing the apparent viscosity of the test samples either through internal (Section 6.2.1.3.) or external (6.2.1.1.) lubrication (3 and 6 phr lubricant).

To investigate the possibility of external lubrication due to the formation of a thin lubricating film at the rubber/metal interface,

FIGURE 7.13: Solvents that dissolve or swell EPDM and the lubricants STRUKTOL WB212, WB16 and A50P.

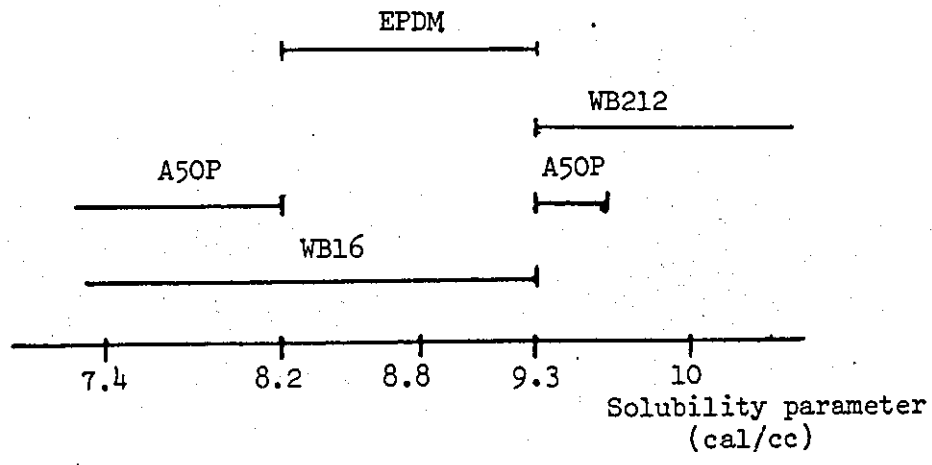
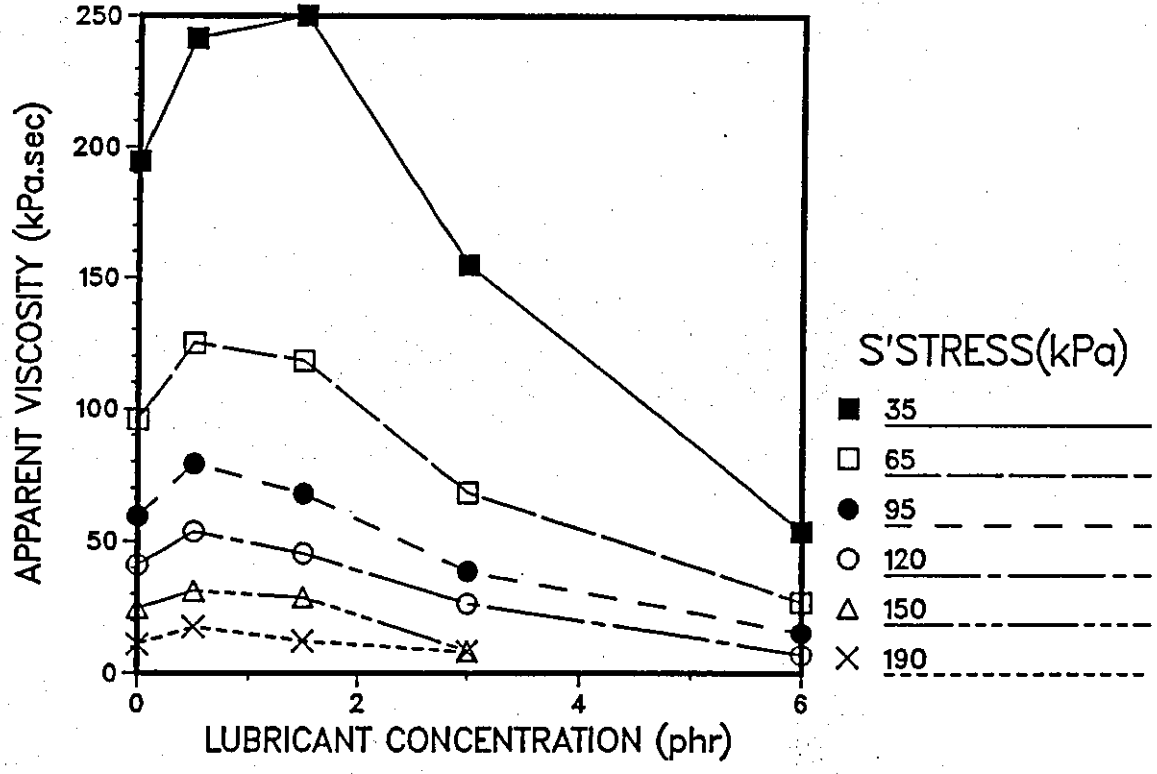


FIGURE 7.14: Apparent viscosity versus lubricant concentration for STRUKTOL WB212 in raw EPDM (Section 7.5.2)



the same test was carried out with the TMS rheometer under similar conditions, but this time with the grooved rotor. The results obtained and plotted in Figure 7.15. show similar values to those obtained with the smooth rotor (Figure 7.14.) suggesting that no external lubrication was occurring with the smooth rotor. The medium compatibility lubricant Struktol WB212 was still acting as an internal lubricant at 6 phr, suggesting that the critical concentration "Cr" (Section 6.2.1.3.) was not reached. The large decrease in the apparent viscosity observed at 3 phr lubricant could be due to the good masking ability of the low compatibility molecules of the lubricant Struktol WB212 (Section 7.5.1.).

7.5.3. Struktol A50P with Raw EPDM

The results obtained for EPDM containing different levels of A50P (0, 0.5, 1.5, 4 and 7 phr) using the TMS rheometer at 100°C with the smooth rotor were plotted in Figure 7.16. In this case, the plots show a smooth exponential decay in the apparent viscosity with 0.5 and 1.5 phr lubricant followed by a sharp drop at 4 phr where the apparent viscosity appeared to have settled. Two explanations can be given:

- 1) At 0.5 and 1.5 phr lubricant the two opposing actions of internal lubrication and chain extension/cross-linking were occurring simultaneously with the lubricating action being the strongest. Chain extension/cross-linking was limited and served only to decrease the lubricating action of the internal lubrication (Section 6.2.1.3.). At 4 phr lubricant, the chain extension/cross-linking reaction reached equilibrium and the internal lubricating effect was decreasing the apparent viscosity

FIGURE 7.15: Apparent viscosity versus lubricant concentration for STRUKTOL WB212 In raw EPDM (Section 7.5.2)

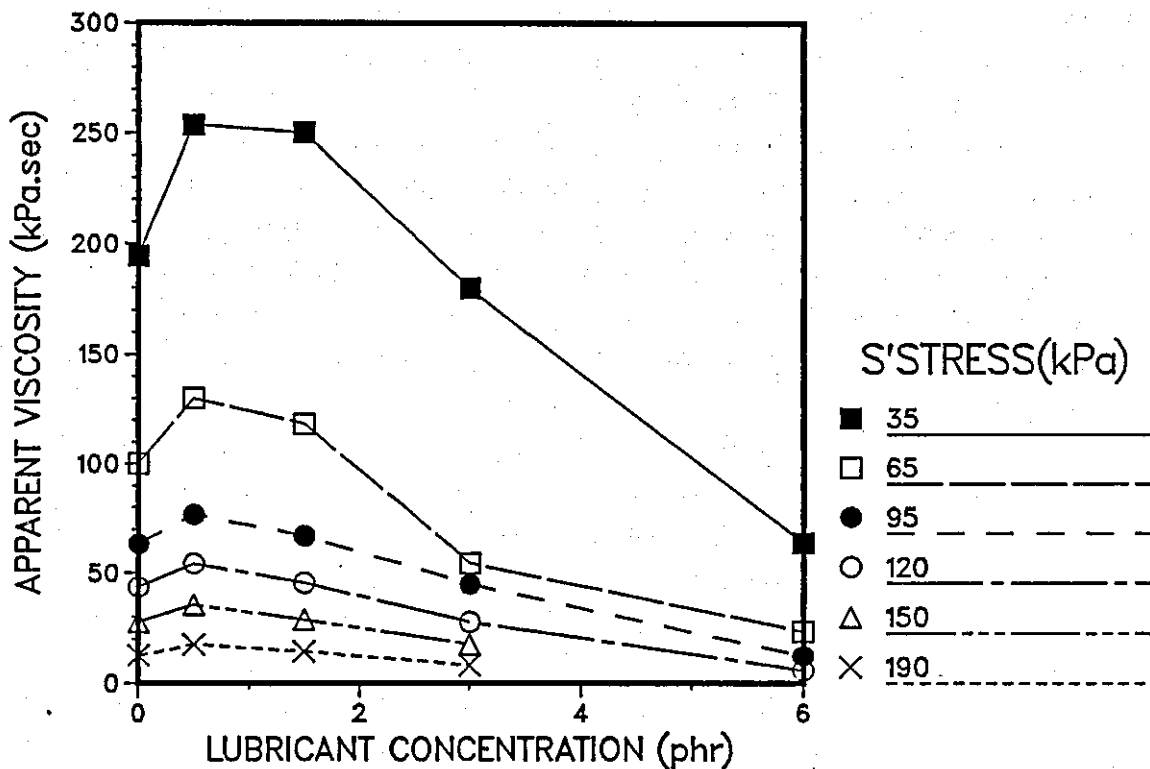
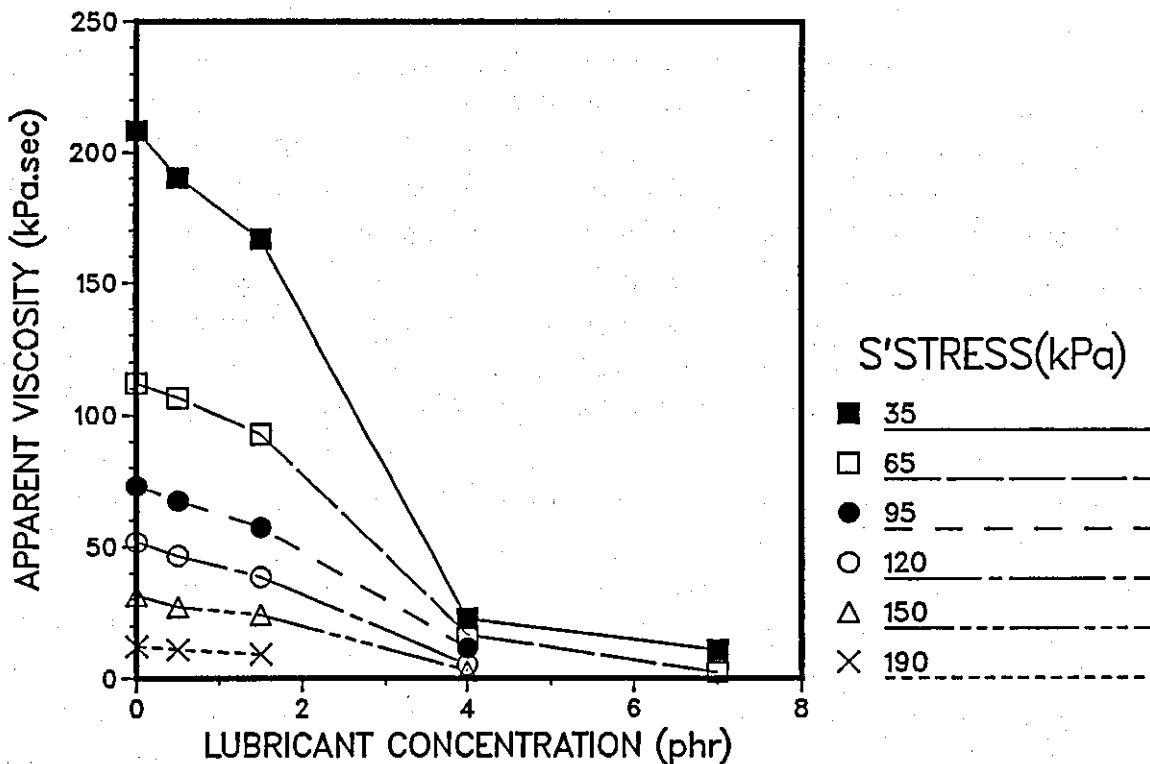


FIGURE 7.16: Apparent viscosity versus lubricant concentration for STRUKTOL A50P In raw EPDM (Section 7.5.3)



of the test sample without interference. At 7 phr lubricant, most of the attraction sites on the elastomer chains have already been masked and the excess lubricant is contained in the test sample without much effect on its rheology.

- ii) At 0.5 and 1.5 phr lubricant the medium compatibility Struktol A50P (Section 7.5.1.) acts as an internal lubricant, decreasing the apparent viscosity of the test sample by masking attraction sites of elastomer chains (Section 6.2.1.3.). At 4 phr lubricant, the lubricant exuded to the rubber/metal interface of the smooth rotor where a thin lubricating film developed, reducing the measured apparent viscosity by external lubrication (Section 6.2.1.1.). The critical lubricant concentration " C_r " at which wall slip developed was between 1.5 and 4 phr lubricant ($1.5 < C_r \leq 4$ phr).

In order to check for external lubrication, the grooved rotor was used on the same sample under similar conditions. The results obtained and plotted in Figure 7.17. appear to be similar to those obtained with the smooth rotor (Figure 7.16.) except for those obtained with 4 phr lubricant at 35 kPa shear stress where a significantly higher apparent viscosity was observed with the grooved rotor. The apparent viscosity results obtained using the smooth and the grooved rotors at 0.5, 1.5 and 4 phr lubricant were plotted against the applied shear stress in Figures 7.18., 7.19. and 7.20. respectively. At 0.5 phr lubricant (Figure 7.18.) the grooved and smooth rotors gave similar results within experimental error. At 1.5 phr lubricant (Figure 7.19.) the smooth rotor showed generally lower

FIGURE 7.17: Apparent viscosity versus lubricant concentration for STRUKTOL A50P In raw EPDM (Section 7.5.3)

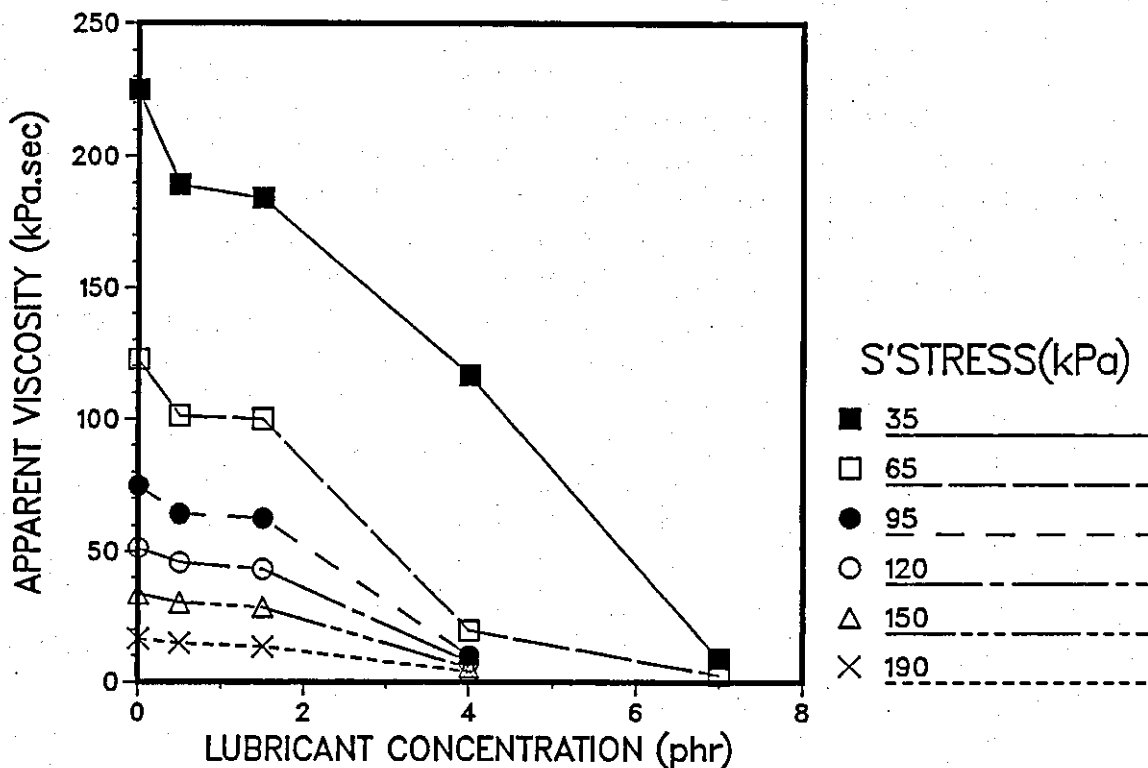


FIGURE 7.18: Apparent viscosity versus shear stress for EPDM at 0.5 phr STRUKTOL A50P using smooth and grooved rotors (Section 7.5.3)

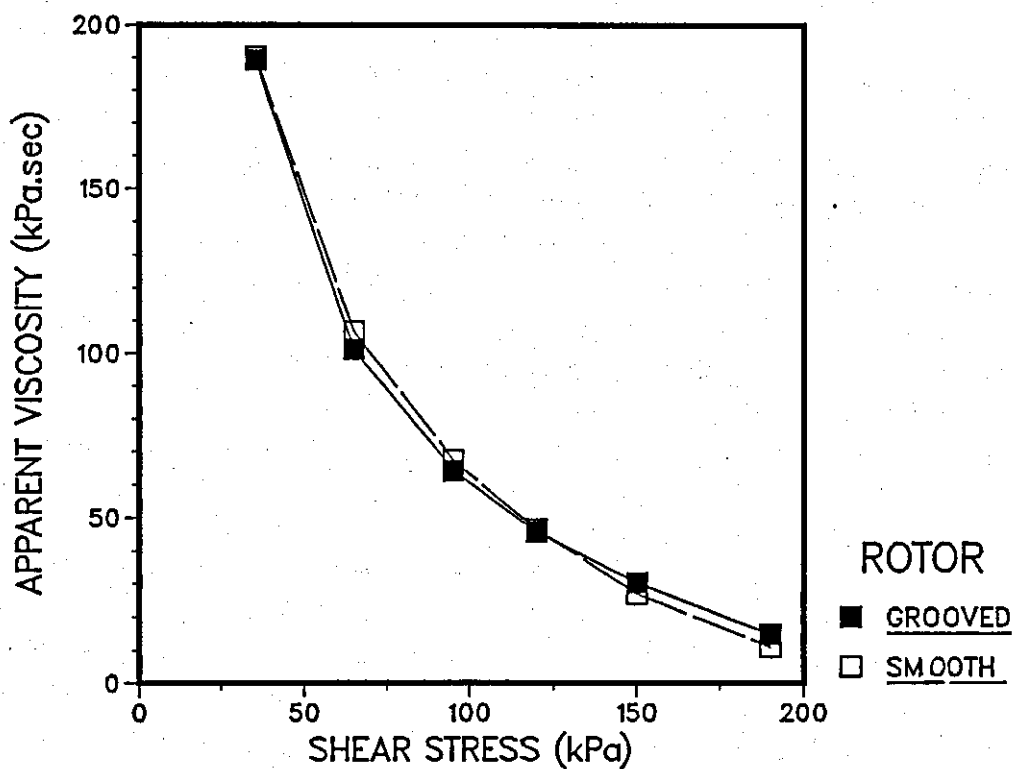


FIGURE 7.19: Apparent viscosity versus shear stress for EPDM at 1.5 phr STRUKTOL A50P using smooth and grooved rotors (Section 7.5.3)

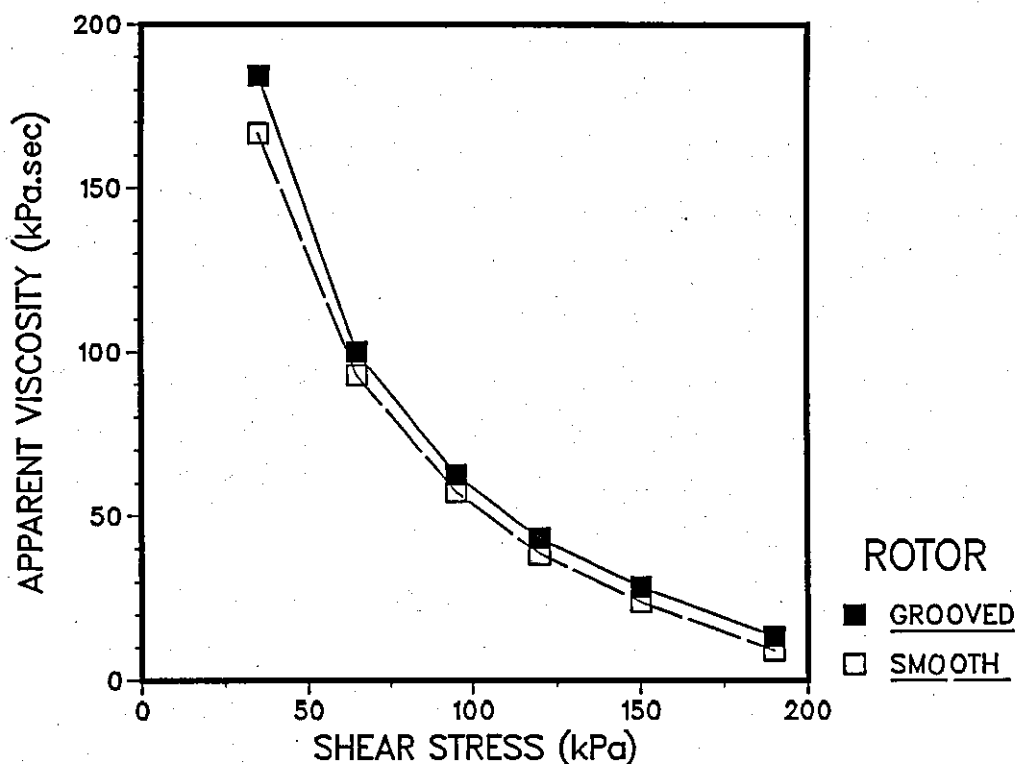
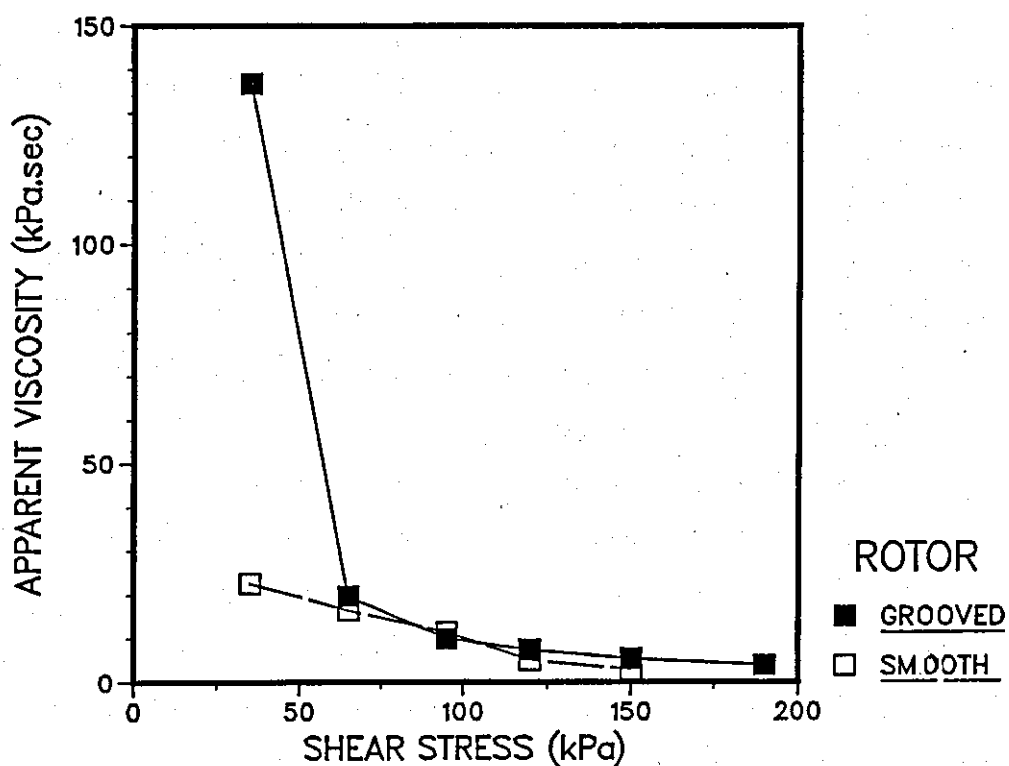


FIGURE 7.20: Apparent viscosity versus shear stress for EPDM at 4 phr STRUKTOL A50P using smooth and grooved rotors (Section 7.5.3)



apparent viscosities. This could imply that partial external lubrication (Section 6.2.1.1.) was occurring, but the effect was insignificant and within experimental error. At 4 phr lubricant, the results obtained with the grooved and the smooth rotors at 35 kPa shear stress show a large difference (~ 83%) in their apparent viscosities indicating that a thin lubricating film had developed at the smooth rotor's surface, decreasing the measured apparent viscosity considerably. At higher shear stress (> 65 kPa) the two rotors showed similar results. The large decrease in the apparent viscosity, when the shear stress was increased from 35 to 65 kPa and the consistency of the results with those obtained with the smooth rotor at higher shear stresses appeared to indicate that external lubrication had developed with the grooved rotor in one of the following ways:

- i) A thin lubricating film had developed between two layers of elastomer in the test sample.
- ii) A lubricating film thicker than the grooves on the rotor's surface had developed (Figure 7.21.).
- iii) A lubricating film had developed at the rotor's surface and over the elastomer within the grooves (Figure 7.22.).

The observations made on samples removed from the rheometer at the end of the experiments carried out on EPDM containing 4 and 7 phr lubricant appeared to support the third explanation. In this case, the presence of the grooves on the rotor's surface served only to shift the position of the critical concentration " C_r " at which external lubrication occurred from $1.5 < C_r < 4$ phr to $4 < C_r < 7$ phr lubricant for shear stresses less than 65 kPa.

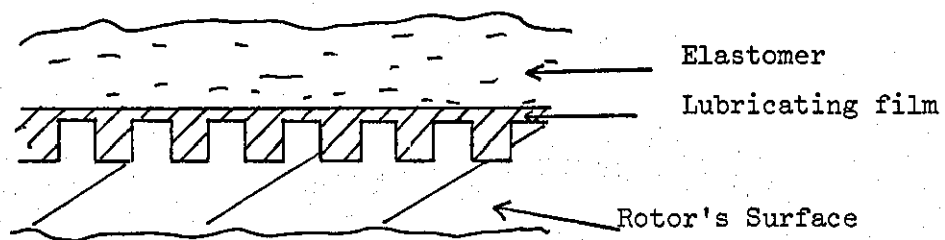


Figure 7.21 : Lubricating film thicker than grooves on rotor's surface.

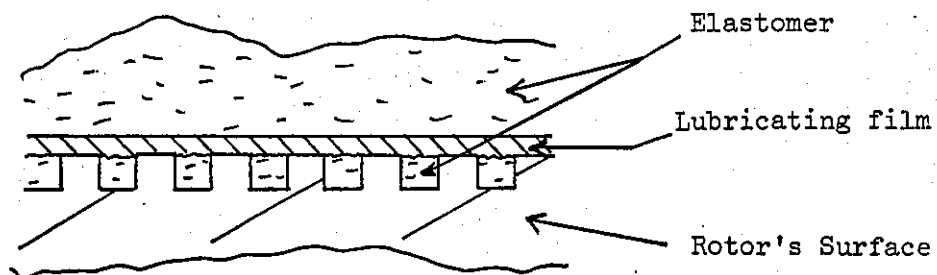


Figure 7.22: Lubricating film on grooved rotor's surface with grooves filled with elastomer.

To summarise, the lubricant Struktol A50P was internally lubricating the test sample with 0.5 and 1.5 phr, but was externally lubricating it at 4 and 7 phr lubricant. No increase in the apparent viscosity due to chain extension/cross-linking was observed as was the case when Struktol A50P was added to the natural rubber compound (Section 5.3.). This could be due to any of the reasons mentioned for the natural rubber compound, but it was becoming more and more evident that the lubricant Struktol A50P did not react with elastomers.

A reason why external lubrication was observed with Struktol A50P and not with WB212 could be attributed to the fact that A50P and WB212 are blends of different materials, with A50P having more incompatible constituents than WB212, which makes it more able to develop a film at the interface (Section 6.2.1.1.).

7.5.4. Struktol WB16 with Raw EPDM

The results obtained for EPDM containing different levels of lubricant Struktol WB16 (0, 0.25, 0.75, 1.5 and 4 phr) using the TMS rheometer at 100°C with the grooved and smooth rotors are plotted in Figures 7.23. and 7.24. respectively. The two plots show similar results where a small increase in the apparent viscosity was observed at 0.5 and 1.5 phr lubricant followed by a small, almost unnoticeable decrease with further additions.

In this case, the highly compatible lubricant Struktol WB16 (Section 7.5.1.) was acting as a solvent (Section 6.2.1.2.). The lubricant molecules had very high attractive forces to some of the

FIGURE 7.23: Apparent viscosity versus lubricant concentration for STRUKTOL WB16 In raw EPDM (Section 7.5.4)

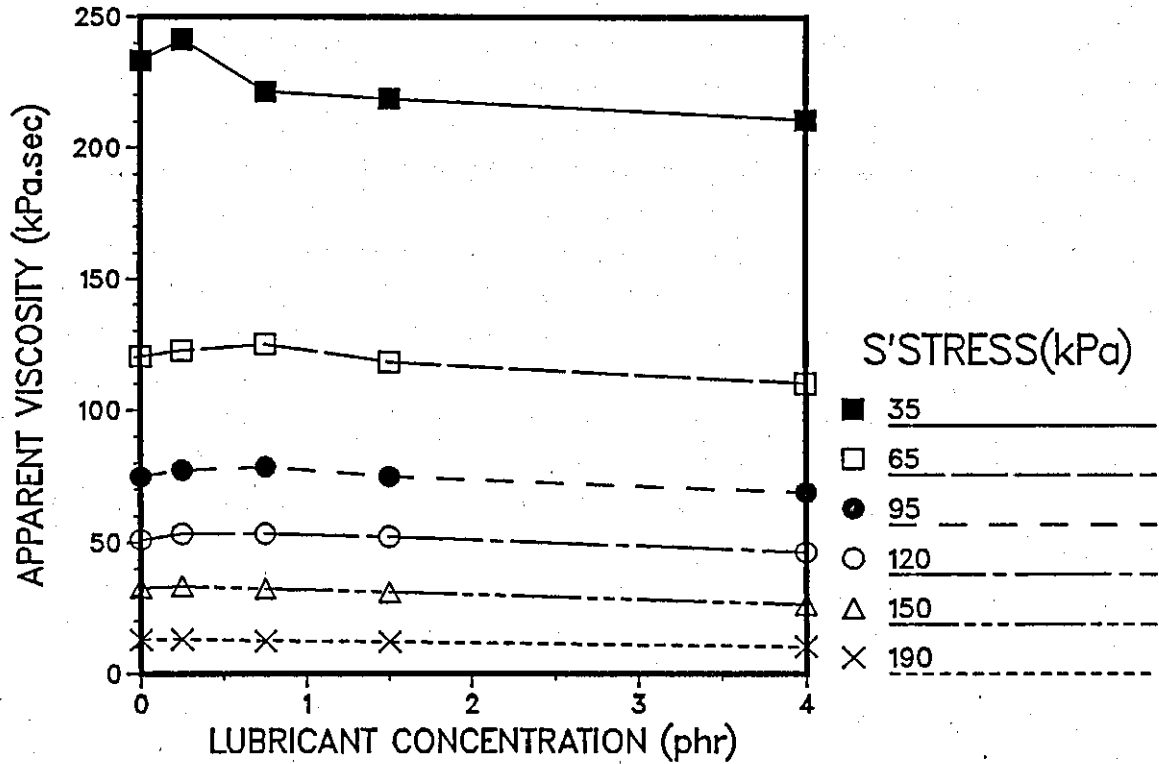
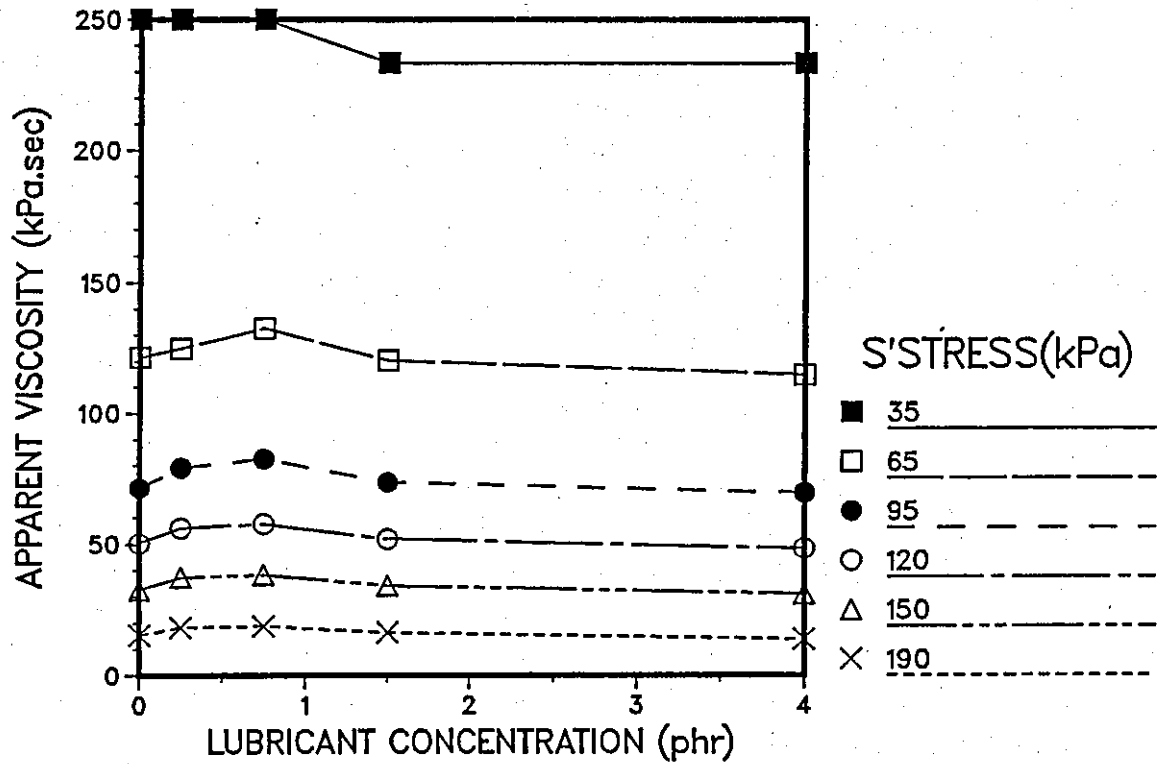


FIGURE 7.24: Apparent viscosity versus lubricant concentration for STRUKTOL WB16 In EPDM (Section 7.5.4)



sites on the elastomer chain offering a large attraction force to neighbouring elastomer chains, therefore not affecting the flow behaviour of the test sample. The effect of solvation can only be felt with large concentrations of lubricants, where disentanglement will occur as a result of swelling.

At 0.5 and 1.5 phr lubricant, a small increase in the apparent viscosity was observed. This indicated that chain extension/cross-linking was occurring due to the presence of the lubricant, as was the case for Struktol WB16 with the natural rubber compound (Sections 5.1. and 5.2.).

7.6. CHAIN EXTENSION/CROSS-LINKING EVALUATION BY SOLVENT

SWELLING MEASUREMENTS

In order to check the occurrence of a chemical reaction with the three process aids (Struktol WB212, WB16 and A50P) and EPDM, an attempt was made to obtain GPC traces of the compounds in the manner described in Section 4.2.3. The attempt failed for the following reasons:

- i) The solvent used by the GPC equipment (THF) was unable to dissolve the EPDM completely at room temperature. After occasional heating of the solution, complete dissolution of the EPDM was attained.
- ii) When injected into the column the pressure gradient across the column started to build-up, indicating a blockage in the column.
- iii) The results obtained at the end of the run showed a wide and unsymmetric distribution curve, making the detection of chain

extension/cross-linking in the manner observed with chlorosulphonated polyethylene (Section 5.6.) impossible.

While trying to dissolve a small amount of EPDM containing different levels of Struktol WB212 in THF for the gel permeation chromatography experiment, it was noticed that it was becoming increasingly difficult to dissolve the sample as the lubricant concentration increased. To verify this observation, the swelling test described in Section 4.2.4. was carried out on samples of EPDM containing different levels of Struktol WB212, A50P and WB16. The experiments were repeated three times on each of the samples. The results obtained were very scattered, but a trend could still be distinguished. The results were plotted as percent weight increase (% swelling) versus lubricant concentration and hand fitted curves were drawn to the observed trends in Figures 7.25., 7.26. and 7.27. respectively.

The results obtained for EPDM containing Struktol WB212 and WB16 show a decrease in the % swelling of the test sample with increasing lubricant concentrations. On the other hand, no change was observed due to the presence of Struktol A50P. This appears to be consistent with the observations made with the TMS rheometer on EPDM (Sections 7.5.2., 7.5.3. and 7.5.4.) and on the natural rubber compounds (Sections 5.1., 5.2. and 5.3.), where Struktol WB212 appeared to be the most reactive lubricant followed by WB16. The lubricant Struktol A50P did not show any increase in the apparent viscosity of the compounds used suggesting that it is inert in this respect.

FIGURE 7.25: %Swelling of EPDM in tetrachloroethane versus STRUKTOL WB212 concentration (Section 7.6)

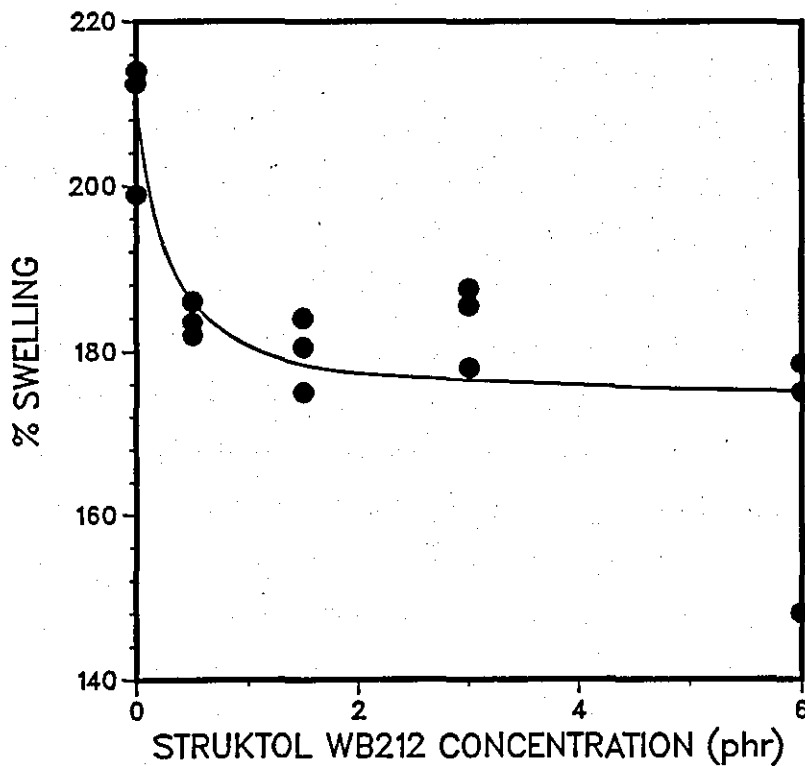


FIGURE 7.26: %Swelling of EPDM in tetrachloroethane versus STRUKTOL A50P concentration (Section 7.6)

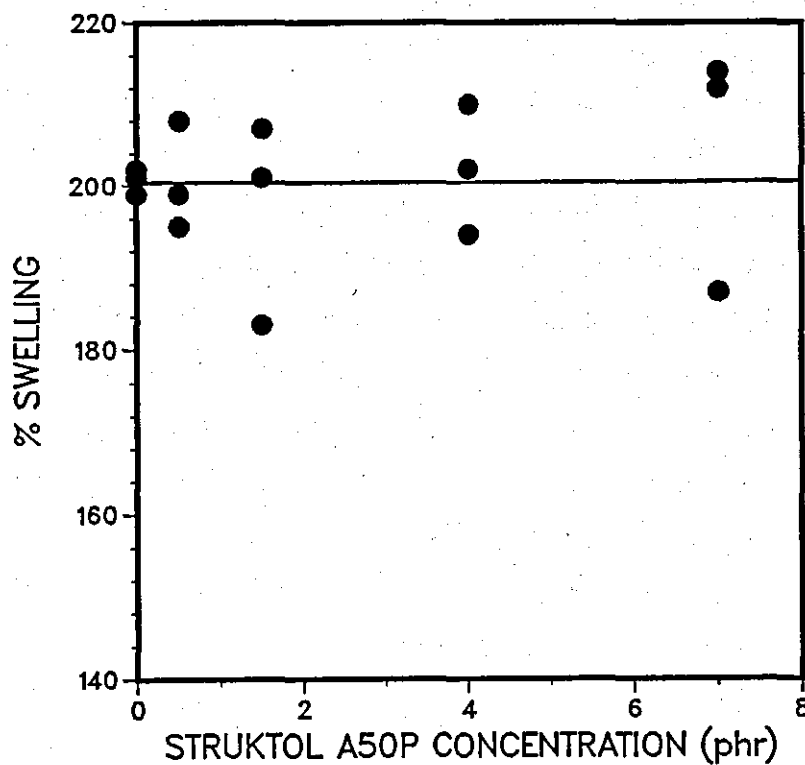


FIGURE 7.27: %Swelling of EPDM in tetrachloroethane versus STRUKTOL WB16 concentration (Section 7.6)

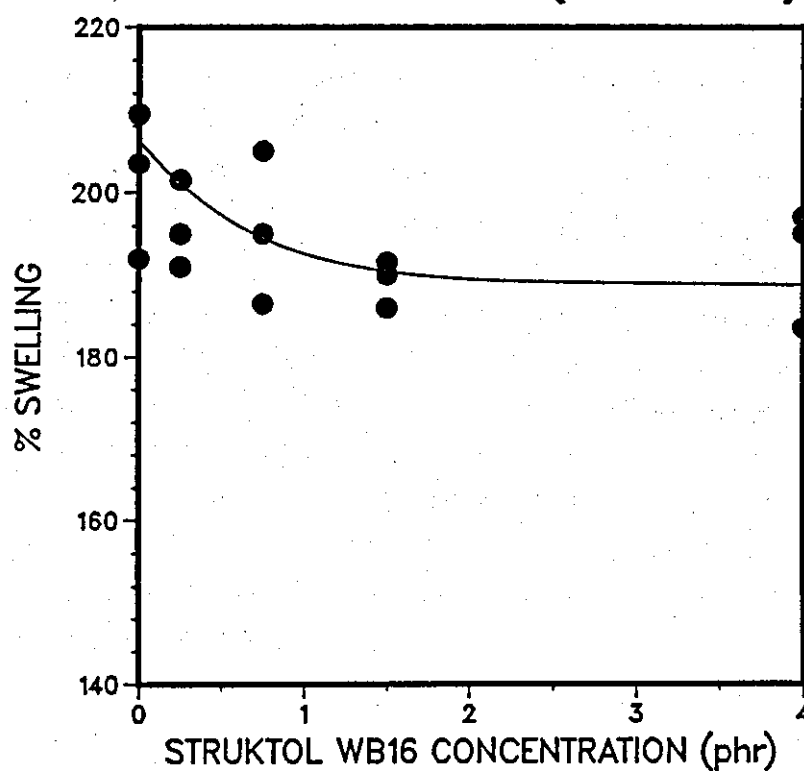
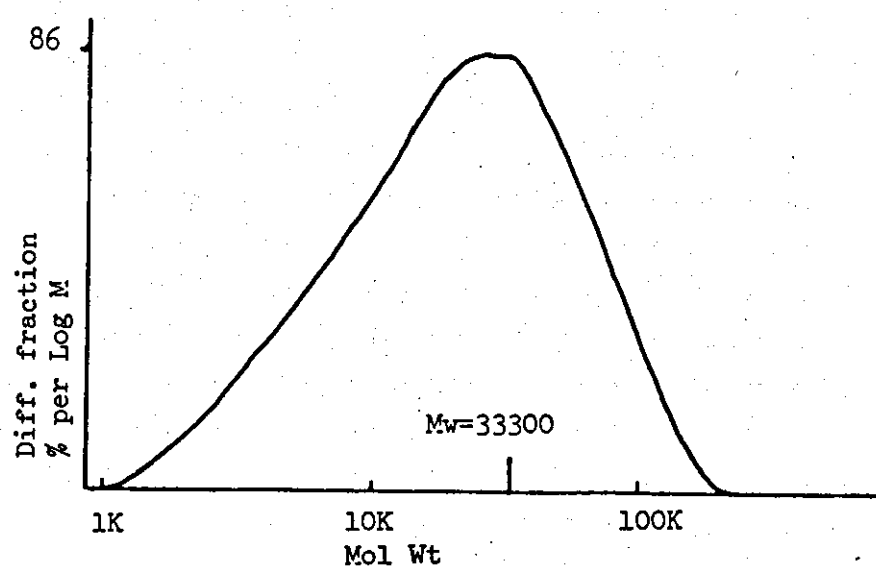


FIGURE 7.28: GPC trace for polyisobutylene grade LM-MS-LC (Section 7.7.1)



7.7. INVESTIGATION OF THE EFFECT OF ELASTOMER MORPHOLOGY ON LUBRICANT ACTION

7.7.1. Molecular Weight Distribution of Test Samples

In order to study the modes of action of lubricants on elastomer compounds of different morphologies, four grades of polyisobutylene from Exxon (Section 4.3.1.1.) were mixed with different levels of lubricant Struktol WB212 (0, 0.5, 1.5, 3 and 6 phr) in the Brabender Plastograph (Section 4.3.2.). The temperature in the mixing chamber was controlled at 100°C and the rotor speed was set to 55 rev/min. The mixing time was two minutes.

The four grades of polyisobutylene had different molecular weight ranges, which were supplied by the manufacturers (Table 4.1.). In order to obtain a better understanding of their molecular weight distributions, gel permeation chromatography (Section 4.2.3.) traces were obtained for the two lower molecular weight polyisobutylene grades, LM-MS-LC and LM-MH-LC (Figures 7.28. and 7.29. respectively). Attempts to obtain GPC traces for the other two grades (MM-L80 and MM-L100) failed because, after injecting the elastomer solutions into the column, a pressure build-up was observed across the column, indicating blockage of the pores in the matrix.

The two traces obtained (Figures 7.28. and 7.29.) show similar characteristics with the only difference being that the one obtained for the grade LM-MH-LC has generally higher molecular weight.

FIGURE 7.29 : GPC trace for polyisobutylene grade LM-MH-LC (Section 7.7.1)

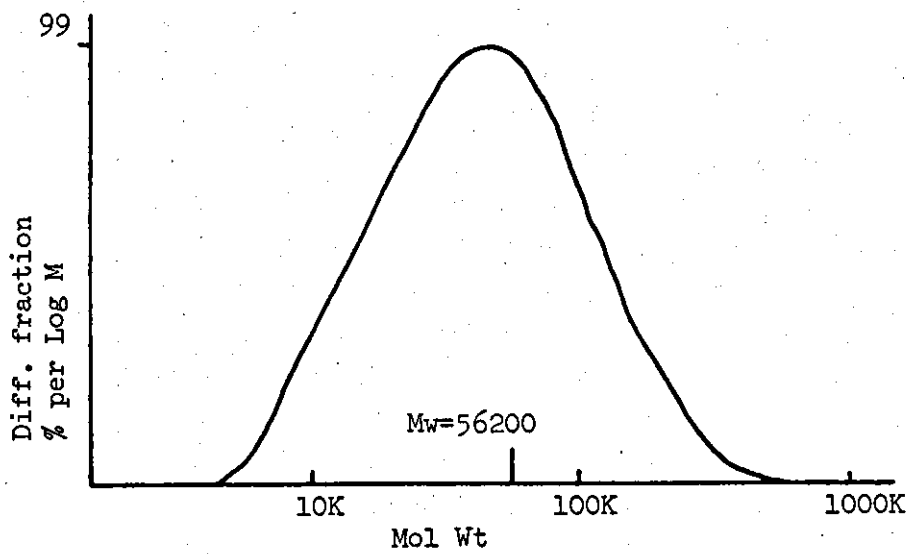
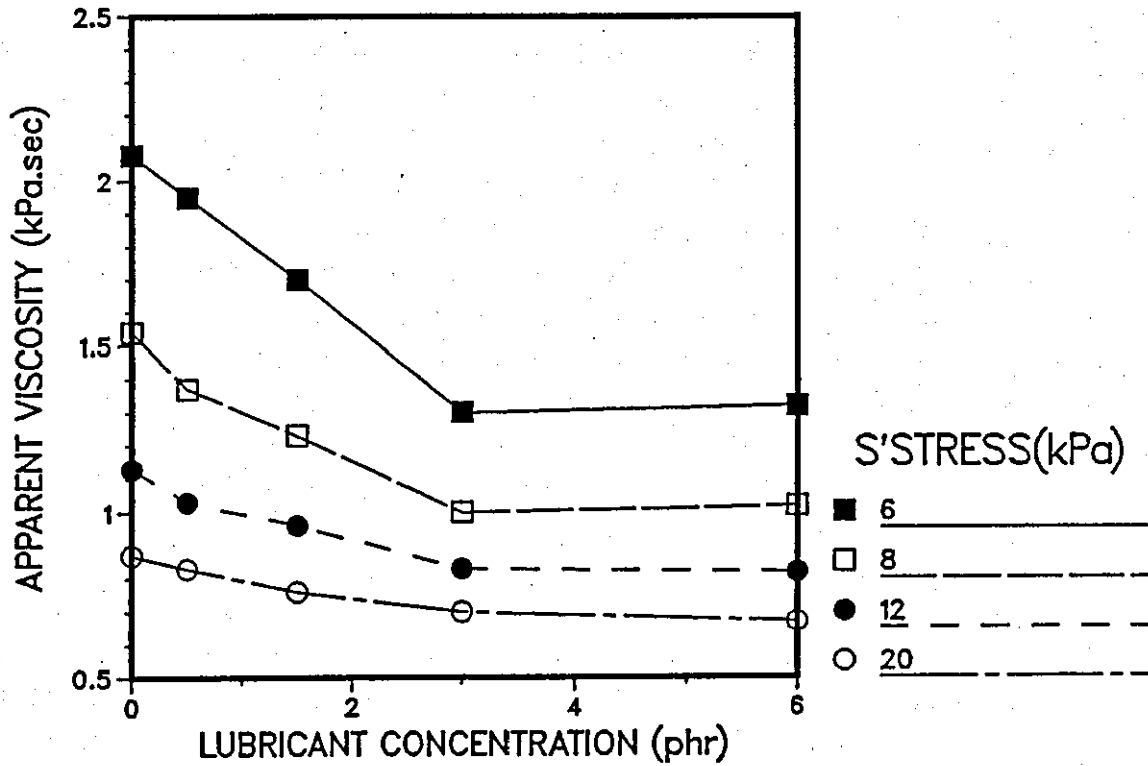


FIGURE 7.30: Apparent viscosity versus lubricant concentration for STRUKTOL WB212 in polyisobutylene grade LM-MS-LC (Section 7.7.2)



7.7.2. Mode of Action of Lubricants on Liquid Polyisobutylene

The TMS rheometer was used at 100°C with the grooved rotor to determine the apparent viscosity versus lubricant concentration relationship for the two liquid polyisobutylene grades, LM-MS-LC and LM-MH-LC, containing different levels of lubricant Struktol WB212. After repeating the experiment three times the results were plotted in Figures 7.30. and 7.31. respectively.

The two grades showed a large difference in their response to lubricant additions. The lower molecular weight sample showed a gradual decrease in the apparent viscosity with increasing lubricant concentration, whereas the higher molecular weight sample (LM-MH-LC) showed an increase with the first two additions of lubricant (0.5 and 1.5 phr), followed by a decrease with 3 phr lubricant where the apparent viscosity appeared to have stabilized.

The increase in apparent viscosity observed with the grade LM-MH-LC can be attributed to chain extension/cross-linking (Section 6.2.3.) brought about by a chemical reaction between the lubricant and elastomer. Since there are no differences in the chemical composition of the two grades studied, the difference in the response observed can only be attributed to their molecular weight distributions (Section 7.7.1.).

It can be seen from the GPC traces of the samples (Figures 7.28. and 7.29.) that the higher viscosity polyisobutylene contains higher molecular weight chains that do not exist in the lower viscosity

FIGURE 7.31: Apparent viscosity versus lubricant concentration for STRUKTOL WB212 in polyisobutylene grade LM-MH-LC (Section 7.7.2)

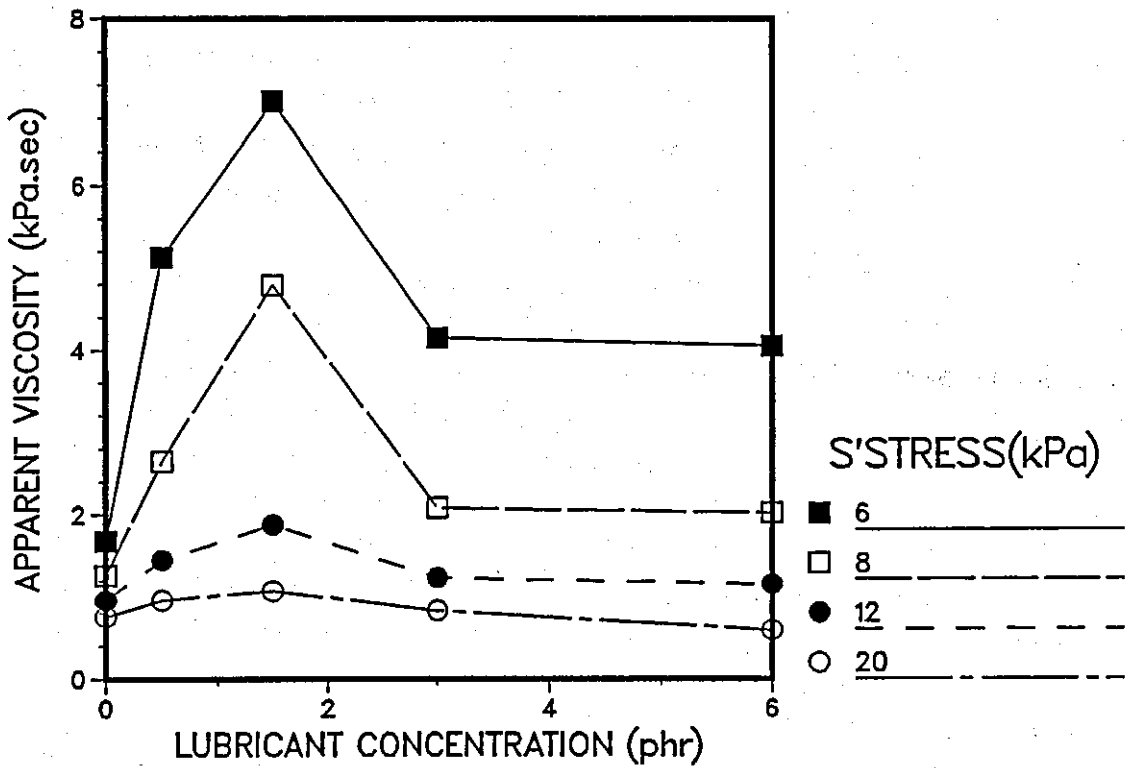
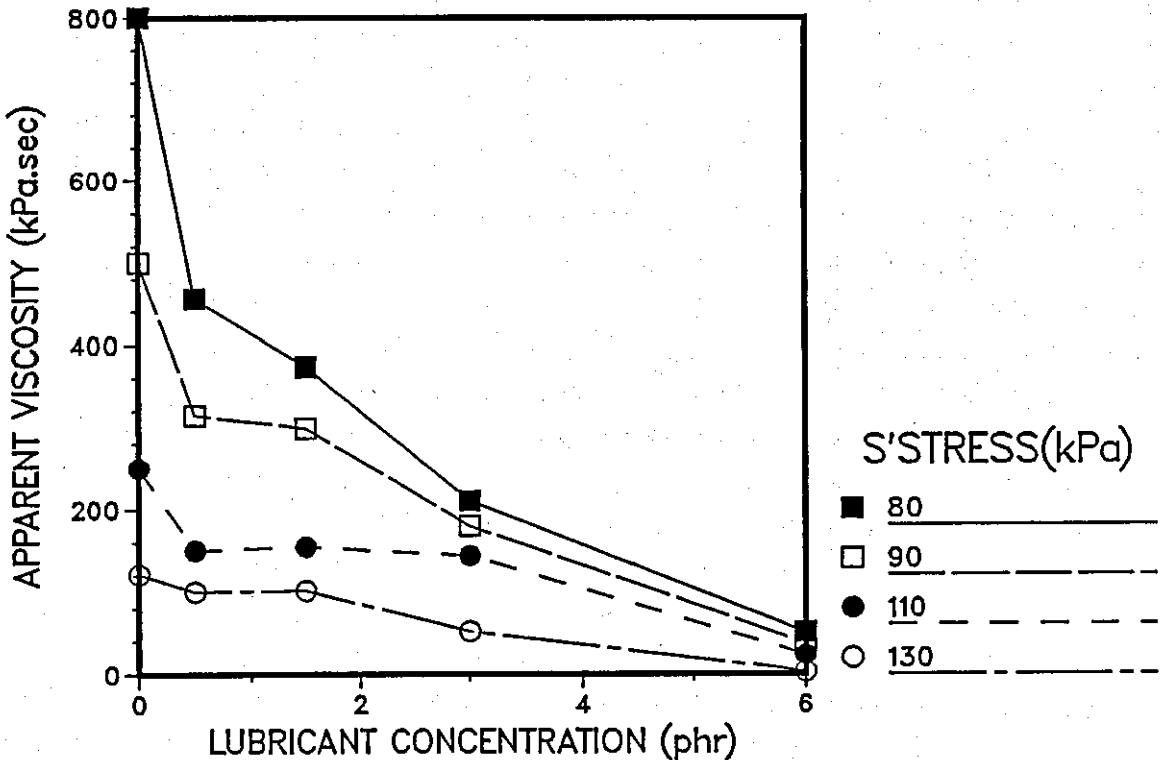


FIGURE 7.32: Apparent viscosity versus lubricant concentration for STRUKTOL WB212 in polyisobutylene grade MM-L80 (Section 7.7.3)



material. A possible explanation for not observing an increase in the lower molecular weight grade of polyisobutylene would be that even though chain extension/cross-linking was occurring, it was not enough to affect the flow of the sample. In the higher molecular weight polyisobutylene case the chain extension/cross-linking effect of the chemical reaction affected the entanglement ratio of the sample enough to increase its resistance to flow.

7.7.3. Modes of Action of Lubricants on Solid Polyisobutylene

A set of three experiments was carried out on each of the two solid polyisobutylene grades, MM-L80 and MM-L100 (Figures 7.32. and 7.33. respectively). A large inconsistency was observed with the results obtained for the high molecular weight polyisobutylene grade MM-L100. This was attributed to the onset of melt fracture (Section 2.3.) indicating that grade MM-L100 was unprocessable under the test conditions of the experiment. To make this argument clearer, the observed apparent viscosities obtained at 0 phr lubricant for grade MM-L100 were about five times lower than those obtained for the lower molecular weight MM-L80. This drop in the apparent viscosity was due to the crumbing of the MM-L100 sample inside the test chamber. This was observed at the end of each of the experiments carried out on grade MM-L100.

The results obtained for grade MM-L80 (Figure 7.32.) showed a large decrease in the apparent viscosity of the test sample (~ 45%) with a small addition of lubricant (0.5 phr) followed by a smaller decrease with 1.5 phr lubricant. At 3 and 6 phr lubricant the results

FIGURE 7.33: Apparent viscosity versus lubricant concentration for STRUKTOL WB212 in polyisobutylene grade MM-L100 (Section 7.7.3)

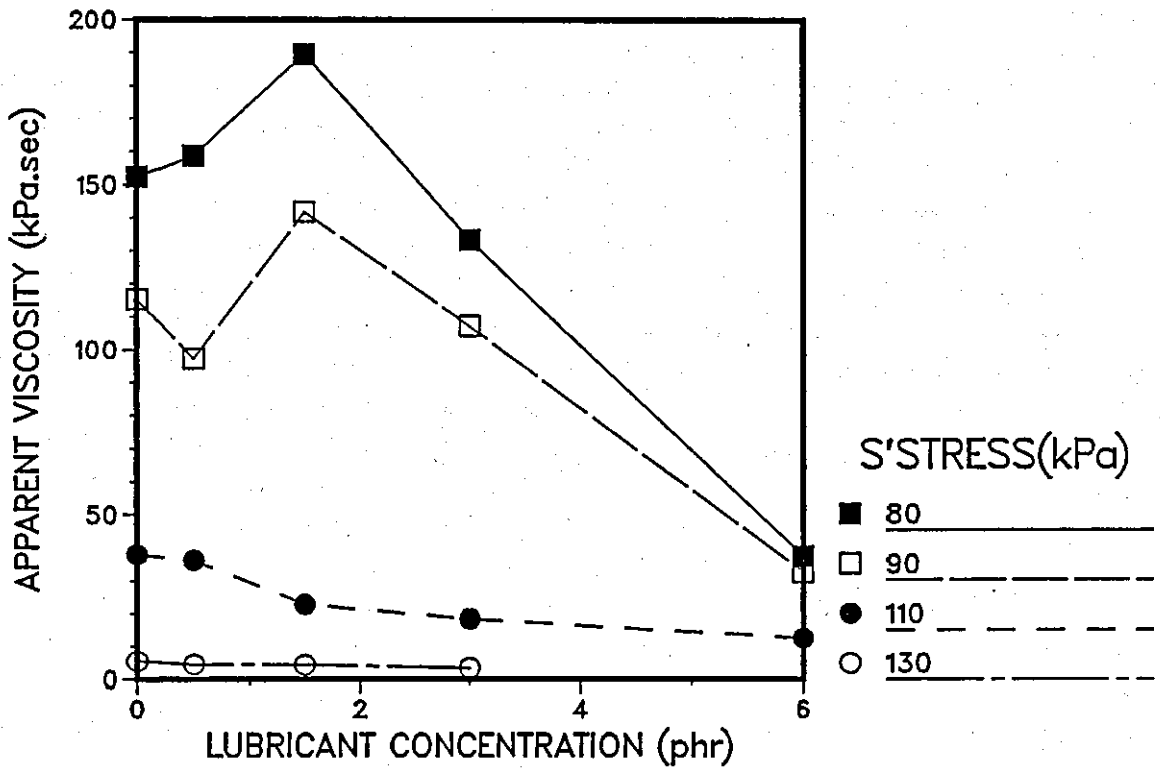
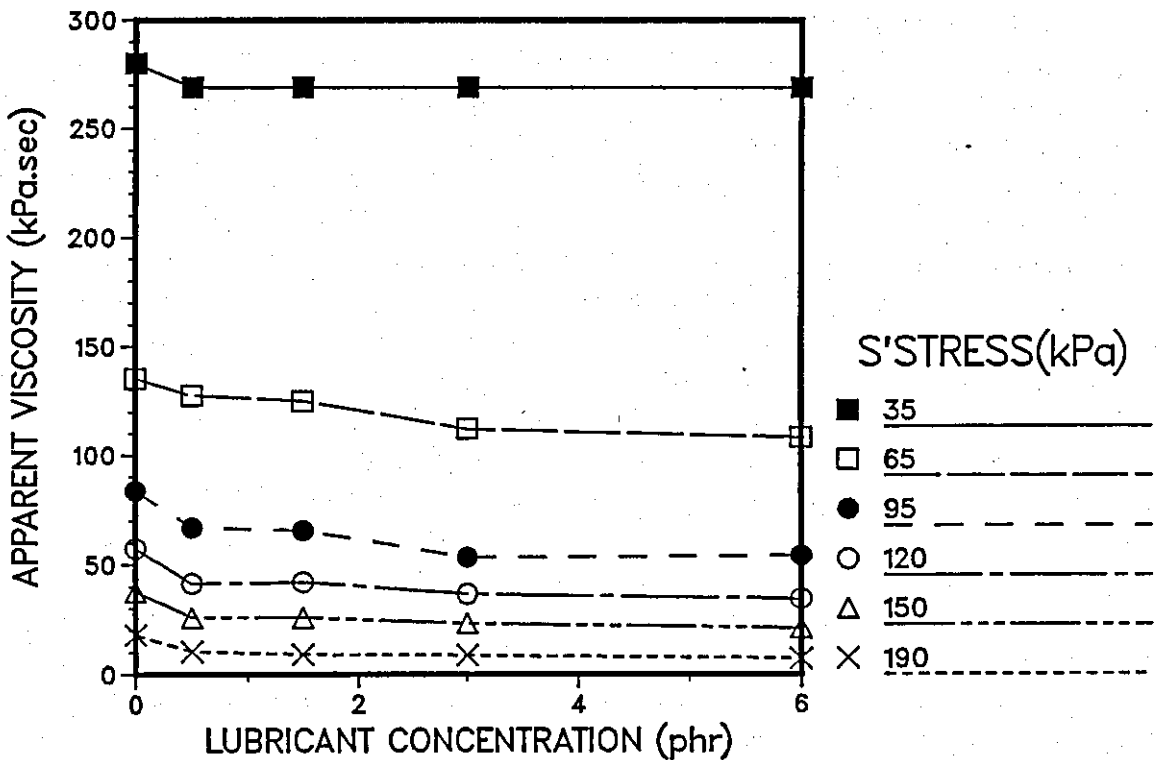


FIGURE 7.34: Apparent viscosity versus lubricant concentration for Sodium Oleate in raw EPDM (section 7.8.1)



collected during the three repetitions of the experiment were very inconsistent and the decrease was attributed to external lubrication (Section 6.2.1.1.), where a thin lubricating film had developed on the surface of the grooved rotor after the grooves on the rotor's surface have been filled with the elastomer (figure 7.7).

The difference in the response observed for the three grades LM-MS-LC (Figure 7.30.), LM-MH-LC (Figures 7.31.) and MM-L80 (Figure 7.32.) to additions of lubricant Struktol WB212 can be explained if the morphology of the samples is taken into consideration. The morphology of the lowest grade of liquid polyisobutylene can be described as comprising of a low concentration of small flow units since it is made up of low molecular weight elastomer chains, where entanglement is less likely to occur. The morphology of the solid polyisobutylene grade (MM-L80), on the other hand, will have a much higher entanglement concentration since it is made of higher molecular weight elastomer chains which are more prone to entanglement. This will encourage the formation of flow units (Section 6.2.2.). The size of the flow units will determine the intensity of the drop in the apparent viscosity observed at the first additions of lubricant. The high molecular weight liquid grade polyisobutylene (LM-MH-LC) appeared to be in the critical region where a small increase in the molecular weight of the sample will affect its mode of flow to a large extent.

At 0.5 phr lubricant the two grades LM-MS-LC and MM-L80 showed a decrease in the apparent viscosity due to internal lubrication. In the first case (Figure 7.30.), the lubricant was acting on individual molecules masking some of the attraction sites and reducing flow

resistivity. In the second case (Figure 7.32.), on the other hand, the lubricant was acting on clusters of elastomer chains entangled into flow units. A small concentration of lubricant (0.5 phr) was needed in this case to decrease the apparent viscosity considerably (~45%) by facilitating the rotation of the flow units. The increase in the chain length of some of the elastomer molecules of grade LM-MS-LC, due to chain extension/cross-linking, was not sufficient to increase the entanglement in the elastomer to a degree where it would affect its mode of flow in the manner observed with grade LM-MH-LC (Figure 7.31.). In the case of the highly entangled grade MM-L80, a small increase in the entanglement ratio gave little change to the structure of the already highly entangled sample, and any effect resulting from it was suppressed by the lubricating action of Struktol WB212.

7.8. INVESTIGATION OF THE MODES OF ACTION OF PURE FATTY

ACID DERIVATIVES

In order to fully understand the effect of a lubricant's chemical structure on its mode of action on elastomers and elastomer compounds, several factors should be taken into consideration: The lubricant's chemical composition, its chain length, the branching of its molecules, its saturation degree, etc... This will require a long and detailed study of the lubricant and the elastomer it will be used with, taking into consideration the various factors affecting the lubricant's mode of action. This is beyond the scope of this study.

A small step into this direction was made in this study by examining the effect of three straight chain saturated fatty acid zinc

salts of different chain lengths and a sodium salt derivative of an unsaturated straight chain fatty acid on the rheological behaviour of EPDM. When tested for compatibility with EPDM (Section 7.5.1.), the four fatty acid salts (Sodium Oleate, Zinc Hexanoate, Zinc Decanoate and Zinc Stearate) (Section 4.3.1.2.) were found to be insoluble in any of the solvents that either dissolved or swelled EPDM indicating that the lubricants and elastomer were of very low compatibility with each other.

7.8.1. The Effect of Sodium Oleate on the Rheology of EPDM

Different levels of fatty acid derivative, Sodium oleate (Section 4.3.1.2.), were incorporated in raw EPDM using the Brabender Plastograph at 100°C. The rotor's speed was set to 55 rev/min. The mixing time was two minutes.

The apparent viscosity versus lubricant concentration relationship was measured using the TMS rheometer at 100°C with the grooved rotor. The results obtained (Figure 7.34.) show a small decrease in the apparent viscosity at 0.5 phr lubricant followed by no further change with further additions.

The decrease in the apparent viscosity at 0.5 phr lubricant can be attributed to internal lubrication, where a small number of attraction sites on the EPDM chains were compatible with the sodium salt which acted on them by masking their effect. This had very little effect on the apparent viscosity of the test sample due to the limited number of compatible sites on the EPDM molecules. The excess lubricant in this

case, instead of exuding to the rubber/metal interface to act as an external lubricating film (Section 6.2.1.1.), was entrapped in the elastomer as an inert filler since the test temperature (100°C) was lower than its melting point (235°C). In order to make sure that the grooved rotor was not inhibiting the occurrence of external lubrication, the smooth rotor was used with the same sample under the same conditions. The results obtained were identical to those obtained with the grooved rotor, within experimental error, confirming that no external lubrication was occurring.

7.8.2. The effect of Zinc Decanoate on the Rheology of EPDM

Zinc decanoate was incorporated into EPDM in different levels (0, 0.5, 1.5, 3 and 6 phr) using the Brabender Plastograph at 100°C. The rotor's speed was set to 55 rev/min and the mixing time was two minutes.

The results obtained using the TMS rheometer at 100°C with the grooved rotor were plotted in Figure 7.25. The plots show a decrease in the apparent viscosity at 0.5 phr lubricant followed by an increase with the low shear stress and a levelling with the higher shear stresses. Even though the elastomer and zinc decanoate were found to be incompatible, there exists a number of attraction sites on the elastomer which will attract some of the zinc decanoate molecules. These will mask the ability of the attraction sites to resist flow, thus reducing the apparent viscosity of the test sample. This was observed at 0.5 phr lubricant where a drop in the apparent viscosity occurred. At higher lubricant concentration the excess lubricant,

FIGURE 7.35: Apparent viscosity versus lubricant concentration for Zinc Decanoate In raw EPDM (Section 7.8.2)

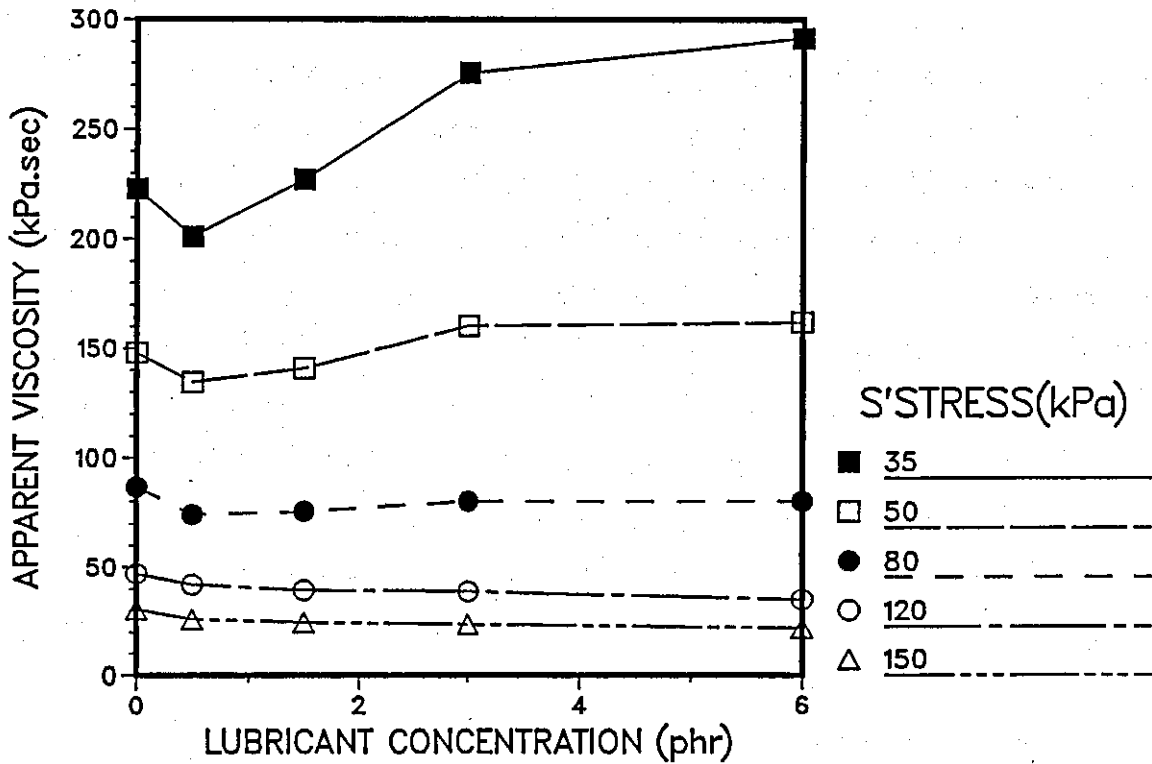
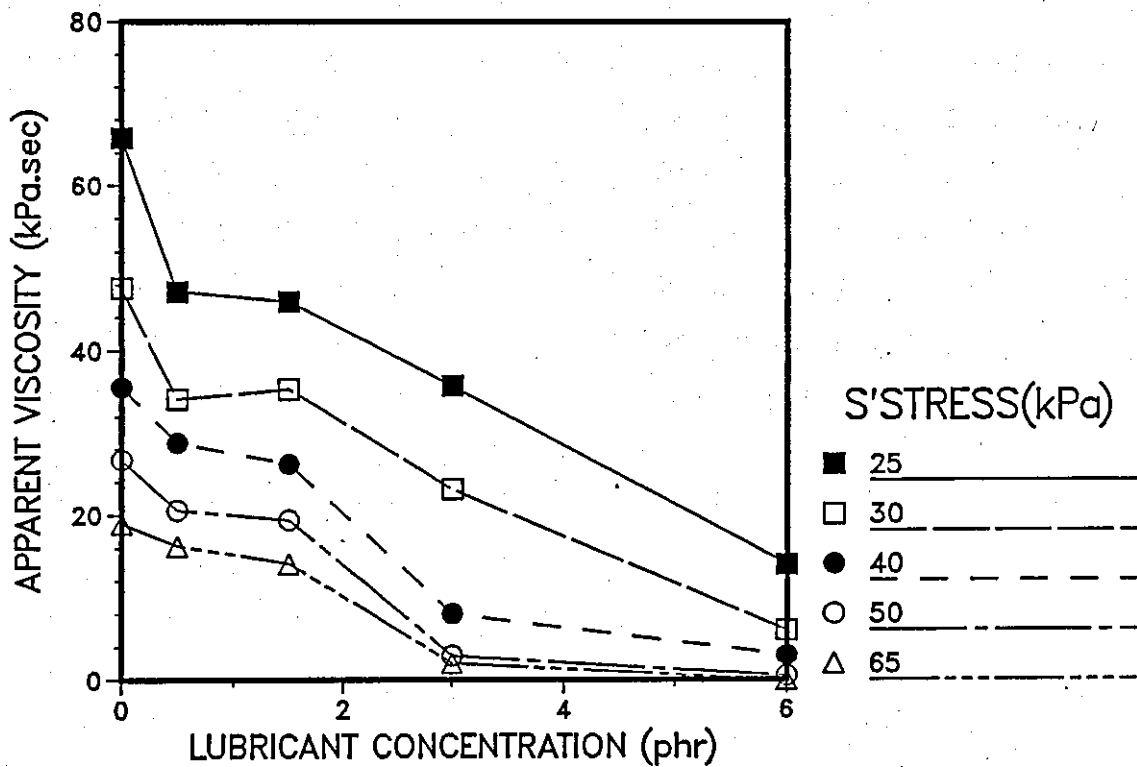


FIGURE 7.36: Apparent viscosity versus lubricant concentration for Zinc Decanoate In raw EPDM at 150°C (Section 7.8.2)



which was in its solid state since its melting point (136.9°C) was higher than the test temperature, was acting as a reinforcing filler, which increased the apparent viscosity of the compound. The plots obtained at higher shear stresses did not show the reinforcing effect of the solid lubricant, probably due to the fact that at high shear stresses the temperature in the test cavity was higher than expected due to shear heating, thus melting the solid lubricant particles (Section 4.4.1.).

Another set of test samples of EPDM containing different levels of zinc decanoate was mixed in the same manner as the previous set, but this time the mixing temperature was 150°C . The results obtained using the TMS rheometer at 150°C with the grooved rotor were plotted in Figure 7.36. In this case, the reinforcing effect observed with the results obtained at 100°C had disappeared completely. The plots show a decrease in the apparent viscosity of the elastomer at 0.5 phr which was attributed to internal lubrication. At higher concentrations (1.5 phr lubricant) the few attraction sites on the elastomer chains compatible with the lubricant were already masked and zinc decanoate was not affecting the rheology of the test sample in any way. At 3 phr lubricant, the excess lubricant exuded to the rubber/metal interface after some of the elastomer had filled the grooves on the rotor (Figure 7.6.) and external lubrication had developed. This was noted at the end of each experiment when the test cavity was cleaned.

Comparison of the lubricating ability of zinc decanoate at 100°C (Figure 7.35.) with that of sodium oleate (Figure 7.34.) at 0.5 phr lubricant showed no significant differences between them.

7.8.3. The Effect of Zinc Hexanoate and Zinc Stearate on the Rheology of EPDM

Different levels of zinc hexanoate and zinc stearate (0, 0.5, 1.5, 3 and 6 phr) were incorporated into EPDM in the Brabender Plastograph at 150°C. The rotor speed was 55 rev/min and mixing time was two minutes. The results obtained with the TMS rheometer at 150°C with the grooved rotor are plotted in Figure 7.37. and 7.38. respectively. The plots show similar trends to those observed with zinc decanoate at 150°C (Figure 7.36.) indicating that the same mechanisms apply.

A comparison between the results obtained with the three zinc salts at 0.5 phr lubricant concentration appeared to indicate that the most effective internal lubricant of them was zinc decanoate followed by zinc hexanoate with zinc stearate being the least efficient. The observations made with all the pure fatty acid derivatives did not provide enough information for a correlation to be made in this respect. More work is needed in this direction before any firm conclusions can be drawn.

FIGURE 7.37: Apparent viscosity versus lubricant concentration for Zinc Hexanoate In raw EPDM at 150°C (Section 7.8.3)

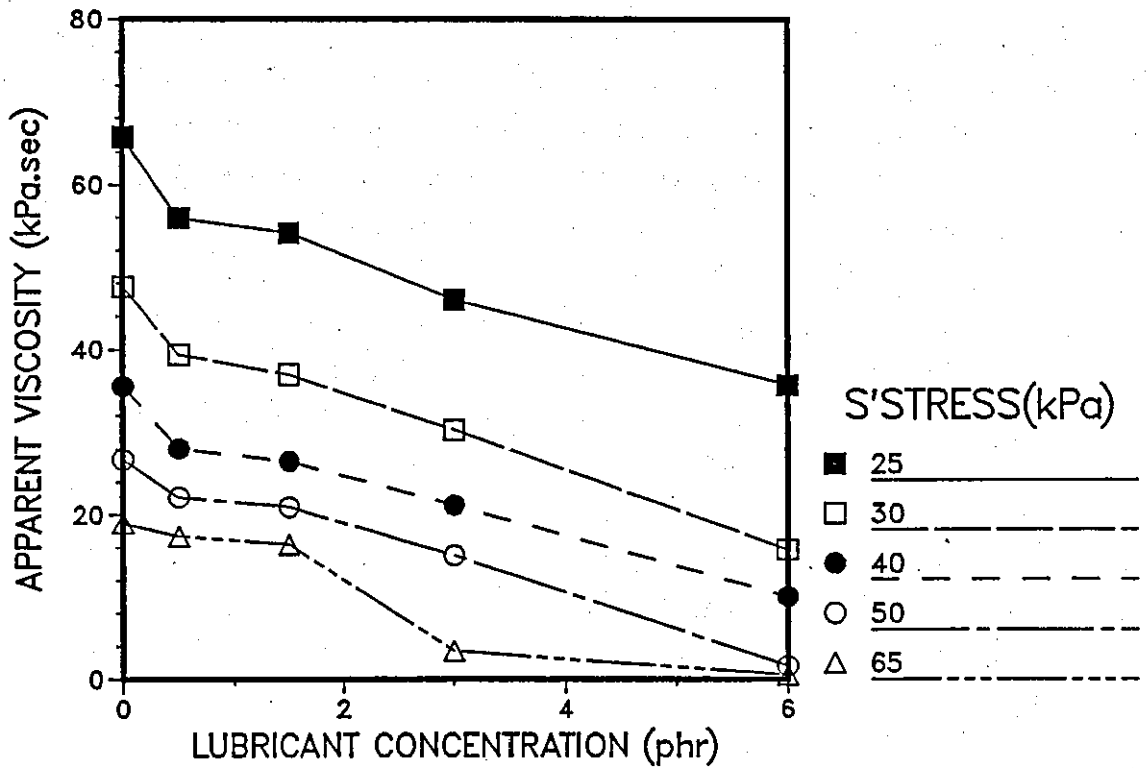
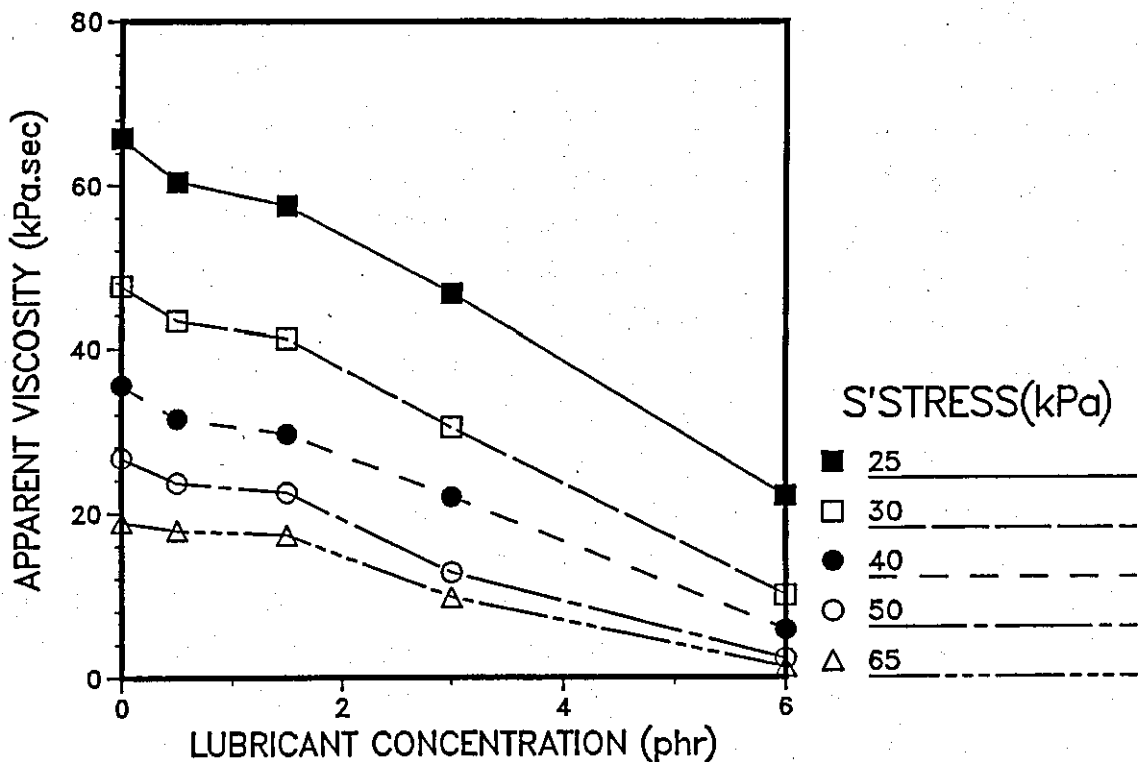


FIGURE 7.38: Apparent viscosity versus lubricant concentration for Zinc Stearate In raw EPDM at 150°C (Section 7.8.3)



7.9. INVESTIGATION OF THE EFFECT OF FILLERS, PROCESS OILS AND OTHER ADDITIVES ON THE MODES OF ACTION OF LUBRICANTS

The results obtained throughout this study showed a definite change in the mode of action of lubricants with the change in the composition of the elastomer compound. The results obtained for compounded and raw chlorosulphonated polyethylene samples (Figures 5.5. and 5.6. respectively) showed only a small shift in the position of chain extension/cross-linking effect due to the addition of carbon black and process oil. A more pronounced difference was observed between the results obtained for raw natural rubber (Figure 7.10.) and a natural rubber compound (Compound 1 (Section 4.3.3.)), containing the same lubricant Struktol WB212 (Figure 5.4.). Another set of natural rubber compound test samples (Compound 3 (Section 4.3.3.)) containing all the ingredients of a compound typical of those found in the rubber industry was mixed in the manner described in Section 4.3.4.2. (iii). The lubricant Struktol WB212 was then incorporated into the compound in different levels (0, 0.5, 1.5, 3 and 6 phr) on the Brabender Plastograph for two minutes at a rotor speed of 55 rev/min and mixing temperature of 100°C. The results obtained with the TMS rheometer at 100°C with the grooved rotor were plotted in Figure 7.39. The results obtained show the same modes of action observed with the previous natural rubber compound, (Compound 1 (Section 4.3.3.)), studied in Section 7.2.1. Internal lubrication of the test sample was interrupted at 1.5 phr lubricant by chain extension/cross-linking. The presence of fillers, process oils and other ingredients had shifted the critical concentration " C_c " (Section 6.2.3.) at which the

FIGURE 7.39: Apparent viscosity versus lubricant concentration for STRUKTOL WB212 In STRUKTOL NR (Section 7.9)

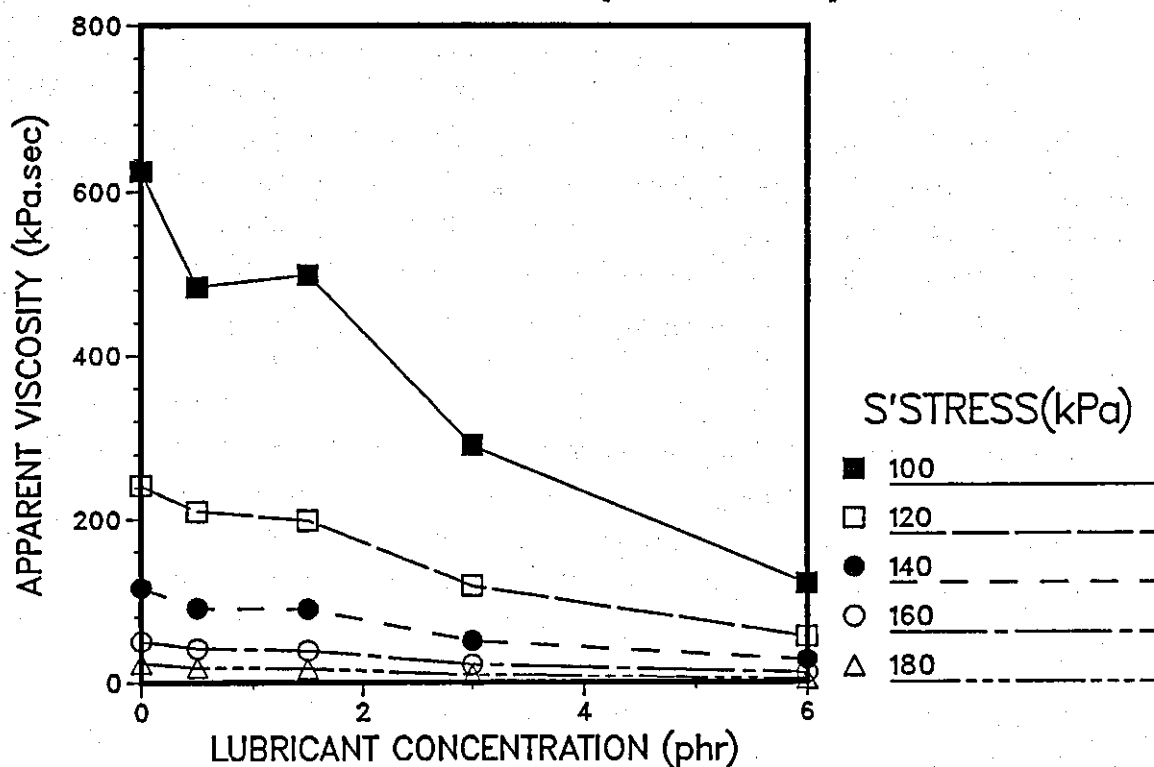
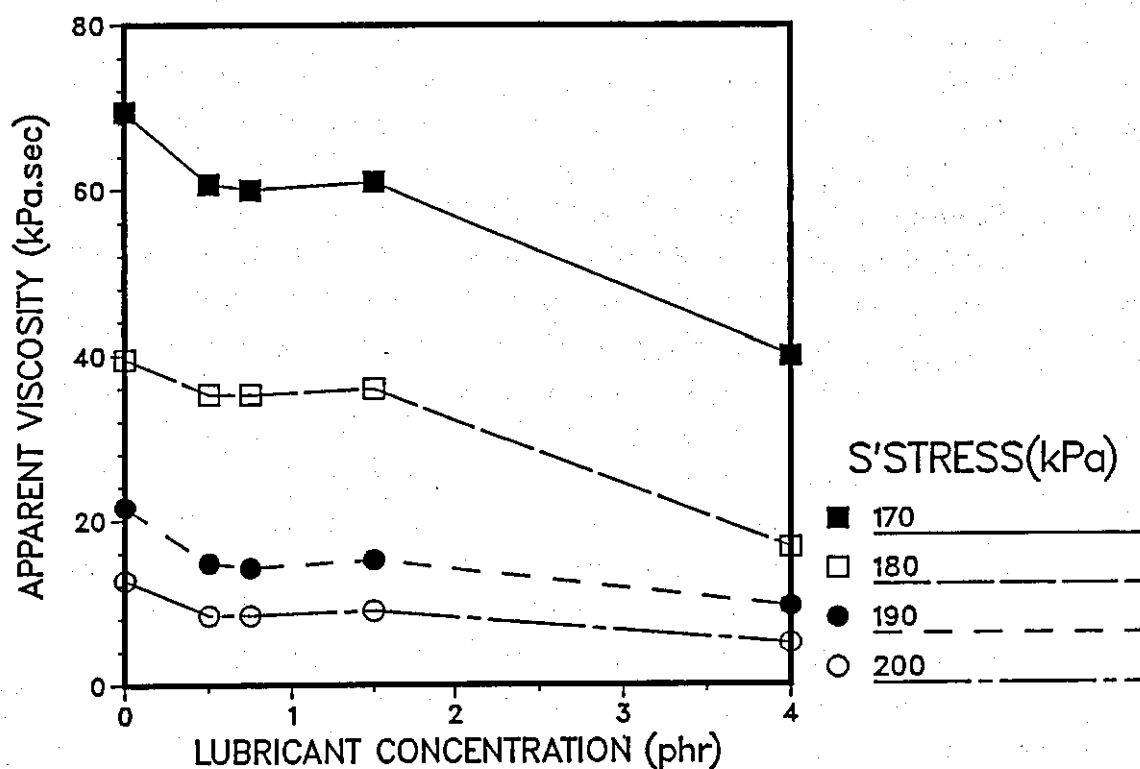


FIGURE 7.40: Apparent viscosity versus lubricant concentration for STRUKTOL WB16 In compounded Natural Rubber at 80°C (Section 7.10)



chain extension/cross-linking effect started to affect the apparent viscosity of the sample.

7.10. INVESTIGATION OF TEMPERATURE EFFECT ON THE MODES OF ACTION OF LUBRICANTS

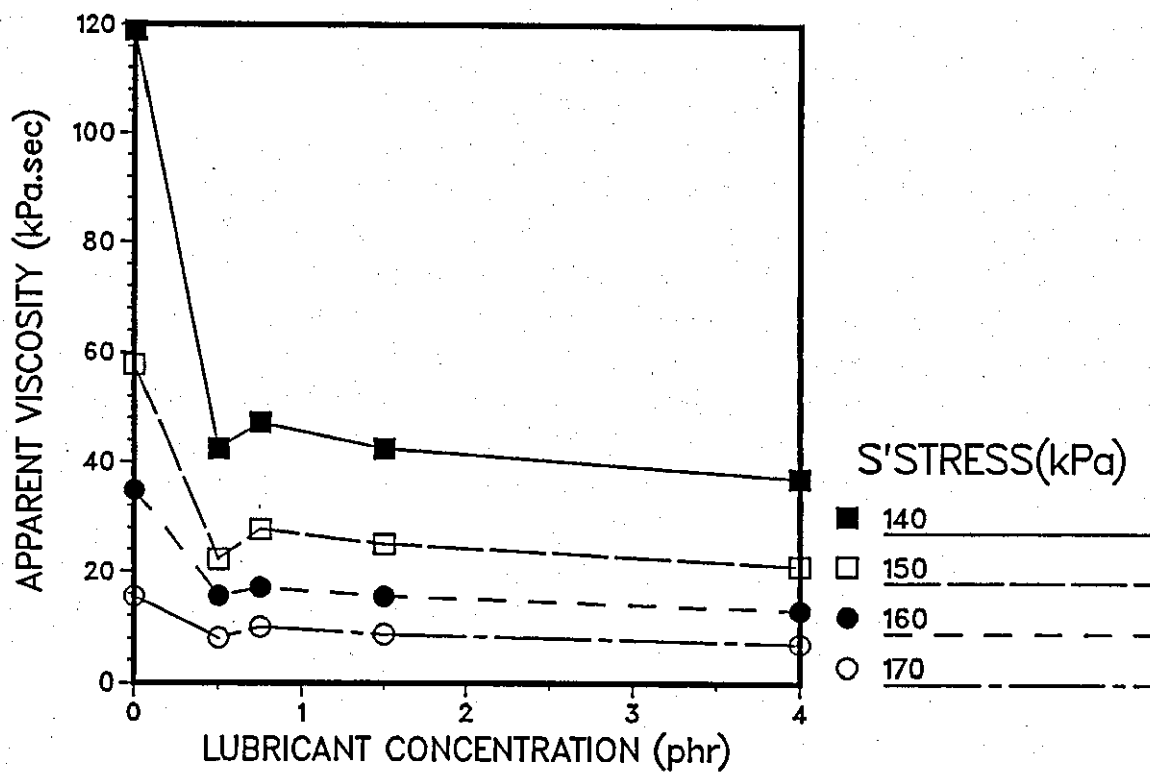
Two batches of a natural rubber compound, (Compound 1 (Section 4.3.3.)), mixed in the manner described in Section 4.3.4.2. (i) with the second batch containing 4 phr Struktol WB16 added to the mix in the final stage were intermixed on the two-roll mill at 100°C to give test samples containing different levels of lubricant (0, 0.5, 0.75, 1.5, and 4 phr). The results obtained on the TMS rheometer at 100°C with the smooth rotor were reported in Section 5.2. and plotted in Figure 5.2.

The results obtained for the same sample and using the same technique at 80°C and 125°C were plotted in Figures 7.40. and 7.41. respectively. The differences in the results obtained at three different temperatures were:

- i) The initial drop in the apparent viscosity observed at 0.5 phr lubricant had increased with increasing test temperature.
- ii) The chain extension/cross-linking effect of the lubricant increasing the apparent viscosity of the test sample appeared to occur at earlier stages and with greater intensity at higher test temperature.

The latter observation can be related to the fact that the intensity and equilibrium of the chemical reaction leading to chain

FIGURE 7.41: Apparent viscosity versus lubricant concentration for STRUKTOL WB16 in compounded Natural Rubber at 125 C (Section 7.10).



extension/cross-linking depend on the temperature of the sample, as do most other chemical reactions. The foregoing observation appears to indicate that the morphology of the elastomer compound was changing, producing an increase in the average size of the flow unit with increasing test temperature (Section 6.2.2.2. and 6.2.2.3.).

Other changes in the modes of action of lubricants due to test temperature were observed in Section 7.8. with EPDM containing Zinc decanoate (Section 7.7.2.). The results were obtained at 100°C and 150°C (Figures 7.35. and 7.36. respectively). The first temperature was lower than the melting point of the lubricant, which stopped the excess lubricant present in the elastomer from exuding to the rubber/metal interface. At 150°C the excess lubricant was able to exude and external lubrication was observed.

Another factor that can be affected by the test temperature is the affinity of the elastomer to the metal surface of the rotor. Higher temperatures will increase the adhesion of the elastomer to the metal surface. The large decrease in the apparent viscosity observed with the natural rubber compound at 80°C (Figure 7.40.) at 4 phr lubricant, which was not observed with the results obtained at higher temperatures, was due to external lubrication. At higher temperatures this was inhibited by the increased affinity of the elastomer to the rotor's surface.

M. Abidin -
please can I see you between
11-12 tomorrow - Tues - if
not convenient we will arrange
another time.

Michael

7.11. RESULTS OBTAINED BY LeBLANC AND LLOYD[29]

A set of results was obtained by LeBlanc and Lloyd[29] using the capillary rheometer for a natural rubber compound containing different levels of a light oil (CIRCOLIGHT RPO) and a lubricant of polymeric origin (BVM001). The results were obtained at 2, 3 and 5 phr lubricant concentrations (Section 2.5.). The light oil was thought by LeBlanc and Lloyd to be acting as an internal lubricant with 2 and 3 phr lubricant. At 5 phr the oil was in excess but did not exude to act as an external lubricant. In contrast the BVM001 was thought to be acting as a Bulk Viscosity Modifier, which is equivalent to solvation (Section 6.2.1.2.), decreasing the apparent viscosity by disentangling and swelling the test sample over the whole range tested.

The model proposed in this study (Chapter 6) would explain the observations made by LeBlanc and Lloyd to be due to internal lubrication in both the light oil and the BVM001 cases. The only difference between the two lubricants being that BVM001 has a higher concentration of compatible materials in its composition than the light oil.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1. CONCLUSION

The apparent viscosity measurements made on elastomers and elastomer compounds containing different levels of lubricants have been the source for a conceptual and a mathematical model describing the modes of action of lubricants. The following conclusions about the proposed models, the lubricants used and the measuring techniques are pertinent:

- 1) The model proposed by LeBlanc and Lloyd[29] was not able to explain all the characteristics of the apparent viscosity versus lubricant concentration relationships observed throughout this study.
- 2) The conceptual model proposed, explaining the different modes of action of lubricants, was found to be capable of rationalising all of the situations encountered throughout this study. The various trends and characteristics of the apparent viscosity versus lubricant concentration curves for the various elastomers and elastomer compounds used could be explained by reference to the lubricant's compatibility with the test sample, the morphology of the test sample and the chemical reactivity of the lubricant with the test sample.

- 3) The proposed mathematical model was shown to fit all the experimental apparent viscosity versus lubricant concentration relationships which it was possible to utilise for this purpose. The model has six parameters, implying that a minimum of six significant data points should be collected before the model can be used. The model is not valid in regions where external lubrication is occurring.
- 4) The lubricants Struktol WB212 and WB16 were found to be chemically reactive with all the elastomers used in the study, leading to chain extension/cross-linking. On the other hand, the lubricant Struktol A50P did not show any signs of reactivity.
- 5) The major reduction of apparent viscosity of the compounded elastomers used in this study occurred at low lubricant concentrations (≤ 1 phr lubricant). At such low concentrations the final physical properties of the rubber compound are unlikely to be adversely affected.
- 6) The excess lubricant existent in an elastomer or elastomer compound can act as a filler or it can exude to the rubber/metal interface and provide external lubrication, depending on processing temperature in relation to lubricant melting point.
- 7) The shear stress level applied was found to change the critical concentration at which external lubrication occurs. An increase in shear stress will encourage the development of a lubricating

film at the rubber/metal interface leading to external lubrication at a lower lubricant concentration.

- 8) The test temperature was found to affect the type of response observed with additions of lubricant by changing the morphology of the test sample.
- 9) The test temperature and the test sample's composition were found to affect the concentration at which the chemical reaction leading to chain extension/cross-linking occurs and the intensity of its effect.
- 10) In order that a lubricant changes the rheological properties of an elastomer or elastomer compound without changing its physical properties, such as tackyness and adhesion, a lubricant has to be acting as an internal lubricant without exuding to the rubber's surface. The chemical composition and structure of the lubricant molecules are an important factor that will determine its mode of action on an elastomer or elastomer compound. The conclusions that can be derived about the lubricant molecules chemical composition and structure are:
 - i) The lubricant molecule should contain attraction sites that will make it compatible with the elastomer molecule. Without such compatibility the lubricant will exude to the rubber's surface.
 - ii) The lubricant molecule should not be able to compete with the elastomer molecules for the attraction sites on a reinforcing

filler. If this occurs, the apparent viscosity of the compound will decrease, but it will also have an adverse effect on the final properties of the product for decreasing the efficiency of the reinforcing filler.

iii) The lubricant molecule should have a structure that will enable it to mask attraction sites on the elastomer molecules efficiently. An added quality would be that a lubricant molecule is able to mask neighbouring attraction sites as well as the primary site to which it is attached.

iv) The lubricant molecule should be inert with respect to the other ingredients in an elastomer compound. If a lubricant reacts with one or more of the additives it will inhibit their performance. Also, if the lubricant reacts with the elastomer, as observed throughout this study, it will increase its apparent viscosity by chain extension/cross-linking.

11) Several characteristics of the grooved rotor of the Negretti TMS biconical rotor rheometer were noted:

i) The rotor torque measurement was influenced by the ability of a sample to flow into and through the grooves, thus change the "apparent size" of the rotor.

ii) A lubricating film could form on the material contained in the grooves resulting in the rotor failing to inhibit slippage.

- 12) The capillary rheometer showed the same apparent viscosity versus lubricant concentration trends as those observed with the TMS rheometer.
- 13) Stress relaxation measurements with the Negretti TMS rheometer gave similar trends to those observed for apparent viscosity versus lubricant concentration results.

8.2. RECOMMENDATIONS

The study is an exploratory investigation of the nature of lubricant action on elastomer compounds. It provides the basis of more detailed studies of the mechanisms proposed and, hopefully, provides assistance for the development of new lubricants for particular processes. Some of the proposals made are speculative and further work is needed in the following areas:

- 1) Investigation should be carried out on the nature of the chemical reaction leading to chain extension/cross-linking of the elastomer chain.
- 2) Experimentation with the effect of different lubricant molecules' structure and composition can give an indication about the optimum chemical characteristics of the lubricant molecule.
- 3) An investigation of the effect of lubricants on a particular industrial process should be carried out in conjunction with the rheological studies. This will explain whether a direct

correlation between the rheological changes and the process improvement is justified.

APPENDIX A

CALIBRATION OF THE TMS RHEOMETER

Five well defined torque values were applied on the shaft of the rotor using the setup described in figure A1 and the corresponding torque values read by the TMS in machine units were presented in table A1.

Figure A1: Calibration instrument of the TMS rheometer

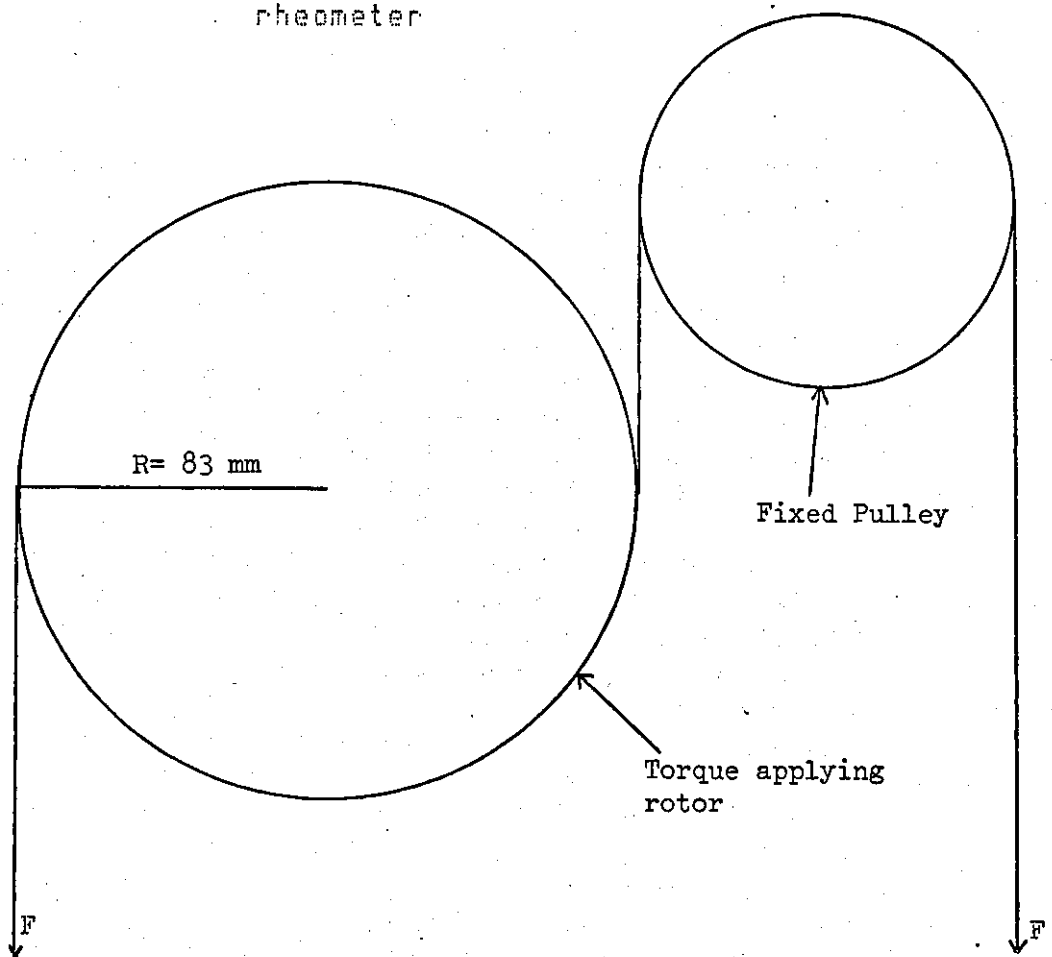


Table A1: Applied torque versus machine values of the TMS rheometer.

Applied weight	Torque (N.M)	Torque (TMS unit)	multiplying fact
3075	1.252	15.2	0.082
6140	2.5	30	0.083
9215	3.75	45.5	0.082
12290	5	60.7	0.082
18435	7.505	89	0.084

Using the dimensions given in figure 4.2 (Section 4.2.1.1), the shear rate can be calculated from the rotor speed with equation 3.2 (Section 3.2). The angular velocity (Rad/sec) is equal to $0.1 \times$ the rotor speed (rev/min) and the cone angle of the rotor can be approximated to 0.1 Radians. The shear rate (1/sec) is then equal to the the rotor speed (rev/min).

Replacing $Y=0.0015\text{m}$ and $R=0.0225\text{m}$ into equation 3.8 (Section 3.2), the shear stress was found to be equivalent to $17.87 \times$ the torque (kPa). The torque (kPa) is equivalent to $0.082 \times$ the torque given in machine units (Table A1), therefore the shear stress (kPa) equal $1.465 \times$ torque (Machine units).

APPENDIX B THE SOFTWARE "TESTER"

```

*****
*   Define the key F1 to act as an emergency stop.   *
*****
10 ON KEY(1) GOSUB 2530
20 KEY(1) ON
*****
*   Definition of array and communication messages with the *
*MPC84. Eg. MSG1$ will transfer or receive data to or from *
*the MPC84 memory addresses: V317,N302,N303,N304,F100 and *
*F101. *
*****
30 DIM TEMP1!(8),TEMP2!(8),TEMP3!(8),TEMP4!(8),TEMP5!(8),
    TEMP7!(8),TEMP8!(8),TEMP9!(8),TEMP10!(8),TEMP11!(8),
    TEMP12!(8),TIM$(10),TRQ$(10)
40 DIM TEMP13!(8),TEMP14!(8)
50 MSG1$="#1,V317,N302,N303,N304,F100,F101#"
60 MSG2$="#1,F102#"
70 MSG3$="#1,F106,V307,V304,V305,N305,N306#"
80 MSG4$="#1,F102,F105,F103#"
90 MSG5$="#1,V310,V312#"
100 MSG7$="#1,F105#"
110 MSG8$="#1,F103#"
120 MSG9$="#1,F104#"
130 MSG11$="#1,F107#"
140 MSG12$="#1,F110#"
150 MSG13$="#1,V333,V334,V335,V336,V337,V340,V341,V342#"
160 MSG14$="#1,V343,V344,V345,V346,V347,V350,V351,V352#"
170 MSG10$="#1,F100,F101,F102,F103,F104,F105,F106,F107#"
*****
*   Zero all flags used and display the Menu.   *
*****
180 TEMP10!(1)=0:TEMP10!(2)=0:TEMP10!(3)=0:TEMP10!(4)=0:
    TEMP10!(5)=0:TEMP10!(6)=0:TEMP10!(7)=0:TEMP10!(8)=0
190 CALL MTYPE (ERRST$,MSG10$,TEMP10!(1))
200 CLS
210 LOCATE 3,30:PRINT"MENU"
220 LOCATE 4,30:PRINT"-----"
230 LOCATE 10,20:PRINT"A)      CREATE A NEW FILE"
240 LOCATE 12,20:PRINT"B)      RUN THE NEWLY CREATED FILE"
250 LOCATE 14,20:PRINT"C)      RUN AN OLD EXISTING FILE"
260 LOCATE 16,20:PRINT
    "D)      RUN THE NEWLY CREATED FILE ON THE SAME SAMPLE"
270 LOCATE 18,20:PRINT
    "E)      RUN AN OLD EXISTING FILE ON THE SAME SAMPLE"
280 LOCATE 20,20:PRINT"F)      PRINTOUT A RESULT FILE"
290 LOCATE 22,20:PRINT"G)      ESCAPE"

```

```

300 LOCATE 24,10:PRINT"PLEASE ENTER YOUR CHOICE:"
310 LOCATE 25,10:PRINT
    "(USE 'F1' FOR EMERGENCY EXIT FROM PROGRAM AT ANY TIME)"
320 X$=INPUT$(1)
330 IF X$="A" THEN 410
340 IF X$="B" THEN 750
350 IF X$="C" THEN CALL MTYPE (ERRST%,MSG10$,TEMP10!(1)):
    GOTO 720
360 IF X$="D" THEN 1750
370 IF X$="E" THEN 1520
380 IF X$="F" THEN 1810
390 IF X$="G" THEN TEMP8!(1)=0:
    CALL MTYPE (ERRST%,MSG8$,TEMP8!(1)):CLS:END
*****
*   When choice "A" is used, start probing for details of   *
*the experiment and save them in a sequential file          *
*****
400 GOTO 300
410 CLS
420 LOCATE 2,30:PRINT"CREATE A NEW FILE"
430 LOCATE 3,30:PRINT"-----"
440 LOCATE 6,10:
    INPUT "ENTER THE NAME OF THE NEW FILE TO BE CREATED: "
    ,DATA$
450 DATA$="A:"+DATA$
460 OPEN DATA$ FOR OUTPUT AS #1
470 LOCATE 8,10:
    INPUT "ENTER THE TEMPERATURE OF THE EXPERIMENT:",TEMP%
480 LOCATE 10,10:
    PRINT"ENTER THE PREHEAT TIME OF THE SPECIMEN:"
490 LOCATE 11,15:INPUT "MINUTES:",MIN%
500 LOCATE 12,15:INPUT "SECONDS:",SEC%
510 CLS:LOCATE 6,10
520 PRINT "THE EXPERIMENT IS TO BE PROGRAMMED IN STEPS.
    EACH STEP CONTAINS THE"
530 PRINT"REQUIRED SHEAR RATE IN RECIPROCAL SECS AND THE
    DURATION IN MINUTES"
540 PRINT "THEN SECONDS. FIRST,ENTER THE NUMBER OF STEPS
    TO BE PROGRAMMED:"
550 INPUT "N= ",NUM%
560 PRINT #1,TEMP%,";",MIN%,";",SEC%,";",NUM%,",";
570 FOR I=1 TO NUM%
580 PRINT "STEP ";I;
590 INPUT;"    SHEAR RATE : ",SPEED!
600 INPUT;"    MINUTES: ",MIN%
610 INPUT "    SECONDS: ",SEC%
620 IF SPEED!=0 THEN SPEED1!=0:SPEED2!=0:GOTO 650
630 IF SPEED!>10 THEN SPEED1!=2:SPEED2!=31250!/SPEED!:
    GOTO 650
640 SPEED1!=20:SPEED2!=31250!/SPEED!/10
650 IF SEC%=0 AND MIN%>0 THEN SEC%=60:MIN%=MIN%-1
660 PRINT #1,SPEED!,";",SPEED1!,";",SPEED2!,";",MIN%,",";
    SEC%,",";
670 NEXT
680 PRINT "FILE IS NOW CREATED. PRESS SPACE BAR TO GO BACK

```

```

        TO MENU."
690 X$=INPUT$(1)
700 IF X$=" " THEN CLOSE #1:GOTO 200
710 GOTO 690
*****
*   When choice "C" is pressed,load the file containing the*
*experimental details and create a sequential file for the *
*collected data.                                           *
*****
720 CLS:LOCATE 6,10
730 INPUT "ENTER THE NAME OF THE FILE TO BE USED: ",DATA$
740 DATA$="A:" + DATA$
750 OPEN DATA$ FOR INPUT AS #1
760 INPUT "ENTER THE NAME OF THE FILE IN WHICH RESULTS ARE
        GOING TO BE STORED:",RESULT$
770 RESULT$="A:" + RESULT$
780 OPEN RESULT$ FOR OUTPUT AS #2
790 INPUT #1,TEMP1!(1),TEMP1!(2),TEMP1!(3),TEMP1!(4)
800 INPUT "ENTER YOUR COMMENTS ABOUT THE RESULT FILE:",A$
810 PRINT#2,A$,";";TEMP1!(1);";";
*****
*   Start sequence 4 (Appendix C) in MPC84, transfer the *
*preprogramed set temperature to the MPC84 and wait for *
*flag F102 in the MPC84 to be raised indicating that the *
*temperature has reached equilibrium.                       *
*****
820 TEMP1!(5)=1:TEMP1!(6)=1
830 CALL MTYPE (ERRST$,MSG1$,TEMP1!(1))
840 CLS:LOCATE 10,10
850 CALL MACPT (ERRST$,MSG2$,TEMP2!(1))
860 IF TEMP2!(1)=0 THEN PRINT
    "WAIT FOR TEMPERATURE TO REACH SET POINT!":
    LOCATE 10,10:GOTO 850
870 CLS:LOCATE 10,10:PRINT
    "TEMPERATURE HAS NOW REACHED SET POINT."
880 SOUND 1000,10
*****
*   Display message for operator to start the experiment *
*after ensuring that the rotor is in its position.        *
*****
890 LOCATE 12,15:PRINT "1)  INSERT SPECIMEN TO BE TESTED"
900 LOCATE 13,15:PRINT "2)  INSERT ROTOR"
910 LOCATE 14,15:PRINT "3)  PRESS ROTOR TO ACTIVATE SWITCH"
920 CALL MACPT (ERRST$,MSG2$,TEMP2!(1))
930 IF TEMP2!(1)=1 THEN 920
940 CLS:LOCATE 20,30:PRINT"STAY CLEAR OF WINDOW!"
950 LOCATE 22,32:PRINT "WHEN READY PRESS SPACE BAR"
960 X$=INPUT$(1)
970 IF X$<>" " THEN 960
980 TEMP3!(1)=1:CLS:LOCATE 20,30:
    PRINT "EXPERIMENT IN PROGRESS!":FLAG=0:CNT!=0
990 INPUT #1,TEMP3!(2),TEMP3!(3),TEMP3!(4),TEMP3!(5),
    TEMP3!(6)
1000 CALL MTYPE (ERRST$,MSG3$,TEMP3!(1))
1010 PRINT #2,"/";TEMP3!(2);"/";";";";

```

```

1020 CALL MACPT (ERRST%,MSG4$,TEMP4!(1))
1030 IF TEMP4!(2)=1 THEN PRINT "S'RATE= ";TEMP3!(2):
      GOTO 1260
1040 GOTO 1020
1050 CALL MACPT (ERRST%,MSG4$,TEMP4!(1))
1060 IF TEMP4!(1)=1 THEN 1100
1070 IF TEMP4!(3)=1 THEN 1470
1080 IF TEMP4!(2)=1 THEN 1200
1090 GOTO 1050
1100 INPUT #1,TEMP3!(2),TEMP3!(3),TEMP3!(4),TEMP3!(5),
      TEMP3!(6)
1110 CALL MTYPE (ERRST%,MSG3$,TEMP3!(1))
1120 CALL MACPT (ERRST%,MSG5$,TEMP5!(1))
1130 PRINT #2,TEMP5!(1);", ";TEMP5!(2);", ";"/";
      TEMP3!(2);"/";", ";
1140 TEMP2!(1)=0:TEMP7!(1)=0:FLAG=1:CNF!=TEMP5!(1)
1150 CALL MTYPE (ERRST%,MSG2$,TEMP2!(1))
1160 CALL MTYPE (ERRST%,MSG7$,TEMP7!(1))
1170 PRINT "TIME= ";TEMP5!(1),"S'STESS= ";TEMP5!(2)
1180 PRINT "S'RATE= ";TEMP3!(2)
1190 GOTO 1050
1200 IF FLAG=1 GOTO 1260
1210 CALL MACPT (ERRST%,MSG5$,TEMP5!(1))
1220 PRINT #2,TEMP5!(1);", ";TEMP5!(2);", ";
1230 PRINT "TIME= ";TEMP5!(1),"S'STESS= ";TEMP5!(2)
1240 TEMP7!(1)=0:CALL MTYPE (ERRST%,MSG7$,TEMP7!(1))
1250 GOTO 1050
1260 CALL MACPT (ERRST%,MSG13$,TEMP13!(1)):
      CALL MACPT (ERRST%,MSG14$,TEMP14!(1))
1270 PRINT #2,CNF!+.1;", ";TEMP13!(1);", ";CNF!+.2;", ";
      TEMP13!(2);", ";CNF!+.3;", ";TEMP13!(3);", ";CNF!+.4;", ";
      TEMP13!(4);", ";CNF!+.5;", ";TEMP13!(5);", ";CNF!+.6;", ";
      TEMP13!(6);", ";
1280 PRINT #2,CNF!+.7;", ";TEMP13!(7);", ";CNF!+.8;", ";
      TEMP13!(8);", ";CNF!+.9;", ";TEMP14!(1);", ";CNF!+1;", ";
      TEMP14!(2);", ";CNF!+1.1;", ";TEMP14!(3);", ";CNF!+1.2;
      ", ";TEMP14!(4);", ";
1290 PRINT #2,CNF!+1.3;", ";TEMP14!(5);", ";CNF!+1.4;", ";
      TEMP14!(6);", ";CNF!+1.5;", ";TEMP14!(7);", ";CNF!+1.6;
      ", ";TEMP14!(8);", ";
1300 PRINT "TIME= ";CNF!+.1,"S'STESS= ";TEMP13!(1)
1310 PRINT "TIME= ";CNF!+.2,"S'STESS= ";TEMP13!(2)
1320 PRINT "TIME= ";CNF!+.3,"S'STESS= ";TEMP13!(3)
1330 PRINT "TIME= ";CNF!+.4,"S'STESS= ";TEMP13!(4)
1340 PRINT "TIME= ";CNF!+.5,"S'STESS= ";TEMP13!(5)
1350 PRINT "TIME= ";CNF!+.6,"S'STESS= ";TEMP13!(6)
1360 PRINT "TIME= ";CNF!+.7,"S'STESS= ";TEMP13!(7)
1370 PRINT "TIME= ";CNF!+.8,"S'STESS= ";TEMP13!(8)
1380 PRINT "TIME= ";CNF!+.9,"S'STESS= ";TEMP14!(1)
1390 PRINT "TIME= ";CNF!+1,"S'STESS= ";TEMP14!(2)
1400 PRINT "TIME= ";CNF!+1.1,"S'STESS= ";TEMP14!(3)
1410 PRINT "TIME= ";CNF!+1.2,"S'STESS= ";TEMP14!(4)
1420 PRINT "TIME= ";CNF!+1.3,"S'STESS= ";TEMP14!(5)
1430 PRINT "TIME= ";CNF!+1.4,"S'STESS= ";TEMP14!(6)
1440 PRINT "TIME= ";CNF!+1.5,"S'STESS= ";TEMP14!(7)

```

```

1450 PRINT "TIME= ";CNT!+1.6,"S'STRESS= ";TEMP14!(8)
1460 FLAG=0:GOTO 1050
1470 PRINT "                                END OF EXPERIMENT"
1480 PRINT " PRESS SPACE BAR TO GO BACK TO MENU"
1490 X$=INPUT$(1)
1500 IF X$=" " THEN CLOSE :GOTO 200
1510 GOTO 1490
*****
*   When option "E" is pressed another experiment is loaded*
*to be applied on the same test sample.                      *
*****
1520 TEMP9!(1)=1:CALL MTYPE (ERRST$,MSG9$,TEMP9!(1))
1530 CLS:LOCATE 6,1
1540 INPUT "ENTER THE NAME OF THE FILE TO BE USED: ",DATA$
1550 DATA$="A:"+DATA$
1560 OPEN DATA$ FOR INPUT AS #1
1570 INPUT"ENTER THE NAME OF THE FILE IN WHICH RESULTS
      ARE GOING TO BE STORED:",RESULT$
1580 RESULT$="A:"+RESULT$
1590 OPEN RESULT$ FOR OUTPUT AS #2
1600 INPUT #1,TEMP1!(1),TEMP1!(2),TEMP1!(3),TEMP1!(4)
1610 INPUT "ENTER YOUR COMMENTS ABOUT THE RESULT FILE: ",A$
1620 PRINT#2,A$;",";TEMP1!(1);",";
1630 TEMP1!(5)=0:TEMP1!(6)=0
1640 CALL MTYPE (ERRST$,MSG1$,TEMP1!(1))
1650 CLS:LOCATE 10,10
1660 TEMP9!(1)=0:CALL MTYPE (ERRST$,MSG9$,TEMP9!(1))
1670 PRINT "WAIT FOR TEMPERATURE TO REACH SET POINT!"
1680 CALL MACPT (ERRST$,MSG11$,TEMP11!(1))
1690 IF TEMP11!(1)=0 THEN 1680
1700 CLS:LOCATE 20,30:PRINT"EXPERIMENT IN PROGRESS!":
      FLAG=0:CNT!=0
1710 TEMP11!(1)=0:CALL MTYPE (ERRST$,MSG11$,TEMP11!(1))
1720 TEMP4!(1)=0:TEMP4!(2)=0:TEMP4!(3)=0
1730 CALL MTYPE (ERRST$,MSG4$,TEMP4!(1))
1740 GOTO 990
1750 TEMP9!(1)=1:CALL MTYPE (ERRST$,MSG9$,TEMP9!(1))
1760 CLS:LOCATE 6,10
1770 OPEN DATA$ FOR INPUT AS #1
1780 GOTO 1570
1790 TEMP8!(1)=0:CALL MTYPE (ERRST$,MSG8$,TEMP8!(1))
1800 GOTO 180
*****
*   When option "F" is pressed, the results collected and *
*stored in a sequential file can be printed out in various *
*formats.                                                    *
*****
1810 CLS:LOCATE 10,20
1820 INPUT"ENTER THE NAME OF YOUR RESULT FILE: ":RESULT$
1830 RESULT$="A:"+RESULT$
1840 OPEN RESULT$ FOR INPUT AS #3
1850 CLS:LOCATE 5,20:PRINT
      "YOU CAN PROGRAM YOUR OUTPUT TO GIVE:"
1860 LOCATE 10,20:PRINT
      "A)          THE LAST 10 RESULTS OF EACH SHEAR RATE"

```

```

1870 LOCATE 12,20:PRINT
    "B)      THE FIRST 'X' RESULT OF EACH SHEAR RATE AT A"
1880 LOCATE 13,28:PRINT
    "CERTAIN STEP VALUE OF 'Y', THEN THE REST"
1890 LOCATE 14,28:PRINT
    "OF THE RESULTS AT A STEP VALUE OF 'Z'."
1900 LOCATE 16,20:PRINT "C)      ALL OF THE RESULTS."
1910 LOCATE 20,2:PRINT "DO YOU WANT TO SEE YOUR RESULTS ON
    THE SCREEN BEFORE CHOOSING HOW YOU WANT THEM PRINTED
    OUT?"
1920 X$=INPUT$(1)
1930 IF X$="Y" GOTO 2020
1940 IF X$<>"N" GOTO 1920
1950 LOCATE 20,2:PRINT
1960 LOCATE 20,2:PRINT "ENTER YOUR CHOICE OF OUTPUT:"
1970 X$=INPUT$(1)
1980 IF X$="A" GOTO 2150
1990 IF X$="B" GOTO 2400
2000 IF X$="C" GOTO 2610
2010 GOTO 1970
2020 INPUT#3,A$:PRINT "COMMENTS: ";A$
2030 INPUT#3,A$:PRINT "TEMPERATURE OF THE EXPERIMENT= ";A$
2040 IF EOF(3) THEN CLOSE #3:GOTO 1840
2050 INPUT#3,A$
2060 B$=LEFT$(A$,1):IF B$="/" THEN 2100
2070 INPUT#3,C$
2080 PRINT "TIME= ";A$,"S' STRESS= ";C$
2090 GOTO 2040
2100 A=LEN(A$):A=A-1
2110 A$=LEFT$(A$,A):A=A-1:A$=RIGHT$(A$,A)
2120 PRINT "S' RATE= ";A$
2130 INPUT#3,A$,C$
2140 GOTO 2080
2150 A%=10
2160 INPUT#3,A$:LPRINT "COMMENTS: ";A$
2170 INPUT#3,A$:LPRINT "TEMPERATURE OF THE EXPERIMENT= ";A$
2180 INPUT#3,A$:GOTO 2320
2190 IF EOF(3) THEN CLOSE #3:GOTO 2360
2200 INPUT#3,A$
2210 B$=LEFT$(A$,1):IF B$="/" GOTO 2280
2220 INPUT#3,C$
2230 FOR J=1 TO A%-1
2240 TIM$(J)=TIM$(J+1):TRQ$(J)=TRQ$(J+1)
2250 NEXT
2260 TIM$(A%)=A$:TRQ$(A%)=C$
2270 GOTO 2190
2280 FOR J=1 TO A%
2290 IF TIM$(J)<>"0" THEN LPRINT"TIME= ";TIM$(J),
    "S' STRESS= ";TRQ$(J)
2300 TIM$(J)="0":TRQ$(J)="0"

```

```

2310 NEXT
2320 A=LEN(A$):A=A-1
2330 A$=LEFT$(A$,A):A=A-1:A$=RIGHT$(A$,A)
2340 LPRINT"S'RATE= ";A$
2350 INPUT#3,A$,C$:GOTO 2230
2360 FOR J=1 TO A%
2370 IF TIM$(J)<>"0" THEN LPRINT"TIME= ";TIM$(J),
    "S'STRESS= ";TRQ$(J)
2380 NEXT
2390 GOTO 200
2400 LOCATE 20,1:INPUT "B:  PLEASE ENTER YOUR 'X' VALUE:",
    A%
2410 PRINT"
2420 LOCATE 21,1:INPUT "B:  PLEASE ENTER YOUR 'Y' VALUE:",
    B%
2430 LOCATE 22,1:INPUT "B:  PLEASE ENTER YOUR 'Z' VALUE:",
    C%
2440 A1%=0:B1%=0:C1%=0
2450 INPUT#3,A$:LPRINT"COMMENTS: ";A$
2460 INPUT#3,A$:LPRINT"TEMPERATURE OF THE EXPERIMENT= ";A$
2470 IF EOF(3) THEN CLOSE #3:GOTO 200
2480 INPUT#3,A$
2490 B$=LEFT$(A$,1):IF B$="/" GOTO 2570
2500 B1%=B1%+1:C1%=C1%+1
2510 INPUT#3,C$
2520 IF A1%<A% AND B1%=B% THEN A1%=A1%+1:B1%=0:GOTO 2560
2530 IF A1%=A% THEN A1%=A%+1:C1%=0
2540 IF C1%=C% THEN C1%=0:GOTO 2560
2550 GOTO 2470
2560 LPRINT"TIME= ";A$,"S'STRESS= ";C$:GOTO 2470
2570 A=LEN(A$):A=A-1:A1%=0:B1%=0
2580 A$=LEFT$(A$,A):A=A-1:A$=RIGHT$(A$,A)
2590 LPRINT"S'RATE= ";A$
2600 GOTO 2470
2610 A1%=1:A%=0:B1%=1:C1%=0:B%=0:C%=1
2620 GOTO 2450
2630 TEMP12!(1)=1
2640 CALL MTYPE (ERRST%,MSG12$,TEMP12!(1))
2645 CALL MTYPE (ERRST%,MSG10$,TEMP10!(1))
2650 I=NUM%:J=A%:CLOSE
2660 END

```

APPENDIX C MPC84 SEQUENCE 4

SEON:004

```
*****
*   Close flag F100 and stop the sequence.   *
*****
```

```
STEP:000
SFCL:F100
HOLD:003.001
```

```
*****
*   Check if the sequence is being run through TESTER   *
*   (Appendix B) or SLIPPER (Appendix D1) and prepare the TMS *
*   rheometer by setting the temperature fed by the IBM PC, *
*   raising the upper die and ram and opening the protective *
*   window.   *
*****
```

```
STEP:001
IFFL:001.F100
SKIP:004
TYPE:006,"[033]H[033]J[033]Y**"
TYPE:006,"THIS SEQUENCE CAN ONLY BE RUN VIA TESTER"
HOLD:004.001
GOTO:001
DSET:003.000.317
DSET:003.001.317
DSET:003.002.317
SDON:J000
SODF:J001
SFCL:F100
```

```
STEP:002
DELY:000.000.002
SDON:J003
SODF:J002
```

```
STEP:002
DELY:000.000.002
SODF:J004
```

```
*****
*   Get the average temperature of the upper die, the lower *
*   die and the ram. If the average temperature has reached *
*   the required level, continue.   *
*****
```

```
STEP:003
FLDT:301.000.003
SETR:V302=(B000+B001+B002)/V301
```

FLOT:301,000,002
SETR:V303=V317+V301
SETR:V306=V317-V301
IFAN:000,V302,V303
AND
IFAN:000,V306,V302
GOTO:004
GOTO:003

* Check if the switch I4 has been activated by the rotor *
*indicating that it is in position. *

STEP:004
SFRS:F102
IFDG:001,I004
GOTO:004
SFCL:F102

* If flag F106 is raised by the IBM PC, close dies, close *
*ram and start filling procedure. *

STEP:005
IFFL:000,F106
GOTO:005
SDON:J004
SDON:J002
SFCL:F106

STEP:006
DELY:000,000,002
SDDF:J000
SDON:J001

STEP:006
DELY:000,N302,N303
CUST:INIT
CUST:CMD,000,000
CUST:CMD,000,005
FLOT:300,000,024
CUST:SET0,300
FLOT:300,000,037
FLOT:301,000,014
SETR:V300=V300*V300*V301
CUST:SET1,300
SDDF:J003
CUST:CMD,000,006

STEP:006
DELY:000,000,036
CUST:CMD,000,007
SDON:J003

STEP:006

DELY:000,000,024
CUST:CMD,000,004
CUST:CMD,000,006

STEP:006
DELY:000,000,036
CUST:CMD,000,007

STEP:006
DELY:000,000,017
SDOF:J003
CUST:CMD,000,005
CUST:CMD,000,006
FLOT:324,000,000

STEP:006
DELY:000,000,015

* If the latest torque value is less or equal to the *
*previous one, the filling procedure is stopped. *

STEP:006
IFAN:002,V324,B003
SKIP:002
SETR:V324=B003
WAIT
CUST:CMD,000,007
SDON:J003

* If flag F120 is raised, go to sequence 5 (Appendix D2) *
*to apply a set of shear stresses on the test sample. *

STEP:006
IFFL:000,F120
GOTO:007
STRT:005,000
RUN :005
SFCL:F120
HOLD:004,007

* Apply the required shear rate on the test sample and *
*read the first 18 torque values at 0.1sec intervals. *

STEP:007
DELY:000,000,015
FLOT:300,000,012
FLOT:353,000,020
SETR:V353=V353/V300
FLOT:310,000,000

STEP:010
DO :N300,D001,N304

BEGN
FLOT:302,000,000
IFAN:002,V302,V304
SKIP:003
CUST:SET0,304
CUST:SET1,305
SKIP:002
CUST:CMD,000,007
SKIP:001
CUST:CMD,000,006
IFIN:001,N306,0000
SKIP:045

STEP:011
SETR:V333=B003*V366

STEP:011
SETR:V334=B003*V366

STEP:011
SETR:V335=B003*V366

STEP:011
SETR:V336=B003*V366

STEP:011
SETR:V337=B003*V366

STEP:011
SETR:V340=B003*V366

STEP:011
SETR:V341=B003*V366

STEP:011
SETR:V342=B003*V366

STEP:011
SETR:V343=B003*V366

STEP:011
SETR:V344=B003*V366

STEP:011
SETR:V345=B003*V366

STEP:011
SETR:V346=B003*V366

STEP:011
SETR:V347=B003*V366

STEP:011
SETR:V350=B003*V366

STEP:011
SETR:V351=B003*V366

STEP:011
SETR:V352=B003*V366
SETR:V310=V310+V353

* Read one torque vaue at a time and raise flag F105 to *
tell the IBM PC to collect the new torque and time values.

STEP:011
SETR:V310=V310+V311
SETR:V312=B003*V366
SFRS:F105
DELY:000,N305,N306
IFIN:001,N300,N304
SKIP:001
SFRS:F102

STEP:011
DELY:000,000,002
ENDB
CUST:CMD,000,007
SFRS:F103

* At the end of the time allocated to the previous shear *
*rate, check whether it is the end of the experiment or if *
*another shear rate should be applied. *

STEP:012
IFFL:001,F103
AND
IFFL:000,F104
GOTO:012
IFFL:001,F103
AND
IFFL:001,F104
GOTO:014

* If the experiment is completed, open window, raise ram *
*open dies. *

STEP:013
SDON:J003
SDON:J000
SDOF:J001

STEP:013
DELY:000,000,003
SDOF:J002

STEP:013

DELY:000,000,003
SDOF:J004
CUST:CMD,000,001
HOLD:004,000
GOTO:000

* If a new experiment is required to be applied on the *
*same test sample, the new test temperature is applied and *
*the experiment repeated. *

STEP:014
IFFL:001,F104
GOTO:014
DSET:003,000,317
DSET:003,001,317
DSET:003,002,317

STEP:015
FLOT:301,000,003
SETR:V302=(B000+B001+B002)/V301
FLOT:301,000,002
SETR:V303=V317+V301
SETR:V306=V317-V301
IFAN:000,V302,V303
AND
IFAN:000,V306,V302
SKIP:001
GOTO:015
SFRS:F107
GOTO:007
ENDS

APPENDIX D

CONSTANT SHEAR STRESS PROGRAMS

Contents:

Appendix D1: THE SOFTWARE SLIPPER

Appendix D2: MPC 84 SEQUENCE 5

APPENDIX D1 THE SOFTWARE "SLIPPER"

```

*****
*   Define the F1 to act as an emergency stop.   *
*****
10 ON KEY(1) GOSUB 1930
20 KEY(1) ON
*****
*   Definition of arrays and communication messages with *
*the MPC84 . Eg. the message MSG3$ will transfer or receive*
*data to or from the MPC84 memory addresses: V356,N357 and *
*N360.   *
*****
30 DIM TEMP1!(8),TEMP2!(8),TEMP3!(8),TEMP4!(8),TEMP5!(8),
    TEMP6!(8),TEMP7!(8),TEMP8!(8),TEMP9!(8),TEMP10!(8),
    TEMP11!(8),TIM$(10),TRQ$(10)
40 MSG1$="#1,F100,F101,F110,F102,F106,F120,F121,F122#"
50 MSG2$="#1,V317,N302,N303,F100,F101,F120#"
60 MSG3$="#1,V356,N357,N360#"
70 MSG4$="#1,F102#"
80 MSG5$="#1,F106#"
90 MSG6$="#1,F110,F121#"
100 MSG7$="#1,F122#"
110 MSG8$="#1,V355,V354#"
120 MSG9$="#1,F124,F123#"
130 MSG10$="#1,F124#"
140 MSG11$="#1,F123#"
*****
*   Zero all flags used and display the menu.   *
*****
150 TEMP1!(1)=0:TEMP1!(2)=0:TEMP1!(3)=0:TEMP1!(4)=0:
    TEMP1!(5)=0:TEMP1!(6)=0:TEMP1!(7)=0:TEMP1!(8)=0:
    TEMP9!(1)=0:TEMP9!(2)=0
160 CALL MTYPE (ERRST%,MSG1$,TEMP1!(1)):
    CALL MTYPE (ERRST%,MSG9$,TEMP9!(1))
170 CLS:LOCATE 3,25:PRINT"TORQUE CONTROL"
180 LOCATE 4,25:PRINT"-----"
190 LOCATE 5,30:PRINT"MENU"
200 LOCATE 6,30:PRINT"-----"
210 LOCATE 10,20:PRINT"A)          CREATE A NEW EXPERIMENT"
220 LOCATE 12,20:PRINT"B)          RUN THE EXPERIMENT"
230 LOCATE 14,20:
    PRINT"C)          RUN AN OLD EXISTING EXPERIMENT"
240 LOCATE 16,20:PRINT"D)          PRINT OUT A RESULT FILE"
250 LOCATE 18,20:PRINT"E)          ESCAPE"
260 X$=INPUT$(1)
270 IF X$="A" THEN 330
280 IF X$="B" THEN 640
290 IF X$="C" THEN 610
300 IF X$="D" THEN 1110
310 IF X$="E" THEN CALL MTYPE (ERRST%,MSG1$,TEMP1!(1)):

```

```

      CALL MTYPE (ERRST%,MSG9$,TEMP9!(1)):CLOSE:END
320 GOTO 260
*****
*   When option "A" is pressed, start probing for the      *
*   results of the experiment and save them in a sequential *
*   file.                                                    *
*****
330 CLS:LOCATE 2,30:PRINT "CREATE A NEW EXPERIMENT"
340 LOCATE 3,30:PRINT"-----"
350 LOCATE 6,10:INPUT"ENTER THE NAME OF THE NEW EXPERIMENT
      TO BE CREATED: ",DATA$
360 DATA$="A:"+DATA$
370 OPEN DATA$ FOR OUTPUT AS #1
380 LOCATE 8,10:
      INPUT"ENTER THE TEMPERATURE OF THE EXPERIMENT: ",TEMP%
390 LOCATE 10,10:
      PRINT"ENTER THE PREHEAT TIME OF THE SPECIMEN:"
400 LOCATE 11,15:INPUT"MINUTES: ",MIN%
410 LOCATE 12,15:INPUT"SECONDS: ",SEC%
420 CLS:LOCATE 6,10
430 PRINT"  THE EXPERIMENT IS TO BE PROGRAMED IN STEPS.
      EACH STEP CONTAINS THE"
440 PRINT"REQUIRED SHEAR STRESS AND THE DURATION IN MINUTES
      AND THEN SECONDS."
450 PRINT"FIRST, ENTER THE NUMBER OF STEPS TO BE PROGRAMED:"
460 INPUT"N=",NUM%
470 PRINT#1,TEMP%:";MIN%:";SEC%:";";
480 FOR I=1 TO NUM%
490 PRINT"STEP ";I;
500 INPUT;"  SHEAR STRESS: ",TRQ!
510 INPUT;"  MINUTES:";MIN%
520 INPUT "  SECONDS:";SEC%
530 TRQ1!=TRQ!/1.4653
540 IF SEC%=0 AND MIN%>0 THEN SEC%=60:MIN%=MIN%-1
550 PRINT#1,TRQ1!;" ";TRQ1!;" ";MIN%:" ";SEC%:" ";
560 NEXT
570 PRINT"FILE IS NOW CREATED.
      PRESS SPACE BAR TO GO BACK TO MENU."
580 X$=INPUT$(1)
590 IF X$=" " THEN CLOSE#1:GOTO 170
600 GOTO 580
*****
*   When choice "C" is pressed, load the file containing  *
*   the experimental details and create a sequential file for *
*   the collected data.                                     *
*****
610 CLS:LOCATE 6,10
620 INPUT"ENTER THE NAME OF THE EXPERIMENT TO BE USED: ",
      DATA$
630 DATA$="A:"+DATA$
640 OPEN DATA$ FOR INPUT AS #1
650 INPUT"ENTER THE NAME OF THE FILE IN WHICH RESULTS ARE
      GOING TO BE STORED: ",RESULT$
660 RESULT$="A:"+RESULT$
670 OPEN RESULT$ FOR OUTPUT AS #2

```

```

680 INPUT #1,TEMP2!(1),TEMP2!(2),TEMP2!(3)
690 INPUT"ENTER YOUR COMMENTS ABOUT THE RESULT FILE:",A$
700 PRINT#2,A$;"":TEMP2!(1);";";
*****
* Start sequence 4 (Appendix C) in MPC84 and raise flag *
*F120 to tell sequence 4 to switch to sequence 5 *
*(Appendix D2) after the filling procedure is completed. *
* Create a sequential file for the collected data. *
*****
710 TEMP2!(4)=1:TEMP2!(5)=1:TEMP2!(6)=1
720 CALL MTYPE (ERRST%,MSG2$,TEMP2!(1))
730 CLS:LOCATE 10,10
740 CALL MACPT (ERRST%,MSG4$,TEMP4!(1))
750 IF TEMP4!(1)=0 THEN PRINT"WAIT FOR TEMPERATURE TO REACH
SET POINT!":LOCATE 10,10:GOTO 740
760 CLS:LOCATE 10,10:PRINT"TEMPERATURE HAS NOW REACHED SET
POINT."
770 SOUND 1000,10
*****
* Display message for operator to start the experiment *
*after ensuring that the rotor is in its position. *
*****
780 LOCATE 12,15:PRINT"1) INSERT SPECIMEN TO BE TESTED"
790 LOCATE 13,15:PRINT"2) INSERT ROTOR"
800 LOCATE 14,15:PRINT"3) PRESS ROTOR TO ACTIVATE SWITCH"
810 CALL MACPT (ERRST%,MSG4$,TEMP4!(1))
820 IF TEMP4!(1)=1 THEN 810
830 CLS:LOCATE 20,30:PRINT"STAY CLEAR OF WINDOW!"
840 LOCATE 22,32:PRINT"WHEN READY PRESS SPACE BAR"
850 X$=INPUT$(1)
860 IF X$<>" " THEN 850
870 TEMP5!(1)=1:CLS:LOCATE 20,30:
PRINT"EXPERIMENT IN PROGRESS!"
880 LOCATE 25,10:
PRINT"(USE 'F1' TO STOP EXPERIMENT AT ANY TIME)"
890 CALL MTYPE (ERRST%,MSG5$,TEMP5!(1))
900 IF EOF(1) THEN 1040
910 INPUT#1, TEMP3!(1),TEMP3!(2),TEMP3!(3),TEMP3!(4)
920 IF EOF(1) THEN TEMP11!(1)=1:
CALL MTYPE (ERRST%,MSG11$,TEMP11!(1))
930 CALL MTYPE (ERRST%,MSG3$,TEMP3!(2))
940 PRINT#2,"/":TEMP3!(1);"/":";";";
950 PRINT "S'STRESS= ":TEMP3!(1)
960 CALL MACPT (ERRST%,MSG7$,TEMP7!(1)):
CALL MACPT (ERRST%,MSG10$,TEMP10!(1))
970 IF TEMP10!(1)=1 THEN TEMP10!(1)=0:
CALL MTYPE (ERRST%,MSG10$,TEMP10!(1)):GOTO 900
980 IF TEMP7!(1)=0 THEN 960
990 TEMP7!(1)=0:CALL MTYPE (ERRST%,MSG7$,TEMP7!(1))
1000 CALL MACPT (ERRST%,MSG8$,TEMP8!(1))
1010 PRINT"S'RATE= ":TEMP8!(1)."ERROR= ":TEMP8!(2)
1020 PRINT#2,TEMP8!(1);";":TEMP8!(2);";";
1030 GOTO 960
1040 CALL MTYPE (ERRST%,MSG1$,TEMP1!(1)):
CALL MTYPE (ERRST%,MSG9$,TEMP9!(1))

```

```

1050 CLOSE
1060 PRINT"                END OF EXPERIMENT"
1070 PRINT" PRESS SPACE BAR TO GO BACK TO MENU"
1080 X$=INPUT$(1)
1090 IF X$=" " THEN 170
1100 GOTO 1080
*****
*   When option "D" is pressed, the results collected and *
* stored in a sequential file can be printed out in various *
* formats. *
*****
1110 CLS:LOCATE 10,20
1120 INPUT"ENTER THE NAME OF YOUR RESULT FILE: ";RESULT$
1130 RESULT$="A:"+RESULT$
1140 OPEN RESULT$ FOR INPUT AS #3
1150 CLS:LOCATE 5,20:
    PRINT"YOU CAN PROGRAM YOUR OUTPUT TO GIVE:"
1160 LOCATE 10,20:
    PRINT"A)   THE LAST 10 RESULTS OF EACH SHEAR STRESS"
1170 LOCATE 12,20:PRINT"B)   THE FIRST 'X' RESULT OF EACH
    SHEAR STRESS AT A"
1180 LOCATE 13,28:PRINT"CERTAIN STEP VALUE OF 'Y',
    THEN THE REST"
1190 LOCATE 14,28:
    PRINT"OF THE RESULTS AT A STEP VALUE OF 'Z'."
1200 LOCATE 16,20:PRINT"C)   ALL OF THE RESULTS."
1210 LOCATE 20,2:PRINT"DO YOU WANT TO SEE YOUR RESULTS ON
    THE SCREEN BEFORE CHOOSING HOW YOU WANT THEM PRINTED
    OUT?"
1220 X$=INPUT$(1)
1230 IF X$="Y" GOTO 1320
1240 IF X$<>"N" GOTO 1220
1250 LOCATE 20,2:PRINT"
1260 LOCATE 20,2:PRINT"ENTER YOUR CHOICE OF OUTPUT:"
1270 X$=INPUT$(1)
1280 IF X$="A" GOTO 1450
1290 IF X$="B" GOTO 1700
1300 IF X$="C" GOTO 1910
1310 GOTO 1270
1320 INPUT#3,A$:PRINT"COMMENTS: ";A$
1330 INPUT#3,A$:PRINT"TEMPERATURE OF THE EXPERIMENT= ";A$
1340 IF EOF(3) THEN CLOSE#3:GOTO 1140
1350 INPUT#3,A$
1360 B$=LEFT$(A$,1):IF B$="/" THEN 1400
1370 INPUT#3,C$
1380 PRINT"S' RATE= ";A$,"ERROR= ";C$
1390 GOTO 1340
1400 A=LEN(A$):A=A-1
1410 A$=LEFT$(A$,A):A=A-1:A$=RIGHT$(A$,A)
1420 PRINT "S' STRESS= ";A$
1430 INPUT#3,A$,C$
1440 GOTO 1380
1450 A%=10
1460 INPUT#3,A$:LPRINT"COMMENTS: ";A$
1470 INPUT#3,A$:LPRINT"TEMPERATURE OF THE EXPERIMENT= ";A$

```

```

1480 INPUT#3,A$:GOTO 1620
1490 IF EOF(3) THEN CLOSE #3:GOTO 1660
1500 INPUT#3,A$
1510 B$=LEFT$(A$,1):IF B$="/" GOTO 1580
1520 INPUT#3,C$
1530 FOR J=1 TO A%-1
1540 TIM$(J)=TIM$(J+1):TRQ$(J)=TRQ$(J+1)
1550 NEXT
1560 TIM$(A%)=A$:TRQ$(A%)=C$
1570 GOTO 1490
1580 FOR J=1 TO A%
1590 IF TIM$(J)<>"0" THEN LPRINT"S' RATE= ";TIM$(J),
    "ERROR= ";TRQ$(J)
1600 TIM$(J)="0":TRQ$(J)="0"
1610 NEXT
1620 A=LEN(A$):A=A-1
1630 A$=LEFT$(A$,A):A=A-1:A$=RIGHT$(A$,A)
1640 LPRINT"S' STRESS= ";A$
1650 INPUT#3,A$,C$:GOTO 1530
1660 FOR J=1 TO A%
1670 IF TIM$(J)<>"0" THEN LPRINT"S' RATE= ";TIM$(J),
    "ERROR= ";TRQ$(J)
1680 NEXT
1690 GOTO 170
1700 LOCATE 20,1:INPUT"B:    PLEASE ENTER YOUR 'X' VALUE:",
    A%
1710 PRINT"
1720 LOCATE 21,1:INPUT"B:    PLEASE ENTER YOUR 'Y' VALUE:",
    B%
1730 LOCATE 22,1:INPUT"B:    PLEASE ENTER YOUR 'Z' VALUE:",
    C%
1740 A1%=0:B1%=0:C1%=0
1750 INPUT#3,A$:LPRINT"COMMENTS: ";A$
1760 INPUT#3,A$:LPRINT"TEMPERATURE OF THE EXPERIMENT= ";A$
1770 IF EOF(3) THEN CLOSE #3:GOTO 170
1780 INPUT#3,A$
1790 B$=LEFT$(A$,1):IF B$="/" GOTO 1870
1800 B1%=B1%+1:C1%=C1%+1
1810 INPUT#3,C$
1820 IF A1%<A% AND B1%=B% THEN A1%=A1%+1:B1%=0:GOTO 1860
1830 IF A1%=A% THEN A1%=A%+1:C1%=0
1840 IF C1%=C% THEN C1%=0:GOTO 1860
1850 GOTO 1770
1860 LPRINT"S' RATE= ";A$,"ERROR= ";C$:GOTO 1770
1870 A=LEN(A$):A=A-1:A1%=0:B1%=0
1880 A$=LEFT$(A$,A):A=A-1:A$=RIGHT$(A$,A)
1890 LPRINT"S' STRESS= ";A$
1900 GOTO 1770
1910 A1%=1:A%=0:B1%=1:C1%=0:B%=0:C%=1
1920 GOTO 1730
1930 TEMP6!(1)=1:TEMP6!(2)=1
1940 CALL MTYPE (ERRST$,MSG1$,TEMP1!(1)):
    CALL MTYPE (ERRST$,MSG9$,TEMP9!(1))
1950 CALL MTYPE (ERRST$,MSG6$,TEMP6!(1))
1960 CLOSE:END

```

APPENDIX D2

MPC84 SEQUENCE 5

SEQN:005

```
*****
*   After completing the filling procedure in sequence 4   *
*(Appendix C) flag F120 indicated that a set of shear    *
*stresses is to be applied by SLIPPER (Appendix D1).      *
*****
```

STEP:000

MANL:B304

FLOT:302,000,012

FLOT:303,000,000

STEP:001

DSET:003,004,303

SETR:B304=V303

```
*****
*   A different set of control parameters will be loaded  *
*into control loop 304 depending on the value of the      *
*required shear stress which will become the set point of *
*the loop.                                                 *
*****
```

STEP:002

DELY:000,000,005

DSET:003,004,356

IFAN:000,V356,V332

SKIP:004

MDVR:000,003,004,017,365

MDVR:000,003,004,025,367

MDVR:000,003,004,033,374

SKIP:003

MDVR:000,003,004,017,357

MDVR:000,003,004,025,361

MDVR:000,003,004,033,362

FLOT:306,306

IFAN:000,V303,V306

SKIP:002

SFRS:F124

GOTO:002

```
*****
*   Read the output value of the loop and implement it as  *
*the angular velocity of the rotor. Also, read the error  *
*value from the loop.                                     *
*****
```

STEP:003

```

IFFL:001,F121
GOTO:004
AUTO:B304
MDVR:000,354,003,004,014
MDVR:000,355,003,004,041
IFAN:002,V303,V355
SKIP:014
IFAN:000,V302,V355
SKIP:005
FLOT:304,000,024
CUST:SET0,304
SETR:V304=V372/V302/V355
CUST:SET1,304
SKIP:007
FLOT:304,000,002
CUST:SET0,304
SETR:V304=V372/V355
CUST:SET1,304
SKIP:002
CUST:CMD,000,007
SKIP:001
CUST:CMD,000,006
SFRS:F122
DELY:000,N357,N360
MANL:B304
SFRS:F124
*****
*   Check if more shear stresses need to be applied.   *
*****
IFFL:000,F123
SKIP:002
SFCL:F123
GOTO:004
GOTO:002

*****
*   At the end of the experiment, open dies, raise ram and *
*open window.                                           *
*****
STEP:004
CUST:CMD,000,007
MANL:B304
DSET:003,004,303
SETR:B304=V303

STEP:005
SDON:J003
SDON:J000
SDOF:J001

STEP:005
DELY:000,000,003
SDOF:J002

STEP:005

```

DELY:000.000.003
SDOF:J004
CUST:CMD.000.001
HOLD:005.000
GOTO:000
ENDS

APPENDIX E

CALCULATIONS AND CORRECTIONS FOR THE DAVENPORT CAPILLARY RHEOMETER

The results obtained with the Davenport capillary rheometer (figure 5.13) were calculated from the data obtained from the pressure transducer and from the ram speed in the following manner:

The flow rate (Q) at a particular ram speed was calculated using equation 4.2. Having calculated the flow rate, the shear rate at the wall of the capillary tube can be calculated using equation 3.15. The shear rate (1/sec) was found to be equal to 60 times the ram speed (cm/min).

The shear stress at the wall of the capillary tube can be calculated from the pressure drops obtained using the two capillary dies of different lengths and similar radii using equation 3.20.

The \ln (shear stress) versus \ln (shear rate) relationship was plotted at the different lubricant concentrations tested. The slopes of the curves were found to be equal to 0.45, 0.33, 0.24 and 0.144 for 0, 0.5, 1.5 and 3phr

lubricant respectively. Using the Rabinowitsch correction the corrected shear rate at the wall of the capillary tube was calculated from equation 3.16.

APPENDIX F

ERROR IN REPORTED APPARENT VISCOSITIES

A set of seven experimental results was obtained from the TMS rheometer at 125 C with the SLIPPER software (Appendix D1) and the smooth rotor. The test sample was a natural rubber compound (Compound 1, (Section 4.3.4)) containing 0.5 phr STRUKTOL WB16 (Section 5.2). The results obtained and their standard deviations of the mean are shown in table F1.

Table F1: Standard Deviations of the Mean at Different Shear Stresses.

Shear stress (kPa)	Average shear rate (1/sec)	Standard dev. (1/sec)	Standard dev. of the mean (1/sec)
120	2.34	0.39	0.15
130	4.84	0.61	0.23
140	8.93	0.95	0.36
150	15.44	1.8	0.68
160	25.03	3.16	1.2
170	50.1	9.97	3.77

Using the t-distribution curve and taking the confidence

limit to be 95%, the degrees of freedom are six, therefore $t = 2.447$. The error in the reported shear rates and % error in the reported apparent viscosities were calculated from the standard deviation of the mean and presented in Table F2.

Table F2: Errors in Reported Shear Rates and Apparent Viscosities.

Shear stress (kPa)	Error for av. shear rate(+or-)	Average app. viscosity (kPa.sec)	Error for app. vis. (+or-)	%Error for app. vis. (+or-)
120	0.37	51.3	7	13.6
130	0.56	26.85	2.8	10.4
140	0.88	15.7	1.4	8.9
150	1.66	9.7	0.93	9.6
160	2.9	6.4	0.67	10.5
170	9.23	3.4	0.53	15.6

The average % error in the reported apparent viscosities was found to be equal to 11.4%.

APPENDIX G

PATTERN SEARCH OPTIMIZATION PROGRAM

```
*****
*   Define all arrays and put the first parameter
*approximations in array XT and the step size in array Y.
*****
10 DIM XT(5),Y(5),N(5),XAT(5)
40 XT(1)=.01:Y(1)=.001
50 XT(2)=2.9:Y(2)=.05
60 XT(3)=4:Y(3)=.5
70 XT(4)=.5:Y(4)=.05
75 XT(5)=.5:Y(5)=.05
*****
*   Set K1 = 4 indicating that after halving the step size
*four times the search routine will be terminated.
*****
80 K1=4:K=0:NUMB=0
90 FLAG1=0:FLAG2=1
*****
*   Set the array A to be equal to zero in all directions.
*****
100 FOR A=1 TO 5
110 N(A)=0
120 NEXT A
*****
*   Check for the end of the search routine by looking at
*the counter K which will show the number of times the step
*size has been halved.
*****
130 IF K=K1 THEN GOTO 800
140 B=XT(1):I=XT(2):T=XT(3):NI=XT(4):Cc=XT(5):
    GOSUB 1000
*****
*   Search in the B direction for minimum error. If B was
*found to give higher error values at B+Y(1) or B-Y(1) then
*change B to the value that gives the lowest error and
*store the change in the array N which then defines a
*direction for movement.
*****
150 MIN=ER
160 B=XT(1)+Y(1):GOSUB 1000
170 FXP1=ER:IF FXP1<MIN THEN MIN=FXP1
180 B=XT(1)-Y(1):GOSUB 1000
190 FXM1=ER:IF FXM1<MIN THEN MIN=FXM1
200 IF MIN=FXP1 THEN N(1)=N(1)+1:XT(1)=XT(1)+Y(1)
210 IF MIN=FXM1 THEN N(1)=N(1)-1:XT(1)=XT(1)-Y(1)
215 B=XT(1)
```

```

*****
* Search in the I direction and save the change made in N*
*****
220 I=XT(2)+Y(2):GOSUB 1000
230 FXP1=ER:IF FXP1<MIN THEN MIN=FXP1
240 I=XT(2)-Y(2):GOSUB 1000
250 FXM1=ER:IF FXM1<MIN THEN MIN=FXM1
260 IF MIN=FXP1 THEN N(2)=N(2)+1:XT(2)=XT(2)+Y(2)
270 IF MIN=FXM1 THEN N(2)=N(2)-1:XT(2)=XT(2)-Y(2)
275 I=XT(2)
*****
* Search in the T direction and save the change made in N*
*****
280 T=XT(3)+Y(3):GOSUB 1000
290 FXP1=ER:IF FXP1<MIN THEN MIN=FXP1
300 T=XT(3)-Y(3):GOSUB 1000
310 FXM1=ER:IF FXM1<MIN THEN MIN=FXM1
320 IF MIN=FXP1 THEN N(3)=N(3)+1:XT(3)=XT(3)+Y(3)
330 IF MIN=FXM1 THEN N(3)=N(3)-1:XT(3)=XT(3)-Y(3)
335 T=XT(3)
*****
* Search in the NI direction and save the change made in N*
*****
340 NI=XT(4)+Y(4):GOSUB 1000
350 FXP1=ER:IF FXP1<MIN THEN MIN=FXP1
360 NI=XT(4)-Y(4):GOSUB 1000
370 FXM1=ER:IF FXM1<MIN THEN MIN=FXM1
380 IF MIN=FXP1 THEN N(4)=N(4)+1:XT(4)=XT(4)+Y(4)
390 IF MIN=FXM1 THEN N(4)=N(4)-1:XT(4)=XT(4)-Y(4)
395 NI=XT(4)
*****
* Search in the Cc direction and save the change made in N*
*****
400 Cc=XT(5)+Y(5):GOSUB 1000
410 FXP1=ER:IF FXP1<MIN THEN MIN=FXP1
420 Cc=XT(5)-Y(5):GOSUB 1000
430 FXM1=ER:IF FXM1<MIN THEN MIN=FXM1
440 IF MIN=FXP1 THEN N(5)=N(5)+1:XT(5)=XT(5)+Y(5)
450 IF MIN=FXM1 THEN N(5)=N(5)-1:XT(5)=XT(5)-Y(5)
451 Cc=XT(5)
*****
* Test for undefined direction i.e. N(1 to 5)=0. *
*****
460 FOR A=1 TO 5
470 IF N(A)<>0 THEN FLAG1=1
480 NEXT A
490 IF FLAG1=0 THEN GOTO 700
500 FLAG1=0
510 IF FLAG2=1 THEN FLAG2=0:GOTO 530
515 PRINT "MIN":MIN:"FXAT":FXAT
*****
* Test for rejection of new base. If new base has higher *
*error value than the old one, go to the old base and *
*re-start the pattern search. *
*****

```

```

520 IF MIN>=FXAT THEN FOR A=1 TO 5:XT(A)=XAT(A):NEXT A:
    GOTO 90
*****
*   Make pattern move to the new base. New base = old base *
* plus N x step size.
*****
530 FOR A=1 TO 5
540 XAT(A)=XT(A)
550 NEXT A
560 FXAT=MIN
570 FOR A=1 TO 5
580 XT(A)=XT(A)+(N(A)*Y(A))
590 NEXT A
600 NUMB=NUMB+1
610 PRINT "ITERATION No=";NUMB;" ERROR=";FXAT;" AT:";XAT(1)
    ;XAT(2);XAT(3);XAT(4);XAT(5);" K=";K
620 GOTO 140
*****
*   If N was equal to zero, halve the step size and add one*
* to the counter K.
*****
700 FOR A=1 TO 5
710 Y(A)=Y(A)/2
720 NEXT A
730 K=K+1:PRINT "K=";K
740 GOTO 100
*****
*   Print messages for operator.
*****
800 PRINT "AFTER ";NUMB;
    "ITERATIONS THE MINIMUM WAS FOUND TO BE ";MIN
805 LPRINT "AFTER ";NUMB;
    "ITERATIONS THE MINIMUM WAS FOUND TO BE ";MIN
810 PRINT " THE COORDINATES ARE ";XT(1);XT(2);XT(3);XT(4)
    ;XT(5)
815 LPRINT " THE COORDINATES ARE ";XT(1);XT(2);XT(3);XT(4)
    ;XT(5)
820 PRINT "THE CALCULATED POINTS ARE:"
825 LPRINT "THE CALCULATED POINTS ARE:"
827 B=XT(1):I=XT(2):T=XT(3):NI=XT(4):Cc=XT(5)
830 FOR X=0! TO 6! STEP .25
835 GOSUB 2000
840 LPRINT "CONC=";X;"VISCOCITY=";Y
845 PRINT "CONC=";X;"VISCOCITY=";Y
850 NEXT X
860 END
*****
*   Subroutine to calculate the least square error criterion*
*****
1000 NO=25.9
1010 X=.5:GOSUB 2000
1020 E1=(12.85-Y)/12.85
1030 X=1.5:GOSUB 2000
1040 E2=(18.85-Y)/18.85
1050 X=3!:GOSUB 2000

```

```

1060 E3=(15.33-Y)/15.33
1070 X=6!:GOSUB 2000
1080 E4=(6!-Y)/6!
1090 NO=44.19
1100 X=.5:GOSUB 2000
1110 E5=(25.61-Y)/25.61
1120 X=1.5:GOSUB 2000
1130 E6=(36.19-Y)/36.19
1140 X=3!:GOSUB 2000
1150 E7=(28.23-Y)/28.23
1160 X=6!:GOSUB 2000
1170 E8=(18.43-Y)/18.43
1180 NO=81!
1190 X=.5:GOSUB 2000
1200 E9=(52.83-Y)/52.83
1210 X=1.5:GOSUB 2000
1220 E10=(70!-Y)/70!
1230 X=3!:GOSUB 2000
1240 E11=(60.09-Y)/60.09
1250 X=6!:GOSUB 2000
1260 E12=(41.79-Y)/41.79
1270 NO=122.22
1280 X=.5:GOSUB 2000
1290 E13=(87.3-Y)/87.3
1300 X=1.5:GOSUB 2000
1310 E14=(99.1-Y)/99.1
1320 X=3!:GOSUB 2000
1330 E15=(123.6-Y)/123.6
1340 X=6!:GOSUB 2000
1350 E16=(72.36-Y)/72.36
1360 NO=180.85
1370 X=.5:GOSUB 2000
1380 E17=(130.77-Y)/130.77
1390 X=1.5:GOSUB 2000
1400 E18=(157.4-Y)/157.4
1410 X=3!:GOSUB 2000
1420 E19=(212.5-Y)/212.5
1430 X=6!:GOSUB 2000
1440 E20=(119.7-Y)/119.7
1450 ER=E1^2+E2^2+E3^2+E4^2+E5^2+E6^2+E7^2+E8^2+E9^2+E10^2
      +E11^2+E12^2+E13^2+E14^2+E15^2+E16^2+E17^2+E18^2+E19^2
      +E20^2
1460 RETURN
*****
*   Subroutine to calculate the apparent viscosity .   *
*****
2000 Y=NO
2010 IF X>CR THEN Y=NO((1-T)*EXP(I*(Cc-X))+T)
2020 Y=Y*((1-B)*EXP(-X*NI)+B)
2040 RETURN

```

APPENDIX H

ERROR FOR % DECREASE IN APPARENT VISCOSITY

Results were obtained from the TMS rheometer at 100 C with the SLIPPER software (Appendix D1) and the smooth rotor. The test sample was a natural rubber compound (Compound 1 (section 4.3.4)) containing different levels of lubricant STRUKTOL WB16 (Section 5.2). If the error in the reported apparent viscosities was taken to be equal to 11%, the error in the %decrease in the apparent viscosities can be calculated using the law of propagation of errors [47].

$$P = A1 - A2 \quad \dots (H1)$$

The error in P (equation H1) will be equal to the square root of the sum of squares of the absolute errors in A1 and A2.

$$P = A1/A2 \quad \dots (H2)$$

The error in P (equation H2) will be equal to the square root of the sum of squares of the relative errors in A1 and A2.

The calculations made are shown in table H1.

Table H1: Calculation of the error in % decrease in the
apparent viscosity at 160 kPa shear stress.

Conc. (phr)	App. vis. (kPa.sec)	Absolute error	Numerator error	Numerator rel.error	%decrease rel.error
0	40	4.4	-	-	-
0.5	17.4	1.91	4.8	0.21	0.24
0.75	16.33	1.8	4.75	0.20	0.23
1.5	17	1.87	4.78	0.21	0.24
4	12.45	1.37	4.61	0.18	0.21

The average relative error in the reported % decrease
in the apparent viscosity was found to be equal to 0.23.

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