SET BEHAVIOUR OF EPICHLOROHDYRIN ELASTOMERS

i.e. epichlorohydrin

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ABSTRACT

Traditionally Epichlorohydrin (ECO) elastomers are cured by thiourea (ETU)-Lead (PbO) curing systems. However, owing to the current concerns regarding health, safety and the environment such systems are now classified as relatively high risk systems. ECO elastomers are widely used as seals and gaskets; in these applications the minimisation of compression-set and compression stress-relaxation is highly desirable. It has been suggested that a curing system designated Zisnet-FPT is not only relatively innocuous but it also has the potential to satisfy property requirements needed for providing adequate sealing efficiency. It is common practice to incorporate acid acceptors, which are merely metal oxides, in ECO rubber mixes in order to neutralise HCl that might be liberated during vulcanisation. However, the addition of acid acceptors enhances the hydrophilic nature of ECO vulcanisates and leads to excessive moisture absorption. Water can plasticise most rubbers leading to high rates of stress-relaxation. In view of the deleterious nature of moisture, several acid acceptors commonly used in ECO elastomers were evaluated. The stiffening of vulcanisates conferred by carbon black was assessed using a relative stiffening parameter, α_f. was found to be greater in ETU-Lead based systems as compared with systems based on Zisnet-FPT. The crosslink densities of both rubber vulcanisates is generally determined by swelling measurements. The effect of various additives incorporated in ECO vulcanisates upon properties either singularly or interactively was assessed using an advanced experimental statistical method known as the Central Composite Rotatable Design (CCRD). The CCRD evaluation revealed that the compression-set behaviour exhibited by the Zisnet-FPT cure system is strongly carbon black-dependent. It was also found that for vulcanisates cured by the traditional curing system the effect of carbon black upon compression-set was negligible. The longevity as assessed by compression-set performance of ECO vulcanisates cured by both systems was evaluated using the classical Arrhenius approach. The relationship between compression-set and stress-relaxation was studied by means of a mathematical model proposed by Ellul and Southern. It was found that there is a broad correlation between compression-set and stress-relaxation provided certain parameters in the model do not vary excessively.

STRUCTURE OF THESIS

This thesis comprises eleven Chapters as follows:

Chapter 1: INTRODUCTION

Chapter 2: LITERATURE REVIEW

Chapter 3: EXPERIMENTAL WORK

Chapter 4: MARCHING MODULUS VULCANISATION

Chapter 5: WATER UPTAKE AND COEFFICIENT OF DIFFUSION

Chapter 6: STIFFENING EFFECT OF CARBON BLACK

Chapter 7: POLYMER-SOLVENT INTERACTION PARAMETER (χ) AND CROSSLINK DENSITY

Chapter 8: STATISTICAL OPTIMISATION OF COMPRESSION-SET

Chapter 9: LONG TERM PREDICTION OF COMPRESSION-SET

Chapter 10: CORRELATION BETWEEN SET AND STRESS-RELAXATION

Chapter 11: CONCLUSIONS AND FUTURE WORK

The reader may find that the description and discussions pertaining to experimental procedures presented in some Chapters are somewhat repetitive. This approach has been purposely adopted in order to provide continuity and to eliminate the monotonous task that might be experienced by the reader in having to refer back to earlier Chapters on matters related to experimental methodology.

LIST OF PAPERS

This thesis is a summary of the following papers:

I M. A. Abdul Wahab, A. S. Farid and K. D. Arunashanthi (2004). Effect of non-lead cure system upon compression set of epichlorohydrin elastomers. *3rd Material Research Conference (MRC3) Proceeding (Institute of Materials, Minerals and Mining)*, London, United Kingdom, 22nd June 2004.

II M A. Abdul Wahab & Dr A Farid (2004). Effect of lead-free cure system upon compression set of epichlorohydrin elastomers, *Rubberchem 2004 (RAPRA) Proceeding, Birmingham*, United Kingdom, 9 – 10 November 2004.

III M.A. Abdul Wahab, A.S Farid, Nicholas Fernando (2005). Long Term Prediction of Set in Epichlorohydrin Elastomers, *4th Material Research Conference (MRC4) Proceeding (Institute of Materials, Minerals and Mining)*, London, United Kingdom, 21st June 2005.

IV M.A. Abdul Wahab, A.S. Farid, K. D. Arunashanthi (2006). Correlation of Stress-relaxation and Compression-set, *Elastomer for Engineering: Future Trend (RIEG) Proceeding (Inst. Of Materials, Minerals and Mining)*, London, United Kingdom, 23rd November 2006.

V M.A. Abdul Wahab, A.S. Farid, Diffusion and Water Uptake of Epichlorohydrin Elastomers with Different Acid Acceptors, *Journal of Rubber Research*, manuscript drafted (2006).

VI M.A. Abdul Wahab, A.S. Farid, Long Term Prediction of Set in Epichlorohydrin Elastomers, *Journal of Elastomers and Plastics*, manuscript drafted (2006).

ACKNOWLEDGEMENT

The lack of comprehensive literature on Epichlorohydrin (ECO) elastomers has provided impetus towards this research work. Most text discussed ECO elastomer in very brief manner and often been grouped together with other rubber materials such as polysulphides, polyethers and various halogenated elastomers under 'miscellaneous' headings. In the present study, Hydrin C2000L was selected based on viscosity and chlorine content which give fair representation of ECO elastomers overall.

For such a wide-ranging literature search, I must acknowledge not only much original research and development work but also many excellent review papers especially those in *Rubber Chemistry and Technology*. Amongst other sources are the publications of *Zeon Chemicals* by Stuart Harris (U.K) and Clark Cable (U.S.A). Most valuable resources are also provided by Ahmed S. Farid whom I am privileged to have as my research supervisor at Polymer Centre, London Metropolitan University for several years. For the time I have spent to write this thesis, my thanks are to my children; Amalin, Amirul and Azri for their patience and understanding. Also thanks to my wife, Shawaleeny, who sacrificed her time and even her own PhD study to ensure the completion of my work. Finally, I would like to thank my parents, Safiyah and Abdul Wahab who for the past 32 years constantly render their support and encouragement in fulfilling my potential.

M. A. A. Wahab
February 2007
London, United Kingdom

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LIST OF ABBREVIATION

ASTM	American Standard Test Method
CCRD	Central Composite Rotatable Design
CR	Chloroprene Rubber
CS	Compression-set
CSR	Compression stress-relaxation
DPG	Diphenyl Guanidine
ECO	Epichlorohydrin
EPDM	Ethylene Propylene Diene Monomer (rubber)
ETU	Ethylene Thiurea
FEF	Fast extrusion furnace
NBR	Nitrile Rubber
NDBC	Nickel-di-n-butyl dithiocarbamate
SRB	Solid Rocket Booster

Chapter 1

INTRODUCTION

This Chapter gives a brief introduction of Epichlorohydrin elastomers (ECO). Fundamental issues related to their vulcanisation, processing as well as their compression-set and stress-relaxation properties are discussed. Aims of the present research programme are outlined at the end of this Chapter.

1.1 ELASTOMER AND SEALING APPLICATION

Ever since 1830s, when Charles Goodyear discovered the vulcanisation of natural rubber with sulphur, elastomers without any doubt became a pre-requisite for the life we live today. The world wide consumption in 2004 was 20,179,000 tonnes *[IRSG, 2006]* in which 59% of it were synthetic rubbers. One of the most important properties of rubber is the ability to successfully return to its original dimension after a deformation; and, to be able to absorb energy on vibration. Although elastomers are often described as elastic materials, in reality they exhibit some degree of liquid-like behaviour as well as elastic characteristics. The liquid-like or viscous behaviour is useful in shaping operations because it generates heat, imparts uniformity in flow behaviour, and thus facilitates the conversion of a rubber mix into a useful product. Viscous behaviour is also useful in the final rubber product because it leads to energy absorption. This attribute enables elastomers to effectively isolate ground-borne vibrations, which would otherwise lead to damage of rigid supports and sensitive electronic equipment. However, in some static applications particularly seals and gaskets, the viscous contribution is detrimental. For instance, if a rubber is compressed, held for a time and then released, one would observe an immediate partial elastic response followed by a slow or retarded response to full recovery. The overall result is that, within a practical time scale, the rubber fails to return to its original dimensions. The amount of compression that is not fully recovered within the time scale of the experiment is known as 'set'. Thus the significance of set in sealing applications is clear: when the mating surfaces in contact with the rubber seal shift (which may be caused by differential mechanical movement or by expansion or contraction) an opening is formed which, if the rubber fails to recover, will produce a leakage path.

In the case of underground flexible pipes conveying gas, natural rubber has been used extensively as a safe, simple and effective sealing material. The position changes drastically when natural rubber is excluded from use in these applications. Present sealing materials i.e. nitrile and chloroprene elastomers are still facing some leakage problems even though it is tolerated in service due to high cost of excavation or indeed because of lack of detection. Thus, it is clearly desirable to assess the potential of much wider range of elastomeric materials which may satisfy the sealing requirements. Attempts were made by Farid *[Farid, 1999; 2000]*, to assess the potential usefulness of such materials as compression seals, valves and diaphragms for use in gas distribution systems. A range of selected elastomers were evaluated and Epichlorohydrin elastomers (ECO) were found to possess the potential to satisfy the requirements stipulated by the authorities.

In terms of sealing applications, albeit its classification is relatively better (see Figure 1.5) compared to current sealing materials i.e. chloroprene, nitrile and EPDM, most engineers would not consider ECO in their sealing applications due to insufficient data and lack of literature that provides evidence that ECO is an adequate sealing material. In high-tech applications such as aerospace, defense and Formula One cars, this concern is amplified by the risk of catastrophic failure caused by sealing materials. One of the examples is the explosion of *Challenger* Space Shuttle at Florida Kennedy Space Center in 1986 which was broadcasted live worldwide. In the Presidential Commission report *[Rogers, Armstrong et al., 1986]* which classified 'cause of accident' and 'contribution cause of accident', the failure of a secondary seal in the Solid Rocket Booster (SRB) was highlighted. Among other factors, such as design, testing, certification, procedures and management, it was found in an investigation that the fatal accident was caused by poor judgment of the launching temperature.

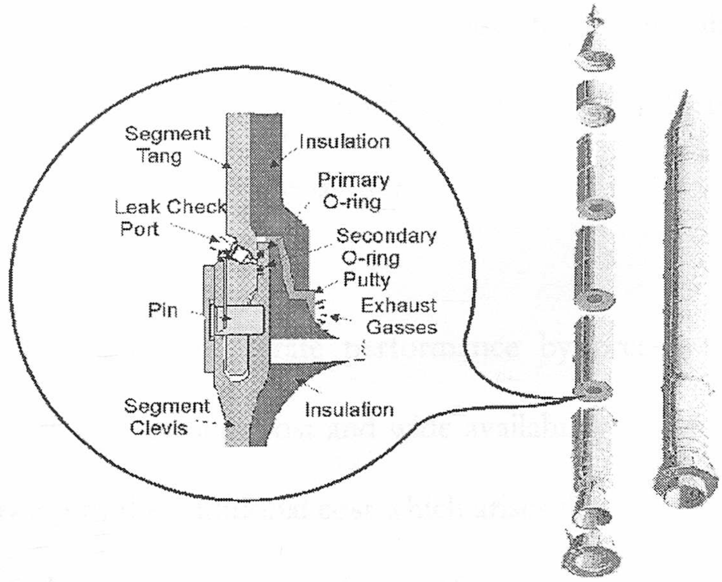


Figure1.1: Position of secondary o-ring in Solid Rocket Booster in *Challenger*

In the investigation, it was reported that the ambient temperature when the space shuttle was launched was at 36°F (2°C), 15 degree lower than the next coldest previous launch. The temperature of the failed SRB joint was estimated as 28°F (-2°C), the coldest of the joint. The temperature of the opposite SRB facing the sun (which did not fail) was estimated at 50°F (10°C). The commission later reported that the experiment showed the compressed o-ring at 75°F (23.8°C) was five times more responsive in returning to its uncompressed shape than a cold o-ring at 30°F (-1°C). In view of the findings, the Commission concluded that the cause of the *Challenger* accident was due to the failure of the pressure seal in the joint of the right SRB. Failure was caused by faulty design which was unacceptably sensitive to a number of factors of which 'the character of materials' was one of the main factors. Neither Morton Thiokol Inc. nor NASA responded adequately to internal warnings about the faulty seal and both organizations did not make a timely attempt to develop and verify a new seal after the initial seal was shown to be deficient. Instead, Thiokol and NASA management came to accept erosion of the seal as 'unavoidable' and 'acceptable'. Clearly, the lack of understanding in rubber materials is not only preventing engineers to use more suitable elastomers (or formulations) for their requirements, but indeed has caused loss of life.

In industrial applications, the moderate performance by present sealing materials is tolerated due to its low replacement cost and wide availability. However, in the long run this proves costly owing to the additional cost which arises from the frequent maintenance cost and down time. In manufacturing industries for example, all dynamic components such as bearings, gears, conveyors and chain need to be sufficiently lubricated to minimise wear and to provide some means of cooling. To ensure efficient lubrication, elastomers play vital roles as various seals, gaskets and diaphragms to ensure correct pressure is maintained or indeed to prevent leakage. This leakage can expose the lubricant to products which are extremely hazardous particularly in food industries. In similar way, foreign materials could enter the lubrication system and will damage the contact surfaces. Undoubtedly, the importance of elastomers in sealing applications is rated very highly. The failure of relatively cheap elastomeric seals could cause expensive losses. Therefore, it is desirable to use sealing elastomers which last longer and from which enough data can be compiled of their performance in order to provide a reliable indication of their service life.

In sealing applications there are four factors to consider in order to minimise failure:

- Correct processing
- Correct design
- Correct material selection
- Correct maintenance

One of the intentions of the present work is to extend the range of usefulness of ECO elastomers by looking at ways of improving formulation design. In industrial applications, it is well-known that o-ring seals often fail prematurely because of improper compound selection, apart from incorrect design. However, as the o-ring design has become almost universal for general applications, the need to improve the compound is inevitable. There are various failure modes of seals due to a diverse range of factors. However, the most common seal failures are illustrated below:

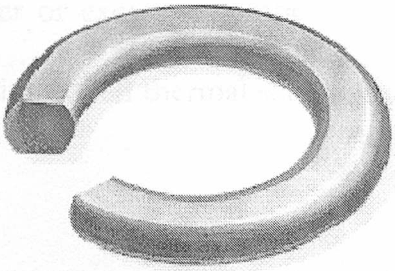


Figure 1.2: Compression-set

In Figure 1.2, the seal exhibits a flat-sided cross-section. These flat sides are surfaces that correspond to the mating seal surfaces. This kind of failure is normally caused by excessive compression, excessive temperature, incomplete cured elastomer, using elastomer with high compression-set and excessive volume swelling in chemical reagents.

To resolve the problem illustrated in Figure 1.2, the obvious solution is to use a low-compression-set elastomer. In the case of excessive swelling, one needs to consider elastomer/liquid compatibility.

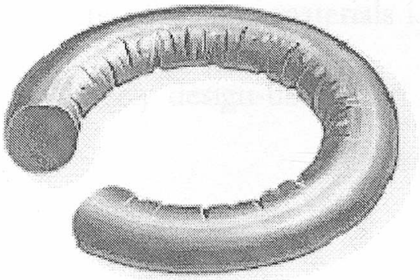


Figure 1.3: Thermal degradation

In Figure 1.3, the seal may exhibit radial cracks located on the highest temperature surfaces. Some elastomers may exhibit sign of softening. The contributing factors are poor thermal properties of elastomer or excessive temperature fluctuations. To minimise this kind of failure, elastomer with improved thermal stability must be considered.

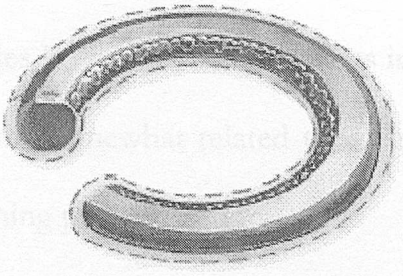


Figure 1.4: Out-gassing or extraction

Figure 1.4 exhibit failure normally observed by reduction in cross-sectional size. The main contributing factor is improper curing of the elastomer and low hardness of elastomers. To rectify this matter, seals must be post-cured and wherever possible, avoid the use of plasticized elastomers.

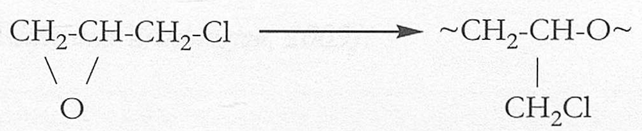
There are many other type of failure of sealing materials i.e. abrasion, extrusion, plasma degradation etc but all these are largely design-based and not directly relevant with the present work.

1.2 EPICHLOROHYDRIN: AN OVERVIEW

1.2.1 Development

ECO is manufactured from propylene through the intermediacy of allyl chloride. The major industrial use of ECO is in the production of glycerine. This process has been commercialised by Shell in 1937. It is also used as a building block in the manufacture of plastics, epoxy resins, phenoxy resins and other polymers. It used as a solvent for cellulose, resins and paints and it has found use as an insect fumigant.

High molecular weight polymers of ECO that were rubbery in nature were founded by E.J. Vandenberg in the Hercules Powder Co. laboratories in 1957 *[Vandenberg, 1982]* using aluminium alkyl catalyst system (somewhat related to Ziegler-Natta catalysts). Essentially the process is one of ring-opening polymerisation.

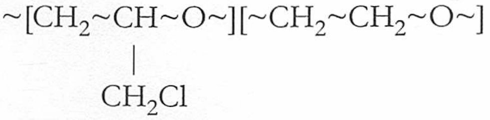


$$\underset{\backslash\ \text{O}\ /}{\text{CH}_2\text{-CH}}\text{-CH}_2\text{-Cl} \longrightarrow \sim\text{CH}_2\text{-}\underset{\substack{|\\ \text{CH}_2\text{Cl}}}{\text{CH}}\text{-O}\sim$$

The product is given an ISO designation: CO rubber. However, in the present work the author has chosen the designation ECO as is commonly used throughout the rubber industry; the ECO designation is used throughout this manuscript regardless of the type of epichlorohydrin rubber (homopolymer, copolymer or terpolymer). The CO designation was derived from the alternative name of the monomer, chloromethyl oxirane.

Apart from its high brittle point of approximately -17°C, this material was found to have excellent ozone, oil and petrol resistance. It also has very low gas permeability together with good heat resistance.

Elastomers were a difficult sell at Hercules since it would have been competing with customers who bought their rosin emulsifiers. But Vandenberg persistence in pursuing the basic research paid off. In the mid 1960s, copolymers (ECO) were prepared by copolymerisation of Epichlorohydrin with ethylene oxide.



$$\sim[CH_2\sim\underset{\underset{CH_2Cl}{|}}{CH}\sim O\sim][\sim CH_2\sim CH_2\sim O\sim]$$

Following this discovery, Hercules licensed manufacturing rights to B. F. Goodrich who marketed the material as *Hydrin* rubber whilst Hercules also commenced manufacture using the tradename *Herclor.* The Epichlorohydrin polymers received an Industrial Research 100 Award (now called R&D 100 Awards) in 1965 as one of the best new products of the year *[Ritter and Washington, 2003].*

In 1977, sulphur-curable grades using allyl glycidlyl ether as third monomer were introduced (AECO) which partly overcame the problem caused by the softening effect by hydroperoxide-containing gasoline (the sour gas problem). Subsequently, in early 1980s two Japanese companies, Nippon Zeon and Osaka Soda commenced manufacture, marketing their products under the names *Gechron* and *Epichlomer* respectively.

Since then ECO and ethylene oxide copolymers have been discovered. ECO elastomers are known for their moderate cost with good oil and gasoline resistance. These properties have rendered ECO elastomers as high-potential elastomers that can be developed further for various engineering applications. This is coupled with their excellent low-temperature flexibility have made them particularly attractive to the automotive industry. ECO elastomers have all the desirable properties that are displayed by nitrile elastomers (NBR) and chloroprene elastomers (CR). Moreover, ECO elastomers have superior gas impermeability compared to most rubbers (comparable to butyl) and are capable of functioning adequately at high service temperatures (comparable to EPDM). ECO elastomers are also classed as 'Arctic capable'.

In 1986 Hercules has decided to exit the business. B. F. Goodrich remains as a domestic supplier. World production facilities for ECO elastomers in 1986 are listed in Table 1.1.

Country	Company	Trade Name	Location	Capacity, metric tons
United States	Hercules	*Herclor*	Hattiesburg, MS	6000
	B. F. Goodrich	*Hydrin*	Avon Lake, OH	2500
Japan	Nippon Zeon	*Gechron*	Tokuyama	600
	Osaka Soda	*Epichlomer*	Kurashiki	1200

Table 1.1: Production of ECO elastomers (IISRP, Worldwide Rubber Statistics 1986)

In 1989, Zeon Chemicals USA Inc. (a wholly owned subsidiary of Nippon Zeon Co Ltd) was founded when Nippon Zeon purchased the synthetic rubber division of the B. F. Goodrich Co. and became the largest ECO elastomers supplier. Since then ECO elastomers were developed and improved greatly by Zeon laboratory. At present, Zeon offers more than 15 different grades and types of ECO elastomers to suit different applications.

The combination of fuel resistance, air ageing, broad temperature range, and moderate cost has assured a large market in the automotive industry. Hose, tubing, seals, gaskets, and coated fabrics are major applications. Rubber-covered rolls, oil field specialties and industrial products also provide a substantial market. The very good low-temperature properties of ECO have led to its use in special military applications such as oxygen mask hose and large gaskets for fuel-transfer systems.

1.2.2 Properties

In essence, ECO elastomers are halogenated linear aliphatic polyethers. The presence of the ether oxygen group has two opposing effects:

- Increase in chain flexibility which depresses T_g (and T_m if the polymer is crystallisable)
- Increase in polarity and hence interchain attraction that will increase T_g and T_m

Other than its vulcanisation issues, ECO elastomers are known for their excellent balance of properties for engineering applications particularly in automotive and marine areas. The presence of oxygen atoms in the polymer backbone imparts flexibility, while saturation in polymer chain provides superior ozone resistance. As ECO elastomers contains about one-third of chlorine (chloromethyl groups) and is polar, it has a very good resistance to oils and fuels (with exception of polar brake fluid). Because of the existence of highly polar and dense chloromethyl groups, ECO elastomers also have excellent permeation resistance. Owing to its balance of properties, these materials are classified by SAE J200 and ASTM D2000, to be in CH 125°C capable category (see Figure 1.5).

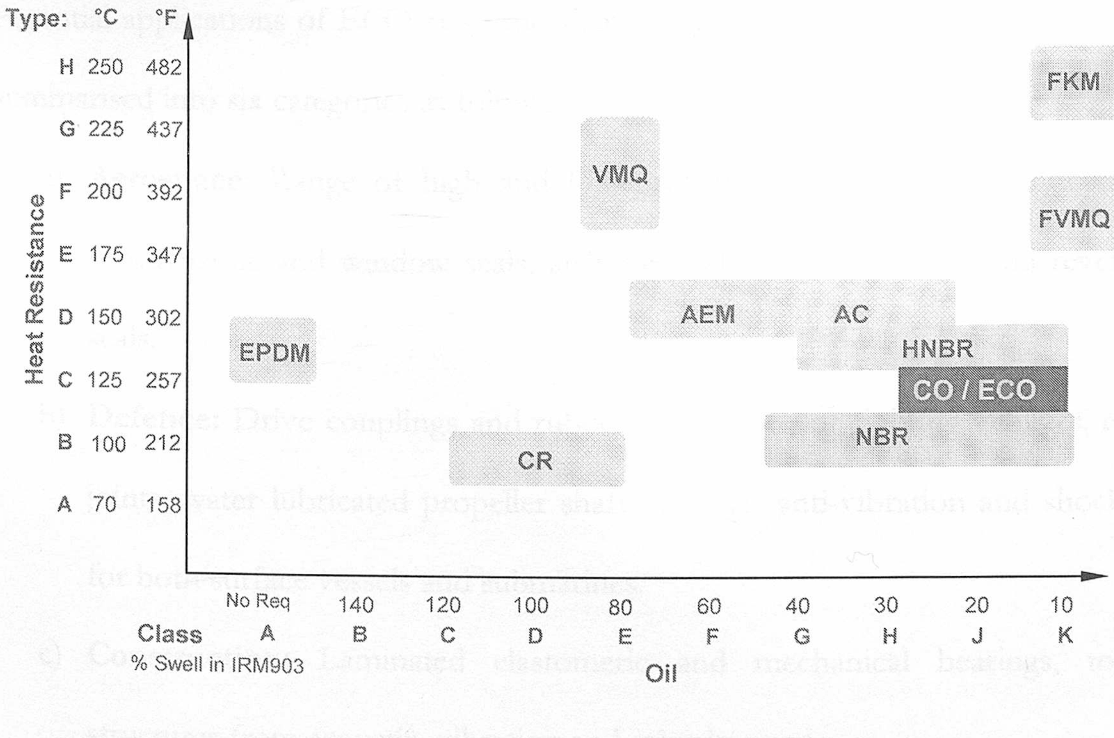


Figure 1.5: Elastomer comparison (*Courtesy of C. Cable, Zeon Chemical USA*)

With suitable compounding, ECO elastomers can be formulated to withstand 70 hours at 150°C in air while being flexible at -40°C (arctic specification). The volume resistivities are as low as 1 x 10^8 ohms-cm. By compounding ECO elastomers with a high structure carbon black such as N472, it is possible to give resistivity values in the conductive range, as low as 1.6 x 10^3 ohms-cm. This can be beneficial in situation where the build-up of a static charge is to be reduced *[Kyllingstad and Cable, 1992]*.

Blending ECO elastomers with other elastomers do not appear in the literature. Although it is possible, there is little evidence that a blend would offer any improvements over the properties offered by either elastomers *[Bhowmick, 2000]*.

1.2.3 Applications

Potential applications of ECO elastomers such as gaskets, o-rings and diaphragms can be summarised into six categories as follows:

a) **Aerospace:** Range of high and low pressure seals, electrical connector covers aerodynamic and window seals, airframe seals, engine mounts and reverse thrust seals.

b) **Defence:** Drive couplings and rubberised wheels for fighting vehicles, expansion joints, water lubricated propeller shaft bearings, anti-vibration and shock mounts for both surface vessels and submarines.

c) **Construction:** Laminated elastomeric and mechanical bearings, to protect structures from acoustic, vibration and seismic events.

d) **Transportation:** Products that provide solutions to problems where flexibility, vibration, noise and electrical isolation are required. Extensively used on the primary and secondary suspension systems of Rail, Truck and Bus.

e) **Engineering:** Vibration isolation mounts for machinery rafts, heavy generators, pump sets and coupling drive systems, rubber diaphragms, seals, accumulator bladders and specialist footwear.

f) **Offshore:** Offshore rubber components which can withstand 'sour' condition (H_2S, CO_2), high temperature and pressure. Drilling components includes pump valve seat, valve liners/seals, drill head rubbers.

1.3 CONTEMPORARY ISSUES

The following issues are recognised and need to be addressed:

- Environment and safety concerns: Hazardous cure systems used in ECO elastomers need to be replaced. Various regulations and directives stipulate strict quantities of lead or ETU in all sorts of applications.
- Engineering considerations: Compression stress-relaxation is a direct measure of the sealing force and this property needs to be minimised to ensure longevity in sealing applications. At present stress-relaxation data is not readily available and most of the time the selection is based on compression-set values.
- Industrial considerations: Specialised procedure (and equipment) in measuring compression stress-relaxation. In general rubber industries desire an alternative and simpler approach from which stress-relaxation behaviour can be obtained.
- Technological issues: Lack of technical information of ECO elastomers in the public domain suggests that further work is required in order to supplement existing technical data.

1.3.1 Environmental and Safety issue: Hazardous cure system

Although ECO elastomers have the potential for development into excellent sealing materials, the fact that many are cured by environmentally problematic lead-based curing systems and thiourea (which is carcinogenic) is a grave concern. Recent legislation which classifies leachable lead as hazardous waste has placed an additional expense burden to rubber manufacturers. European legislation *[Directive, 2000]* has been introduced prohibiting the use of lead, cadmium, mercury and hexavalent chromium (IV) for all new cars and trucks from July 2003. This will affect ECO elastomers directly as it has been used for fuel hose (Volkswagen), air duct (Mercedes), fuel tubes (Ford), emission tube (Nissan) and fuel hose (Chrysler) *[Abraham, Burczak et al., 2003]*. Although some exceptions and exemptions may exist, elimination where avoidable has become mandatory. In USA, the existing lead leachate limits stipulated by EPA (Environmental Protection Agency) have added urgency to the removal of lead-based materials from rubber compounds. The imposition of 5mg/l lead leachate limits indicate that not enough lead can be used in ECO compounds to be an effective and viable cure system. In addition, the presence of lead can cause a silver-grey bloom especially on steam cured parts. This is one of the major quality issues especially in coloured rubber products. The colouring agent is usually one of the most expensive ingredients in a compound. It is often very sensitive to curing conditions and to other curing ingredients. Furthermore, lead also known for severely fouling mould cavities. This is thought to be due to both lead complexes and ethylene thiourea (ETU) depositing onto the mould surface during vulcanisation. Apart from known toxicity, thiourea is also known as carcinogenic (material can cause cancer) as well as teratogenic (material that can cause malfunction or defect in foetus or embryo). These issues have led to the investigation of alternative cure systems, especially non-lead-based vulcanisation systems. The alternative system sought needs to be conducive to contemporary issues regarding safety, recycling and environment without compromising their excellent properties. This work no doubt requires significant acquisition of data to supplement the lack of information in present literature on ECO elastomers.

1.3.2 Engineering issue: Compression stress-relaxation (CSR)

CSR is considered as the most direct measure of sealing capacity. It gives the force a rubber article would exert on a solid sealing surface as a function of time. However, as the stress-relaxation tests present some experimental difficulties, industries tend to use a simpler test which is known as compression-set although the information given by this test is somewhat limited. The debate about the use of compression-set and stress-relaxation, as a predictor of seal performance is not new. Morell and Watson *[Morell and Watson, 1976]* suggested that compression-set and compression stress-relaxation have different non-linear relationships to the basic processes and hence are not expected to correlate with each other i.e. network formation during compression is not expected to have significant effect on compression stress-relaxation but markedly reduces recovery on release of compression. But Farid *[Farid, 1996; 1999]* suggested set and stress-relaxation in elastomers at elevated temperature arise from chemical changes that occur in the rubber network. Therefore, in principle they are connected. Previous work by Ellul and Southern *[Ellul and Southern, 1985]* also demonstrated that it is possible to model the CSR based on compression-set data.

1.3.3 Industrial issue: Testing and properties

Practically, compression-set is preferable because of its simplicity. It also does not require highly-skilled workers to perform compression-set tests as the procedure is very robust. CSR on the other hand, requires expensive and specialised equipment and is susceptible to human error. Therefore the development of theoretical or empirical relationships between stress-relaxation and compression-set is highly desirable for the rubber and allied industries.

1.3.4 Technological issue: Lack of technical data

The lack of technical information on ECO elastomers has somewhat restricted their growth in many applications. Although existing applications in certain areas such as automotives and petrochemicals has strengthened their reputation as viable materials for extreme applications, the absence of important information of essential properties has excluded them from wider applications. Therefore, it is desirable to acquire, validate and publish pertinent data for ECO elastomers in terms of: diffusion behaviour, filler effects, solvent-polymer interaction parameter values (χ), network characterisation and life prediction. It is noteworthy that all the aforementioned properties are believed to be important in attempting to obtain an overall assessment of ECO elastomers as a sealing material.

1.4 AIMS OF PROPOSED STUDY

In order to fully appreciate the benefits of ECO elastomers as an important engineering elastomer several aspects of its behaviour need to be investigated. This includes: seeking safe and environmentally friendly alternative curing systems; plasticization effects due diffusion and water absorption; crosslinked network characterisation; life prediction methodology and developing reliable relationships between set and stress-relaxation. It is hoped that the findings from the proposed study will engender confidence in ECO as a viable engineering material and lead to its wider adoption.

At the onset one should take note of a few peculiar features displayed by ECO rubber mixes as these are of fundamental relevance in the present work. For instance, ECO mixes (cured by lead-based system) are known to exhibit marching-modulus-cures (this phenomenon will be explained in due course), which leads to problems in attempting to obtain reliable cure times. Thus, it is desirable to establish a reliable method for estimating reliable vulcanisation times in such cases. Several methods are available for determining reliable cure times but the 'Analytical Method' seemed the most appropriate and was consequently adopted; the procedure will be discussed more fully later on. In terms of set, it is known that lead-based vulcanisation systems are far superior than most. As we wish to find a more benign curing system it is important to develop an equivalent non-lead-based vulcanisation system. No fewer than eight alternative cure systems have been proposed *[Harris, 2000]*; but, in terms of minimising set the Zisnet-FPT system appears to be the most promising. It is desirable and informative to commence work using a statistical approach (factorial design of experiments) in order to locate optimum set performance of ECO compound for the vulcanisation systems mentioned above. The statistical approach can lead to the recognition of various vulcanisation systems that would be appropriate in terms of minimising set and CSR. ECO is a polar rubber and as such susceptible to moisture absorption; moreover moisture has plasticizing effect in most rubbers leading detrimental behaviour in terms of CSR and compression-set at ambient and low temperatures. Therefore it is important that one understands the migratory nature of water in ECO rubber compounds by way of diffusion behaviour. Concerning diffusion, it would be expedient to study the diffusion behaviour of ECO elastomers containing lead-based and non-lead-based acid acceptors; particularly in view of the general belief that lead-based systems tend to absorb low levels of moisture.

Crosslink density has a profound influence on chemical and mechanical properties of rubbers in general. The way in which crosslink density affects CSR and compression-set is obviously important in this work and therefore determining crosslink density for ECO compounds is a fundamental aim of the present investigation. As will be explained at the appropriate juncture, crosslink density experiments on rubbers usually involve swelling of rubber vulcanisates in appropriate solvents. If this approach is used then one must have knowledge of the polymer-solvent interaction parameter. Unfortunately, so far as the author is aware, no reliable polymer-solvent interaction parameter values are available in the literature for ECO elastomers. Thus, an important preliminary aspect of the work described here was to determine the polymer-solvent interaction parameter for a particular ECO/liquid system. Since compression-set is a relatively simple test it is desirable to attempt to develop a relationship between this property and CSR; as may be inferred from earlier comments CSR is a fundamental property for assessing behaviour of seals but it is relatively difficult to measure. Many engineering products, such as seals used in underground applications, once installed are difficult to assess for routine testing or replacement and therefore it is helpful to have in place reliable life-extrapolation techniques to quantify longevity. The present study includes an extensive investigation in this area.

As a general summary the aims of the present work are:

a) To replace hazardous cure systems used for ECO with alternative benign systems, such as as Zisnet-FPT. A statistical approach known *Central Composite Rotatable Design (CCRD)* to optimise the curing system is used.

b) To develop a correlation between properties related to sealing efficiency such as compression-set and stress-relaxation on the basis that the former property is easier to determine than the latter.

c) To supplement the current body of literature on ECO elastomers in terms of diffusion, filler effects, polymer-solvent interaction parameter values (χ) and network characterisation.

d) Attempt to develop a reliable life-prediction methodology for assessing longevity.

In an attempt to achieve the preceding aims the work was divided into six areas of individual study; these are reported and discussed in subsequent chapters.

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Chapter 2

LITERATURE REVIEW

This chapter discusses the main body of literature that is currently available for ECO elastomers but which pertinent to this investigation. ECO is discussed specifically in relation to Hydrin® tradename, the grade used in present work.

2.1 EPICHLOROHYDRIN ELASTOMERS

ECO elastomers are available in both a homopolymer (poly-epichlorohydrin) and a copolymer [poly(epichlorohydrin-*co*-ethylene oxide)]. There is also a terpolymer. Essentially a copolymer with a cure-site monomer allows greater freedom in crosslinking chemistry. Within the various classes, there are a range of molecular weights available for specific compounding and application. Zeon Chemicals alone offers about 15 different ECO elastomers as shown in Table 2.1 under the trade name *Hydrin*®. Each *Hydrin*® elastomer grade has certain properties unmatched by other grades and other elastomers. *Hydrin*® H is outstanding in its low gas permeability and ozone resistance. It is about three times as impermeable to air as butyl rubber. Vulcanisates of both *Hydrin*® H and *Hydrin*® C2000 exhibit extremely low swell in ASTM oils, aliphatic solvents and aromatic fuels. Both have low hysteresis but *Hydrin*® H has high damping characteristics at room temperature.

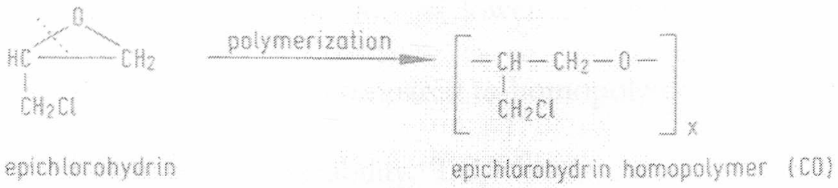
Hydrin® C2000 has low damping, and relatively constant hardness and flexibility over a wide temperature range. It has true low-temperature flexibility, not just a low brittle point. This puts *Hydrin*® C2000 elastomers in the oil-resistant, low-temperature class with polysulfide and fluorinated rubbers. It is also inherently static dissipative and can impart unique dielectric properties to polymer blends and compounds, spanning the range from conductive through static dissipative to highly insulating, while retaining their flexibility, strength, dynamic properties and oil resistance. Certain grades of the raw polymers are soluble and have sufficient tack to make them of interest for adhesives. When *Hydrin*® H, *Hydrin*® C2000 series or *Hydrin*® T3000 series elastomers are blended, the properties are generally intermediate and proportional to the amount of each polymer.

Hydrin Grade	Mooney Viscosity	S.G	Tg (°C)	Special Properties / Applications
H (45, 55, 65, 75)	40-80	1.37	-21	Outstanding ozone and gas permeation resistance. Used for fuel hose, vibration mounts, adhesives, and gaskets.
H1100	52-65	1.35	-26	Copolymer of ECH and Allyl Glycidal Ether (AGE) for improved ozone resistance. Can be sulphur or peroxide cured.
C2000	90-102	1.28	-41	Fuel pump diaphragms, hose, coated fabrics and vibration mounts. Can also impart antistatic properties to plastics.
C2000L	65-75	1.28	-41	Low viscosity version of Hydrin C2000.
C2000LL	53-65	1.28	-41	Lower viscosity version of Hydrin C2000.
C2000XL	40-52	1.28	-41	Lowest viscosity version of Hydrin C2000 for optimum injection flow.
T3000	80-94	1.28	-43	Terpoylmer of ECH/EO/AGE. Sulphur curable with improved milling properties and can be blended with all other elastomers.
T3000L	65-79	1.28	-43	Low viscosity Hydrin T3000.
T3000LL	50-64	1.28	-43	Lowest viscosity version of Hydrin T3000 for optimum injection flow.
T3100	63-77	1.30	-36	High AGE content terpolymer for enhanced 'sour gasoline' & ozone resistance.
T3100	63-77	1.30	-36	High AGE content terpolymer for enhanced 'sour gasoline' & ozone resistance.
T3102	80-100	1.30	-38	Highest ECH content terpolymer for improved heat and permeation resistance.
T3105	70-80	1.28	-41	High ECH and AGE content terpolymer for improved heat & ozone resistance.
T3106	53-67	1.28	-48	Highest EO content terpolymer for best low-temperature properties and enhanced electrostatic dissipative properties. Used in low-temperature hoses, air inlet ducts, and laser printer rolls.
T5010	75-100	1.27	-40	Has the best mill release and processing.

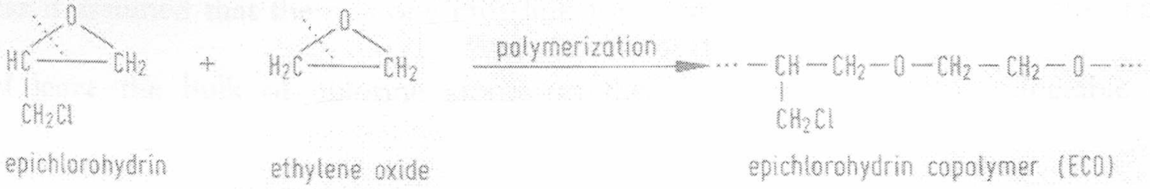
Table 2.1: Various grades and types of ECO elastomers by Zeon

Properly formulated compounds have the smooth mill processing and good building tack of polychloroprene and natural rubber. *Hydrin*® T3000 can be blended with conventional elastomers such as SBR or nitrile because of its similar cure characteristics. This allows compounding at maximum cost efficiency, by using only specific amount of *Hydrin*® necessary to obtain desired properties. *Hydrin*® T3000 rubbers can also be used to improve the properties of conventional rubber without adding excessive costs. The low-temperature properties and fuel and oil resistance of *Hydrin*® T3000 are the same as for *Hydrin*® C2000. While heat resistance and compression-set are reduced with sulphur cures, these properties are improved when a peroxide cure is used. ECO elastomers can be divided into three types:

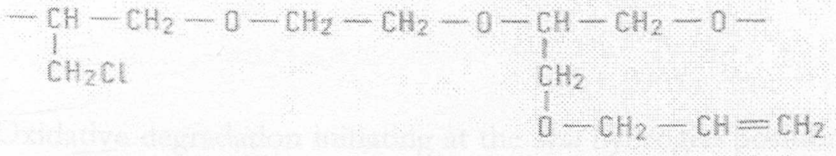
a) homopolymers of ECO designated as CO



b) copolymers of ECO and ethylene oxide (about 40%) designated as ECO



c) terpolymer of ECO, ethylene oxide and unsaturated monomer (allyl glycidyl ether) designated as GECO according to ASTM 1418. The unsaturated monomer provides double bonds in side chains pendant from the fully saturated backbone to enable sulphur cures to be obtained.



$$-\underset{\substack{|\\ CH_2Cl}}{CH}-CH_2-O-CH_2-CH_2-O-\underset{\substack{|\\ CH_2\\ |\\ O-CH_2-CH=CH_2}}{CH}-CH_2-O-$$

Homopolymer (CO) is basically described as a saturated polyether with a polar character imparted by the chloromethyl side group. The 38% chlorine content provides the fuel resistance and promotes flame retardancy. The copolymer (ECO) has lower chlorine content, about 26%; it has improved low-temperature flexibility imparted to it by ethylene oxide monomer but higher fuel swell due to lower chlorine content. With a glass transition temperature (T_g) below -40°C compared to homopolymer (CO) value of -20°C, ECO has superior low-temperature flexibility. Terpolymer cure-site monomer allows a broad application of peroxide, peroxide/coagent, and sulphur cure mechanisms. The very polar chloromethyl group common to CO and ECO elastomers not only creates the basic oil resistance but is also the crosslinking site in these elastomers. During the crosslinking process it assumed that there is one crosslink for every 130 – 200 repeating units. This would leave the bulk of chlorine atoms on the chloromethyl groups vulnerable to dehalogenation.

Only C2000L (copolymer) was used in present work. This grade is similar to T3000L in many ways and could give fair representation of ECO elastomers in general.

Previous work by Yamada *[Yamada, Arai et al., 1973]* and Nakamura *[Nakamura, Mori et al., 1974]* proved conclusively that ageing occurs in two steps:

- Step 1: Oxidative degradation initiating at the *beta* hydrogen position following the thermal decomposition mechanism for alkylene oxides.
- Step 2: Subsequent formation of hydroperoxide creating chloroketone structure that decomposes, yielding HCl.

Therefore the mechanism of protection for long-term heat stability dictates both an antioxidant (step 1) and an HCl acceptor (step 2). Typical antioxidants are metal dithiocarbamates: nickel dibutyldithiocarbamate (NBC), nickel diisobutyl dithiocarbamate (NIBC) and nickel dimethyldithiocarbamate (NMC). Typical HCl acceptors are red lead oxide and magnesium oxide. Zinc oxide should be avoided as they become strong Lewis acid and promote rapid elastomer breakdown *[Farid, 1999]*.

Low temperature properties of ECO elastomers are particularly good as was previously mentioned. The ether (oxygen) linkage in the backbone is highly mobile, much like the siloxy linkage in the silicone rubber backbone. Long term ageing characteristics are a function of operating temperature. The antioxidant and HCl acceptor ingredients are essentially sacrificial. On depletion of these agents, there is typically a reversion to lower-molecular weight materials. Fluid resistance values in terms of automotive environment are available from Zeon Chemicals whose bulletins contained very encouraging information with respect to long-term utilisation of CO and ECO elastomers. A major problem is with the sour (peroxidised) gasoline, which causes an attack similar to that described as step 2 of the ageing process. Specific compounding can minimise sour gasoline attack but cannot completely stop it *[Mori and Nakamura, 1984]*. Aqueous and nonaqueous electrolytes should be avoided as they promote nucleophilic attack on the chloromethyl group, causing rapid breakdown.

The crosslinking of CO and ECO elastomers can progress by several mechanisms each utilising nucleophilic displacement *[Bhowmick, 2000]* of the chlorine from the chloromethyl group using:

i. Ethylene thiourea (nucleophilic, crosslinker), red lead oxide (acid acceptor)

ii. Amine accelerator (nucleophile), thiadazole complex (crosslinker), barium carbonate (acid acceptor), magnesium oxide (acid acceptor)

iii. Diphenyl guanidine (nucleophile), 2-4-6-trimercapto-*s*-triazine (crosslinker), magnesium oxide (acid acceptor)

The terpolymer may be crosslinked through the reactive double bond that is pendant to the backbone by the following cure systems:

i. peroxide/coagent, peroxide

ii. sulphur and organic accelerators

iii. 2-4-6-trimercapto-*s*-triazine and organic accelerators

The various crosslinking mechanisms are discussed in detail by Mori and Nakamura *[Mori and Nakamura, 1984]*, and Kyllingstad *[Kyllingstad and Cable, 1992]*. Mixing can be carried out on both open mill and internal mixers. ECO elastomers are known for their high viscosity and consequently their rapid heat build-up tendencies should be treated accordingly. Processing aids are critical for mill release. An incorrect selection can interfere with cure rate or promote rapid ageing. Fillers are typically furnace-type blacks of the reinforcing variety *[Kyllingstad and Cable, 1992]*. N500 types are used in plasticizer-free formulations. N700 types are used to offset the softening effects of plasticizer while maintaining tensile strength and hardness. Non-black fillers, specifically hydrated silicas are reported *[Fetterman, 1973]* to give improve dry-heat ageing properties.

Although blending different types of ECO elastomers will improve their properties and certain grades, the manufacturer suggested that T3000 can be used to improve conventional rubber *[Zeon, 1999]*, although blends with other elastomers do not appear in literature.

2.2 THIOUREA-LEAD CURE SYSTEM

At present, within the rubber industry, the use of lead-based compounds has aroused concerns over environmental and processing issues. Present vulcanisation systems which employ lead (PbO or Pb_3O_4) and Ethylene Thiourea (ETU) are considered hazardous. ETU has been used as a curative for ECO elastomers for the past 30 years and still remains the preferred curative for optimum compression-set. It is activated with a lead containing compound, usually *Litharge* or red lead oxide. Previous work by Farid *[Farid, 1999]* showed that lead based acid acceptors particularly Pb_3O_4 gave the lowest set values, which are desirable, especially at high temperatures. Although this system has served the industry well, there have been problems associated with this cure system *[Houeto, Bindoula et al., 1995]*. In 1969 the FDA (Food and Drug Administration) in the USA found that when ETU was administered in the diet of rats at a dosage of 250 ppm, it induced significant number of thyroid tumours *[Innes, Ulland et al., 1969]*. Subsequently it was found that when a solution of ETU was applied to the skin of pregnant rats, it induced a high proportion of foetal abnormalities in the offspring. As a result there has been an intensive search for an alternative to ETU. However, the British Rubber Manufacturers' Association through its Health Advisory Committee have advised that there was insufficient evidence to warrant a ban on the use of ETU and recommended that it should be used either in masterbatch form or as a palletised compound to ensure minimum exposure on workers *[Parkes, 1974]*. The same precautions should also be taken to prevent lead from becoming airborne *[DuPont, 2003]*. Women of child bearing age should also be protected from contact with these chemicals by excluding them from areas involved with mixing, milling and vulcanisation. Other than increasing consumer's awareness of environment, health and safety, recent legislation which classifies materials with leachable lead as hazardous waste also has placed an additional expense burden on fabricators using the ETU-lead cure system. In addition to the known toxicity of lead and the reported carcinogenicity and teragonaity of ETU, the presence of lead can cause a silver-grey bloom on steam cured parts. Also, cure systems containing lead are known for fouling a mould cavity rather severely. This is thought to be the lead compounds depositing onto the mould surface during vulcanisation process. Non-lead systems have been shown to foul the mould much less. These issues have led to the investigation of some new ideas as well as re-evaluation of other known cure systems for ECO elastomers and to provide data that shows the way in which non-lead cure systems affect properties. Several alternative vulcanisation systems have been introduced *[Harris, 2000]*.

2.3 ALTERNATIVE CURE SYSTEM

There are at least 8 known alternative cure systems which have potential to replace the existing ETU-Lead system. They are Echo MPS, Zisnet Triazine, Sulphur, Dynamar, Peroxide etc. Although these systems give various advantages in relation to properties such as tensile, heat resistance, hardness, elongation and conductivity, most of them give detrimental effects in terms of compression-set behaviour.

a) ETU/MgO system

This system replaced Lead with MgO. Although problems caused by Lead such as mould fouling could be eliminated, the hazard from ETU is still there. In typical formulation, between 5.0 – 2.0 pphr of ETU is used as curative in combination with 3.0 – 5.0 pphr MgO as acid acceptor. The most common retarder for this system is Sulfasan, used at 0.2 – 1.0 pphr. The heat resistance is almost comparable to standard (ETU-Lead) with cost index of 1.0.

b) Zisnet-FPT (triazine)

This system used Zisnet-FPT (triazine) between 0.5 – 1.0 pphr as curative with $CaCO_3$ and MgO as acid acceptors at 5.0 and 3.0 respectively. The known accelerator is DPG while common retarder is Vulkalent EC, both used between 0.0 – 1.0 pphr. Santogard PVI could also be used as retarder although it can cause bad odour. Among advantages of this system; not a regulated waste substance, flexible cure system (can accelerate or retard easily), no lead-bloom and less mould fouling. The compression-set is nearly as good as ETU-Lead system and the relative cost index is 1.0. Some known disadvantages are high water volume swells approximately 46% (although can be reduced by untreated silica) as well as low tensile strength.

c) Echo MPS™

This system employed thiodiazole type curative 4.0 – 5.0 pphr and $BaCO_3$ or MgO as acid acceptors 3.0 – 7.0 pphr. It use Echo A as accelerator at 0.0 – 2.0 pphr. The Echo cure system was known for its high degree of moisture sensitivity, sometimes causing winter and summer formulations to be developed. The Echo MPS cure ingredient eliminates the high degree of moisture sensitivity, allowing for more consistent cure rates year round. The ingredients of the cure package must be carefully selected to avoid scorch times that are too short for a given process. Up to 1.0 pphr of retarder may be needed to obtain the desired scorch time. The main disadvantage of this system is it relative cost index of 1.3 – more expensive.

d) Vanax 829

This system use thiodiazole derivate as curative at 0.5 – 1.5 pphr with MgO or $CaCO_3$ as acid acceptor at 3.0 – 5.0 pphr. The accelerator is not desirable as it scorch time is very quick. Recently, Vanax 829 (thiadiazole) has been found to be a very effective non-lead cure system, giving high tensile strengths with much higher elongation values than other CO/ECO cure systems. Although the relative cost index is 1.0, the compression-set is significantly higher. The drawback is short scorch times. The Vanax 829 cure system is very fast and the use of an accelerator can quickly lead to scorch problems. The use of a retarder is highly reommended. Using less than 3 phr of MgO is recommended to help increase scorch time. If the MgO is reduced, then 5 phr of calcium carbonate should used to ensure enough acid acceptor is present.

e) Dynamar

Dynamar 5157 (propriety of bis-phenol) is used as accelerator at 1.0 – 2.0 pphr with Dynamar 5251Q as acid acceptor at 8.0 – 12.0 pphr. Dynamar 5166 (phosphonium salt) is used as accelerator at 0.5 – 2.0 pphr. Retarder is not needed and this system gives very good adhesion to fluoropolymers. Among its disadvantages, apart from long curing time it also very expensive with relative cost index of 1.5.

The more conventional cure systems, peroxide and sulphur, can be used for the Hydrin polymers containing the allyl glycidyl ether (AGE) - GECO and Hydrin H1100 (possibly GCO). This is because the AGE introduces unsaturation in a side chain. The double bonds allow the traditional rubber crosslinking or vulcanisation.

f) Sulphur

This system employed sulphur and TMTM as curatives between 0 – 6.0 pphr and 1.0 – 2.0 pphr respectively. This is together with CaO or Calcium Stearate at 3.0 – 5.0 pphr while addition of TMTD or MBTs are optional. This cure system produced high elongation with excellent shelf life. However, its disadvantages are high compression-set and slightly worse heat ageing.

g) Peroxide

This system employed Di-Cup 40C, Vul-Cup 40C and possess all advantages by peroxide cure. However its relative cost index is 1.1 and it is not possible to postcure.

Typical formulations and properties of these systems are tabulated in Table 2.2 and Table 2.3.

	ECHO MPS	VANAX 829	DYNAMAR	SULPHUR	PEROXIDE	ZISNET	ETU/Lead	ETU/MgO
Hydrin C2000L	100.00	100.00	100.00			100.00	100.00	100.00
Hydrin T 3102				100.00	100.00			
Stearic Acid	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Vulanox MB2	1.00		1.00	1.00	1.00	1.00	1.00	1.00
Naugard 445		1.00						
Vanox MTI		0.50						
N-330 Black	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00
Calcium Carbonate		5.00				5.00		
Red Lead - 90%							5.00	
Magnesium Oxide								5.00
Barium Carbonate	4.00							
ECHO MPS	3.00							
ECHO A	1.00							
Vanax 829		1.00						
Dynamar RC 5251			15.00					
Dynamar 5166			1.80					
Dynamar 5157			1.50					
Calcium Stearate				4.00				
TMTM				1.00				
Sulphur				0.50				
Potassium Stearate					3.00			
Calcium Oxide					4.00			
Di-Cup 40C					1.00			
Zisnet F-PT						0.80		
DPG						0.50		
Vulcalent E/C						0.50		
ETU - 75%							1.50	1.50
Total	160.00	158.50	170.30	157.50	160.00	158.80	158.50	158.50

Table 2.2: Formulations of various alternative systems (*Courtesy S. Harris, Zeon UK*)

One of the most promising alternative systems is Zisnet-FPT (triazine) *[Hashimoto, Inagami et al., 1986]*. Zisnet-FPT is chosen due to its potential to optimise properties pertinent to sealing applications. It is a unique curative newly developed by Nippon Zeon Co. Ltd for ECO elastomers, a safer curing system with the same efficiency of curing characteristics as ETU with red lead. This is shown by Table 2.3 where compression-set is comparable to that of ETU-Lead system.

	ECHO MPS	**VANAX 829**	**DYNAMAR**	**SULPHUR**	**PEROXIDE**	**ZISNET**	**ETU/Lead**	**ETU/MgO**
SCORCH T5, mins @ 125°C	4.1	5.5	5.3	10.1	7.9	4.3	3.5	6.7
Cure Rate - T90 @ 160°C	50.3	50.2	41.5	36.7	41	53.5	38.4	48.5
Cure Rate - T90 @ 200°C	9.9	12.2	8	12.5	11.7	11.8	10.7	16
ORIGINALS- Cured 15' @200°C								
Hardness - Shore A	77	76	81	73	74	77	80	71
Tensile Strength, MPa	18.6	17.2	16.1	19.5	17.4	13.9	18.8	18.6
Elongation, %	230	620	150	510	410	280	240	310
Tear, Die C, ppi	170	NT	230	380	270	310	250	260
Comp.Set - 22 Hrs @ 125°C	22	65	30	65	32	29	26	44
Air Ageing - 70Hrs @ 125°C								
Tensile Change %	-6	12	-12	-18	-19	-2	-11	-16
Elongation Change %	-22	-44	-17	-67	-46	-39	-33	-39
Hardness Change	3	6	5	8	3	4	3	3
Ageing in Distilled Water - 72 Hrs @ 90°C								
Water Swell %	46	NT	39	33	36	46	13	58
Shelf Life (Weeks)	1 to 2	1 to 2	2	4	4	2	2	2
Cost Index	1.3	1	1.5	1	1.1	1	1	1

Table 2.3: Vulcanisate properties of alternative systems (*Courtesy S. Harris, Zeon UK*)

Zisnet-FPT provides better heat resistance than that of ETU-lead system especially when Magnesium monoxide is added as acid acceptor. Moreover, a remarkable improvement on mould fouling and compression-set for ECO elastomers are also realised. It provides the most promising balance in terms of overall properties, cost, and more importantly producing compression-set comparable to the traditional lead-based system. Work has been done by Zeon Chemicals© and initial results have shown good recovery properties which are almost comparable to superior set properties produced by lead-based systems.

It should be noted in passing that the present author has used the statistical CCRD procedure in an attempt to optimise set properties using Zisnet-FPT and in so doing tried to obtain similar characteristics to that of the equivalent lead-based system; this matter is discussed in more detail at the appropriate place. The curing mechanism for Zisnet-FPT suggested by the manufacturers *[Nippon, 1989]* is shown in Figure 2.1.

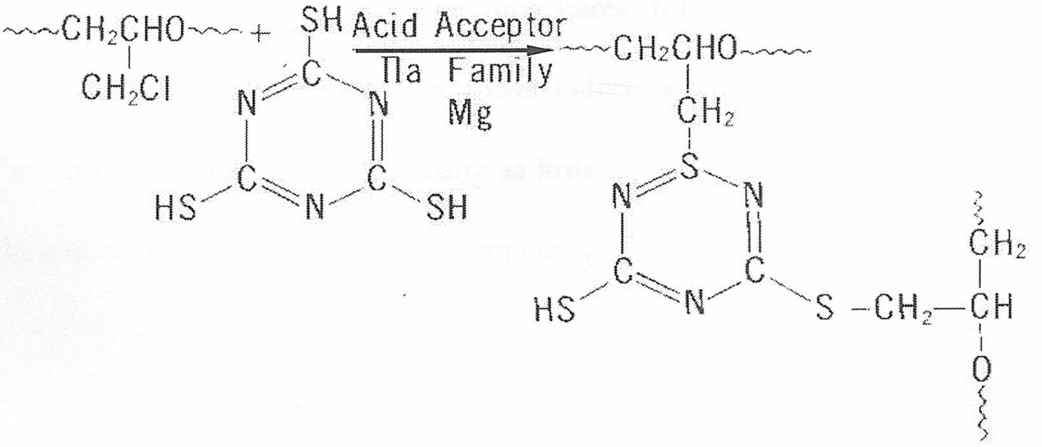


Figure 2.1: Mechanism of Zisnet-FPT curing *[Nippon, 1989]*

2.4 MARCHING MODULUS VULCANISATION

Polyepichlorohydrin elastomers (ECO) of CO (homopolymer) and ECO (copolymer) are fully saturated and therefore traditional rubber cure systems are not viable with them. Since the introduction of commercial ECO elastomers in the 1960s, the most commonly used cure system has been ETU activated with lead, usually Pb_3O_4 (red lead oxide). However, in almost all cases, this system produces marching modulus cures. This is exhibited by a slow but constant increase in torque beyond approximately 90% cure during the vulcanisation process. Continuing the process beyond this point is not economical and unnecessary as its improvement is usually very marginal. For many reasons discussed in more detail in Chapter 4, it is desirable to establish a technique to determine the maximum modulus in such cures. Various techniques can be used to satisfactorily deduce the maximum modulus in marching cure vulcanisates. One of the most popular techniques is known as the 'Analytical method' *[Rigbi, 1996]*. This technique is used throughout the research work due to its high degree of accuracy and reproducibility. This method is originally used to reconstruct an entire rheogram by using mathematical strategy provided the trace produced goes beyond the incubation or induction time. Apart from analysing marching cures, this method is also useful if one encounters a situation in which there is a power failure or the tracing pen fails to operate correctly beyond induction period. By using as little as two points, the maximum torque, T_{max}, can be calculated and therefore optimum cures i.e. 95% cure, can be determined.

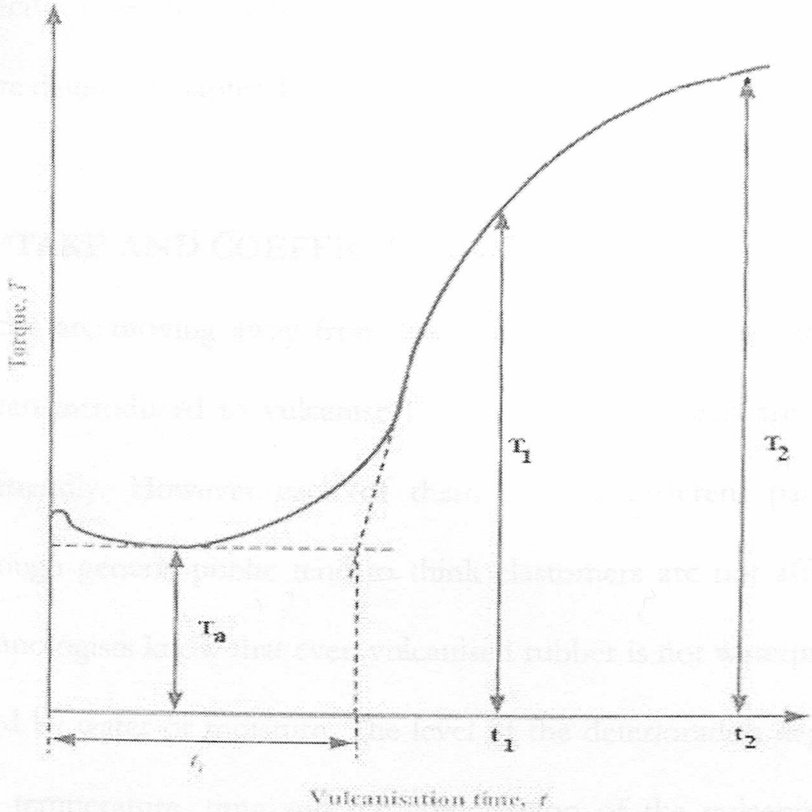


Figure 2.2: Typical marching modulus cure rheogram

The analytical method is used where the T_{max} can be calculated mathematically from equation:

$$T_{\max} = T_a + \frac{T_1 - T_a}{1 - \exp[-k(t_1 - t_i)]} \qquad (2.1)$$

It is also possible to plot several points in order to reconstruct the rheogram beyond the point of failure by using the following expression:

$$T_t = T_a + (T_\infty - T_a)\left[1 - \exp\left[-k\left(t - t_i\right)\right]\right] \qquad (2.2)$$

where t is a specific time in minutes. The application of this mathematical strategy is explained in more detail in Chapter 4.

2.5 WATER UPTAKE AND COEFFICIENT OF DIFFUSION

As most industries are moving away from lead-containing materials, various alternative systems have been introduced to vulcanise ECO elastomers which are safer and more environmental friendly. However each of them imparts different particular physical properties. Although general public tend to think elastomers are not affected by water, most rubber technologists know that even vulcanised rubber is not waterproof and can be adversely affected by water or moisture. The level of the deterioration depends upon the purity of water, temperature, time and the composition of the vulcanisate. Numerous previous work on water absorption has been published dealing with vulcanised rubber and raw rubber, for example, Boggs and Blake *[Boggs and Blake, 1926]* and Lowry and Kohman *[Lowry and Kohman, 1927]* have shown that the water absorption decreased with the advancing state of vulcanisation, although their work was more concerned with the process mechanism rather than filler and accelerator effects. Winkelmann and Croakman *[Winkelmann and Croakman, 1930]* concluded that the increased volume loading of any given filler had very little effect on water absorption. However, Skinner and Drakeley *[Skinner and Drakeley, 1933]* in his work found the absorption of water appears to decrease with increasing amounts of filler. They also found *litharge* (PbO) was one of the accelerators that showed higher absorption than the unaccelerated base mix. *Litharge* is widely used in conjunction with ETU as curative for ECO elastomers. This has become the industry norm for this elastomer for many years *[Parkes, 1974]*. However, the toxicity of lead and the reported carcinogenaity of ETU have led to investigation of non-lead cure systems for ECO elastomers. Various alternative systems have been studied by *Zeon Chemicals* but as mentioned previously the most promising system is Zisnet-FPT. This is due to the good balance of properties obtained, although these properties are also determined by component monomer composition and not the cure chemistry alone. However Zisnet-FPT has one notable disadvantage, that is high water volume swelling *[Harris, 2000]*, which can be as high as 46% *[Briggs, Edwards et al., 1962]*, although it can be reduced by untreated silica. This is a major disadvantage for the new system as water absorption proves detrimental to sealing applications. It also means that ECO compounded with Zisnet-FPT system may require caution in terms compound shelf-life. Abraham, Burczak and Cable *[Abraham, Burczak et al., 2003]* suggested that the shelf-life may only be one to three weeks and can be shorter in conditions of high humidity. In the present study, the water uptake of Zisnet-FPT system and its diffusion coefficient were investigated and compared to that of an ETU-based system with different acid acceptors. In Chapter 5, work pertaining to the diffusion and water uptake of six lead-based systems with different acid acceptors are discussed and compared with a typical Zisnet-FPT system. Carbon black is generally excluded in diffusion studies due to the confounding problems arising from it in terms of interpretation of the diffusion phenomena *[Amerongen, 1964]*.

2.6 STIFFENING EFFECT OF CARBON BLACK

The stiffening effect, α_f, of carbon black on vulcanisate is one of various measure of reinforcement and has been well established *[Wolff and Wang, 1993]*. When a carbon black is incorporated into a compound, the maximum torque (in rheometer) during the vulcanisation increases. The ratio between the torque increase of the loaded compound, $T_{\max} - T_{\min}$, and that of the gum, $T^o_{\max} - T^o_{\min}$, was found to be directly proportional to filler loading. The slope of the linear plot showing the relative torque increase as a function of filler concentration was defined as α_f *[Wolff, 1969; Wolff, 1970]*:

$$\frac{T_{\max} - T_{\min}}{T^o_{\max} - T^o_{\min}} - 1 = \alpha_f \frac{m_f}{m_p} \tag{2.3}$$

where m_p is the mass of the polymer in the compound and m_f is the mass of the filler compound.

Changes in primary particle size or surface area of a given filler have no influence on α_f but its value does depend on carbon black structure. It can be therefore concluded that α_f is a measure of the secondary network of carbon black, i.e. the 'remaining structure' after mixing. This was confirmed by graphitisation; Boonstra *[Boonstra, 1982]* showed that α_f is one of the properties that change very little after deactivation of carbon black surface by graphitisation. This is because the structure cannot change significantly during heat treatment.

In the present work two vulcanisation systems were used. Therefore, it is vital to investigate and to quantify the magnitude of the stiffening effect on each system. Clearly, if the stiffening effects are different in both systems, it is very likely to affect the end properties such as compression-set and stress-relaxation in addition to the effect from cure systems itself. Farid has described a way *[Farid, 2004]* to characterise the effect of filler on vulcanisates by a simple method using the Monsanto Rheometer. The procedure is based on measuring the difference in torque of compounded stocks containing different filler loadings. This procedure is discussed in detail in Chapter 6.

In general, there are mainly four different mechanisms that are responsible for the reinforcing action of the carbon black in rubber materials:

- The hydrodynamic effect
- Rubber-carbon black interaction
- Occluded rubber
- Filler networking

The hydrodynamic effect has its origin in the viscosity of fluids. If a particle is introduced into a fluid, the flow field is perturbed in relation to that of the pure fluid, increasing the viscosity *[Funt, 1988]*. It was originally stated by Einstein in 1906 *[Einstein, 1906]* through the equation

$$\eta_f = \eta_u \left(1 + 2.5c\right) \tag{2.2}$$

which described how the viscosity of fluid, η_u, is changed to η_f with the introduction of spherical particles at a concentration c. In terms of carbon black filled rubber it may be explained as a reduction in the volume fraction of the soft part (the rubber), and this increases the modulus of the material.

The rubber-carbon black interactions improve the adhesion between polymer and filler and thereby prevent large scale molecular slippage. These interactions are full of nuances and will not be discussed here in detail. *Occluded rubber* refers to the rubber that is hidden within the carbon black aggregates, not available to take part in deformation on loading *[Wolff, Wang et al., 1993]*. This partially immobilised rubber behaves more like the filler than the polymer matrix.

Filler networking also known as 'secondary network', is the agglomeration of carbon black aggregates into a kind of filler particles network. The aggregates are held together by Van der Waal type of forces and will be effective only if deformation is small. It has be suggested that the stiffening effect, α_f, is largely attributed to this secondary network *[Wolff and Wang, 1993]*.

2.7 SOLVENT-POLYMER INTERACTION (χ) AND CROSSLINK DENSITY

The properties of vulcanisate are greatly affected by crosslink density, particularly properties in compression as well as in tension. A method for measurement of true crosslink density of cured rubber samples has been sought for many years. Generally two different methods are available:

- stress-strain technique, and
- volume-swelling technique.

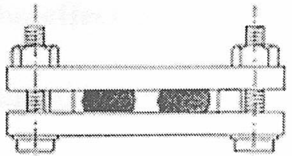
For stress-strain technique, whenever possible, the 'compression' technique is much preferred rather than 'tension'. This is due to the fact that relationship between stress and strain given by 'compression' will obey the Gaussian theory of rubber elasticity much more closely as compared with tension or simple extension. In recent years there has been renewed interest in the question of swelling of crosslinked rubber networks. Much work has been done to study the accuracy and reliability of the swelling technique *[Westlinning and Butenuth, 1961]*. The swelling technique is not affected by non-affine effects of elastomers and it also eliminates viscoelastic effects. For the reasons just stated, the swelling method provides both accuracy and excellent reproducibility. Thus volume-swelling methods are used throughout the present work. McKenna *[McKenna and Flynn, 1990]* in his work has shown the dependency of crosslink density to the polymer-solvent interaction parameter, χ.

Upon immersion in a good solvent, crosslinked elastomers will absorb a portion of the solvent and subsequently swell rather than dissolving completely. The extent of equilibrium swelling represents a balance between two physical aspects. The free energy of mixing will cause the solvent to penetrate and try to dilute the crosslinked elastomer. This entropic increase may be enhanced by increasing the temperature. As the polymer chains in the crosslinked elastomer network begin to elongate under the swelling action of the solvent, they generate an elastic retractive force in opposition to this deformation and therefore limit the magnitude of the deformation. The volumetric swelling reaches steady state or equilibrium when the two forces balance each other. Given that the steady state swelling ratio is a direct function of extent of crosslinking in the sample, swelling experiments are simple and low-cost techniques to characterise polymer networks. In general applications, at the simplest level of analysis, swelling measurements can be used for quality control and serve as an indexing tool for polymer systems with different levels of crosslinking. At the more advanced academic level of analysis, by knowing the value of the interaction parameter χ and the molar volume of the swelling liquid one can calculate the crosslink density, molecular weight between crosslinks, and the number of crosslinks/chain. As the crosslink density will undoubtedly affect the properties of vulcanisates it is important to quantify it.

In terms of determining crosslink density, samples were treated according to the method used by Morris *[Morris and Thomas, 1995]* to isolate the rubber from the non-rubber constituents. Cold extraction was used to remove extractable non-rubber materials from the samples without causing changes to their network character. Hayes' method *[Hayes, 1986]* was used to determine the polymer-solvent interaction parameter. This technique is discussed in more detail in Chapter 7.

2.8 STATISTICAL OPTIMISATION OF COMPRESSION-SET

Some essential aspects concerning compression-set can be summarised as follows:



Compression Set Test Fixture

$$\%\ \text{Comp Set} = \frac{\text{original height} - \text{recovered height}}{\text{original height} - \text{compressed height}} \times 100$$

- Measure ratio of **elastic** to **viscous** component of elastomers to a given deformation.
- Test: 25% compression (of original sample's height) at a given time and temperature. The dimension is measured after the load is removed.
- Compression-set is the percentage of the original compression (25%) that is **not recovered** (known as **set**).
- Most beneficial for production quality control, easy to perform with a simple device.
- Various test methods: ISO 815 (ambient & high temperature), ISO 1653 (Low temperature), ASTM D395 (Ambient & high temperature), D1229 (Low temperature)

The study of compression-set (and stress-relaxation) of ECO elastomers is based on previous work by Farid *[Farid, 1999]* who studied the effect of essential additives on set and stress-relaxation in ECO elastomers. However, this study was done by using traditional screening variables approach. This approach does not allow an accurate assessment of the interaction of various essential factors or additives influencing set and stress-relaxation in ECO elastomers.

Traditional screening method is also known as 1-FAT (one factor at a time) in which one factor was changed at a time in type or level of use. This method only detects and quantifies the effect of single factor at one time thus making it impossible to investigate possible interactions. The term 'interactions' refers to a special relationship in which two or more factors or variables affect processes (or properties) when acting together compared to how they act individually. 'Interactions' does not always occur, but they are sometimes extremely important and 1-FAT experiments by their nature are not capable of finding such interactions. Therefore to resolve this issue the experiment was re-designed in accordance with suitable statistical techniques.

Generally, there are four major statistical techniques adopted into design of experiment; Factorial, Response Surface, Mixture and Taguchi *[Vecchio, 1997]*. Each of them has their own advantages and limitations. For example, **Factorial** designs allow the simultaneous study of the effects that several factors may have on a process. When performing an experiment, varying the levels of the factors simultaneously rather than one at a time is efficient in terms of time and cost, and also allows for the study of interactions between the factors. Interactions are the driving force in many processes. Without the use of factorial experiments, important interactions may remain undetected. **Response surface** methods are used to examine the relationship between a response and a set of quantitative experimental variables or factors. These methods are often employed after a vital few controllable factors are identified. It is also very useful to find the factor settings that optimise the response. Designs of this type are usually chosen when curvature is suspected in the response surface. **Mixture** experiments are a special class of response surface experiments in which the product under investigation is made up of several components or ingredients. In the simplest mixture experiment, the response (the quality or performance of the product based on some criterion) depends on the relative proportions of the components. In contrast, in a factorial design, the response varies depending on the amount of each factor. **Taguchi** designs are used for robust parameter design, in which the primary goal is to find factor settings that minimize response variation, while adjusting (or keeping) the process on target. Taguchi designs provide powerful and efficient method for designing products that operate consistently and optimally over a variety of conditions.

In present work, a technique known as Central Composite Rotatable Design *(CCRD)* is used to optimise compression-set. *CCRD [Vecchio, 1997]* is an advance experimental design based on a factorial design that uses five levels of each factor to generate a full data set suitable for response surface methods. It is very useful in investigating the interaction effect of different compounding ingredients by systematically varying the quantity of each using set criteria as dictated in *CCRD*. The property measured is subjected to the whole variable set where a statistical analysis is performed. From the application of regression analysis, the significant factor (or factors together) can be determined and the response surface equation can be established. Once the data is acquired, this equation is capable of calculating the end properties by manipulating the value of the factors without having to repeat the arduous actual experiment process.

As it is desirable to introduce a safer vulcanisation system as an alternative to existing lead-based vulcanisation systems, it is envisaged that *CCRD* techniques would be useful in locating optimum performances. This is to ensure that the non-lead vulcanisation system can be used without compromising the properties, particularly compression-set.

2.9 LONG TERM PREDICTION OF SET PROPERTIES

In engineering applications compression-set is sometimes known as retention loss. It occurs when the clamping force exerted by the bolting of actuator casings causes the elastomer to relax. The elastomer squeezed between the casing flanges tends to relax over time to a value that it then sustains. While the relaxation is more related to stress, the amount that does not recover to its original dimension is known as set. Additional tightening of the casing bolts will not change this value greatly since it is intrinsic to the material. The same applies to various applications pertaining to set, for example seals, gaskets and diaphragms. In the past for applications such as underground flexible pipes conveying town gas, elastomers have been used extensively as a safe, simple and effective sealing material. The life prediction in this particular application proves to be vital because of inadequate failure detection or indeed due to high maintenance or replacement costs especially caused by the excavation. Thus, when faced with such situations, it is clearly desirable to develop a means of predicting service life which could give an indication on end-of-life time. Two approaches are well known for long term prediction; these are based on the Arrhenius model and the WLF (William-Landel-Ferry) equation.

The Arrhenius approach is the most widely used for evaluating accelerated test results involving the effect of temperature. Service lifetimes have been estimated for the thermal ageing of ECO elastomers with an ETU-lead system and for the ageing with a Zisnet-FPT system. Predictions using the Arrhenius model usually do not take into account oxygen-diffusion-controlled oxidation. In the case of ECO elastomers, extrapolations are determined by the effect of thermal ageing on compression-set properties. WLF approach is normally use when the physico-chemical mechanisms are dominant. It is appropriate for lifetime predictions when polymer ageing is controlled by a viscoelastic process, for instance relaxation or creep. This method use time/temperature shifts where it is very effective in analysing creep behaviour in contrast to compression-set. In present work, the compression-set of elastomers containing both curing systems is obtained from temperature-time plots carried out at various temperatures. 20% set is taken as the failure criterion; the method is essentially that which is proposed by the British Gas Engineering Standard *[British and Gas, 1984]*.

2.10 CORRELATION BETWEEN SET AND STRESS-RELAXATION

Stress-relaxation in compression (CSR) is considered as the most direct measure of sealing capacity. It gives the force (or stress) a rubber article would exert on a solid sealing surface as a function of time. However, as the stress-relaxation test presents some experimental difficulties, industries tend to use a simpler test which is known as compression-set (CS) although the information given seems limited. The debate about the use of compression-set and stress-relaxation, as a predictor of seal performance is not new. Morell and Watson *[Morell and Watson, 1976]* suggested that compression-set and compression-relaxation have different non-linear relationships to the basic processes and hence are not expected to correlate with each other i.e. network formation during compression is not expected to have a significant effect on compression stress-relaxation but markedly reduces recovery on release of compression. But Farid *[Farid, 1996; 1999]* suggested set and stress-relaxation in elastomers at elevated temperature arise from chemical changes that occur in the rubber network. Therefore, in principle they are connected.

Practically, compression-set is preferable because of its simplicity. Therefore the production of extensive data correlating compression-set, stress-relaxation and seal performance is highly desirable. Previous work by Ellul and Southern *[Ellul and Southern, 1985]* found that there is a broad correlation between compression-set and stress-relaxation as predicted theoretically. A reasonable correlation was found between stress-relaxation and compression-set. Although it is insufficient to predict accurately values of one physical quantity from another, it is suggested that the correlation is adequate for ranking purposes of sealing behaviour of different compounds. The investigation to see whether this correlation can be extended to the present range of ECO elastomers is reported in Chapter 10.

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Chapter 3

EXPERIMENTAL WORK

This Chapter reports on general procedures regarding sample preparation, processes and materials handling. However, as the nature of some experiments are somewhat complex and vary significantly from one to the next, their specific details are given in appropriate Chapters; references to these Chapters will be given here.

3.1 MATERIALS

The base polymer used was Hydrin C2000L (copolymer) supplied by Zeon Chemicals. A list of intrinsic properties of raw ECO is given in Table 3.1.

Properties	C2000L
Chlorine content, (% by weight)	26.0
Mooney viscosity (ML 1+4 100°C)	65-75
Specific gravity, (g/cm^3)	1.28
Tg (°C)	-38

Table 3.1: Intrinsic properties of raw ECO *[Zeon, 1999]*

The curing system known as Zisnet-FPT was supplied by Zeon Chemicals, Wales. ETU was supplied by Robinson Brothers (UK) Ltd as 75% (wt/wt) active in a binder system. Fast extrusion furnace (FEF) carbon black (N550) was supplied by Cabot Carbon (UK); it is commonly used in rubber formulations designed for sealing applications. FEF carbon black has a relatively large particle size and high structure which leads to low rates of primary or physical stress-relaxation. In order to overcome processing difficulties *[Zeon, 2000; 2000]*, two processing aids were used in conjunction. The first was zinc stearate, in the form of powder which was supplied by Omya (UK) Ltd. The second was a complex zinc soap of partly unsaturated fatty acid within the $C_{12} - C_{18}$ range; supplied by Schill and Seilacher GmBH Hamburg, Germany via their UK distributor, International Adhesive Ltd under the trade name 'Struktol A60'. Zinc stearate was used to control the degree of splitting and tearing of ECO during mill-mixing. The complex zinc soap on the other hand, was used to improve the flow characteristics of ECO mixes and to reduce the degree of surface bloom in vulcanisates fabricated from ECO mixes. Nickel di-n-butyldithiocarbamate (NBC) was used as protective agent, supplied by Flexsys Rubber

Chemicals, Wales under the trade name NDBC; it was supplied in the form of green powder. The accelerator used in conjunction with Zisnet-FPT was Diphenyl guanidine (DPG), supplied by Omya United Kingdom. DPG was supplied under the trade name DPG 75; this material was 75% active in a polyethylene binder.

3.2 MASTERBATCH AND COMPOUNDING

A masterbatch technique was used to prepare various mixes used in the present study. A 2500 cm^3 Francis Shaw Intermix (Manchester, United Kingdom) was used for the masterbatch preparation. The internal mixer was set to operate at a rotor speed of 44 revolutions per minute, under a ram pressure of about 0.70 MPa. The fill factor used was 75% and the batch masses were about 3462 g. Seven masterbatches were prepared in order to produce 32 mixes. The discharge temperatures were all within 80-90°C. All seven masterbatches were prepared according to the time schedule outlined in Table 3.2. At the end of each mixing schedule the masterbatches were refined on a 0.45 m two-roll mill operating at an even speed of 15 revolutions per minute with roll surface of 50 ± 5°C. At the end of the mill refining operation, each masterbatch was end passed six times on a tight nip to ensure uniform distribution of ingredients. This operation took about 6-10 minutes.

Time elapse (min)	Action
0	Add ECO
1	Add 1/3 of FEF
3	Add a further 1/3 of FEF
6	Add a further 1/3 of FEF
9	Sweep down
11	Discharge

Table 3.2: Mixing schedule of masterbatch

Each masterbatch was sheeted out at approximately 6-8 mm in thickness. Material losses due to mixing were less than 0.5%; this percentage loss is considered quite acceptable for mixing operations as far as elastomers are concerned.

Typical base formulation is given by Table 3.3.

Ingredient	pphr
ECO	100.0
Stearic acid	1.0
Struktol A60	1.0
Zinc stearate	1.0

Table 3.3: Base formulation

In attempt to minimise the variations between masterbatches, about 50 g was taken from each masterbatch and was cross-blended to give a series of homogenised FEF-containing mixes. ETU, litharge and NBC were incorporated on a laboratory 0.3 m two-roll operating at a friction speed 1.25:1. Roll surface temperature were maintained at approximately 50 ± 5°C. The mixing procedure was carried out according to the schedule outlined in Table 3.4.

Time elapse (min)	Action
0	Add masterbatch to mill with surface at temperature of 50 ± 5°C
1	Add stearic acid and processing aid (zinc stearate, Struktol A60)
3	Add protective agent (NBC), curative (ZISNET) and acid acceptor ($CaCO_3$/MgO)
6	Sweep and cross-cut from each side of a sheet of rotating rubber
9	Six time end-roll on a tight nip, allow to band for one minute
11	Sheet off at a thickness 4-5 mm

Table 3.4: Mixing schedule of mixes with different combination of factors

3.3 VULCANISATION

The determination of the vulcanisation characteristics were carried out on a Monsanto Oscillating-disc rheometer (ODR) S100. It was maintained at a temperature of $170 \pm 0.5°C$ and set so that it would operate at strain amplitude of $\pm 3°$ of arc. The extent of crosslinking is given by the difference between maximum torque and minimum torque. The vulcanisation time, t_{95}, is the time (in minute) corresponding to a torque value of: $0.95 \times$ (maximum torque-minimum torque) + (minimum torque). However, due to the marching-modulus nature of the cure, the conventional way of determining the optimum cure could not be used; instead the method proposed by Rigbi *[Rigbi, 1996]* was adopted as will be explained later. A Bradley and Turton (Kiddermaster, UK), double-daylight, steam press was used for the the moulding process. For each mix, several cylindrical discs of 13.0 ± 0.5mm diameter and 6.3 ± 0.3mm thickness were compression-moulded on a steam press at $170 \pm 2°C$. The moulding times used were those corresponding to t_{95} values calculated from the rheograms of respective mixes. Post-curing process was carried out according to Farid's work which is explained in detail elsewhere *[Farid, 1996]*. Previous work by Kyllingstad *[Kyllingstad and Cable, 1992]* showed that the post-curing process reduces the set further. In Principle, the post-curing method used in the present work involved inserting compression–moulded ECO test pieces in a circulating air oven for 5 hours at a temperature of $150 \pm 1°C$. All test pieces were conditioned in an open laboratory environment at temperature of $23 \pm 2°C$ for at least 16 hours before testing. This is to allow sufficient time for vulcanisates to attain a state of thermal equilibrium.

For specific procedures and methods of determining specific properties and characteristics outlined below the reader should refer to the Chapters indicated.

3.4 MARCHING MODULUS VULCANISATION

For experimental details, see Chapter 4.

3.5 WATER UPTAKE AND COEFFICIENT OF DIFFUSION

For experimental details, see Chapter 5.

3.6 STIFFENING EFFECT OF CARBON BLACK

For experimental details, see Chapter 6.

3.7 SOLVENT-POLYMER INTERACTION (χ) AND CROSSLINK DENSITY

For experimental details, see Chapter 7.

3.8 STATISTICAL OPTIMISATION OF COMPRESSION-SET

For experimental details, see Chapter 8.

3.9 LONG TERM PREDICTION OF SET PROPERTIES

For experimental details, see Chapter 9.

3.10 CORRELATION BETWEEN SET AND STRESS-RELAXATION

For experimental details, see Chapter 10.

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Chapter 4

MARCHING MODULUS VULCANISATION

The aim of this chapter is to establish a reliable technique to determine the maximum torque of ECO rubber mixes which produce rheograms displaying marching-modulus characteristics. Having found a way of determining the maximum torque of ECO rubber mixes exhibiting this marching behaviour it would then be possible to produce vulcanisates that are both consistent and reproducible in terms of crosslinking and mechanical behaviour.

It was found that the 'Analytical Technique' developed by Rigbi [Rigbi, 1996] was the most facile in terms of interpreting marching-modulus cure traces and was therefore the adopted procedure in the present work. Based on a simple explanation of Rigbi's method by Farid [Farid, 2002], the rheograms were reconstructed and the maximum torques were successfully determined thus allowing optimum cure times to calculated. The utility and reliability of the method was demonstrated by using a Zisnet-FPT curing system.

4.1 OVERVIEW

ECO elastomers are normally vulcanised by lead-based systems. Apart from its processing and environmental issues, rubber technologists also need to deal with the difficulties in locating the optimum cure state. This is due to the 'marching-modulus' nature of the ECO elastomers cured by ETU-Lead systems. The marching-modulus cure can be described as gradual but continuous increase in torque that shows no tendency to reach a constant torque value within a reasonable time scale, say within 60 minutes. Although vulcanisation times corresponding to maximum torque, $T_{\max}$, at 'plateau' are desirable in order to obtain optimum cure levels, it is economically unwise to continue the cure process beyond approximately 90% cure for most commercial rubber products. It is generally found that imparting cure levels to rubber stocks beyond 90% cure leads only to a marginal increase in the state of cure. In view of the preceding remarks it is clearly desirable to establish a method by which maximum torque values can be determined by extrapolation or interpolation for rubber mixes that require unacceptably long periods of time to reach constant or plateau torque values. It is in this area that the present author has found the Analytical Method to be most useful.

The application of Analytical method has been explained by Rigbi *[Rigbi, 1996]*. The original purpose of the method was to reconstruct an entire rheogram, using a mathematical strategy, of a cure trace that has prematurely terminated thus leaving only a partial cure profile (possibly due to instrument or power failure). This can be done provided the trace that is produced goes beyond the incubation or induction time. As mentioned briefly, this proves useful if one encounters a situation in which there is power failure or the tracing pen fails to operate correctly beyond induction period. The main attraction of this method is based on the realisation that by using as little as two data points, the whole rheogram can be reconstructed and maximum torque can be calculated and subsequently used to determine the optimum cure time.

4.2 ANALYTICAL METHOD

Consider a marching-modulus rheogram as illustrated below:

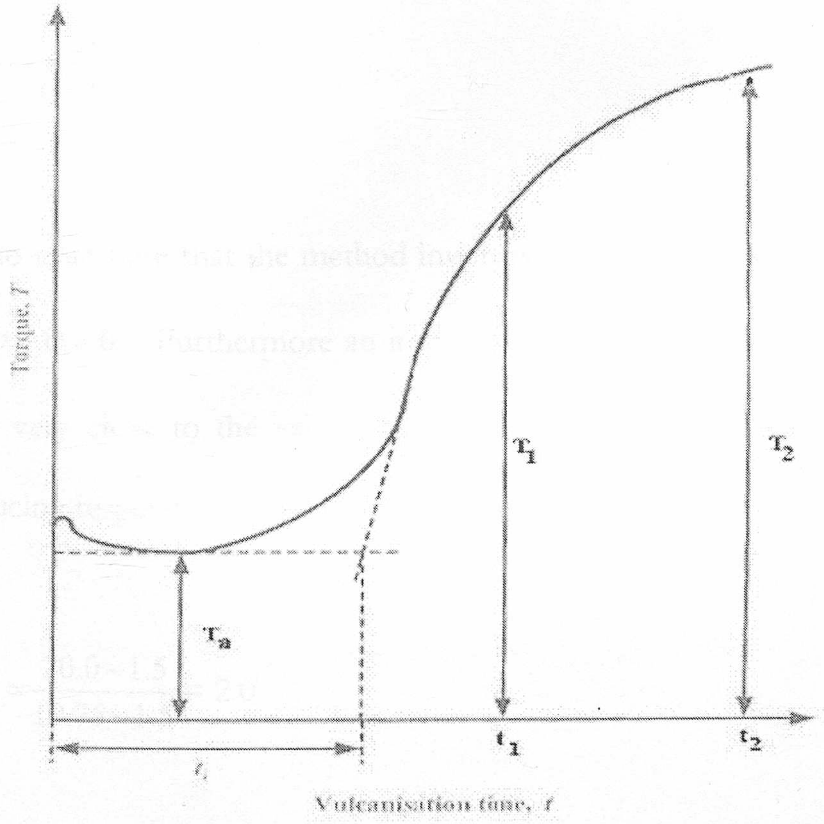

Figure 4.1: Typical incomplete rheogram or rheogram with marching-modulus

The maximum torque, $T_{\max}$, may be calculated from the following equation (note the significance of the parameters given in the equation is indicated in Figure 4.1:

$$T_{\max} = T_a + \frac{T_1 - T_a}{1 - \exp[-k(t_1 - t_i)]} \tag{4.1}$$

The application of the Rigbi method is best demonstrated by carrying out an actual calculation using some typical values. Hence, with the aid of the diagram shown in Figure 4.1 consider the following situation. Let torque T_2 be 60.0 dNm and T_1 be 50.0 dNm corresponding to times t_2 (20.0 minutes) and t_1 (10.75 minutes) respectively. In addition, suppose that the induction time, t_i is 1.5 minute. We now introduce the expression:

$$s = \frac{t_2 - t_i}{t_1 - t_i} \tag{4.2}$$

It is important to note here that the method involves solving a quadratic equation of the form: $z^2 - rz + (r-1) = 0$. Furthermore an important prerequisite of the method is that s must always be very close to the value of 2.0. In view of the preceding precautionary remarks, introducing respective values into (4.2) gives:

$$s = \frac{20.0 - 1.5}{10.75 - 1.5} = 2.0 \tag{4.3}$$

We now assume that T_a is 13.0 dNm. The next step is to determine the ratio r which is defined by the expression:

$$r = \frac{T_2 - T_a}{T_1 - T_a} \tag{4.4}$$

Introducing appropriate values into equation (4.4) gives:

$$r = \frac{60-13}{50-13} = 1.2702 \tag{4.5}$$

The solution to our quadratic equation, notably $z^2 - rz + (r-1) = 0$ is given by the general 'quadratic formula' $z = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$, two z values are obtained, that is z_1 =0.9999 and z_2 =0.2702. The parameter z is given by

$$z = \exp[-k(t_1 - t_i)] \tag{4.6}$$

Introducing z_1 and z_2 into equation (4.6) enables us to calculate the constants, k_1 and k_2; the values are 0.0000 and 0.1414 respectively. The above mathematical procedure has now provided values for all the parameters in equation (4.1) thus allowing the determination of $T_{\max}$. The k_1 value of 0.0000 is clearly not possible; leaving only a k_2 value of 0.1414 to be inserted into equation (4.1). Finally, we obtain a $T_{\max}$ value of 63.70 dNm.

It is also possible to plot several points in order to reconstruct a rheogram beyond the point at which the trace has prematurely ended by using the expression:

$$T_t = T_a + (T_\infty - T_a)\left\{1 - \exp\left[-k\left(t - t_i\right)\right]\right\} \tag{4.7}$$

where *t* is the general time in minutes. Calculation based on (4.7) if *t* is 100 minutes then T_{100} is 63.70 dNm. Using typical values and applying equation (4.7), the complete reconstruction process produces a rheogram of the type shown in Figure 4.2 below:

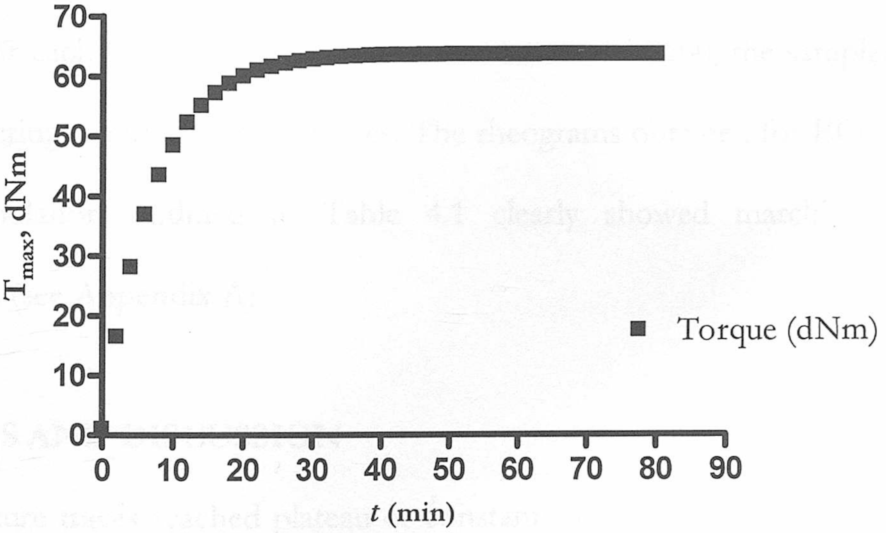

Figure 4.2: Reconstruction of a rheogram (after the induction time)

4.3 EXPERIMENTAL WORK

The work described here is concerned with testing the reliability of the Rigbi method discussed in 4.2. The base rubber formulation upon which the present work was based is given in Table 4.1.

Ingredient	pphr
ECO (C2000L)	100.0
Stearic acid	1.0
Struktol A60	1.0
Zinc stearate	1.0
ETU	2.5
NBC	2.0
Litharge	5.0
FEF N550	50.0

Table 4.1: Base formulation for marching-modulus

The essential ingredients for an ETU-lead system are: curing agent (ETU), protective agent (NBC), acid acceptor (Litharge) and filler (FEF N550). Rubber mixes based upon the formulation given in Table 4.1 were prepared according to the procedures described in Chapter 3. Five samples were taken from any given mix and the cure times were determined for each by using a *Monsanto* rheometer model S100; the samples were tested at 170°C covering a period of 60 minutes. The rheograms obtained for ECO mixes based on the formulation outlined in Table 4.1 clearly showed marching-modulus-type characteristics (see Appendix A).

4.4 RESULTS AND DISCUSSION

Most of the cure traces reached plateau or constant torque values at around 60 minutes. As the main objective of the present work was to assess the validity of the Rigbi method two points were taken from the cure traces (after the incubation time); one in the linear region immediately after the minimum torque and another near the area in which approximately 90% cure level was achieved. Using the two data points along with their corresponding times the maximum torques were calculated in the manner described in Section 4.2. The results are given in Table 4.2 under the third column entitled 'Calculated (dNm)'. In Table 4.2, the first column under the heading 'Plotter (dNm)' refers to data obtained from a rheogram as plotted on an electronic flat bed recorder. The second column in the Table records the data from an electronic readout. Comparison of the data delineated in the first and second columns clearly indicates some degree of incongruity in the results. The data afforded by the electronic readout appears to be about 5% lower than that given by the plotter.

Sample	Plotter (dNm)	Electronic readout (dNm)	Calculated (dNm)
1	125.00	118.40	121.95
2	112.00	106.10	104.29
3	108.50	102.00	109.91
4	114.00	107.20	105.77
5	113.00	106.90	112.78

Table 4.2: Maximum torque values for ETU-Lead system compounds

The reason for this discrepancy is not entirely known and experience has shown that this anomaly is a salient feature of the instrument. Nevertheless, the variation is not a serious issue provided the actual crosslink density of any given ECO rubber mix is correlated with either of the two sources providing the data. In such a case it simply becomes a matter of preference.

The calculated standard deviations of $T_{\max}$ values are generally within 5% of either plotter or electronic readout values. Figure 4.8 indicates that the calculated values are of sufficient accuracy for the approximation of $T_{\max}$. It was anticipated at the onset that all ETU-lead based mixes used in the present work would exhibit Marching-modulus cure profiles and therefore the method just described was used widely.

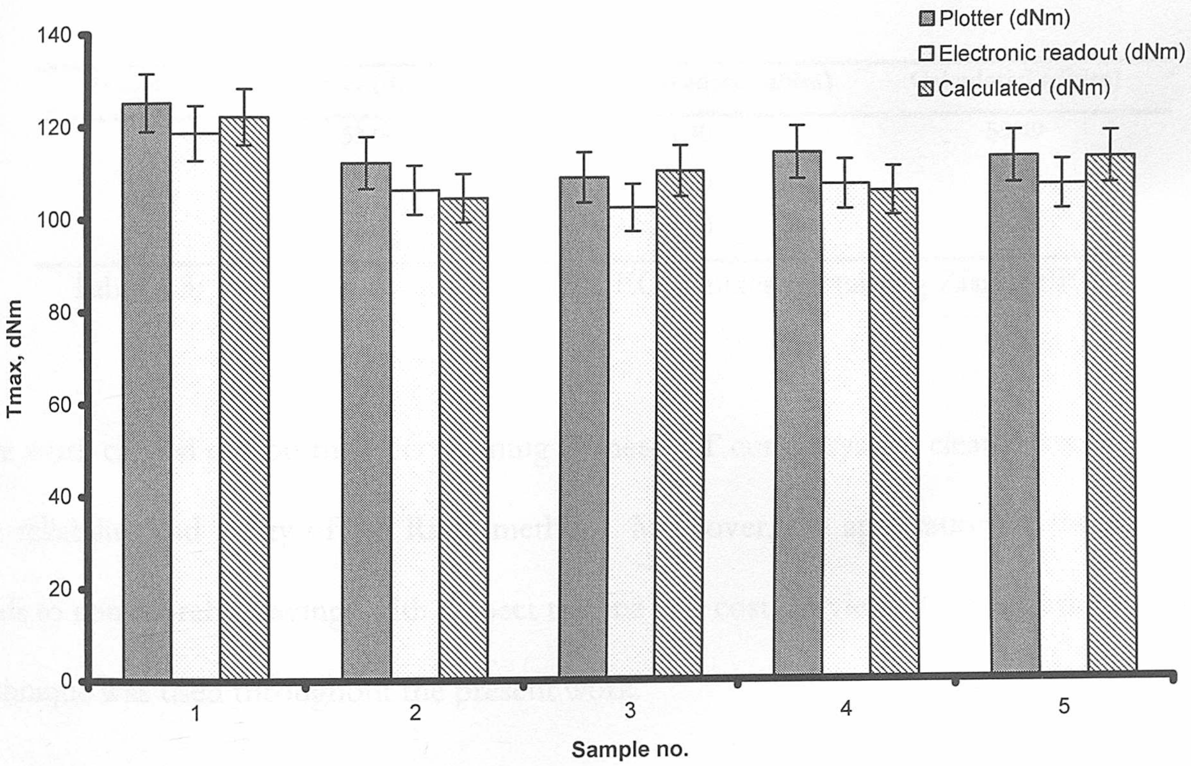

Figure 4.8: Comparison of $T_{\max}$ values from various sources for the ETU-Lead system

In order to demonstrate the reliability of the Rigbi method further, a similar analysis was carried out on ECO mixes based on Zisnet vulcanisation systems. Here, three samples were taken and their cure times determined using the same rheometer as described previously. The rheograms of the aforementioned samples are reproduced in Appendix A.

Table 4.3 delineates the maximum torque values for the three Zisnet-FPT samples in terms of readings obtained from the following sources: 'Plotter', 'Electronic readout' and 'Calculated'. Comparison of the data given in Table 4.3 indicates that the calculated maximum-torque values are in good agreement with those obtained from the two remaining sources.

Sample	Plotter (dNm)	Electronic readout (dNm)	Calculated (dNm)
1	53.00	51.40	55.49
2	59.00	57.60	60.93
3	78.00	77.00	80.25

Table 4.3: Maximum torque values for ECO mixes containing Zisnet-FPT

The work carried out on mixes containing Zisnet-FPT curing system clearly demonstrates the reliability and utility of the Rigbi method. Moreover, the application of the method leads to considerable savings with respect to time and cost. In view of these desiderata the technique was used throughout the present work.

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Chapter 5

WATER UPTAKE AND COEFFICIENT OF DIFFUSION

This chapter characterises and discusses water absorption or water uptake behaviour of ECO vulcanisates. The diffusion coefficient, D, was determined using water absorption measurement; such measurements were based on simple gravimetric weighing procedures. Characterisation of ECO vulcanisates in terms of migration of water is considered important because water absorption can effectively plasticise some polymers and engender high rates of stress-relaxation and thereby vitiate sealing performance.

5.1 INTRODUCTION

As mentioned earlier ECO elastomers are normally vulcanised by lead-based systems; and, as was explained previously these systems have aroused concerns over environmental and processing issues. Various alternative systems have been introduced which are safer and more environmental friendly. However each of these systems has its own peculiarities. In a relatively recent study *[Wahab, Farid et al., 2004; 2004]* the compression-set of ECO elastomers was investigated and the Zisnet-FPT system was found to be most promising in terms of matching the set properties of ECO vulcanisates containing traditional ETU-lead systems. However, an initial study by the manufacturers *[Harris, 2000]* of the Zisnet-FPT system showed that vulcanisates containing this system were prone to absorbing large amounts of water leading high levels of volume swelling, up to approximately 46%; although this can be reduced with the incorporation of untreated silica. This is a major disadvantage of the novel Zisnet-FPT system. In the light of the foregoing remarks, it was thought expedient to determine the diffusion behaviour of six lead-based systems containing different acid acceptors. The results were then compared with the diffusion characteristics of ECO elastomers containing the favourable Zisnet-FPT system.

5.2 EXPERIMENTAL WORK

5.2.1 Material

The base polymer used was ECO elastomer which was supplied under the trade name Hydrin C2000L; the supplier was Nippon Zeon Co. Ltd., Wales. Intrinsic properties of raw ECO elastomers are given in Table 5.1. The Zisnet-FPT was used as a vulcanisation system which was also supplied by Nippon Zeon Co. Ltd, Wales. ETU was supplied by Robinson Brothers (UK) Ltd as 75% active material in a binder system. Fast extrusion furnace (FEF) carbon-black-filler having an ASTM classification of N550 was used; this filler is particularly suitable for rubbers designed for sealing applications. FEF has a relatively large particle size and high structure which leads to very low rates of primary or physical stress-relaxation of rubbers containing it. Cabot Carbon, Ellesmere Port, United Kingdom, supplied FEF carbon black.

Properties	**C2000L**
Chlorine content, (% by weight)	26.0
Mooney viscosity (ML 1+4 100°C)	65-75
Specific gravity, (g/cm^3)	1.28
Tg (°C)	-38

Table 5.1: Intrinsic properties of raw ECO *[Zeon, 1999]*

Due to intrinsic and widely acknowledged processing difficulties encountered with ECO it was thought desirable to use three processing aids together. The first of these was zinc stearate, in the form of powder which was supplied by Omya, United Kingdom. The second was a complex zinc soap of partly unsaturated fatty acid within the C_{12} – C_{18} range; this was supplied by Schill and Seilacher GmBH Hamburg, Germany via their UK distributor, International Adhesive Ltd under the trade name 'Struktol A60'. The third is known as Vanfre AP2/SP2 which was supplied by Brenntag UK Ltd, Surrey. Zinc stearate was used to control the degree of splitting and tearing of ECO elastomers during mill-mixing. The complex zinc soap on the other hand, was used to improve the flow characteristics of ECO mixes and to reduce the degree of bloom in vulcanisates made from ECO mixes. Nickel di-n-butyldithiocarbamate (NBC) was used as protective agent, supplied by Flexsys Rubber Chemicals, Wales under the trade name of NDBC in the form of green powder. Seven different acid acceptors were used in the present study. All of them were supplied by Omya, Surrey, UK. These were; Litharge (PbO), 90% dispersion on chlorinated polyethylene binder, supplied under the trade name K(HRL)D-90; Red lead (Pb_3O_4) , 80% in polymeric binder supplied under name K(RD)-80PE; Magnesium oxide (MgO), 80% active supplied under trade name Maglite D; Calcium oxide (CaO), 80% dispersion on ethylene-proplyene as carrier supplied under trade name Garosorb 80P, Zinc oxide (ZnO) 80% dispersion in polymeric binder; 80% dispersion of dibasic lead phosphate on chlorinated polyethylene as carrier supplied under the trade name K(DPS)D-80 or Dyphos; 80% dibasic lead phthalate on chlorinated polyethylene as binder supplied under trade name K(DYT)D-80P or Dythal. For Zisnet FPT system, the accelerator used in conjunction with Zisnet-FPT was Diphenyl guanidine (DPG), supplied by Omya United Kingdom. It was supplied under the trade name DPG 75 in the form of 75% active in polyethylene binder.

5.2.2 Mix Formulation

The formulations used in this stage of the study are delineated in Table 5.2. It can be seen that six different acid acceptors have been utilised, notably, litharge, red lead, MgO, CaO, ZnO and Dyphos/Dythal. Note that for the non-lead-based system, ETU has been replaced with Zisnet-FPT and DPG as accelerator and a combination of acid acceptors, that is, $CaCO_3$/MgO used in the ratio 5:3.

Ingredients	**Mix 1**	**Mix 2**	**Mix 3**	**Mix 4**	**Mix 5**	**Mix 6**	**Mix 7**
Hydrin C2000L	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Nickel dibutyl dithiocarbamate	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Struktol A60	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Vanfre AP2	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ethylene thiurea (75%)	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Zinc stearate	1.0	1.0	1.0	1.0	1.0	1.0	1.0
FEF N550	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Litharge (90%)	5.0						
Read lead (K-RD-80PE)		5.0					
MgO (Maglite D) (80%)			3.0				3.0
Calcium Oxide (80%)				3.0			
Zinc oxide (80%)					3.0		
Dyphos (80%)						5.0	
Dythal (80%)						7.0	
Zisnet-FPT							2.5
Calcium Carbonate (Britomya)							5.0
Diphenylguanidine(DPG) (75%)							0.2

Table 5.2: Mix formulations containing various acid acceptors

5.2.3 Preparation of Mixes

ECO masterbatches were prepared in the manner described previously and the method will not be reiterated here. It should be merely noted that after having prepared the required number of masterbatches each masterbatch was subjected to the following treatment: refining on a 0.45 m two-roll mill operating at an even speed of 15 revolutions per minute with a roll surface temperature of 50 ± 5°C. At the end of the mill refining operation, each masterbatch was end passed six times on a tight nip to ensure uniform distribution of ingredients. This operation took about 6-10 minutes. At the end of the end-passing procedure each masterbatch was sheeted out at approximately 6-8mm in thickness. Material losses due to mixing were less than 0.5% which is considered acceptable for internal and open-mill mixing. In an attempt to minimise the variations between masterbatches, about 50 g was taken from each masterbatch and was subsequently cross-blended. The foregoing procedures produced a series of ECO-FEF black masterbatches ready for receiving other materials.

All other ingredients were added to the cross-blended masterbatches on a laboratory 0.3m two-roll operating at a friction speed 1.25:1. Roll surface temperatures were maintained at approximately 50 ± 5°C. The mixing procedure was carried out according to the schedule outlined in Table 5.3.

Time elapse (min)	Action
0	Add masterbatch to mill with surface at temperature of 50 ± 5°C
1	Add stearic acid and processing aid (zinc stearate, Vanfre SP2, Struktol A60)
3	Add protective agent (NBC), curative and acid acceptor
6	Sweep and cross-cut from each side of a sheet of rotating rubber
9	Six time end-roll on a tight nip, allow to band for one minute
11	Sheet off at a thickness 4-5 mm

Table 5.3: Mixing schedule

5.2.4 Vulcanisation

The determination of the vulcanisation characteristics were carried out on a Monsanto Oscillating-disc rheometer (ODR) S100. It was operated at 170 ± 0.5°C using a strain amplitude of $\pm 3°$ of arc. The extent of crosslinking is given by the difference between maximum torque and minimum torque. The optimum cure time, t_{95}, is determined corresponding to a torque value T_{95} given by $0.95 \times$ (maximum torque-minimum torque) + (minimum torque). A Bradley and Turton (Kiddermaster, United Kingdom), double-daylight, steam press was used for the moulding process. For each mix, several very thin sheets of approximately 1mm thickness were compression-moulded on a steam press at

170 ± 2°C. The moulding times used were those corresponding to the T_{95} values calculated from the rheogram of respective mixes. The cure times were between 27 to 35 minutes. Post-curing process was carried out according to work by Farid which is explained elsewhere*[Farid, 1999]*. All compression–moulded ECO test pieces were placed in a circulating air oven which was maintained at a temperature of 150 ± 1°C for 5 hours. All test pieces were conditioned in an open laboratory environment at temperature of 23 ± 2°C for at least 16 hours before testing. This is to allow sufficient time for vulcanisates to attain a state of thermal equilibrium. The humidity was not measured but based on National Physical Laboratory (NPL), typical relative humidity (%RH) for UK is 50% at 20°C, at 1013.25 mbar *[NPL, 2002]*.

5.2.5 Water uptake and coefficient of diffusion

Various measurement techniques of diffusion and coefficient have been comprehensively discussed elsewhere *[Ahmad, Tinker et al., 1994]* . Generally measurement of the diffusion coefficient of liquids in rubbers fall into two categories; those where the concentration profiles are measured with time and another is where the total amount of liquid which has entered the sample is recorded as a function of time. The first method normally measure optically (refractive index changes) but the application is limited to transparent rubber. The second method is less accurate but does not require optical transparency and can be determined fairly simply at any time gravimetrically. In the present work, the second method is used where an ordinary analytical balance is quite satisfactory. The mass uptake is plotted against square root of time. Three samples were cut from each vulcanised sheet. Using test piece cutter designed for the purpose, square-shaped samples were cut using a single stroke of a hand press. The thickness of each sample was measured using a Mercer type 259 dial or thickness gauge with a precision of 0.01mm. Each sample was weighed three consecutive times in grams to four decimal places and the mean mass recorded. The density of each sample was measured according to method recommended by the British Standards Institute (BSI) described in *[BS903, 1980]*. The area (*A*) of any given sample was determined by utilising the following expressions:

$$\rho = \frac{M}{V} \tag{5.1}$$

where ρ is density (g/cm^3), M is mass (g) and V is volume (cm^3).

For the square samples used in the present study:

$$\rho = \frac{M}{At} \tag{5.2}$$

In the above expression, t represents the thickness. Hence the area (in cm^2) is obtained from:

$$A = \frac{M}{\rho t} \tag{5.3}$$

For the diffusion experiments, any given sample was completely submerged in distilled water whilst being suspended from nylon thread in a glass bottle. It should be noted a nylon thread was used instead of a conventional cotton thread because the latter shows rapid water absorption which might confound the results. Suspension was effected by fitting a specially-designed hook to the underside of a cap that fitted tightly over the neck of the glass bottles. The bottles, with the entire contents, were then placed in a continuously stirred water bath maintained at a temperature at 25+0.5°C. During the early initial period of the diffusion experiment, the samples were weighed regularly at hourly intervals for the first 24 hours; this regularity was subsequently reduced to once every 24 hours during the next seven days. The intervals were then extended to 36 to 48 hours after the second week as the rate of water uptake reduced. As regards the weighing procedure the following method was adopted: samples were removed from the water and the excess water on the surface was removed using filter paper. After having removed the excess water, the samples were placed in sealed weighing bottles in order to minimise evaporation of water from the samples during weighing. The diffusion experiments were carried out in triplicate. The duration of the diffusion experiments were 60 days. Table 5.4 gives the data that was used to determine the areas of the diffusion samples.

Mix	Sample	Density (g/cm³)	Weight (g)	Thickness (mm)	Area (mm²)
1	a	1.3977	0.4109	0.98	299.96
	b		0.4272	0.99	309.75
	c		0.4243	0.98	309.74
2	a	1.3767	0.3311	0.78	308.37
	b		0.2963	0.74	292.19
	c		0.2824	0.67	307.69
3	a	1.3802	0.2379	0.54	319.15
	b		0.2135	0.49	313.51
	c		0.1906	0.45	304.57
4	a	1.3121	0.2249	0.51	338.25
	b		0.2391	0.57	321.58
	c		0.2249	0.55	311.64
5	a	1.3622	0.2596	0.62	309.00
	b		0.2776	0.66	307.22
	c		0.2641	0.64	302.93
6	a	1.3741	0.2104	0.48	321.18
	b		0.2447	0.54	331.78
	c		0.2375	0.56	310.49
7	a	1.2225	0.1895	0.42	366.23
	b		0.2210	0.51	352.16
	c		0.2570	0.65	325.05

Table 5.4: Densities and determination of area of samples

5.3 RESULT S

The maximum water uptake can be determined from plots shown by Figure 5.1 to 5.7

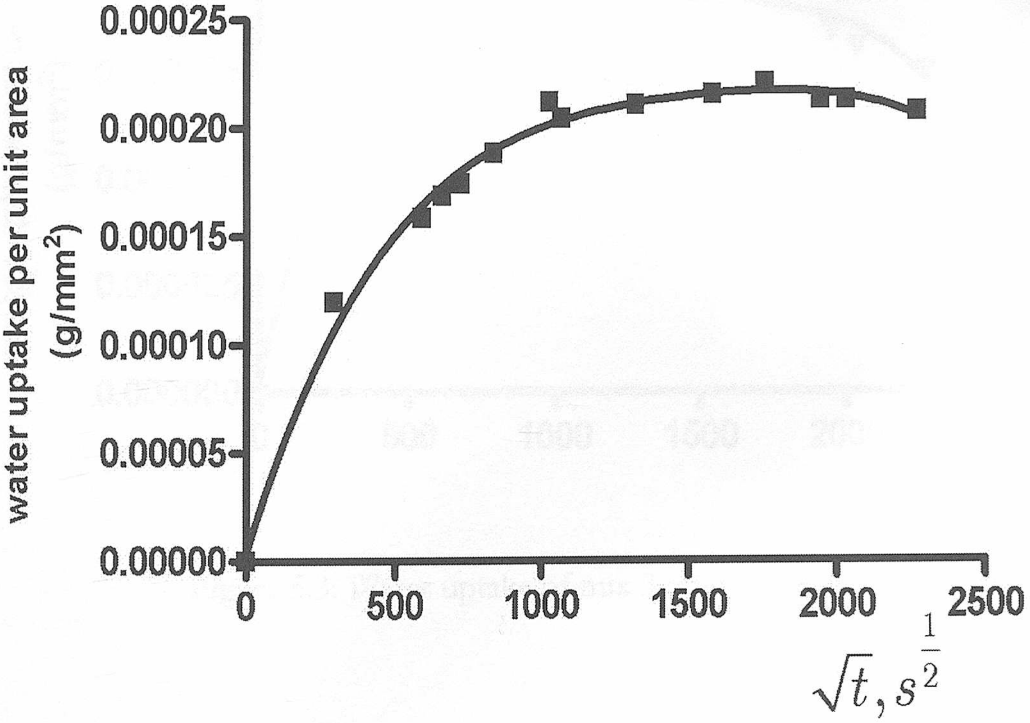

Figure 5.1: Water uptake of mix 1 after 60 days

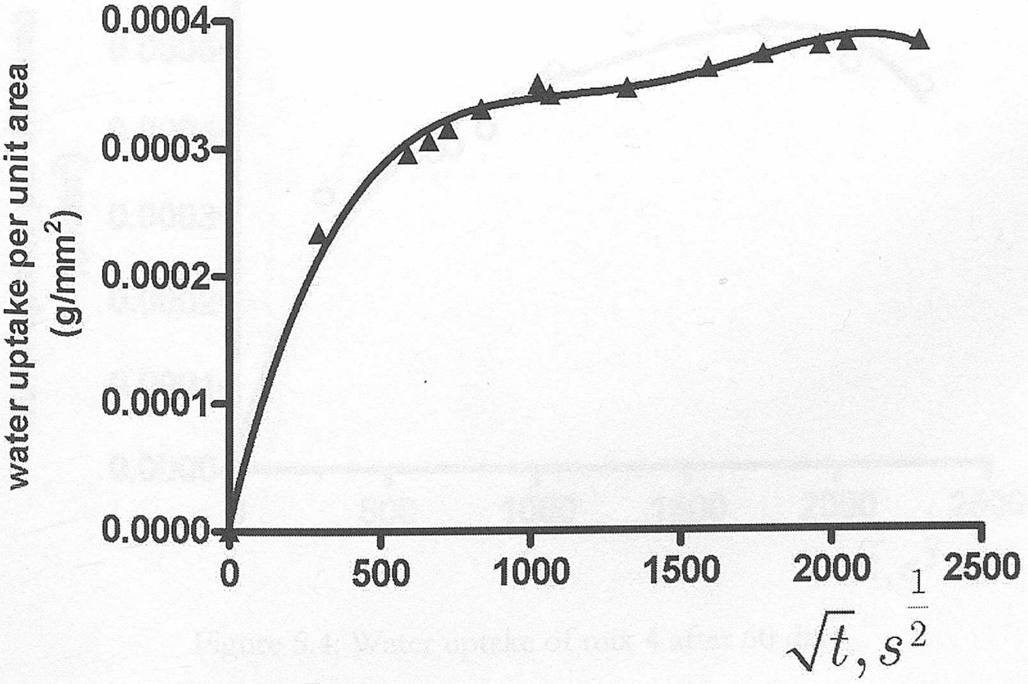

Figure 5.2: Water uptake of mix 2 after 60 days

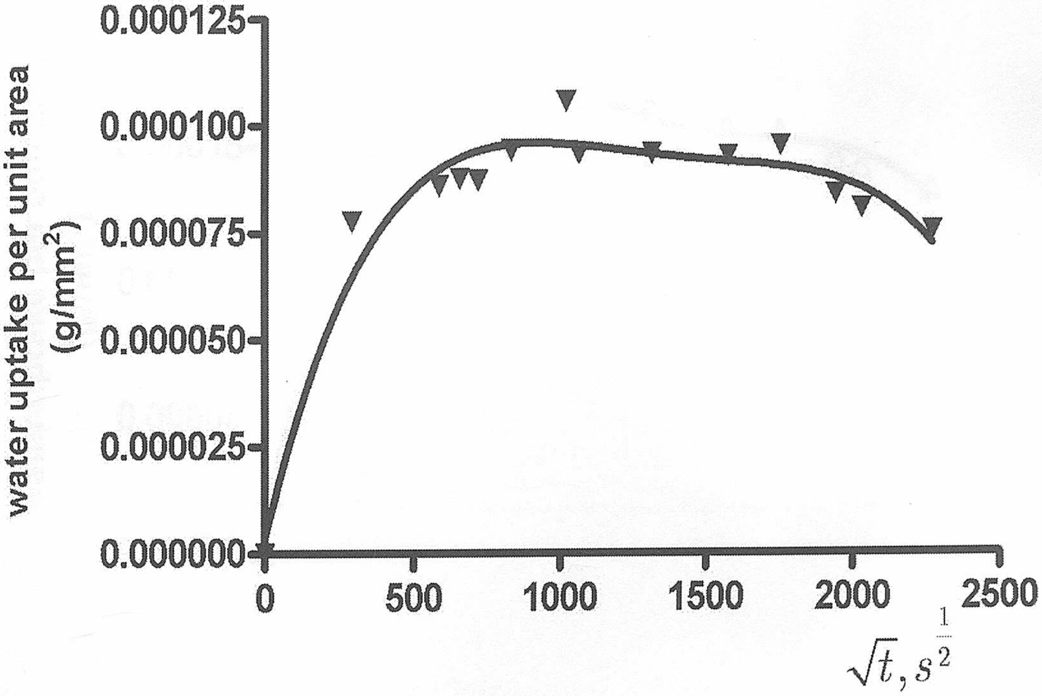

Figure 5.3: Water uptake of mix 3 after 60 days

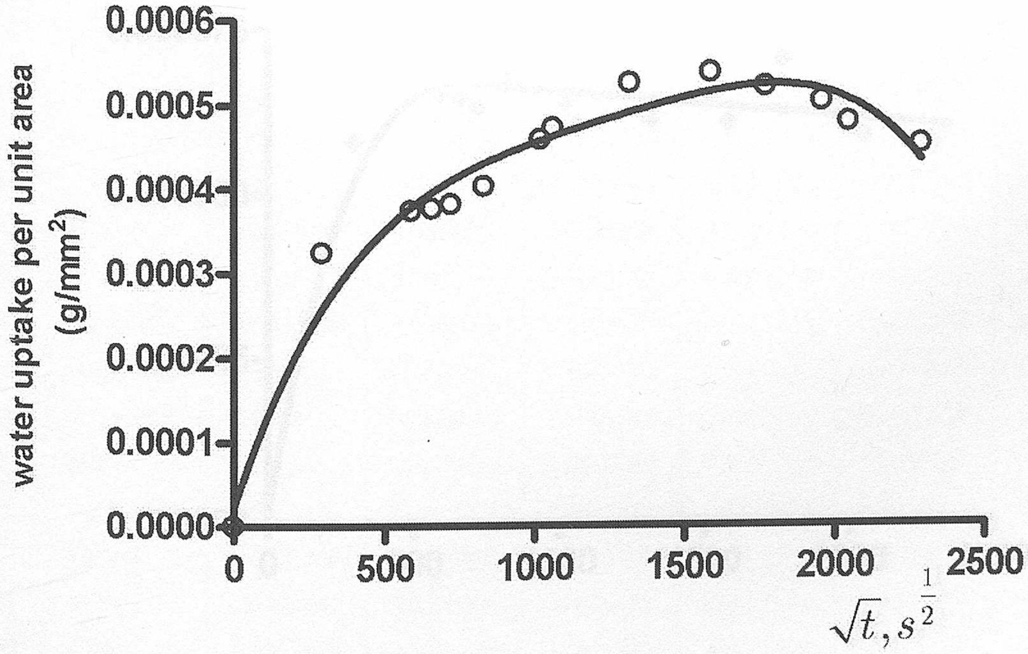

Figure 5.4: Water uptake of mix 4 after 60 days

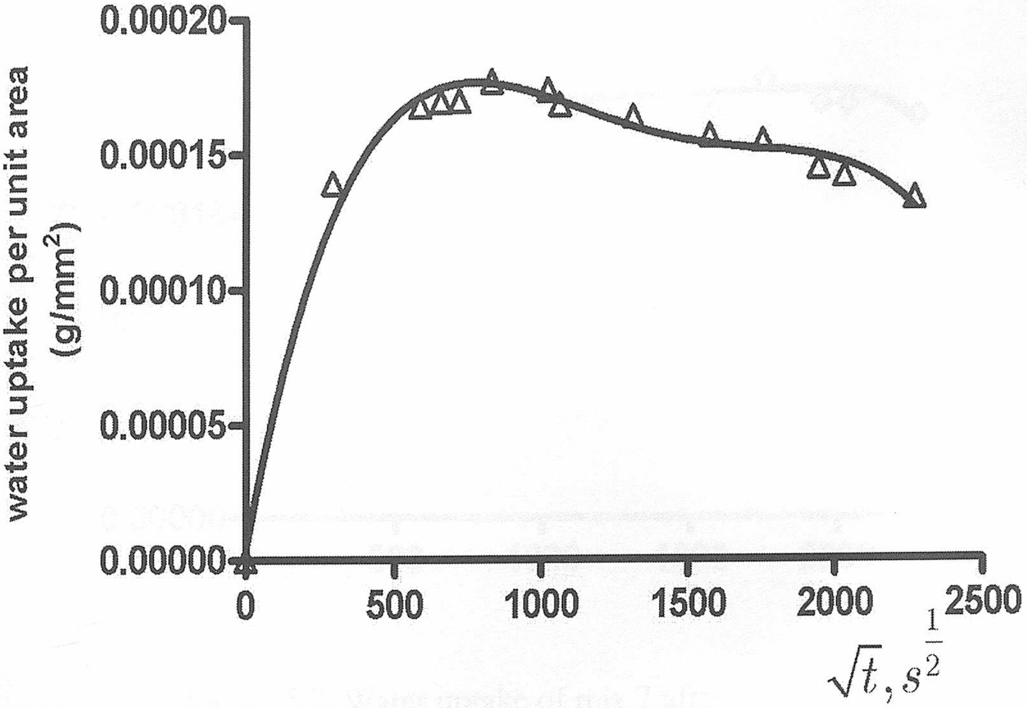

Figure 5.5: Water uptake of mix 5 after 60 days

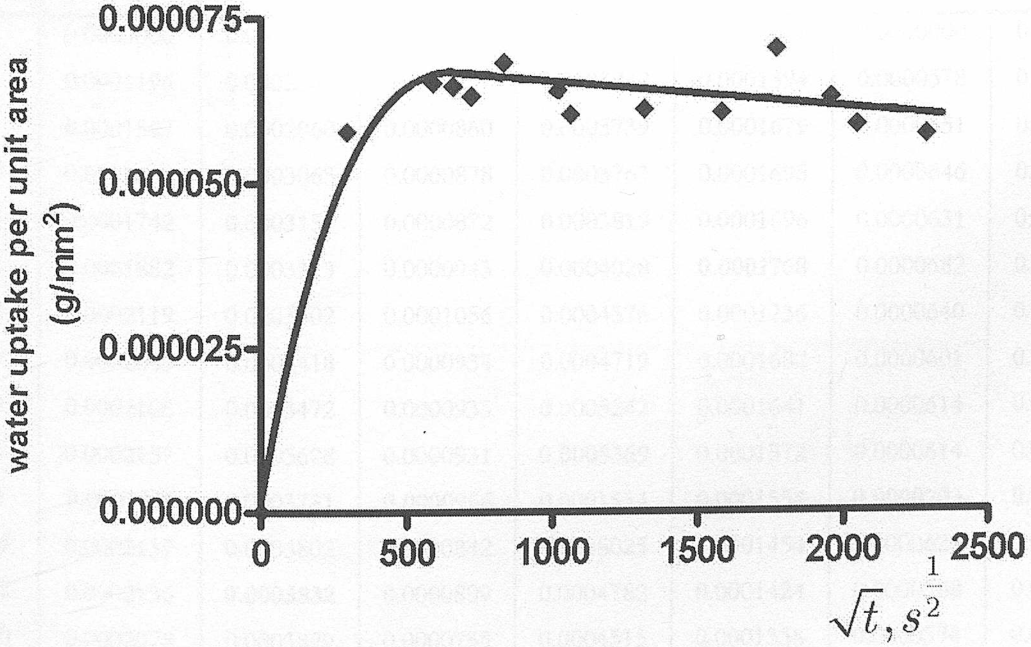

Figure 5.6: Water uptake of mix 6 after 60 days

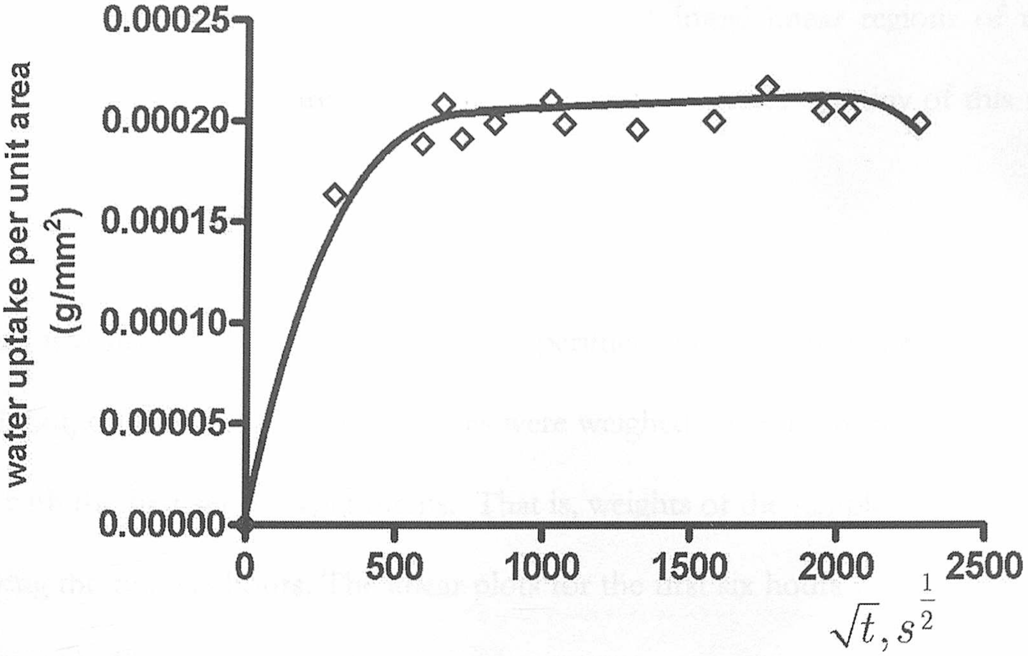

Figure 5.7: Water uptake of mix 7 after 60 days

The summary of the water uptake is shown by Table 5.5.

Time	Water uptake (g/mm^2) for 60 days						
(hour)	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7
0	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
24	0.0001196	0.0002344	0.0000777	0.0003242	0.0001394	0.0000578	0.0001889
96	0.0001587	0.0002960	0.0000860	0.0003739	0.0001679	0.0000651	0.0001889
120	0.0001686	0.0003065	0.0000878	0.0003763	0.0001695	0.0000646	0.0002082
144	0.0001742	0.0003157	0.0000872	0.0003819	0.0001696	0.0000631	0.0001914
192	0.0001882	0.0003313	0.0000943	0.0004028	**0.0001768**	0.0000682	0.0001987
288	0.0002119	0.0003502	0.0001056	0.0004576	0.0001736	0.0000640	0.0002101
312	0.0002045	0.0003418	0.0000934	0.0004719	0.0001682	0.0000601	0.0002010
480	0.0002108	0.0003472	0.0000935	0.0005242	0.0001641	0.0000614	0.0001964
696	0.0002157	0.0003628	0.0000931	**0.0005369**	0.0001572	0.0000614	0.0002018
864	**0.0002211**	0.0003731	**0.0000956**	0.0001554	0.0001554	**0.0000703**	**0.0002173**
1056	0.0002137	0.0003802	0.0000842	0.0005025	0.0001454	0.0000629	0.0002057
1152	0.0002136	**0.0003832**	0.0000809	0.0004782	0.0001424	0.0000588	0.0002056
1140	0.0002078	0.0003829	0.0000755	0.0004515	0.0001338	0.0000574	0.0001996

Table 5.5: Average water uptake (of different mixes) with time of 60 days

In terms of determining the diffusion coefficient the initial linear regions of the plots shown in Figures 5.1 to 5.7 are of interest and therefore greater scrutiny of this region is necessary.

To further investigate this region, the same experimental procedure as detailed above was followed; but, on this occasion the samples were weighed much more frequently than was the case with the first set of experiments. That is, weights of the samples were taken every hour during the first six hours. The linear plots for the first six hours water uptake of each mix is shown in Figure 5.8 to 5.14.

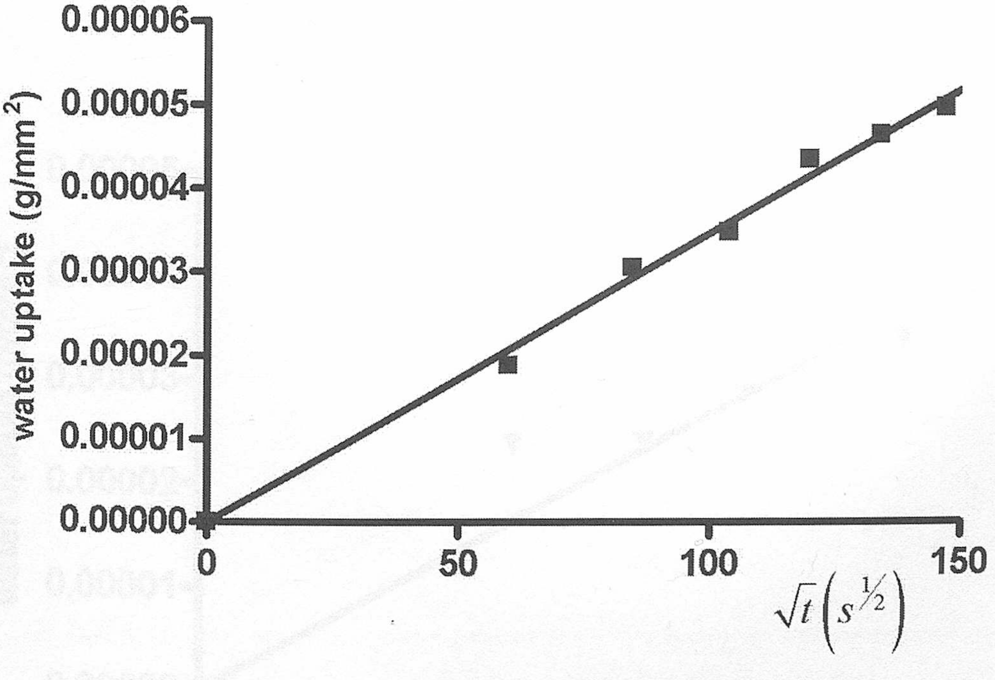

Figure 5.8: Linear plot of Mix 1

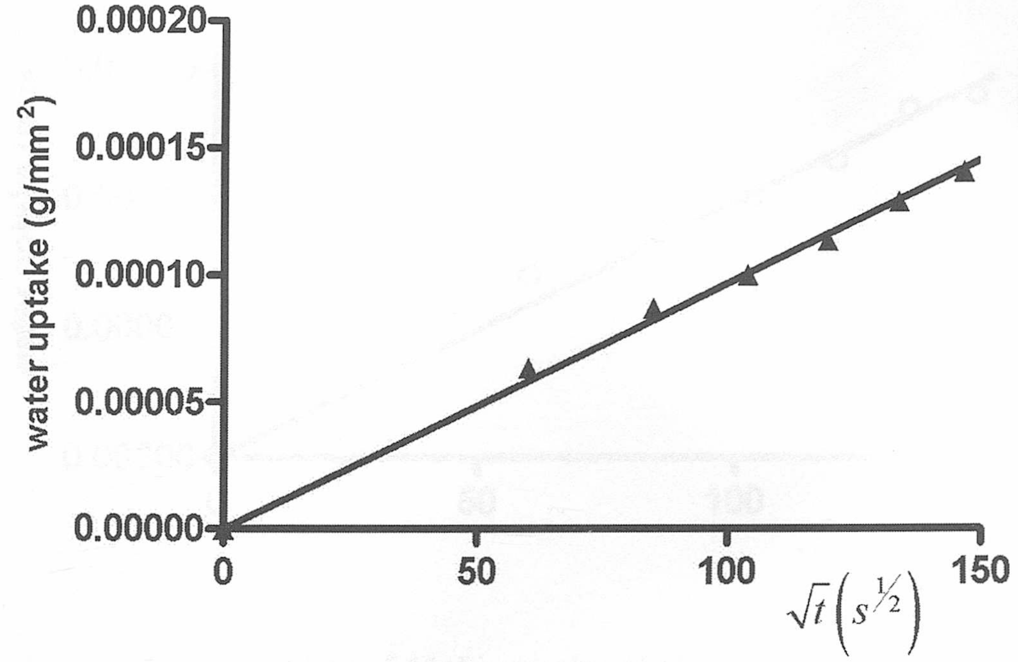

Figure 5.9: Linear plot of Mix 2

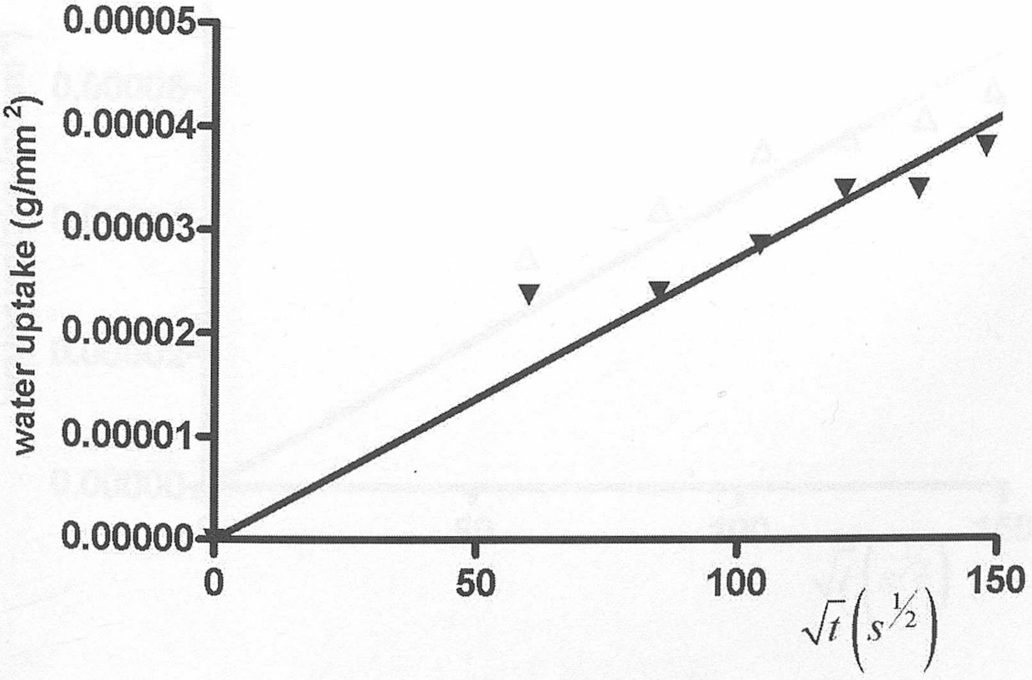

Figure 5.10: Linear plot of Mix 3

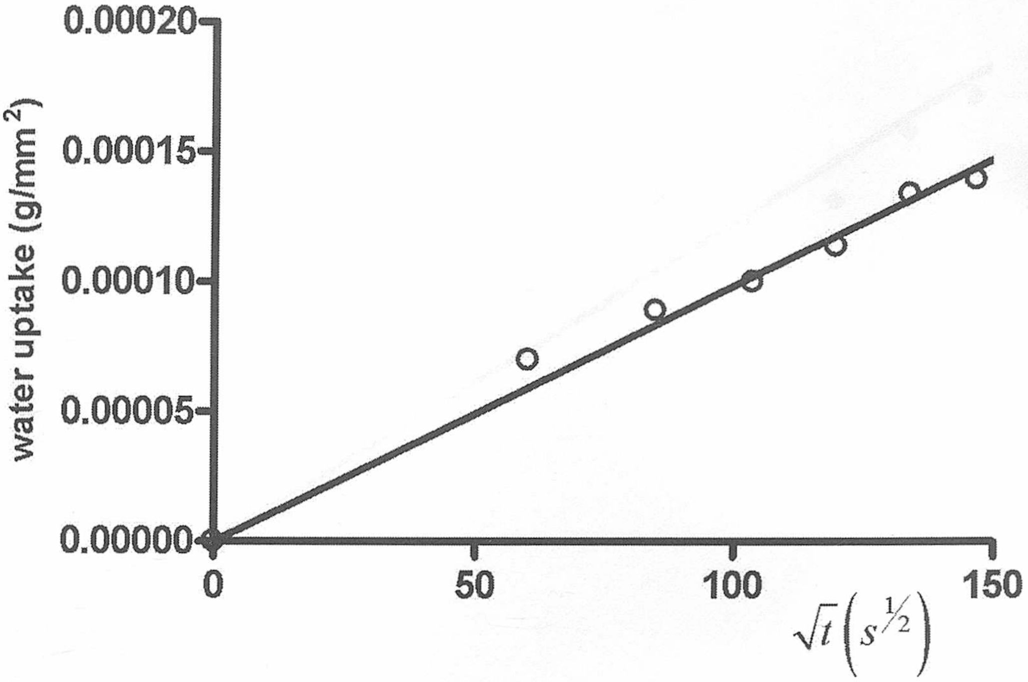

Figure 5.11: Linear plot of Mix 4

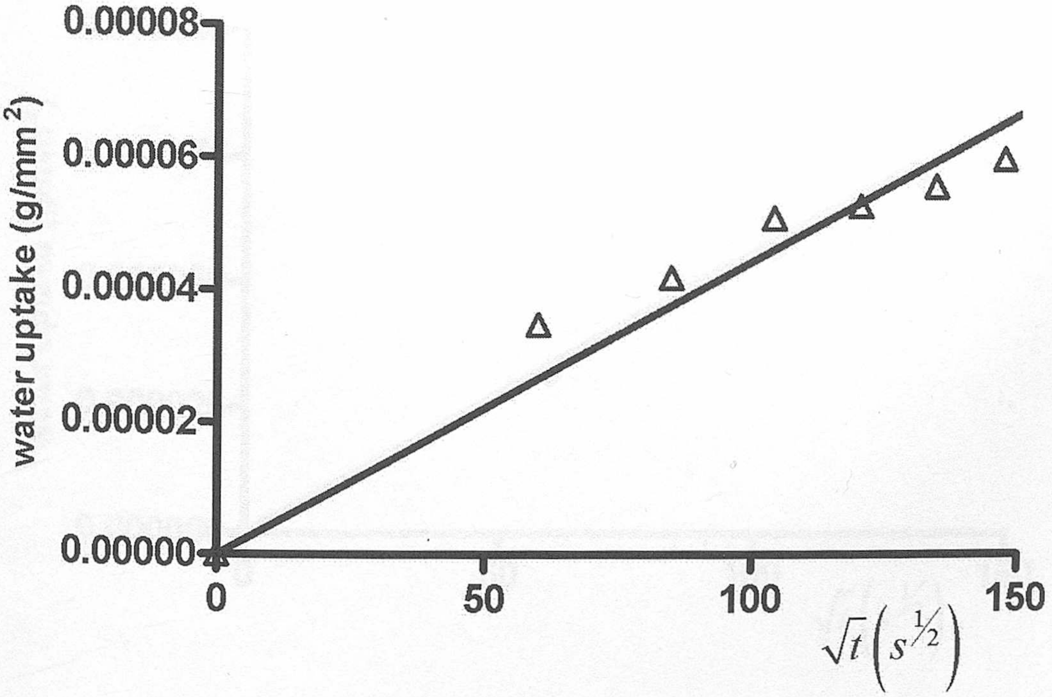

Figure 5.12: Linear plot of Mix 5

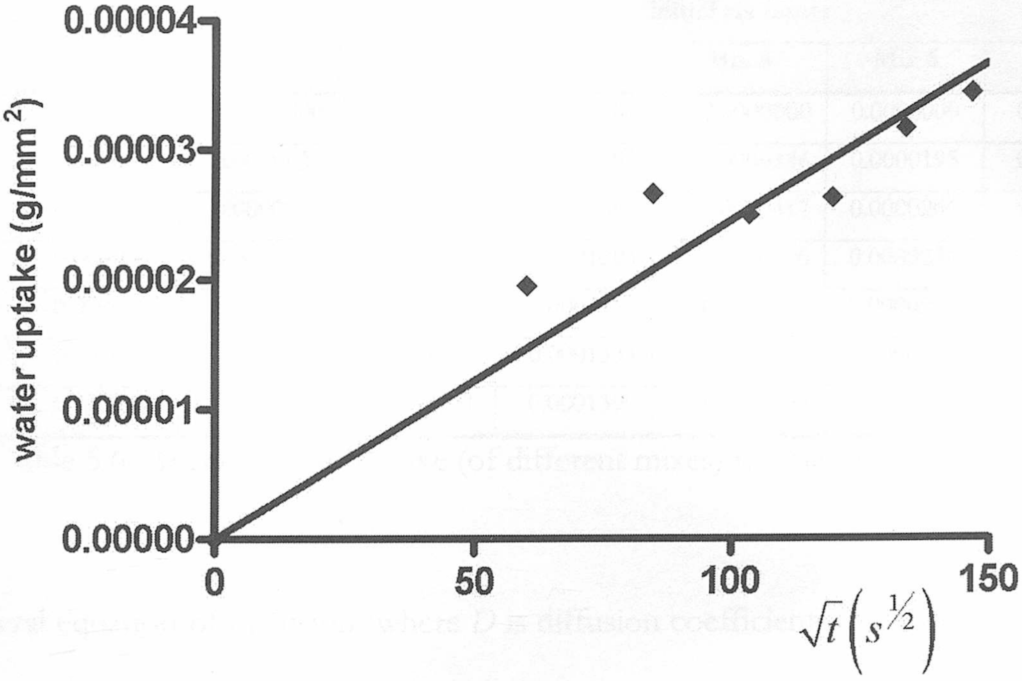

Figure 5.13: Linear plot of Mix 6

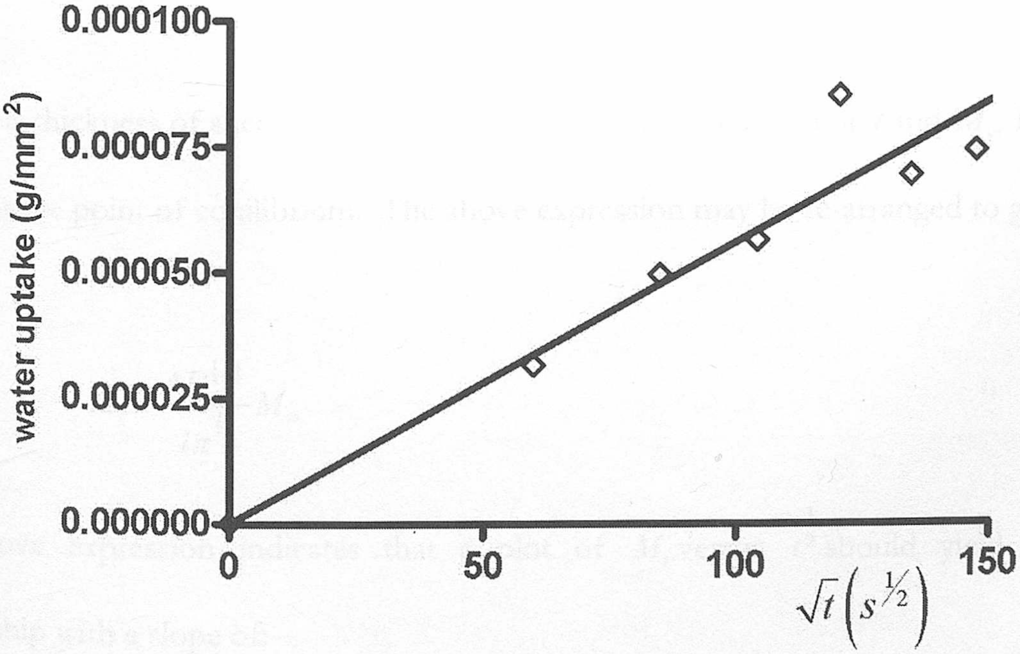

Figure 5.14: Linear plot of Mix 7

The water uptake results for the first six hours are tabulated in Table 5.6.

Time	**Water uptake (g/mm^2) for initial six hours**						
(hour)	**Mix 1**	**Mix 2**	**Mix 3**	**Mix 4**	**Mix 5**	**Mix 6**	**Mix 7**
0	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
1	0.0000187	0.0000632	0.0000237	0.0000697	0.0000346	0.0000195	0.0000314
2	0.0000303	0.0000867	0.0000239	0.0000889	0.0000417	0.0000266	0.0000495
3	0.0000345	0.0001003	0.0000285	0.0001003	0.0000506	0.0000250	0.0000563
4	0.0000432	0.0001138	0.0000338	0.0001140	0.0000524	0.0000263	0.0000849
5	0.0000461	0.0001292	0.0000339	0.0001344	0.0000554	0.0000317	0.0000692
6	0.0000494	0.0001410	0.0000380	0.0001399	0.0000595	0.0000344	0.0000740

Table 5.6: Average water uptake (of different mixes) for the first six hours

The general equation of diffusion (where *D* is diffusion coefficient) that defines the initial linear region is given by *[Ahmad, Tinker et al., 1994]*:

$$\frac{M_t}{M_\infty} = \frac{4D^{\frac{1}{2}}t^{\frac{1}{2}}}{l\pi^{\frac{1}{2}}} \qquad (5.4)$$

Where l is thickness of sheet, M_t is water uptake per unit area at time t and M_∞ is water uptake at the point of equilibrium. The above expression may be re-arranged to give:

$$M_t = \frac{4D^{\frac{1}{2}}t^{\frac{1}{2}}}{l\pi^{\frac{1}{2}}}M_\infty \qquad (5.5)$$

The above expression indicates that a plot of M_t versus $t^{\frac{1}{2}}$ should yield a linear relationship with a slope of:

$$\frac{4D^{\frac{1}{2}}M_\infty}{l\pi^{\frac{1}{2}}} \qquad (5.6)$$

The slope is the maximum uptake rate in the unit of $g/mm^2s^{\frac{1}{2}}$. Clearly, the slope is related to D by:

$$D = \left[\frac{(\text{slope})\, l\pi^{\frac{1}{2}}}{4M_{\infty}} \right]^2 \tag{5.7}$$

As an example to show the way in which the above expression is used, consider Mix 1 which contains litharge as the acid acceptor. On inserting the respective experimental values for the mix containing litharge we obtain:

$$D_1 = \left[\frac{\left(0.0000003427\, g/mm^2 s^{\frac{1}{2}}\right)(0.9822mm)\,\pi^{\frac{1}{2}}}{4\left(0.0002211 g/mm^2\right)} \right]^2 \tag{5.8}$$

$D_1 = 4.55 \times 10^{-7}$ mm²/s or 4.55×10^{-13} m²/s

In this way, values of D were determined for all other mixes used in the present study, as shown in Table 5.7.

Mix	Cure system/ Acid Acceptor	Max. water uptake* *(g/mm²)*	Time to max uptake* (hour)	Max. uptake rate $(g/mm^2s^{\frac{1}{2}})$	$D \times 10^{-13}$ *(m²/s)*
1	ETU/Litharge	0.0002211	864	0.0000003427	4.552
2	ETU/Red lead	0.0003832	1152	0.0000009694	6.656
3	ETU/MgO	0.0000956	864	0.0000002725	3.918
4	ETU/CaO	0.0005369	696	0.0000004410	0.388
5	ETU/ZnO	0.0001768	192	0.0000009844	24.936
6	ETU/Dyphos/Dythal	0.0000703	864	0.0000002446	6.511
7	Zisnet-FPT/$CaCO_3$/MgO	0.0002173	864	0.0000005593	3.624

Table 5.7: Summary of results (*Based on 60 days)

5.4 DISCUSSION

Rubber, and in some case the additives it contains will absorb moisture. In some applications the absorption of water has a deleterious effect on performance; this is certainly so for elastomers used in sealing applications that are exposed to moisture. The level of the deterioration depends upon the water temperature, the contact period with water or moisture and also the composition of the vulcanisate. Numerous previous works on water absorption have been published concerning vulcanised rubber and raw rubber. Boggs and Blake *[Boggs and Blake, 1926]* and Lowry and Kohman *[Lowry and Kohman, 1927]* have shown that the water absorption decreased with the advancing state of vulcanisation, although their work was more concerned with the mechanism of water absorption rather than the effect engendered by fillers and accelerators. Winkelmann and Croakman *[Winkelmann and Croakman, 1930]* were of opinion that the increased volume loading of any given filler had very little effect on water absorption. However, Skinner and Drakeley *[Skinner and Drakeley, 1933]* in his work found the absorption of water appears to decrease with increasing amounts of filler. They also found that litharge (type of lead used throughout present work) was one of the acid acceptors that showed higher absorption. Litharge is widely used in conjunction with ethylene thiurea (ETU) as a curative for ECO. This has become the industry norm for this elastomer for many years *[Parkes, 1974]*. As mentioned previously, Zisnet-FPT system suffers from the disadvantage of showing substantial volume swelling in the presence of moisture or water *[Harris, 2000]*; as high as 46%. The volume swell caused by water can be substantially reduced by incorporating untreated silica. The high moisture uptake displayed by the Zisnet-FPT system suggests that ECO mixes containing this system may have a limited shelf-life and therefore caution needs to be exercised in terms of storage and the conditions of storage. Abraham, Burczak and Cable *[Abraham, Burczak et al., 2003]* suggested that critical conditions can be reached within three weeks and may even be sooner in high humidity conditions. In the present study, the water uptake of Zisnet-FPT system and its diffusion coefficient were investigated and compared to that of ETU system with various acid acceptors.

Different water uptake characteristics were observed in ECO mixes with different acid acceptors. Each acid acceptor was used at a concentration recommended by the respective manufacturer. Formulations of ECO mixes containing the various acid acceptors are given in Table 5.2. Preliminary diffusion experiments were carried out with two objectives in mind. In the first place, the water uptake during a period 60 days was monitored as a way of understand the rudiments of long term behaviour. The second objective was to ascertain the time required to reach maximum water uptake. In reference to Figures 5.1 to 5.7 it is clearly seen that the point of maximum water uptake has been surpassed. Continuing the diffusion experiments beyond the periods indicated in Figures 5.1 to 5.7 were considered undesirable because samples commenced showing signs of weight reduction; probably due to 'leaching'. The leaching phenomenon is thought to occur as a result of the egression of water-soluble matter in the bulk of the samples. The extraction of water-soluble materials was manifested as minute clear crystals (possibly metal salt residues) found in the water. For most of the samples the point of maximum water uptake was attained after approximately 500 hours of immersion except for Mix 5 (ZnO) which reached a maximum value in a relatively much shorter period, notably after about 192 hours. The rapid attainment of the point of maximum water uptake for the ECO mix containing ZnO is thought to be attributed to its very high diffusion coefficient, that is 24.936×10^{-13} m^2/s.

Most of the mixes exhibited highest rates of water uptake within 24 hours of immersion in water as was observed in the 60-day experiments (see Figures 5.1 to 5.7). In order to assess the reproducibility of the water uptake method used in the present study, diffusion experiments were repeated covering a period of 24 hours and taking measurements with much greater frequency than previously. The results are shown in Figures 5.8 to 5.14. With some obvious slight exceptions, in general Figures 5.8 to Figure 5.14 clearly indicates a well-defined linear region reflecting a constant rate of water uptake. The linear regions allowed the determination of *D* values; these are presented in Figure 5.15.

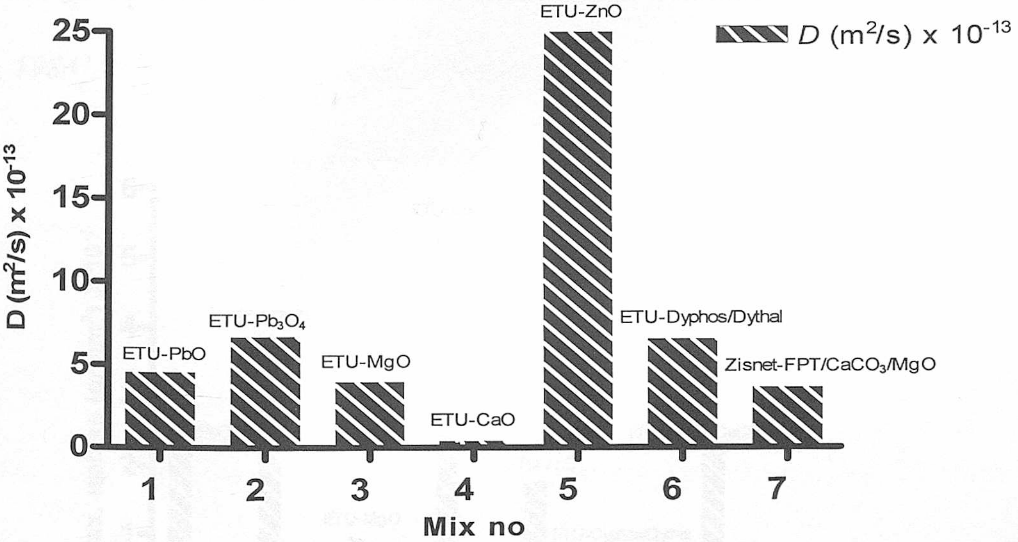

Figure 5.15: Diffusion coefficient of Mix 1 to 7

Any given mix that reaches the point of maximum water uptake in the shortest time does not necessarily imply that it will absorb the greatest amount of water. Mix 4 (CaO) was anticipated as having the highest water uptake as is confirmed in the present diffusion experiments; it did however require a relatively longer period to achieve it (approximately 1152 hours) as it displayed the lowest *D* value. Mix 2 (Red Lead) and Mix 7 (Zisnet and

CaCO3/MgO) also exhibited high water uptake values. Figure 5.16 clearly shows that Mix 5 (ZnO) gave the highest *D* value thus indicating rapid water absorption characteristics.

Generally, the diffusion coefficients of liquids in different elastomers are related to their glass transition temperatures. ECO is an elastomers that has a low T_g (-40°C) and therefore exhibits a reasonable degree of flexibility at low temperatures. However due to the presence of chlorine which is polar by nature, ECO has very low gas permeability about one third of butyl rubber. Butyl rubber is known for its impermeability owing to its large methyl group that causes steric hindrance to the rotation of its molecular segments *[Southern, 1984]*.

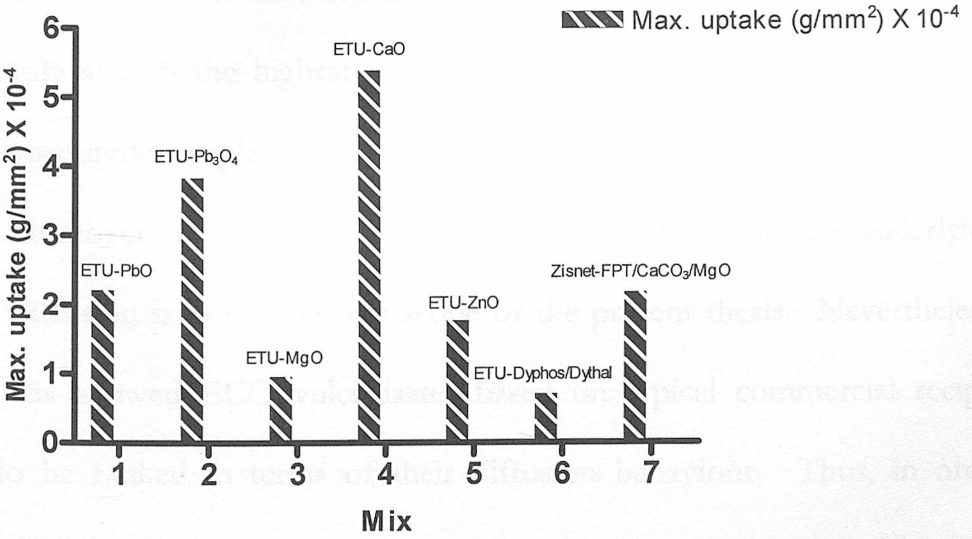

Figure 5.16: Maximum water uptake per unit area (*g/mm²*) of each mix

The presence of particulate fillers, such as, carbon black, whiting or clay reduces the diffusion coefficient according to the simple theory proposed by Maxwell *[Maxwell, 1891]*. The effect however is too small and often negligible.

Previous work by Ahmad, Tinker and Aubrey *[Ahmad, Tinker et al., 1994]* concluded that there is a reasonable correlation between diffusion coefficient and crosslink density. Southern *[Southern, 1984]* asserted that the general levels of crosslink density normally encountered in vulcanised rubbers produce only a minimal effect on the diffusion behaviour. He also concluded that generally fillers do not have much influence on the diffusion of liquids in elastomers. This summation however is not applicable to elastomers which contain liquids, that is, plasticizers or extenders, where the situation is more complicated.

It is widely accepted that a mix with a higher diffusion coefficient, *D*, will absorb water faster than a mix with a lower diffusion coefficient. However, mixes with high *D* values do not necessarily absorb the highest amount of water. Owing to so many uncertain parameters an unequivocal explanation of the diffusion behaviour of ECO vulcanisates is not possible. Moreover, a comprehensive study of the thermodynamics underlying the mechanism of diffusion is not within the scope of the present thesis. Nevertheless, the present work has allowed ECO vulcanisates based on typical commercial recipes or formulations to be ranked in terms of their diffusion behaviour. Thus, in order of decreasing coefficient-of-diffusion values the acid acceptors can be ranked as follows: ZnO, red lead, dyphos/dythal, litharge, MgO, Zisnet, CaO. It is generally believed that acid acceptors, which are merely metal oxides, may react with hydrochloric gas that is given off during high-temperature vulcanisation to form metal chloride salts. Such salts are hydrophilic by nature and therefore will attract moisture *[Farid, 1999]*.

In order for the reader to appreciate the rudiments and complexities of the diffusion mechanism a fleeting account of the work of Karuppiah *[Karuppiah, 1987]* is appropriate here. This worker proposed a model for the equilibrium water absorption of natural rubber containing hydrophilic materials; his arguments with annotations by the present author are as follows: Consider a rubber vulcanisate containing a water soluble impurity. If the rubber vulcanisate containing the impurity is placed in a solution of this impurity and allowed to equilibrate then two simultaneous mechanisms are thought to take place as the sample approaches equilibrium. First, water diffuses into the rubber phase. Second, some of the water that has absorbed into the rubber phase will come into contact with the hydrophilic impurities and form droplets of solution around the impurities. The concentration gradient developed between the droplets of solution and the water in the rubber phase promotes further passage of water into the droplets causing them to grow against the elastic pressure of the surrounding rubber network. Equilibrium is attained when the pressure within the droplets is equal to the pressure exerted by the rubber hydrocarbon network. By considering the pressure balance between the osmotic pressure of the aqueous solution in which the vulcanisate is immersed, the osmotic pressure of the internal droplets; and, the elastic pressure of the rubber network the following expression is derived.

$$\frac{c_0}{M_0}=\frac{c_i\rho_w}{(c_w-s)M_i}-\frac{G}{2RT}\left(5-\frac{4}{\lambda}-\frac{1}{\lambda^4}\right) \qquad (5.9)$$

In the above expression c_0 is the concentration of the solute in the external solution in which the rubber vulcanisate is immersed and M_0 its molecular weight; c_i and M_i are the concentration of and molecular weight of the hydrophilic impurity respectively in the rubber; c_w is the total concentration of water in the rubber vulcanisate; s is the concentration of water dissolved in the rubber phase only; G is the shear modulus of the rubber; λ is the extension ratio of the droplet solution; R is the Universal Gas Constant and T is the absolute temperature. The shear modulus is given by

$$G = \frac{\rho RT}{M_c} \tag{5.10}$$

In equation (5.10), ρ is the density of the rubber hydrocarbon and M_c is the molecular weight between crosslinks. Introducing equation (5.10) into expression (5.9) gives

$$\frac{c_0}{M_0} = \frac{c_i \rho_w}{(c_w - s) M_i} - \frac{\rho}{2M_c}\left(5 - \frac{4}{\lambda} - \frac{1}{\lambda^4}\right) \tag{5.11}$$

In the above expression $\rho/2M_c$ is simply the crosslink density of the rubber vulcanisate and may be conveniently represented by $[X]$. Hence, equation (5.11) may be written as

$$\frac{c_0}{M_0} = \frac{c_i \rho_w}{(c_w - s) M_i} - [X]\left(5 - \frac{4}{\lambda} - \frac{1}{\lambda^4}\right) \tag{5.12}$$

If the liquid in which the rubber vulcanisate is immersed is not a solution but simply water then the term c_0/M_o is zero. Hence, for a rubber vulcanisate immersed in water equation (5.12) simplifies to

$$\frac{c_i \rho_w}{(c_w - s) M_i} = [X]\left(5 - \frac{4}{\lambda} - \frac{1}{\lambda^4}\right) \qquad (5.13)$$

Re-arrangement of equation (5.13) leads to the desired result. That is

$$(c_w - s) = \frac{c_i \rho_w}{M_i} \bullet \frac{1}{[X]} \bullet \left[5 - \frac{4}{\lambda} - \frac{1}{\lambda^4}\right]^{-1} \qquad (5.14)$$

It should be appreciated that the term $(c_w - s)$ represents the amount of water present as droplets within the rubber vulcanisate. Clearly, equation (5.14) indicates that water absorption of rubbers in the presence of hydrophilic substances is a function of the concentration and molecular weight of the substance as well as the crosslink density of the rubber network.

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Chapter 6

STIFFENING EFFECT OF CARBON BLACK

It should be noted that ECO mixes used in the previous Chapter did not contain carbon-black filler. This was a deliberate omission in order to highlight the effect of each acid acceptors per se. Carbon black is known to reduce the water absorption capabilities of vulcanisates and undoubtedly confound the effect engendered by acid acceptors. Nevertheless, carbon black is an essential ingredient for commercial rubber compounds; consequently it is considered important to acquire some understanding of the reinforcing potential of carbon-black filler in ECO vulcanisates. This Chapter reports and discusses the effects of carbon black on ECO vulcanisate properties cured by the present range of vulcanisation systems. A greater degree of stiffening was found in ECO vulcanisates based on ETU-Lead compared with that of ECO vulcanisates containing the Zisnet-FPT system. This finding is significant because it facilitates the optimisation of the curing system. The necessity for optimisation will be made clear in the subsequent Chapter.

6.1 INTRODUCTION

In order to understand the potential differences in vulcanisates cure by the Lead-ETU and Zisnet-FPT systems a preliminary study on the effect of carbon black was deemed appropriate. Essentially, equal amounts of a given grade of carbon black were added to the ECO mixes containing the two different curing systems and the 'stiffening' effect of carbon black on each of them were investigated. As previously explained in 2.6, the stiffening effect, α_f, is directly proportional to the carbon black loading.

6.2 STIFFENING EFFECT

The method used to study this behaviour was explained by Farid *[Farid, 2004]* but the initial work was carried out by Wolff *[Wolff, 1970]*. Consider a typical Monsanto theometer trace for a rubber compound containing a given concentration crosslinking agent as shown in Figure 6.1.

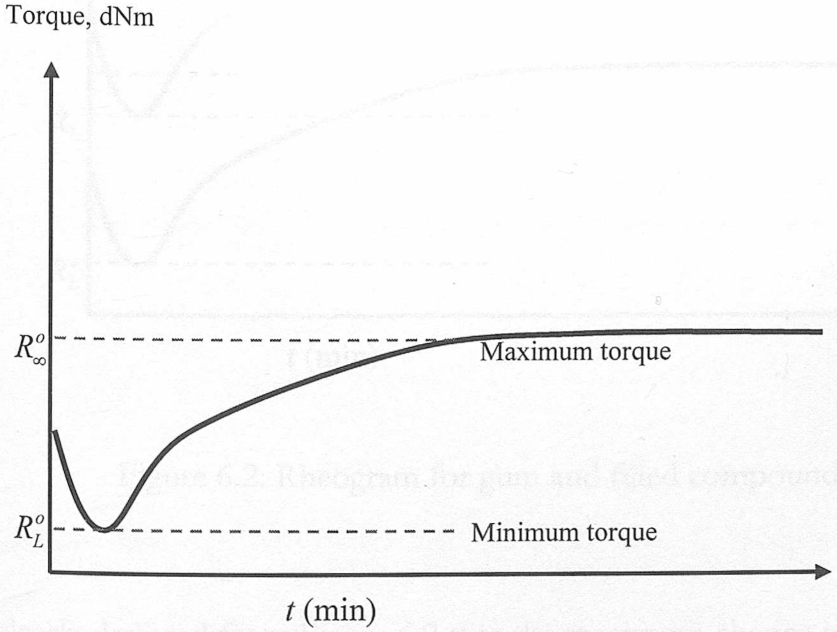

Figure 6.1: Typical rheogram for a gum (unfilled) rubber

If a known quantity of a given grade of carbon black is added to the same compound, then it is reasonable to assume that R_L^o will increase due to increase in viscosity. It is expected that the parameter R_∞^o will also be raised as depicted in Figure 6.2.

In Figure 6.2, the upper trace signifies a rubber mix containing *a* grams of carbon black per 100 grams of rubber. If a number of other rubber mixes containing increasing levels of carbon black concentration were analysed then a series of rheometer traces (in which the maximum change in torque would increase with increasing carbon black levels) would be obtained.

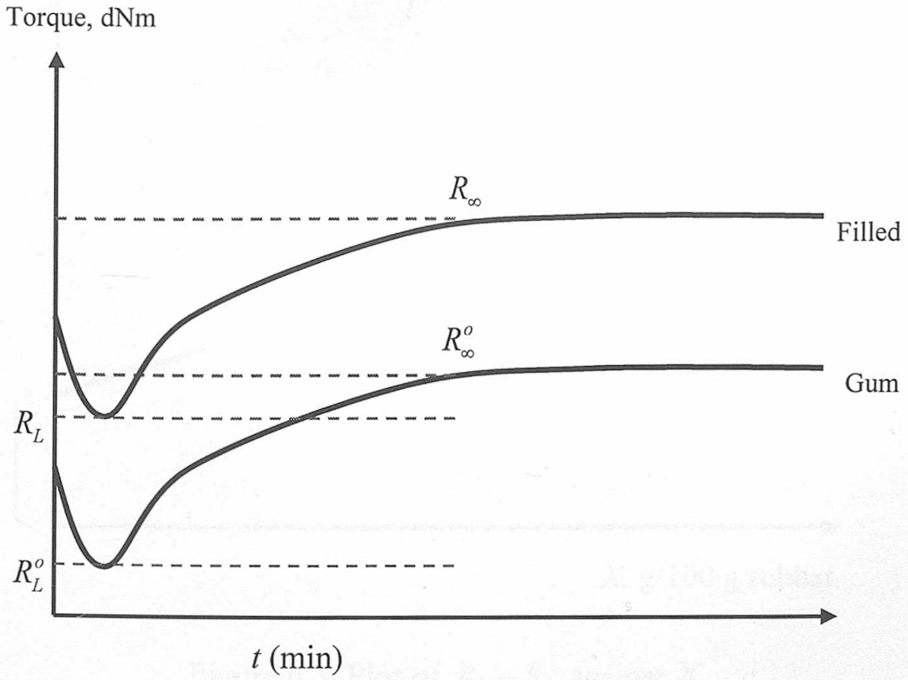

Figure 6.2: Rheogram for gum and filled compound

It may be clearly deduced from Figure 6.2 that the maximum change in torque for a filled rubber is given by,

$$R_\infty - R_L$$

The maximum change in torque is assumed to be proportional to the concentration of carbon black. In the present work, filler concentration is defined as the amount of filler in grams per 100 grams of rubber. Thus,

$$R_\infty - R_L \propto X \tag{6.1}$$

where X is the filler concentration.

Based on proportionality behaviour, consider a plot of $R_\infty - R_L$ against X as follows:

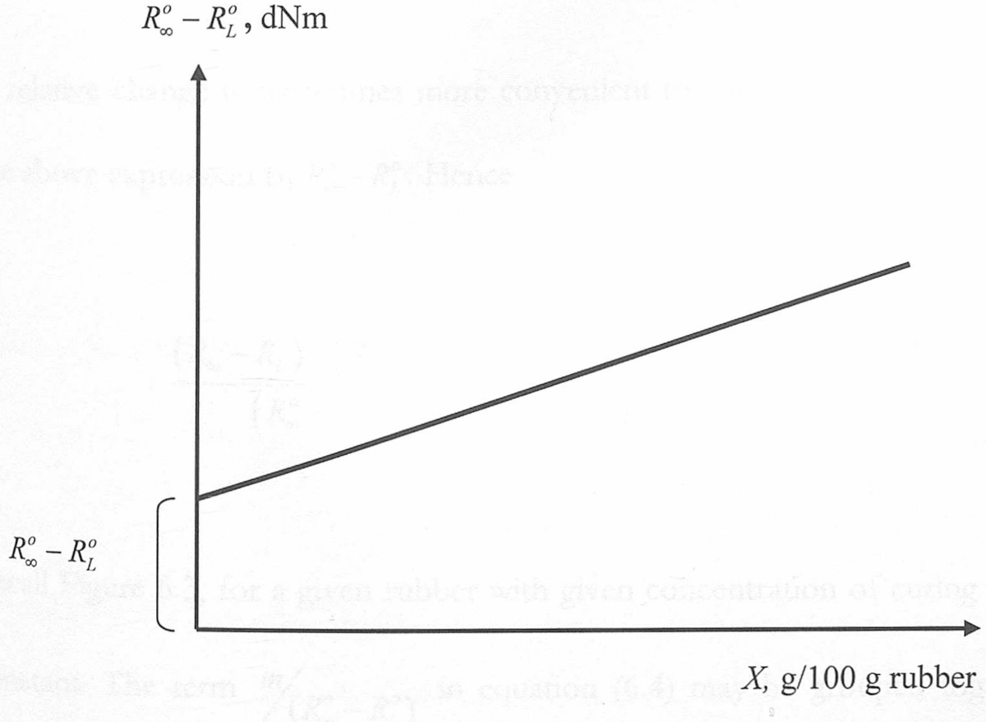

Figure 6.3: Plot of $R_\infty - R_L$ against X

It is clear that the intercept on the vertical axis (see Figure 6.3) represents the maximum change in torque of a rubber mix without carbon black. Therefore, the maximum change in torque of the gum rubber is $R_\infty^o - R_L^o$.

The linear equation of the plot is

$$R_\infty - R_L = \left(R_\infty^o - R_L^o\right) + mX \tag{6.2}$$

m is the gradient or slope of the straight line.

Equation (6.2) can be re-arranged to give

$$\left(R_\infty - R_L\right) - \left(R_\infty^o - R_L^o\right) = mX \tag{6.3}$$

A relative change is sometimes more convenient to analyse in which case we may divide the above expression by $R_\infty^o - R_L^o$. Hence

$$\frac{\left(R_\infty - R_L\right) - \left(R_\infty^o - R_L^o\right)}{\left(R_\infty^o - R_L^o\right)} = \frac{m}{\left(R_\infty^o - R_L^o\right)} X \tag{6.4}$$

Recall Figure 6.3, for a given rubber with given concentration of curing agent, $R_\infty^o - R_L^o$ is constant. The term $m / (R_\infty^o - R_L^o)$ in equation (6.4) may be grouped together to provide common constant α_f. Therefore,

$$\alpha_f = \frac{m}{\left(R_\infty^o - R_L^o\right)} \tag{6.5}$$

Introducing (6.5) into (6.4) gives,

$$\frac{\left(R_\infty - R_L\right) - \left(R_\infty^o - R_L^o\right)}{\left(R_\infty^o - R_L^o\right)} = \alpha_f X \tag{6.6}$$

Thus, a plot of, $\dfrac{\left(R_\infty - R_L\right) - \left(R_\infty^o - R_L^o\right)}{\left(R_\infty^o - R_L^o\right)}$ versus X, should yield a linear plot with slope α_f.

For a deeper understanding of the signification of α_f, we may re arrange (6.6) to give

$$\alpha_f = \frac{\dfrac{\left(R_\infty - R_L\right) - \left(R_\infty^o - R_L^o\right)}{\left(R_\infty^o - R_L^o\right)}}{X} \tag{6.7}$$

From expression (6.7), it can be deduced that α_f represents the 'relative stiffening action' of the filler per unit concentration of filler. Note, α_f is a dimensionless parameter.

6.3 EXPERIMENTAL WORK

For each curing system, five compounds with 0, 10, 20, 30, 40 and 50 pphr of FEF (N550) carbon black were prepared. Three samples of each compound were taken and their cure properties were determined using the Monsanto Rheometer S100. The base formulations are given in Table 6.1.

Ingredient	ETU-lead, pphr	Zisnet-FPT, pphr
ECO	100.0	100.0
Stearic acid	1.0	1.0
Struktol A60	1.0	1.0
Zinc stearate	1.0	1.0
ETU	2.5	-
NBC	2.0	2.0
Litharge	5.0	-
FEF N550	from 0 to 50	from 0 to 50
Zisnet FPT	-	1.0
$CaCO_3/MgO$	-	5.0
DPG	-	0.2

Table 6.1: Base formulations of ECO mixes containing FEF carbon black

6.4 RESULTS AND DISCUSSION

The cure times of the mixes containing various levels of carbon black (0 to 50 pphr) were determined at 170°C covering a period of 60 minutes. The range was set to 200 dNm and the arc was fixed at ±3°. To demonstrate the typical effects of various loadings of carbon black rheograms for Zisnet-FPT system are shown in Appendix B.

The effect of carbon black on torque for both systems is shown in Tables 6.2 and 6.3.

Carbon black (pphr)	Min. torque, R_L (dNm)	Max. torque, R_∞ (dNm)	$R_\infty - R_L$ (dNm)	$\frac{(R_\infty - R_L) - (R_\infty^o - R_L^o)}{(R_\infty^o - R_L^o)}$
0	10.2	64.0	53.9	0.0000
10	10.3	85.0	74.7	0.3885
20	10.7	97.0	86.1	0.6041
30	10.0	105.0	95.0	0.7658
40	11.0	115.0	103.9	0.9331
50	10.5	127.3	116.6	1.1710

Table 6.2: Torque against carbon black loading for the ETU-Lead system

Carbon black (pphr)	**Min. torque,** R_L **(dNm)**	**Max. torque,** R_∞ **(dNm)**	$R_\infty - R_L$ **(dNm)**	$\frac{(R_\infty - R_L)-(R_\infty^o - R_L^o)}{(R_\infty^o - R_L^o)}$
0	10.1	62.4	52.3	0.0000
10	10.3	64.5	54.2	0.0363
20	10.9	74.8	63.9	0.2218
30	10.0	82.6	72.6	0.3881
40	11.1	89.5	78.4	0.4990
50	10.7	95.4	84.7	0.6195

Table 6.3: Torque against carbon black loading for the Zisnet-FPT system

It is apparent that the minimum torque, R_L, for all ECO mixes, irrespective of the cure system used, appears to be reasonably consistent. The minimum torque may be regarded as an indication of the mix viscosity. A fleeting inspection of the results delineated in Tables 6.2 and 6.3 suggests that the increase in relative torque is directly proportional to the carbon black loading concentration. Confirmation of this proportionality is clearly apparent from the plots of $\frac{(R_\infty - R_L)-(R_\infty^o - R_L^o)}{(R_\infty^o - R_L^o)}$ versus carbon black concentration given in Figure 6.10.

The r^2 values for each of the two plots shown in Figure 6.10 are 0.9538 and 0.9729 corresponding to ETU-Lead and Zisnet-FPT systems respectively. These values indicate a reasonably good level of linear dependence.

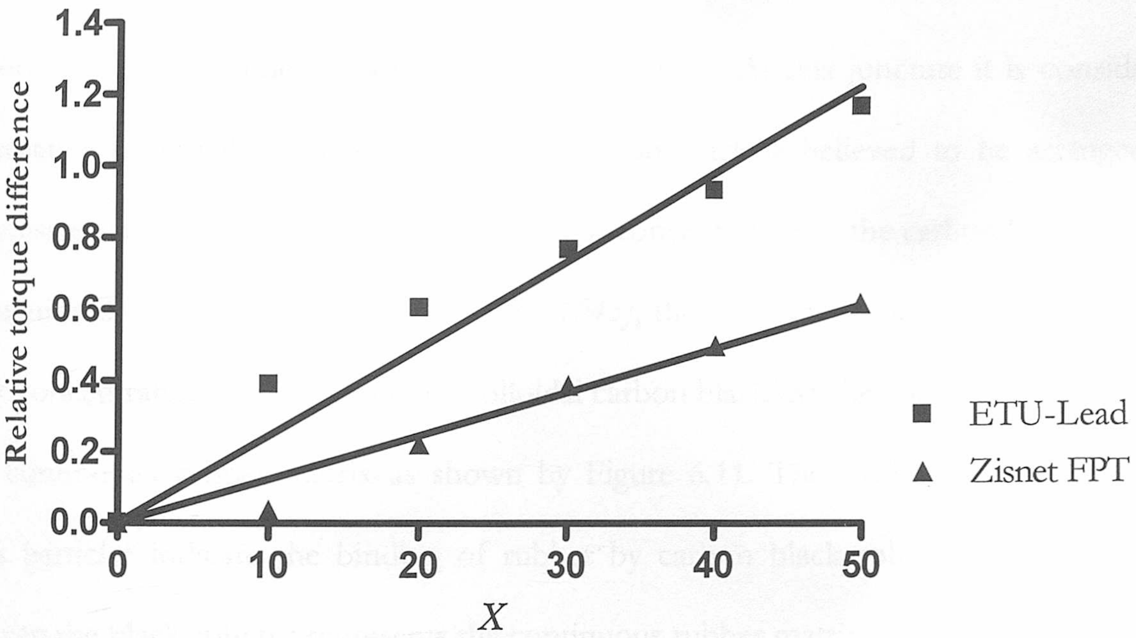

Figure 6.10: Plot of $\frac{\left(R_\infty - R_L\right)-\left(R_\infty^o - R_L^o\right)}{\left(R_\infty^o - R_L^o\right)}$ against carbon black concentration, X

From the plots shown in Figure 6.10 the following expressions may be deduced

For ETU-Lead system: $\frac{\left(R_\infty - R_L\right)-\left(R_\infty^o - R_L^o\right)}{\left(R_\infty^o - R_L^o\right)} = 0.02451X$,

where α_f is 0.02451

For Zisnet FPT system: $\frac{\left(R_\infty - R_L\right)-\left(R_\infty^o - R_L^o\right)}{\left(R_\infty^o - R_L^o\right)} = 0.01225X$,

where α_f is 0.01225

Clearly from the results obtained hitherto we deduce that α_f, for a given type or grade of carbon black, is dependent upon the cure system used. At this juncture it is considered informative to visualise the way in which carbon black is believed to be arranged in vulcanisates at various loadings. Three ranges of concentration of the carbon black may be distinguished. As described by Guth *[Guth, 1945]*, the first range is up to 10% of carbon black concentration. In this range the colloidal carbon black may be considered suspended in a continuous rubber matrix as shown by Figure 6.11. The shaded areas around the black particles indicate the binding of rubber by carbon black sphere. The white area between the black spheres represents the continuous rubber matrix.

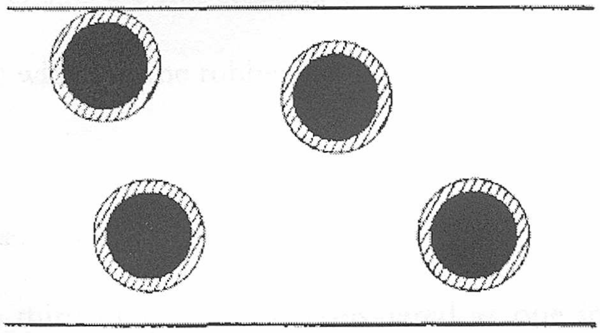

Figure 6.11: Model for the rubber-carbon black up to 10% concentration

The second range is up to 30% concentration where the carbon black chains develop, leading to a carbon black network interpenetrating the rubber network. This is shown by Figure 6.12.

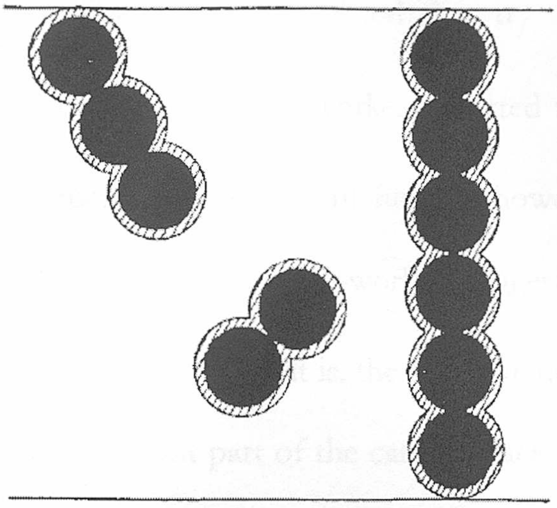

Figure 6.12: Model for rubber-carbon black in the second range up to 30% concentration

Chain formation may lead to continuous bridge between the boundaries of rubber-black system. In general, the chains are not straight. In this range, the chain as a whole (rather than individual spheres) will bind the rubber.

The third range describes a situation in which the concentration is greater than 30%. The situation posed by this third range may be considered as one in which carbon black is diluted by the rubber. Figure 6.13 illustrates the cubic packing of the spheres.

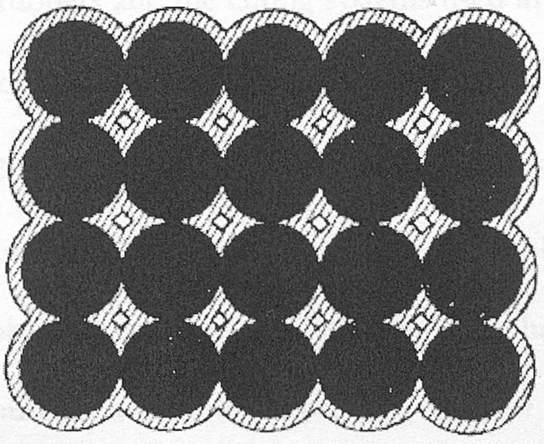

Figure 6.13: Model for rubber-carbon black system in third range of concentration

Wolff and Wang *[Wolff and Wang, 1993]* postulated that α_f of all furnace blacks is independent of the type of cure system; these workers asserted that α_f is dependent on primarily the carbon black structure. The present findings however are contrary to the views expressed by Wolf and Wang. Wolff and co-workers suggested that α_f is a measure of the in-rubber structure of carbon blacks, that is, the structure that remains after mixing. It is generally believed that a significant part of the carbon black network is destroyed by shear deformation during mixing. The remnant carbon black network could be destroyed further by the action of the cure rheometer; in this instrument the angular movement of the rotor in which the rubber is embedded is normally ±3° of arc which is equivalent to approximately 20% strain *[Dannenberg and Stokes, 1949]*. However, in the opinion of the present author this is unlikely because the carbon black network that remains after mixing is 'persistent structure' and is held together tenaciously; it is difficult to envisage how the relatively gentle and benign oscillatory action of a rheometer rotor is capable of disintegrating a formidable carbon black network. In view of the foregoing remarks there is clearly some degree of doubt as to whether α_f is indeed a measure of a 'secondary' network formed by carbon black in the higher region of carbon black concentration; particularly for the ECO rubbers and the curing systems used in the present investigation. Having dismissed the notion that α_f is perhaps a measure of a tenuous secondary structure in so far as ECO vulcanisates are concerned it is nevertheless informative to expound on the present state of knowledge concerning carbon-black network formation. The subsequent paragraph is devoted to this aspect. After having reviewed pertinent current knowledge the author will then proceed to present his own views on this interesting matter in an attempt to interpret the results of the present study.

Filler aggregates in the polymer matrix have a tendency to associate to agglomerates especially at high loadings. This leads to chain-like filler structures or clusters. These somewhat complex arrangements are generally known as secondary structures or filler-network. Previous work *[Voet and Cook, 1968] [Voet, Sircar et al., 1969]* has revealed that carbon blacks with smaller particles and higher structure have a greater tendency to undergo filler networking. This belief is based on the evaluation of electrical properties of dynamically and statically strained carbon black filled vulcanisates.

As remarked earlier, it is believed that α_f is affected chiefly by the formation of a secondary network; however, there is no experimental evidence to show how it is constructed. That is, whether it is formed by direct contact between filler aggregates or via layer of immobilised rubber on the filler surface although the latter seems to be most plausible route. There is no evidence in the literature that suggests α_f is affected by the cure system. However, the present findings clearly allude to some kind of interaction between the cure system and the carbon-black network. It is generally known that the surfaces of furnace carbon blacks are replete with chemical groups, such as, ketones, aldehydes, carboxylic acid groups and so forth. Thus, it is feasible that the nature of the surface chemistry exhibited by carbon blacks may lead to a chemical or chemi-physical interaction between the filler surface and the vulcanisation system. If such an interaction were to exist then this would certainly explain the differences in the stiffening action (as reflected by the α_f values) between the ECO mix containing ETU-lead and that containing Zisnet-FPT. Moreover, assuming that a kind of undefined interaction between the filler surface and the curing system exists then the work described here implies that the ETU-lead system has a greater affinity than does Zisnet-FPT for the carbon-black filler surface (see Figure 6.10). In addition, the results of the work described here suggest that a lower concentration of the ETU-lead system may be used in order to produce ECO vulcanisates with comparable moduli to those containing Zisnet-FPT. This may have significant commercial implications; but, more importantly the use of lower concentrations of ETU-lead compositions than typically recommended is clearly a welcome proposition in view of the present-day concerns with health risks and environmental issues associated with the use of ETU-lead systems.

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Chapter 7

POLYMER-SOLVENT INTERACTION PARAMETER (χ) AND CROSSLINK DENSITY

Many physical and mechanical properties of elastomers in general depend upon the concentration of crosslinks within the bulk of the elastomer. Therefore, in order to obtain the correct level and to control the in-service properties of rubber vulcanisates it is essential that the crosslinked network structure is characterised in terms of concentration of crosslinks; and, in some cases crosslink type. Probably the most facile way of determining crosslink concentrations is by using equilibrium-swelling methods as will be explained later in this Chapter. The successful application of the swelling technique depends upon knowing the value of an essential thermodynamic parameter known as the polymer-solvent interaction parameter χ*. Values of* χ *can be readily found in the literature for various general-purpose rubbers paired with most common solvents or liquids; however, there appears to be a paucity of information in reference to special-purpose rubbers, such as ECO. Therefore, the main objective of the work described in the present Chapter is to determine a reliable value of* χ *for both ETU-lead and Zisnet-FPT systems. Based on measurements carried out under equilibrium conditions* χ *values were calculated using the familiar Flory-Rehner relationship [Flory and Rehner, 1943]. Having acquired knowledge of* χ *crosslink densities were subsequently determined.*

7.1 INTRODUCTION

A reliable method for measuring the true crosslink density of a cured rubber has been sought for many years. Generally, two different approaches are used. One of which is based on stress-strain behaviour in simple extension and the other on equilibrium volume-swelling measurements. In terms of using stress-strain procedures, it is often said that measurements in compression are preferred rather than simple extension. This preference is based on the observation that the stress-strain relationship in compression agrees remarkably well with the predictions of the Gaussian theory of rubber elasticity *[Treloar, 1975]*. However, this does not imply futility of simple extension methodology; simple extension techniques are perfectly acceptable provided certain assumptions upon which the theory is based are not violated. In recent years there has been renewed interest in techniques involving swelling of crosslinked rubber networks. Much work has been done to study the accuracy and reliability of swelling techniques in general. There are two major advantages of the swelling approach that makes it highly desirable for academic investigation. First, the swelling technique is not affected by non-affine effects that are generally encountered during stress-strain measurements of dry rubbers. Second, as a consequence of the isotropic expansion of the rubber network during swelling any complications arising from viscoelastic effects is eliminated. A further advantage of the swelling method is the high degree of reproducibility that is normally achieved.

Upon immersion in good solvent, crosslinked elastomers, as opposed to uncrosslinked types, will absorb a portion of the solvent and subsequently swell rather than dissolving completely. The extent of swelling represents a competition between two forces. The free energy of mixing will cause the solvent to penetrate and try to dilute the crosslinked elastomer. This entropic increase may be enhanced by increasing the temperature. As the polymer chains in the crosslinked elastomer network begin to elongate under the swelling action of the solvent, they generate an elastic retractive force in opposition to this deformation. The crosslinks will limit the magnitude of the deformation. The volumetric swelling reaches steady state when the two forces balance each other. Given that the steady state swelling ratio is a direct function of extent of crosslinking in the sample, swelling experiments are simple and low-cost methods that may be used to characterise polymer networks. At the simplest level of analysis, swelling measurements can be used for quality control and serve as an indexing tool for polymer systems with different levels of crosslinking. At a higher level of analysis, by knowing the value of the interaction parameter, χ, the crosslink density, molecular weight between crosslinks, and number of crosslinks/chain can be computed.

7.2 THEORY: NETWORK AND CROSSLINK DENSITY

A polymer network can be defined as an assemblage of many long polymer chains that are connected to each other through chemical bonds, called crosslinks, resulting in a three-dimensional structure (Figure 7.1). To show rubber-like properties, materials have to fulfil three requirements as follows *[Treloar, 1975]*; the presence of long chain-like molecules with freely rotating links; weak secondary forces between the molecules; and, an interlocking of the molecules at a few places along their length to form a three-dimensional network.

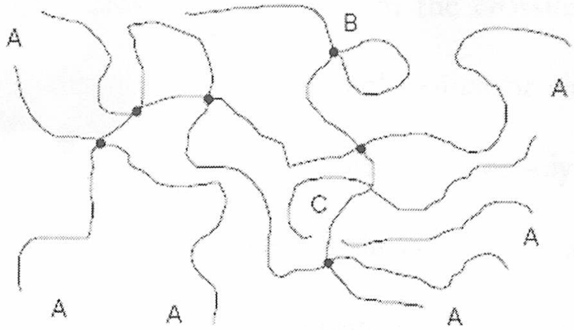

Figure 7.1: Model of a rubber network. (A) loose chain ends, (B) elastically inactive loop, (C) chain entanglement, (•) chemical crosslink.

Through the introduction of crosslinks, the chains are prevented from sliding over each other and the rubber becomes elastic. Besides chemical crosslinks, chain entanglements can also contribute appreciably to the elasticity of the polymer network. They can be of either a permanent or a temporary nature. The concept of entanglements has been discussed, and even questioned, during many decades. However, today it is more or less accepted that entanglements contribute to the elastic forces in rubber materials *[Boyd and Phillips, 1993]*. When filler is introduced, polymer-filler interactions appear and will also contribute to the three-dimensional network. Opposing these three mechanisms of networking are loose chain ends and elastically ineffective loops. By their non-restricted mobility, the former increase the free volume of the material (no crosslinks that tighten the chain end). Chain loops may be formed during vulcanisation and will lower the number of elastically effective chains in the material.

The term crosslink density can be expressed as the number of crosslink points or number of elastically effective chains per unit volume. Theses two quantities are proportional to each other, and their exact relationship depends on the functionality of the crosslink points, i.e. the number of chains that radiate from the crosslink. Henceforth crosslink density will be defined as the number of crosslink points or simply crosslinks per unit volume of rubber. Furthermore, crosslink density is inversely related to the average molecular weight of the chains between the crosslinks, which is also a way to express the network structure. The value of crosslink density may be in the order of 10^{-3} to 10^{-5} mol/cm^3 for a typical rubber material, corresponding to 15 to 1500 monomer units between the crosslinks. Crosslink density is fundamental for polymeric networks, as it determines many physical properties of the resulting material *[Coran, 1994]*. Figure 7.2 shows schematically the way in which some properties of a rubber vulcanisate generally depend on the crosslink density.

Crosslink density can be measured in principally three different ways; by stress-strain measurements, evaluation by the Mooney-Rivlin equation *[Mooney, 1940]*, *[Rivlin, Mullins et al., 1955]*, by determination of the elastic modulus at a certain temperature in the rubbery plateau zone *[Saville and Watson, 1967]* and, by swelling measurements using the Flory-Rehner equation *[Flory and Rehner, 1943]*.

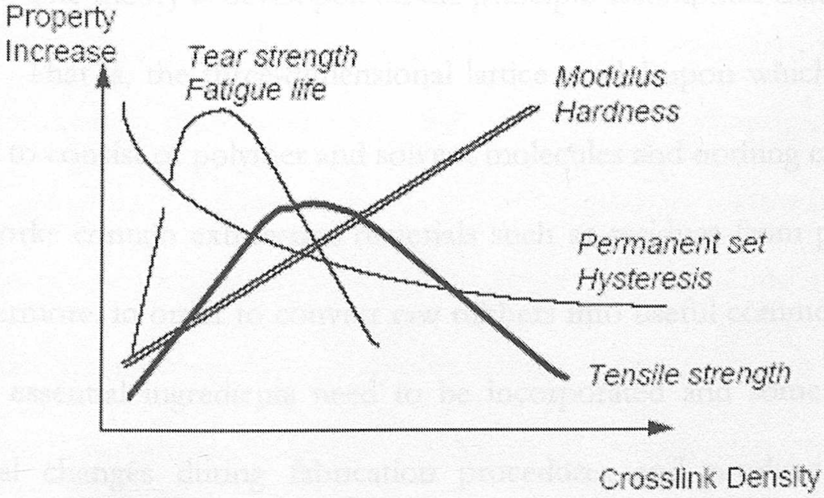

Figure 7.2: Some properties of a elastomer affected by crosslink density *[Bellander, 1998]*

These methods are not absolute but have to be calibrated in some way and therefore some degree of caution is required in handling the data. Different methods will give different results partly due to the time scale of the measurements *[Hagen, Salmen et al., 1997]*. The swelling measurement, which is an equilibrium method, normally gives lower contributions from entanglements because the time scale of the experiment is such that it allows considerable disentangling of temporary entanglements. DMTA measurements, on the other hand, which are often performed at a frequency of 1 Hz will show a much larger proportion of entanglements as there is little time for appreciable disentangling to occur. However, a quantitative measure of crosslink density is valuable, especially for relative comparisons of similar elastomers. In the present work, equilibrium swelling measurements have been used throughout to determine the degree of crosslinking.

7.3 EXPERIMENTAL WORK

Before describing the experimental work a few remarks concerning the application of the lattice theory of Flory and Rhener *[Flory and Rehner, 1943]* need to be brought to the attention of the reader as these are pertinent to the experimental methods that will be described shortly. The theory is developed on the principle assumption that the molecular network is ideal. That is, the three-dimensional lattice model upon which the theory is based is assumed to consist of polymer and solvent molecules and nothing else. However, real rubber networks contain extraneous materials such as residues from polymerisation reactions. Furthermore, in order to convert raw rubbers into useful commercial products a wide range of essential ingredients need to be incorporated and some of these will undergo chemical changes during fabrication procedures and produce by-products. Clearly therefore, a conventional rubber vulcanisate is not a pure material and far removed form the ideal description assumed by the lattice theory. In order for real rubber networks to conform to theory they need to be subjected to a rigorous regime of pre-treatment. The objective of this pre-treatment is to remove or extract, as far as possible, non-rubber constituents. Some additives, of course, form an intrinsic part of the network and therefore cannot be removed. In such cases appropriate correction factors are sometimes employed. The experimental descriptions that follow simply reflect some of the foregoing ideas.

As described in previous Chapters, mixing was carried out on a two-roll mill using the formulation given in Table 7.1.

Ingredient	**pphr**
ECO	100.0
Stearic acid	1.0
Struktol A60	1.0
Zinc stearate	1.0

Table 7.1: Base formulation

The following additives were added to the base formulation: 2.5 pphr of ETU, 5.0 pphr of Litharge (lead) and 2.0 pphr of NBC. The resulting ECO mix was cured into flat sheets (thickness of approximately 1.0 mm) at 170°C for a period corresponding to the optimum cure time determined from a Monsanto rheometer. The cured or vulcanised sheets were allowed to cool to room temperature. When the sheets had cooled sufficiently samples were cut from them having dimensions of approximately 25 mm × 25 mm × 1.0 mm. An azeotropic mixture was prepared for the extraction of certain non-rubber materials comprising acetone, chloroform and methanol (ACM) in the ratio 312:291:274 by volume

[Russell, 1969]; the liquids used for the azeotropic mixture were supplied by Aldrich Ltd, UK. The boiling temperature (b.p.) of the mixture was determined by heating it in a specially designed glassware that allowed the introduction of a thermometer that could be suspended directly above the solvent without immersion. The mixture was gradually heated until it reached its boiling state and produced a superheated vapour. The temperature of the superheated vapour was about 58°C.

Having cut samples of appropriate dimensions and prepared the azeotropic mixture, each sample was weighed in grams to four decimal places and subsequently placed in an azeotropic mixture (or constant boiling mixture) maintained at room temperature for a period of 24 hours in order to pre-swell the samples in order to facilitate the extraction process. Immediately after the pre-swelling period the samples were subjected to cold extraction in a special soxhlet extractor using the ACM mixture for 24 hours. This apparatus was specially modified in such a way that the vapour can be cooled in order to allow cold extraction. At the end of the 24-hour period, the ACM mixture in the soxhlet extractor was discarded and replaced with fresh ACM in order to remove sol. Having introduced fresh ACM mixture, the extraction process was repeated for another period of 24 hours. At the end of the second period of extraction, the samples were removed from the apparatus, placed in labelled containers and kept in a dry, cool and dark environment until required. In passing it should be remarked that cold extraction was used in preference to hot extraction in order to prevent further network maturing reactions taking place during the extraction process.

The azeotrope mixture is used not only because it completely extracts certain non-rubber constituents of the crude rubber (for example, fatty acids, quebrachitol and sterols in case of natural rubber), but it is also capable of completely extracting such reagents as emulsifying agents, anti-oxidants and other similar materials used in manufacturing synthetic rubbers. The extraction process may also remove some resins, free sulphur, mineral oils, wool grease, saponifiable waxes, paraffin wax, ceresin, pine tar, dyestuffs, organic accelerators and anti-oxidants and/or their decomposition products.

Equilibrium volume-swelling of ACM-extracted samples representing the two curing systems (ETU-lead and Zisnet-FPT) were carried out in trichloroethane and chloroform at a temperature of 25 ± 2°C. For any given swelling liquid (trichloroethane or chloroform) and sample the swelling procedure was conducted in the following way: An extracted sample was weighed accurately in grams to 4 decimal places and placed in a sealed glass bottle containing the swelling liquid. In order to ensure that all sides of the sample were exposed to the swelling liquid, the sample was totally submerged in the swelling liquid by suspending it from a nylon thread. The jar with contents was placed in a thermostatically controlled water bath maintained at a temperature of 25 ± 2°C. In order to minimise degradation of the sample, the whole arrangement was protected from direct sunlight by strategic positioning. The sample was weighed periodically until a state of equilibrium was achieved; this state was deemed to have been attained when the sample reached a constant mass. The experiment was performed in triplicate using both swelling liquids, that is, trichloroethane and chloroform. Having reached a state of equilibrium, the sample was dried in vaccuo at 40±3°C. The sequence of experimental events are summarised in Figure 7.3.

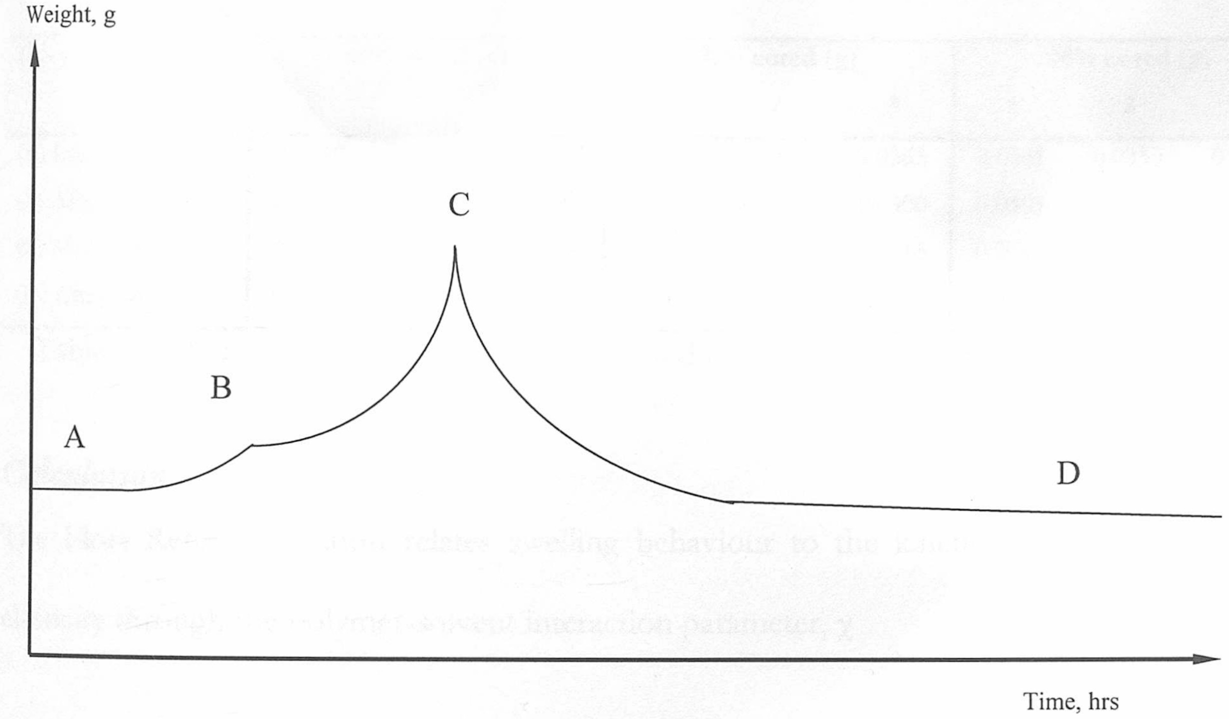

Figure 7.3: A is initial weight, B is weight during extraction, C is maximum weight of swollen sample, D is constant weight upon drying.

7.4 RESULTS

The results obtained are reported and discussed separately for each curing system.

7.4.1 ETU-Lead System

The equilibrium swelling results for the three levels of cure are summarised in Tables 7.2 and 7.3.

(Stages) weight	50% cured (g)			70% cured (g)			90% cured (g)		
	1	2	3	1	2	3	1	2	3
(A) Initial weight	0.0343	0.0338	0.0335	0.0360	0.0366	0.0362	0.0357	0.0357	0.0338
(B) After extraction	0.0308	0.0298	0.0294	0.0323	0.0317	0.0320	0.0312	0.0317	0.0297
(C) Max. swelling	0.0930	0.0974	0.0915	0.0999	0.1032	0.1009	0.1022	0.1617	0.0965
(D) After drying	0.0306	0.0295	0.0294	0.0305	0.0320	0.0321	0.0317	0.0323	0.0305

Table 7.2: Weights (in grams) for samples cured by ETU-Lead system in Trichloroethane

(Stages) weight	50% cured (g)			70% cured (g)			90% cured (g)		
	1	2	3	1	2	3	1	2	3
(A) Initial weight	0.0348	0.0346	0.0339	0.0374	0.0374	0.0363	0.0341	0.0355	0.0354
(B) After extraction	0.0287	0.0295	0.0297	0.0324	0.0297	0.0300	0.0301	0.0316	0.0302
(C) Max. swelling	0.2169	0.2126	0.2159	0.2403	0.2316	0.2315	0.2043	0.2222	0.2148
(D) After drying	0.0300	0.0301	0.0298	0.0317	0.0314	0.0319	0.0288	0.0315	0.0296

Table 7.3: Weights (in grams) for samples cured by ETU-Lead system in Chloroform

Calculation

The Flory-Rehner equation relates swelling behaviour to the kinetic theory of rubber elasticity through the polymer-solvent interaction parameter, χ

$$-\left[\ln(1-\upsilon_r)+\upsilon_r+\chi\upsilon_r^2\right]=\nu V_s\left(\upsilon_r^{1/3}-\frac{2\upsilon_r}{f}\right) \qquad (7.1)$$

where υ_r is the volume fraction of rubber in the swollen sample, ν is the number of effective network chains/cm^3 of rubber (the network density), V_s is the molar volume of the solvent, and f is the functionality of the crosslinks (usually assumed to be 4). The parameter ν is a constant and assumed not to change with swelling pressure. Essentially, the swelling data from using the two swelling liquids on samples of different network densities provide solvable simultaneous equations for χ_1 and χ_2; the subscripts appended to χ identify the swelling liquid used. The method of calculation is based on the procedure proposed by Hayes *[Hayes, 1986]*.

The molar volumes of the two swelling liquids were determined as follows *[Barikani and Hepburn, 1992]*

$$V_s = \frac{M_s}{\rho_s} \tag{7.2}$$

where M_s is the molecular weight of the swelling liquid and ρ_s its density. M_s for trichloroethane ($C_2H_3Cl_3$) is 133.42 g/mol and its ρ_s value is 1.338 g/cm^3. Hence, using equation (7.2) V_s for trichloroethane is 99.716 mol/cm^3. In terms of chloroform ($CHCl_3$), M_s and ρ_s values are 119.38 g/mol and 1.492 g/cm^3 respectively. Hence, the V_s value for chloroform is 80.0134 mol/cm^3. The volume fraction of polymer in the swollen state at equilibrium, υ_r, was calculated according to the method described by Barikani *[Barikani and Hepburn, 1992]* using the following equation:

$$\upsilon_r = \frac{m_1 d_s}{m_1\left(d_s - d_r\right) + m_2 d_r} \tag{7.3}$$

where m_1 is the weight of polymer before swelling, m_2 is the weight of the polymer after swelling, d_s is the density of solvent and d_r is the density of polymer.

The results of the volume fraction of rubber in a swollen sample at equilibrium for the ETU-lead system in relation to the two swelling liquids are given in Table 7.4 below.

Solvent	υ_r **50% cured**	υ_r **70% cured**	υ_r **90% cured**
1,1,1-trichloroethane	0.3751	0.3681	0.3598
Chloroform	0.1714	0.1690	0.1753

Table 7.4: Equilibrium υ_r values for samples cured by ETU-Lead system

Using the calculated υ_r and V_s values equation (7.1) may be solved. Thus for the 50% cured sample in trichloroethane

$$-\left[\ln(1-0.3751)+0.3751+\chi_T(0.3751)^2\right]=v(99.716)\left[(0.3751)^{1/3}-\frac{2(0.3751)}{4}\right] \tag{7.4}$$

Expression (7.4) reduces to

$$v = 1.786\times10^{-3} - 2.644\times10^{-3}\,\chi_T$$

In the above expression χ_T represents the polymer-solvent interaction parameter for trichloroethane.

Similarly, for the 50% cured sample in chloroform

$$-\left[\ln(1-0.1714)+0.1714+\chi_C(0.1714)^2\right]=v(80.0134)\left[(0.1714)^{1/3}-\frac{2(0.1714)}{4}\right] \tag{7.5}$$

Expression (7.5) reduces to

$$v = 4.42\times10^{-4} - 7.82\times10^{-4}\,\chi_C$$

In the above expression χ_C represents the polymer-solvent interaction parameter for chloroform.

Similar calculations as described were carried out to determine ν for the remaining 70% and 90% cured samples in terms of χ_T and χ_C. The equations thus obtained are listed as follows.

50% cured samples:

$$\nu = 1.786\times10^{-3} - 2.644\times10^{-3}\chi_T \tag{7.6}$$

$$\nu = 4.42\times10^{-4} - 7.82\times10^{-4}\chi_C \tag{7.7}$$

70% cured samples:

$$\nu = 1.712\times10^{-3} - 2.551\times10^{-3}\chi_T \tag{7.8}$$

$$\nu = 4.30\times10^{-4} - 7.62\times10^{-4}\chi_C \tag{7.9}$$

90% cured samples:

$$\nu = 1.626\times10^{-3} - 2.443\times10^{-3}\chi_T \tag{7.10}$$

$$\nu = 4.62\times10^{-4} - 8.14\times10^{-4}\chi_C \tag{7.11}$$

Assuming that ν is constant for any given level of cure; and, that it does not change with swelling pressure equations (7.6) to (7.11) are reduced to the forms given below:

50% cured sample: $\chi_T = 0.5083 + 0.2958\chi_C$

70% cured sample: $\chi_T = 0.5026 + 0.2987\chi_C$

90% cured sample: $\chi_T = 0.4765 + 0.3332\chi_C$

The magnitudes of the numbers in the above equations are very small and it is difficult to appreciate the way in which χ_T and χ_C vary with respect to each other. Therefore, it was thought expedient to plot χ_T against χ_C using for each of the above equations using fictitious values of χ_C. The plots are shown in Figure 7.4. According to the tenets of solution theory the polymer-solvent interaction parameter should be independent of the degree of crosslinking. On the basis of this principle it is easily deduced from Figure 7.4 that χ_C and χ_T values are 0.81 ± 0.04 and 0.75 ± 0.00 respectively for the system cured by ETU-lead.

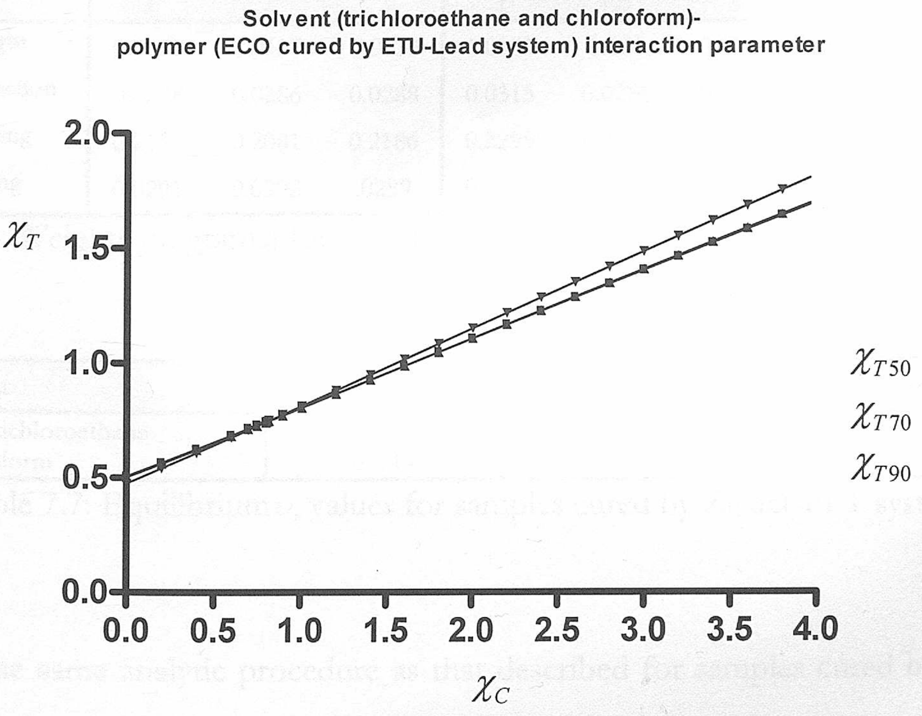

Figure 7.4: Plots of linear equations for ETU-Lead system

7.4.2 Zisnet-FPT System

The equilibrium swelling data obtained for samples cured by the Zisnet-FPT system were treated in a similar manner as described above. Tables 7.5 and 7.6 show the swelling data in relation to trichloroethane and chloroform respectively for samples cured by the Zisnet-FPT system; Table 7.7 gives the υ_r data for the two swelling liquids.

(Stages) Weight	**50% cured**			**70% cured**			**90% cured**		
	1	2	3	1	2	3	1	2	3
(A) Initial weight	0.0334	0.0329	0.0326	0.0351	0.0357	0.0373	0.0348	0.0347	0.0329
(B) After extraction	0.0299	0.0289	0.0285	0.0314	0.0308	0.0311	0.0303	0.0308	0.0288
(C) Max. swelling	0.0922	0.0966	0.0907	0.0990	0.1024	0.1001	0.1006	0.0982	0.0948
(D) After drying	0.0297	0.0286	0.0285	0.0296	0.0311	0.0312	0.0308	0.0314	0.0296

Table 7.5: Weights (in grams) for samples cured by Zisnet-FPT system in Trichloroethane

(Stages) Weight	**50% cured**			**70% cured**			**90% cured**		
	1	2	3	1	2	3	1	2	3
(A) Initial weight	0.0339	0.0337	0.0330	0.0365	0.065	0.0354	0.0332	0.0346	0.0345
(B) After extraction	0.0278	0.0286	0.0288	0.0315	0.0288	0.0291	0.0292	0.0307	0.0293
(C) Max. swelling	0.2154	0.2081	0.2186	0.2295	0.2175	0.2193	0.1781	0.2196	0.2054
(D) After drying	0.0291	0.0292	.0289	0.0308	0.0305	0.0310	0.0279	0.0306	0.0287

Table 7.6: Weights (in grams) for samples cured by ETU-Lead system in Chloroform

Solvent	υ_r **50% cured**	υ_r **70% cured**	υ_r **90% cured**
1,1,1-trichloroethane	0.3644	0.3621	0.3586
Chloroform	01714	0.1740	0.1829

Table 7.7: Equilibrium υ_r values for samples cured by Zisnet-FPT system

Repeating the same analytic procedure as that described for samples cured by the ETU-lead system we obtain the following sets of equations.

For 50% cured samples:

$$\nu = 1.673\times10^{-3} - 2.503\times10^{-3}\chi_T \tag{7.12}$$

$$\nu = 4.42\times10^{-4} - 7.82\times10^{-4}\chi_C \tag{7.13}$$

For 70% cured samples:

$$\nu = 1.65\times10^{-3} - 2.473\times10^{-3}\chi_T \tag{7.14}$$

$$\nu = 4.55\times10^{-4} - 8.03\times10^{-4}\chi_C \tag{7.15}$$

For 90% cured samples:

$$\nu = 1.614\times10^{-3} - 2.428\times10^{-3}\chi_T \tag{7.16}$$

$$\nu = 5.01\times10^{-4} - 8.78\times10^{-4}\chi_C \tag{7.17}$$

Invoking the same assumptions as before we obtain similar relationships between χ_T and χ_C. These relationships are expressed as follows.

50% cured sample: $\chi_T = 0.4918 + 0.3124\chi_C$

70% cured sample: $\chi_T = 0.4832 + 0.3247\chi_C$

90% cured sample: $\chi_T = 0.4584 + 0.3616\chi_C$

Again, plots are produced representing the above expressions using fictitious values of χ_C. These plots are presented in Figure 7.5.

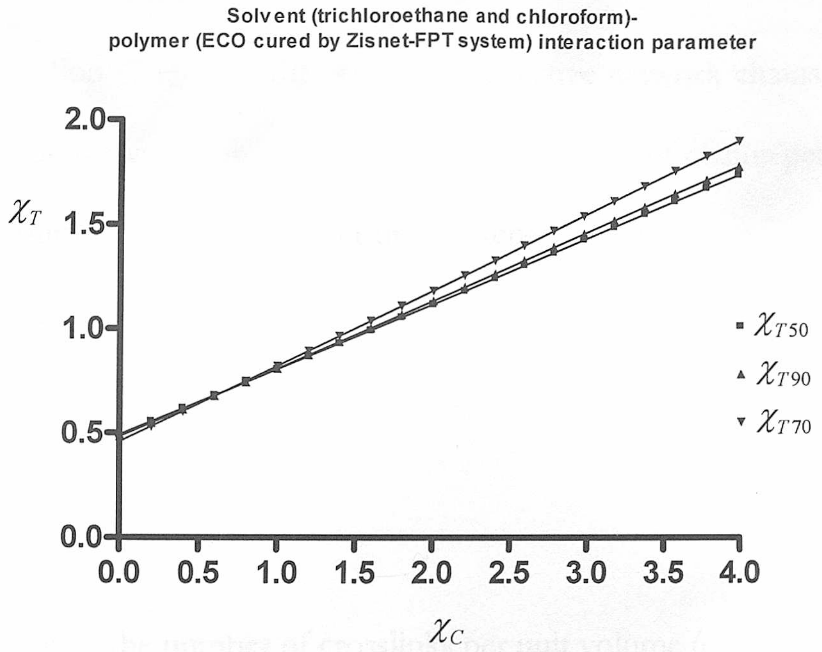

Figure 7.5: Plots of linear equations for Zisnet-FPT system

From the plots, the values of χ_C and χ_T were found to be 0.67 ± 0.03 and 0.70 ± 0.00 respectively. The χ_C and χ_T values for vulcanisates cured by each of the two curing systems are given in Table 7.8.

ETU-Lead system		**Zisnet-FPT system**	
χ_C	χ_T	χ_C	χ_T
0.81	0.75	0.67	0.70

Table 7.8: χ values for the two curing systems

7.5 CROSSLINK DENSITY

Recall that in equation (7.1), ν is the number of effective network chains/cm^3 of rubber (in other words, the network density). In general, the number of chains per unit volume is always twice the number of crosslinks per unit volume. Therefore,

$$\nu = 2\left(\frac{\rho}{2M_C}\right) \tag{7.18}$$

where $\frac{\rho}{2M_C}$ represents the number of crosslinks per unit volume (cm^3) of rubber and

Introducing (7.18) into (7.1) leads to the following expression

$$-\left[\ln\left(1-\upsilon_r\right)+\upsilon_r+\chi\upsilon_r^2\right]=\frac{\rho}{M_C}V_s\left(\upsilon_r^{1/3}-\frac{2\upsilon_r}{f}\right) \tag{7.19}$$

On re-arrangement of the above equation the network chain density may be obtained directly

$$\frac{\rho}{M_c}=\frac{-\left[\ln\left(1-\upsilon_r\right)+\upsilon_r+\chi\upsilon_r{}^2\right]}{V_s\left(\upsilon_r{}^{1/3}-\frac{\upsilon_r}{2}\right)} \tag{7.20}$$

Using the χ values given in Table 7.8 the crosslink densities of ECO vulcanisates is easily found, as shown in Tables 7.9 to 7.12.

Vulcanisate (ETU-Lead system)	υ_r	$\frac{\rho}{2M_C}$ mol/cm^3 ($\times 10^{-5}$)	$\frac{1}{2M_C}$ mol/g ($\times 10^{-5}$)
50%	0.3751	9.8298	7.7696
70%	0.3681	10.0720	7.8690
90%	0.3598	10.3030	8.0489

Table 7.9: Crosslink densities and υ_r values for ECO vulcanisates (trichloroethane)

Vulcanisate (ETU-Lead system)	υ_r	$\frac{\rho}{2M_C}$ mol/cm^3 ($\times 10^{-5}$)	$\frac{1}{2M_C}$ mol/g ($\times 10^{-5}$)
50%	0.1714	9.5486	7.4598
70%	0.1690	9.3511	7.3055
90%	0.1753	9.8706	7.7114

Table 7.10: Crosslink densities and υ_r values for ECO vulcanisates (chloroform)

Vulcanisate (Zisnet-FPT system)	υ_r	$\frac{\rho}{2M_C}$ mol/cm^3 ($\times 10^{-5}$)	$\frac{1}{2M_C}$ mol/g ($\times 10^{-5}$)
50%	0.3644	4.1030	3.1352
70%	0.3621	4.1489	3.2414
90%	0.3586	4.3461	3.3954

Table 7.11: Crosslink densities and υ_r values for ECO vulcanisates (trichloroethane)

Vulcanisate (Zisnet-FPT system)	υ_r	$\frac{\rho}{2M_C}$ mol/cm^3 ($\times 10^{-5}$)	$\frac{1}{2M_C}$ mol/g ($\times 10^{-5}$)
50%	0.1714	4.0776	3.1857
70%	0.1740	4.1429	3.2366
90%	0.1829	4.3559	3.4031

Table 7.12: Crosslink densities and υ_r values for ECO vulcanisates (chloroform)

7.6 DISCUSSION

The work described in this Chapter involves a two-solvent method to determine the polymer-solvent interaction parameter, χ. Knowledge of this parameter is essential for determining reliable crosslink densities by equilibrium swelling methods. In the treatment described here, the polymer-solvent interaction parameter was introduced to account for the acknowledged vagaries inherent in using different solvents and polymers for the swelling data collected. It has been argued the χ is not a constant *[Hergenrother and Hilton, 2003]*; nevertheless this parameter has often been used as such without presenting much difficulty in interpreting results pertaining to rubber networks.

It will be recalled that in determining crosslink densities of ECO vulcanisates of one description or another two swelling liquids were utilised, that is trichloroethane and chloroform. It was found that for any given ECO vulcanisate the crosslink density was dependent upon the type of swelling liquid used; this was surprising. Generally, samples that were allowed to attain equilibrium swelling in trichloroethane showed higher crosslink densities as compared with chloroform as the swelling liquid. In principle the crosslink density of a given vulcanisate should not be a function of the type of swelling liquid used. However, there is a distinct possibility that highly compatible swelling liquids may cause excessive isotropic expansion of the rubber network leading to chain scission and consequently engendering an apparent reduction in crosslinks. Therefore, in terms of the present work, it is perhaps not too surprising to find that the liquid that gave the lowest υ_r value (thus indicating a high degree of swelling) also reflected the lowest crosslink density.

In the present work carbon black filler was deliberately excluded in order to eliminate complications during measurements of crosslink densities. Filler, particularly carbon black, has the capacity to restrict expansion of the network during the swelling process.

This often leads to over-estimates of crosslink densities of rubber networks. It has been stated *[Gent and Hartwell, 2003]* that for a recipe containing 50 phr of HAF carbon black, the effective degree of crosslinking is twice that of the corresponding unfilled compound. Thus, both swelling and modulus measurements on swollen samples indicate that the effective degree of crosslinking is somewhat higher in filled rubbers compared with corresponding unfilled rubbers, even though the actual degree of crosslinking is may be the same. It is possible to compensate for the restriction imposed by the filler during swelling *[Kraus, 1966]*, however, the compensation method proposed by Kraus is based on a theory that is far too simplistic to be of any real practical benefit; for instance, the theory rather erroneously assumes that carbon black does not interfere with the mechanism of crosslinking. Thus, in the opinion of the present author the application of the Kraus correction is merely nothing more than a mathematical exercise and of little practical use.

The complexity of various types of crosslinks in relation to determining crosslink densities has been briefly discussed by Hergenrother *[Hergenrother and Hilton, 2003]*. Some attempts have been made to measure ν using methods other than swelling *[Flory, 1953; Komoroski, Shockcor et al., 1986]*, but little information is presented on the way in which ν relates to χ and υ_r. The most convenient method currently available involves using tensile retraction to measure ν, then subsequently rearranging the Flory-Rehner equation to solve for χ followed by plotting the response obtained as a function of υ_r. This method is not discussed in the present work.

The χ values of ECO vulcanisates cured by ETU-Lead and Zisnet-FPT systems were found to cover the range between 0.75 to 0.81 and 0.67 to 0.70 respectively. The crosslink density of ECO cured by the ETU-Lead system was found to be $7.6940\times10^{-5} \pm 0.2714$ mol/g, about twice the value of that cured by the Zisnet-FPT system, that is, $3.2662\times10^{-5} \pm 0.1101$ mol/g. Clearly, as the crosslink density increases so too does the modulus.

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Chapter 8

STATISTICAL OPTIMISATION OF COMPRESSION-SET

In this work, a technique known as Central Composite Rotatable Design (CCRD) is used. CCRD [Vecchio, 1997] is an advanced experimental design methodology based on a factorial system that uses five levels of each factor or independent variable to generate a full data set suitable for utilising response surface methods. It is very useful in investigating the interaction effect of different compounding ingredients or additives by systematically varying the quantity of each. The property measured is presented as a function of a set of variables dictated by the design; the relationship is then subjected to a statistical analysis, notably regression analysis. From the regression analysis, the significant factor (or factors together) can be determined and the response surface equation can be established. Once the data is acquired, this equation is capable of calculating the end properties by manipulating the factor(s) without having to do the actual experiment. As it is desirable to introduce a safer vulcanisation system as an alternative to the existing lead-based vulcanisation systems, it is envisaged that CCRD technique would be useful in locating optimum performances. This is to ensure that the non-lead vulcanisation system can be used without compromising the properties, particularly compression-set.

8.1 INTRODUCTION

The study of set (and stress-relaxation) of ECO elastomers is based on previous work carried out by Farid *[Farid, 1999]* who studied the effect of essential additives on set and stress-relaxation in ECO elastomers. However, this study was done by using traditional screening variables approach. This approach does not allow an accurate assessment of the interaction of various essential factors or additives influencing set and stress-relaxation in ECO elastomers. Traditional screening method is also known as 1-FAT (one factor at a time) in which one factor was changed at a time in type or level of use. This method only detects and quantifies the effect of single factor at one time, and makes it impossible to investigate 'interactions' between variables or factors. The 'interactions' is a special relationship in which two or more factors act differently and indicate the way in which they affect a process (or properties) together compared to how they affect it individually. 'Interactions' may not always occur, but they are sometimes extremely important and 1-FAT experiments by their nature are not capable of finding such interactions. Therefore to resolve this issue the experiment was re-designed in accordance with suitable statistical techniques.

8.2 EXPERIMENTAL WORK

Much of the descriptive account of the experimental work pertaining to the preparation of ECO vulcanisates has already been given in previous Chapters; however, for the sake of completeness and convenience it will be reiterated here. The base polymer used was Hydrin C2000L (copolymer) supplied by Zeon, Wales. A list of intrinsic properties of raw ECO is given in Table 8.1. The Zisnet-FPT vulcanisation system was supplied by Nippon Zeon Co. Ltd, Wales. ETU was supplied by Robinson Brothers (UK) Ltd as 75% active material in a binder system. Fast extrusion furnace (FEF) carbon black (N550) was supplied by Cabot Carbon (UK); it is especially used in rubber compounds for sealing applications. This filler has a relatively large particle size and high structure and therefore produces very low rates of primary or physical stress-relaxation in rubber vulcanisates.

Properties	C2000L
Chlorine content, (% by weight)	26.0
Mooney viscosity (ML 1+4 100°C)	65-75
Specific gravity, (g/cm^3)	1.28
Tg (°C)	-38

Table 8.1: Intrinsic properties of raw ECO *[Zeon, 1999]*

Due to the widely acknowledged processing difficulties *[Zeon, 2000; 2000]* associated with ECO rubbers, two processing aids were used together. The first was zinc stearate, in the form of powder which was supplied by Omya, United Kingdom. The second was a complex zinc soap of partly unsaturated fatty acid within the $C_{12} - C_{18}$ range. It is supplied by Schill and Seilacher GmBH Hamburg, Germany via their UK distributor, International Adhesive Ltd under the trade name 'Struktol A60'. Zinc stearate was used to control the degree of splitting and tearing of ECO elastomers during mill-mixing. The complex zinc soap on the other hand, was used to improve the flow characteristics of ECO mixes and to reduce the degree of bloom in vulcanisates made from ECO mixes. Nickel di-n-butyldithiocarbamate (NBC) was used as protective agent, supplied by Flexsys Rubber Chemicals, Wales under the trade name of NDBC in the form of green powder. The accelerator used in conjunction with Zisnet-FPT was Diphenyl guanidine (DPG), supplied by Omya United Kingdom. It was supplied under the trade name DPG 75 in the form of 75% active material in a polyethylene binder.

8.2.1 Mix Formulation

The base formulation is given in Table 8.2. For the ETU-lead system, an experimental design comprising four factors was used. These four factors were: curing agent (ETU), protective agent (NBC), Acid acceptor (Litharge) and filler (FEF N550).

Ingredient	ETU-lead, pphr	Zisnet-FPT, pphr
ECO	100.0	100.0
Stearic acid	1.0	1.0
Struktol A60	1.0	1.0
Zinc stearate	1.0	1.0
ETU	2.5	-
NBC	2.0	2.0
Litharge	5.0	-
FEF N550	50.0	50.0
Zisnet FPT	-	1.0
$CaCO_3/MgO$	-	5.0
DPG	-	0.2

Table 8.2: Base formulation for CCRD studies

For the Zisnet-FPT system, five factors were used. That is: Curing agent (Zisnet-FPT), acid acceptor ($CaCO_3/MgO$), filler (FEF N550), protective agent (NBC) and activator (DPG). All factors were systematically varied as dictated by the CCRD methodology. Thirty-one mixes were prepared for the four-factor design and thirty-two mixes in the five-factor design. The centre point and the design step of each factor are shown in Table 8.3.

Factors/variables	Curing agent (ETU)	Protective agent (NBC)	Acid acceptor (LITHARGE)	Filler (FEF N550)
Centre point (code 0)	2.5	2.0	5.0	50.0
Design step	1.0	0.5	2.0	10.0

Table 8.3: Centre point value and design step for the ETU-lead system

Factors/variables	Curing agent (ZISNET FPT)	Protective agent (NBC)	Acid acceptor ($CaC0_3/MgO$)	Filler FEF N550	Activator (DPG)
Centre point (code 0)	1.0	2.0	5.0	50.0	0.2
Design step	0.2	0.5	2.0	10.0	0.08

Table 8.4: Centre point value and design step for the Zisnet-FPT system

Five levels are assigned to each factor or variable, as identified by following codes:

$$-\alpha \quad -1 \quad 0 \quad 1 \quad \alpha$$

In the above coding system, α is determined by the following expression

$$\alpha = 2^{k/4}$$

In the definition of α given above, k represents the number of independent variable or factors that are considered in the design. In the four-factor experimental design comprising curing agent (ETU), protective agent (NBC), acid acceptors (Litharge) and filler (FEF N550), the α-value is given by

$$\alpha = 2^{4/4} = 2.0\,.$$

On the other hand, for a five-factor experimental design α-value is given by

$$\alpha = 2^{5/4} = 2.378$$

The assignment of the centre point and design step values is based on prudent judgement and experience in the sense that the experimenter must intuitively know the demarcations of the optimum operating window of the system under scrutiny. Having determined the centre point and design step values, real values are assigned to the codes. The design codes and the expressions used to convert them into real values are given in Table 8.5.

Codes	Expression for conversion to real values
- *a* (star point)	(Centre point real value) + (design step real value)(-*a*)
-1 (factorial point)	(Centre point real value) - (design step real value)
0 (centre point)	Centre point real value
+1 (factorial point)	(Centre point real value) + (design step real value)
+ *a* (star point)	(Centre point real value) + (design step real value)(*a*)

Table 8.5: Codes and conversion to real experimental values

8.2.2 Preparation of Mixes

A masterbatch technique was used to prepare various mixes used in the present study. A 2500 cm^3 Francis Shaw Intermix (Manchester, United Kingdom) was used for the masterbatch preparation. The internal mixer was set to operate at a rotor speed of 44 revolutions per minute, under a ram pressure of about 0.70 MPa. The fill factor used was 75% and the batch masses were about 3462 g. Seven masterbatches were prepared; these were considered sufficient to produce the required 32 mixes. The discharge temperatures were all within 80-90°C. All seven masterbatches were prepared according to the time schedule outlined in Table 6. At the end of each mixing schedule the masterbatches were refined on a 0.45 m two-roll mill operating at an even speed of 15 revolutions per minute with a roll surface temperature of 50 ± 5°C. At the end of the mill refining operation, each masterbatch was end passed six times on a tight nip to ensure uniform distribution of ingredients. This operation took about 6-10 minutes. Each masterbatch was sheeted out at approximately 6-8 mm in thickness. Material losses due to mixing were less than 0.5%; this value is considered reasonable for a mixing operation of this nature. In attempt to minimise the variations between masterbatches, about 50 g was taken from each masterbatch each time and was cross-blended to give a FEF-filled batch for each compound. ETU, litharge and NBC were incorporated on a laboratory 0.3m two-roll operating at a friction speed 1.25:1. Roll surface temperatures were maintained at approximately 50 ± 5°C. The mixing procedure was carried out according to the schedule outlined in Tables 8.7 and 8.8.

Time elapse (min)	Action
0	Add ECO
1	Add 1/3 of FEF
3	Add a further 1/3 of FEF
6	Add a further 1/3 of FEF
9	Sweep down
11	Discharge

Table 8.6: Mixing schedule of masterbatch

Time elapse (min)	Action
0	Add masterbatch to mill with surface at temperature of 50 ± 5°C
1	Add stearic acid and processing aid (zinc stearate, Struktol A60)
3	Add protective agent (NBC), curative (ZISNET) and acid acceptor ($CaCO_3$/MgO)
6	Sweep and cross-cut from each side of a sheet of rotating rubber
9	Six time end-roll on a tight nip, allow to band for one minute
11	Sheet off at a thickness 4-5 mm

Table 8.7: Mixing schedule of mixes with different combination of factors or variables

8.2.3 Vulcanisation

The determination of the vulcanisation characteristics were carried out on a Monsanto Oscillating-disc rheometer (ODR) S100; operating at 170 ± 0.5°C using a strain amplitude of ± 3° of arc. In the case of rheograms that produce plateau-type profiles the extent of crosslinking is generally taken as the difference between maximum torque and minimum torque. The time, t_{95}, (in minute) corresponding to a torque value of 0.95 (maximum torque-minimum torque) + (minimum torque) was used as vulcanisation time. However, due to marching modulus nature of the cures found here, the approach suggested by Rigbi *[Rigbi, 1996]* was utilised (see Chapter 4 for a detailed account of this method) to calculate the maximum torque. A Bradley and Turton (Kiddermaster, United Kingdom), double-daylight, steam press was used for the moulding process. For each mix, several cylindrical discs of 13.0 ± 0.5 mm diameter and 6.3 ± 0.3 mm thickness were compression-moulded on a steam press at 170 ± 2°C. Moulding times used were those corresponding to t_{95} values calculated from the rheograms of the respective mixes. Post-curing process was carried out according to Farid's work which is explained elsewhere *[Farid, 1996]*. Previous work by Kyllingstad *[Kyllingstad and Cable, 1992]* showed that the post-curing procedure reduces the set further. All compression–moulded ECO test pieces were placed in a circulating air oven which was maintained at a temperature of 150 ± 1°C for 5 hours. All test pieces were conditioned in an open laboratory environment at a temperature of 23 ± 2°C for at least 16 hours before testing. Conditioning was carried out in order to allow sufficient time for vulcanisates to attain a state of thermal equilibrium.

8.2.4 Compression-set

The test was performed according to ISO 815:1991(E) prepared by the Technical Committee ISO/TC 45 (Rubber and Rubber Products), Sub-Committee SC2 (Physical and Degradation Tests). Type B test pieces were used. This test-piece is in the form of a cylindrical disc of diameter 13mm ± 0.5mm and thickness 6.3mm ± 0.3mm. The spacer used for the type B test piece has a height of 4.8 mm maximum and 4.7 mm minimum. A constant strain of 25% was used. The compression-set test was performed at a constant temperature of 125°C ± 2°C using a circulating air oven. The duration of the test was 22 hours and silicone oil was used as lubricant. At the end of the 22-hour period, the test pieces were quickly released from the imposed strain allowed to recover freely on a wooden bench at room temperature for a period of 30 ± 3 minutes. On completion of the recovery process for the assigned time, the thicknesses of the test-pieces were re-measured to the nearest 0.01mm. The compression-set, expressed in percentage of the initial compression, was calculated using the following formula

$$\%\text{Compression-set} = \frac{h_o - h_1}{h_o - h_s} \times 100$$

In the above compression-set expression, h_o is the initial thickness (mm) of the test piece, h_1 is the thickness (mm) after recovery, h_s is the height (mm) of the spacer. Three test pieces were tested for each mix the mean taken as representing the compression-set; standard deviations were also calculated in order to assess the magnitude of errors.

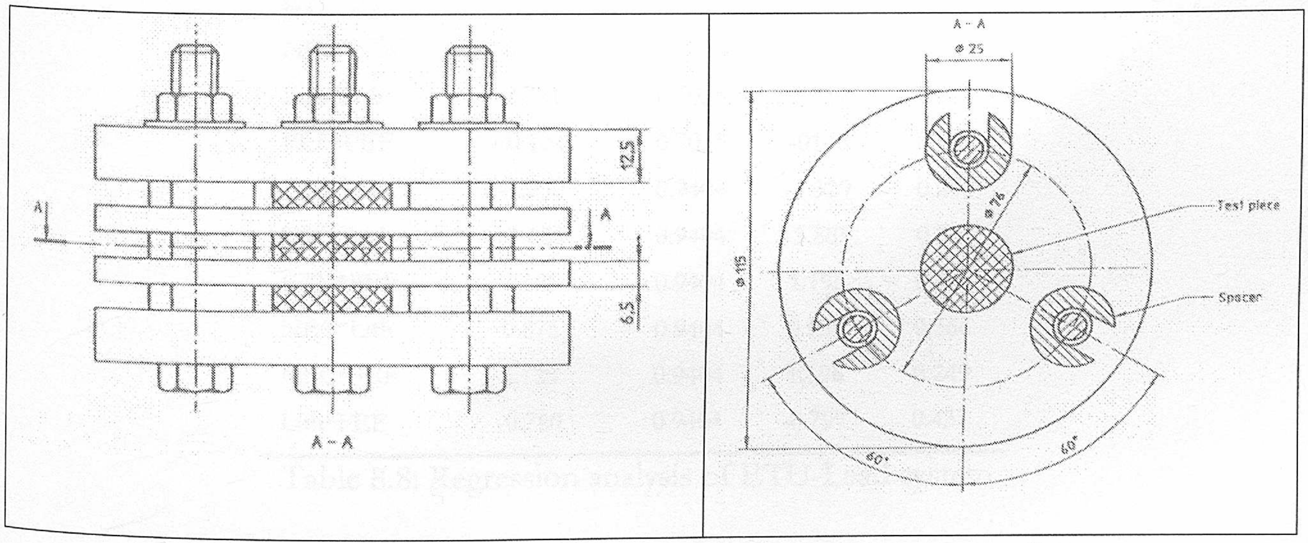

Figure 8.1: Elevated and plan view of compression-set test jig

8.3 DATA ANALYSIS

In the previous work on compression set *[Wahab, 2003]*, two sets of results were obtained from each cure system, at low temperature (30°C) and high temperature (100°C), using a compression period of 168 hours. In the present study, the test condition was changed to a temperature of 125°C and a test period 22 hours. The data were subjected to response surface analysis where factors and interactions affecting compression-set were identified. The analysis was performed using commercially available statistical analysis software *[Minitab©, 1972-2004]*. The results of the analysis are given in Table 8.8 for the ETU-lead system; in Table 8.8, T and P denote the usual T-statistic and probability values.

Term	Coefficient	SE Coef	T	P
Constant	15.000	1.4218	10.550	0.000
ETU	3.833	0.7679	4.992	0.000
NBC	-0.167	0.7679	-0.217	0.831
Lith	-5.417	0.7679	-7.054	0.000
FEF	1.333	0.7679	1.736	0.102
ETU*ETU	2.021	0.7035	2.873	0.011
NBC*NBC	0.521	0.7035	0.740	0.470
Lith*Lith	2.771	0.7035	3.939	0.001
FEF*FEF	-0.104	0.7035	-0148	0.884
ETU*NBC	-1.250	0.9404	-1.329	0.249
ETU*Lith	-3.625	0.9404	-3.885	0.366
ETU*FEF	1.125	0.9404	1.196	0.249
NBC*Lith	0.875	0.9404	0.930	0.366
NBC*FEF	1.125	0.9404	1.196	0.249
Lith*FEF	-0.750	0.9404	-0.797	0.437

Table 8.8: Regression analysis of ETU-Lead system

All factors and interactions that have P-values (probability) less than 0.1 were considered significant and were included in the response surface equation. For the ETU-lead system, the response surface equation is

$$Set_{(22hr,\ 125C)} = 15.0+3.833e-5.417l+2.021e^2+2.771l^2-3.65el \qquad (8.1)$$

where *e* signifies ETU and *l* represents litharge.

The response surface equation (8.1) is highly significant in the sense that the terms have low P-values. The statistical F-ratio value was found to be 8.64; this value is higher than the tabulated $F_{5\%}$ value of 2.373. Because $F_{reg}>F_{5\%}$, the equation (8.1) is deemed to have explanatory power. Rather surprisingly, FEF was found to be insignificant in terms of set at 125°C. However, there is a highly significant 'interaction effect' between ETU and Litharge as indicated by a P value of 0.001 (see Table 8.8). Figure 8.2 shows a graphical prediction of set properties based on equation (8.1).

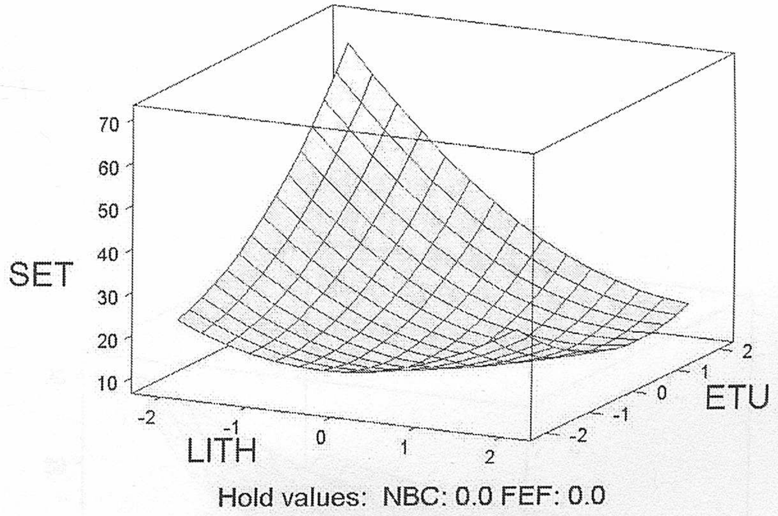

Figure 8.2: Surface plot effect on set of ETU-lead system at 125°C after 22 hours

For the alternate Zisnet-FPT system, the result of analysis is shown in Table 8.9.

Term	Coefficient	SE Coeff	T	P
Constant	21.475	0.6287	34.159	0.000
ZISNET	-1.474	0.2970	-4.965	0.000
NBC	0.467	0.2970	1.573	0.144
CACO3/MG	-1.067	0.2970	-3.592	0.004
FEF	0.669	0.2970	2.252	0.046
DPG	-0.673	0.2970	-2.266	0.045
ZISNET*ZISNET	0.915	0.2184	4.188	0.002
NBC*NBC	0.207	0.2184	0.950	0.363
CACO3/MGO*CACO3/MGO	0.119	0.2184	0.545	0.597
FEF*FEF	0.207	0.2184	0.950	0.363
DPG*DPG	0.119	0.2184	0.545	0.597
ZISNET*NBC	0.125	0.3880	0.322	0.753
ZISNET*CACO3/MGO	0.250	0.3880	0.644	0.533
ZISNET*FEF	-0.125	0.3880	-0.322	0.753
ZISNET*DPG	-0.125	0.3880	-0.322	0.753
NBC*CACO3/MGO	0.625	0.3880	1.611	0.136
NBC*FEF	0.250	0.3880	0.644	0.533
NBC*DPG	-0.750	0.3880	-1.933	0.079
CACO3/MG*FEF	0.375	0.3880	0.966	0.355
CACO3/MG*DPG	0.125	0.3880	0.322	0.753
FEF*DPG	0.000	0.3880	0.000	1.000

Table 8.9: Regression analysis of Zisnet-FPT system

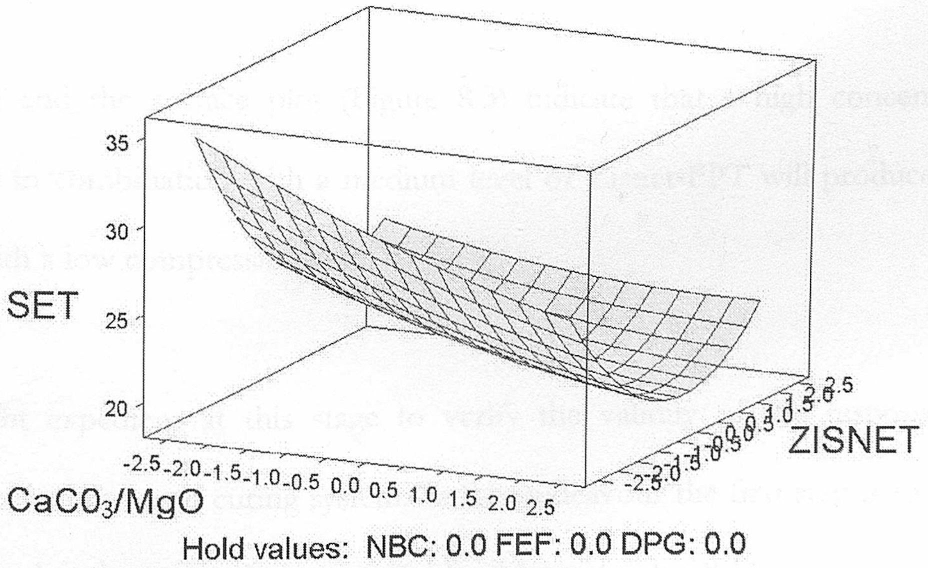

Figure 8.3: Surface plot effect on set of Zisnet-FPT system at 125°C after 22 hours

For the alternate Zisnet-FPT system, the following equation was obtained:

$$Set_{(22hr,\ 125C)} = 21.475-1474z-1.067c+0.669f-0.673d+0.915z^2-0.75nd \tag{8.2}$$

In the above response equation, z, c, f, d and n denotes Zisnet-FPT, $CaCO_3/MgO$ (5:3), FEF, DPG and NBC respectively.

Equation (8.2) has an F-value of 3.83 and a P-value of 0.013 indicating a high degree of significance. In contrast to the ETU-Lead system, which showed that FEF was insignificant in terms of affecting compression-set, the Zisnet-FPT system however indicates that FEF is clearly significant in terms of influencing set (consider the low P-value in Table 8.9). This behaviour is with consistent with the results of previous work published elsewhere *[Wahab, Farid et al., 2004]*. The only 'interaction effect' that is deemed to be significant in terms of set behaviour is between NBC and DPG. Figure 8.3 shows a graphical prediction of set properties based on equation (8.2).

The equation and the surface plot (Figure 8.3) indicate that a high concentration of $CaCO_3/MgO$ in combination with a medium level of Zisnet-FPT will produce an ECO vulcanisate with a low compression-set.

It was thought expedient at this stage to verify the validity of the response surface equations obtained for each curing system. In this endeavour the first step is to randomly select design codes; these are tabulated in Tables 8.10 and Table 8.11.

Ingredient\Compound	1	2	3	4	5
ETU	-2	2	1	-1	2
NBC	2	0	-2	2	1
LITH	1	1	0	-1	-2
FEF N550	1	-1	2	1	0

Table 8.10: Randomised codes of the confirmation compounds for ETU-lead system

In order to prepare the appropriate mixes corresponding to the coded values given in Table 8.10, all codes were converted to real values using expressions given in Table 8.5 to obtain their actual quantities. The codes were introduced into each equation to predict the Set at 125°C. The experimental results were then compared against the predicted values.

Ingredient\Compound	1	2	3	4	5
ZISNET FPT	-2.378	2.378	1	-1	2.378
$CaCO_3$/MgO	2.378	0	-2.378	2.378	1
NBC	1	1	0	-1	-2.378
FEF N550	1	-1	2.378	1	0
DPG	1	1	-1	-2.378	0

Table 8.11: Random codes of the confirmation compounds for Zisnet-FPT system

8.4 RESULT AND DISCUSSION

Using response surface equations (8.1) and (8.2), the set properties of each system were calculated by introducing design codes as variables. The experimental results were measured from the actual compression-set of five confirmation mixes and were compared to the calculated values.

The predicted compression-set properties obtained from the response surface equations and their experimental values are summarised in Table 8.12. It can be seen from the results presented in the Table that only some of the experimental results were successfully predicted by the response equations.

Compound	**ETU-Lead system** **%Set at 125°C (22 hours)**		**Zisnet-FPT system** **%Set at 125°C (22 hours)**	
	Predicted	**Experimental**	**Predicted**	**Experimental**
1	20.0 ± 2.4	29.8 ± 1.0	26.9 ± 3.5	34.9 ± 1.6
2	20.9 ± 2.4	20.9 ± 1.7	21.1 ± 3.3	18.4 ± 0.6
3	20.9 ± 2.0	22.0 ± 1.1	27.2 ± 2.1	28.5 ± 1.4
4	17.8 ± 2.0	18.0 ± 0.4	26.4 ±3.1	30.2 ± 1.4
5	67.2 ± 2.3	48.8 ± 0.3	24.7 ± 3.1	29.6 ± 1.7

Table 8.12: Comparison between the predicted and experimental results

The plots showing predicted and experimental values of compression-set are shown in Figures 8.4 and 8.5. It is found that although coincidence of some of the predicted and experimental measurements is not excellent there is however a clear indication that the response equations do successfully predict the general trend. Trend prediction is appropriate for ranking purposes. It is also apparent that generally, the predicted values are slightly lower than experimental values; it is possible that a more complex response equation containing a greater number of terms may give an accurate prediction.

In Figure 8.4, it can be seen that the ECO vulcanisate predicted to have high set (for instance, compound number 5) corresponds well with the experimental result, although it does not match the value exactly. In general, the standard error for the calculated values did not exceed 2.4% in the ETU-Lead system and 3.5% in the Zisnet-FPT system. On the other hand, the errors generated in the experimental work were significantly lower (0.3 - 1.7%) in both systems; this is clearly indicative of good reproducibility.

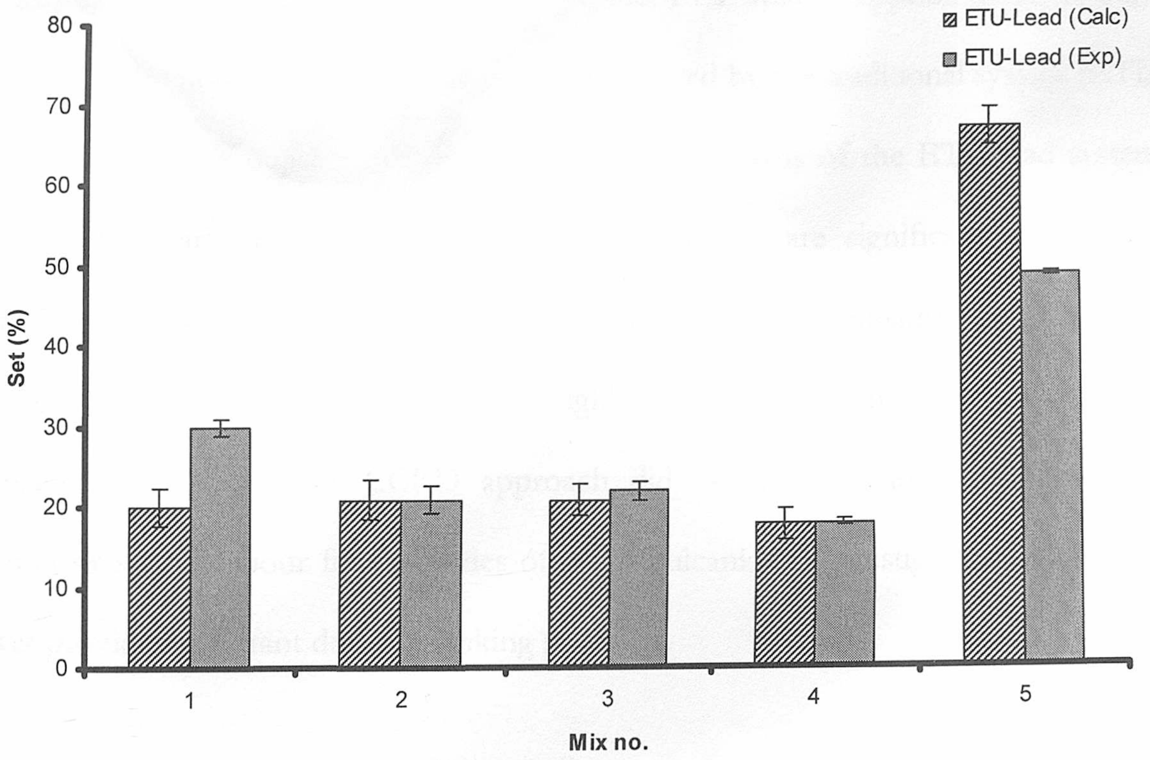

Figure 8.4: Compression-set of ETU-Lead system at 125°C after 22 hours.

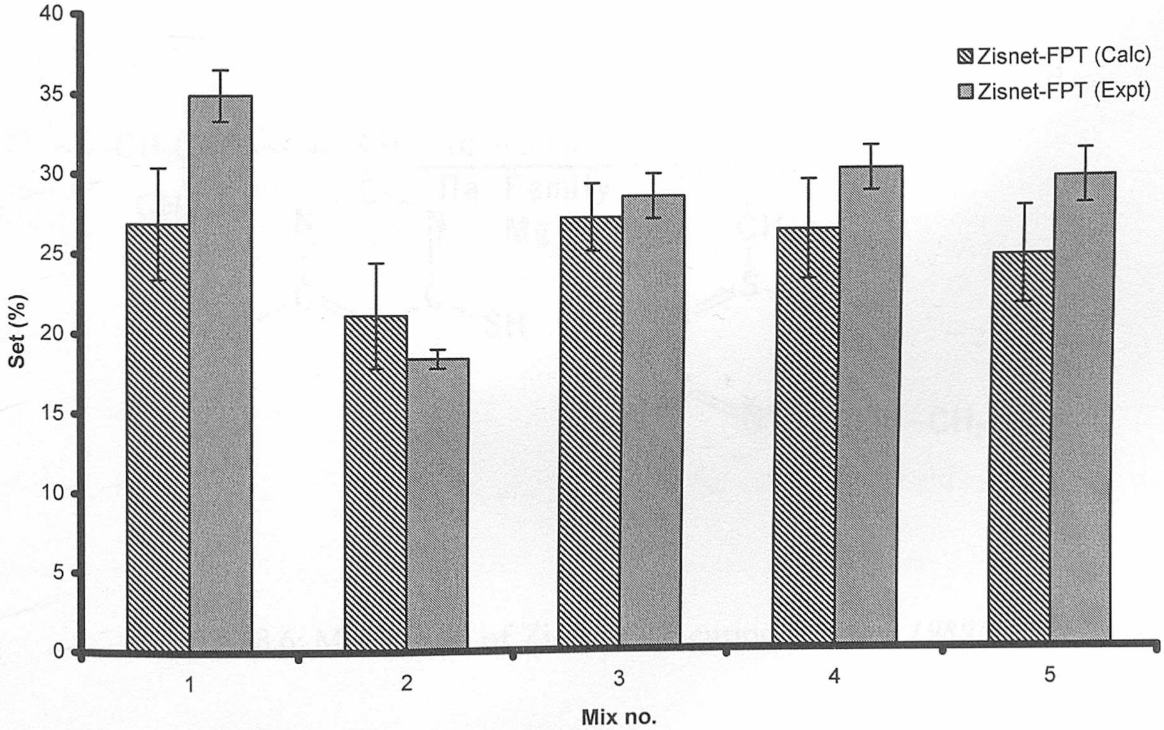

Figure 8.5: Compression-set of Zisnet-system at 125°C after 22 hours.

The compression-set of ECO containing the Zisnet-FPT system appears to be strongly carbon-black dependent. On the other hand, ECO cured by the traditional system (ETU-lead) shows negligible dependence on carbon black. In terms of the ETU-lead system, equation (8.1) clearly shows that only ETU and Litharge are significant in affecting compression-set. So far as the Zisnet-FPT system is concerned, equation (8.2) indicates FEF, Zisnet-FPT and $CaCO_3/MgO$ are all highly significant in terms of controlling the set behaviour. Although the CCRD approach did not provide an entirely accurate prediction of set behaviour for the series of ECO vulcanisates investigated here, it does however provide important data for ranking purposes.

It is not yet fully understood the way in which carbon black interacts with other ingredients, especially Zisnet-FPT ($C_3H_3N_3S_3$). The curing mechanism for Zisnet-FPT as revealed by the manufacturers *[Nippon, 1989]* is shown in Figure 8.6.

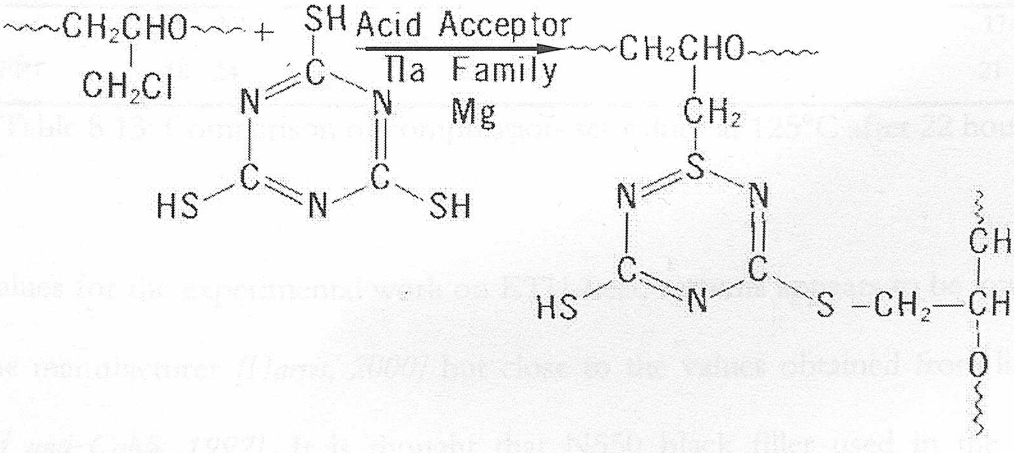

Figure 8.6: Mechanism of Zisnet-FPT curing *[Nippon, 1989]*

It is initially thought that the localised cyclic structure of Zisnet-FPT is non-reactive and will not react with carbon black. However, the present studies on compression-set indicate the possibility of some degree of FEF interaction, perhaps secondary in nature. This interaction appears to have a strong influence on the recovery process which forms part of the compression-set test. In the ETU-Lead system however, this interaction appears to be absent. In consideration of the view that interaction occurs in one curing system but not the other for a common rubber leads to the conclusion that the interaction is likely to be caused by the type of curing system.

The reader should note that the formulations used in the present work for preparing ECO mixes was based on information gleaned from literature *[Kyllingstad and Cable, 1992]*. The compression-set values obtained from literature *[Kyllingstad and Cable, 1992]* and from the manufacturers *[Harris, 2000]* are presented in Table 8.13. For comparison, experimental and predicted compression-set values are also included in the same Table.

Cure system	**Literature values**	**Manufacturer's values**	**Experimental values**	**Predicted values**
	Set (%)	**Set (%)**	**Set (%)**	**Set (%)**
ETU-Lead	18 - 20	26	15 - 17	17- 19
Zisnet-FPT	18 - 24	22	20 - 22	21 - 24

Table 8.13: Comparison of compression-set values at 125°C after 22 hours

The set values for the experimental work on ETU-Lead systems appears to be lower than that of the manufacturer *[Harris, 2000]* but close to the values obtained from literature *[Kyllingstad and Cable, 1992]*. It is thought that N550 black filler used in the present experimental work may be primarily responsible for the comparatively low set; in the manufacturer's recipe N330 black filler was used which has a smaller particle size as compared with N550 black. In addition, N550 carbon black has higher DBP number (that is, 121) than N330 (that is, 102) which indicates that N550 has a higher structure level compared with N330 *[Eirich, Erman et al., 1994]*. Large particle size, high structure carbon blacks can give low rates of primary physical stress-relaxation *[Farid, 1999]*. In other words, carbon black fillers of this nature give rapid recovery leading to low set. Moreover, poor dispersion can sometimes lead high set values *[Farid, 2002]*.

The possible interaction between FEF and in Zisnet-FPT is an interesting aspect to consider. It is possible to neutralise the surface of FEF black by graphitisation *[Boonstra, 1982]* and thereby eliminate the possibility of secondary interactions that might occur with innate additives present in the bulk of the rubber, such as FEF black. Comparison of the set behaviour of two ECO vulcanisates, one containing conventional FEF and the other graphitised FEF should shed some light on the matter.

In general, it may be concluded that response surface equations obtained from CCRD studies has proved very useful for ranking the set behaviour of ECO elastomers.

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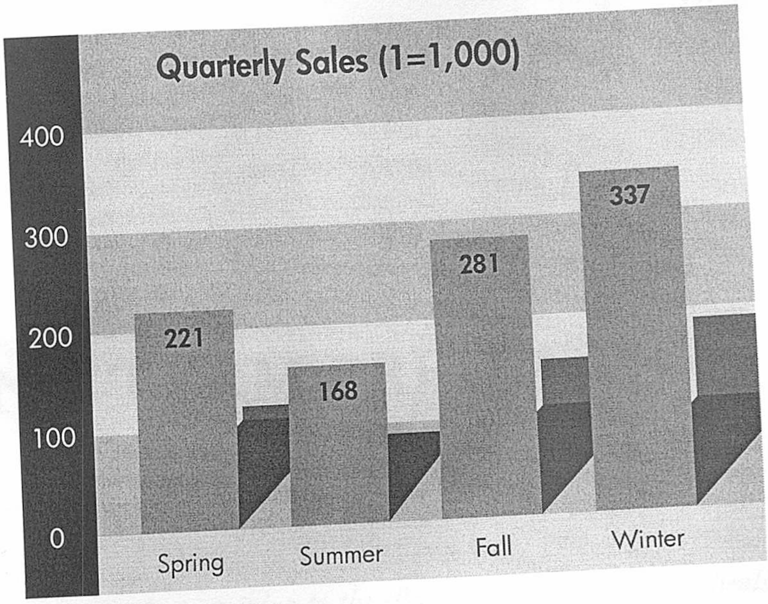

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Chapter 9

LONG TERM PREDICTION OF SET PROPERTIES

The previous chapter reported and discussed the results pertaining to the effect of compounding ingredients on compression-set behaviour. As an important adjunct to this work, a statistical method was introduced which allowed the possibility of optimising and predicting compression-set. However, in order for the set behaviour to serve any real purpose it must be related to rubber products used in service. Products that are of interest here are those which are difficult to monitor on a routine basis owing to restrictions on access; for example, seals used in underground pipelines or in off-shore applications. In such situations it is desirable to have a means of assessing longevity and long-term stability using life-extrapolation methods. This Chapter presents and utilises some selected procedures for predicting long-term set properties of ECO rubbers cured by ETU-Lead and Zisnet-FPT vulcanisation systems. Using the classical Arrhenius approach it was found that compression-set properties of ECO vulcanisates based on the ETU-Lead system was far superior in terms of longevity as compared with ECO vulcanisates cured by the Zisnet-FPT system.

9.1 INTRODUCTION

As mentioned earlier, presently within the rubber industry the use of lead-based compounds has aroused concerns over environmental and processing issues *[Innes, Ulland et al., 1969; Parkes, 1974; Wahab, Farid et al., 2004]*. ECO elastomers are traditionally vulcanised by lead-based system for the past 40 years. Hence, it is expedient to seek non-lead based curing system and investigate the way in which they can influence relevant properties, such as compression set. There are several non-lead systems available to be used in ECO. One of which is Zisnet FPT and is claimed to give optimum compression set*[Hashimoto, Inagami et al., 1986; Zeon, 1989; 1996; Harris, 2000]*. In engineering application the compression set is sometimes known as retention loss. It occurs when the clamping force exerted by the bolting of actuator casings causes the elastomer to relax. The elastomer squeezed between the casing flanges tends to relax over time to a value that it then sustains. While the relaxation is more related to stress, the amount that does not recover to its original dimension is known as set. Additional tightening of the casing bolts will not change this value greatly since it is intrinsic to the material. The same applies to various applications pertaining to set i.e. seals, gaskets and diaphragms. In the case of applications, such as underground flexible pipes conveying gas, elastomers have been used extensively as a safe, simple and effective sealing material. The life prediction in this particular application proves to be vital because of inadequate failure detection or indeed due to high maintenance cost especially caused by excavation. Thus, when faced with such restrictions, it is clearly desirable to have in place a reliable way of predicting service life. In the most general terms, the present work entails the determination of compression set of ECO vulcanisates over a range of temperatures and time. 20% set is used as the failure criterion and the determination of time to failure is carried out in accordance with the method proposed by British Gas Engineering Standard *[Gas, 1984]*. The investigation is based on previous work carried out by Farid *[Farid, 1996; 1999; 1999]*.

9.2 EXPERIMENTAL WORK

9.2.1 Materials

The base polymer used was Hydrin C2000L, an ECO copolymer supplied by Nippon Zeon, Wales. A list of intrinsic properties of raw ECO is given in Table 9.1.

Properties	C2000L
Chlorine content, (% by weight)	26.0
Mooney viscosity (ML 1+4 100°C)	65-75
Specific gravity, (g/cm^3)	1.28
Tg (°C)	-38

Table 9.1: Intrinsic properties of raw ECO *[Zeon, 1999]*

The Zisnet-FPT curing system was supplied by Zeon Chemicals Ltd, Wales. ETU was supplied by Robinson Brothers (UK) Ltd as 75% active in a binder system. Fast extrusion furnace (FEF) carbon black (N550) was supplied by Cabot Carbon (UK). As mentioned previously, FEF filler has a relatively large particle size and high structure which leads to very low rates of primary or physical stress-relaxation. To aid processing, *[Zeon, 2000]* two processing aids were used together. The first was zinc stearate, in the form of powder which was supplied by Omya, United Kingdom. The second was a complex zinc soap of partly unsaturated fatty acid within the $C_{12} - C_{18}$ range; supplied by Schill and Seilacher GmBH Hamburg, Germany via their UK distributor, International Adhesive Ltd under the trade name 'Struktol A60'. Zinc stearate was used to control the degree of splitting and tearing of ECO mixes during mill-mixing. The complex zinc soap was used to improve flow characteristics of ECO mixes and to reduce the degree of blooming in vulcanisates. Nickel di-n-butyldithiocarbamate (NBC) was used as protective agent, supplied by Flexsys Rubber Chemicals, Wales under the trade name of NDBC in the form of green powder. The accelerator used in conjunction with Zisnet FPT was Diphenyl guanidine (DPG), supplied by Omya United Kingdom. It was supplied under the trade name DPG 75 in the form of 75% active in a polyethylene binder.

9.2.2 Mix Formulation

The base formulation is given by Table 9.2.

Ingredient	pphr
ECO	100.0
Stearic acid	1.0
Struktol A60	1.0
Zinc stearate	1.0
Carbon black FEF N550	50.0

Table 9.2: Base formulation

For the preparation of a mix containing Zisnet-FPT, the following ingredients were added to the base mix: 1.0 pphr Zisnet-FPT, 0.2 pphr DPG, 2.0 pphr NBC, 5.0 pphr $CaCO_3$ and 3.0 pphr MgO. On the other hand, preparation of a mix containing the alternative ETU-Lead system involved the addition of the following to the base mix: 2.5 pphr of ETU, 5.0 pphr of Litharge (lead) and 2.0 pphr of NBC.

9.2.3 Preparation of Mixes

A masterbatch technique was used to prepare various mixes used in the present study. A 2500 cm³ Francis Shaw Intermix (Manchester, United Kingdom) was used for the masterbatch preparation. The internal mixer was set to operate at a rotor speed of 44 revolutions per minute, under a ram pressure of about 0.70 MPa. The fill factor used was 75%. The discharge temperatures were all within 80-90°C. All masterbatches were prepared according to the time schedule outlined in Table 3. At the end of each mixing schedule the masterbatches were refined on a 0.45 m two-roll mill operating at an even speed of 15 revolutions per minute with roll surface of 50 ± 5°C. At the end of the mill refining operation, each masterbatch was end passed six times on a tight nip to ensure uniform distribution of ingredients. This operation took about 6-10 minutes. Each masterbatch was sheeted out at approximately 6-8mm in thickness. Material losses due to mixing were less than 0.5%. In attempt to minimise the variations between masterbatches, about 50 g was taken from each masterbatch each time and was cross-blended to give a FEF batch for each compound. ETU, litharge and NBC for ETU system, and Zisnet, DPG and NBC for Zisnet system were incorporated on a laboratory 0.3m two-roll operating at a friction speed 1.25:1. Roll surface temperature were maintained at approximately 50 ± 5°C. The mixing procedure was carried out according to the schedule outlined in Table 9.4.

Time elapse (min)	Action
0	Add ECO
1	Add 1/3 of FEF
3	Add a further 1/3 of FEF
6	Add a further 1/3 of FEF
9	Sweep down
11	Discharge

Table 9.3: Mixing schedule of masterbatch

Time elapse (min)	Action for ETU system	Action for Zisnet system
0	Add masterbatch to mill with surface at temperature of 50 ± 5°C	Add masterbatch to mill with surface at temperature of 50 ± 5°C
1	Add stearic acid and processing aid (zinc stearate, Struktol A60)	Add stearic acid and processing aid (zinc stearate, Struktol A60)
3	Add NBC, ETU and Litharge	Add NBC, Zisnet and DPG
6	Sweep and cross-cut from each side of a sheet of rotating rubber	Sweep and cross-cut from each side of a sheet of rotating rubber
9	Six time end-roll on a tight nip, allow to band for one minute	Six time end-roll on a tight nip, allow to band for one minute
11	Sheet off at a thickness 4-5 mm	Sheet off at a thickness 4-5 mm

Table 9.4: Mixing schedule of mixes with different combination of factors

9.2.4 Vulcanisation

The determination of the vulcanisation characteristics were carried out on a Monsanto Oscillating-disc rheometer (ODR) S100. It was operated at $170 \pm 0.5°C$ using strain amplitude of $\pm 3°$ of arc. The extent of crosslinking is given by the difference between maximum torque and minimum torque. The vulcanisation time, t_{95}, is the time (in minute) corresponding to a torque value of: $0.95 \times$(maximum torque-minimum torque) + (minimum torque). However, owing to the marching modulus nature of the cures, the method proposed by *[Rigbi, 1996]*, as discussed in Chapter 4, was used in interpret the rheograms. A Bradley and Turton (Kiddermaster, United Kingdom), double-daylight, steam press was used for the moulding process. For each mix, several cylindrical discs of 13.0 ± 0.5 mm diameter and 6.3 ± 0.3 mm thickness were compression-moulded on a steam press at $170 \pm 2°C$. The moulding times used were those corresponding to the t_{95} values calculated from the rheogram of respective mixes. Post-curing process was carried out according to Farid's work *[Farid, 1996]*. Previous work by Kyllingstad *[Kyllingstad and Cable, 1992]* showed that post curing advances the state of cure and reduces set. All compression–moulded ECO test pieces were placed in a circulating air oven which was maintained at a temperature of 150 ± 1°C for 5 hours. All test pieces were conditioned in an open laboratory environment at temperature of 23 ± 2°C for at least 16 hours before testing. The conditioning was necessary in order to allow sufficient time for vulcanisates to attain a state of thermal equilibrium.

9.2.5 Compression-set

The test was performed according to ISO 815:1991(E) prepared by the Technical Committee ISO/TC 45 (Rubber and Rubber Products), Sub-Committee SC2 (Physical and Degradation Tests). Type B test pieces were used; that is, a cylindrical disc of diameter 13mm ± 0.5mm and thickness of 6.3mm ± 0.3mm. Spacer dimensions for type B test pieces have a height of 4.8mm maximum and 4.7mm minimum. 25% constant strain was used at various temperatures as indicated in Tables 8.5 and 8.6. These temperatures were maintained in a circulating-air oven. The duration of test was 1 to 7 days and silicone oil was used as lubricant. On completion of test period, the test pieces were quickly released from the imposed strain and allowed to recover at room temperature on a wooden bench for 30 minutes. After 30 ± 3 minutes, the thicknesses were measured to the nearest 0.01mm. The compression-set, expressed in percentage of the initial compression, is given by the formula:

$$\%\text{Compression-set} = \frac{h_o - h_1}{h_o - h_s} \times 100$$

In the above expression, h_o is the initial thickness (mm) of the test piece, h_1 is the thickness (mm) after recovery, h_s is the height (mm) of the spacer. Three test pieces were tested and the mean taken as representing the compression-set; errors were assessed using standard deviations. Table 9.5 gives the compression-set data for ECO vulcanisates cured by the ETU-lead system. The results delineated in Table 9.5 are also represented graphically in Figure 9.1.

Day	Set at 100°C	Set at 120°C	Set at 140°C	Set at 160°C	Set at 170°C
1	7.5±0.41	10.6±0.72	32.8±2.46	40.6±2.24	80.6±0.10
2	11.1±0.22	21.1±0.40	45.0±3.00	66.0±1.99	99.1±0.13
3	12.2±0.25	27.7±0.88	54.7±3.28	88.5±1.11	n/a
4	12.8±1.68	32.2±0.04	63.1±1.62	94.4±3.60	n/a
5	16.3±0.70	34.5±0.67	63.9±2.12	n/a	n/a
6	15.9±1.74	43.2±1.49	69.1±3.60	n/a	n/a
7	20.5±0.61	45.3±1.39	69.8±0.39	n/a	n/a

Table 9.5: Compression-set (%) of ETU-Lead system at different temperatures and times

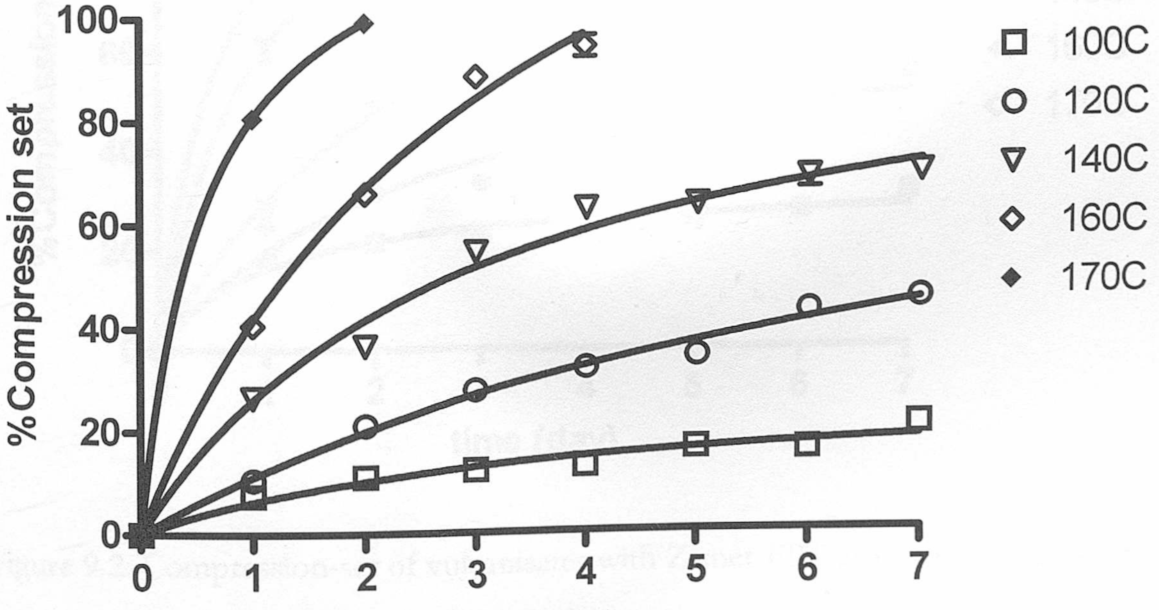

Figure 9.1: Compression-set of vulcanisate with ETU-lead system at various temperatures

Compression-set data for the ECO vulcanisates based on the Zisnet-FPT system are given in Table 9.6; and, the same data is represented graphically in Figure 9.2.

Day	Set at 100°C	Set at 120°C	Set at 140°C	Set at 160°C	Set at 170°C
1	17.9±0.94	25.4±1.16	29.7±2.21	60.3±3.76	73.3±2.87
2	21.8±0.97	31.7±0.82	48.4±2.83	79.7±0.80	92.9±1.47
3	23.9±0.45	33.7±2.12	60.3±1.92	92.5±0.22	95.3±0.72
4	24.0±1.87	40.9±0.87	67.6±0.54	93.8±0.23	n/a
5	26.9±1.03	43.6±0.91	72.1±0.66	96.7±0.64	n/a
6	28.2±1.22	51.9±0.85	79.8±1.24	n/a	n/a
7	31.9±1.10	55.8±0.87	79.5±1.38	n/a	n/a

Table 9.6: Compression-set (%) of Zisnet system at different temperature and time

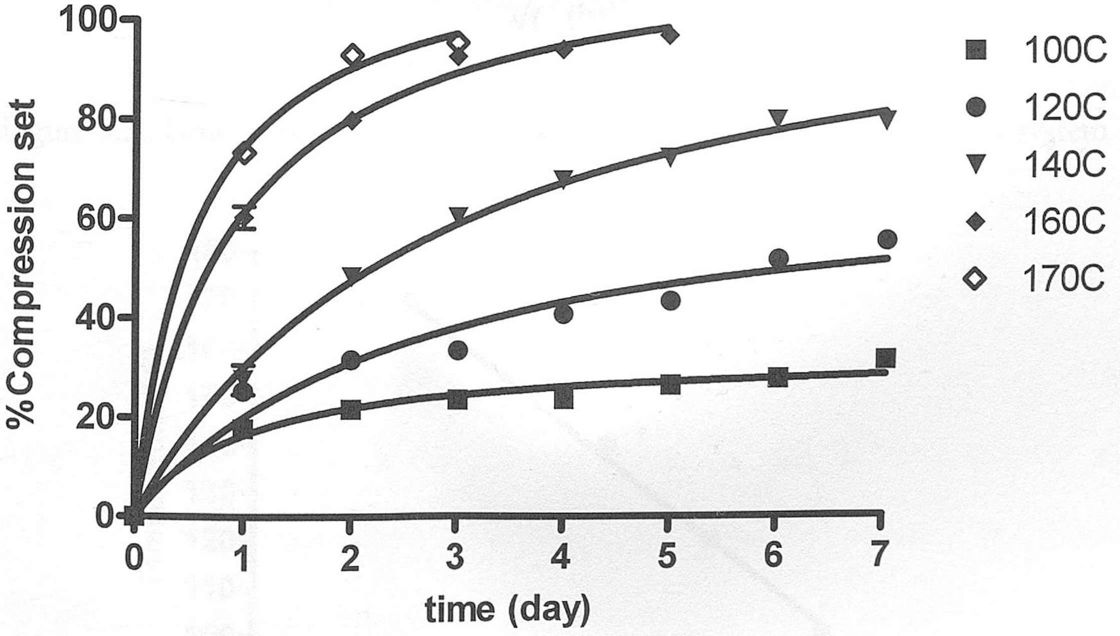

Figure 9.2: Compression-set of vulcanisates with Zisnet-FPT at various temperatures

9.3 RESULT AND DISCUSSION

9.3.1 Empirical Method

Recall that 20% set is used as the failure criterion. At each temperature, the time to reach 20% set was determined and plotted against the square root of time as shown in Figures 9.3 and 9.4 for both curing systems.

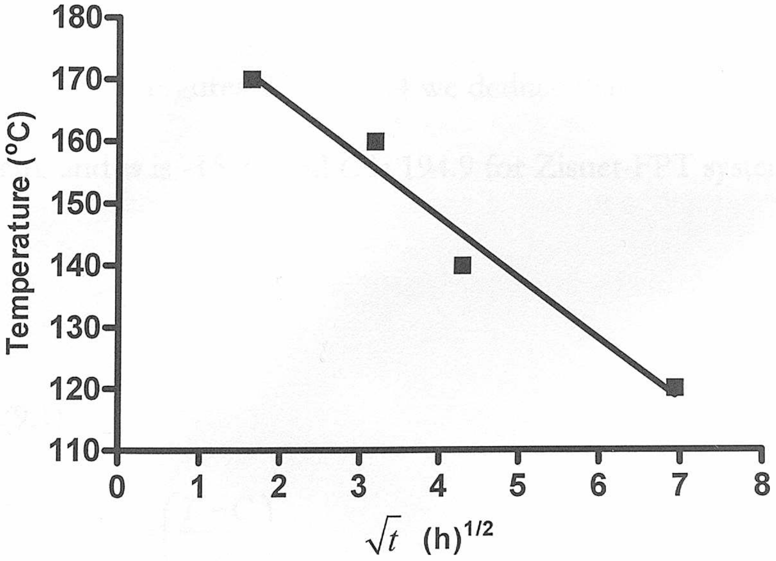

Figure 9.3: Time to reach 20% set at various temperatures for ETU-lead system

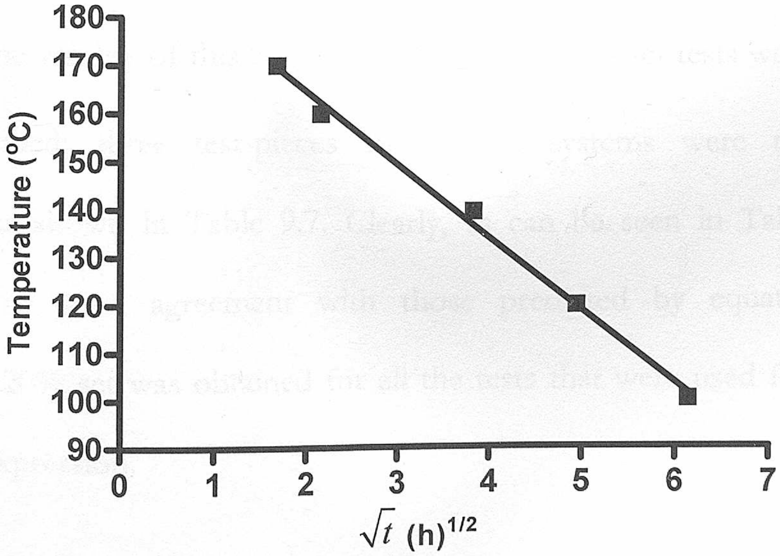

Figure 9.4: Time to reach 20% set at various temperatures for Zisnet-FPT system

In relation to Figures 9.3 and Figure 9.4, if T is temperature and t_{20} is time to reach the 20% failure criterion, then the general equation representing the plots is given by

$$T = m\sqrt{t_{20}} + C \tag{9.1}$$

In the above expression m is the gradient and C is the intercept on the T axis.

From the plots shown in Figures 9.3 and 9.4 we deduce that m is -9.735 and C is 186.4 for ETU-Lead system, and m is -15.24 and C is 194.9 for Zisnet-FPT system.

Verification

From equation (9.1),

$$t_{20} = \left(\frac{T - C}{m}\right)^2 \tag{9.2}$$

Hence, t_{20} at different temperatures for both systems can be calculated using equation (9.2). To test the validity of this equation, the compression-set tests were repeated and t_{20} values determined; three test-pieces from both systems were tested at different temperatures as shown in Table 9.7. Clearly, as can be seen in Table 9.7, the results obtained are in good agreement with those predicted by equation 9.1. That is, approximately 20% set was obtained for all the tests that were used for confirmation of the empirical expression.

Sample	Temperature (°C)	Hour, t_{20}	Set (%)
ETU	135	27.88	20.9±1.77
	145	18.09	20.0±1.88
	165	4.83	19.3±1.02
Zisnet	130	18.14	22.1±1.75
	155	6.85	20.8±1.64
	165	3.85	21.3±1.51

Table 9.7: Compression-set of both systems at different temperature using t_{20}

As further evidence of the reliability of equation 9.1 the results in Table 9.7 are superimposed onto Figures 9.3 and 9.4 to generate two new Figures, namely 9.5 and 9.6. Again, these Figures clearly demonstrate the reliability of equation 9.1.

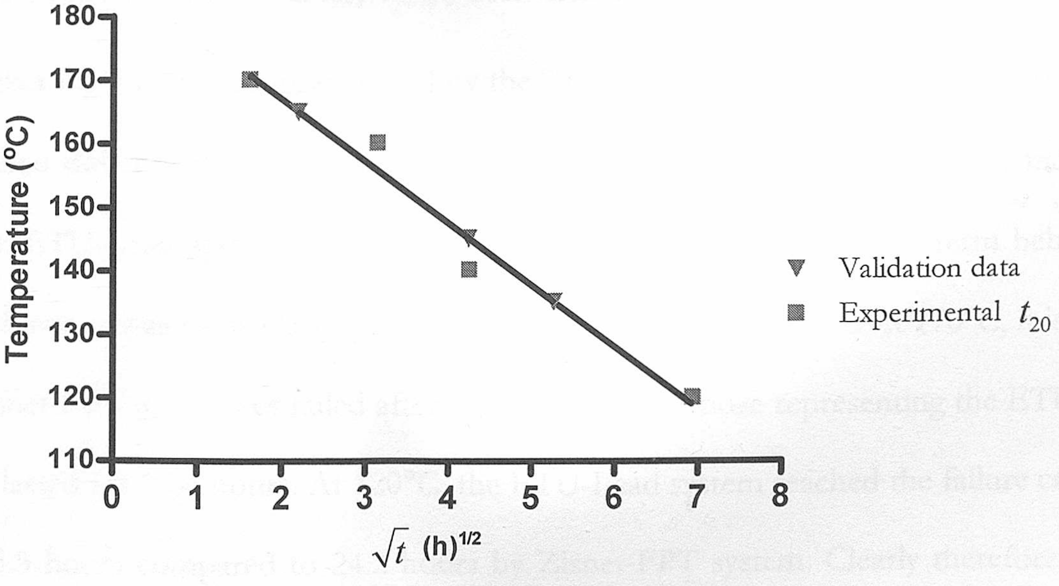

Figure 9.5: Experimental values on time to reach 20% set for ETU-lead system

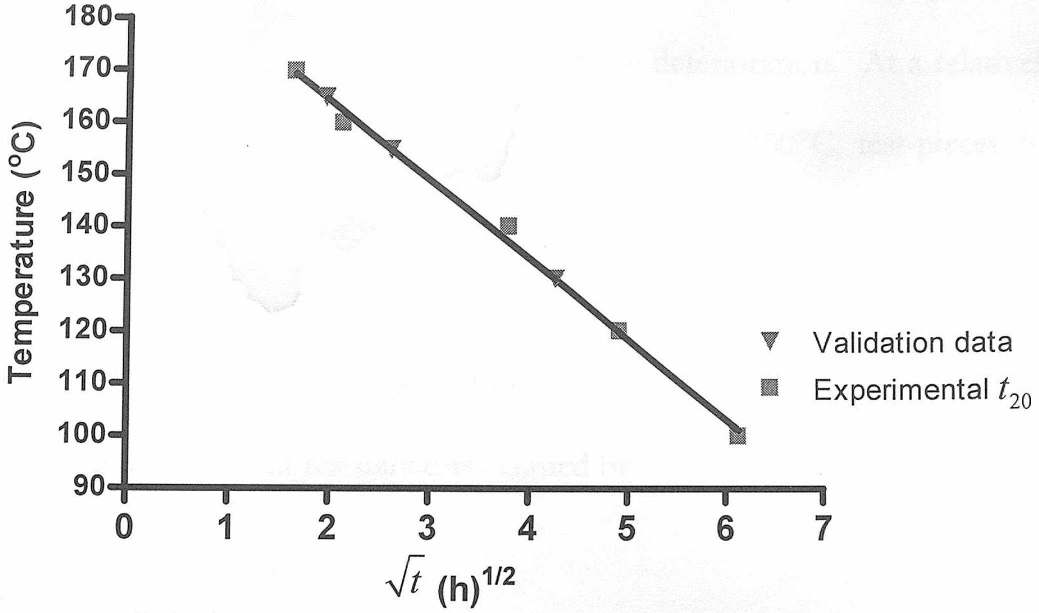

Figure 9.6: Experimental values on time to reach 20% set for Zisnet-FPT system

Based on time to failure values, $t_{f=20}$, determined from equations (9.1) or (9.2), it was found that the ECO vulcanisate cured by the Zisnet-FPT system reached the failure value faster than did the ECO vulcanisate containing the ETU-Lead system. Thus, indicating that the ETU-Lead system is the superior of the two in terms of long term behaviour. This behaviour was particularly significant at the lower temperatures. At 170°C, it is found that Zisnet-FPT test-pieces failed after 2.67 hours while those representing the ETU-Lead system lasted for 2.84 hours. At 120°C, the ETU-Lead system reached the failure criterion after 46.5 hours compared to 24.2 hours by Zisnet-FPT system. Clearly therefore, ECO elastomers cured by the traditional ETU-lead system is considerably more robust than that containing the Zisnet-FPT system.

At 170°C the test-pieces representative of the Zisnet-FPT system suffered heavy deterioration after 72 hours; beyond this period, the test-pieces showed appreciable loss in elasticity. On the other hand, under identical conditions, test-pieces prepared from the ETU-Lead system only survived for 48 hours before deterioration. At a relatively lower temperature a similar trend was observed, for instance at 160°C, test-pieces from the Zisnet-FPT and ETU-Lead systems lasted 120 hours and 96 hours respectively. These observations suggest that although ECO vulcanisates cured by the Zisnet-FPT system are unable to match the compression-set produced by the ETU system, they nevertheless appear to possess better heat resistance as claimed by the manufacturer *[Harris, 2000]*.

9.3.2 Arrhenius Relationship

Another property prediction technique is that due to the Arrhenius relationship *[Arrhenius, 1889]*. This relationship is derived from the Arrhenius reaction rate equation proposed by the Swedish physical chemist Svandte August Arrhenius in 1887. This relationship is the most commonly accepted and most widely used model; particularly in situations in which permanent effects of temperature occur. The Arrhenius relationship given by

$$k(T) = A.e^{\left[\frac{-E}{RT}\right]} \tag{9.3}$$

Taking the natural logarithm of the above expression gives

$$\ln k(T) = \frac{-E}{RT} + A \tag{9.4}$$

In the above expression, $k(T)$ is the reaction rate for the process at an absolute temperature T, E is the activation energy, R is the gas constant and A is the frequency factor.

In order to apply the Arrhenius methodology to predict long-term compression-set behaviour it is expedient to consider the diagram shown in Figure 9.7. The diagram shown in Figure 9.7 represents the various stages involved in a typical compression-set experiment. In reference to the diagram, h_o is the original height, h_c is the compressed height and h_r is the recovered height of the test piece. The percentage recovery, R, is defined as amount recovered per amount compressed.

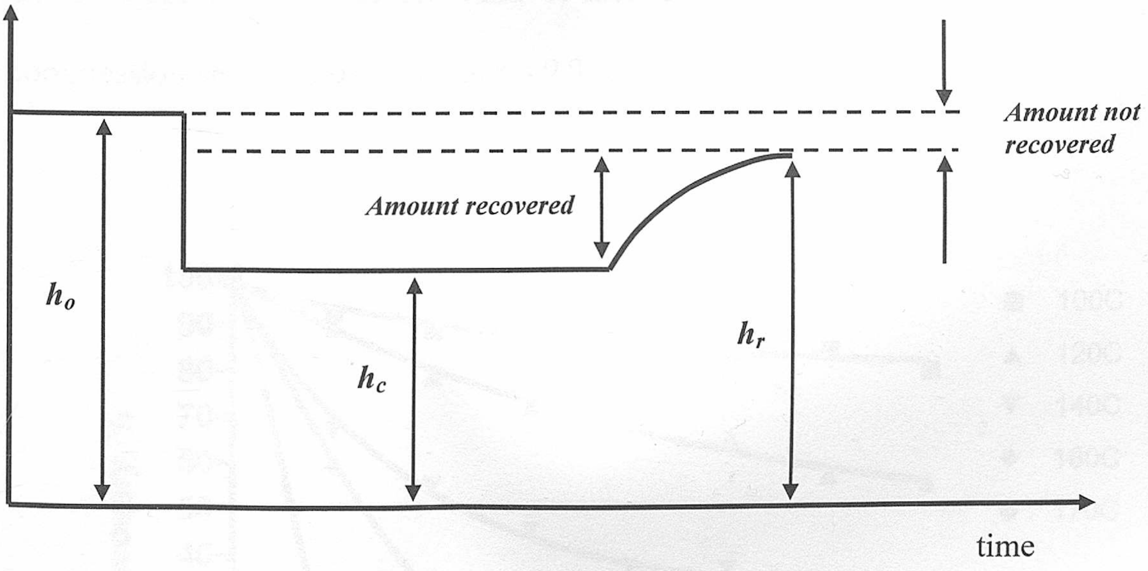

Figure 9.7: Various stages in a compression-set test

Therefore from diagram, we deduce

$$R(\%) = \left(\frac{h_r - h_c}{h_o - h_c} \right) \times 100 \tag{9.5}$$

In contrast, percentage compression-set, S, is defined as amount not recovered per amount compressed. Hence:

$$S = \left(\frac{h_o - h_r}{h_o - h_c} \right) \times 100 \tag{9.6}$$

Noting equations (9.5) and (9.6) we deduce that

$$\frac{S}{100} + \frac{R}{100} = 1$$

$$R = 100 - S \tag{9.7}$$

From equation (9.7), knowing the compression-set values determined earlier it is a simple matter to determine the recovery. Plots of recovery versus time using equation (9.7) on the compression-set are shown in Figures 9.8 and 9.9.

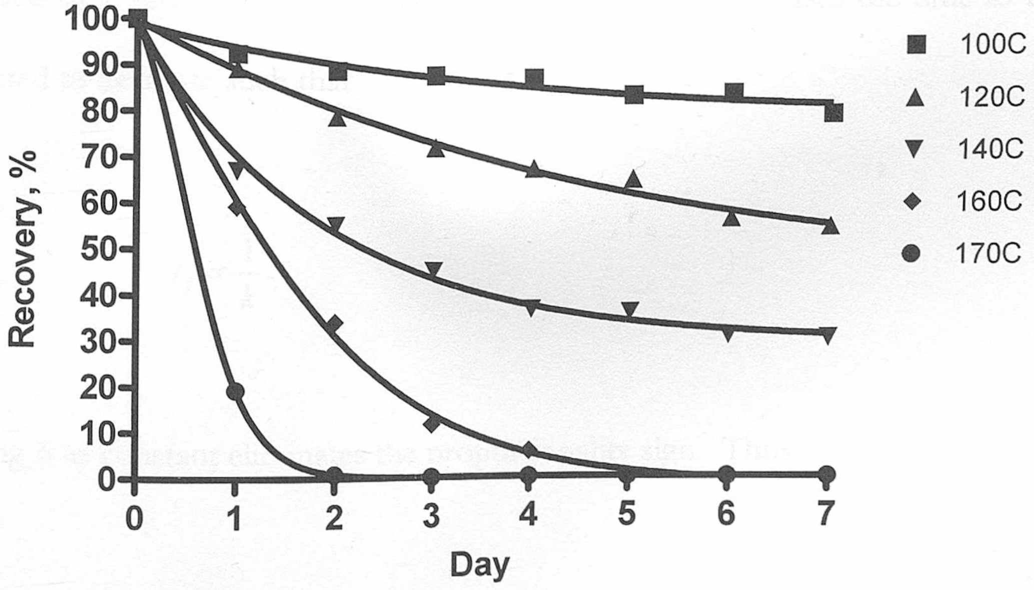

Figure 9.8: Recovery of ETU-Lead samples at various temperatures and times

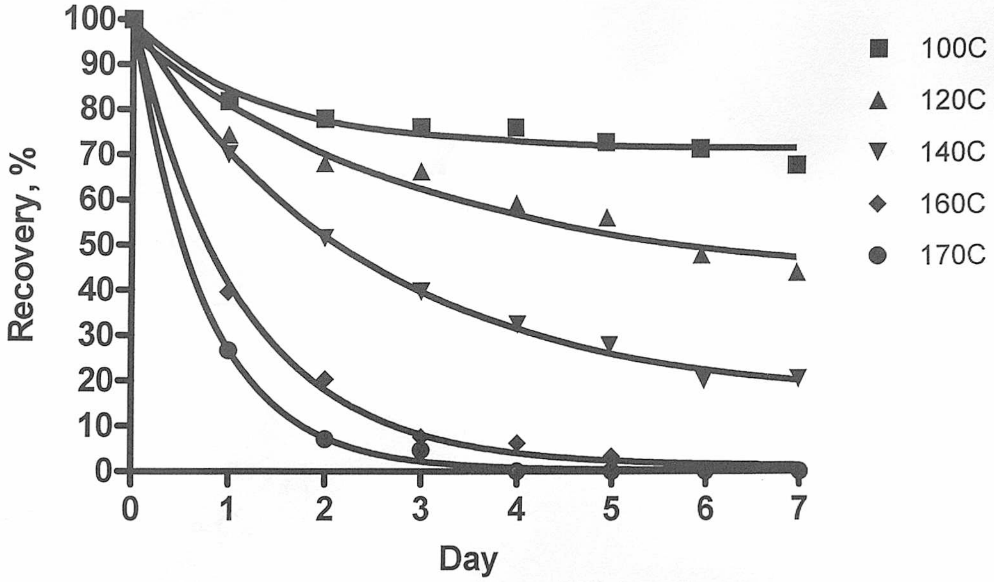

Figure 9.9: Recovery of Zisnet-FPT samples at various temperatures and time

The common threshold value used for establishing a general maximum temperature of use is 50% change in property *[Brown, 2001]*. In this work however, 80% recovery is used to correspond with 20% set which is the specified failure criterion used in the present study. Since recovery (or set) is due to chemical reactions then the rate of reaction may be characterised by a rate constant, k. As the rate of reaction increases the time to failure, t_f is expected to decrease such that

$$t_f \propto \frac{1}{k} \tag{9.6}$$

Introducing B as constant eliminates the proportionality sign. Thus

$$t_f = \frac{B}{k} \tag{9.7}$$

k is related by the Arrhenius expression,

$$k = A.e^{\frac{-E}{RT}} \tag{9.8}$$

Introducing (9.8) into (9.7) gives,

$$t_f = C.e^{\left(\frac{E}{RT}\right)} \tag{9.9}$$

In the above expression *C* is another constant to replace the constants *A* and *B*. Taking natural logarithms of expression (9.9) gives

$$\ln t_f = \ln C + \frac{E}{R}.\frac{1}{T} \tag{9.10}$$

Equation (9.10) suggests that a plot of ln t_f against $1/T$ should yield a straight-line relationship. Such plots generated from current compression-set data (see Figures 9.10 and 9.11 for the respective curing systems) confirm this linear relationship.

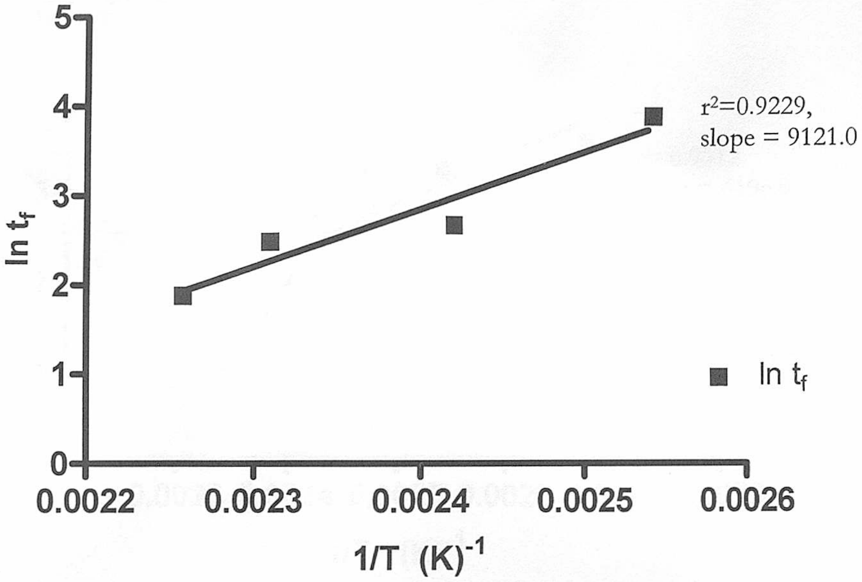

Figure 9.10: Arrhenius plot for the ETU-Lead curing system

From Figure 9.10, the slope, E/R is 9121.0 K and intercept on vertical axis, ln C, is (-19.23). The time to failure, t_f, at any particular temperature can be predicted by equation (9.10). For example, at 25°C (298K), the parameter $1/T$ is 0.003356, therefore on introducing these values in equation (9.10) gives

$$\ln t_f = \left[\left(\frac{E}{R}\right)\left(\frac{1}{T}\right)\right] - 19.23 \tag{9.11}$$

$$t_f = 87324 \text{ hours} \approx 9.96 \text{ years}$$

Thus, based on the above calculation it appears that at 25°C, vulcanisates based on the ETU-Lead should be able to maintain their integrity for up to 10 years.

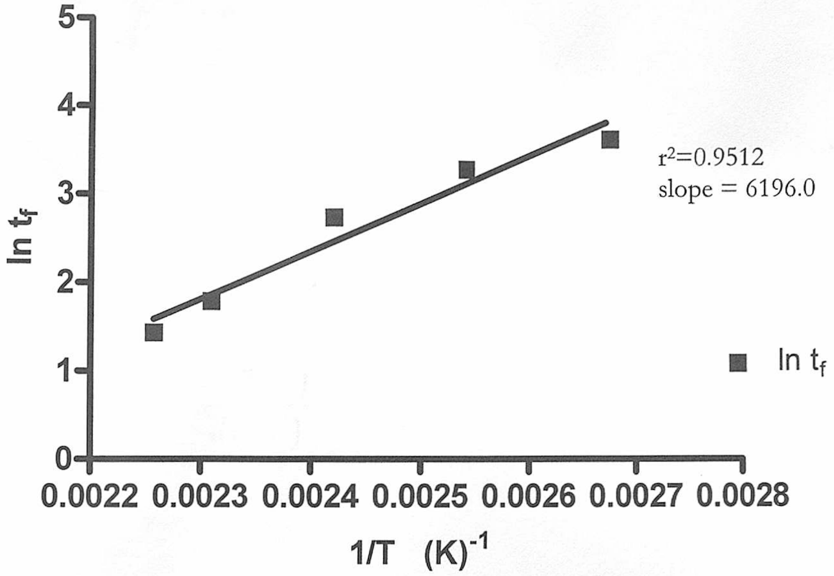

Figure 9.11: Arrhenius plot for the Zisnet-FPT curing system

Consider now a similar calculation as that just described for the Zisnet-FPT curing system. For this system, we find that from Figure 9.11 the value of the slope is 6196.0 K and the value for ln C of is (-12.73). Introducing both values into equation (9.10) we obtain a t_f value of about 132 days. Clearly, the value of t_f for the Zisnet-FPT system is considerably lower than that of the ETU-lead system. These results confirm the earlier findings based on the empirical relationship.

Knowing the value of the Gas Constant, R, that is, 8.314 x 10^{-3} kJ mol^{-1}K^{-1}, the activation energy, E_a can also be determined. Recall, the relationship

$$\ln t_f = \ln C + \frac{E}{R} \cdot \frac{1}{T} \tag{9.12}$$

Differentiating the above expression with respect to $1/T$ gives

$$\frac{d\left(\ln t_f\right)}{d\left(1/T\right)} = \frac{E}{R} \tag{9.13}$$

Hence, we deduce that

$$E = R \bullet \frac{d\left(\ln t_f\right)}{d\left(1/T\right)} \tag{9.14}$$

Referring to Figures 9.10 and 9.11 we clearly deduce that

$$E = R \times \left(\text{Slope of plots of } t_f \text{ versus } 1/T\ \right) \tag{9.15}$$

The slopes of the plots for the ETU-Lead and Zisnet-FPT systems are 9121.0 K and 6196.0 K respectively. Introducing these values into equation (9.15) yields the activation energies for the ETU-Lead system, E_E, and for the Zisnet system, E_Z, these values are 75.8320 kJmol^{-1} and 51.5135 kJmol^{-1} respectively. Clearly, the activation energy in of the ETU-Lead system is greater than that of Zisnet-FPT system. Measured activation energies are sometimes found in the literature and could be used to make an approximation from a single point measurement. Some measure of safety can be built in by assuming a conservative value for activation energy. A crude way of applying this principle is the use of the rule-of-thumb generality that reaction rate doubles for every 10°C rise in temperature.

The results given in Table 9.8, particularly at low temperatures, indicates that time predictions obtained from the empirical relationship are significantly shorter than those predicted from the Arrhenius relationship. As temperature is increased, the prediction becomes increasingly more comparable and there appears to be closer agreement. Both the empirical and theoretical relationships predict that the ETU-lead system is superior to the Zisnet-FPT sytem in terms of longevity.

Temperature (°C)	**Empirical relationship, t_{20} (Hour)**		**Arrhenius relationship, t_f (Hour)**	
	Zisnet	**ETU**	**Zisnet**	**ETU**
170	2.67	2.84	4.88	6.93
160	5.24	7.35	6.44	9.65
140	12.98	22.72	11.65	19.64
120	24.15	46.52	22.39	42.97
100	38.78	78.77	46.15	102.26
25	124.28	274.87	1650.10	7446.53

Table 9.8: Comparisons of both relationships

It should be noted that the empirical method involves the use of basic mathematical transforms to obtain simple linear relationships and therefore has no theoretical foundation. On the other hand, the Arrhenius relationship is based on theoretical considerations and for this reason there is greater credibility attached to it. Care needs to be taken when applying the Arrhenius methodology to investigate properties under accelerated ageing of thick samples; in bulkier samples chemical processes may become diffusion controlled. It is generally assumed that the activation energy is independent of temperature and that the chemical changes relate directly to the physical properties measured, for example, set and recovery. In complex reactions, this assumption may not be entirely valid as shown by Le Huy and Evrard *[Huy and Evrard, 1998]*.

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Chapter

10

CORRELATION BETWEEN SET AND STRESS-RELAXATION

The present Chapter is related to finding a meaningful relationship between set and stress-relaxation. In industry, set behaviour has always been regarded as an efficient way of assessing sealing performance. However, many argue that stress-relaxation should be the principle property by which sealing behaviour should be ranked. There is some justification for taking this view in the sense that stress-relaxation measurements are carried out on vulcanisates that are in a continuous state of strain whereas compression-set measurements require vulcanisates to undergo a recovery or relaxation period without restraint. The main reason for the popularity of the compression-set approach is that the method is very facile, cheap, and efficient; moreover, it does not require specialised apparatus. Nevertheless, in view of the importance that is placed upon stress-relaxation as a way of effectively monitoring sealing performance it is desirable to develop a relationship between stress-relaxation and compression-set. Such a relationship will clearly couple experimental convenience with a reliable parameter for assessing sealing behaviour. On the basis of the preceding remarks, the object of the present Chapter is to investigate the extent to which compression-set results can be used to indicate stress-relaxation behaviour. In this endeavour a mathematical model proposed by Ellul and Southern [Ellul and Southern, 1985] is employed. It was found that the model was sufficient for ranking purposes.

10.1 INTRODUCTION

Compression stress-relaxation (CSR) is considered as the most direct measure of sealing capacity. It gives the force a rubber article would exert on a solid sealing surface as a function of time. However, as the stress-relaxation tests present some experimental difficulties, industries tend to use a simpler test which is known as compression-set (CS) although the information it provides is considered limited. The debate about the use of compression-set and stress-relaxation, as a predictor of seal performance is not new. Morell and Watson *[Morell and Watson, 1976]* suggested that compression-set and compression stress-relaxation have different non-linear relationships to the basic processes and hence are not expected to correlate with each other, that is, network formation during compression is not expected to have significant effect on compression stress-relaxation but markedly reduces recovery on release of compression. But Farid *[Farid, 1996; 1999]* argued that set and stress-relaxation in elastomers at elevated temperatures arise from chemical changes that occur in the rubber network; therefore, in principle they are connected. Previous work by Ellul and Southern *[Ellul and Southern, 1985]* found that there is a broad correlation between compression-set and stress-relaxation as predicted theoretically for a wide range of elastomers.

Although elastomers are often described as elastic materials, in reality they exhibit some degree of liquid-like behaviour as well as elastic characteristics. The liquid-like or viscous behaviour is useful in shaping operations because it generates heat, imparts uniformity in flow behaviour, and thus facilitates the conversion of a rubber mix into a useful product. Viscous behaviour is also useful in the final rubber product because it leads to energy absorption, which is why elastomers are very effective in isolating ground-borne vibrations, which would otherwise lead to damage of rigid supports and sensitive electronic equipment. However, in some static applications, particularly seals and gaskets, the viscous contribution is detrimental. For instance, if a rubber is compressed, held for a time, and then released one would observe an immediate partial elastic response followed by a slow or retarded response to full recovery. The overall result is that, within a practical time scale, the rubber fails to return to its original dimensions. The amount of compression that is not fully recovered within the time scale of the experiment is known as set. Thus the significance of set in sealing applications is clear: when the mating surfaces in contact with the rubber seal shift (which may be caused by differential mechanical movement or by expansion or contraction) an opening is formed which, if the rubber fails to recover, will produce a leakage path. The efficiency of rubber seal may be influenced by a number of factors, but one of the most important properties is its stress-relaxation. Although it is considered as the most direct measure of sealing efficiency, in practice compression-set is preferable owing to its simplicity. Therefore the production of extensive data correlating compression-set and stress-relaxation in order to acquire a deeper understanding upon seal performance is highly desirable. Previous work by Ellul and Southern *[Ellul and Southern, 1985]* found that there is a reasonable broad correlation between compression-set and stress-relaxation. Although it is insufficient to predict accurately values of one physical quantity from another, it is suggested that the correlation is adequate for ranking purposes of sealing behaviour of different rubber compounds. The aim of the present work is to investigate whether this correlation can be applied to the present range of ECO elastomers using two distinct vulcanisation systems. Farid *[Farid, 1996; 1999; 1999]* has proposed that the ECO elastomers is the most promising elastomer as it could potentially satisfy many requirements which considered useful for sealing applications.

10.2 THEORY

Ellul and Southern *[Ellul and Southern, 1985]* used two-network theory of Tobolsky *[Andrew, Tobolsky et al., 1946]* to develop a mathematical model that relates the permanent set, S, to the extension ratio, λ, and to the ratio of the number of network chains unbroken, N_u, to those formed in the deformed state, N_x. That is

$$S = \left\{ \left[\frac{\lambda^3 - 1}{\left(N_u / N_x \right) \lambda^2 + 1} + 1 \right]^{\frac{1}{3}} - 1 \right\} \frac{100}{\lambda - 1} \qquad (10.1)$$

A detailed explanation of the theory and its derivation of the equation is available elsewhere *[Ellul and Southern, 1985]*. Thus, only the most salient points of the theory will be given here.

In compression-set measurements, λ is less than unity and S then signifies compression-set. Equation (10.1) has been used successfully in tension experiments to predict permanent set from the difference between continuous and intermittent stress-relaxation measurements *[Andrew, Tobolsky et al., 1946]*. However, this approach is not beneficial in this work as the interest is on continuous stress-relaxation and compression-set only.

In attempting to obtain a theoretical relationship between CS and CSR, Ellul *[Ellul and Southern, 1985]* assumed that the network chains formed in the deformed state and those lost under the same condition, N_x arise from two sources; namely, the recombination of broken cross-links and the introduction of new cross-links giving

$$N_x = f(N_o - N_u) + N_n \qquad (10.2)$$

In the above expression f is the fraction of broken chains which become reconnected, N_n is the number of chain produced by new cross-links and N_o is the number of chains originally present.

Re-arranging (10.2) gives,

$$\frac{N_u}{N_x} = \frac{N_u/N_o}{f(1 - N_u/N_o) + N_n + N_n/N_o} \qquad (10.3)$$

The relative stress in continuous deformation, F` is given by $F = N_u/N_o$.

Introducing the relationship for F into equation (10.3) gives

$$\frac{N_u}{N_x} = \frac{F}{f(1-F) + N_n + N_n/N_o} \qquad (10.4)$$

Introducing equation (10.4) into (10.1) gives,

$$S=\left\{\left[\frac{\lambda^3-1}{\{F/[f(1-F)+N_n/N_o]\}\lambda^2+1}+1\right]^{\frac{1}{3}}-1\right\}\frac{100}{\lambda-1} \tag{10.5}$$

Equation (10.5) is the desired relationship between compression-set, *S*, and relative stress, *F*. It is an implicit assumption that the values of f and N_n/N_o are not affected by the ageing behaviour. It is plausible to introduce a relationship of the form

$$\frac{N_n}{N_o}=k\left(\frac{N_o-N_u}{N_o}\right)^{\alpha} \tag{10.6}$$

$$\frac{N_n}{N_o}=k(1-F)^{\alpha} \tag{10.7}$$

Hence, using the relationship above, equation (10.5) becomes,

$$S=\left\{\left[\frac{\lambda^3-1}{\{F/[f(1-F)+k(1-F)^{\alpha}]\}\lambda^2+1}+1\right]^{\frac{1}{3}}-1\right\}\frac{100}{\lambda-1} \tag{10.8}$$

By introducing speculative values for k, α, and f it is possible to obtain a general correlation between stress-relaxation and compression-set, provided the constants k, α and f do not vary too much for the vulcanisates tested.

10.3 EXPERIMENTAL WORK

10.3.1 Material

The base polymer used was Hydrin C2000L (copolymer), supplied by Zeon Chemicals, Wales. The Zisnet-FPT was used as a vulcanisation system supplied by Nippon Zeon Co. Ltd, Wales. ETU was supplied by Robinson Brothers (UK) Ltd as 75% active in a binder system. Fast extrusion furnace (FEF) carbon black (N550) was supplied by Cabot Carbon (UK). This filler has a relatively large particle size and high structure which lead to very low rates of primary or physical stress-relaxation. Due to nature of processing difficulties *[Zeon, 2000; 2000]*, two processing aids were used together. The first was zinc stearate, in the form of powder which was supplied by Omya, United Kingdom. The second was a complex zinc soap of partly unsaturated fatty acid within the $C_{12} - C_{18}$ range. It is supplied by Schill and Seilacher GmBH Hamburg, Germany via their UK distributor, International Adhesive Ltd under the trade name 'Struktol A60'. Zinc stearate was used to control the degree of splitting and tearing of ECO during mill-mixing. The complex zinc soap on the other hand, was used to improve the flow characteristics of ECO mixes and to reduce the degree of bloom in vulcanisation made from ECO mixes. Nickel di-n-butyldithiocarbamate (NBC) was used as protective agent, supplied by Flexsys Rubber Chemicals, Wales under the trade name of NDBC in the form of green powder. The accelerator used in conjunction with Zisnet FPT was Diphenyl guanidine (DPG), supplied by Omya United Kingdom. It was supplied under the trade name DPG 75 in the form of 75% active material in a polyethylene binder.

10.3.2 Mix Formulation

The formulations used are given in Table 10.1.

Ingredient	ETU (pphr)	Zisnet (pphr)
ECO (C2000L)	100.0	100.0
Stearic acid	1.0	1.0
Struktol A60	1.0	1.0
Zinc stearate	1.0	1.0
ETU	2.5	-
Litharge	5.0	-
Zisnet FPT	-	1.0
$CaC0_3/MgO$	-	5.0
DPG	-	0.2
FEF N550	50.0	50.0
NBC	2.0	2.0

Table 10.1: Formulations used

10.3.3 Preparation of Mixes

Formulations in Table 10.1 are based on compounds used elsewhere*[Wahab, Farid et al., 2004]*. A masterbatch technique was used to prepare various mixes. A 2500 cm^3 Francis Shaw Intermix (Manchester, United Kingdom) was used for the masterbatch preparation. The internal mixer was set to operate at a rotor speed of 44 revolutions per minute, under a ram pressure of about 0.70 MPa. The fill factor used was 75% and the batch masses were about 3462 g. Seven masterbatches were prepared in order to produce 32 mixes. The discharge temperatures were all within 80-90°C. All seven masterbatches were prepared according to the time schedule outlined in Table 9.3. At the end of each mixing schedule the masterbatches were refined on a 0.45 m two-roll mill operating at an even speed of 15 revolutions per minute with roll surface of 50 ± 5°C. At the end of the mill refining operation, each masterbatch was end passed six times on a tight nip to ensure uniform distribution of ingredients. This operation took about 6-10 minutes. Each masterbatch was sheeted out at approximately 6-8 mm in thickness. Material losses due to mixing were less than 0.5%. In attempt to minimise the variations between masterbatches, about 50 g was taken from each masterbatch each time and was cross-blended to give a FEF batch for each compound. ETU, litharge and NBC were incorporated on a laboratory 0.3 m two-roll operating at a friction speed 1.25:1. Roll surface temperature were maintained at approximately 50 ± 5°C. The mixing procedure was carried out according to the schedule outlined in Table 10.3.

Time elapse (min)	Action
0	Add ECO
1	Add 1/3 of FEF
3	Add a further 1/3 of FEF
6	Add a further 1/3 of FEF
9	Sweep down
11	Discharge

Table 10.2: Mixing schedule of masterbatch

Time elapse (min)	Action
0	Add masterbatch to mill with surface at temperature of 50 ± 5°C
1	Add stearic acid and processing aid (zinc stearate, Struktol A60)
3	Add protective agent (NBC), curative (ETU or ZISNET) and acid acceptor (Litharge or $CaCO_3/MgO$)
6	Sweep and cross-cut from each side of a sheet of rotating rubber
9	Six time end-roll on a tight nip, allow to band for one minute
11	Sheet off at a thickness 4-5 mm

Table 10.3: Mixing schedule of mixes

10.3.4 Vulcanisation

The determination of the vulcanisation characteristics were carried out on a Monsanto Oscillating-disc rheometer (ODR) S100. It was operated at 170 ± 0.5°C using strain amplitude of ± 3° of arc. The extent of crosslinking is given by the difference between maximum torque and minimum torque. The vulcanisation time, t_{95}, is the time corresponding to M_{95}, given by 0.95×(maximum torque-minimum torque) + (minimum torque). However, due to marching modulus nature of the cure, the approach suggested by Rigbi *[Rigbi, 1996]* was used to calculate maximum torque and subsequently, T_{95}. A Bradley and Turton (Kiddermaster, United Kingdom), double-daylight, steam press was used for the moulding process. For each mix, several cylindrical discs of 13.0 ± 0.5mm diameter and 6.3 ± 0.3mm thickness were compression-moulded on a steam press at 170 ± 2°C. Moulding times used were those corresponding to the T_{95} values calculated from the rheogram of respective mixes. Post-curing process was carried out according to Farid's work *[Farid, 1999; 2000]*. Previous work by Kyllingstad *[Kyllingstad and Cable, 1992]* showed that post-curing can substantially reduce set. All compression–moulded ECO test pieces were placed in a circulating air oven which was maintained at a temperature of 150 ± 1°C for 5 hours. All test pieces were conditioned in an open laboratory environment at temperature of 23 ± 2°C for at least 16 hours before testing. This is to allow sufficient time for vulcanisates to attain a state of thermal equilibrium.

10.3.5 Stress-relaxation and compression-set

The test-pieces used for stress-relaxation experiments were identical to those used for compression-set tests. For any given test-piece the compression stress-relaxation procedure was as follows: A compression cage was fitted to an Instron tensometer (model 1026); the compression cage is device that is designed in such a manner as to allow force measurements to be conducted in compression. A test piece is placed centrally as possible in the compression cage and the test-piece is then strained to 25% compression and subsequently held at this strain. The compressive force at the fixed compression is then monitored as a function of time. If a test temperature other than that of room temperature is required then the compression cage and fittings are enclosed within an environmental thermal cabinet adjusted to give the required temperature. An excellent compendium of the compression stress-relaxation test using the compression cage is given by Ellul *[Ellul and Southern, 1985]*. At the end of the compression stress-relaxation test, the test-piece is removed and allowed to recover freely on a wooden bench for 30 minutes; at the end of the 30-minute recovery time the height of the test-piece is measured. Thus, knowing the original height of the test-piece, the compressed height and the final height at the end of the recovery period it is a simple matter to determine the compression-set (see previous Chapters for method of determination) of the same test-piece that was subjected to compression stress-relaxation. For any given ECO compound, three test-pieces were tested in the manner described above and the mean value of compression stress-relaxation and set was recorded.

10.4 RESULTS AND DISCUSSION

10.4.1 Reproducibility

In order to assess the reproducibility of the compression stress-relaxation test, three samples were tested for period 6 hours and the results are shown in Figure 10.1. Note that the force measured in experimental work is in N.

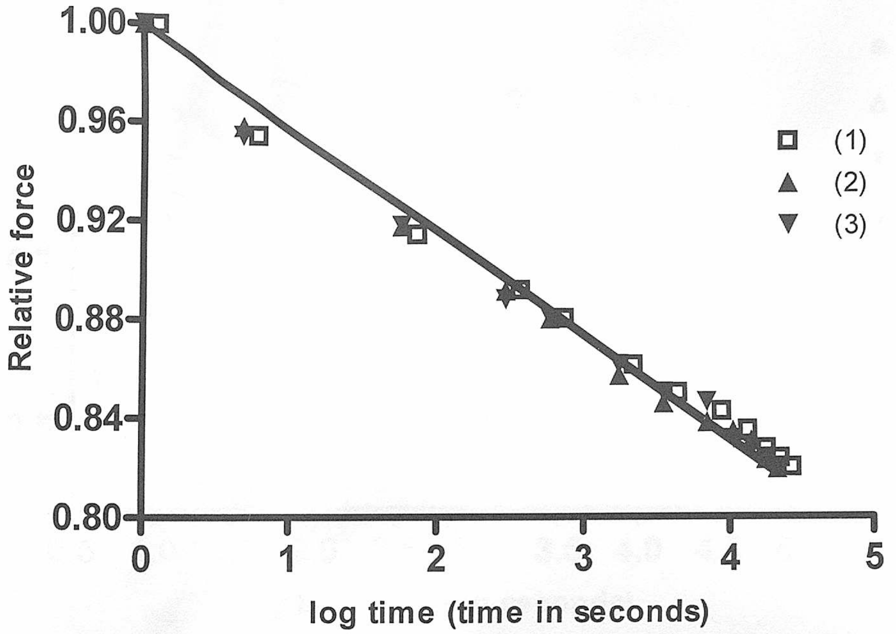

Figure 10.1: Reproducibility of CSR of ETU-lead system at 23°C
(plots were nudged to 0.1N to avoid overlapping)

Based on the slope of the linear relationship shown in Figure 10.1, the mean rate of stress-relaxation is 4.2% per decade and the standard deviation is 0.4%. These results indicate good reproducibility.

10.4.2 Effect of temperature

Compression stress-relaxation experiments were carried out at temperatures between 40°C to 180°C. The results are shown in Figures 10.2 and Figure 10.3 for the ETU-lead system and the Zisnet-FPT system respectively.

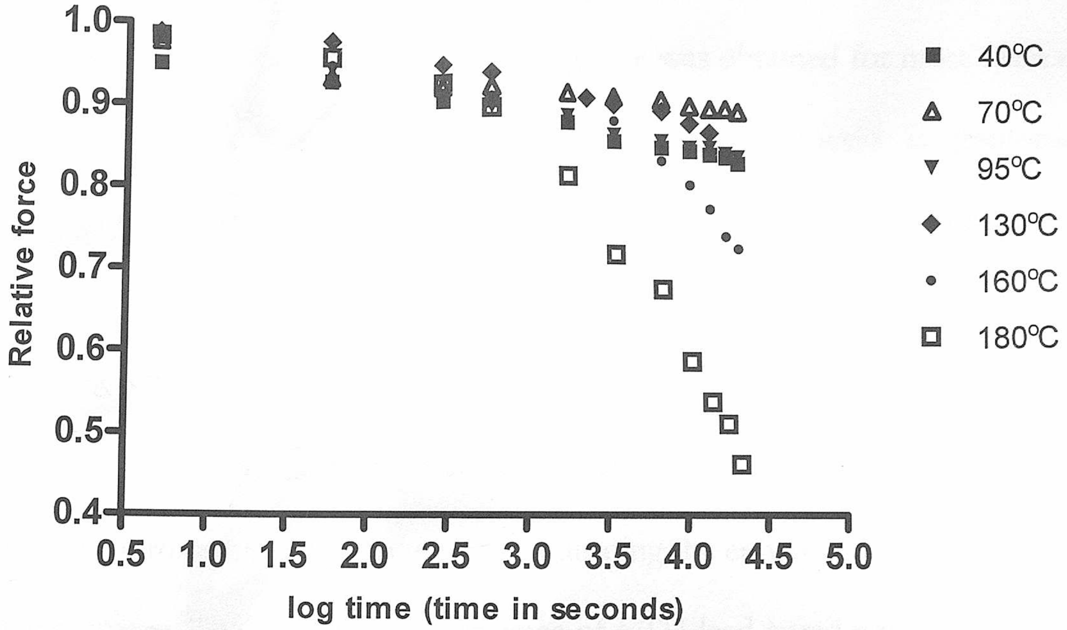

Figure 10.2: Effect of temperature on CSR of vulcanisates using ETU-Lead system

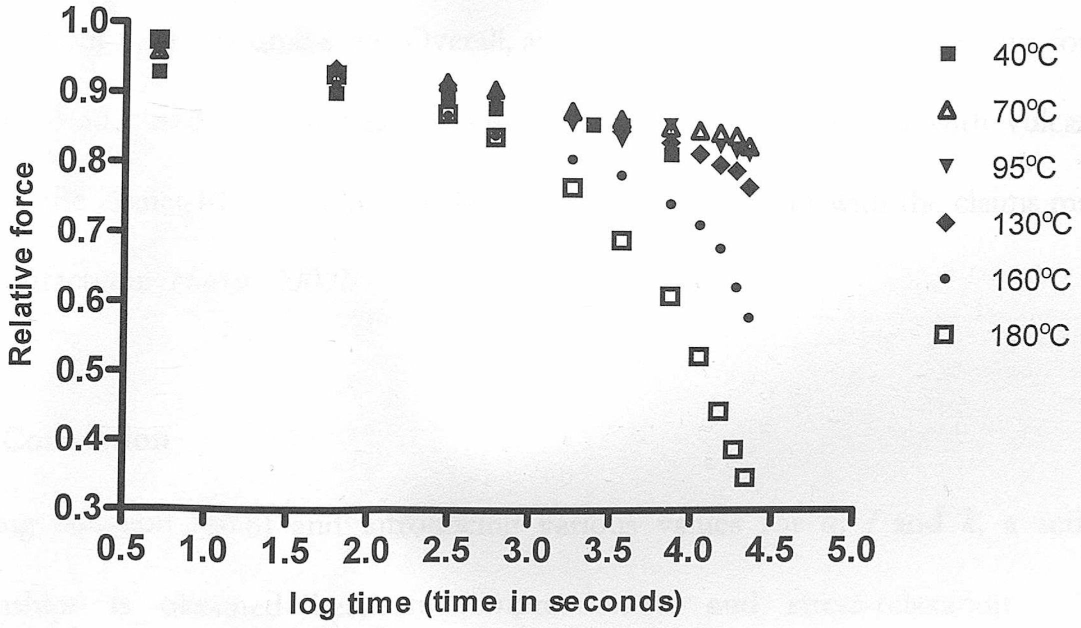

Figure 10.3: Effect of temperature on CSR of vulcanisates using Zisnet-FPT system

As anticipated, increasing the temperature leads to increasing rate of stress-relaxation. A linear relationship between relative force and log time was obtained for most cases up to a temperature of 95°C; this indicates that the relaxation process is predominantly viscoelastic in nature. For the ETU-lead system it was found that the rate increased from 3.4% per decade at 95°C, to 31.4% per decade at 180°C; as for the Zisnet system at the corresponding temperatures, the increase was from 6.8% per decade to 45.1% per decade. Appreciable increases in the rates of stress-relaxation were observed at 180°C for both systems after approximately 30 minutes thus indicating the enhanced chemical degradation at this temperature. The excellent performance of ETU-lead cured vulcanisates is further demonstrated by its ability to maintain higher relative forces over the present temperature range. The chemical changes as reflected by the sharp inflexions of the curves of relative force against time for both ETU-lead and Zisnet-FPT cured systems appeared to take place at about the same time-scale. Overall, at any given temperature, the relative force for the ETU-lead cured vulcanisates is consistently higher as compared with vulcanisates cured by the Zisnet-FPT system. This behaviour is in agreement with the claims made by the manufacturer *[Harris, 2000]*.

10.4.3 Correlation

By using equation (10.8) and introducing various values for *a, f* and *k*, a series of relationships is obtained between compression-set and stress-relaxation. These relationships, using specific values of *a, f* and *k*, are represented by curves *(a), (b), (c)* and *(d)* in Figure 10.4.

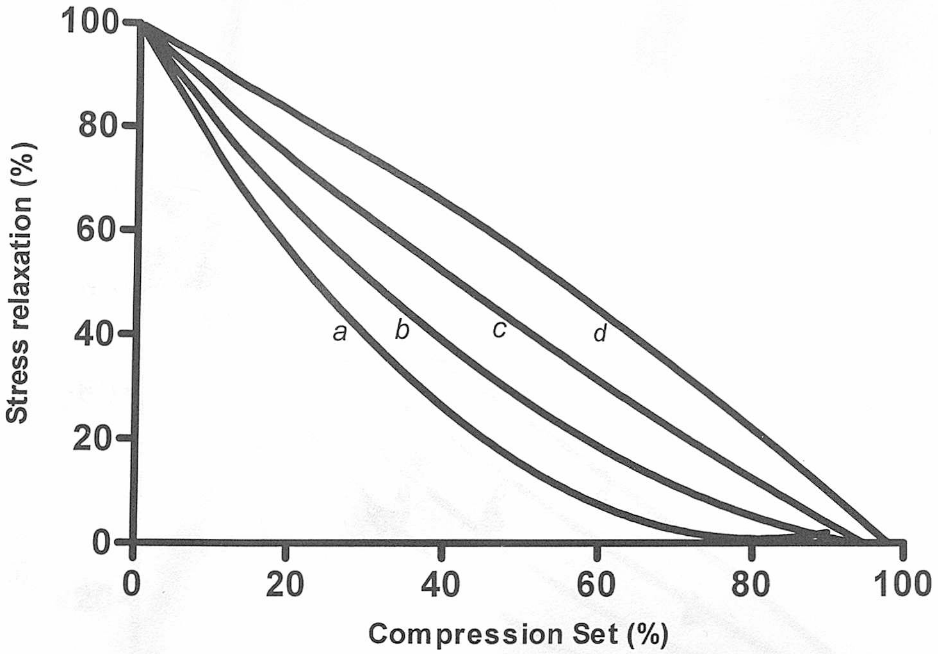

Figure 10.4: Theoretical relationship between CSR and compression-set. Curve a, f=0.125, k=0; curve *b*, f=0.25, k=0; curve *c*, f=0.5, k=0; curve *d*, f=0.1, k=0.

The compression-set and stress-relaxation data obtained in the present investigation at various temperatures for all vulcanisates are tabulated in Table 10.4.

Temp	**ETU-lead system**						**Zisnet system**					
(°C)	**Sample 1 (%)**		**Sample 2 (%)**		**Sample 3 (%)**		**Sample 1 (%)**		**Sample 2 (%)**		**Sample 3 (%)**	
	CSR	CS	CSR	CS	CSR	CS	CSR	CS	CSR	CS	CSR	CS
23	82.4	1.6	84.1	1.5	82.8	1.5	82.4	0.2	82.4	1.0	82.4	1.6
40	83.0	1.7	84.7	3.6	83.6	2.0	83.0	0.8	83.0	1.1	83.0	1.1
70	89.3	3.5	87.0	1.7	84.0	2.1	82.4	1.6	82.4	3.4	82.4	0.6
95	83.8	5.3	83.8	5.3	83.8	2.8	81.3	5.8	81.3	7.5	81.3	8.9
130	83.0	7.2	83.0	10.3	83.0	8.2	73.9	9.6	73.9	12.2	73.9	10.1
160	72.6	17.9	72.6	19.1	72.6	18.5	58.1	29.6	58.1	28.1	58.1	27.7
180	46.2	37.4	46.2	35.8	46.2	36.4	34.8	34.0	34.8	32.0	34.8	34.0

Table 10.4: Compression-set and stress-relaxation data at various temperatures

By superimposing the data given in Table 10.4 with the curves shown in Figure 10.4, Figure 10.5 is obtained.

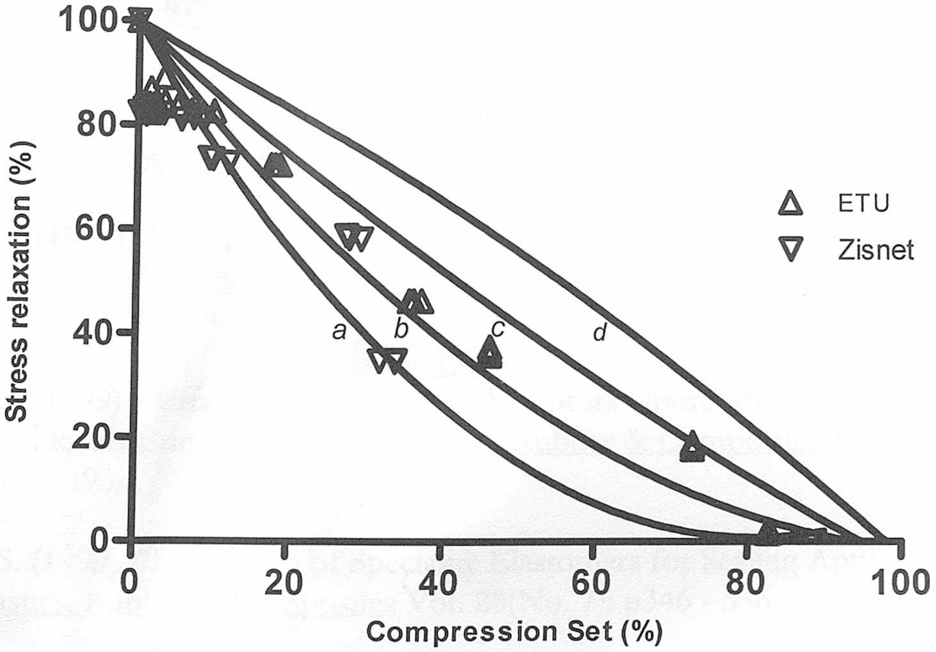

Figure 10.5: Relationship between CSR and compression-set for the two cure systems at various temperatures (23°C, 70°C, 95°C, 130°C, 160°C and 180°C after 6 hours).

Figure 10.5 shows that vulcanisates based on the Zisnet-FPT system predominantly fall on curve *(a)* where *f* (fraction of broken chains which become reconnected) is 0.125. On the other hand, vulcanisates cured by the ETU-lead system show an affinity for curve *(b)* which is associated with a higher *f*-value of 0.25. Comparison of the results indicates that the vulcanisates produced by the ETU-lead system have a higher fraction of broken chains which become reconnected. At a given *F*, the *S* (set) increases with increase in *f* values. Ellul and Southern *[Ellul and Southern, 1985]* are of opinion that, provided the constant *k*, α and *f* do not vary too much, the theoretical curves form a relatively narrow envelope. The work presented here indicates that there is a broad correlation between compression stress-relaxation and compression-set.

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Chapter 11

CONCLUSIONS AND FUTURE WORK

The first section of this chapter concludes the findings of the present work. The second section delineates the possibilities for potential further work based on the findings of the present investigation when considered in its entirety.

11.1 CONCLUSIONS

The main issues surrounding the present investigation are summarised below:

a) The ETU-Lead system traditionally used to vulcanise ECO elastomers is now considered hazardous. ETU is a known carcinogenic while Lead causes various problems in manufacturing and has raised environmental concerns.

b) Compression stress-relaxation (CSR) measurements require fairly sophisticated apparatus and this may cause problems for the main and supporting rubber industries. For such industries compression-set measurements are simple, facile and require little expertise. CSR measurements give a direct measure of sealing efficiency; however, compression-set is considered an important secondary requirement. Indeed, owing to the simple nature and ease of interpretation of compression-set measurements it is highly desirable to establish a meaningful relationship between CSR and set.

c) The lack of technical data on ECO elastomers in the literature has prevented field engineers from selecting better materials for correct sealing applications. At present, automotive and industrial engineers have to rely on Nitrile, Chloroprene and EPDM as well as Viton for their engineering applications. This has somewhat limited the advancement and development in various engineering sectors such as automotive, defence and aerospace.

In order address some of the issues delineated above, the present work aims to:

a) To replace the hazardous cure system of ECO elastomers by introducing an alternative system known as Zisnet-FPT. In order to ensure the new system is able to match the superior set properties produced by ETU-Lead system, the new system was optimised by utilising a technique known as the response surface method or *Central Composite Rotatable Design (CCRD)*.

b) To examine the possible correlation between properties related to sealing such as set and stress-relaxation by using a mathematical approach. By using data from simple compression-set tests, it was possible to estimate CSR indirectly.

c) To acquire a deeper understanding of the behaviour of ECO elastomers in terms of: diffusion, effect of filler, solvent-polymer interaction parameter (χ), crosslink density, response to optimisation by statistical approach as well as long term prediction of properties. All the aforementioned properties are believed to be important in attempting to obtain an overall assessment of ECO elastomers as a sealing material.

The results obtained in Chapter 4 show that vulcanisates cured by ETU-Lead systems give marching- modulus cure behaviour. The Zisnet-FPT system however, does not have this problem and its maximum torque can be measured in the conventional way within a typical cure period i.e. 60 minutes. Although the introduction of Zisnet-FPT systems in ECO elastomers may eliminate marching-modulus cure issues altogether, other systems may display distinct marching-modulus type traces. In such situations it is necessary to devise a technique that can be used to assess reliable vulcanisation times of cure traces that fail to reach plateau values such as those displayed by ETU-Lead systems. In endeavouring to do this consistency is ensured and a homogenised cure level (95%) particularly for ETU-Lead based vulcanisates are feasible thus providing a fair and unbiased comparison with vulcanisates based on Zisnet-FPT systems.

In present work, a method known as the 'Analytical Method' introduced by Rigbi *[Rigbi, 1996]* is used. Two points were taken from the rheogram after the 'induction period' and the maximum torque, $T_{\max}$, was calculated. The detailed procedure is discussed in Chapter 4. The results from this method were rigorously verified by experimental results; tests were carried out in triplicate and were randomly repeated. As a further verification of the 'Analytical Method' the procedure was repeated for rheograms produced from Zisnet-FPT cure systems which displayed distinct 'plateau' states. It was found that this technique satisfactorily calculated the $T_{\max}$ with approximately 5% deviation. The work carried out on Zisnet-FPT samples clearly demonstrates the reliability and utility of the Rigbi method. The application of this method also leads to considerable savings with respect to time and cost.

In the present work, the diffusion coefficient, *D,* of ECO elastomers was determined by means of simple gravimetric technique. This was done by measuring the water uptake of vulcanisates based on ETU-lead curing systems but containing various acid acceptors. Different acid acceptors have been known to produce variable water uptake characteristics. The vulcanisate based on Zisnet-FPT system was also included for comparison. Square shaped samples with nominal thicknesses (1.0 mm) were immersed in distilled water at a temperature of 25± 0.5°C. The samples were individually weighed every hour for the first 6 hours. The weighing frequency was subsequently reduced to once in several hours or to once a day depending on the rate of water uptake. The whole process took about 60 days. Generally, after the sixty-day period, no further significant water absorption was observed and the samples appeared to reach equilibrium states. A detailed procedure of the method just described is given in Chapter 5. The mixes based on

ETU-Litharge and Zisnet-FPT reached their maximum water uptake values at about the same time (approximately after 860 hours). The mix based on the ETU-ZnO combination was the first to reach maximum water uptake, that is, after approximately 190 hours.

As the rates of water uptake were at their maximum during the initial stage of immersion, it was expedient to analyse the first 6 hours of absorption in more detail. Based on this analysis, linear plots were obtained in which the slopes allowed the determination of diffusion coefficients, *D,* for each vulcanisate. The *D* value for ETU-Litharge system was found to be slightly higher than that of Zisnet-FPT system with values 4.552 $\times 10^{-13}$ m^2/s and 3.624 $\times 10^{-13}$ m^2/s respectively. The mix designated as ETU-CaO gave the lowest value of all, that is, 0.388 $\times 10^{-13}$ m^2/s. On the other hand, the system based on the ETU-ZnO combination gave the highest *D* values, for instance, 24.936$\times 10^{-13}$ m^2/s.

Vulcanisates with characteristically high *D* values absorbed water at a faster rate as compared to those with lower values. This is confirmed by the mix containing ETU-ZnO, which reached its maximum water uptake in the shortest period. However, the mix with highest *D* value does not necessarily absorb the highest amount of water. In this case, it is clear that the *D* value is a measure of 'rate' of water uptake rather than magnitude of absorption. There is no significant difference between ETU-Lead system and Zisnet-FPT systems in terms of their *D* values.

The complexities of the diffusion mechanism were discussed briefly in Chapter 5. Previous work by Karuppiah *[Karuppiah, 1987]* suggest two simultaneous mechanisms that take place as samples approaches equilibrium water absorption: First, water diffuses into the rubber phase. Second, some of the water absorbed into the rubber phase will come into contact with the hydrophilic impurities and form droplets of solution around the impurities. Equilibrium is attained when the pressure within the droplets is equal to elastic pressure of the surrounding rubber network.

Carbon black is one of the most important components in the manufacture of rubber products, with consumption second only to elastomer itself. This is particularly so when it was discovered to be an 'active' filler in elastomers at the beginning of 1960s. In one of the most well-documented accounts, Kraus *[Kraus, 1965]* has reported a phenomenon using the term *reinforcement* which has a profound effect on today's rubber industry. Therefore it was considered important to quantify the reinforcing effect of carbon black in ECO elastomers both in the ETU-Lead and Zisnet-FPT systems. In the present work, a simple method based on torque measurements obtained from a typical rheogram was used. Both cure systems were systematically loaded with different levels of carbon black ranging from 0 – 50 pphr. At each filler level, the increase in torque was measured and recorded. This procedure is discussed in its entirety in Chapter 6. As anticipated, the torque measurements were found to increase proportionally with increases in carbon black loading. The relative differences in torque for both systems were plotted against filler loading, *X,* which produced linear plots. Finally, the slopes, α_f, were calculated. The dimensionless parameter α_f values of vulcanisates based on the ETU-Lead systems and Zisnet-FPT systems were found to be 0.02451 and 0.01225 respectively. The α_f value for ETU-Lead system was almost twice that of the Zisnet-FPT system.

Although Wolff and Wang *[Wolff, Wang et al., 1993]* suggested that α_f of all furnace blacks is independent of the cure system, they asserted that α_f is dependent on the carbon black structure primarily. Wolff and co-workers suggested that α_f is a measure of the structure that remains after mixing; and, it is generally believed that a significant part of the carbon black network is destroyed mainly by shear deformation during mixing. However, in the opinion of the author this is unlikely because the carbon black network that remains after mixing is 'persistence structure' and is held together tenaciously. Therefore, there is some degree of doubt whether α_f is indeed a measure of 'secondary network'.

It is generally known that the surfaces of carbon blacks are replete with chemical groups such as ketones, aldehydes, carboxylic acid groups and so forth. Thus, it is plausible that the nature of such surface chemistry may lead to a chemi-physical interaction between filler surface and vulcanisation system. If such interaction were to exist then this would certainly explain the differences in the stiffening action as reflected by α_f values.

Crosslink density measurements are founded on swelling procedures using the well-known Flory-Rehner equation *[Flory and Rehner, 1943]*. The χ values (solvent-polymer interaction parameter) were determined based on the two-solvent method as explained by Hayes *[Hayes, 1986]*. The samples that were allowed to attain equilibrium swelling in trichloroethane showed lower degree of swelling as compared with chloroform as the swelling liquid. The low degree of swelling indicated by high υ_r values is a reflection of high crosslink density.

The carbon black was deliberately excluded to eliminate complications during measurement of crosslink densities. Filler, especially carbon black, has the capacity to restrict the expansion of the network during swelling process. This often leads to over-estimates of the crosslink densities of rubber networks. It was found that the crosslink density produced by ETU-Lead system was on average 7.679×10^{-5} mol/g, nearly twice as high compared to the Zisnet-FPT system which produced a value of 3.2662×10^{-5} mol/g. As the crosslink density increases, so too does the modulus.

As the ETU-Lead formulation used in the present work gives higher crosslink density than the Zisnet-FPT formulation, it is generally believed that its compression-set properties are also more superior and more stable. To understand the 'interaction' between rubber chemicals in the vulcanisation system, an advanced method known as *CCRD* was employed. The experimental work was systematically designed in order to investigate any possible response (in terms of compression-set) due to 'interactions' between two or more 'factors', in this case, selective rubber additives. It was found that the ETU-Lead curing showed a insignificant response to carbon black. It is also found that the 'interaction effect' between ETU and Litharge is highly significant in terms of compression-set behaviour. On the other hand, the compression-set for samples containing Zisnet-FPT system is highly 'dependent' on carbon black. Although the way in which carbon black interacts with other ingredients, especially with Zisnet-FPT, is not yet fully understood, *CCRD* has provided a useful means of identifying additives that significantly affect the properties, in this case compression set. The *CCRD* methodology generates response equations; thereby allowing selective manipulation of compounding ingredients to give the desired set properties. The results have shown that the calculated set properties from the response equations have successfully mirrored the experimental results. The accuracy of this procedure was rigorously examined. More than five hundred compression-set tests were systematically carried out according to the design demanded by the *CCRD* approach.

It was also thought desirable to attain some level of understanding on the way in which compression-set of ECO elastomers varies in long-term applications. Knowledge in this matter is important because most rubber products that depend upon compression-set for their integrity, such as gaskets, seals, o-rings cannot be monitored easily during service. Studies pertaining to long-term prediction of compression-set was based upon the 'Arrhenius Relationship' *[Arrhenius, 1889]*. Detail procedures are discussed in Chapter 9. The results have shown that ETU-Lead systems consistently give longer service times before reaching a specific failure criterion. The Arrhenius approach indicated that the ETU-Lead samples should be able to maintain their integrity for up to 10 years. The Zisnet-FPT was predicted to last up to 132 days before it reach the failure limit. However, it is worth noting that in industrial applications the failure limit is normally 50% (based on original dimensions) *[Brown, 2001]* as opposed to the stringent failure criterion used in present work, that is, 20%.

Long-term compression-set studies gave activation energies of 75.8320 $kJmol^{-1}$ and 51.5135 $kJmol^{-1}$ for the ETU-Lead and Zisnet-FPT systems respectively. This data is very useful as it can be used to approximate longevity by measuring the change in compression-set at single temperature only.

Previous work *[Ellul and Southern, 1985]* has shown that there is broad correlation between compression-set properties and compression stress-relaxation. The mathematical expression developed by Ellul and Southern was used in this work. The results were found to be satisfactory although the value *f*, fraction of broken chains which become reconnected, for Zisnet-FPT system is somewhat lower at 0.125. This indicates lower fraction of broken chains that become reconnected. ETU-Lead systems, on the other hand, have a slightly higher *f* value of 0.25. (Note, *f* is a dimensionless constant). This phenomenon could largely be due to higher crosslink density produced in the ETU-Lead system resulting in a greater possibility of broken chains that become reconnected. Overall, the trends that were observed and the mathematical approach introduced by Ellul *[Ellul and Southern, 1985]* proved to be compatible. Although it is safe to rank the stress-relaxation of ECO elastomers from compression-set behaviour, the use of this model to calculate their absolute values to predict one or the other properties must be used with great caution.

In short, the present work can be summarised as follows:

- The technique to deal with marching modulus cure was satisfactorily established.
- The water uptakes of different cure systems were measured. This is important as different acid acceptors (in ETU-based system) would take up different levels of water absorption which can vitiate set properties and stress-relaxation.
- The stiffening effect of carbon black on both systems was examined. The results have provided some information on the stiffening effect of carbon black on both cure systems.

- The solvent-polymer interaction parameter, χ, of ECO elastomers, which is not readily available in the literature, has been determined. This value is necessary to determine the crosslink density of ECO elastomers produced by systems containing various curing recipes using the Flory-Rehner relationship.
- The response surface equations were generated by using the *CCRD* methodology. This procedure allowed the compression-set of ECO elastomers to be optimised without resorting to repetitive arduous experimental procedures. These equations were rigorously verified.
- The compression-set in long term applications was predicted using both the Empirical approach*[British Gas, 1984]* and the Arrhenius relationships*[Arrhenius, 1889]*. The Zisnet-FPT system was found to have a shorter service time. The activation energies of ECO vulcanisates for both cure systems were determined. These values can be used to predict the service life by measuring the changes of a given elastomer property at one temperature.
- The mathematical model developed by Elull *[Ellul and Southern, 1985]* was examined and found to be useful in correlating compression-set and stress-relaxation. Although it must be used with great care, it has enabled one to calculate the stress-relaxation values from compression-set measurements. This is useful for ranking purposes.

In addressing the issues outlined at the beginning of this chapter, the Zisnet-FPT system should not be considered a panacea. Although it has been available for some time, improvement is still under way. From the present work, it has become clear that the ingredients in the Zisnet-FPT formulation need to be optimised. These include ingredients such as $CaCO_3/MgO$, carbon black (FEF), DPG as well as Zisnet-FPT itself. It is hoped that the findings of the present work will significantly supplement the technical data in the public domain and thereby facilitate the selection process.

11.2 FUTURE WORK

Although ECO elastomers have been commercially available for some time, it is still fairly new in the field of sealing applications. It has not been used extensively as one would hope; one suspects that this may be due to lack of fundamental technical data, not to mention problematic cure systems which might cause environmental concerns. In 1966, when U.S Army developed new propulsion system for their LANCE missile, several elastomers were considered to be used for sealing applications (as it involved bipropellant liquid-propulsion). Due to its extreme operating condition (from -40°C to 60°C), in the end the LANCE Project researchers settled for Chlorobutyl rubber *[McManus and Piken, 1966]*. The properties of Butyl rubber are approximately equivalent to Chloroprene. However, ECO elastomers are far more superior. In his report, McManus clearly states that the selection of Butyl was only for short term exposure and urged rubber and chemical industries to continue their development to meet the stringent challenges for such an application. Here, ECO is a likely candidate for such an application.

Based on the work carried out thus far, it is thought the following future work may provide important insights:

- Further investigation of the interaction between carbon black and the Zisnet-FPT system. An interesting approach would be to graphitise carbon black in order to eliminate the surface reactivity of the black.

- Study the set and stress-relaxation of both cure systems; but, with equivalent crosslink densities. Although different types of crosslink will be obtained, it would be interesting to find out if the equal amount of crosslinks (per gram of rubber) could produce comparable set properties. This could enhance longevity in ECO containing the Zisnet-FPT system.
- Re-examine present formulations in terms of improving longevity. Present response surface equations are designed to optimise the magnitude of compression-set and not longevity.

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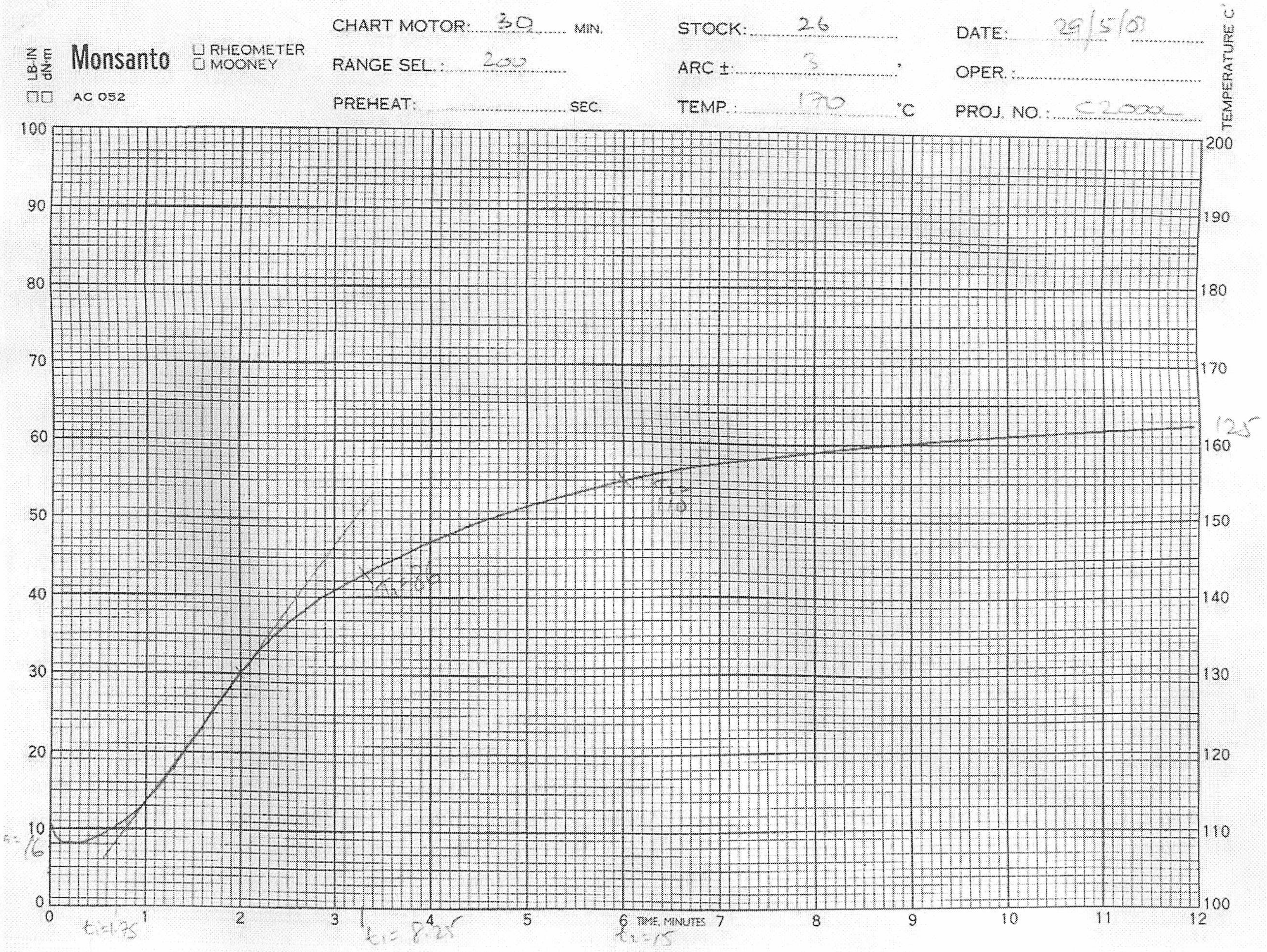
APPENDIX A

Marching modulus cure rheograms for Chapter 4.



Monsanto ☐ RHEOMETER ☐ MOONEY

LB-IN ☐ dN·m ☐

AC 052

CHART MOTOR: 30 MIN.

RANGE SEL.: 200

PREHEAT: SEC.

STOCK: 26

ARC ±: 3 °

TEMP.: 170 °C

DATE: 29/5/08

OPER.:

PROJ. NO.: C2000

ETU-Lead system sample 1 (stock no. 26)

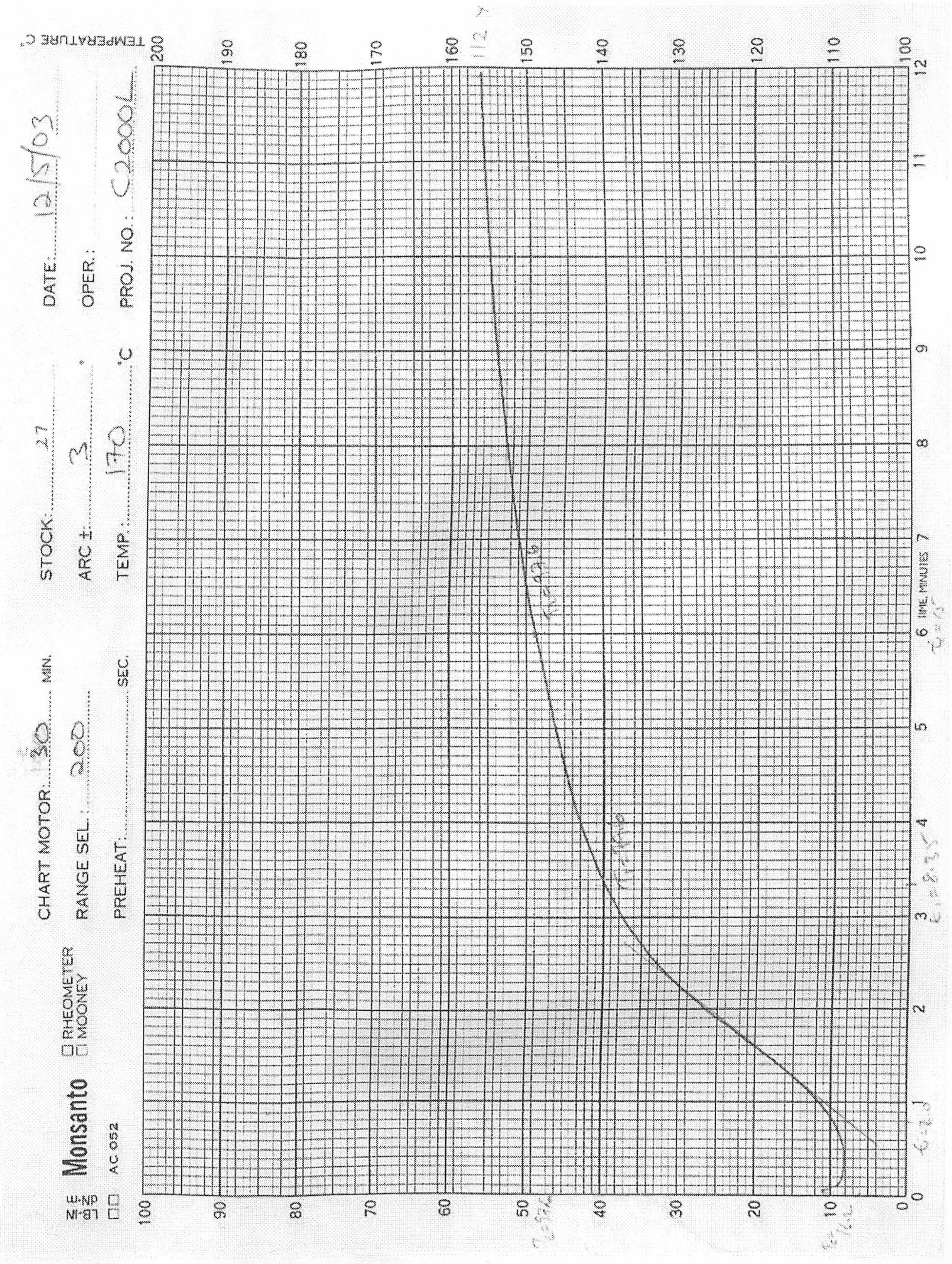
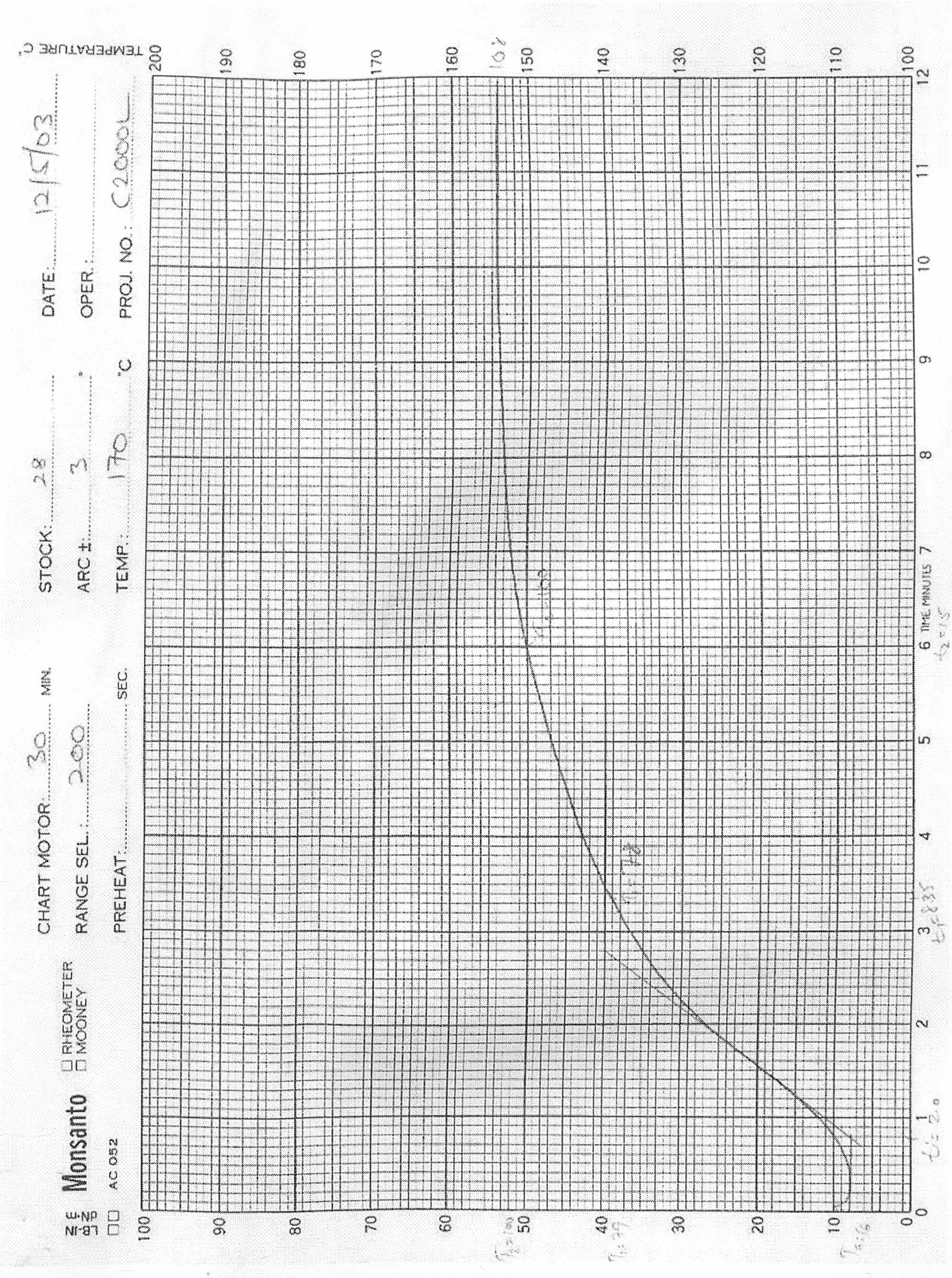


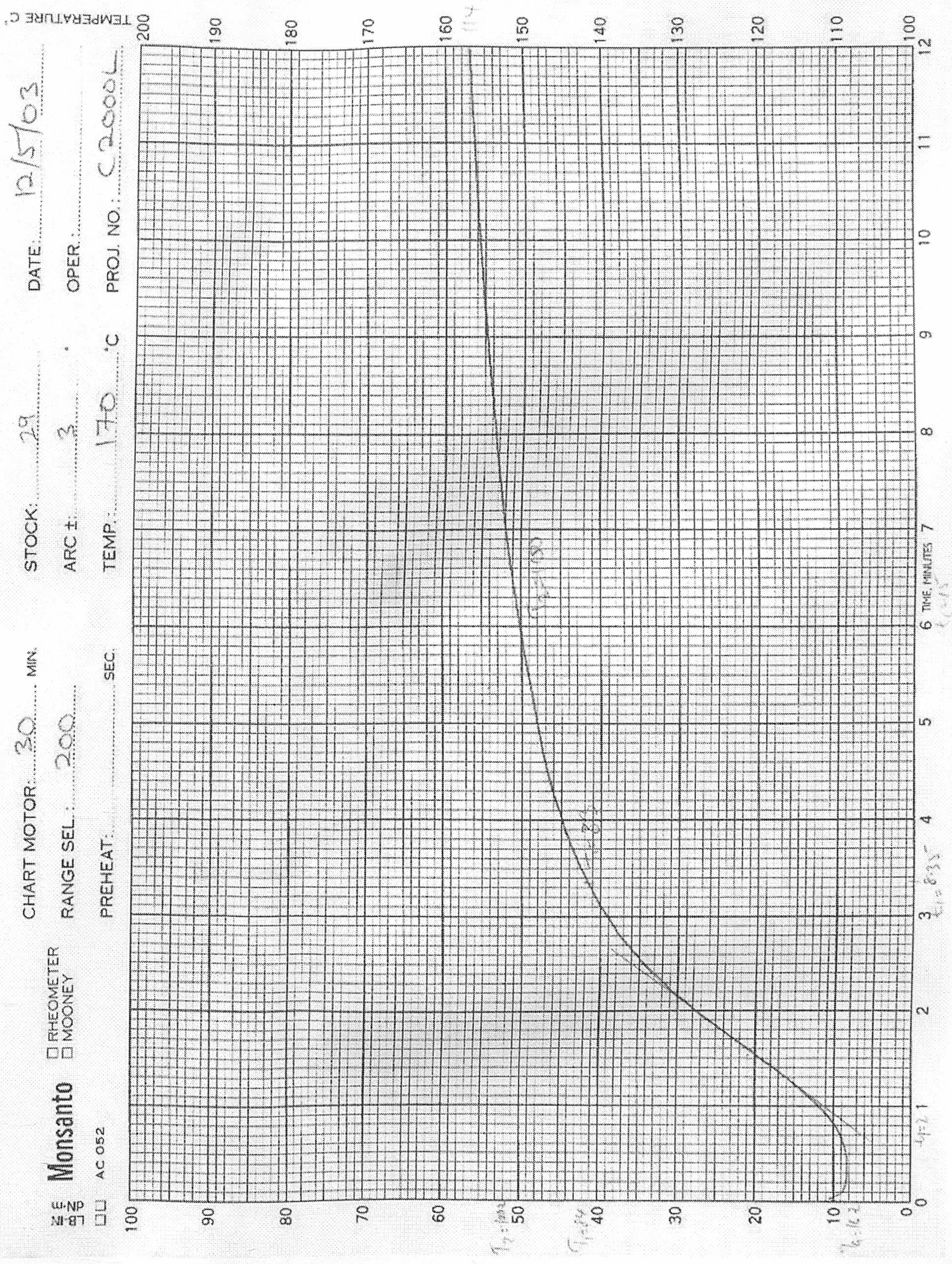
CHART MOTOR: 30 MIN.
RANGE SEL.: 200
PREHEAT: SEC.
STOCK: 27
ARC ±: 3 °
TEMP.: 170 °C
DATE: 12/5/03
OPER.:
PROJ. NO.: C2000L

ETU-Lead system sample 2 (stock no. 27)



Monsanto
AC 052
☐ RHEOMETER
☐ MOONEY
CHART MOTOR: 30 MIN.
RANGE SEL.: 200
PREHEAT: SEC.
STOCK: 28
ARC ±: 3 °
TEMP.: 170 °C
DATE: 12/5/03
OPER.:
PROJ. NO.: C2000L

ETU-Lead system sample 3 (stock no. 28)



ETU-Lead system sample 4 (stock no. 29)

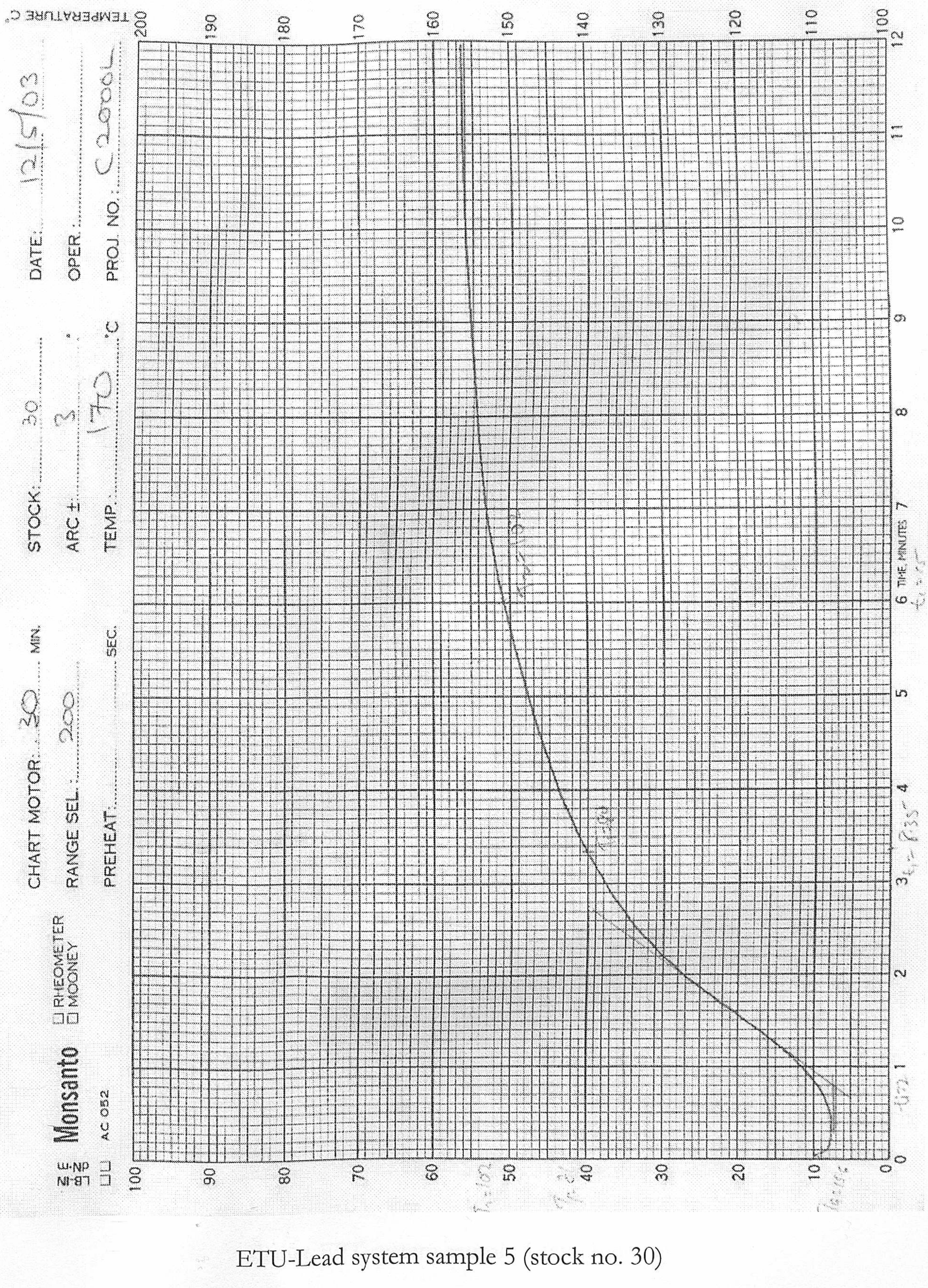
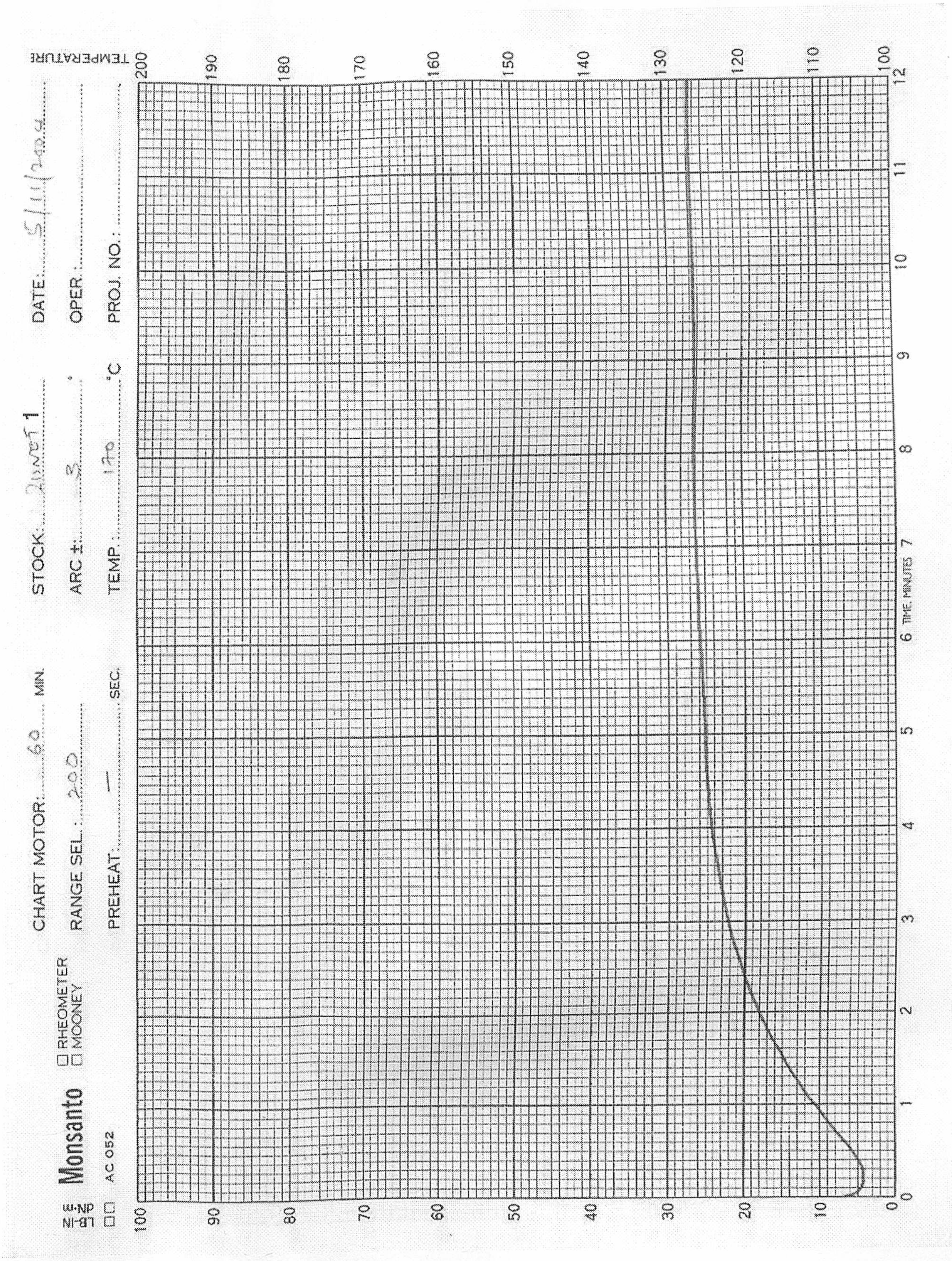


CHART MOTOR: 30 MIN.
RANGE SEL.: 200
PREHEAT: SEC.
STOCK: 30
ARC ±: 3 °
TEMP.: 170 °C
DATE: 12/5/03
OPER.:
PROJ. NO.: C200L

ETU-Lead system sample 5 (stock no. 30)



Monsanto ☐ RHEOMETER ☐ MOONEY

AC 052

☐ LB-IN ☐ dN·m

CHART MOTOR: 60 MIN.

RANGE SEL.: 200

PREHEAT: — SEC.

STOCK: Zisnet 1

ARC ±: 3 °

TEMP.: 170 °C

DATE: 5/11/2004

OPER.:

PROJ. NO.:

Zisnet-FPT system sample 1 (stock no. 1)

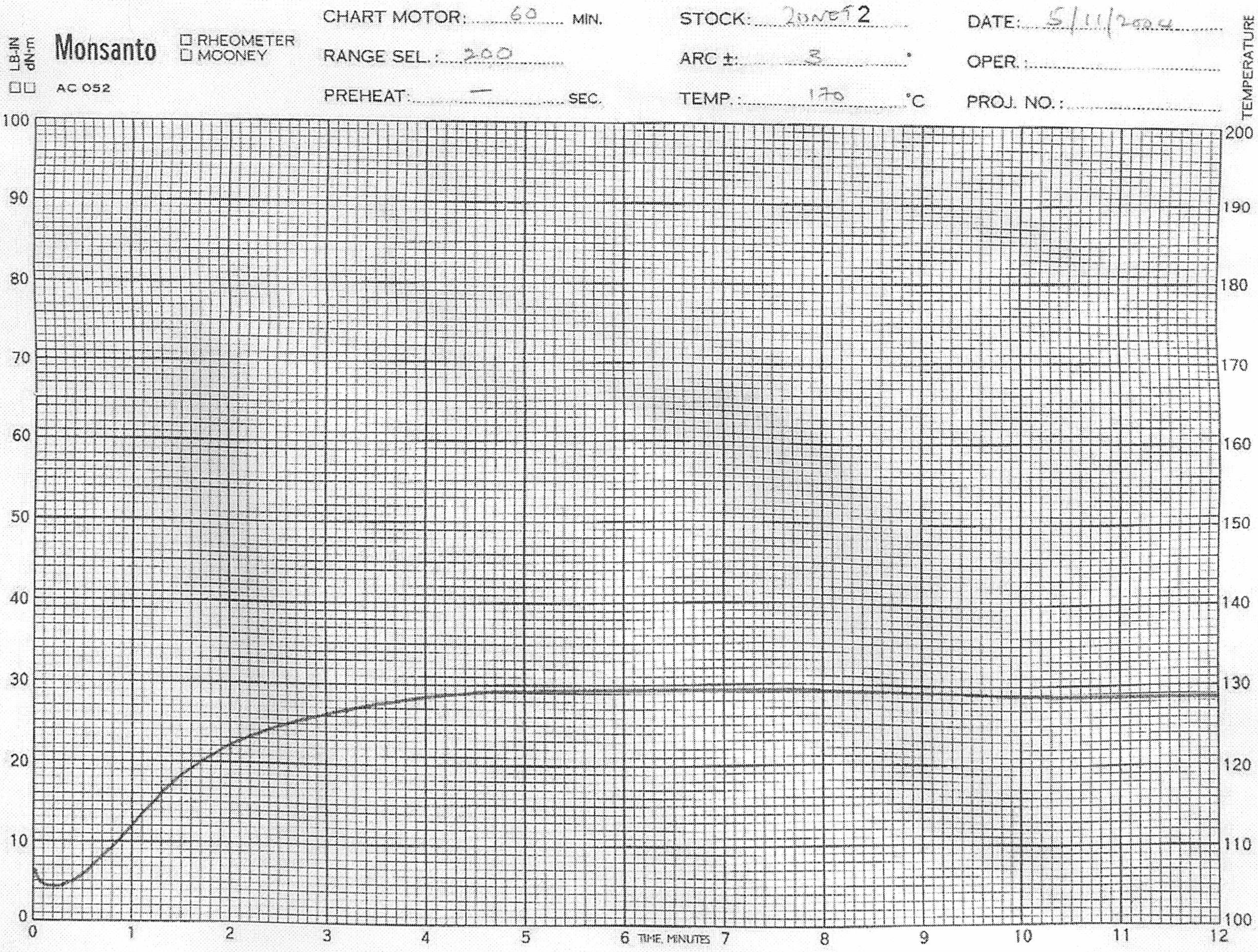


CHART MOTOR: 60 MIN.

RANGE SEL.: 200

PREHEAT: — SEC.

STOCK: ZSNET 2

ARC ±: 3 °

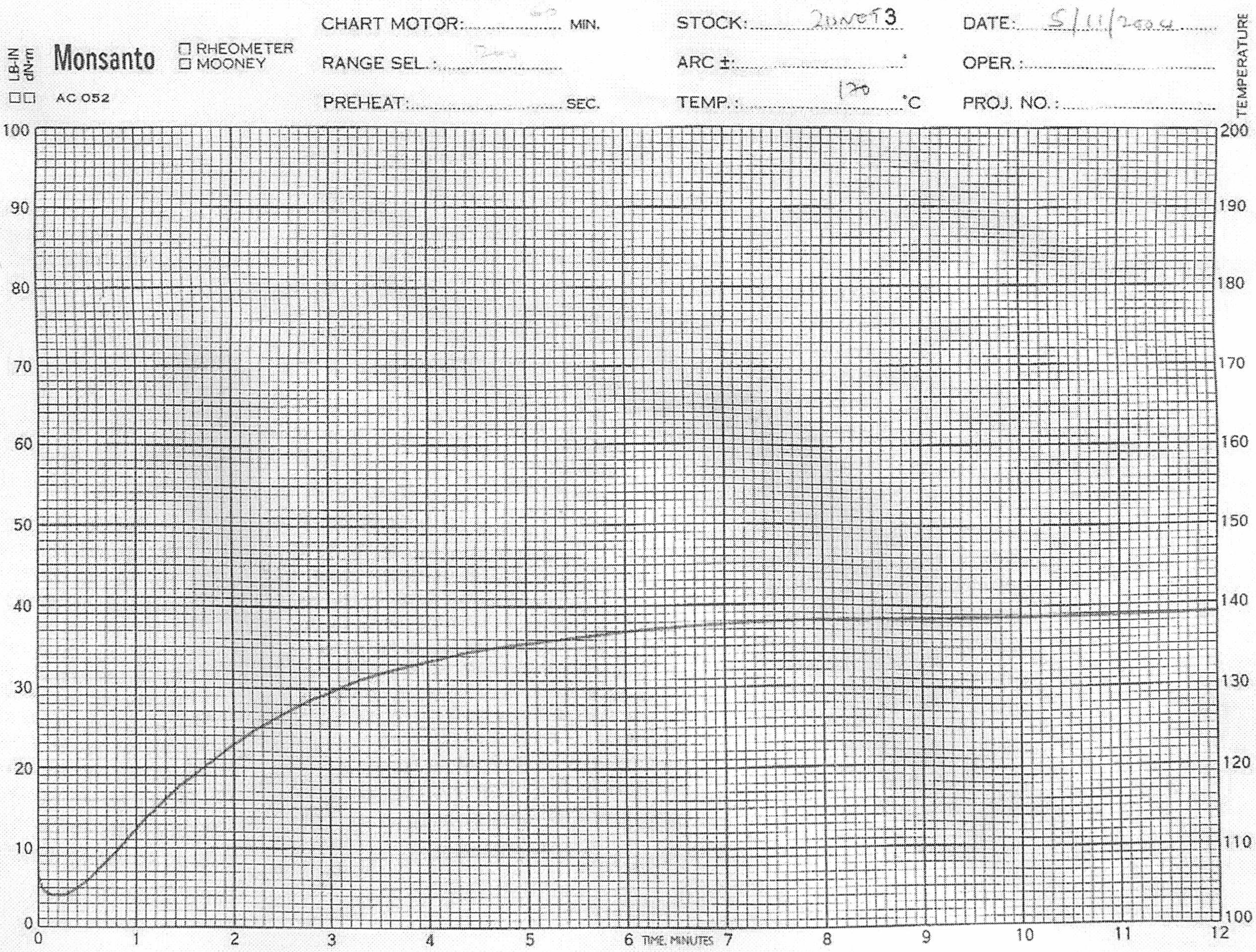
TEMP.: 170 °C

DATE: 5/11/2004

OPER.:

PROJ. NO.:

Zisnet-FPT system sample 2 (stock no. 2)



Monsanto ☐ RHEOMETER ☐ MOONEY
☐ LB-IN ☐ dN·m
AC 052

CHART MOTOR: 60 MIN.
RANGE SEL.: 200
PREHEAT: SEC.

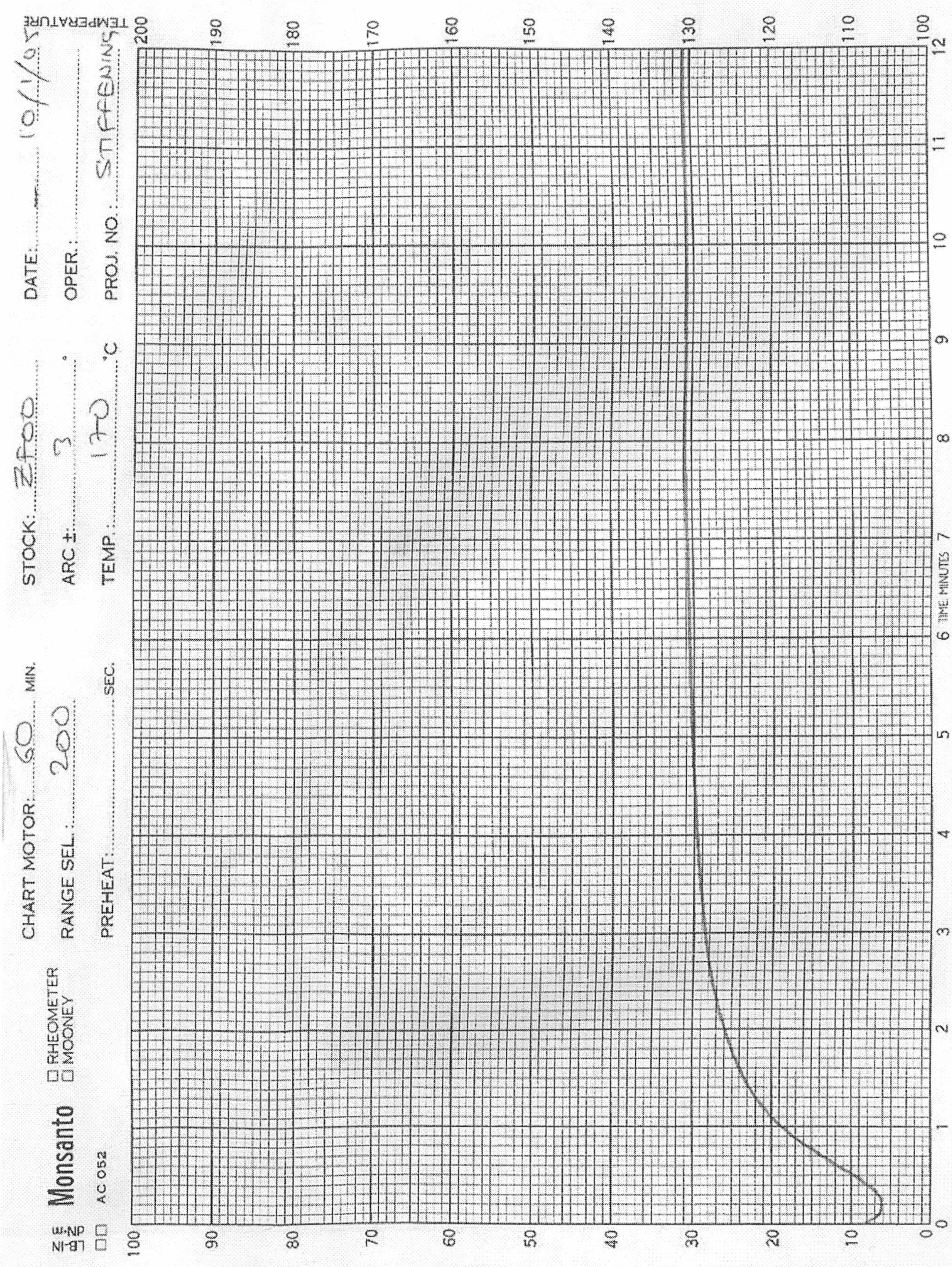
STOCK: Zisnet3
ARC ±: °
TEMP.: 170 °C

DATE: 5/11/2004
OPER.:
PROJ. NO.:

Zisnet-FPT system sample 3 (stock no. 3)

APPENDIX B

Rheograms (different filler concentration) for Chapter 6.



LB-IN ☐ dN·m ☐

AC 052

Monsanto ☐ RHEOMETER ☐ MOONEY

CHART MOTOR: 60 MIN.

RANGE SEL.: 200

PREHEAT: SEC.

STOCK: ZF00

ARC ±: 3

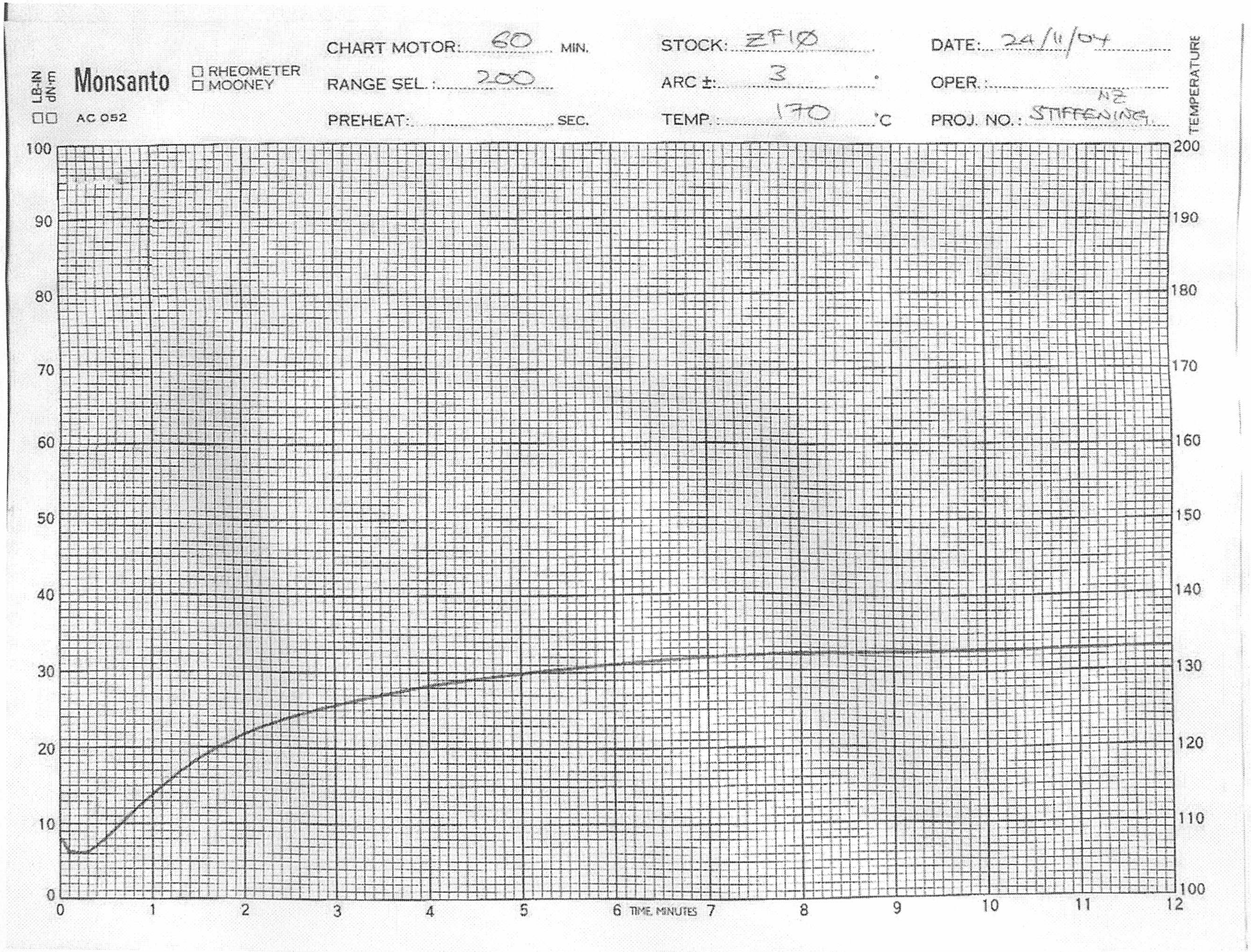
TEMP.: 170 °C

DATE: 10/1/05

OPER.:

PROJ. NO.: STIFFENING

Gum rubber (0 pphr of FEF carbon black)



Monsanto ☐ RHEOMETER ☐ MOONEY

☐ LB-IN ☐ dN·m

AC 052

CHART MOTOR: 60 MIN.

RANGE SEL.: 200

PREHEAT: SEC.

STOCK: ZF10

ARC ±: 3 °

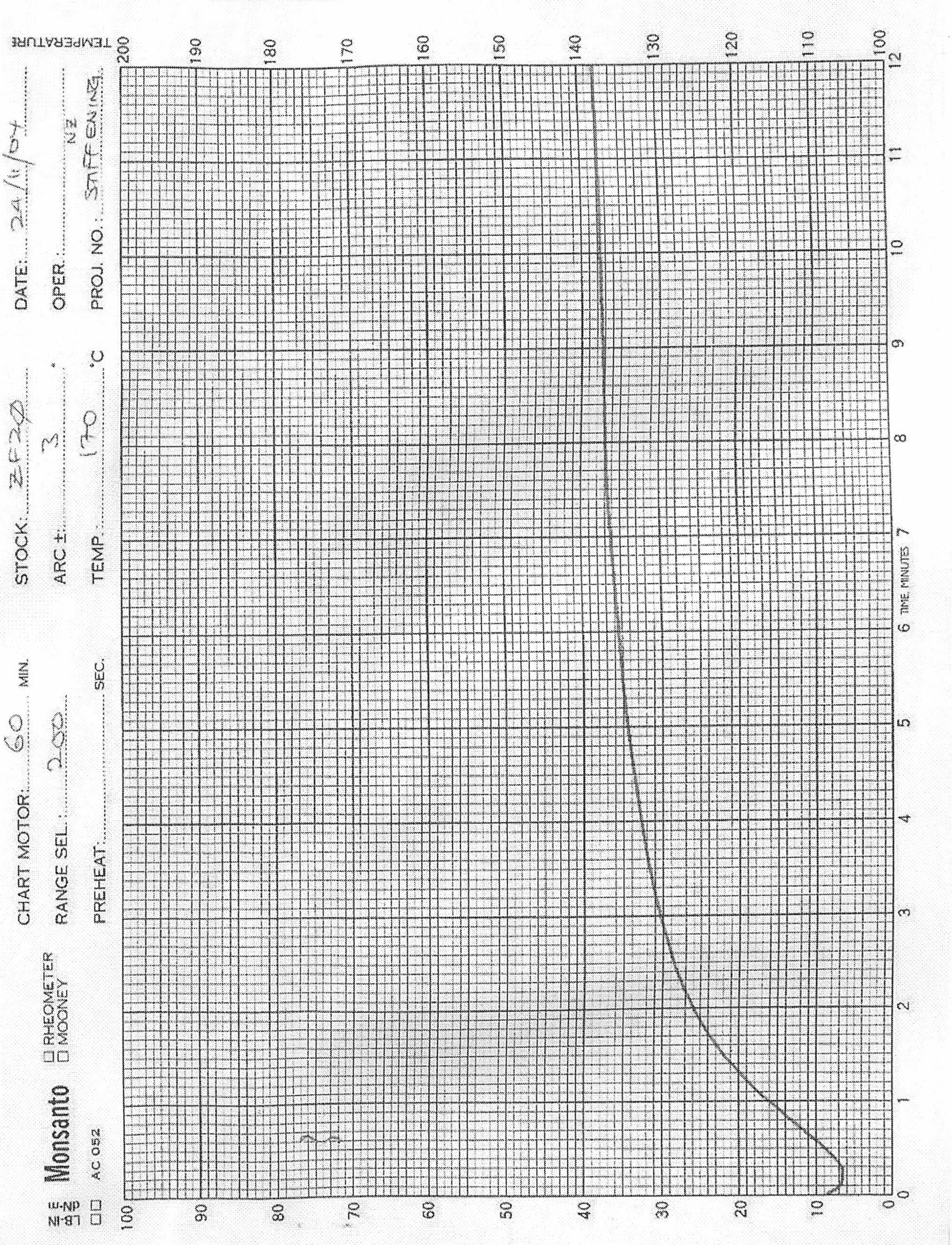
TEMP.: 170 °C

DATE: 24/11/04

OPER.: NZ

PROJ. NO.: STIFFENING

10 pphr of FEF carbon black



Monsanto ☐ RHEOMETER ☐ MOONEY

☐ LB-IN ☐ dN-M

AC 052

CHART MOTOR: 60 MIN.

RANGE SEL.: 200

PREHEAT: SEC.

STOCK: ZF20

ARC ±: 3 °

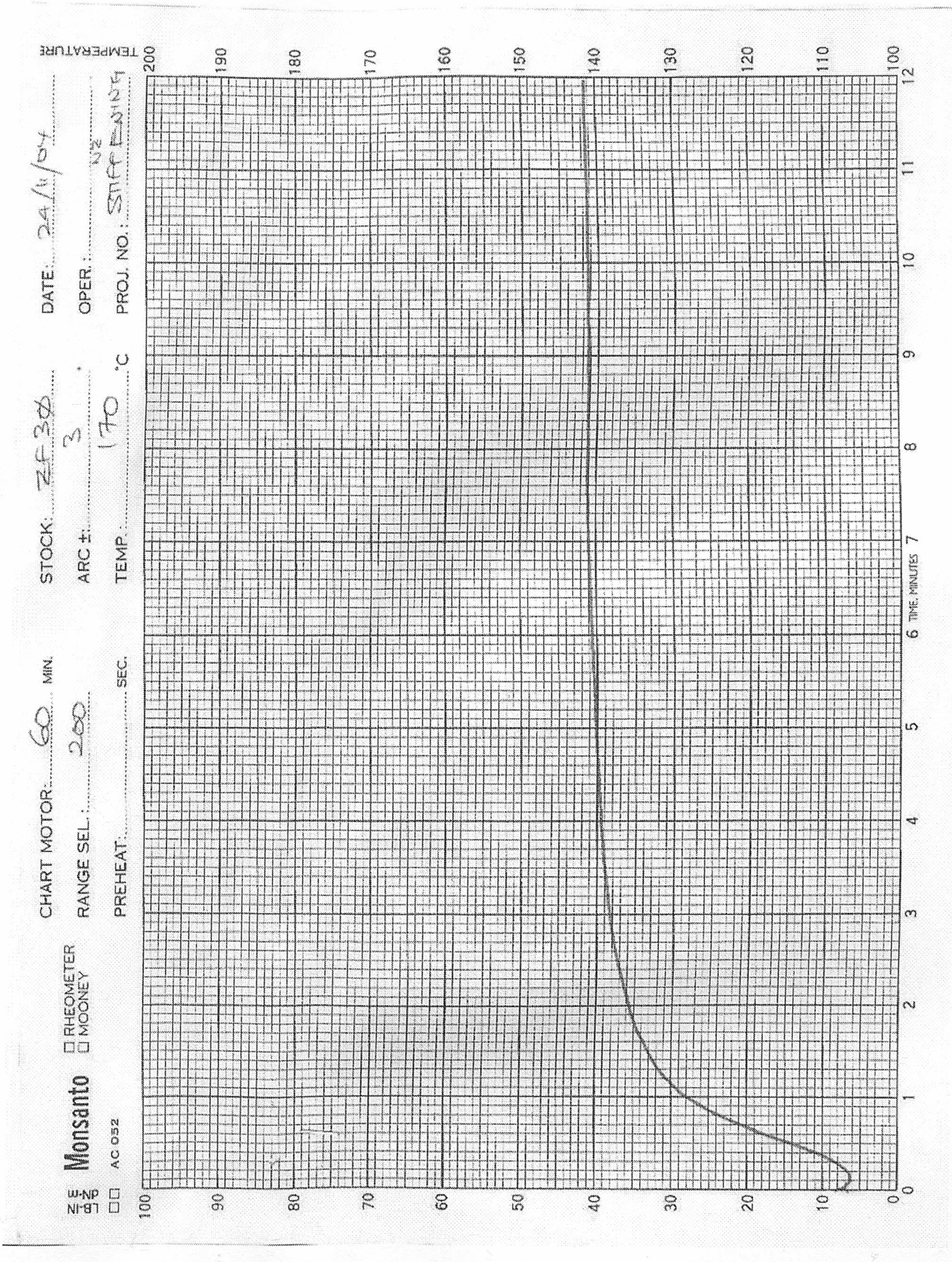
TEMP.: 170 °C

DATE: 24/11/04

OPER.: NZ

PROJ. NO.: STAFF ENG.

20 pphr of FEF carbon black



Monsanto ☐ RHEOMETER ☐ MOONEY

☐ LB-IN ☐ dN-m

AC 052

CHART MOTOR: 60 MIN.

RANGE SEL.: 200

PREHEAT: SEC.

STOCK: ZF 30

ARC ±: 3 °

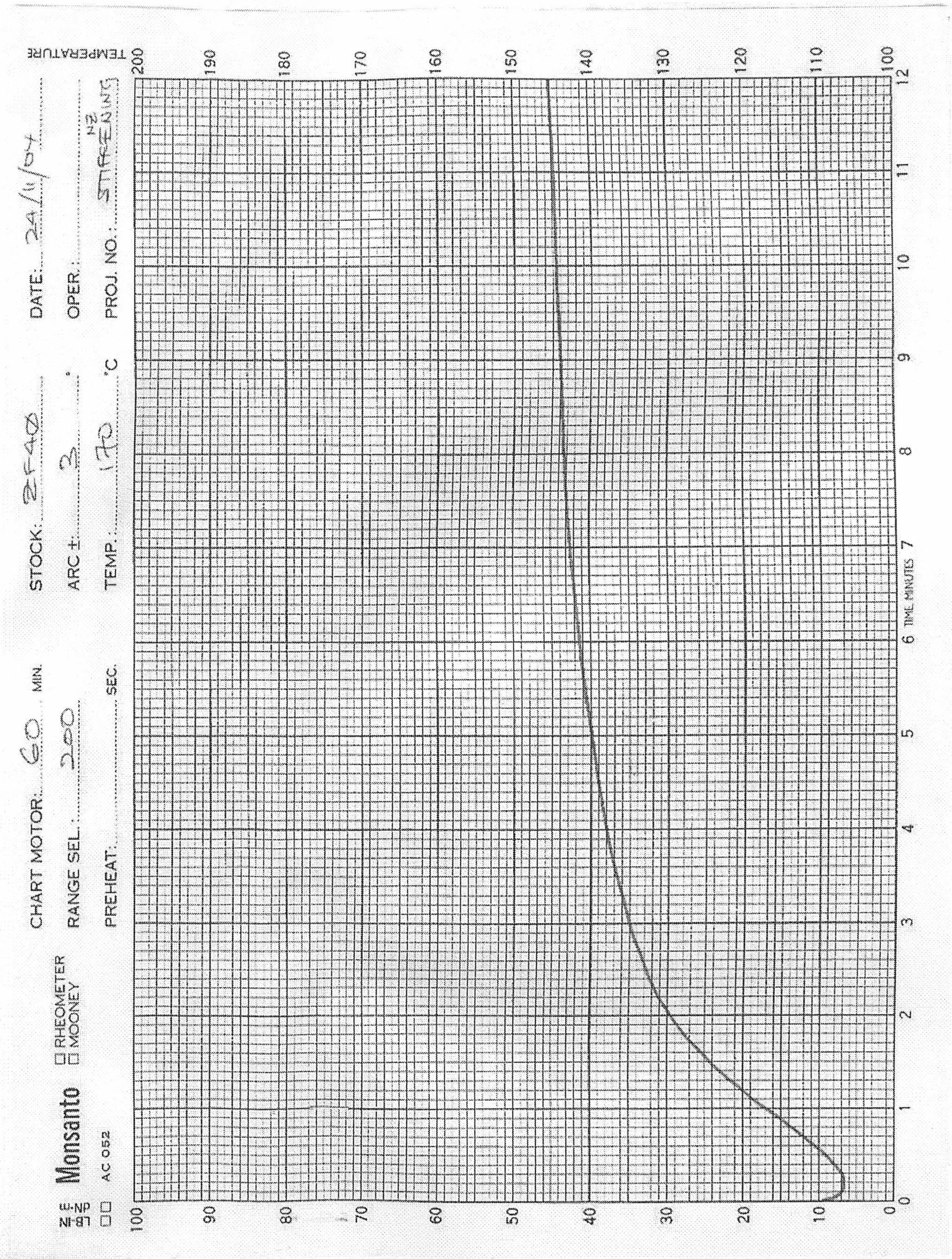
TEMP.: 170 °C

DATE: 24/11/04

OPER.: N2

PROJ. NO.: STIFFENING

30 pphr of FEF carbon black



Monsanto AC 052

☐ LB-IN ☐ dN-m

☐ RHEOMETER ☐ MOONEY

CHART MOTOR: 60 MIN.

RANGE SEL.: 200

PREHEAT: SEC.

STOCK: ZF40

ARC ±: 3 °

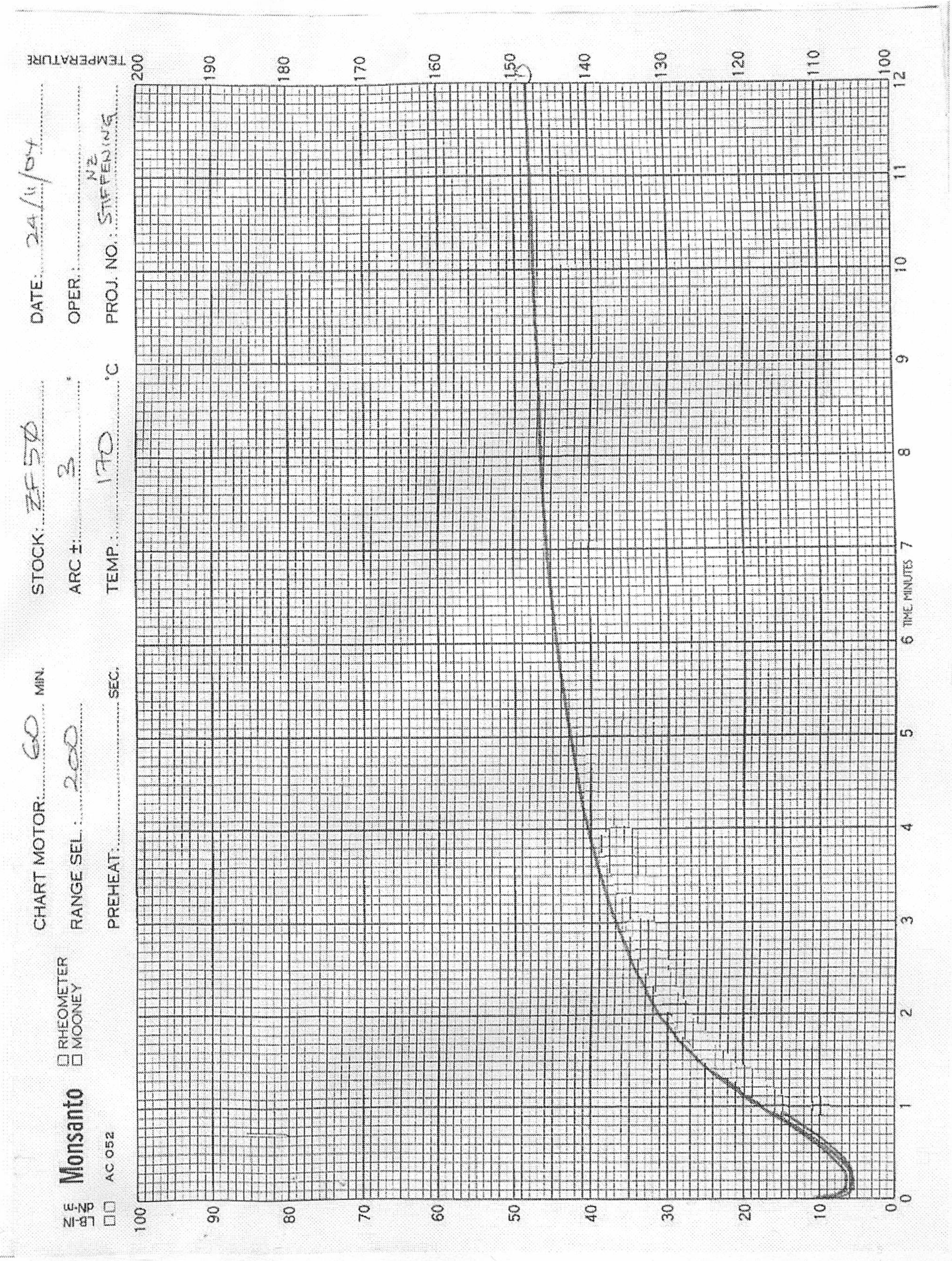
TEMP.: 170 °C

DATE: 24/11/04

OPER.:

PROJ. NO.: Mz STIFENING

40 pphr of FEF carbon black



50 pphr of FEF carbon black