# STUDIES ON SHORT SISAL FIBRE REINFORCED NATURAL RUBBER COMPOSITES

A THESIS SUBMITTED TO
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IN CHEMISTRY UNDER THE FACULTY OF SCIENCE

BY
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INDIA,
DECEMBER 1992

Dedicated to
My Teachers & Parents

# CERTIFICATE

This is to certify that the thesis entitled 'STUDIES ON SHORT SISAL FIBRE REINFORCED NATURAL RUBBER COMPOSITES' is an authentic record of the research work carried out by Mr. SIBY VARGHESE under our joint supervision and guidance, during the period from February 1989 to December 1992, in partial fulfilment of the requirements of the degree of Doctor of Philosophy, under the Faculty of Science of Mahatma Gandhi University. The work presented in this thesis has not been submitted for any other degree or diploma earlier. It is also certified that Mr. SIBY VARGHESE has fulfilled the course requirements and passed the qualifying examination for the Ph.D. Degree of Mahatma Gandhi University.

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# DECLARATION

I, SIBY VARGHESE, hereby declare that the thesis entitled **'STUDIES ON SHORT SISAL FIBRE REINFORCED NATURAL RUBBER COMPOSITES'** is a bonafide record of the research work done by me and that no part thereof has been presented earlier for any degree or diploma of any other university.

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# PREFACE

Reinforcement of elastomers with short fibres combines the rigidity of the fibre with the elasticity of rubber. The resulting composites are used in many applications especailly in hoses and V-belts. Currently a lot of research is being carried out in this field. However, no systematic study has been reported till date, on sisal fibre reinforced natural rubber composites. Therefore, a detailed investigation has been carried out on the above mentioned composite with special reference to the effects of chemical treatment of fibre, bonding agent, fibre loading and fibre orientation.

The subject matter of the thesis is presented in eight chapters.

The first chapter consists of a detailed review of the earlier work in the field of fibre reinforced polymer composites and the scope of the present work.

The experimental techniques and the details of the equipments used are described in chapter two.

Chapter three describes the mechanical properties of short sisal fibre reinforced natural rubber composites. The effects of acetylation, aspect ratio, concentration of fibre and bonding agent on the properties of short sisal fibre reinforced natural rubber composites are evaluated in this chapter.

The dynamic mechanical properties of NR composites filled with untreated and acetylated short sisal fibres are described in chapter four.

In chapter five, the melt rheological behaviour of acetylated sisal fibre reinforced natural rubber composites is described.

Chapter six describes the stress relaxation behaviour of acetylated short sisal fibre reinforced natural rubber composites.

The results of the investigation, on the solvent swelling of the composites filled with both untreated and acetylated fibre are presented in chapter seven.

The eighth chapter describes the degradation behaviour of short sisal fibre reinforced natural rubber composites containing acetylated and untreated fibre.

# GLOSSARY OF TERMS

$\Delta E$ = Activation energy for viscous flow
$\tau_{wa}$ = Apparent wall shear stress
$\dot{\gamma}_{wa}$ = Apparent shear rate at wall
XNBR = Carboxylated nitrile rubber
$L_c$ = Critical fibre length
Ap = Cross sectional area of the plunger
$d_c$ = Diameter of capillary
$d_e$ = Diameter of extrudate
EPDM = Ethylene propylene diene monomer rubber

$V_f$ = Fibre volume fraction
$W_f$ = Fibre weight fraction
$n'$ = Flow behaviour index
F = Force on plunger
$T_g$ = Glass transition temperature
HMT = Hexamethylene tetramine
HMMM = Hexamethoxy methyl melamin
HRH = Hexa-Resorcinol-Hydrated Silica
HDPE = High density polyethylene
L = Length of the fibre
$E''$ = Loss modulus
LDPE = Low density polyethylene
$\tau_y$ = Matrix yield stress
$\tan\delta$ = Mechanical loss factor
$T_m$ = Melting temperature
$E_L$ = Modulus of the composite in the longitudinal direction

$E_T$ = Modulus of the composite in the transverse direction

$Q_t$ = Mole uptake of the solvent/100 gm of polymer

NR = Natural rubber

CBS = N-cyclohexyl 2-benzthiazylsulphenamide

NBR = Nitrile rubber

SEM = Scanning electron microscope

$\eta$ = Shear viscosity

E' = Storage modulus

$\sigma_o$ = Stress at zero time

$\sigma_t$ = Stress at 't' time

$\sigma_{fu}$ = Ultimate fibre strength

$\sigma_{cu}$ = Ultimate composite strength

R = Universal gas constant

UTM = Universal Testing Machine

$V_m$ = Volume fraction of matrix

$V_I$ = Volume fraction of rubber in unswollen state

Q = Volumetric flow rate

$E_f$ = Young's modulus of fibre

$E_m$ = Young's modulus of matrix

# CONTENTS

# CHAPTER I

# INTRODUCTION

The mechanical properties of elastomers can successfully be improved by adding reinforcing ingredients, such as carbon black and silica. Lately it has become evident that the addition of a suitable short fibre results in further improvement in mechanical properties. Reinforcement of elastomers with short fibres combines the rigidity of the fibre with the elasticity of rubber. The industrial application of continuous fibre reinforcement of elastomers in many products such as tyres, hoses, V-belts, gaskets and oil seals is well known. The extent to which discontinuous fibre can approach the performance of a continuous cord, depends critically upon its modulus relative to that of the matrix. Performance of a short fibre-rubber composite depends on several factors, such as preservation of high aspect ratio (average length to diameter ratio of the fibre), control of fibre orientation, generation of a strong fibre-rubber interface, establishment of a high state of dispersion and optimum quality of the rubber compound to accommodate and facilitate stress transfer.

## I.1 Advantages of short fibres in comparison to cord reinforcement

In products such as conveyor belts and tyres, elastomers reinforced with continuous cords are used. The characteristics of this type of reinforcement are the following. The cord-rubber composite remains quite flexible both parallel to the direction of major reinforcement and more specially in the normal direction because (1) the reinforcement does not alter the rubber properties on a microscopic level and (2) the cords themselves are free to slide past each other in shear as the part is flexed. The reinforcing members are loaded directly and efficiently by the forces applied to the part, negating concern about stress transfer. In continuous fibre reinforced composites, the bonding to the rubber phase is critical in many applications. The reinforcement by continuous cord can be placed exactly into orientation patterns comprising either a single direction or a multiplicity of directions, represented by a laminate structure that optimizes mechanical performance.

On the other hand, reinforcement with short fibres also offers some attractive features. Advantages in using short fibre composite must represent negative attributes of the cord reinforcement.

The advantages of using short fibre composites are ease of fabrication, better economics at both the incorporation (mixing) and fabrication stages, high green strength, reduced and controlled shrinkage in moulded products, improved solvent resistance, better thermal ageing, and improved cut and tear resistance. The manufacture of a complex shaped engineering article is easily accomplished with short fibre composite which is impracticable from elastomers reinforced with continuous fibres.

Short fibres can be incorporated directly into the rubber compound along with other additives and the compounds are amenable to the conventional standard rubber processing operations such as extrusion, calendering and compression, injection or transfer moulding. Since the additional work such as dipping, wrapping, laying and placing of fibres generally associated with continuous cord reinforcement can be avoided, economic advantages are possible in the case of short fibre reinforced articles.

In general, well dispersed short fibres reinforce the rubber phase uniformly and their benefits can therefore be interpreted in terms of an improved set of rubber properties. Cord reinforcement, on the other hand, is more inhomogeneous with mechanical properties, widely different from those of the unreinforced matrix. Low concentrations ( $<$ 1 per cent, v/v) of discontinuous fibre reinforcement can be used to modify slightly the rubber behaviour which is very beneficial. Thus the distributes of short fibre reinforcement must be based on the difference from both non-reinforced compounds and cord-rubber composites.

## I. 2 Comparison with fibre reinforced plastics

It is interesting to have a comparison between the short fibre reinforcement of elastomers and thermoplastics. The high modulus of the plastic matrix in comparison to a rubbery material allows a more efficient transfer of stress to the short reinforcing fibre. The parameter $E_f/E_m$, which is the ratio of the Young's modulus of the fibre to that of the matrix, determines the length of fibre that is required for reinforcement.

Indeed, low performance unregenerated cellulose and textile fibres such as rayon, nylon and polyester have found some degree of acceptance for rubber reinforcement. Unfortunately these materials do not satisfy some other requirements such as high temperature performance for the more demanding automotive applications.

Another obstacle to short fibre-rubber composite development is the difficulty in handling reinforced stocks in the free surface processing that is conventional in rubber industry. The higher modulus and reduced elasticity and elongation to fracture of the reinforced compound cause bagging on mill and calender rolls.

Finally, in product manufacture, reinforced plastics offer a performance that allows them to compete with metals in a number of surface and structural applications.

Short fibre reinforced elastomers only behave more like unreinforced plastics.

## I. 3 Component materials

### I. 3.1 Types of fibre reinforcement

The reinforcement of an elastomer by short fibres is mainly governed by (a) the aspect ratio of the fibre (length divided by effective diameter) (b) the adhesion of the fibre to the matrix (c) its dispersion in the matrix (d) flexibility of the fibre to enable processing without breakage[1, 2]. A review of the numerous types of short fibres, their properties and shortcomings as reinforcements for polymer, is given by Milewski[3]. It has been suggested that an aspect ratio of around 100 to 200, develops good adhesion with the matrix and is flexible enough to be processable without breakage[2-5]. On the other hand, Chakraborty et al.[6] have observed that an aspect ratio of 12 gives optimum reinforcement in the case of jute fibre-carboxylated nitrile rubber (XNBR)system, while Murthy and De[7, 8] have reported that an aspect ratio of 12 in the case of short jute fibre-natural rubber (NR) system, and 32 in the case of short jute fibre-styrene butadiene rubber (SBR) system are sufficient for good reinforcement of the composites. The following types of fibres have been used for short fibre reinforcement.

### I. 3.1.1 Cellulose fibre

Short cellulose fibres are found to provide good reinforcement when mixed with matrices. The major advantages associated with cellulose fibres are (1) they are resistant to breakage during mixing (2) their rough surface causes good mechanical anchor with rubber. However compounds of high strength was unattainable because of the poor bonding between the fibre and the matrix. The use of finely divided wood cellulose in rubber by Goodloe and coworkers is the earliest reported work in this field [9, 10].

Unregenerated wood cellulose fibre is a highly reinforcing material for rubbers [11]. The Young's modulus of this fibre is in the range of 15 to 30 MPa, which is about 104 times greater than that of the rubber matrices. Hence the composite stiffness, resulting from reinforcement, is more dependent upon the aspect ratio of the fibre than on the mechanical strength. Since the cellulose fibres are derived from woody plants, they are ribbon shaped rather than round. In addition, their supple nature, tempered by plasticization by absorbed water, allows them to buckle easily without breakage during processing [12]. Hence the initial aspect ratio (before processing) of around 100 or more is preserved in the composite offering good reinforcement.

The source determines the actual dimension of a cellulose fibre. Typical measurements are recited by Britt[13] and by Ott and Spurlin[14]. Since reinforcement efficiency is actually related to the ratio of length to the smallest dimension, this effective aspect ratio is more, of the order of 300, indicating high reinforcing potential for the cellulose fibre. Moreover the surface contains active hydroxyl groups and fibrils to act as bonding sites for a strong interface[15].

Although the average tensile strength of wood pulp fibres of about 300 MPa is only a quarter that of glass fibre or 60% that of nylon fibre[13, 16], it is still effective in rubber composite because in short fibre composites, failure commonly occurs in the matrix around fibres lying at an angle to the applied stress and the high strength (inorganic) reinforcements tend to be brittle and break during processing.

The pulping and drying conditions will influence the tensile strength and modulus of cellulose fibre[17, 18]. Besides , these properties are functions of the moisture content of the fibres which is usually about 8 per cent in contact with 30 per cent RH air[19].

### I. 3.1.2 Glass fibre

The suitability of glass fibre as a reinforcing material for rubber has been extensively investigated because of their high potential as reinforcing agents for plastics[20]. Although high initial aspect ratio can be obtained with glass fibre, their brittleness causes breakage of the fibres during processing. The aspect ratio can thus be drastically reduced, and reinforcement would become less effective. As with the synthetic fibres the surface of glass fibre is also not very reactive and good bonding is hard to achieve[13]. Many investigators have considered short glass fibres for reinforcing rubber because of the high modulus, high resilience and low creep[21-23]. Czarnecki and White[12] have reported the mechanism of glass fibre breakage and severity of breakage with time of mixing. The extent of fibre-matrix adhesion and physical properties of short glass fibre reinforced NR[24] and SBR[8] have been studied by Murthy and De. Manceau[25] has reported that glass fibres have a markedly lower reinforcing capability than cellulose fibres but can undergo higher elongation.

### I. 3.1.3 Asbestos fibre

In view of the poor performance as a reinforcing element in rubber and the health hazards involved in using it, asbestos ranks to little priority. Asbestos fibre is mainly used when working conditions are severe, eg. brake linings and gaskets. The proportion of fibre to rubber in these applications is normally high and the rubber acts only as a binder. The use of asbestos fibre bonded with neoprene to improve the dimensional stability of roofing sheet of unvulcanized chlorosulphonated polyethylene has been reported by Bohmhamel[26]. Brokenbrow et al.[27] have studied asbestos fibre reinforcement of rubbers. They have observed that as the length of the asbestos fibre decreases, the tensile strength of the composite increases. This is because of the poor bonding between fibre and rubber matrix. In NBR a significant improvement in the physical properties was registered when asbestos fibre treated with isocyanate coupling agent was used. Vershchev et al.[28,29] studied the rheological characteristics of asbestos fibre-rubber composite[28,29].

### I. 3.1.4 Miscellaneous fibres

Various natural materials, some of which comprise of biomass wastes, are potential source for rubber reinforcement. This includes silk [30], jute [31], bagasse[32] and others.

The use of asbestos, flax, and cotton fibres to reinforce various types of rubber including NR, SBR, BR has been reviewed by Zuev et al.[33]. In these composites, fibre orientation is shown to be an important parameter. The physico-chemical properties, including fatigue life and thermal expansion strongly depend on the anisotropy resulting from fibre orientation.

A unique polyolefin fibre is used by Blanc and Evrard as reinforcement for SBR[34]. The improved performance from the hybrid composites comprising of cellulose in conjunction with chopped textile fibre has been reported by Boustany and Coran[35]. Moghe[2] also reported on hybrid composites.

In literature the in situ generation of plastic reinforcing fibres within an elastomer matrix has been discussed[36, 37]. The mixture containing a melt mixed fibre forming thermoplastic polymer is extruded above the glass transition temperature (Tg) or crystalline melting temperature (Tm) of the said polymer. After the temperature of the extrudate drops below the Tg or Tm, it is drawn to impart molecular orientation to the fibrous plastic phase. Anisotropy can be controlled by the directions and amounts of extension. Leonard[38] explained the technology for producing polytetrafluoroethylene fibrils in a rubber stock during compounding. Coran and Patel[39] used this process to reinforce chlorinated polyethylene with nylon fibrils.

### I. 3.2 Elastomer types

Short fibres find application in essentially all conventional rubber compounds. Though natural rubber and EPDM are often used [21-23], SBR, neoprene and nitrile rubber have also received much attention [40-46]. The effects of adhesion and orientation of chopped nylon fibres on the tensile strength of isoprene rubber composites have been discussed by Dzyura and Serebro[47] For steel wire reinforcement also they have given a similar treatment[48].

Various types of elastomers used as composite matrices are discussed below.

### I. 3.2.1 Thermoplastic elastomers (TPEs)

The chemical and physico-mechanical properties of glass fibre reinforced butanediolpolytetramethyleneglycol terephthalic acid thermoplastic elastomer is discussed by Kane.[49] He explained the oxidative stability, flammability and U.V resistance of these composites. The use of glass and carbon fibres to reinforce TPEs is reviewed by Aoki[50]. The use of chopped glass fibre as reinforcement for general classes of thermoplastic elastomers has been reported by Theberge and Arkles[51].

### I. 3.2.2 Silicone rubber

The in situ generation of short fibre, by graft polymerization in silicone elastomers has been reviewed by Warrick et al.[52]. Eccersly[53] reviewed the short cellulose and carbon fibre reinforcement of silicone rubber. Marinik[54] used blast furnace slag fibres for increasing the modulus of silicone rubber. Sieron usec carbon fibres to improve the high temperature resistance of the silicones [55,56].

### I. 3.2.3 Fluoro elastomers

The improved physico-chemical properties of fluoro rubbers by reinforcement with chopped polyamide fibres have been reported[57]. Other fibre reinforcements are covered by Grinblat et al.[58].

### I. 3.2.4 Urethane elastomers

Using chopped glass fibres, Moghe reinforced urethane, EPDM, and EP rubbers [59]. Kutty and Nando [60,61] studied the reinforcement of polyurethane using short aramid fibre. A new urethane rubber that can be reinforced by glass fibres was introduced by Turner et al. [62]. Lin et al. [63] optimized the cost performance properties of RIM (reaction injection moulding) urethane, reinforced with 15 to 30 wt. per cent of 1.5 mm milled fibre glass. They compared the use of 1, 4-butanediol and ethylene glycol as crosslinking agents over a broad base of physical and mechanical properties.

## I. 4 Bonding systems

The performance and properties of a short fibre-rubber composite are mainly governed by the bonding between the fibre and rubber. A good level of adhesion between the fibre and the rubber is obtained by modifying the fibre surface by some chemical treatment or by the incorporation of an external bonding agent. The bonding agent may either be a liquid or a solid (dry form) one. In the liquid form, the fibre is coated with this liquid bonding agent, which is then dried and this pretreated fibre is used for reinforcement. In the dry bonding system the bonding ingredients are incorporated directly into the compound during mixing, which form a resin during vulcanization. This bonding resin binds the fibre to the rubber more effectively. The commonly used bonding systems are HRH (Hexamethylenetetramine-resorcinol-hydrated silica), RH (Resorcinol-Hexamethylenetetramine) and RFL (Resorcinol-formaldehyde latex) dip.

The major additives of these systems are resorcinol and a methylene donor. The most widely used donors are hexamethylenetetramine (HMT) and hexa-methoxymethyl melamin (HMMM). These two materials will give moderate levels of adhesion. This can be significantly increased, by a factor of two, by using hydrated silica of fine particle size.

Essentially this system works by the production of resorcinol formaldehyde resin, which migrates to the rubber/fibre interface, where it reacts to bond the two components together. The role of silica is not fully understood. It would appear to act by retarding the cure of the rubber, thereby allowing longer time for the migration of resin to the fibre-rubber interface[64].

As this system acts by migration of the active materials to the interface, it is essential that a sufficient reserve of these be present in the rubber compound. Otherwise, back migration of the adhesion promoters into the bulk of the standard compound will deplete the concentration at the fibre interface below that required for satisfactory adhesion.

This in situ bonding system can be used with many elastomers, giving acceptable level of adhesion and can give significant improvement even with the very low unsaturation elastomers such as IIR and EPDM.

## I. 5 Effects of rubber compounding ingredients

In most formulations there are many ingredients which are required as standard ones in compounding ie., fillers curatives, antidegradents etc., but these are seldom considered for their effects on the adhesion properties of the resultant compound.

The majority of rubber-fibre composites are based on carbon black filled compounds and, on the whole, the type of black used does not have a great effect on the level of adhesion obtained[65]. The reinforcing siliceous fillers also give good levels of adhesion but non-reinforcing white fillers usually show lower levels of measured adhesion. MBTS (Mercaptobenzthiazole) gives the highest adhesion level. If the thiazole is activated, either internally as in the sulphenamides or with a secondary amine based accelerator such as DPG, the level of adhesion is reduced. This amine based activation has much lesser effect than that with the faster thiuram or dithiocarbamate activation.

Greater reduction in the adhesion level is caused by the reduction of sulphur concentration. The EV system, based on CBS only gives around 60 per cent of the level of adhesion obtained with the conventional dosages. When free sulphur is eliminated, either with the thiuram sulphurless system or with a sulphur donor, virtually no adhesion is obtained.

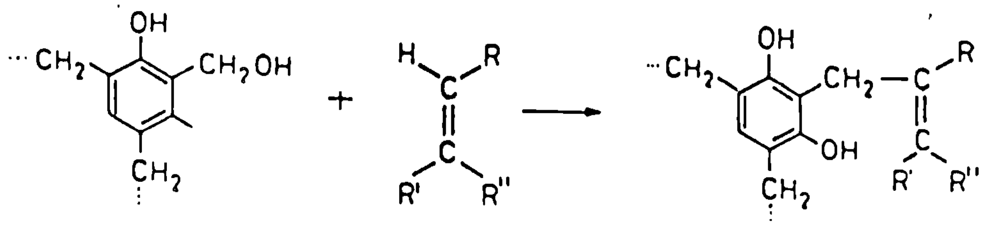
Other materials which can adversely affect adhesion are the process oils and plasticizers.

## I. 6 Mechanism of adhesion

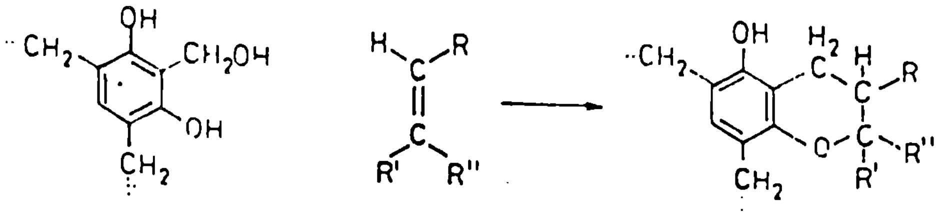
Basically the mechanism of adhesion can be separated into two areas (a) adhesion between the bonding resin and the rubber and (b) between the bonding resin and the fibre. There is also some contribution to the total bond by reaction of the resin component with the rubber either with the active hydrogen in the polymer chains or by chroman formation. This is generally only a minor contribution. There is obviously some purely mechanical contribution, arising from the penetration of the polymer into the structures of the fibre.

The chemical bonding accounts for the remaining adhesion. With rayon (cellulosic) and nylon direct covalent bond with the resin and the fibre contributes significantly to the total adhesion. The mechanism postulated is shown below. The reaction with both rayon and nylon are condensation reactions between methoxy groups on the resin with active hydroxyl or amide groups in the fibre polymer chain respectively.

A. **WITH 'ACTIVE HYDROGEN'**

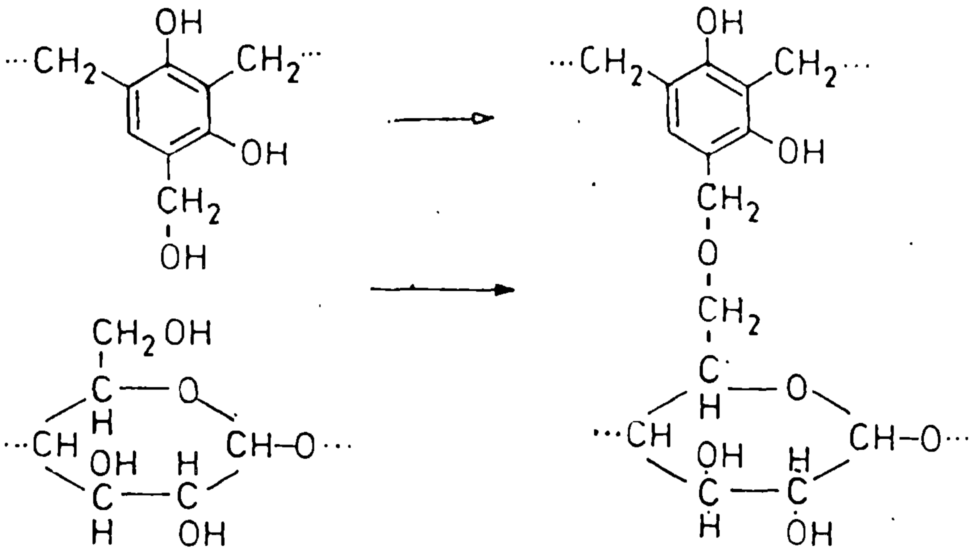


B. **CHROMAN FORMATION**

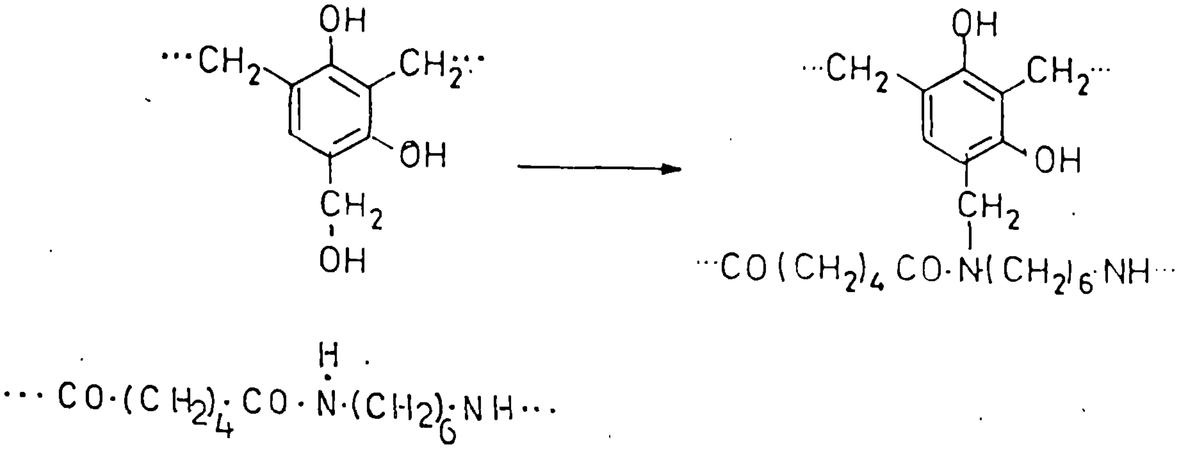


Possible Reactions Between
Resorcinol Resin and Unsaturated Rubbers

A. WITH CELLULOSICS



B. WITH POLYAMIDES



Possible Reactions

Between Resorcinol Resin and Fibres

The tricomponent system (HRH) consisting of hexamethylenetetramine, resorcinol and fine particle hydrated silica generally can be used for most rubber and fibre combinations. Good bonding was obtained with HRH system when used with various fibres in natural and nitrile rubber. Derringer[22] concluded that the HRH system is not effective with polyester fibre in any elastomer matrix. O'Connor[66] compared the HRH system with RH (resorcinol and hexamethylenetetramine alone),and HMMM alone in various short fibre-natural rubber composites. None of the systems worked for glass fibre. The RH system worked best for nylon and cellulose. HMMM showed some bonding only with aramid fibre. It is more active in the presence of resorcinol[67]. Carbon fibre showed best results with HRH.

Foldi[21] applied resorcinol formaldehyde latex (RFL) dip on nylon fibre in a NR-SBR matrix and found the reinforcing ability actually reduced. Various modifications of the later formulation have appeared in the literature to improve bonding between polyester glass fibre.

## I. 7 Preparation of composites

For short fibre composites, good dispersion of the fibre is necessary to achieve the full advantage of the fibre reinforcement. Due to the high viscosity of rubber compound they are generally compounded in high intensity mixers. Mixing of short fibres with rubber can be done in conventional mixers. Depending on the type of fibre, emphasis should be given either on dispersive mixing or on distributive mixing. Distributive mixing increases the randomness of the minor constituents within the major base material without further size reduction, while dispersive mixing serves to reduce the agglomerate size. Brittle fibres such as glass or carbon, break severely during mixing and hence these fibres need more distributive mixing whereas organic fibres such as cellulose and nylon require more of dispersive mixing due to their tendency to agglomerate during mixing.

While it is obvious that short fibres require dispersive mixing, it must not be neglected that high dispersive force might as well result in severe fibre damage. Hence an optimum dispersive force should be employed so that the force is just sufficient to overcome the aggregate entanglements. Goettler and Shen[15] have reviewed intensive mixing of short fibres in rubber.

## I. 8 Fibre dispersion

An essential requisite for high performance composite is good dispersion of the fibres. Two major factors which contribute towards fibre dispersion are (a) level of fibre-fibre interaction and (b) fibre length. It is found that naturally occurring fibres such as cellulose tend to agglomerate during mixing as a result of hydrogen bonding. A pretreatment of fibres at times is necessary to reduce fibre-fibre interaction. Such treatments include making of predispersions and formation of salt film on the surface. Leo and Johansson[68] have described predispersions of polyester, chopped glass and rayon fibres in neoprene latex for better mixing into CR or SBR rubber. Goettler[69] has reported that cellulose pulp may be dispersed directly into a concentrated rubber masterbatch or into the final compound. It is sufficiently wetted to reduce fibre to fibre hydrogen bonding. In the latter case even the bonding agents can be incorporated in the film and it is thus slightly more advantageous than the former. Secondly, the fibre length should be small enough to facilitate better dispersion. According to Derringer[22] the commercially available fibres such as nylon, rayon, polyester and acrylic, must be cut into smaller lengths of approximately 0.4 mm for better dispersion. The dispersion of fibres can be improved by adding fibre first in banbury. Goettler[69] has shown that a dimensionless dispersion number which is a function of fibre length, rotor diameter, rotor tip clearance, mixing chamber volume, rotor speed and mixing time, is a reliable parameter for short fibre mixing.

## I. 9 Fibre breakage

The length of fibre in a composite is a critical parameter. The fibre should not be too long to entangle with one another and cause dispersion problems, or too short, so that it does not offer sufficient stress transfer area and effect reinforcement. Many investigators[21, 22, 42] have studied the importance of fibre length and its influence on the properties of the composite. O'Connor[66] has studied the extent of fibre breakage, after processing and vulcanization and concluded that fibre breakage and distribution of fibre length occur only in the uncured stock during processing and not in the cured vulcanizate. The severity of fibre breakage depends primarily on two factors: (a) type of the fibre (b) its initial aspect ratio. Glass and carbon fibres being brittle, possess low bending strength and suffer severe damage during mixing unlike cellulose and nylon fibres which are flexible and hence highly resistant to breakage. Another factor controlling the extent of fibre breakage is the shear force generated during mixing which is particularly high in cases where the compound viscosity is high. Higher the shear force more severe will be the fibre breakage. The lower reinforcing effect of glass fibre is due to the severe reduction in its length compared to cellulose fibre during mixing[66]. De and co workers [6] Murthy and De[8] and Murthy[24] have studied the breakage of jute and glass fibres in NR, SBR and NBR and found that the breakage of glass fibre is more severe compared to that of jute fibre. A comparative account of fibre breakage is given in Table I.1.

## I. 10 Processing characteristics

The processing characteristics of rubber compounds can be significantly improved by addition of short fibres. Murthy and De [7,70] have studied processing characteristics of short jute and glass fibre filled NR, that of SBR by Murthy[24] and that of NBR by Setua[30] both in the presence and absence of carbon black. In the case of short jute fibre-NR compounds a considerable improvement is observed in the green strength at a loading of 25 phr of fibre. In the presence of carbon black a further increase in green strength is observed. Mill shrinkage is reduced considerably in the case of fibre filled mixes while carbon black does not affect it significantly. A continuous decrease in mill shrinkage with increase in fibre loading for short glass fibre-NR compounds has been observed in the absence of carbon black. But in the presence of carbon black upto a loading of 15 phr of fibre, mill shrinkage decreases and at higher fibre loading (75 phr) there is a slight increase in mill shrinkage due to high compound viscosity which results in fibre breakage. In the case of SBR, addition of fibres improves the green strength of the fibre filled mixes and the presence of carbon black further enhances it. Mill shrinkage for jute-SBR system is lower than that for glass-SBR system, while the extent of fibre breakage is more in the latter compared to that in the former. In the case of short jute-XNBR system[6], addition of fibres to the mixes increases the Mooney viscosity and reduces the Mooney scorch time.

## I. 11 Fibre orientation

### I. 11.1 Effect on flow behaviour

During processing and subsequent fabrication of short fibre-rubber composites the fibres orient preferentially in a direction depending on the nature of the flow eg: convergent, divergent, shear or elongational as explained by Goettler et al.[71]. If the flow is of convergent type the fibres align themselves in the direction of flow. The divergent type of flow causes alignment of fibres away from the direction of flow. In the case of shear flow, the fibre alignment can be from random to unidirectional depending on the shear rate and if the flow is of elongational type the fibres orient themselves in the direction of the applied stress. The direction and extent of fibre orientation are controlled by the magnitude and direction of viscosity gradient. (eg. either positive or negative). In a convergent flow, the flow accelerates because of a reduction in the cross-sectional area of the channel, the viscosity gradient becomes positive and the fibres tend to align in the direction of flow making a small angle with the flow axis[72].

### I.11.2 Effect of different processing techniques

All the conventional rubber processing techniques are applicable to short fibre composites as well. Goettler described extrusion[73-75] and injection moulding[76] of short fibre composites. Milling, represents the allied operation of calendering, is commonly utilized for preparation of specimen sheets for property evaluation [21, 77-81]. A detailed review of short fibre orientation is given by Mc Nally[82]. Campbell[83] has reported that when the rubber matrix containing the dispersed fibres is made to flow in a non-turbulent manner the fibres are turned and become aligned or oriented in the direction of the matrix.

#### I.11.2.1 Milling

Milling is a simple method by which the fibre orientation can be controlled. A high degree of fibre orientation can be achieved by repetitive folding and passing through a two roll mill, as described by Boustany and Coran[1].

The effect of mill parameters such as number of passes, nip gap and mill roll speed ratio on fibre orientation has been studied by Moghe[72]. For a particular direction of fibre orientation, the composite modulus, ultimate elongation and the breaking stress were found to be independent of mill roll speed ratio and number of passes and he concluded that the maximum fibre orientation was achieved during the first mill pass making additional passes almost unnecessary. Mill opening, however, was found to have an influence on the physical properties of the composites. The composite modulus in all directions of fibre orientation increased with decreasing mill opening although the effect of mill opening on the ultimate elongation and breaking stress of the composites was not significant. A mill was used by Foldi[21] to orient various organic filaments into several types of rubber stock. The brittle glass and wire fibres were found to fracture to such an extent that reinforcement of the rubber sheet was compromised.

### I. 11.2.2 Extrusion

Goettler and Lambright[84] developed a technique for controlling fibre orientation in extrusion by the use of an expanding mandrel die. A detailed discussion on the design of extrusion dies for controlling fibre orientation is given by Goettler et al.[74, 84, 85]. The major application of these dies is in the hose extrusion[79]. But it also applies to profile dies in the extrusion of tyre component strips[73].

### I. 11.2.3 Calendering

In calendering, the fibre orientation occurs preferentially in the machine direction. Calendering can achieve about the same level of fibre orientation in the machine direction as in conventional extrusion[74].

It is the flow of the rubber matrix which aligns the fibres during the above mentioned processing techniques. A new process for aligning magnetically responsive fibre in a magnetic field has been described by Timbrell[86]. However, coating fibres with metals is tedious and for this technique to be viable for rubber composites magnetic force has to be applied before vulcanization begins.

## I. 12 Fibre orientation and Fibre orientation distribution

It is impossible to achieve all the fibres aligned in one particular direction. In all cases there will be a distribution of fibre orientation. Maximum level of fibre orientation included 80-90% fibres oriented within ± 10 degree to normal alignment direction[76]. Different methods employed to determine fibre orientation include the tearing of a cured sheet prepared in an open mill which indicated the preferential fibre orientation as the tear path, which proceeds easily in a direction parallel to the fibre orientation. Contact microradiography has been applied to short fibre reinforced plastics to determine the fibre orientation distribution[88]. De and coworkers[6, 31, 89] have used scanning electron microscopy (SEM) of the fracture surfaces to determine fibre orientation.

The swelling in fibre-rubber composites, becomes anisotropic as the swelling is restricted in the direction of fibre alignment. Hence, anisotropic swelling has been used by several researchers to determine the fibre orientation. Coran et al.[44] showed that the linear deformation due to swelling is a simple trignometric function of the angle between the direction of measurement and the orientation. The theoretical aspects of swelling have been considered by Daniels [90]. Li et al.[81] have studied the swelling behaviour of bonded and oriented composites containing various levels of treated short cellulose fibres embedded in a vulcanized EPDM matrix. The swelling ratio measured by the eccentricity of the critical shape was compared with the mechanical anisotropy of the fibre-rubber composites and a satisfactory correlation was established. Rigbi and Sabatov[91] have reported their results of a theoretical study of the swelling constraint imposed by fibrillar fibre. Anisotropic swelling behaviour in short jute and glass fibre SBR composites both in the presence and absence of carbon black was reported by Murthy and De [8].

Effect of fibre orientation preferentially in the machine direction on the anisotropy in mechanical properties of the fibre-rubber composites has been discussed by Derringer[22]. The mode of composite fracture depends, to a certain extent, on the angle between the direction of application of the load and the principal fibre orientation direction[79]. The composite fracture takes place through fibre breakage when this angle lies between 0-10 degrees, as a result of shear when the angle lies between 10 to 60 degrees and when it lies between 60-90 degrees the matrix failure leads to total failure of the composite. As the distribution of fibre orientation is usually unavoidable all these modes of failure overlap and none can be identified in isolation. This distribution can be used as a basis for the theoretical prediction of the strength of the composites. The composite modulus can be related to the angle between the principal fibre orientation and the direction of applied stress as,

$$\frac{1}{E_{\phi}} = \frac{\sin^2\phi}{E_T} + \frac{\cos^2\phi}{E_L} \qquad \ldots\ldots \quad (I.1)$$

where $E_L$ and $E_T$ are the moduli of the composite in the longitudinal and transverse orientations, respectively. The drawback in this case is that $\phi$ cannot be determined exactly and in any case it becomes single valued. Moghe[59] proposed a simple mathematical model which takes into account a probability distribution function in any direction during fibre orientation for a number of short fibre - rubber composites. He compared mill mixed (oriented) with Brabendar mixed (randomly oriented) composites. He modified Halpin-Tsai's equation[92], which predicts the modulus of a unidirectionally oriented composite, for the randomly oriented composites using a single parameter called orientation strain and concluded that the modulus of a perfectly oriented composite obtained from Halpin-Tsai's theory is six times that of a randomly oriented one. A practical application of this analysis in characterizing calendering and extrusion processes in view of orientation and physical properties has also been discussed. In literature, suspension rheology has been used to study the fibre orientation behaviour [93]. Fukuda and Chow[94] used a probabilistic approach based on Halpin-Tsai's equation to suit composites containing a distribution of fibre orientation.

## I. 13 Application of fibre orientation

The importance of preferential fibre orientation is immediately apparent in various short fibre filled rubber products. In V-belts, for example, the base compound is required to withstand compressive forces allowing sufficient flexibility in the axial direction simultaneously, thus, transversely oriented fibres are more suitable in this case[95-96]. In the case of randomly oriented composites the swelling is restricted in both the length and width directions and hence the swelling takes place only in the thickness direction. Thus the oil seals made out of them tighten after swelling. Similarly the fibre orientation in the circumferential direction is more suitable in the case of hose construction [74].

## I. 14 Critical fibre length

The interfacial shear force developed at the fibre-rubber interface depends to a great extent on the level of fibre - rubber adhesion. Unlike in continuous cord reinforced composites, fibre ends play a significant role in the determination of ultimate properties in short fibre reinforced rubber composites. Hence, optimum fibre reinforcement involves the concept of a critical fibre length where the fibre is stressed to its maximum during stress transfer. A theoretical analysis by Broutman and Aggarwal[97] on the mechanism of stress transfer between the fibres of uniform radius and length with the matrix gave the following expression for critical fibre length($L_c$),

$$\frac{L_c}{d} = \frac{\sigma_{fu}}{2\tau_y} \qquad \ldots\ldots \quad (I.2)$$

where, d = fibre diameter, $\sigma_{fu}$ = ultimate fibre strength, $\tau_y$ = matrix yield stress in shear. It has also been suggested that while comparing various fibres of different radii it would be more appropriate to consider aspect ratio in place of fibre length.

## I. 15 Design properties

Chow[98] and Kardos[99] have given a good review of models for predicting the elastic moduli as a function of the shape of the reinforcing particle. The mechanical properties of short fibre composites are intermediate between those containing continuous filaments or cords and particulate filled materials. This is particulary true of the responses in a direction parallel to that of the fibres when they are highly aligned. Short fibres are nearly identical to continuous fibres in their transverse properties [100].

Boonstra[101] reported the use of particulate fillers in elastomer reinforcement. Paipetis and Grootenhuis [102,103] developed the dynamic properties of viscoelastic composites in comparison with particulate and long fibre reinforcements. The effects of the shape, size and orientation of the fibre reinforced material are studied. It has been reported that the composite plays a frequency dependent response[104].

The mechanical properties of short fibre composites are related to the aspect ratio, concentration, state of dispersion and the degree of adhesion to the matrix. These variables are again influenced by bonding agent and other additives that might interact with matrix. The effect of bonded versus unbonded fibres on the properties such as heat build up, static and dynamic compression, permanent set, rupture elongation and low elongation moduli have been discussed by Das[104].

The fibrous composites of natural rubber and synthetic rubbers are reported by Aleksandrov[105]. Frenkel et al.[106] reported the incorporation of long (30 mm) chopped textile fibres into rubber in a random way. Hamed and Li[107] reported the physico-mechanical properties of EPDM rubber-cellulose fibre composites.

## I. 16 Tensile strength

The theories to explain the mechanism of stress-strain properties in continuous and discontinuous fibre reinforced plastics are applicable to short fibre reinforced rubber composites, subject to certain modifications and the theories applicable to particulate filler reinforced rubbers may also be extrapolated to low aspect ratio fibre composites. Broutman and Krock[108] have developed theories for polymer composites where elastomer matrices can be considered as a special case.

For a perfectly aligned and properly bonded unidirectional continuous fibre composite the rule of mixtures is applicable and is given by

$$\sigma_{cu} = \sigma_f \; v_f + \sigma_m \; v_m \qquad \ldots\ldots \quad (I.3)$$

where, $\sigma_{cu}$ = ultimate composite strength, $\sigma_f$ = ultimate fibre strength, $\sigma_m$ = matrix strength at the maximum fibre stress, $v_f$ = volume fraction of fibre, $v_m$ = volume fraction matrix. However, as short fibres have ineffective stress transfer near the ends, they cannot be stressed to their maximum. Rosen[109] has discussed the effect of fibre length on tensile properties and used shear-log analysis to explain the mechanism of stress transfer. The response of tensile strength to a variation in the volume loading of fibre is a complex one. For strain crystallizing rubbers (eg. NR and CR), the tensile strength first decreases up to a certain volume fraction of fibre as a result of the dilution effect, even when the fibres are properly bonded to the rubber matrix[31]. The minimum fibre loading value depends upon the nature of the fibre, nature of the rubber, bonding level and state of dispersion and is different for different fibre-elastomer systems. Derringer[22] has postulated certain empirical equations relating volume fraction and aspect ratio of the fibres to the tensile strength, modulus and elongation at break.

For non-crystallizing rubbers where the strength of the unfilled matrix is poor (e.g. SBR), the presence of even a small fraction of fibre increases the overall strength of the composite. Dzyura[110] and Murthy and De[8] have reported that the tensile strength does not drop in the case of non-strain hardening SBR. But if the matrix strength is increased with the help of reinforcing carbon black the tensile strength is found to decrease[8].

The above discussed theoretical consideration holds good for unidirectional composites and for randomly oriented composites when the load is applied along the direction of principal fibre orientation. But, when the fibres are aligned transversely to the direction of the applied stress, the fracture of the composites takes place mainly through the matrix and the fibres do not affect the strength properties significantly. There are many references pertaining to the effect of the angle between the principal fibre direction and the direction of application of stress. The maximum composite strength can be achieved if the angle is '0' degree and it decreases as the angle increase from 0 to $90^{o}$, giving the lowest value at $90^{o}$.

Moghe[80] reported the variation of physical properties of the composite with the direction of fibre orientation. He proposed an expression for the strength of the composite, in which the orientation parameter has been taken into account. The ultimate composite strength is given by

$$\sigma_{cu} = \sigma_f V_f F (L_c/\bar{L}) C_o + \sigma_m (1 - V_f) \quad \ldots. \text{ (I.4)}$$

where, $\sigma_{fu}$ = ultimate fibre strength

$V_f$ = volume fraction of fibre

$\sigma_m$ = matrix strength at the max. fibre stress

$L_c$ = critical fibre length

$C_o$ = orientation parameter

$L$ = length of the fibre

Dzyura[110] proposed that the strength of a rubber-fibre composite may be described by the additivity rule provided that adhesion and orientation coefficents are introduced and true influence of the matrix is considered. In order to determine the dependence of composite strength on the filler loading, he used a theoretical diagram proposed by Kelly and Tyson[111] for computing the efficiency of filamentary reinforcement of metals and expressed the strength of rubber-fibre composites as

$$\sigma_c = \sigma_f V_f (1-Li/2L) K + \sigma_m V_m \quad \ldots.. \text{ (I.5)}$$

where, $\sigma_c$ = composite strength

$\sigma_f$ = strength of the fibre

$V_f$ = volume fraction of fibre

$\sigma_m$ = strength of the matrix at its maximum attainable deformation

$L$ = length of the fibre

$K$ = coefficient of fibre orientation.

$L_i$ = ineffective length of the fibre and is calculated on the condition that the force required for breaking the fibre is equal to the maximum shear force on the fibre-rubber bonding.

$$Li = \frac{\sigma_f \cdot d}{2\tau} \qquad \text{...... (I.6)}$$

where d = diameter of the fibre and $\tau$ = the minimum shear stress on boundary. Dzyura[110] found that the orientation coefficient depends not only on the method of processing but also on the fibre concentration and is different for different fibre-rubber composition. The influence of the matrix on the value of $\sigma_c$ was reported to be dependant not on the matrix strength ($\sigma_m$) but on its streching resistance at the maximum composite deformation $\sigma'_m$. For the composite with a higher $\sigma'_m / \sigma_m$ ratio (as in the case of NR) there exsists a minimum in tensile strength vs fibre concentration curve. But for composite with higher ( $\sigma_m'/\sigma_m$ ) ratio approaching unity, this minimum is not observed and the lower the value of $\sigma_m'/\sigma_m$ ratio higher the increase in relative strength $\sigma_c$ as compared to $\sigma$

## I. 17. Tear strength

The tear resistance of composites reinforced with short fibres is considerably higher than that for other rubber composites. Beatty and Hamed[112] and Beatty and Miksch [113] have reported that low loading (<5 per cent) of short fibres causes an increase in tear strength of a composite above that of the non-reinforced rubber matrix. The increase in the tear strength of the composite is reflected in the improved resistance to cutting and chipping of heavy-duty and off the road tyre treads applications. De and coworkers[6-8] have reported that in the case of composites of short jute fibres, with NR, SBR and XNBR systems a sharp increase in tear strength occurs upto a certain fibre concentration and then remains almost constant with increasing fibre concentration.

## I. 18. Fatigue and hysteresis properties

Generally, short fibre reinforcement particularly at high fibre loading and high strains has an adverse effect on flex fatigue. Fatigue failure is associated with crack generation and its propagation in the matrix, followed by dewetting and destruction of the fibre-matrix bond. In addition, increased stiffness makes the composite brittle and cause early failure under fatigue. It has been reported that the flex cracking resistance is slightly more when the fibres are oriented transversely than when they are oriented longitudinally[31]. The fatigue caused by repeated loading in tension and compression in the case of cellulose fibre-rubber composites was studied by Boustany and Arnold[42]. Derringer[23] pointed out that the composite containing 9 phr rayon exhibits lower heat build up and permanent set than carbon black (FEF. 50 phr) reinforced vulcanizate. Heat build up for reinforced composites is higher than that for the unfilled vulcanizates[42]. Many investigators[6, 8, 24, 31] have explained that the mechanical damping near the fibre-matrix interface at high frequencies accounts for higher heat build up and is in part responsible for low fatigue life of these composites.

## I. 19. Creep

Addition of short fibres to an elastomer reduces the creep substantially[114]. Coran et al.[44] have reported on the creep behaviour of short cellulose fibre reinforced NR composites. Derringer[23]discussed the advantages of short glass fibre composites over FEF black filled composites with reference to their creep behaviour. As a first approximation, the creep of the composites compared to that of the unfilled polymer should be reduced by about the same factor as the ratio of the two moduli of the materials. The time dependant failure of fibre reinforced elastomers under cyclic strain conditions has been discussed by Moghe[115]. Since the composites have high modulus, the same strain conditions induce higher stresses in composites as compared to the elastomers.

## I. 20. Modulus and elongation at break

Addition of short fibres to rubber compounds always increases the modulus[116]. Guth et al.[117] derived a formula for the modulus of a fibre reinforced rubber

$$G = Go\ (1 + 0.67\ f\ C + 1.62\ f^2\ C^2) \quad \ldots\ldots \quad (I.7)$$

where, Go = modulus of unfilled rubber vulcanizates.

C = volume concentration of the fibre

f = length to diameter ratio of the fibre

when 'f' is in the range 10-50, a moduli between $10^2$-$10^3$ can be achieved if there is good adhesion between fibre and matrix. The other principal difference is very low elongation at break values of the short fibre-rubber composites compared to those of the elastic unfilled rubber vulcanizates. O' Connor [66] studied a range of fibres at 16-17 volume per cent concentrations in the presence of bonding system. He showed how the elongation at break originally at 620 per cent can be reduced eg., to 63 per cent with glass, to 96 per cent with carbon, to 13 per cent with Kevlar and cellulose and to 40 per cent with nylon. At the same time the composite's hardness increased from 60 shore A to the range of 86 to 93 shore A for the fibres studied. Derringer[23] suggested that the rapid loss of elongation with increased fibre loading is due to good fibre-matrix adhesion and ultimate elongation is a good index of fibre-matrix adhesion especially at higher fibre loading.

## I. 21. Applications

Short fibres can find application where the continuous fibres are now being used. If the aspect ratio and adhesion of short fibres to rubbers can be suitably controlled, short fibres can conveniently replace continuous cord as they offer flexibility in both design and processing. Various applications involving short fibre reinforcement of elastomers have been reviewed by Campbell[83]. The shrinkage during vulcanization in cup seals manufactured from cotton fibre reinforced NBR has been reported by Orlov et al.[118]. Ratliff[119] has investigated the advantages of short cellulose fibres over nylon in providing dimensional stability to air cylinder packing cups. Lueers[20] has studied the reinforcement of rubber with discontinuous glass fibres and explored the applications of these composites. The main applications of short fibre reinforced rubber composites are discussed below.

### I.21.1. V-belts

In V-belts short fibre rubber composites must be transversely oriented so that fibres can offer good resistance to compressive forces with better flexibility in axial direction.

V-belts are designed by considering the fact that the compressive force acts in the transverse direction and the fatigue in axial direction. Here the anisotropy of those fibre-rubber composites which exhibit high modulus in transverse direction and low modulus coupled with high flexibility in the axial direction was found to be very useful. Rogers[95] and Yantinskaya et al.[96] have studied the use of short cellulose fibre along with polyester fibre as reinforcement for V-belt compounds.

Cellulose fibre composites have higher anisotropy, increased flex life in the DeMattia cut growth test and are more easily dispersable than other fibres. The effects of EPDM compound formulation on the thermal degradation of various fibre types of belting products have been studied by Shinda and Hazelton[120].

### I.21.2. Hoses

In the area of hoses, short fibres are used as a replacement in knit or spiral wound cords. The main advantages are easy processing, economy and higher production rates. The braiding operations can be-excluded by using short fibre reinforcement without affecting the physical properties adversely. Goettler et al.[74, 75, 84, 85] have reported extensively on the production and performance of short fibre reinforced hoses.

They have studied short fibre reinforcement in the production of heater hoses, radiator hoses and fuel hoses as the composites provide necessary burst strength in them. Extrusion shaping of curved hoses in which both the inner and outer portions of the hose are moved out of concentricity in a programmed sequence to produce hoses with bends has also been reviewed[84].

### I.21.3. Tyres

Short fibre can be used in all parts of tyre construction due to its high green strength. They find application in the construction of tyre inners and in tyre tread as they have high chipping and chunking resistance. Inoue et al.[121] have reported improvement in modulus and cut/crack resistance of urethane rubber composites when chopped organic fibres viz. nylon, polyester, polyacrylonitrile etc. are added to them.

Boustany and Coran[122] have recommended other tyre applications. The extrusion of a bead filler stock containing short glass fibres to increase stiffness has been reported by Dzyura et al.[45]. Goettler[67] has studied the extrusion of treated cellulose fibre reinforced rubber profiles with controlled fibre orientation and their use as tyre components. The advantages of using rubber-fibre composite in extending the service life of tractor tyres have been described by Dzyura et al.[123] Nesiolovskaya et al.[124] have studied the use of a modified fibrous filler in tyre tread compounds.

### I.21.4. Other applications

Georgieva and Vinogradova[125] have studied the application of cotton and other cellulose fibre reinforced thermoplastic polyisoprene as sheeting in shoe construction. The use of cellulose fibre-EPDM composites for automotive applications has been reviewed[19]. The high degree of anisotropy of fibre-rubber composites helps in designing products such as tubing, where the swell can be minimised with decreasing elasticity.[22]

The application of Sandoweb fibres in rubber goods such as diaphragms, roofing, sheeting, moulding and sealants has been described[22].

## I. 22 Scope of the work

The use of particulate fillers like carbon black and silica in rubber compounds imparts better serviceability as a result of superior reinforcement to elastomers. The continuous cord reinforcement is well known in many applications such as tyres, V-belts, hoses, gaskets etc. But the additional work such as dipping, coating, wrapping, braiding, ply making etc. associated with continuous fibre reinforcement creates economic and processing problems. Hence the quest for a suitable replacement of continuous fibre led to the discovery of short fibre reinforcement.

Though the short fibres have a variety of applications in plastics, its applicability in elastomers is yet not fully explored. Many authors have studied the physical and mechanical properties of short fibre reinforced elastomer composites and the suitability of their application in different products. But a systematic study on the processing characteristics of fibre-rubber composites, the effects of fibre-matrix adhesion, fibre dispersion, fibre orientation, and the temperature dependence of strength properties etc. is still lacking. In the present study an attempt has been made to cover all these parameters, in the case of natural rubber short sisal fibre composites.

Due to the limited supply and high price of synthetic rubbers and the increase in price of NR, there is an urgent need for ensuring a judicious use of the available supply of rubber and rubber products. In this context sound knowledge about the various ways in which rubber products fail during service is important. In the case of short fibre-reinforced rubber composites the failure may be due to weak fibre-rubber interface, premature failure as a result of the insufficient quantity of fibres, loss of fibres during abrasion or fibre breakage during processing. Studies on the failure mechanism of short jute and glass fibre reinforced NR, SBR and NBR composites have been reported[6-8,24]. However no detailed study on the failure modes of short sisal fibre reinforced rubber composites is reported.

Among the various natural fibres, sisal fibre is of particular interest since its overall mechanical properties are superior to those of other fibres. Another objective associated with the use of fillers in rubber is to cheapen the product. Use of natural fibres in rubber is expected to further bring down the production cost. However no information is available regarding the use of sisal fibre as a reinforcing filler for rubber. In this context, the present work deals with the utilization of a cheap, naturally occurring material in rubber.

In short fibre-NR composites, the tricomponent drybonding system (Hexa-resorcinol-silica) is generally used to produce adhesion between the fibre and the rubber matrix. But in the case of cellulose fibres, use of silica has very little effect on adhesion properties[66] Hence we replaced the tricomponent system by a dicomponent system consisting of hexa and resorcinol only. A relative proportion of the two components of the drybonding system was necessary to produce optimum adhesion at a particular fibre concentration. Even in the presence of the bonding system the adhesion between sisal fibre and NR is poor. Hence we modified the fibre surface for better bonding by a chemical treatment. Since the sisal fibre is a cellulosic one, it contains a number of free reactive hydroxyl groups. Hence acetylation is a suitable method to modify the fibre surface. The mechanism of fibre-rubber adhesion through the bonding resin is also established.

In the case of short fibre-rubber composites, the level of adhesion cannot be ascertained quantitatively and hence a qualitative assessment of the same is to be made. Measurements of stress-strain characteristics, physical properties, restricted swelling, SEM studies on the failure mechanism of the composites etc. are useful in solving this problem.

During service the products fabricated out of short fibre-rubber composites may generate heat due to hysteresis, or they may be exposed to elevated temperatures, $\gamma$- radiation or ozonised air. Therefore, there is a need to study the effect of these degrading agents on the properties of short fibre rubber-composites.

With the advent of new processing machinery which are extrusion oriented, the quest for the knowledge of rheological behaviour of short fibre-filled rubber compounds has increased.

To throw light on the above unsolved problems connected with short sisal fibre-NR composites, studies on the following aspects were undertaken.

1. The mechanical properties of the natural rubber-short sisal fibre composites.
2. Dynamic mechanical properties of short sisal fibre reinforced natural rubber composites.

3. Rheological behaviour of short sisal fibre reinforced natural rubber composites.

4. Stress relaxation behaviour of short sisal fibre reinforced natural rubber composites.

5. Behaviour of natural rubber-short sisal fibre composites towards organic solvents.

6. Degradation behaviour of natural rubber-short sisal fibre composite in presence of $\gamma$- radiation , heat and ozone.

In all the above cases, the effects of acetylation of the fibre, fibre loading, orientation of the fibre and presence of bonding agent have been explained.

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Table I.1. **Severity of breakage of different fibres**

| Research group | Type of fibre | Type of matrix | Fibre length before processing (mm) | 1/d | Fibre length after processing (mm) | 1/d |
|---|---|---|---|---|---|---|
| J.E. O'Connor[66] | Glass | NR | 6.35 | 488 | 0.22 | 17 |
| J.E. O'Connor[66] | Carbon | NR | 6.35 | 794 | 0.18 | 22 |
| J.E. O'Connor[66] | Cellulose | NR | 2.0 | 167 | 1.20 | 100 |
| J.E. O'Connor[66] | Aramid | NR | 6.35 | 529 | 1.33 | 111 |
| J.E. O'Connor[66] | Nylon | NR | 6.35 | 254 | 4.51 | 180 |
| D.K. Setua[30] | Silk | NR | 6.00 | 333 | 1.31 | 73 |
| S.K. Chakraborty et al.[6] | Jute | XNBR | 6.00 | 130 | 0.58 | 12 |
| D.K. Setua[30] | Silk | NBR | 6.00 | 500 | 0.92 | 77 |
| L. Czarnecki and J.L. White[12] | Glass | Polystyrene | 0.19 | - | 0.50 | - |
| L. Czarnecki and J.L. White[12] | Aramid | Polystyrene | 1.27 | - | 0.49 | - |

# CHAPTER II

# MATERIALS AND EXPERIMENTAL

The details of the materials used and experimental techniques adopted in the present investigation are given in this chapter.

## II.1. Materials used

### II.1.1. Natural rubber

The natural rubber (NR) used for the study was technically specified form of rubber, obtained from the Rubber Research Institute of India, Kottayam. This rubber satisfied the Bureau of Indian Standards specifications for ISNR-5 grade natural rubber. The specification parameters and their limits for the ISNR-5 grade NR are given in Table II.1. The rubber from the same lot has been used in a particular experiment, since the basic properties such as molecular weight, molecular weight distribution and the contents of non-rubber constituents of NR are affected by clonal variation, season, use of yield stimulants and methods of preparation[1,2].

### II.1.2. Sisal fibre

Sisal fibre (Agave sisalana) was obtained from local sources. The sisal fibre is extracted from the plant Agave sisalana which is available in plenty in the southern parts of India. The chemical constitution of sisal fibre is given in Table II.2. The fibre was washed thoroughly with water and dried in an air oven at 80°C for 4 - 6 h., before being chopped into the desired length for fibre treatment and composite preparation.

### II.1.3. Rubber chemicals

Commercial grade accelerator N-cyclohexyl benzthiazyl sulphenamide (CBS) and antioxidant 2,2,4-trimethyl 1,2 dihydroquinoline polymerised (TDQ) used for the study were obtained from the Alkali and Chemical Corporation of India Ltd., Rishra.

### II.1.4. Other chemicals

Zinc oxide (specific gravity - 5.5), stearic acid (specific gravity 0.92) and elemental sulphur (specific gravity - 1.9) used in the study were chemically pure grades.

### II.1.5. Special chemicals

Resorcinol (specific gravity - 2.36) and hexamethylenetetramine (specific gravity 1.33) were of chemically pure grades and were obtained from Aldrich Chemical Company.

### II.1.6. Solvents

Benzene, pentane, hexane, heptane and octane were of analytical grade.

## II.2. Chemical treatment of fibre

Sisal fibre chopped to a length of 10 mm when used as such is designated as the untreated fibre. Acetylated fibre was prepared from the raw sisal fibre as per the methods reported by Chand et al.[3] by immersing the chopped fibre (10 mm) in 18% aqueous sodium hydroxide solution at 35°C for 1 h. It was washed with water several times and then dried. This fibre was soaked in glacial acetic acid for 1 h. at 35°C, decanted and then soaked in acetic anhydride containing two drops of concentrated sulphuric acid for five minutes. The fibre was filtered through a Buchnor funnel, washed with water and freed from acid and then dried in an oven at 70°C for 24 h. The acetylated fibre was kept in polythene bags to prevent moisture absorption.

## II.3. Preparation of compounds

### II.3.1. Composite preparation

The composites were prepared in a two-roll laboratory model open mixing mill (150 x 300 mm) at a nip gap of 1.3 mm and at a friction ratio of 1:1.25. Nip gap, mill roll speed ratio, time of mixing and temperature of the rolls were kept the same for all mixes. In order to disperse resorcinol homogeneously in the mixes, it was added in molten state[4]. Similarly finely powdered hexamethylenetetramine was used for the purpose of homogeneous mixing. Orientation of the fibre in the mill grain direction was achieved by repeated passing of the uncured compound through a tight nip[5].

### II.3.2. Time of optimum cure

Optimum cure times at 150°C were determined by using Monsanto rheometer (model R-100). The optimum cure time corresponds to the time to achieve 90 per cent ($t_{90}$) of the cure calculated from the formula,

$$\text{Optimum cure} = [0.9\,(L_f - L_i) + L_i] \qquad \text{......(II.1)}$$

In the cases where the rheographs show maximum or plateau, $L_f$ and $L_i$ are the maximum and minimum torques respectively. But in the case of rheographs showing marching modulus, optimum cure time was calculated as follows. Two tangents AC and BC were drawn on the rheograph as shown in Figure II.1. They meet each other at point C. The points of contact (A and B) of the tangents and rheograph were connected by a straight line AB. The middle point O of the straight line was connected with point C (point of interaction of the two tangents). The line CO cuts the rheograph at point T. The time corresponding to the modulus at point T of the rheograph was taken as the optimum cure time.

### II.3.3. Moulding of test samples

Blanks cut from the uncured sheet were marked with the direction of the mill grain and were vulcanized at 150°C in a hydraulic press having steam heated platens to their respective cure times, as obtained from Monsanto rheometer. Test pieces were punched out from the moulded sheet along and across the direction of fibre orientation for tensile and tear tests. The orientations of fibres along and across the grain direction are shown in Figure II.2. Test samples for other tests such as abrasion resistance, compression set, ozone resistance etc. were directly moulded out.

### II.3.4. Fibre breakage

Shear forces during mixing cause breakage of the fibres. Extent of fibre breakage and the fall in the mean aspect ratio (average length to diameter ratio) of the fibres from its original value (before mixing) was determined by dissolution of the mixes in benzene, followed by extraction of the fibres and examination of length and diameter of the extracted fibres by a polarizing microscope under reflected light. A batch size of 200 fibres was taken and the distribution of fibre length was assessed using an optical microscope.

## II.4. Physical tests

At least three specimens per sample were tested for each property and the mean of these values was reported. Excepting hardness, resilience and abrasion in the Du Pont abrasion tester, the other tests were carried out both along (longitudinally oriented fibres) and across (transversely oriented fibres) the grain direction. In the case of hardness and compresssion set the direction of fibre alignment is normal to the direction of application of load.

### II.4.1. Modulus, tensile strength and elongation at break

In the present work, these tests were carried out using a Zwick Universal Testing Machine model 1474 according to ASTM test method D 412 - 51 T. Samples were punched out from vulcanized sheets both along and across the grain directions using a dumb-bell die (C-type). The thickness of the narrow portion was measured by a bench thickness gauge. The above tests were carried out at room temperature (28 ± 2°C) and at a cross-head speed of 500 mm per minute.

### II.4.2. Tear resistance

This property was tested as per ASTM D 624-81 test method, using unnicked 90° angle test specimens which were punched out from the moulded sheets, along the mill grain direction. This test was also carried out in the Zwick UTM, at a cross-head speed of 500 mm per minute and at 28 ± 2°C. The tear strength values are reported in kN/m.

### II.4.3. Hardness

As per ASTM D-2240-81 test method, the hardness of the samples was measured using a Shore A type Durometer, which employed a calibrated spring to provide the indenting force. Since the hardness reading decreased with time after firm contact between the indentor and the sample, the reading was taken immediately after the establishment of firm contact.

### II.4.4. Abrasion resistance

The abrasion resistance of the samples was tested using a Du pond abrader. In this machine, two test pieces, each having 2 cm square surface, are simultaneously held against an abrasive paper disc which rotates at a speed of 40 rpm. The normal load on the samples was 3.26 Kg and the silicon carbide abrasive paper used for the test was of grain size 320. The samples were abraded for 10 min. after an initial conditioning period of 5 min. Seperate abrasive discs were used for each sample. The abrasion loss of the samples was calculated and expressed as volume loss in $cm^3$ $h^{-1}$.

### II.4.5. Compression set

The compression set was measured according to ASTM D 395-71 (method B). The samples (1.25 cm thickness and 2.8 cm diameter) in duplicate, compressed to give 25 per cent deflection, were kept in an air oven at 70°C for 22 h. After the heating period, the compression was released, the samples were cooled to room temperature for half an hour and final thickness was measured. The compression set was calculated using the equation

$$\text{compression set (\%)} = \frac{t_o - t_f}{t_o - t_s} \times 100 \quad \ldots\ldots \quad (II.2)$$

where $t_o$ and $t_f$ are the initial and final thickness of the specimen, respectively and $t_s$, the thickness of the spacer bar used.

### II.4.6. Rebound resilience

The rebound resilience of the composites was measured using Dunlop Tripsometer (BS 903, Part 22, 1950). The sample was held in position by applying vacuum. It was conditioned by striking the indentor six times. The temperature of the specimen holder and the sample was kept constant at 35°C. Rebound resilience was calculated as,

$$\text{Rebound resilience (\%)} = \frac{1 - \cos\Theta_2}{1 - \cos\Theta_1} \times 100 \quad \ldots\ldots \quad (II.3)$$

where $\Theta_1$ and $\Theta_2$ are the initial and rebound angles respectively. $\Theta_1$ was $45^o$ in all cases.

## II.5. Melt flow studies

### II.5.1 Equipment details

A capillary rheometer attached to a Zwick UTM model 1474 was used to carry out the melt flow studies. The extrusion assembly consisted of a barrel, made of hardened steel, mounted on a special support, underneath the moving cross-head of the Zwick UTM. A hardened steel plunger, which is accurately ground to fit inside the barrel is held to the load cell extension. An insulating ring thermally isolates the barrel from the rest of the machine and prevents heat losses due to conduction. The capillary is inserted at the bottom of the barrel and is locked using a clamping device. The capillary is made of tungsten carbide. The barrel was heated using a three zone temperature control system. The difference between the successive temperature zones in the barrel was kept at 5°C and the temperature of the lower zone, where the capillary is located, is taken as the test temperature.

The moving cross-head of the Zwick UTM runs the barrel at a constant speed irrespective of the load on the melt, maintaining constant volumetric flow rate through the capillary. The cross-head speed can be varied from 0.5 mm/min. to 500 mm/min. giving shear rates ranging from 3 $s^{-1}$ to 3000 $s^{-1}$ for a capillary of l/d= 40. Forces corresponding to specific plunger speeds were recorded on a strip chart recorder. These values were converted into shear stresses.

### II.5.2. Test procedure

The sample to be tested was placed inside the barrel which was maintained at the test temperature. The sample was forced down to the capillary using the plunger attached to the cross-head. After a warming up period of three minutes, the melt was extruded through the capillary at pre-selected speeds of the cross-head. The melt height in the barrel before extrusion was kept the same in all experiments and the machine was operated to give ten different plunger speeds. Each plunger speed was continued until the recorded force was stabilized, before changing to the next speed. Forces corresponding to specific plunger speeds were recorded. The force and cross-head speed were converted into apparent shear stress ($\tau_w$) and shear rate ($\dot{\gamma}_w$) at the wall by using the following equations[6].

$$\tau_w = \frac{F}{4\, A_p\, (l_c/d_c)} \qquad \ldots\ldots \quad (II.4)$$

$$\dot{\gamma}_w = \frac{(3n'+1)}{4n'} \, \frac{32\, Q}{\pi\, d_c^{\,3}} \qquad \ldots\ldots \quad (II.5)$$

where

$F$ = Force applied at a particular shear rate

$A_p$ = Cross sectional area of the plunger

$l_c$ = Length of the capillary

$d_c$ = Diameter of the capillary

$Q$ = Volume flow rate

$n'$ = Flow behaviour index, defined by $\frac{d\,(\log \tau_w)}{d\,(\log \dot{\gamma}_{wa})}$

$\dot{\gamma}_{wa}$ = Apparent wall shear rate

$\dot{\gamma}_w$ = Actual shear rate at wall n' is determined by regression analysis of the values of $\tau_w$ and $\dot{\gamma}_{wa}$ obtained from the experimental data. The shear viscosity '$\eta$' was calculated as

$$\eta = \frac{\tau_\omega}{\dot{\gamma}_\omega} \qquad \ldots\ldots \quad (II.6)$$

The shear stress at the wall requires correction as suggested by Bagely[7]. But the correction factor diminishes as the length to diameter ratio increases. For a capillary having $\frac{l}{d}$ ratio 40, it is assumed that the correction factor is negligible. For the analysis of the data, the following assumptions were also made:

1. There is no slip at the capillary wall.
2. The material is incompressible.
3. The fluid is time independent.
4. The flow pattern is constant along the capillary.
5. The flow is isothermal.
6. The flow properties are independent of hydrostatic pressure.

### II.5.3. Extrudate swell

It is expressed as the diameter of the extrudate to that of the capillary used. The extrudate emerging from the capillary was collected without any deformation. The diameter of the extrudate was measured after 24 h. rest period using a WILD Stereomicroscope model M 650 at several points on the extrudate. The average value of 10 readings was taken as diameter ($d_e$) of the extrudate and swelling index was calculated as $(d_e/d_c)$ where $d_c$ is the diameter of the capillary. For each sample, the extrudate swell at two different shear rates was determined.

## II.6. Degradation studies

### II.6.1. Ozone cracking

The ozone test chamber manufactured by MAST Development Company, USA, was used to study ozone cracking. The chamber provided an atmosphere with a controlled concentration of ozone and temperature. Ozone concentration used was 50 pphm which is generated by an UV quartz lamp. The test was carried out as per ASTM D-1149-81 specification. The test was conducted at 38.5°C

### II.6.2. Radiation studies

Test samples (2 ± 0.2 mm thick) were irradiated with $\gamma$-rays from a $^{60}$Co source in a gamma chamber. The samples were irradiated for different radiation doses at a dose rate of 0.321 Mrad/h in air at room temperature. The mechanical properties were measured before and after irradiation.

### II.6.3. Thermal ageing

Test samples (2 ± 0.2 mm thick) were aged at 100°C for three and five days in an oven. The tensile and tear strengths were measured before and after ageing. The percentage retention of properties after ageing was calculated.

## II.7. Scanning electron microscopy studies

The scanning electron microscopy (SEM) photomicrographs given in this work were obtained using JEOL 35 C model scanning electron microscope, the principle of which is given in Figure II.3 [8]. The fracture surfaces were carefully cut from the failed test specimens without touching the surface and were sputter-coated with gold within 24 h. of testing. The SEM observations were made within 24 h. of gold coating. The fractured specimens and the gold coated samples were stored in a desiccator till the SEM observations were made. There should not be any change in the fracture pattern when the SEM observations were made one month after gold coating[9]. The operating conditions of the SEM are summarised in Table II.3.

## II.8. Dynamic mechanical properties

The dynamic mechanical properties of NR-Sisal composites were measured using a dynamic mechanical analyser (Polymer Laboratories DMTA MK-II), consisting of a temperature programmer and a controller. It measures dynamic moduli (both storage and loss) and damping of the specimen under oscillatory load as a function of temperature. The experiment was conducted at a strain amplitude of 64 $\mu$m and a frequency of 10 Hz. The heating rate of the samples was 1°C/min. Liquid nitrogen was used to achieve sub ambient temperature. The mechanical loss factor $\tan\delta$ and dynamic moduli (E' and E") were calculated with a micro computer.

## II.9. Stress relaxation

The stress relaxation measurements were carried out in a Zwick Universal Testing Machine model 1474. The dumb-bell shaped test specimen was pulled to desired strain level (20-70%) at fixed strain rate of 0.016 $s^{-1}$. The test was carried out at room temperature. The stress was recorded as a function of time on a chart paper initially at a higher speed and later at a lower speed. The ratio $\sigma_t/\sigma_o$ is plotted against logarithm of time, $\sigma_t$ and $\sigma_o$ being stresses at time t and that at zero time, respectively.

## II.10. Swelling studies

For swelling studies, vulcanized composites were cut circularly (diameter 1.94 cm). The thickness of the composite was measured using a micrometer screw gauge. Dry weights of the cut samples were taken before immersion in the liquid contained in air tight weighing bottles. The samples were removed from the bottles at periodic intervals, the wet surface was quickly dried using a piece of blotting paper and weighed immediately in air tight weighing bottles. During swelling any change in the diameter and thickness of the sample was determined by means of a vernier caliper and a micrometer, respectively.

The uptake of the liquid by the polymer during swelling was expressed as moles of liquid sorbed by 100 g. of the polymer. This method was found to be more convenient for comparison of sorption data and was adopted by many researchers[10,11].

To determine the volume fraction of rubber in the unswollen vulcanizate, the test specimen was weighed both in air and water. The difference between the two weights gave the volume of the samples. Using the base formulation, the amount of rubber present in the weighed sample of each specimen and its volume were calculated. From these data the volume fraction of rubber present in dry specimen was calculated and it is denoted as $V_I$. These dry specimens were then swollen in solvents upto equilibrium swelling volume. Volume of swollen samples was determined by hexane displacement method. The displaced volume of hexane was corrected for actual volume of swollen samples by multiplying them with density of hexane. From this, the volume fraction of rubber in the swollen sample was calculated.

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Table II.1. Specifications for ISNR-5 grade natural rubber

| Parameters | Limit | Actual value |
|---|---|---|
| Dirt content, % by mass, max | 0.05 | 0.03 |
| Volatile matter, % by mass, max | 0.80 | 0.50 |
| Nitrogen, % by mass, max | 0.60 | 0.30 |
| Ash, % by mass, max | 0.50 | 0.40 |
| Initial plasticity, $P_0$, min. | 30 | 38 |
| Plasticity retention index PRI , min. | 60 | 78 |

Table II.2. Chemical constitution of sisal fibre

| | | |
|---|---|---|
| Cellulose | - | 78% |
| Hemi cellulose | - | 10% |
| Lignin | - | 8% |
| Waxes | - | 2% |
| Ash | - | 1% |

Table II.3. Operating conditions of the SEM

| | |
|---|---|
| Specimen position, tilt, degree | adjustable |
| Maximum resolution, nm | 0.5 |
| Spot size, angstrom | 640 |
| Emission current, amp. | 26 |
| Aperture, microns | 200 |
| H.T., Kv | 25 |
| Depth of focus | high |

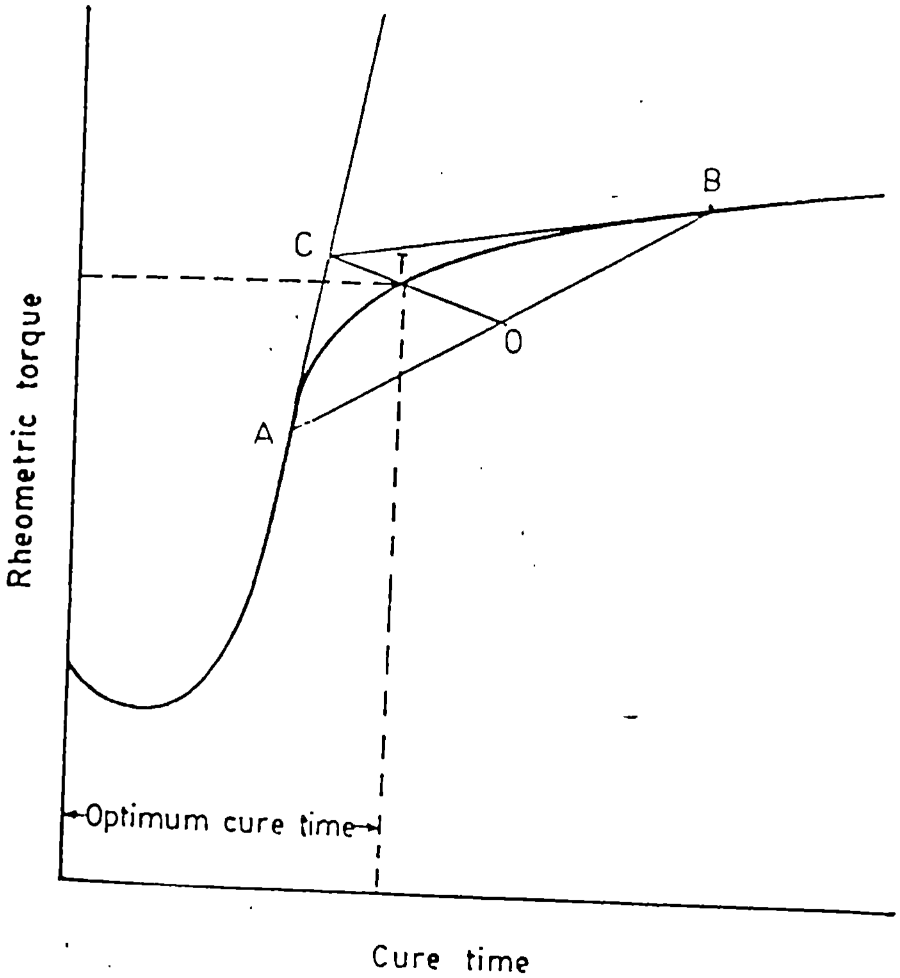

Figure II.1. Determination of optimum cure time by modified tangent method.

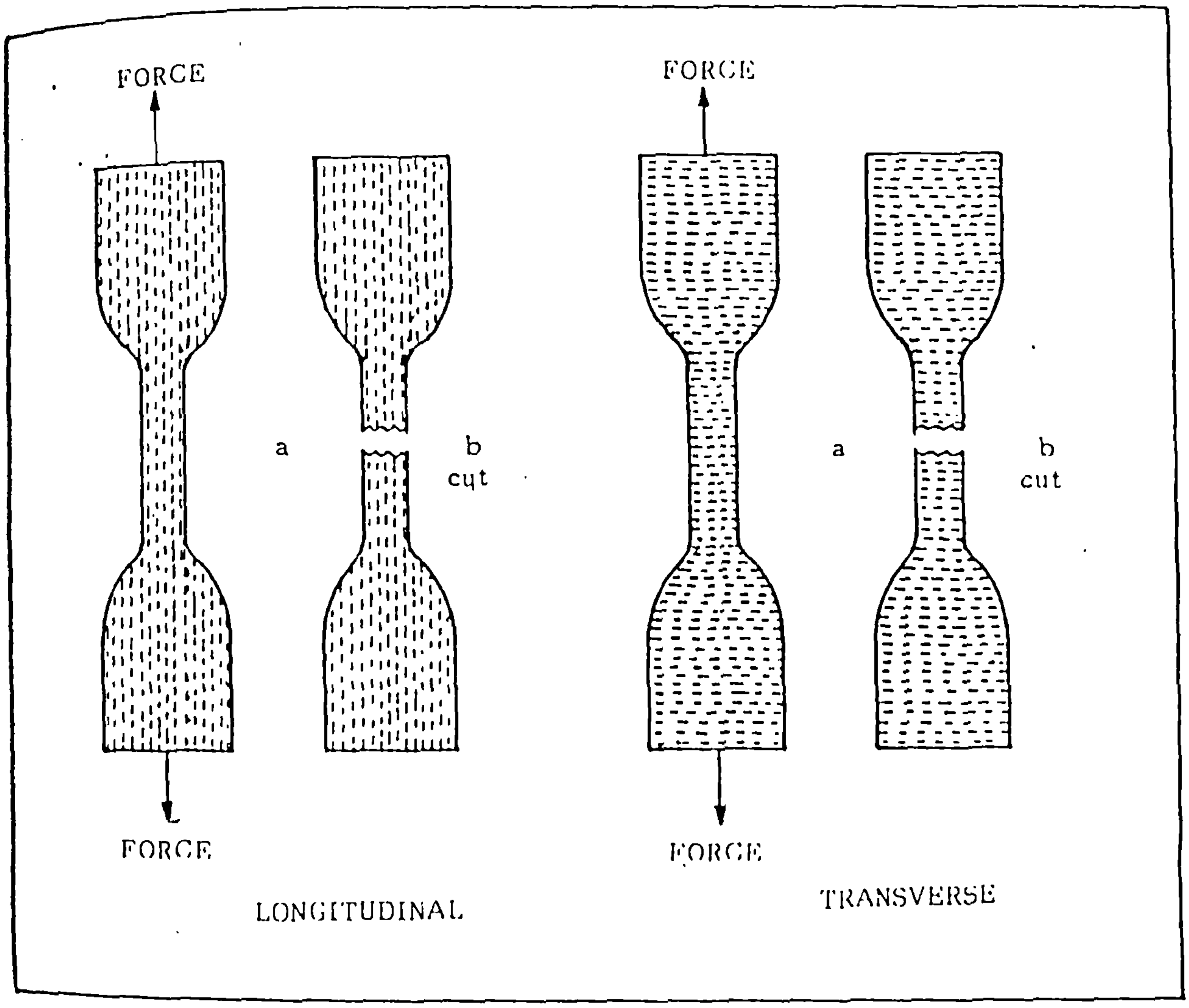

Figure II.2. Longitudinal and transverse orientation of the fibre.

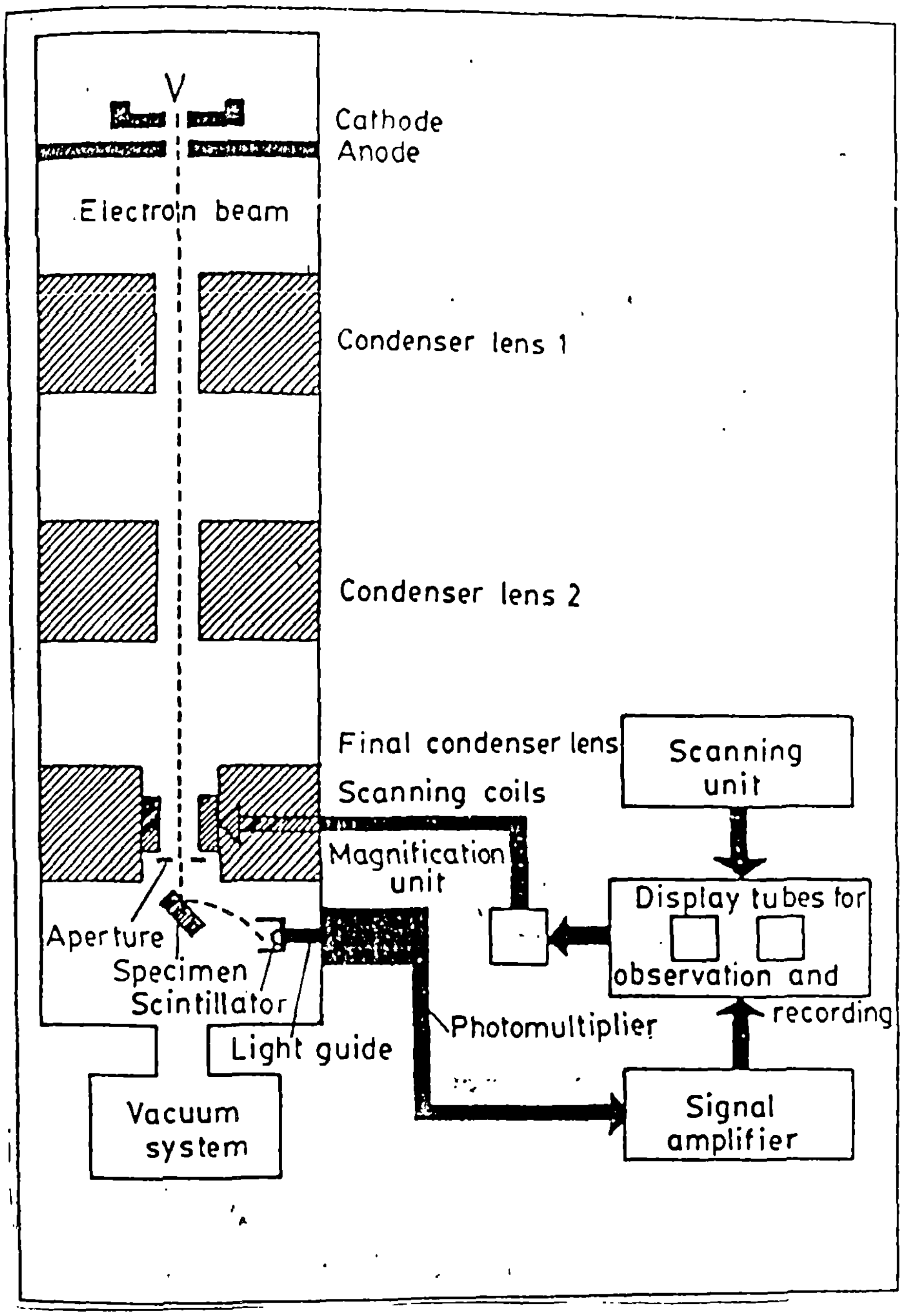

**Figure II.3.** Schematic construction of a scannin electron microscope.

# CHAPTER III

## MECHANICAL PROPERTIES OF SHORT SISAL FIBRE-NATURAL RUBBER COMPOSITES

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The results described in this chapter have been published in the _Indian Journal of Natural Rubber Research_, Vol.4, No.1, P. 55 (1991).

Short fibre reinforced elastomer composites are well known because of the easy processing and low cost coupled with high strength. These composites are also amenable to standard rubber processing techniques, such as extrusion, calendering and various types of moulding techniques[1-6]. Most of the properties of fibre composites strongly depend on microstructural parameters such as fibre diameter, fibre length, volume fraction of fibre, orientation of fibre and the bonding between the fibre and the rubber. The fibre-rubber interfacial bonding can be improved by modifying the fibre surface by chemical treatment or by adding an external bonding agent. The length of the fibre should be above a critical length for effective stress transfer from the matrix to the fibre to occur, which in turn depends on the bonding between the fibre and the matrix. Similarly, reinforcing effect of the fibres at low volume fraction is pronounced only when good mechanical bonding exists between the fibre and the matrix.

Several types of elastomers have been used as matrices for natural fibre composites[7-10]. Jute, silk and coir have been used as reinforcing material for natural rubber (NR)[7,10]. Sisal fibre has been studied as a reinforcing material in plastics[11,12]. However, no systematic study has been reported on the use of sisal fibre in rubbers. The physical properties of sisal fibre is superior to other naturally occurring fibres and its worldwide production is high (6 lakhs tonnes per year) as compared to other naturally occurring fibres. Since the raw sisal fibre has very poor adhesion with non-polar matrices, its surface has to be modified by chemical treatment.

Results of the investigations on the cure characteristics and mechanical properties of NR-short sisal fibre composites are reported in this chapter. The study includes effects of acetylation, aspect ratio, volume loading of the fibre and a dry bonding system on the above properties. The formulations of the mixes are given Tables III.1 & III.2.

## III.1. Cure time

The optimum cure times of the mixes J to S and that of A to I are given in Tables III.2 and III.3, respectively. It is clear that on increasing the fibre loading, the optimum cure time remains almost constant (J to S). This trend is observed for the mixes containing both acetylated and untreated fibre. In the presence of bonding agent the optimum cure time is lower for mixes containing acetylated fibre when compared with that of compounds containing untreated fibre at the same loading. Presence of silica affects cure time. This is evident from increased optimum cure times of mixes G, D and F compared with that of E (Table III.3). Silica retards cure probably by absorbing the curatives[15]. Incorporation of resorcinol and hexamethylenetetramine as dry bonding agent also does not affect cure. This is evident from the optimum cure times of mixes E, H and I compared to that of B (Table III.3). However, in the case of both acetylated and untreated fibre-filled composites the optimum cure time is slightly lower when the fibre loading is 40 phr (Table III.2).

## III.2. Effect of critical fibre length

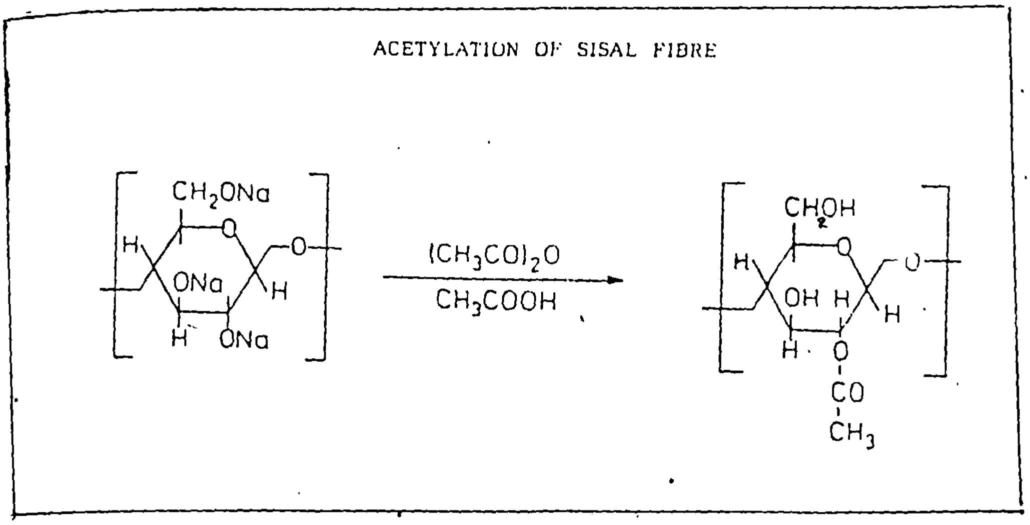
Compounds H, E and I have the same ingredients except that they contain acetylated fibre having lengths 6 mm, 10 mm and 15 mm, respectively (Table III.1). Shear forces during mixing orient most of the fibres along the grain direction. It also causes breakage of fibres. The extent of fibre breakage in the above mixes was evaluated by dissolution of the compound in benzene, followed by the extraction of fibre and examination of fibre length by a polarising microscope. The breakage analysis data of the mixes H, E and I are given in Table III.4. However, no measurable change in average diameter (0.103 mm) occurred during mixing. From the data, it is seen that in mix E, majority of fibres were having an aspect ratio of 20 to 60 (2 to 6 mm length) after breakage. This mix had an original fibre length of 10 mm. Even though an aspect ratio of 100 to 200 is generally required for effective stress transfer in short fibre-elastomer composites[3], in the case of jute fibre-rubber composites, aspect ratio as low as 40 was reported to be sufficient for reinforcing rubber matrix, since there was very good adhesion between the fibre and rubber[7].

In the present case it is seen that reinforcement is high for the mix which contained fibres having an original length of 10 mm, as evidenced by the higher tensile strength and modulus (Table III.3) of mix E compared to those of mix H. Mix E contained a total of 65.4 per cent of the fibre in the range of 2-6 mm length after breakdown (Table III.4). The tensile strength and modulus of mix I were comparable to those of mix E and not to those of mix H, even though it contained almost the same level of fibres (59.9 per cent) having length in the range 2-6 mm as that of mix H. This is likely to be due to the presence of 18.4 per cent fibres having a final length in the range of 6-10 mm. These observations indicate that an original fibre length of 10 mm is essential and sufficient for getting reinforcement in natural rubber-short sisal fibre composites. Hence further studies reported in this work were conducted using fibres having 10 mm length.

## III.3. Effect of chemical treatment

One of the most important factors for obtaining good reinforcement by fibre in a rubber-fibre composite is adequate adhesion between the rubber matrix and fibre[2]. Adhesion between the fibre and rubber depends upon the structure and polarity of these materials. As reported earlier by Chand et al.[L3] the surface of sisal fibre can be modified by aqueous alkali treatment at elevated temperature followed by acetylation and this was found to improve its adhesion to some extent. The surface of sisal fibre, both acetylated and untreated, was examined by means of scanning electron microscope. The surface structures of raw and acetylated fibres are shown in Figures III.1a & III.1b, respectively. The treatment caused the fibre to fibrillate into the ultimate. In addition, the treated surface is highly rough and this facilitates mechanical bonding with rubber matrix.

It is possible to explain the mechanism of bonding involved between treated fibre and rubber molecule. The cellulosic hydroxyl groups in the fibre are relatively unreactive, since they form strong hydrogen bonds. Alkali treatment before acetylation may destroy the hydrogen bonding in cellulosic hydroxyl groups, and cause partial removal of lignin thereby making them more reactive. Considering the ring structure of cellulose, a possible route for acetylation may be as given in Scheme 1.

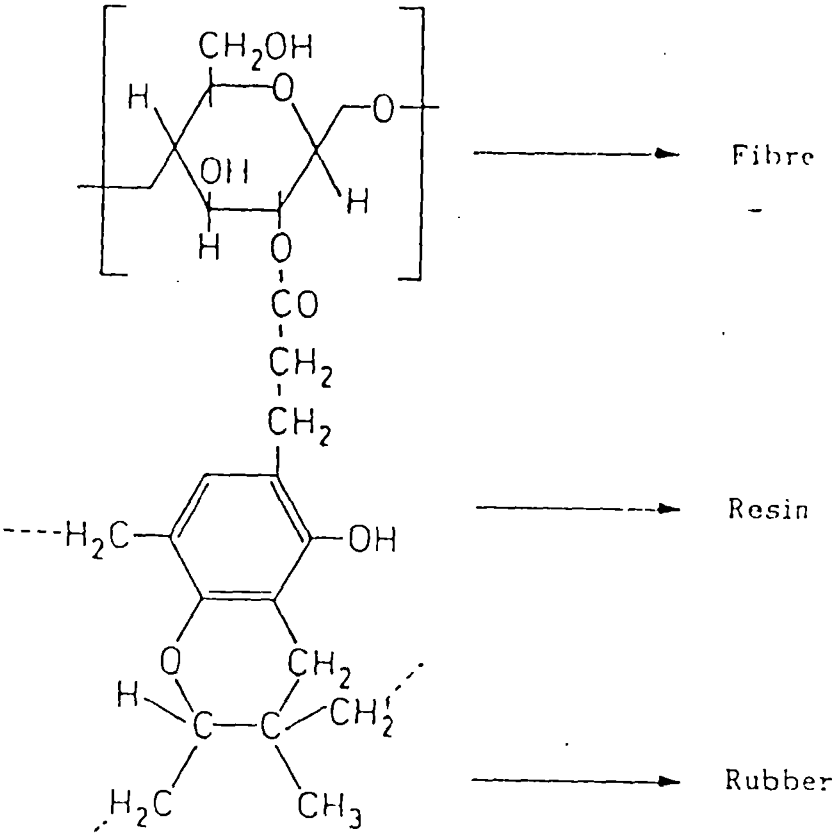


Scheme 1

The acetylation of sisal fibre supported by IR spectrum has been reported[13]. The hydrogen atom on the acetyl carbon atom becomes more reactive due to the presence of the carbonyl group. This may form chemical link with active sites on rubber, thereby improving adhesion. This is evident from the difference in strength of the composites containing acetylated and untreated fibres. In mixes A & C (Table III.1) untreated fibre was used whereas mixes B and D contained acetylated fibres. The properties of vulcanizates given in Table III.3, indicate that compound B has higher modulus and tensile strength and lower elongation at break compared with those of compound A. Similarly, between compounds C and D, the latter showed higher modulus, tensile strength and tear strength and lower elongation at break. The effect of acetylation of fibre in improving the properties of the composites is also reflected in the properties of compounds P,Q,R and S as compared with those of K,L,M and N respectively.

## III.4. Effect of bonding agent

It has already been established that a tricomponent system consisting of hexamethylenetetramine, resorcinol and fine particle silica (HRH system) can be used as a bonding agent for most rubber and fibre combinations[3]. Bonding by HRH system involves a condensation reaction between resorcinol and the methylene donor (Hexa) which takes place during vulcanization and silica is reported to accelerate this reaction. The bonding resin acts as an intermediate in binding rubber and the fibre[16]. The bonding between rubber and acetylated fibre through the bonding resin is likely to have followed Scheme 2.



Scheme 2

Mixes A and B containing no bonding agent have very poor mechanical properties compared to mixes C and D which contained the bonding agent (Table III.3). Acetylation of the fibre further enhanced the effect of bonding agent as seen from the higher modulus, tensile strength and tear strength of compound D compared with those of compound C. In terms of the reactivity of the OH groups in the fibre and steric effects of the resin, acetylation of the fibre is expected to make the bonding of the resin with fibre and rubber easier. The bonding between acetylated fibre and rubber can well be understood from SEM photomicrograph of tensile fractured surface of mix R (Figure III.1c.). Due to good bonding between fibre and rubber matrix, fibres are broken during tensile failure. The broken ends of the fibres protruding in the fracture surface can be seen from the photomicrograph . Figure III.1d is the SEM photomicrograph of acetylated fibre stripped out from mix E during tensile testing. It is interesting to note that rubber particles are adhered to the fibre due to good bonding between the treated fibre and the rubber.

## III.5. Effect of silica

In short sisal fibre-natural rubber composites the effect of silica in the HRH dry bonding system was found to be contrary to its normal functioning in short fibre-rubber composites. Silica in the HRH system was found to decrease the mechanical properties of the composites. Compounds E,F,D and G (Table III.1) contained 0, 5, 8.75 and 10 parts of hydrated silica, respectively. It is observed that the tensile strength, modulus and tear strength of compounds G, D and F were lower than those of compound E. However, the decrease in these properties was not proportional to the quantity of silica. It indicated that a small quantity of silica is sufficient to influence the bonding characteristics of the RH system in this particular case. O'Connor[2] also made similar observations with nylon and cellulosic fibres and established that the RH system is better than the HRH system. Hence in the succeeding experiments the RH system was used as the bonding agent.

## III.6. Effect of fibre content

Table III.2 gives formulations of mixes J to S. Here we have varied concentration of the fibre (10 mm length) from 0 to 40 phr both in the case of untreated and acetylated fibre.

In the case of untreated fibre, up to 17.5 per cent volume loading, tensile strength in the longitudinal direction decreased and thereafter the strength increased (Figure III.2a). For acetylated fibre,upto 12 per cent volume loading tensile strength in the longitudinal direction decreased and thereafter increased. In transverse orientation of the fibre (Figure III.2b) tensile strength decreased continuously with increase in fibre concentration, both for acetylated and untreated fibre. Greater hindrance to the progress of fracture front is experienced when fibres are oriented longitudinally (ie., perpendicular to the fracture surface). Breakage and pull-out of the fibre take place mainly when fibres are oriented in the longitudinal direction, whereas for transversely oriented fibre the crack progresses in the direction of fibre alignment. Tensile strength in the longitudinal direction of fibre orientation is, therefore, always greater than that in the transverse direction of orientation. Lower tensile strength of mixes K to S compared with that of mix J which contained no fibre may be due to two reasons. (1) The optimum cure time of the rubber compound at a temperature of 150°C may not be sufficient to develop the maximum adhesive strength through resin formation. (2) At low volume loadings, fibre acted as flaws rather than helping in load transfer. But at sufficiently higher loadings, fibre acted as a load transfer medium and the tensile strength showed an increasing trend beyond this critical level. In the case of acetylated fibre the minimum quantity required for this was observed to be about 12 per cent (v/v) whereas for the untreated fibre the minimum value was found to be about 17 per cent (v/v). This indicated that for the treated fibre effective load transfer could take place at lower loadings because of the better bonding realized.

Both untreated and acetylated fibres were found to improve tear strength of the composite to a considerable extent (Figures III.3a & III.3b). However in mixes containing untreated fibre (K to N), the increase in tear strength was less compared with the increase in compounds containing acetylated fibre (P to S). The same pattern is observed in the transverse fibre orientation also (Figure III.3b). The higher tear strength of composites having longitudinally oriented fibre is due to the obstruction of tear path by well bonded longitudinally oriented fibres, as explained earlier. This could not take place in the case of composites having transverse fibre orientation[5]. The longitudinal and transverse fibre orientation of mix Q is shown in Figures III.3c & III.3d respectively.

Elongation at break drops drastically with loading of fibre (Figures III.4a & III.4b). In the case of composites containing the acetylated fibre the extent of drop is much higher than that in the untreated fibre composites. Elongation at break in the transverse direction also registered the same trend but with considerably higher values (Figure III.4b). From the variation of tensile strength and elongation at break, it can be understood that untreated fibre is less effective in load transfer whereas acetylated fibre functions effectively as a reinforcing filler beyond a loading of 12 per cent (v/v). This is further supported by the modulus of the composites shown in Figure III.5. The modulus at 10% elongation was much higher for the acetylated fibre composites compared with that containing untreated fibre at all loading.

Compression set increased steadily with increase in volume loading of fibre (Figure III.6). The rate of increase in set, however, decreased as the loading was increased. But set was lower for the composites having acetylated fibre. It has been reported that this behaviour is due to buckling of the fibre taking place invariably when the closely packed fibres are compressed in the direction of their alignment[7]. Good adhesion between the acetylated fibre and rubber reduced the extent of buckling of the fibre resulting in reduced set for the compounds containing acetylated fibre. Hardness of the composites increased sharply with volume loading of the fibre (Figure III.7). The reinforcing effect of acetylated fibre was reflected in hardness also.

Abrasion loss decreased with increase in fibre concentration in the composite (Figure III.8a). In this case also the acetylated fibre composites showed better resistance to abrasion compared with those containing the untreated fibre. Abrasion involves many basic processes such as cutting, chipping, tearing, fatigue, etc. Better abrasion resistance of the acetylated fibre composites may be resulting from the combination of higher tear strength, tensile strength and modulus achieved through better bonding with the rubber matrix. The SEM photomicrographs of the abraded surfaces of the samples of mix S are given in Figures III.8b & III.8c. From these photomicrographs it is well understood that the fibres effectively hinder the chipping and cutting of rubber. A magnified portion of the abraded surface (Figure III.8c) shows that better bonding of the rubber and fibre helps in reducing the loss of rubber during abrasion.

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**Table III.1. Formulations of mixes A to I**

| | A | B | C | D | E$^{+}$ | F | G | H$^{++}$ | I$^{+++}$ |
|---|---|---|---|---|---|---|---|---|---|
| Natural Rubber | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Stearic Acid | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Zinc Oxide | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Resorcinol | 0 | 0 | 8.75 | 8.75 | 8.75 | 8.75 | 8.75 | 8.75 | 8.75 |
| Hexa$^{*}$ | 0 | 0 | 5.6 | 5.6 | 5.6 | 5.6 | 5.6 | 5.6 | 5.6 |
| Silica | 0 | 0 | 8.75 | 8.75 | 0 | 5 | 10 | 0 | 0 |
| Sisal fibre (untreated) | 35 | - | 35 | - | - | - | - | - | - |
| Sisal fibre (acetylated) | - | 35 | - | 35 | 35 | 35 | 35 | 35 | 35 |
| T D Q$^{**}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| C B S$^{***}$ | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| Sulphur | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |

* Hexamethylenetetramine

** 2:2:4 trimethyl 1,2 dihydroquinoline polymerised

*** N-cyclohexyl-2-benzthiazylsulphenamide

\+ Fibre length 10 mm

++ Fibre length 6 mm

+++ Fibre length 15 mm

Table III.2. **Formulations of mixes J to S**

| | J | K | L | M | N | P | Q | R | S |
|---|---|---|---|---|---|---|---|---|---|
| Natural Rubber | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Stearic Acid | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Zinc Oxide | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Resorcinol | 0 | 2.5 | 5 | 7.5 | 10 | 2.5 | 5 | 7.5 | 10 |
| Hexa | 0 | 1.6 | 3.2 | 4.8 | 6.4 | 1.6 | 3.2 | 4.8 | 6.4 |
| Sisal fibre (untreated) | 0 | 10 | 20 | 30 | 40 | - | - | - | - |
| Sisal fibre (acetylated) | - | - | - | - | - | 10 | 20 | 30 | 40 |
| T D Q | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| C B S | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| Sulphur | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |
| Cure time at $150^{\circ}C$ (min.) | 12.5 | 12.5 | 13.5 | 13 | 11 | 11.5 | 12.5 | 12.5 | 10.5 |

Table III.3. Properties of mixes A to I

| | Orientation | A | B | C | D | E | F | G | H | I |
|---|---|---|---|---|---|---|---|---|---|---|
| Cure time at 150$^{o}$C min. | - | 10.5 | 11.5 | 15.5 | 13.5 | 11.5 | 13.5 | 13.5 | 11 | 12.5 |
| Modulus for 10% elongation (MPa) | L | 2.56 | 5.03 | 8.73 | 10.8 | 13.2 | 10.2 | 10.9 | 9.67 | 13 |
| | T | 1.02 | 0.93 | 1.78 | 1.90 | 1.84 | 5.32 | 2.51 | 1.25 | 1.11 |
| Modulus for 20% elongation (MPa) | L | 3.11 | 5.05 | - | - | - | - | - | - | - |
| | T | 1.36 | 1.62 | 2.80 | 3.15 | 3.10 | 3.6 | 3.9 | 2.02 | 1.81 |
| Tensile strength (MPa) | L | 4.53 | 5.79 | 8.4 | 11.70 | 14.9 | 11.7 | 10.9 | 10.87 | 14.9 |
| | T | 3.73 | 4.49 | 4.76 | 5.04 | 6.61 | 5.26 | 5.22 | 4.16 | 5.11 |
| Tear strength (kNm$^{-1}$) | L | 47.6 | 47.3 | 66.8 | 86.76 | 87.5 | 85.3 | 86.4 | 62.25 | 82.3 |
| | T | 38.8 | 40.76 | 64.36 | 63.36 | 66.2 | 69.16 | 67.5 | 52.08 | 56.5 |
| Elongation at break (%) | L | 388 | 213 | 22 | 20 | 17 | 19 | 15 | 18 | 18 |
| | T | 576 | 586 | 88 | 115 | 126 | 82 | 60 | 147 | 122 |

Table III.4. **Fibre breakage analysis data**

| Length after breakage, range, mm | H 6mm. (Original) | E 10mm. (Original) | I 15mm. (Original) |
|---|---|---|---|
| 0-2 | 40.7% | 19% | 21.7% |
| 2-4 | 33.9% | 43% | 43.3% |
| 4-6 | 25.4% | 22.4% | 16.6% |
| 6-8 | - | 12% | 11.7% |
| 8-10 | - | 3.4% | 6.7% |

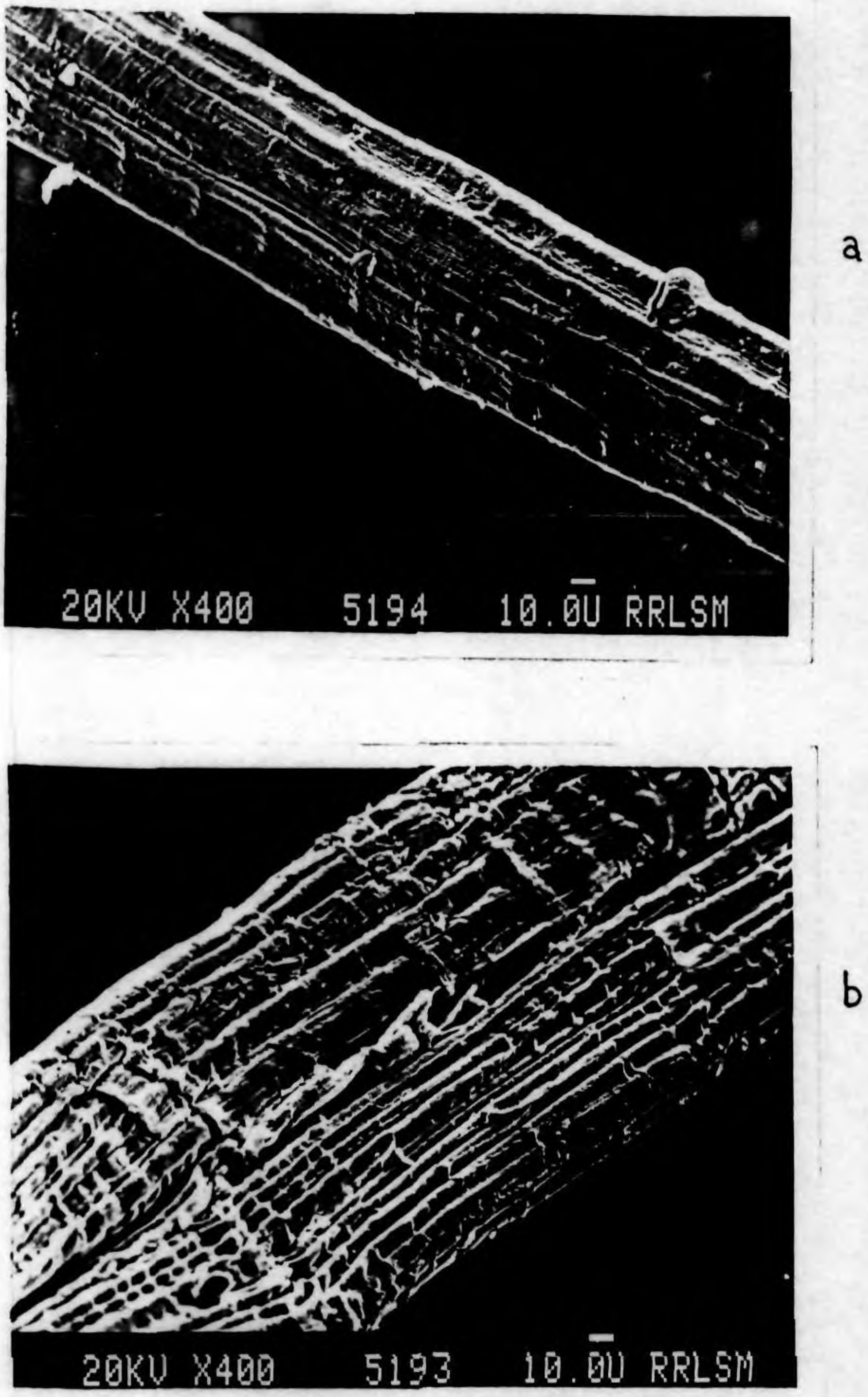
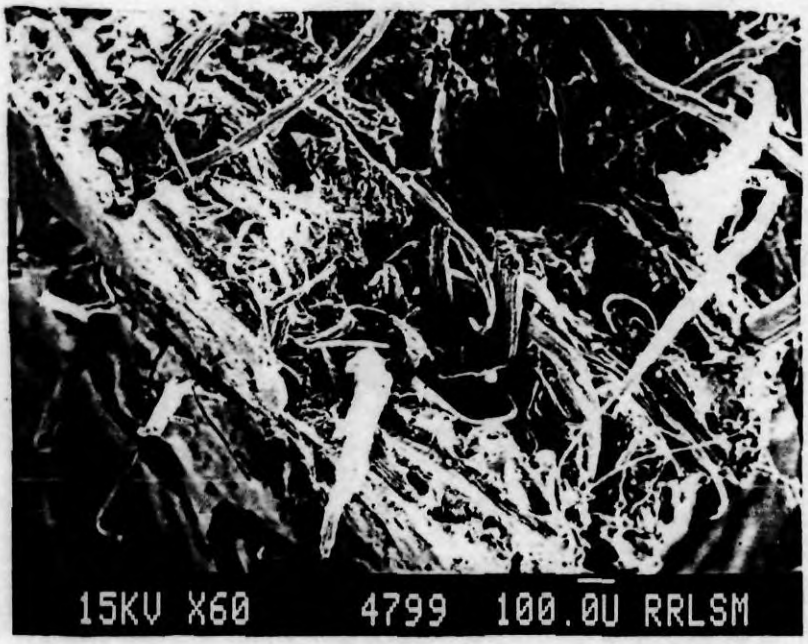


**Figure III.1a.** SEM photomicrograph of the surface of the raw sisal fibre.

**1b.** SEM photomicrograph of the surface of acetylated sisal fibre.



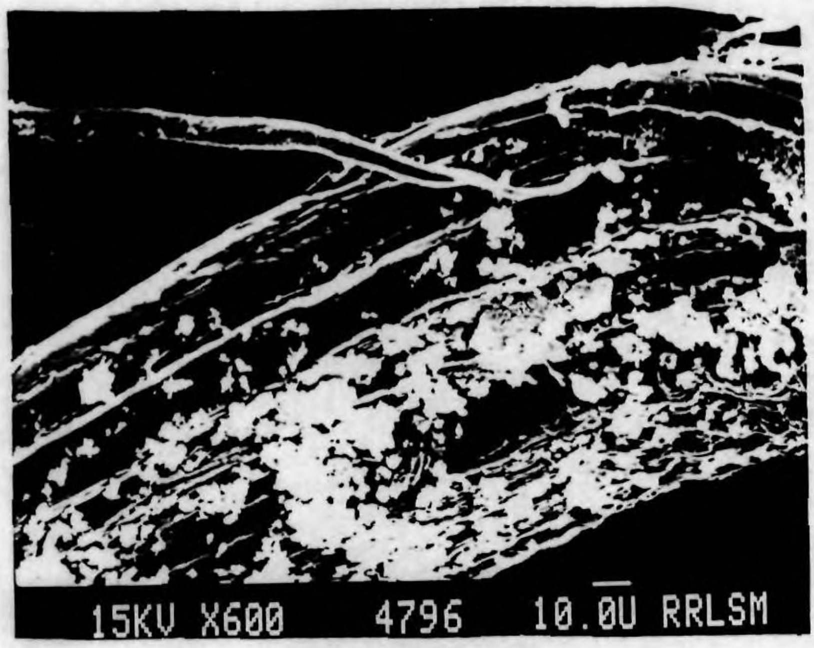


**Figure III.1c.** SEM photomicrograph of tensile fracture surface of mix R showing good adhesion.

**1d.** SEM photomicrograph of the surface of acetylated sisal fibre stripped out from mix E during tensile testing.

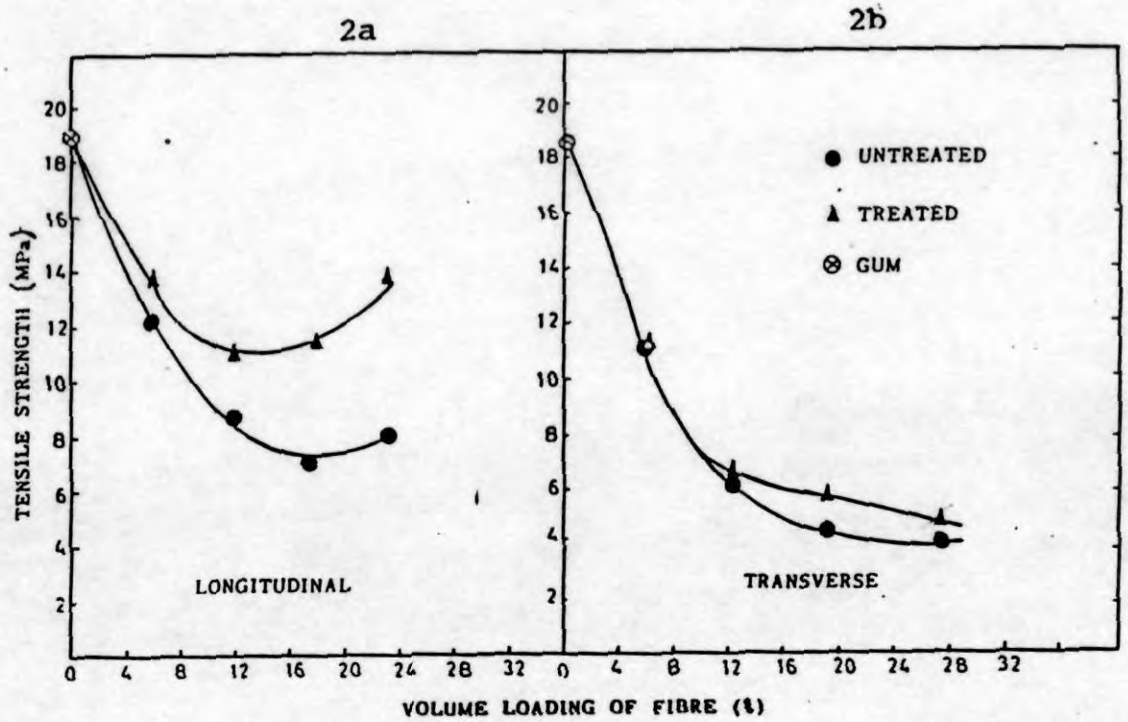


Figure III.2a. Variation of tensile strength with volume loading of fibre in the longitudinal direction.

2b. Variation of tensile strength with volume loading of fibre in the transverse direction.

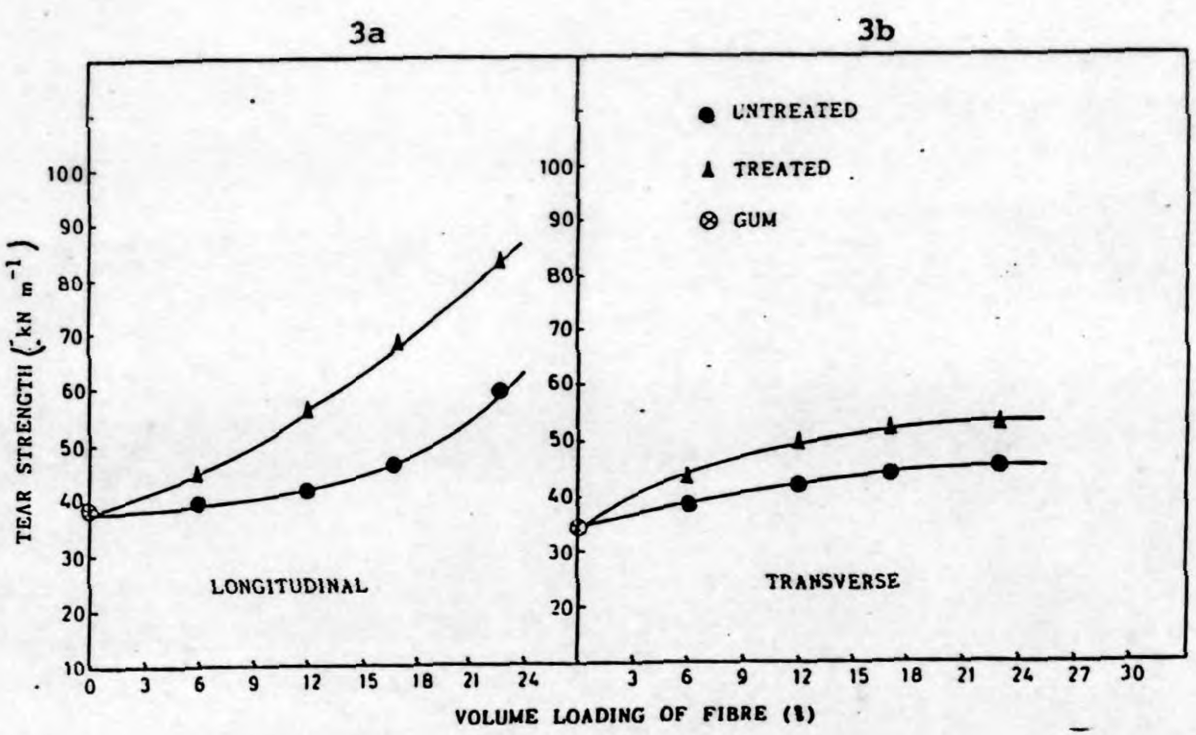
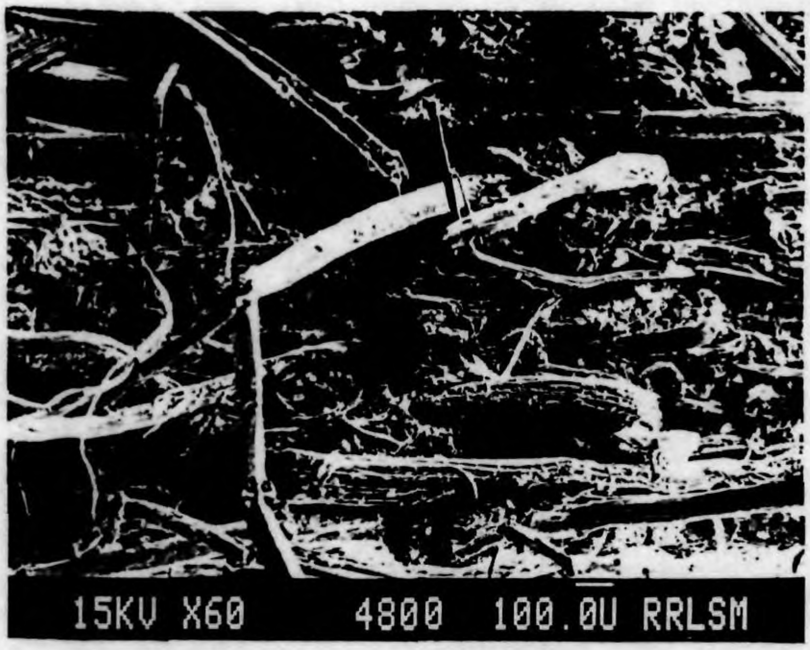


Figure III.3a. Variation of tear strength with volume loading of fibre in the longitudinal direction.

3b. Variation of tear strength with volume loading of fibre in the transverse direction.

c



d

**Figure III.3c.** SEM photomicrograph of the tear fracture surface of mix Q showing longitudinal fibre orientation.

**3d.** SEM photomicrograph of the tear fracture surface of mix Q showing transverse fibre orientation.

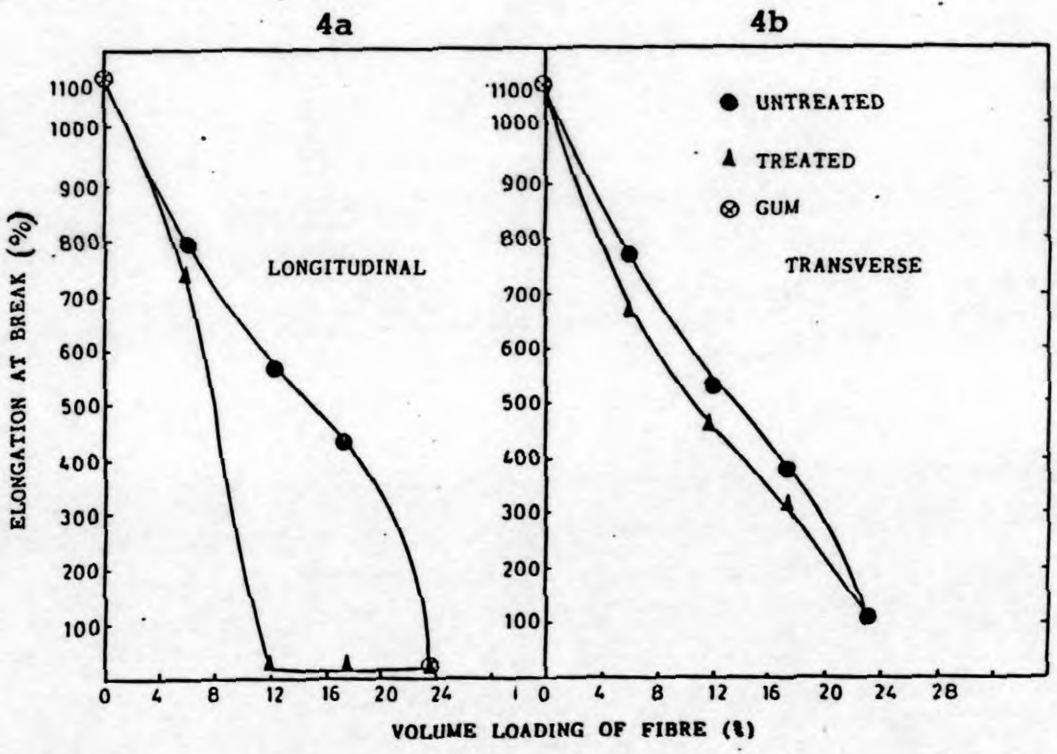


Figure III.4a. Variation of elongation at break with volume loading of fibre in the longitudinal direction.

4b. Variation of elongation at break with volume loading of fibre in the transverse direction.

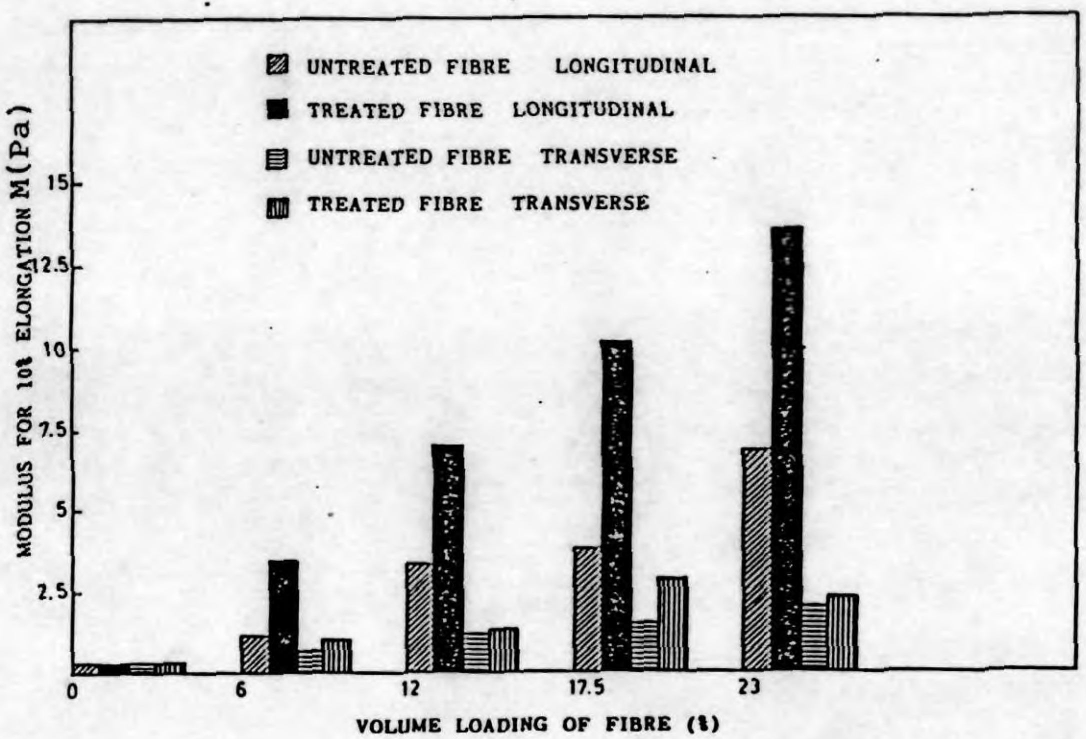


Figure III.5. Variation of modulus at 10 per cent elongation with volume loading of fibre.

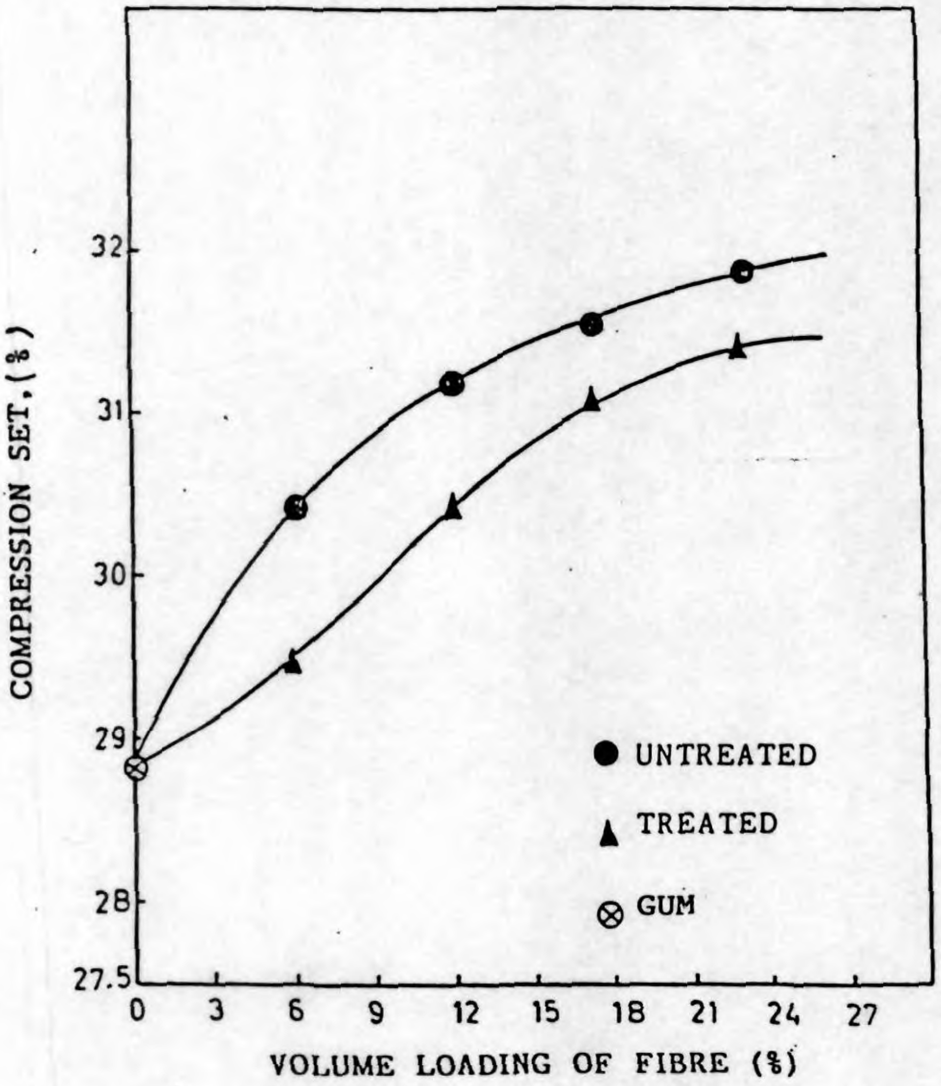


Figure III.6. Variation of compression set with volum loading of fibre.

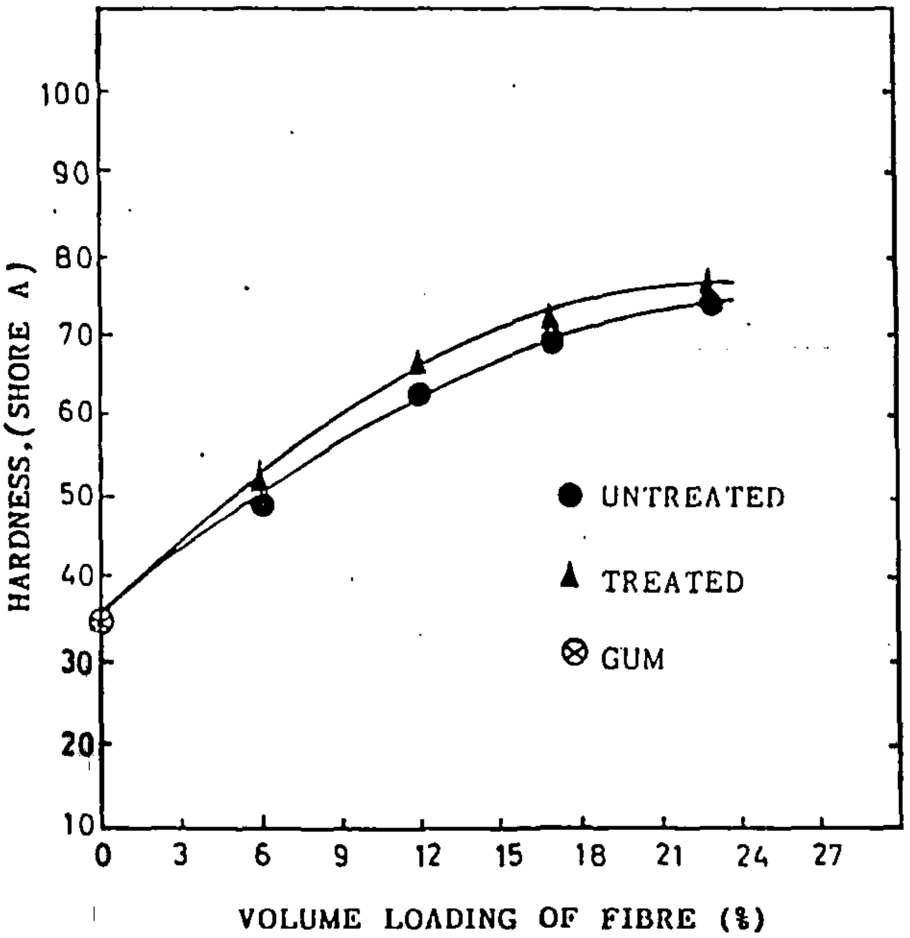


**Figure III.7.** Variation of hardness with volume loading of fibre.

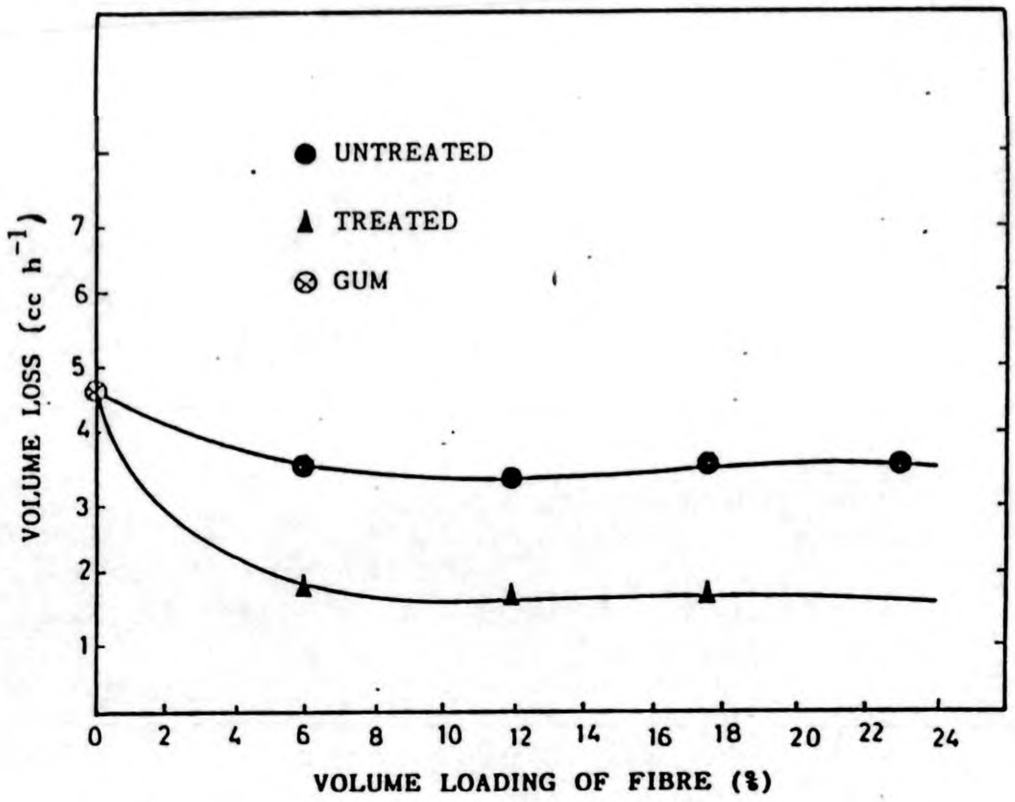
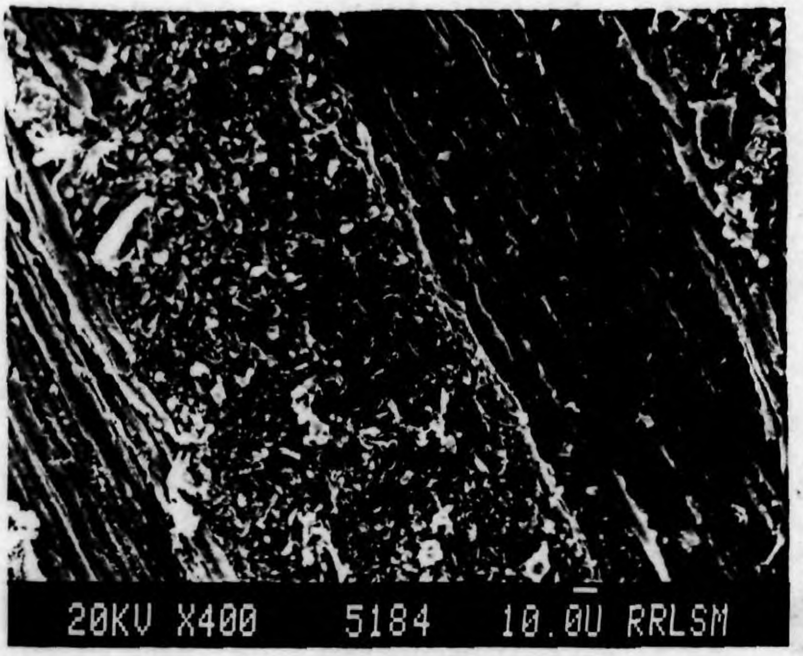


Figure III.8a. Variation of abrasion loss with volume loading of fibre.

b



c

**Figure III.8b.** SEM photomicrograph of abraded surface of mix S.

**8c.**. SEM photomicrograph of magnified abraded surface of mix S.

# CHAPTER IV

# DYNAMIC MECHANICAL PROPERTIES OF SHORT SISAL FIBRE-NATURAL RUBBER COMPOSITES

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The results described in this chapter have been accepted for publication in the Indian Journal of Natural Rubber Research.

Dynamic mechanical properties describe the response of materials to periodically varying strain or stress and are usually measured as functions of frequency or temperature. The loss modulus (E") is a measure of energy dissipated as heat and the storage modulus (E') accounts for the elastic energy stored and recovered in cyclic deformation. The ratio of loss modulus to storage modulus gives the loss tangent (tan $\delta$ ) which indicates the damping characteristics of the material.

Rubber products generally undergo dynamic stressing during service. Therefore, their behaviour in dynamic load application is highly important. In dynamic applications, bonding between the fibre and rubber plays an important role. Ashida et al.[1] have investigated the dynamic mechanical properties of nylon-chloroprene rubber composites, highlighting the effects of absorbed water on dynamic modulus. Carvalho and Bretas[2] have investigated the correlation between interface morphology and dynamic mechanical properties of thermoplastics-carbon fibre composites. Recently, Otaigbe[3] has reported on the dynamic mechanical properties of nylon 6-continuous glass fibre composites at four levels of fibre loading. The influence of fibre-matrix adhesion on the viscoelastic properties of short jute fibre and short glass fibre reinforced rubber composites has been studied by Murthy and De[4,5]. However, till date no detailed study on the dynamic mechanical properties of short sisal fibre reinforced natural rubber composites has been reported.

In this chapter the dynamic mechanical properteis of short sisal fibre reinforced natural rubber composites are described. The effects of acetylation of fibre, fibre orientation, fibre loading, bonding agent and temperature on the dynamic mechanical properties have been investigated. Attempts have been made to correlate the variation in dynamic mechanical properties with the strength of adhesion between fibre and matrix. The formulations of the mixes are given in Table IV.1. The details of the experimental procedure for the measurement of dynamic mechanical properties are given in chapter II.

## IV.1. Effect of acetylation

Figure IV.1 shows the effect of temperature on the storage modulus (E') of the composites containing acetylated and untreated fibres as a function of fibre loading. It is clear from the figure that the addition of both untreated and acetylated fibre increases the storage modulus. But the effect is more pronounced in the case of acetylated fibre than that of the untreated one, at same loading. This is due to the fact that the matrix gets stiffened by the addition of acetylated fibres which are well bonded to the rubber matrix. This indicates the importance of fibre-matrix adhesion in improving the viscoelastic properties of short fibre composites. With the increase of temperature, the storage moduli of both acetylated and untreated composites are decreased. The decrease may be due to the deterioration of the fibre-matrix adhesion at higher temperatures[5]. The effect of temperature on the loss modulus (E") of the composites is shown in Figure IV.2. As in the case of storage modulus, the loss modulus of the composites increased with fibre loading and the effect is more predominant in the case of acetylated fibres due to the strong fibre-matrix adhesion. The damping properties of the composites can be understood from the plot of tan $\delta$ against temperature as shown in Figure IV.3. It is interesting to note that the tan $\delta$ values increased with increase of fibre loading. High interfacial bonding between acetylated fibres and the rubber matrix is evident from their higher tan $\delta$ values as compared with those of the untreated fibre composites. In general the tan $\delta$ values decrease with the increase of temperature and the decrease is sharper at higher loading (>10%) of acetylated fibres.

From Figures IV.1, IV.2 & IV.3, it can be concluded that the fibre-matrix adhesion influences the viscoelastic properties of the composites. When there is no bonding between the fibre and matrix, the fibre can slip past from the matrix under tension, but when there is bonding between the fibre and the matrix, there will be shear at the interface between matrix and fibre, which leads to increased mechanical loss. The high storage modulus of the well bonded composite supports the fact that the load transfer between the fibre and the matrix occurred through the strong fibre-rubber interface. Ashida and coworkers[1] have reported that in the case of cord-rubber composite, the cords do not contribute to mechanical loss in the absence of adhesion and therefore the mechanical loss of the unbonded cord-rubber composite will be lower than that of rubber. But in the case of short fibre reinforced rubber composites, when the bonding between the fibre and rubber is poor, the fibre ends will be free and act as stress raisers and thus contribute to the mechanical loss[4]. However, the values of mechanical loss will increase with increase in adhesion level.

## IV.2. Effect of bonding agent

Unlike the continuous cord reinforcement in which the adhesion can be determined quantitatively with the help of H-test, the quantitative determination of adhesion is extremely difficult in the case of short fibre reinforced composites. However it can be assessed by SEM analysis of the fracture surfaces or by stress-strain curves. Figure IV.4 gives the stress-strain curves of mix L and mix Q containing 20 phr each of untreated and acetylated fibre, respectively. The well bonded, longitudinally oriented fibres in mix Q impart very high modulus and give low elongation for the composite. But in mix L, the tensile strength increases upto the yield point and thereafter it decreases due to the poor bonding between the fibre and rubber. The importance of a strong fibre-rubber interface and its role on the viscoelastic properties can be better understood from Figure IV.5, which shows the variation of E' of mixes B and E with temperature. Mix B contained no bonding agent while in mix E, a bonding agent consisting of resorcinol, and hexamethylenetetramine is incorporated (in both the cases acetylated fibres are used). Hence the high modulus of mix E compared with that of mix B is attributed to the strong fibre-rubber interface created by the bonding agent. This is further confirmed by SEM studies. Figure 6a gives the SEM photomicrograph of tensile fractured surface of mix B containing treated fibre without bonding agent. The long stems of the fibre protruding out of the rubber matrix indicate that the fibres were pulled out of the rubber matrix under tension due to poor bonding. Figure IV.6b gives SEM photomicrograph of tensile fractured surface of mix Q which contained the treated fibre and the bonding agent. The broken ends of the fibre indicate that the fibres were well bonded to the matrix. Unlike Figure IV.6a in this case no debonding can be observed. Careful examination of the fracture surface indicated that the failure is brittle type as evident from the presence of fracture lines in different planes. The brittle nature of the composite is associated with the strong matrix-fibre interactions. The stress-strain curve also supports this view.

## IV.3. Effect of fibre orientation

Figure IV.7 shows the effect of orientation of the fibres on the viscoelastic properties of mix P. From this figure, it is clear that storage modulus remains almost constant with the entire temperature range (25-150°C) of the experiment. Even though the loading of the fibre in the composite is the same (10 phr), the longitudinally oriented fibre composite has high modulus compared to that of transverse fibre orientation. When the fibres are in the direction of application of load, the load will be borne by the fibre also and hence a high modulus is obtained[6-10]. This will not happen when the fibre orientation is perpendicular to the direction of application of load (transverse orientation).

## IV.4. Effect of fibre loading

Figure IV.8 shows the variation of dynamic storage modulus(E') and tan $\delta$ with volume loading of fibre at a temperature of 35°C and at a frequency of 10 Hz. It can be seen that the dynamic storage modulus showed a continuous increase with volume loading. But higher modulus value is always registered by composites containing treated fibres than those containing untreated fibre at same loading. This is associated with the strong fibre-rubber interface adhesion in acetylated fibre composite.

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1, 104(1
0,945
1971).

*Table IV.1.* ***Formulations of mixes***

| Ingredients | B | E | J | K | L | M | N | P | Q | R | S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Natural rubber | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Stearic acid | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Zinc oxide | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Resorcinol | 0.0 | 8.75 | 0.0 | 2.5 | 5.0 | 7.5 | 10.0 | 2.5 | 5.0 | 7.5 | 10.0 |
| Hexa[1] | 0.0 | 5.6 | 0.0 | 1.6 | 3.2 | 4.8 | 6.4 | 1.6 | 3.2 | 4.8 | 6.4 |
| Sisal fibre (untreated) | 0.0 | 0.0 | 0.0 | 10.0 | 20.0 | 30.0 | 40.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Sisal fibre (acetylated) | 35.0 | 35.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 10.0 | 20.0 | 30.0 | 40.0 |
| T D Q[2] | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| CBS[3] | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| Sulphur | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |

1. Hexamethylenetatramine
2. 2:2:4 trimethyl 1,2 dihydroquinoline polymerised.
3. N-cyclohexyl-2-benzthiazylsulphenamide

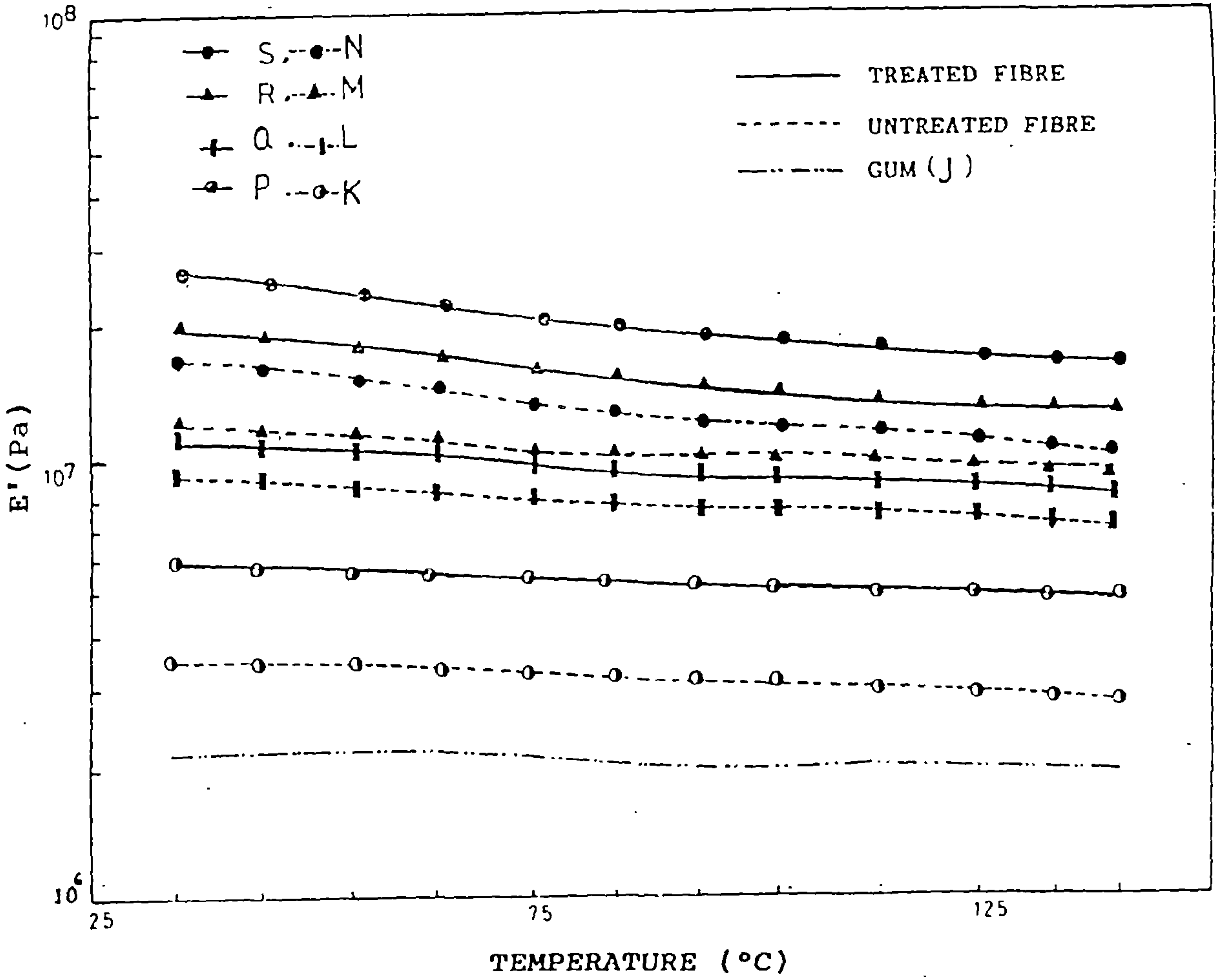

Figure IV.1. Variation of E' with temperature at a frequency of 10 Hz of the mixes J, K, L, M, N, P, Q, R and S.

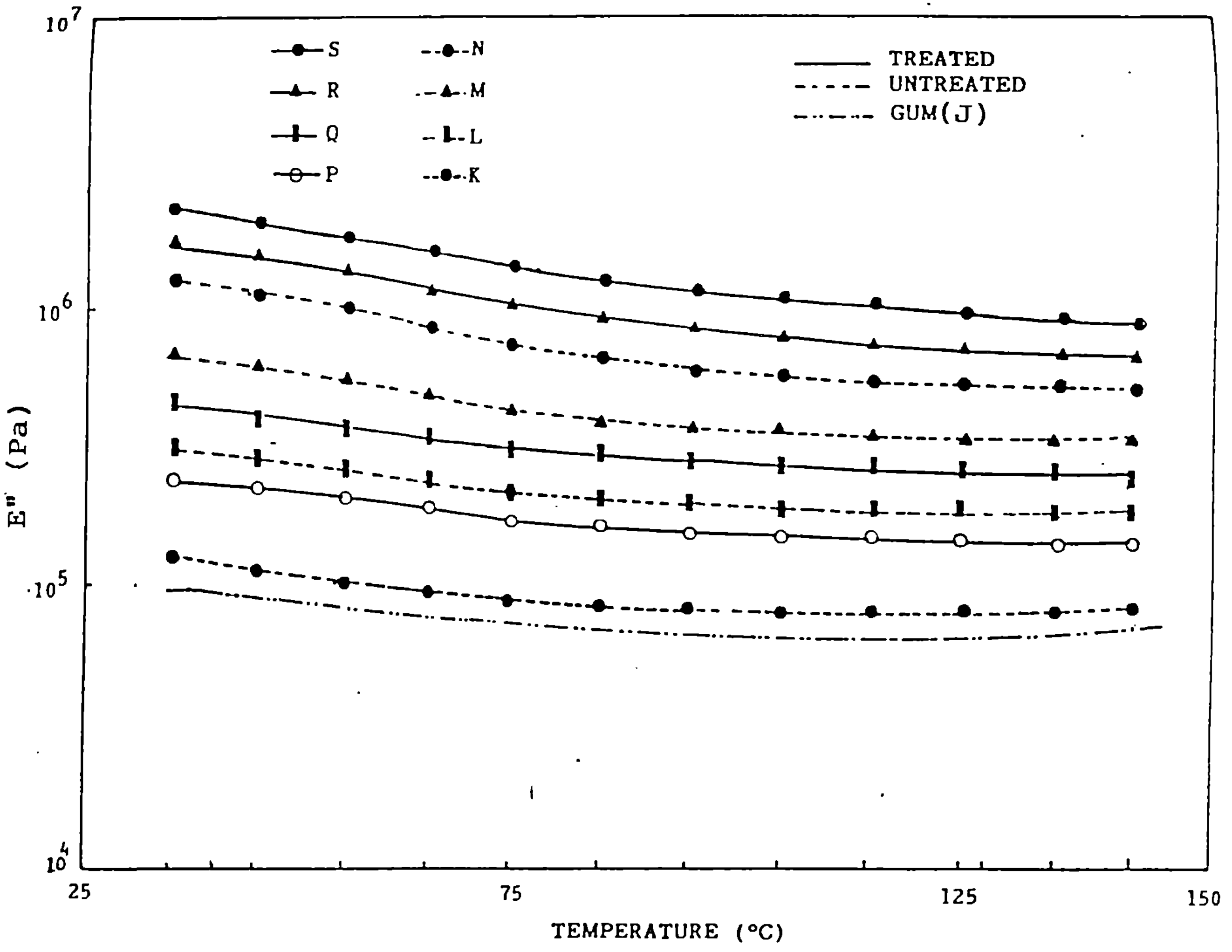

Figure IV.2. Variation of E" with temperature at a frequency of 10 Hz of the mixes J, K, L, M, N, P, Q, R and S.

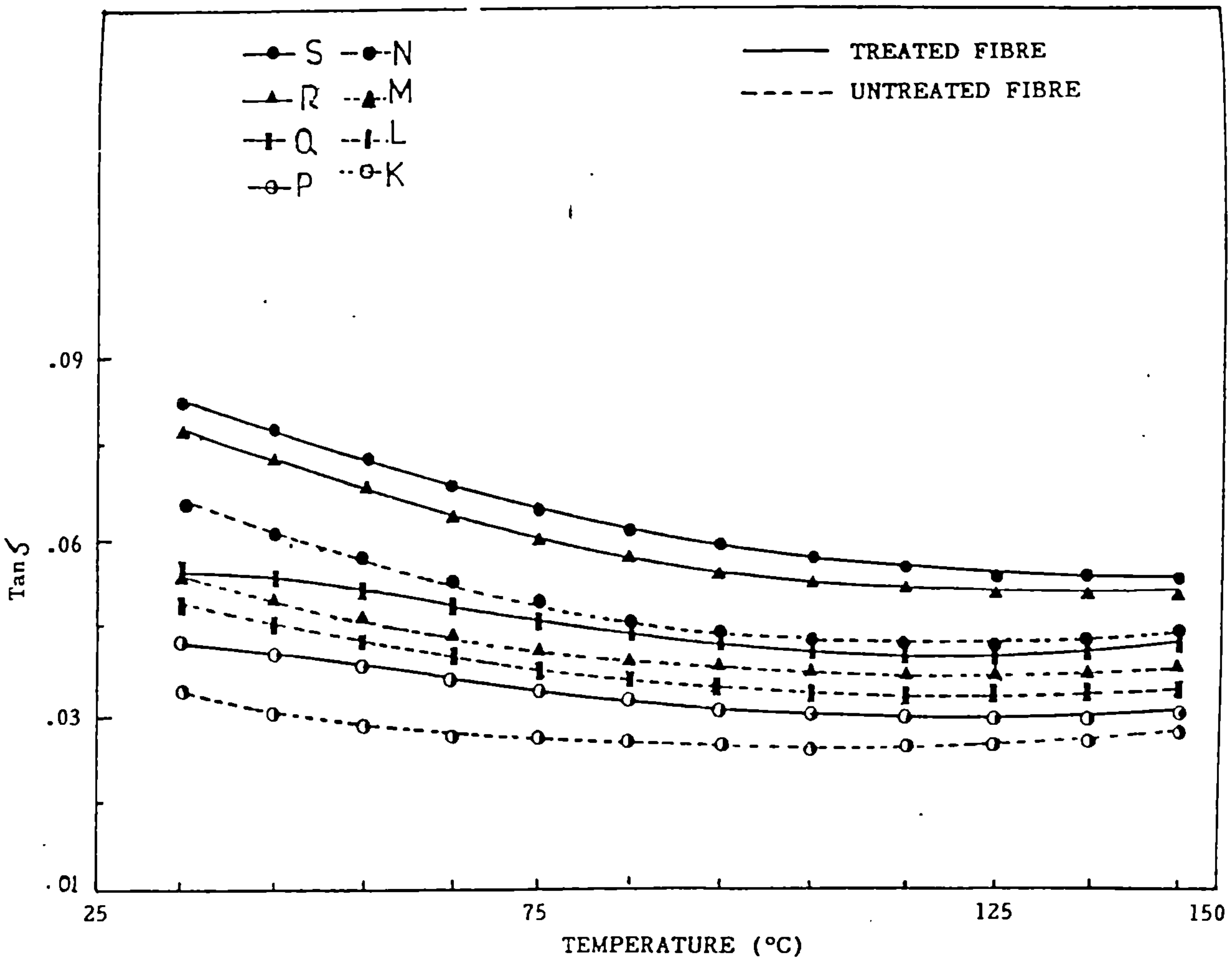

Figure IV.3. Variation of tan δ with temperature, at a frequency of 10 Hz of the mixes J, K, L, M, N, P, Q, R and S.

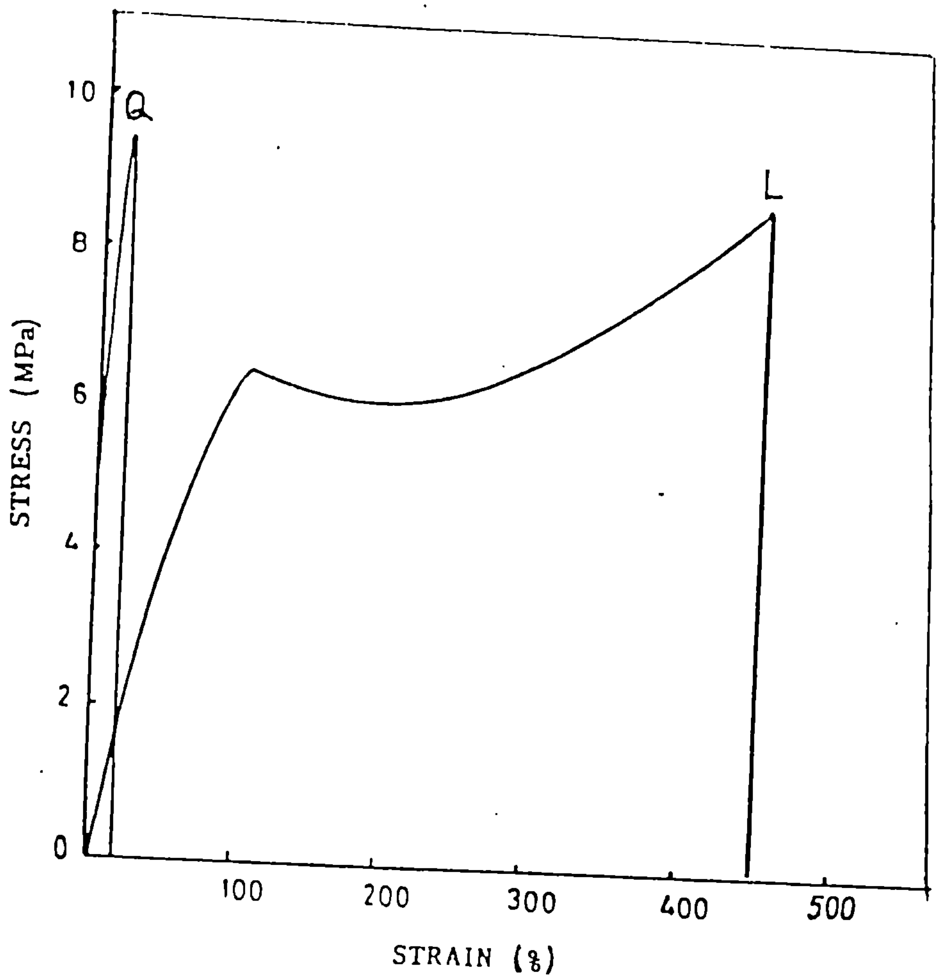

Figure IV.4. Stress strain curves of mixes L and Q.

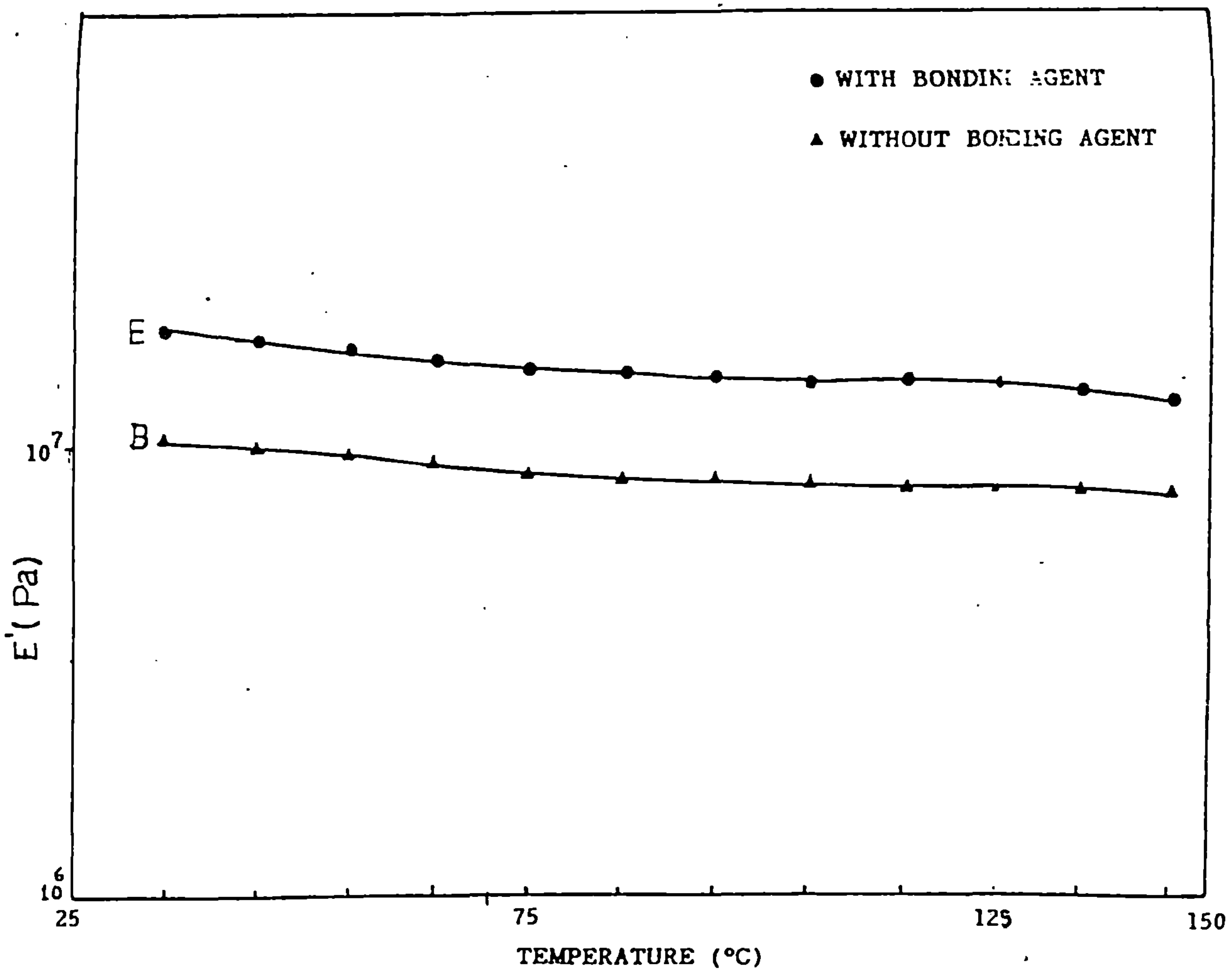

Figure IV.5. Variation of E' with temperature, at a frequency of 10 Hz, of mixes B and E.

**Figure IV.6a.** SEM photomicrograph of the tensile fracture surface of mix B

**6b.** SEM photomicrograph of the tensile fracture surface of mix E

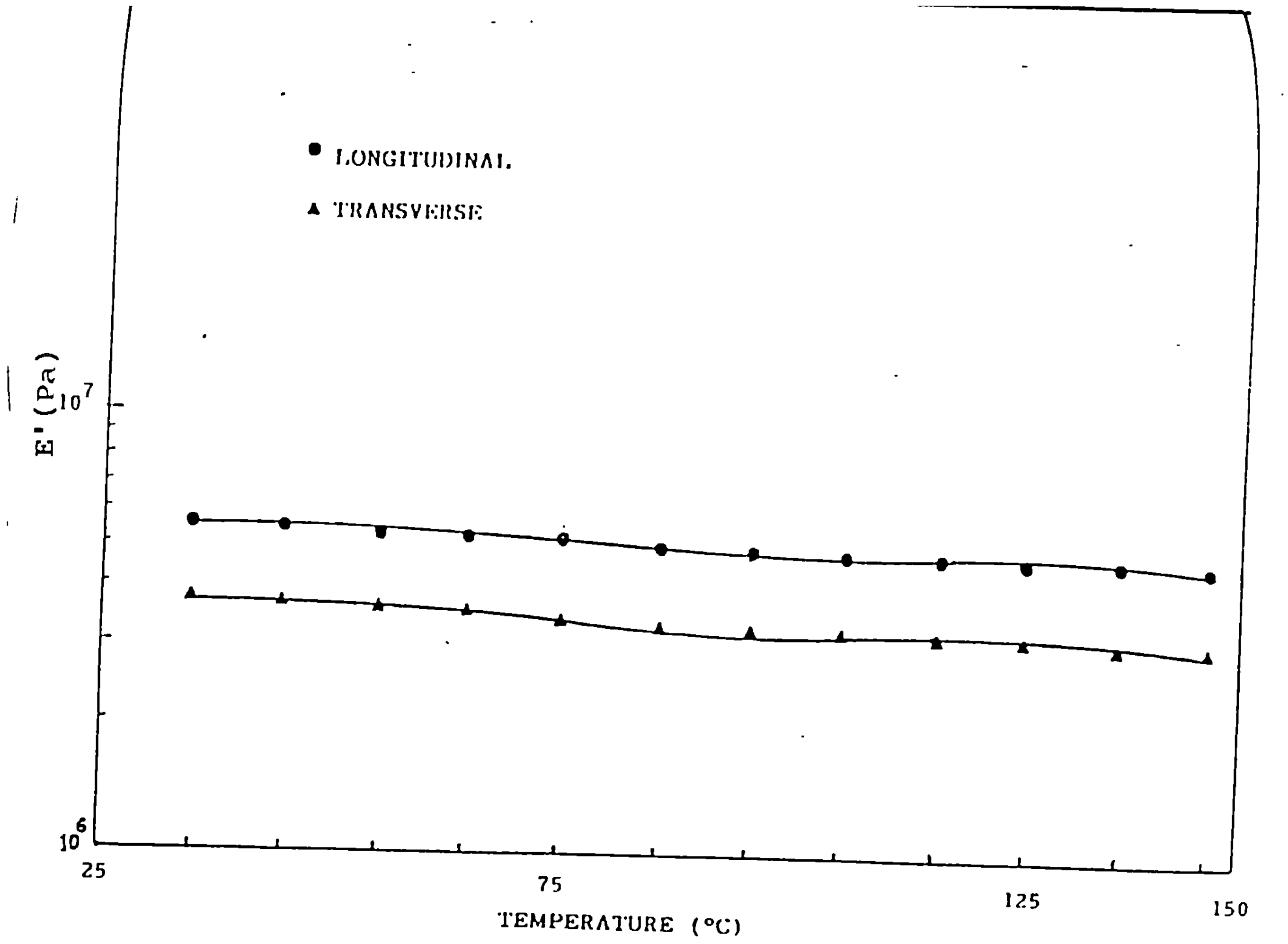

Figure IV.7. Variation of E' with temperature at a frequency of 10 Hz of mix P in the longitudinal and transverse directions.

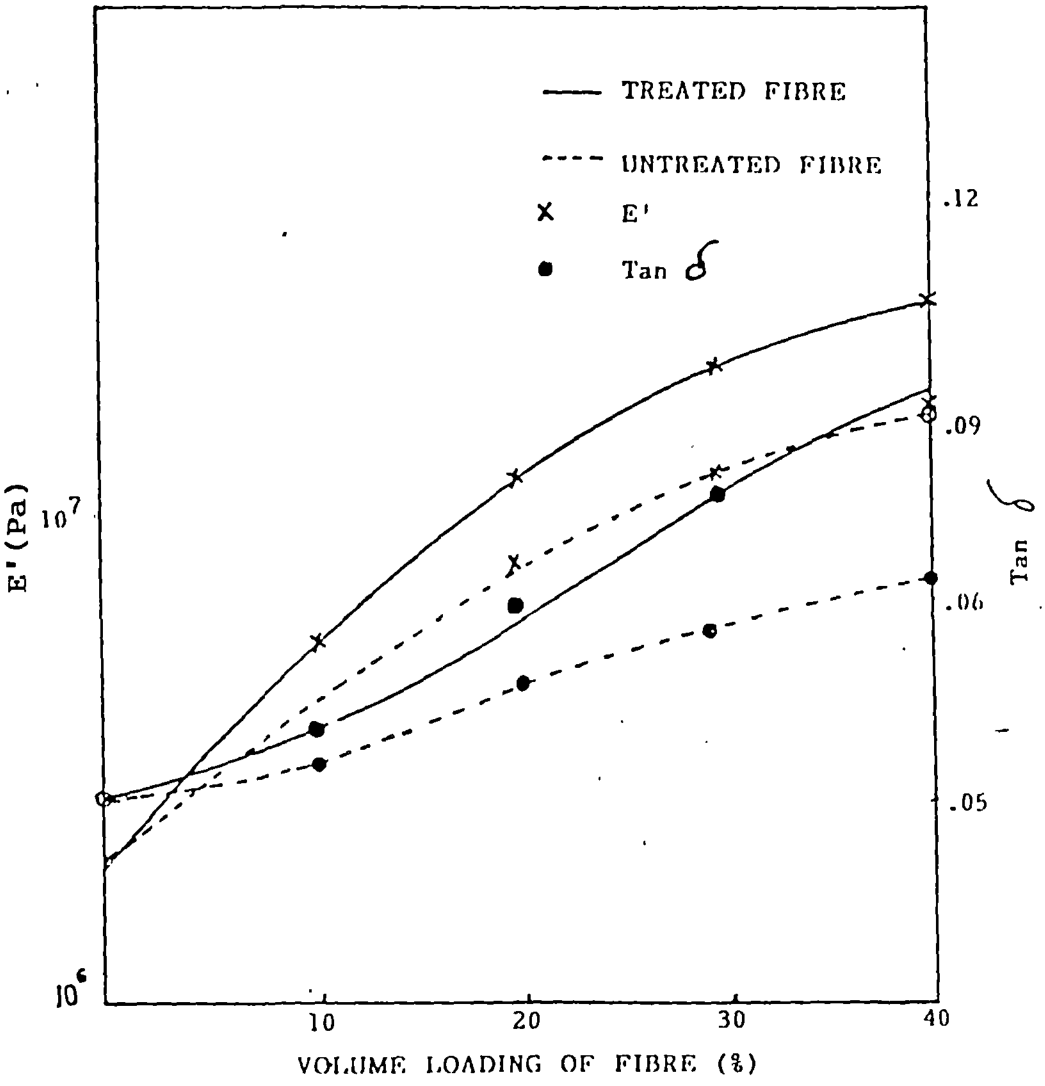

Figure IV.8. Variation of E' and tan δ against fibre loading at 35°C.

# CHAPTER V

# RHEOLOGICAL BEHAVIOUR OF SHORT SISAL FIBRE-NATURAL RUBBER COMPOSITES

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The results described in this chapter have been accepted for publication in Plastics, Rubber, Composites, Processing and Applications.

Since the processing of polymer in most cases involves flow of the material, a thorough understanding of the flow characteristics of the composite is essential. Brydson[1] indicated the need for rheological studies and their importance in selecting a polymer and its processing conditions. Studies on the rheological behaviour and the extrusion characteristics of polymer melts have been reported by White and Tokita[2] and White[3,4]. Viscosity data and melt elasticity behaviour at different temperatures are highly useful in selecting the processing conditions and also to design processing instruments. Several studies have been reported on the rheological behaviour of short fibre reinforced polymer composites. Setua[5] studied the rheological behaviour of short silk fibre filled elastomers and confirmed the pseudoplastic nature of the composites. The rheological behaviour of short jute fibre composite has been studied by Murthy et al.[6] and they found that viscosity-shear rate relationship was similar to that found in other fibre-filled polymer melts. Crowson et al.[7] reported the rheology of short glass fibre reinforced thermoplastics and concluded that the fibres in the composite orient along the flow direction when the flow is convergent and at 90$^{o}$ to the flow direction in a divergent flow. The fibre alignment increases with die length and flow rate. The dependence of die swell on the l/d ratio of the capillary has been studied extensively by many researchers[8-10]. Recently the rheology of short aramid fibre reinforced thermoplastic polyurethane has been reported by Kutty et al.[11]. They concluded that the pseudoplastic behaviour of the melt decreases with increase in temperature.

This chapter of the thesis presents the results of the studies on the rheological behaviour and extrudate morphology of acetylated and untreated short sisal fibre reinforced natural rubber composites. The rheological properties such as viscosity and flow behaviour index have been studied with special reference to the effect of fibre loading, temperature and shear rate. The extrudate morphology of the composites has been studied as a function of fibre loading and extrusion shear rates.

The rheological characteristics were evaluated in the temperature range of 80 to 110°C, since the processing temperatures of these materials are in this range. Shear rates ranging from 8 to 8331 $s^{-1}$ were selected for the study so as to cover the processing conditions such as compression moulding (shear rate, $10s^{-1}$) and injection moulding (shear rate $10^3$ $s^{-1}$). The morphology of the sample extruded at 100°C was studied by SEM. The experimental techniques used for the rheological measurements and for evaluating the extrudate morphology are given in chapter-II. The formulations of the mixes are given in Table V.1.

## V.1. Fibre breakage

Figure V.1 shows the fibre length distribution of mix E before and after extrusion through the capillary at three different shear rates. Due to the shear forces generated during mixing in the two roll mill, the fibre has undergone severe breakage and the initial 10 mm length of the sisal fibre is converted to varying sizes. It can be observed that the maximum population is between 2 to 4mm length and only 3 per cent of the fibre retains the original length after mixing. During extrusion, the fibre undergoes further breakage and the percentage of fibre having less than 4 mm length increased considerably. This may be due to the fact that the kinked fibres resulted from mixing, again undergo final break up during extrusion. From the figure, it is also clear that as the shear force increases, the population of the fibre having length less than 2 mm increases rapidly and at a shear rate of 3300 $s^{-1}$ more than 50 per cent of the fibres have less than 2 mm length.

## V.2. Effect of shear rate on viscosity

Figure V.2 shows the variation of shear viscosity with shear stress at $100^{\circ}$C. From this figure, it is evident that the composites behave like a pseudoplastic material as the shear viscosity decreased with the increase in shear stress. Polymer compounds containing particulate fillers also show pseudoplastic nature at low loading but at high loading dilatant behaviour is observed in certain cases[1]. It is seen that on increasing fibre loading, the shear viscosity increased continuously and at all shear stresses the unfilled composite registered the minimum viscosity. In the case of fibre filled composites, the high viscosity compared to the gum compound is due to the fact that the presence of fibre restricts molecular mobility under shear. Within the same mix, as the shear stress increases the shear viscosity decreases. This is due to the fact that at high shear stress fibres also get oriented along with rubber molecules[11].

The presence of short sisal fibre increased the shear viscosity of NR at low shear stress much more than that at high shear stress. This is due to the change in fibre distribution and orientation that take place with shear stress. This orientation of fibre during shear flow can be understood from the SEM photomicrographs of the extrudates of mixes R and U. Figures V.3a & V.3b show the cut surface of the extrudate of mix R at shear rates 3.33 $s^{-1}$ and 333.3 $s^{-1}$, respectively. The fibres, seen as an aggregate mass along the periphery at lower shear rate (Figure V.3a) are distributed uniformly at high shear rate

(Figure V.3b). Similar is the case with untreated fibre also. Figures V.3c & V.3d are the photomicrographs of the extrudates of mix U containing 30 phr untreated fibre extruded at shear rates 3.33 $s^{-1}$ and 333.3 $s^{-1}$, respectively. At low shear rate, the fibres are mainly concentrated at the periphery, which at higher shear rate formed a uniform dispersion throughout the matrix.

## V.3. Effect of temperature on viscosity

The variation of shear viscosity with temperature and shear stress of mixes Q and T is shown in Figure V.4. It is clear that as temperature increases shear viscosity decreases. But in the shear rate range of 166-1666 $s^{-1}$ viscosities show wide variations with temperature. However, below 110°C, the viscosity at high shear stress region has little effect on temperature. Dependence of melt viscosity on temperature is shown in Figure V.5, as the semilogarithmic plots of $\eta$ vs. 1/T. In this equation, $\eta$ is related to absolute temperature (T) by the following equation:

$$\eta = A.e^{\Delta E/RT} \qquad .....(V.1)$$

where A is a constant, characteristic of the polymer. $\Delta E$ is the activation energy and R is the universal gas constant. From the slope of the plots, $\Delta E$ values are calculated for mixes Q and T. Fibre loading in mixes Q and T is the same but in mix Q bonding agent is incorporated while mix T does not contain any bonding agent. The activation energy of both the mixes are the same and is equal to 0.46 cal/mol. The magnitude of the activation energy is a measure of the difficulty of molecular unit to jump from one equilibrium state to another. Since the activation energy of both the systems are the same, it can be concluded that the temperature sensitivity of mixes Q and T are same. In other words, addition of resorcinol and hexamethylenetetramine does not alter the temperature sensitivity.

## V.4. Flow behaviour index

The effects of temperature and bonding agent on the flow behaviour indices of the samples are given in Figure V.6. The magnitude of n' indicates the extent of pseudoplastic or non-Newtonian behaviour of the composite. From this figure it is clear that n' decreases as the temperature is increased from 80 to 110°C. This indicates that the melt becomes more pseudoplastic as the temperature is increased. Mix Q shows a lower n' than mix T at all temperatures. The variation of n' with fibre loading is shown in Figure V.7. It is seen that the n' decreases sharply by the addition of 6% (v/v) of fibre followed by levelling off at higher loading.

## V.5. Extrudate distortion

The extrudates have been examined for distortion and it is found that this is negligible at 80 and 90°C. When the temperature is raised to 100°C, the extrudates are found to be distorted. Photograph of the composites extruded at 100°C and at three different shear rates is shown in Figure V.8. It is clear that presence of fibre reduces the extrudate distortion at high shear rates and at 35 phr fibre loading (sample E), the distortion is remarkably low.

## V.6. Melt elasticity

### V.6.1. Die swell

Table V.2 gives the die swell ($d_e/d_c$) of the gum and fibre filled mixes at 100°C, at three different shear rates. In the case of gum compound the die swell increased continuously with increasing shear rate. The die swell is a relaxation phenomenon. When the molten polymer flows through the capillary, shearing tends to maintain molecular orientation of polymer chains. When the melt emerges from the die, molecules tend to recoil leading to the phenomenon of die swell[1]. The elastic recovery of the polymer chain is influenced by parameters such as stress relaxation, crosslinking, presence of fillers etc. It is seen that die swell decreases by the addition of fibres. The reduction of die swell in presence of fibres has been reported earlier[11]. Mix Q which contains the bonding agent has low die swell at all shear rates when compared with mix T, which contains no bonding agent.

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Table V.1. **Formulation of mixes**

| Ingredients | O | J | P | Q | R | E | T | U |
|---|---|---|---|---|---|---|---|---|
| Natural rubber | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Stearic acid | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Zinc oxide | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Resorcinol | 2.5 | 0.0 | 2.5 | 5.0 | 7.5 | 8.75 | 0.0 | 0.0 |
| Hexa* | 1.6 | 0.0 | 1.6 | 3.2 | 4.8 | 5.6 | 0.0 | 0.0 |
| Sisal fibre (acetylated) | 0.0 | 0.0 | 10.0 | 20.0 | 30.0 | 35.0 | 20.0 | 0.0 |
| Sisal fibre (untreated) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 30.0 |
| TDQ** | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| CBS*** | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| Sulphur | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |

* Hexamethylenetetramine
** 2:2:4 trimethyl 1,2-dihydroquinoline polymerized
*** N-cyclohexyl-2-benzthiazylsulphenamide

Table V.2. **Die swell of composites at different shear rates**

| Mix | Die swell<br>$33.32\ s^{-1}$ | <br>$333.2\ s^{-1}$ | <br>$3332\ s^{-1}$ |
|---|---|---|---|
| $O_{(0)}$ | 1.58 | 1.62 | 1.97 |
| $J_{(0)}^{**}$ | 1.53 | 1.68 | 1.97 |
| $P_{(10)}$ | 1.14 | 1.21 | 1.17 |
| $Q_{(20)}$ | 1.01 | 1.06 | 1.04 |
| $R_{(30)}$ | 1.00 | 1.06 | 1.04 |
| $E_{(35)}$ | 1.00 | 1.00 | 1.00 |
| $T_{(20)}^{**}$ | 1.06 | 1.09 | 1.09 |
| $U_{(30)}^{*}$ | 1.00 | 1.03 | 1.04 |

Figures in brackets indicate the fibre loading

* Untreated fibre

** Without bonding agent

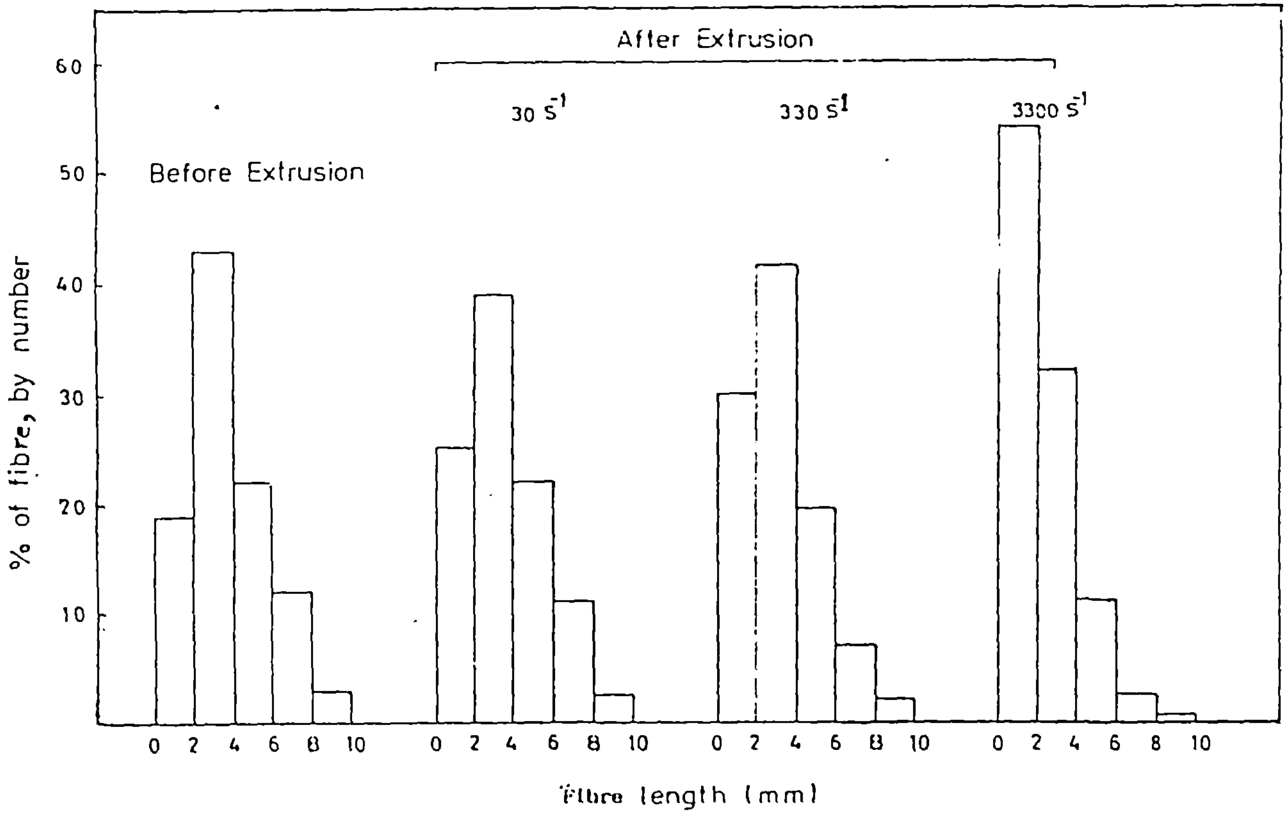


**Figure V.1.** Fibre length distribution of mix E before and after extrusion through the capillary at three different shear rates.

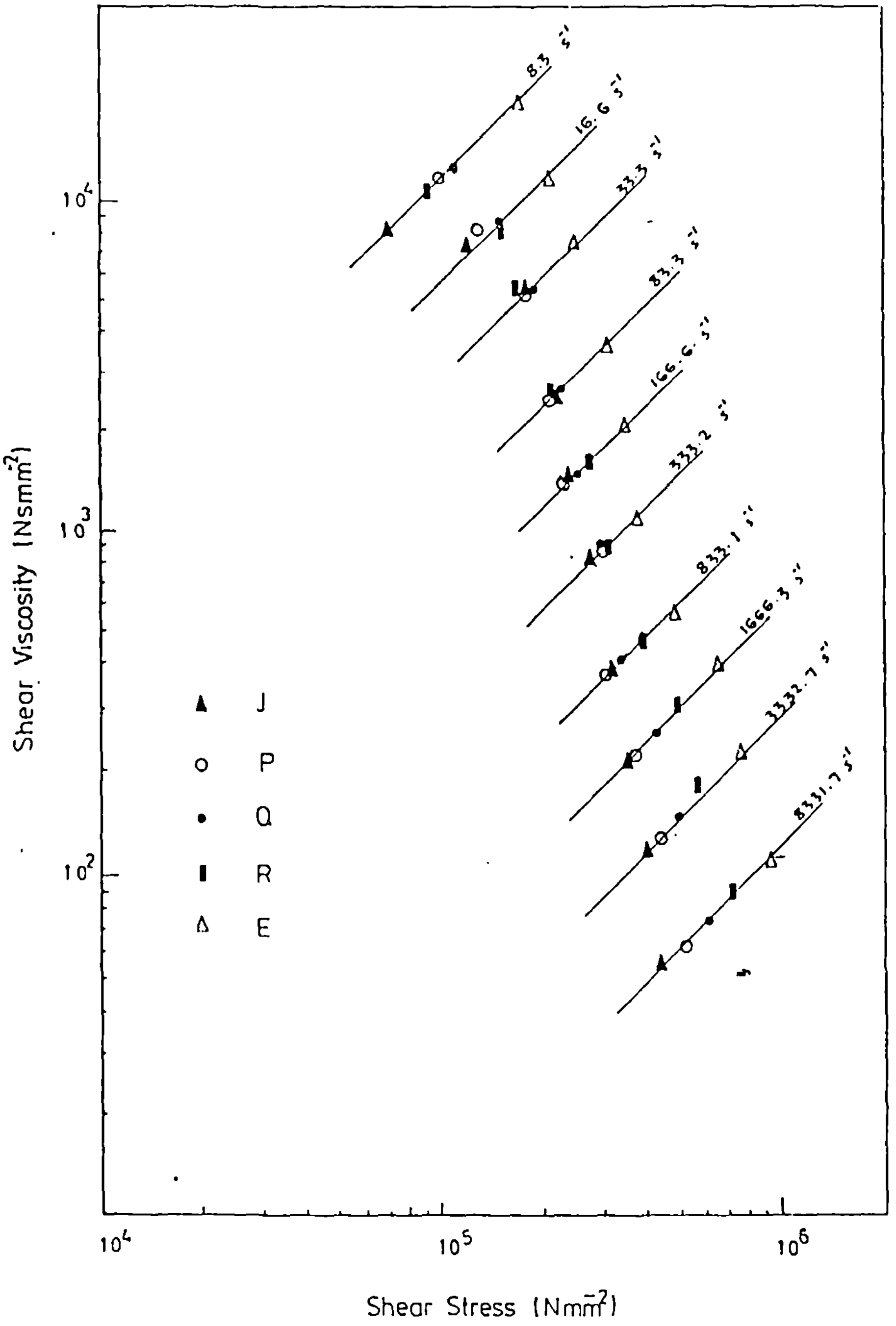
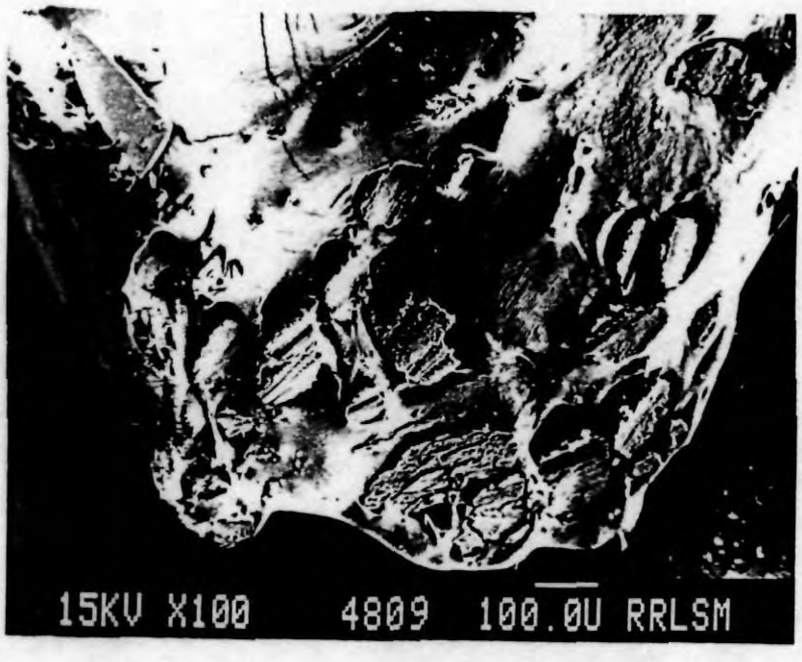


**Figure V.2.** Variation of shear viscosity with shear stress at 100°C of mixes J, P, Q, R and E.

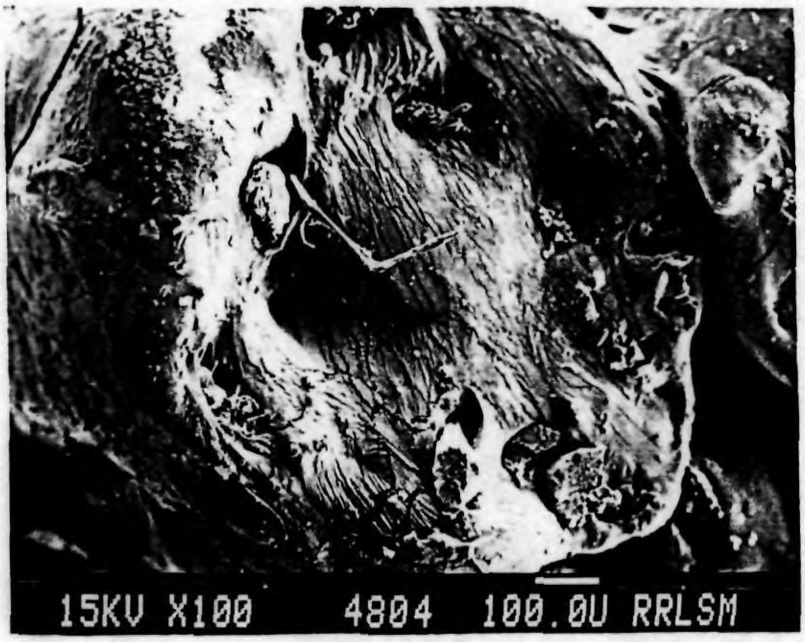
a



b

**Figure V.3a.** SEM photomicrograph of the cut surface of the extrudate of mix R at a shear rate of 3.33 $s^{-1}$

**3b.** SEM photomicrograph of the extrudate of mix R at a shear rate of 333.3 $s^{-1}$.



c

d

**Figure** **V.3c.** SEM photomicrograph of the cut surface of the extrudate of mix U at a shear rate of 3.333 s$^{-1}$

**3d.** SEM photomicrograph of the cut surface of the extrudate of mix U at a shear rate of 333.3 s$^{-1}$.

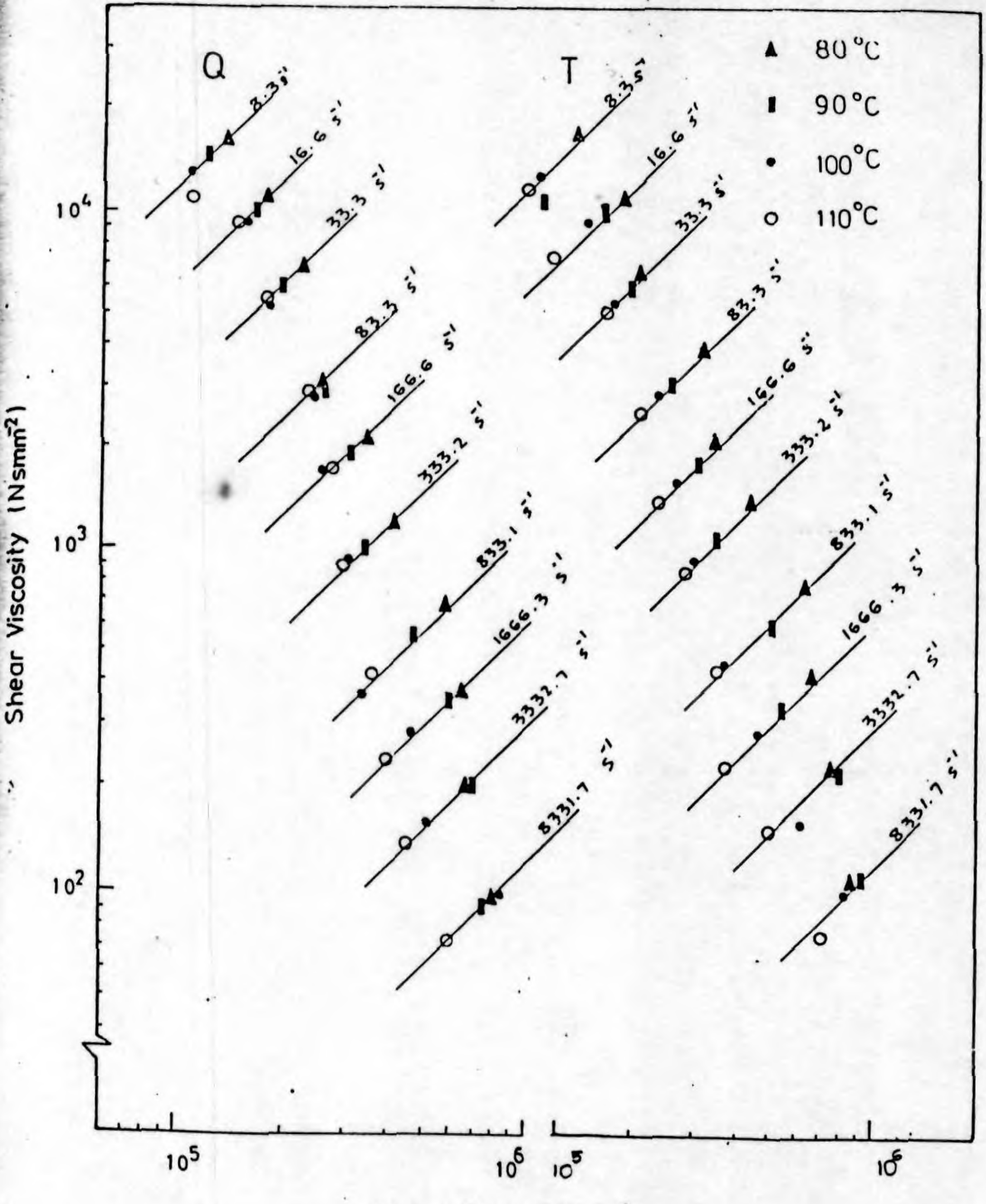


Figure V.4. Variation of shear viscosity with temperature and shear rate of mixes Q and T.

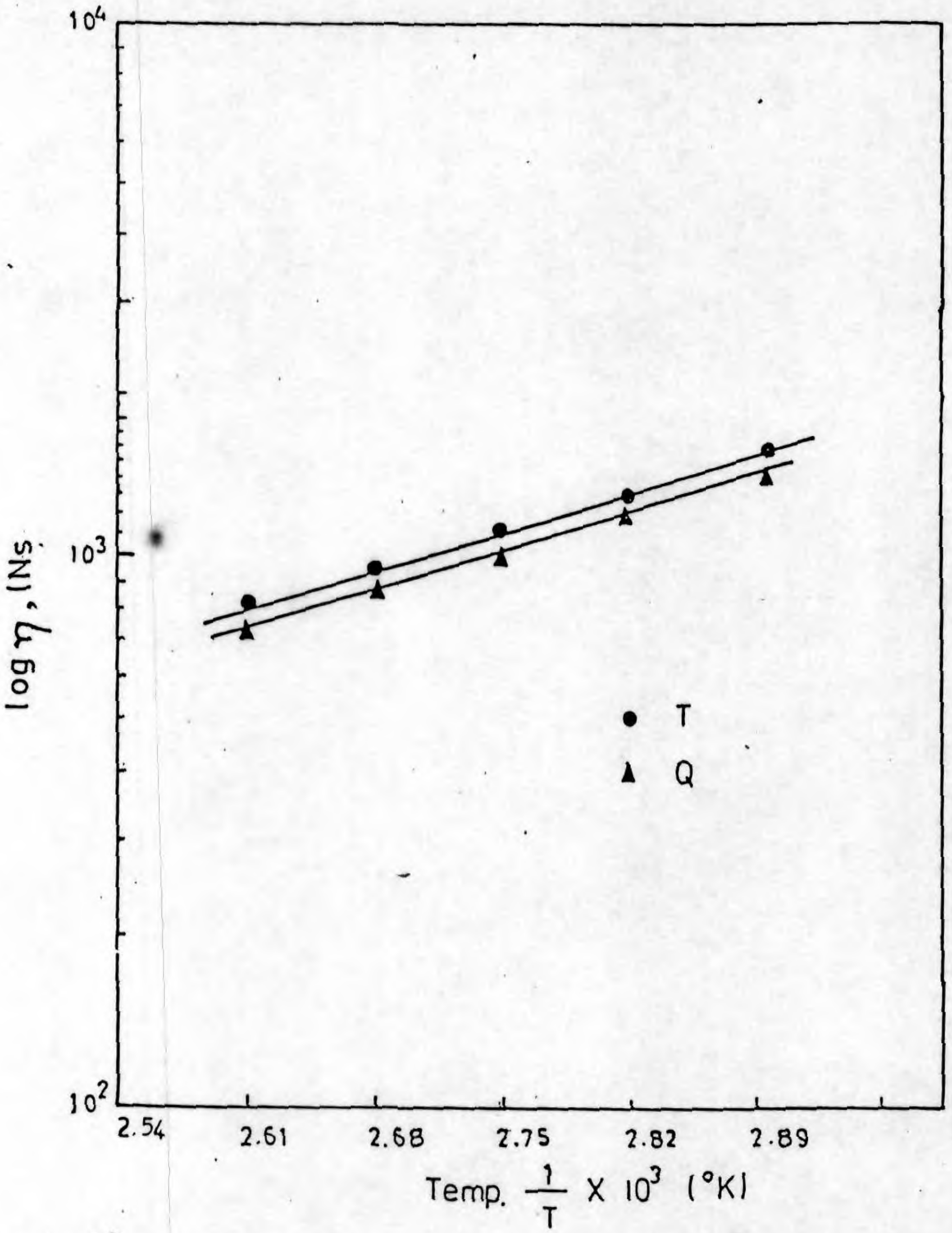


**Figure V.5.** Variation of melt viscosity with temperature of mixes Q and T.

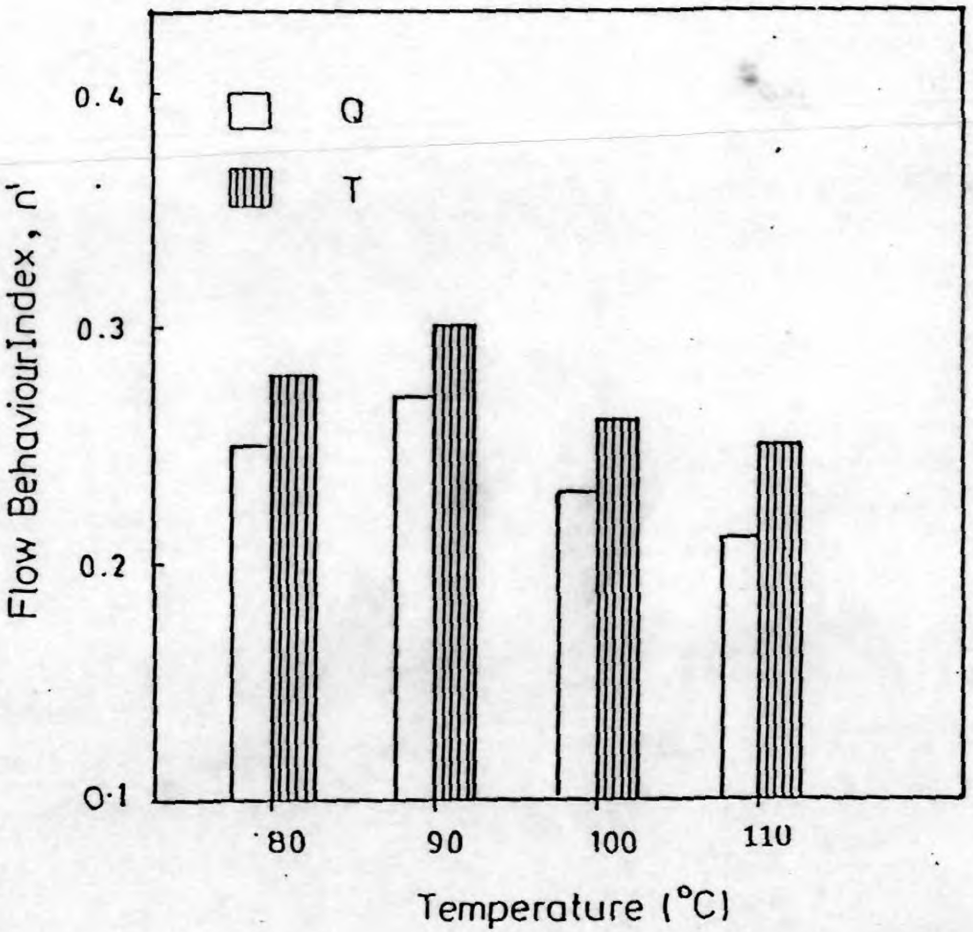


Figure V.6. Effects of temperature and bonding agent on the flow behaviour indices of mixes Q and T.

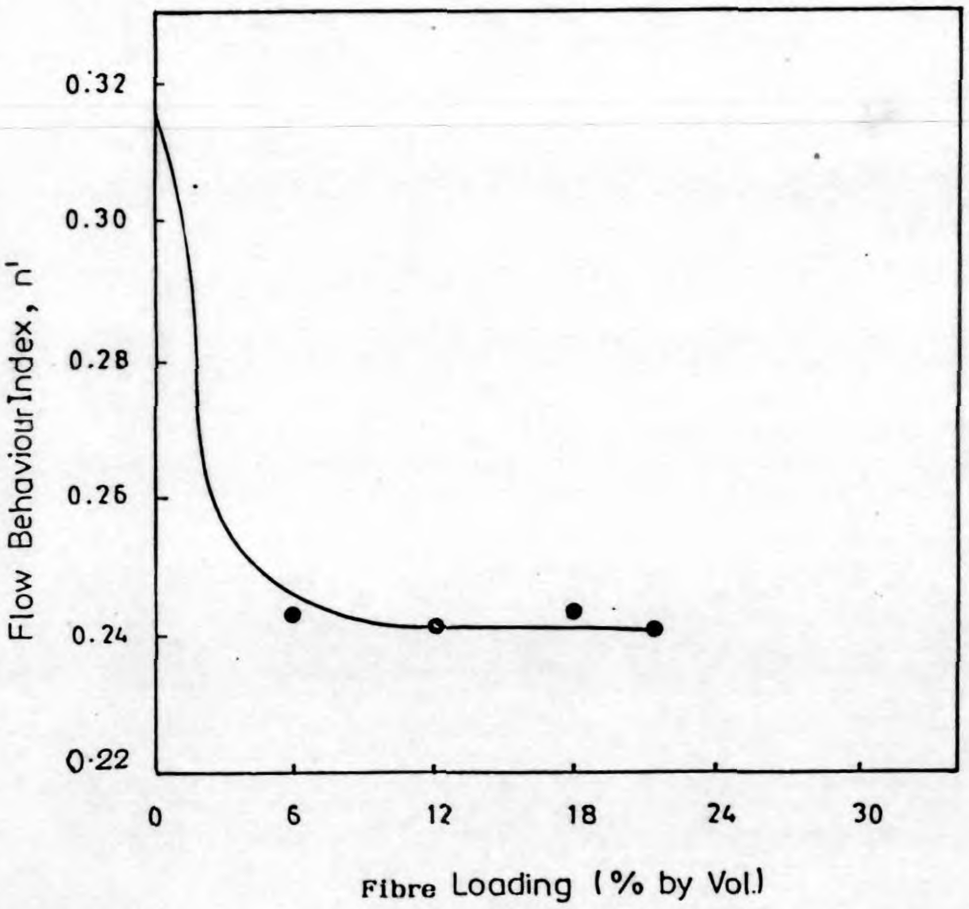


Figure V.7. The variation of flow behaviour index (n') with fibre loading.

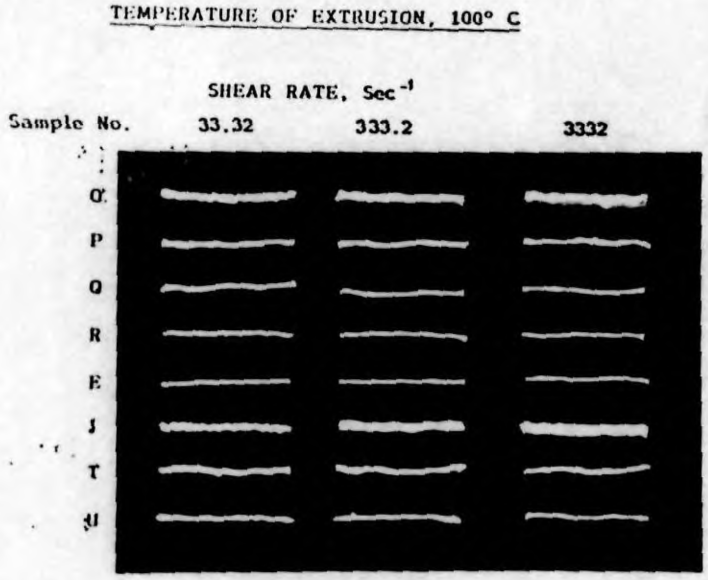


Figure V.8. Optical photograph showing the effect of shear rate and fibre loading on the deformation of extrudates of mixes O, P, Q, R, E, J, T and U.

# CHAPTER VI

# STRESS RELAXATION BEHAVIOUR OF SHORT SISAL FIBRE-NATURAL RUBBER COMPOSITES

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Part of the results described in this chapter has been

1) Communicated to the Journal of Applied Polymer Science.
2) Presented at the Eigth Annual Meeting Polymer Processing Society (PPS 8) held in New Delhi, India, March 24-27 (1992).

The increasing use of short fibre composites in static and dynamic applications led to the importance of stress relaxation measurements. Vulcanized rubbers when subjected to constant deformation undergo a marked relaxation of stress both at low and high temperatures[1]. The stress under a constant deformation decays by an amount substantially proportional to the logarithm of the period in the deformed state. The stress relaxation behaviour of short jute fibre reinforced nitrile rubber composites has been studied in detail by Bhagawan et al.[2] They reported the existence of a two stage relaxation pattern in these composites. Flink and Stenberg[3] studied the stress relaxation behaviour of short cellulose fibre reinforced natural rubber composites by using plots of $E_{(t)}/E_{(t=0)}$ vs. log t, where $E_{(t)}$ is the stress at a given time and $E_{(t=0)}$ is the initial stress. They reported that the stress relaxation measurement would give a clear idea about the level of adhesion in fibre-rubber composites. Stress relaxation behaviour of short aramid fibre reinforced thermoplastic polyurethane has been studied by Kutty and Nando[4]. They reported a two step relaxation mechanism for the unfilled stock and a three stage relaxation process for the filled stock. However, the stress relaxation behaviour of short sisal fibre reinforced natural rubber has not yet been reported. In this chapter the results of the studies on the stress relaxation behaviour of acetylated short sisal fibre reinforced natural rubber composites with special reference to the effects of strain level, fibre loading, bonding agent and temperature are presented. The experimental procedure adopted for this study has been given in chapter II. The formulations of the mixes are given in Table VI.1.

## VI.1. Fibre breakage

Figure VI.1 shows the distribution of the length of the extracted fibres after mixing. It is seen that the initial 10 mm length of the fibre was reduced due to the high shear force generated during mixing and majority of the fibres (65%) have a length of 2-6 mm after mixing.

## VI.2. Effect of strain level

Figure VI.2 is the stress relaxation plot, $(\sigma_t/\sigma_o)$ vs. log t, of the gum vulcanizate (mix J) at different strain levels. $\sigma_t$ is the stress at a particular time and $\sigma_o$ is the stress at t = 0. The rate ($0.061\ s^{-1}$) at which the initial strain attained, is kept constant for all samples. It is seen that the experimental points for gum compound fall on a straight line, showing that the relaxation process involved only a single process. There are two important mechanisms which can lead to stress relaxation in a crosslinked elastomer[5]. (1) Physical stress relaxation due to molecular rearrangements requiring little primary bond formation or breakage, (2) Chemical stress relaxation due to chain scission, crosslink scission, or crosslink formation. Under normal conditions, both physical and chemical stress relaxations will occur simultaneously. However, at typical ambient temperatures, the rate of chemical relaxation in a rubber like NR is very small and the relaxation behaviour is dominated by the physical process except that for very long periods. Here the relaxation patterns of the samples were studied at different elongation. However, it is interesting to note that the rates of stress relaxation obtained for all the extensions studied are almost constant. According McKenzie and Scanlan[6], the slope of stress relaxation plot of unfilled NR was independent of strain upto levels at which stress induced crystallization occurs. It was also concluded that the mechanism is a physical one probably involving the protracted rearrangement of molecular chains or aggregates[1]. In the present case also it is seen that the stress relaxation of the gum compound is independent of strain levels as indicated by almost parallel straight line plots (Figure VI.2).

Unlike the case of gum vulcanizates, the experimental points for the fibre filled composites fall on two intersecting straight lines (Figures VI.3 & 4). The stress relaxation curves consisting of two straight lines of unequal slopes indicate that a different mechanism of relaxation operates in the case of short fibre filled composites: one that operates at shorter time (<200 s) and another that is prominent at the later stages of relaxation. It appears that a new relaxation mechanism operates in the fibre filled composites and contributes significantly to the observed relaxation. It might arise from the progressive failure of rubber-fibre attachment either at the surface of the fibre or by the rupture of the rubber molecule attached to them[1]. The point of intersection of these two straight lines is the time at which a change over from one mechanism to another takes place. The characteristics of the two mixes (J & V) can be realised from their slopes and intercepts given in Table VI.2. The slopes and intercepts were calculated using a linear regression method. The contribution by an earlier process of relaxation is calculated as reported by McKenzie and Scanlan[6] by dividing the difference of the two intercepts by the intercept of the first line at t = 1s. The values obtained are given in Table VI.2.

In mix V, which contained no bonding agent, the initial relaxation pattern increased with strain level. This is because of the fact that the adhesion through weak bonds formed between acetylated fibre and rubber breaks as the strain level is increased. In mix W which contained the bonding agent, the pattern of relaxation is the same as that in the case of mix V but the initial relaxation rate remained almost constant with strain level. Due to good bonding, there is improved adhesion between fibre and rubber resulting in a strong interface. Therefore relaxation at the interface is not at all affected by low strain level. However, as in mix V, higher strain levels led to faster relaxation of stress in this case also. The second phase of relaxation, which is primarily due to the polymer remains constant.

## VI.3. Effect of bonding agent

In Figure VI.5, the stress relaxation curves of mixes J, V and W at 30% elongation are presented. The compound J (gum) has the lowest rate of relaxation at 30% elongation. It has been shown earlier that the initial relaxation increases with strain level in a weak fibre-rubber interface, whereas it remains almost constant in a strong interface. By comparing the cross over time at same extensions of mix V and mix W (Table VI.2) we can have a clear idea about the level of adhesion between the fibre and the rubber in these two compounds. Mix W always registered a higher cross over time. This suggests that the initial relaxation is faster in a weak interface and hence a low cross over time for mix V. But in a strong interface as in mix W, the initial relaxation process is long and takes more time for the initiation of the second phase of the relaxation process.

From Table VI.2, it is seen that in the case of mix V the contribution of the early process changes from 21% to 7% as the strain level is varied from 20 to 70%. But in the case of mix W which contained the bonding agent the contribution is nearly constant and independent of strain level.

## VI.4. Effect of fibre content

Figure VI.6 illustrates the effect of fibre loading (mixes J, P and W) on stress relaxation at 50% strain level. The rate of relaxation increases with fibre content and also the time at which the earlier relaxation mechanism stops is shifted to a higher value (Table VI.3). According to the theory of strain amplification, owing to the inextensibility of the filler[7], the strain in the elastomer matrix is greater than the overall strain, resulting in the rubber phase having an instantaneous modulus higher than that for a gum rubber at equivalent extension. Derham[8] showed that the stress relaxation rate increases with carbon black loading. Similar results are obtained with short jute fibre filled NBR composites[2].

The results obtained in the present study are in agreement with these findings. The stress-strain relation of particulate filled vulcanizates has been shown by Mullins and Tobin[7] in which substantially all of the observed extension is attributed to the deformation of 'softened regions' with properties similar to those of the corresponding unfilled vulcanizate. The amount of material in the softened state rises with imposed extension by a progressive breakdown of the original 'rigid' structure. The fractional extension of the softened regions will be quite large, even when the imposed extension is small. Thus, even at small imposed extensions the regions taking part in the deformations are very highly strained. Relaxation of stresses would therefore be expected to proceed as in highly stretched unfilled rubber. The same mechanism is expected to take place in fibre filled composites since here also the relaxation rate increased with strain level.

## VI.5. Effect of ageing

Ageing produces interesting effects on the relaxation behaviour of NR-sisal fibre composites (Figure VI.7). Stress relaxation measurements have been made after ageing the samples at 70 and 100$^{o}$C for four days (Table VI.3). In the case of mix V (without bonding agent), the initial relaxation rate decreased with ageing. This may be due to the fact that some of the reactive groups in the treated fibre surface may be activated at high temperature to form bonds with rubber. The chemical stress relaxations due to chain scission or crosslink scission cause a sharp increase of the later stages of relaxation rate of mix V aged at 100°C. The relaxation curve of mix W aged at 70°C registered the maximum cross over time and contribution to the initial relaxation. This is because of the fact that the full strength of the bonding resin is developed during ageing, which helps in obtaining better adhesion between the fibre and rubber resulting a strong interface. On the contrary the second phase relaxation process of mix W aged at 100°C shows a sudden decrease in relaxation rate. There are two competing mechanisms leading to relaxation in the second stage: (1) chemical relaxation due to chain scission, (2) the bonding resin formation. Between these two competing processes, the degradation by molecular break down shows predominant effect on the relaxation process.

### VI.6. Effect of fibre orientation

The effect of fibre orientation on relaxation of stress is investigated for mixes V and W at 30% strain (Figure VI.8). For the initial process, even in the presence of bonding agent, composites containing fibres oriented longitudinally have high relaxation rate than those of composites with transverse fibre orientation (Table VI.4). In mix V it is observed that the slope of the initial rate of relaxation curve in the transverse direction is only half of that in the longitudinal direction. In transverse fibre orientation, the fibres are aligned perpendicular to the direction of force application and the major relaxation is due to the polymer. In both the mixes, the transversely oriented fibre composites have lower cross over time. In transverse fibre orientation, the fibre-rubber interface has very little role in stress transfer and the initial relaxation process which is entirely due to the fibre-rubber linkage shifts quickly to the second relaxation process.

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Table VI.1. Formulations of mixes

| Ingredients | J | V | W | P |
|---|---|---|---|---|
| Natural rubber | 100 | 100 | 100 | 100 |
| Zinc oxide | 5 | 5 | 5 | 5 |
| Stearic acid | 1.5 | 1.5 | 1.5 | 1.5 |
| Sisal fibre (acetylated) | - | 15 | 15 | 10 |
| Resorcinol | - | - | 3.75 | 2.5 |
| Hexa * | - | - | 2.4 | 1.6 |
| T D Q ** | 1 | 1 | 1 | 1 |
| CBS *** | 0.6 | 0.6 | 0.6 | 0.6 |
| Sulphur | 2.5 | 2.5 | 2.5 | 2.5 |

* Hexamethylenetetramine
** 2:2:4 trimethyl 1,2 dihydroquinoline polymerised
*** N-cyclohexyl-2-benzthiazylsulphenamide

Table VI.2. **Results of stress relaxation measurements**

|  | Strain (%) | Slope (negative) |  | Difference | Intercept |  | Difference | Contribution to Initial mechanism (%) | Cross ov time (sec) |
|---|---|---|---|---|---|---|---|---|---|
|  |  | Early | Later |  | Early | Later |  |  |  |
| Mix J | 20 | 0.0427 | - | - | 0.9761 | - | - | - | - |
|  | 30 | 0.0481 | - | - | 0.9736 | - | - | - | - |
|  | 50 | 0.0500 | - | - | 0.9906 | - | - | - | - |
|  | 70 | 0.0520 | - | - | 0.9797 | - | - | - |  |
| Mix V | 20 | 0.0854 | 0.0125 | 0.0729 | 0.9529 | 0.7532 | 0.1997 | 20.9 | 180 |
|  | 30 | 0.0880 | 0.0109 | 0.0771 | 0.9243 | 0.7574 | 0.1669 | 18.1 | 160 |
|  | 50 | 0.0892 | 0.0164 | 0.0576 | 0.9571 | 0.8083 | 0.1488 | 15.5 | 120 |
|  | 70 | 0.0912 | 0.0196 | 0.0655 | 0.9270 | 0.8697 | 0.0573 | 6.9 | 91 |
| Mix W | 20 | 0.0834 | 0.0440 | 0.0394 | 0.8819 | 0.7353 | 0.0866 | 9.8 | 200 |
|  | 30 | 0.0800 | 0.0450 | 0.0346 | 0.9115 | 0.8434 | 0.0681 | 7.5 | 180 |
|  | 50 | 0.0848 | 0.0509 | 0.0339 | 0.9387 | 0.8848 | 0.0539 | 5.7 | 140 |
|  | 70 | 0.0853 | 0.0809 | 0.0044 | 0.9600 | 0.8621 | 0.0960 | 9.9 | 120 |

*Table VI.3.* ***Effect of fibre concentration and ageing in stress relaxation***

| | Strain (%) | Slope (negative) | | Difference | Intercept | | Difference | Contribution to initial mechanism (%) | Cross over time (sec.) |
|---|---|---|---|---|---|---|---|---|---|
| | | Early | Later | | Early | Later | | | |
| Effect of fibre content | | | | | | | | | |
| Mix J (no fibre) | 50 | 0.0500 | - | - | 0.9906 | - | - | - | - |
| Mix P (10 phr) | 50 | 0.0792 | 0.0503 | 0.0288 | 0.9836 | 0.8346 | 0.149 | 15.1 | 120 |
| Mix W (15 phr) | 50 | 0.0848 | 0.0509 | 0.0339 | 0.9387 | 0.8848 | 0.053 | 5.7 | 140 |
| Effect of ageing | | | | | | | | | |
| Mix V | 30 | 0.0880 | 0.0109 | 0.0771 | 0.9243 | 0.7574 | 0.1669 | 18.1 | 160 |
| Ageing at 70°C for 4 days | 30 | 0.0701 | 0.0178 | 0.0523 | 0.8220 | 0.6227 | 0.199 | 24.2 | 165 |
| Ageing at 100°C for 4 days | 30 | 0.0518 | 0.0794 | 0.0276 | 0.8369 | 0.9949 | 0.158 | - | 199 |
| Effect of ageing | | | | | | | | | |
| Mix W | 30 | 0.0800 | 0.0450 | 0.0346 | 0.9115 | 0.8434 | 0.0681 | 7.5 | 180 |
| Ageing at 70°C for 4 days | 30 | 0.0701 | 0.0394 | 0.0307 | 0.8224 | 0.7476 | 0.075 | - | 150 |
| Ageing at 100°C for 4 days | 30 | 0.0397 | 0.0680 | 0.0280 | 0.7558 | 0.8130 | 0.057 | - | 50 |

Table VI.4. Dependence of stress relaxation on fibre orientation

| | Slope (negative) | | Difference | Intercept | | Difference | Contribution to initial mechanism (%) | Cross over time (sec) |
|---|---|---|---|---|---|---|---|---|
| | Early | Later | | Early | Later | | | |
| Effect of fibre orientation | | | | | | | | |
| Mix W | | | | | | | | |
| Longitudinal (30) | 0.0800 | 0.0450 | 0.0346 | 0.9115 | 0.8434 | 0.0681 | 7.5 | 200 |
| Transverse (30) | 0.0640 | 0.0701 | 0.0011 | 0.9172 | 0.4882 | 0.0709 | - | 140 |
| Mix V | | | | | | | | |
| Longitudinal (30) | 0.0880 | 0.0109 | 0.0771 | 0.9245 | 0.7574 | 0.1669 | 13.1 | 160 |
| Transverse (30) | 0.0405 | 0.0565 | 0.0160 | 0.9983 | 0.9912 | 0.0071 | - | 120 |

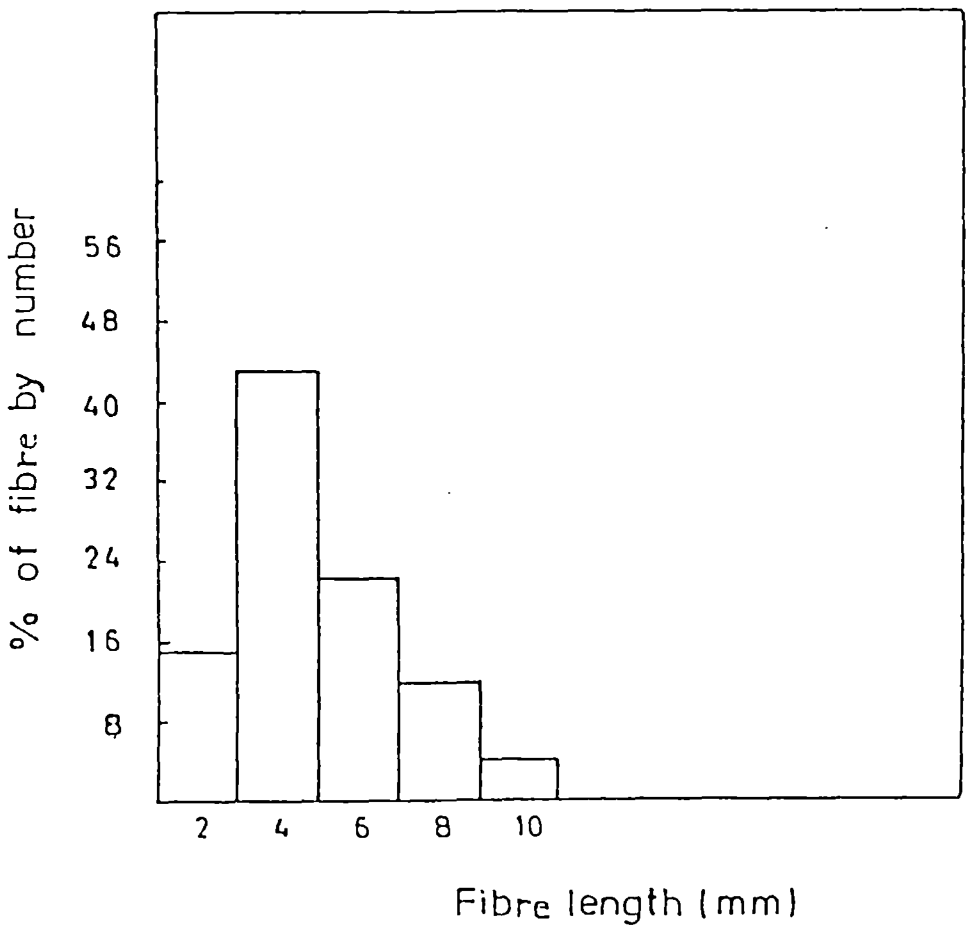

Figure VI.1. Distribution of the fibre length of mix-W after mixing.

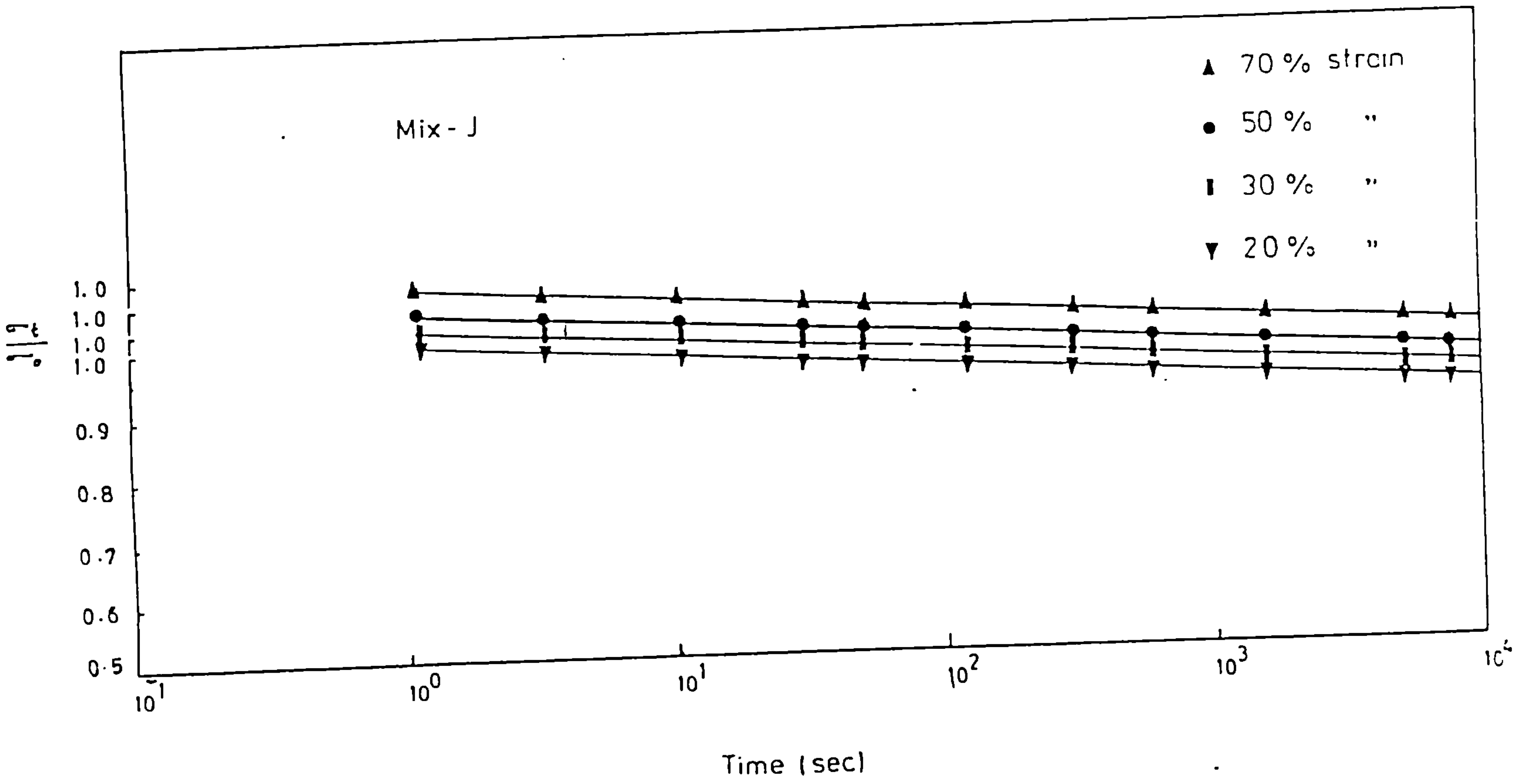

Figure VI.2. Stress relaxation curves of the mix J at different strain levels.

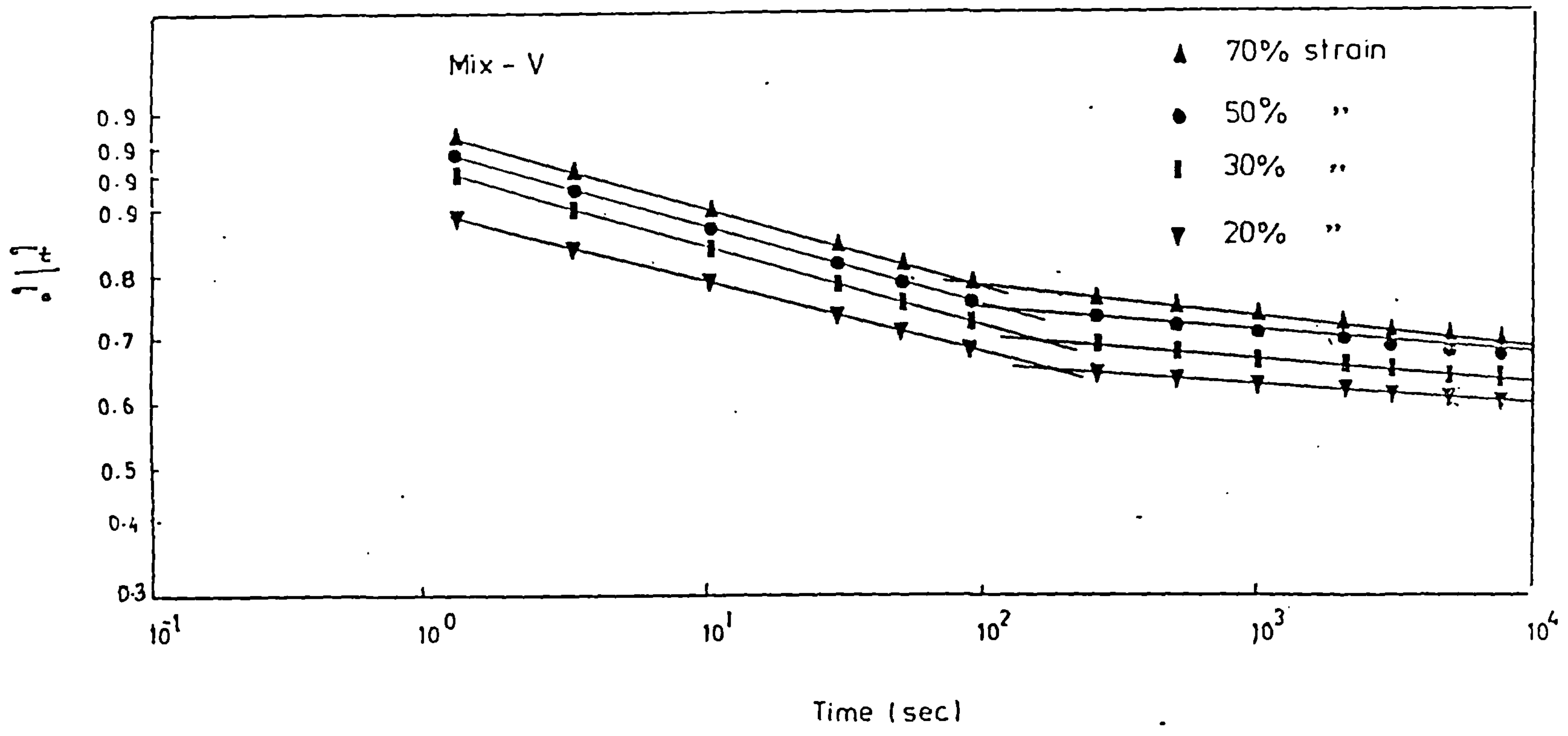

Figure VI.3. Stress relaxation curves of the mix V at different strain levels.

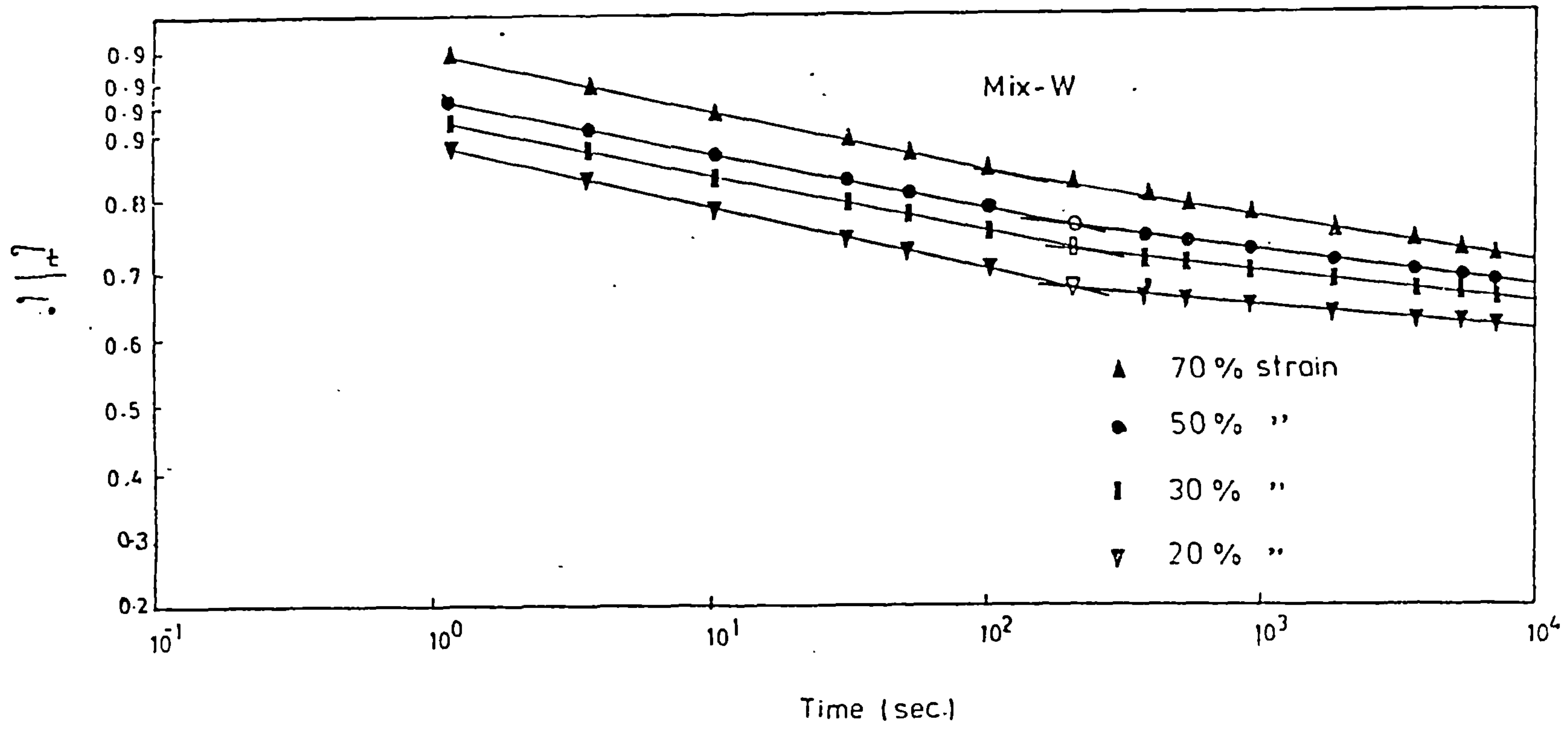

Figure VI.4. Stress relaxation curves of the mix W at different strain levels.

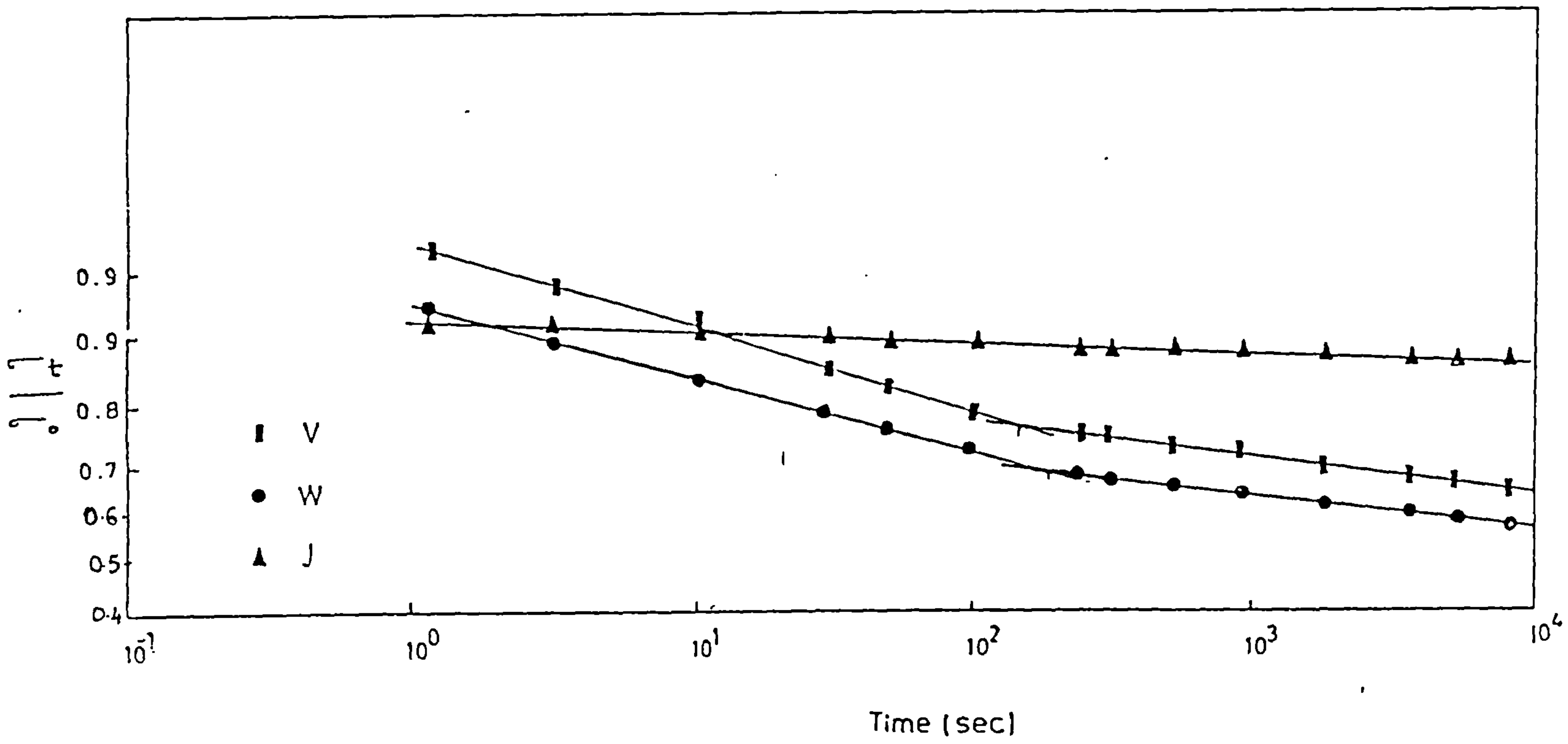

Figure VI.5. The stress relaxation curves of mixes J, V and W at 30% elongation.

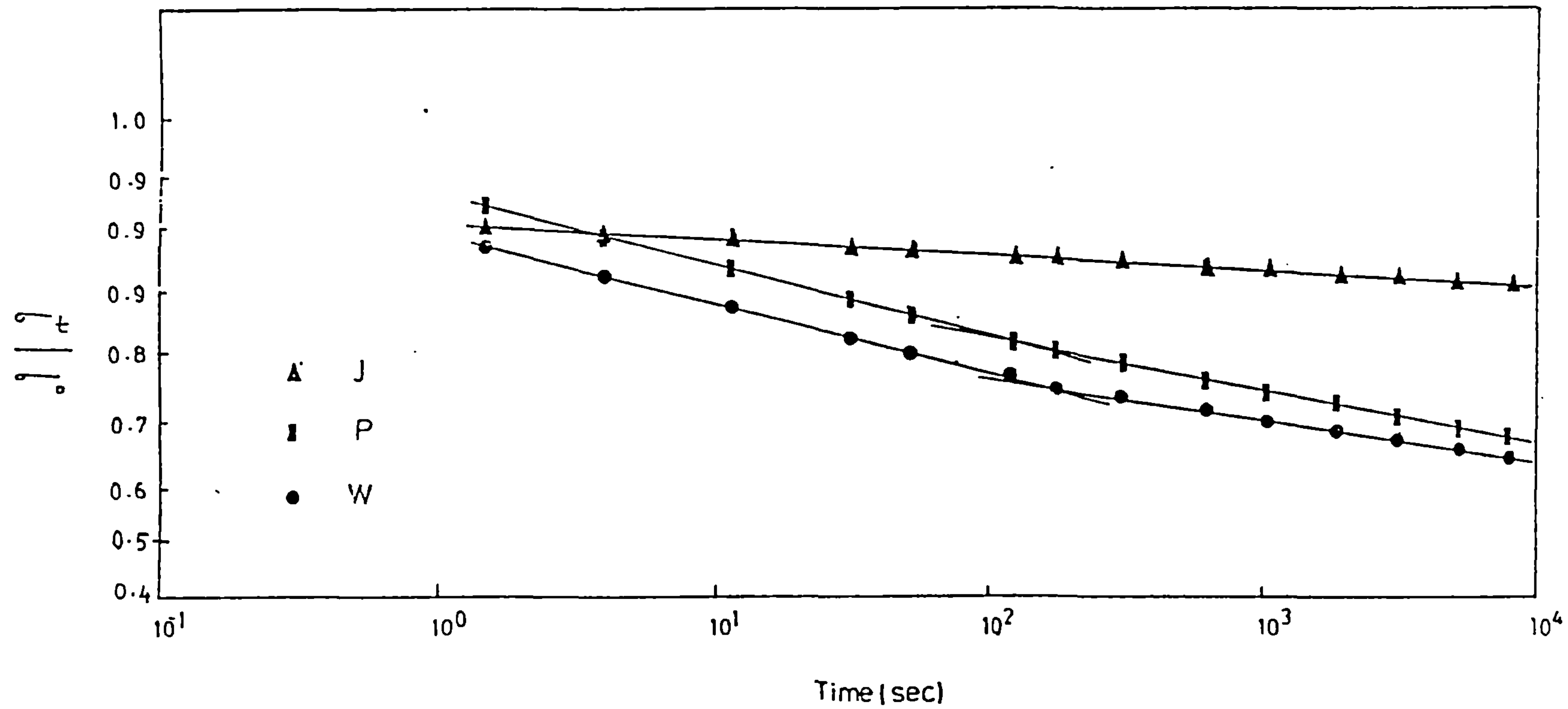

Figure VI.6. The effect of fibre loading on stress relaxation at 50% strain level of mixes J, P and W.

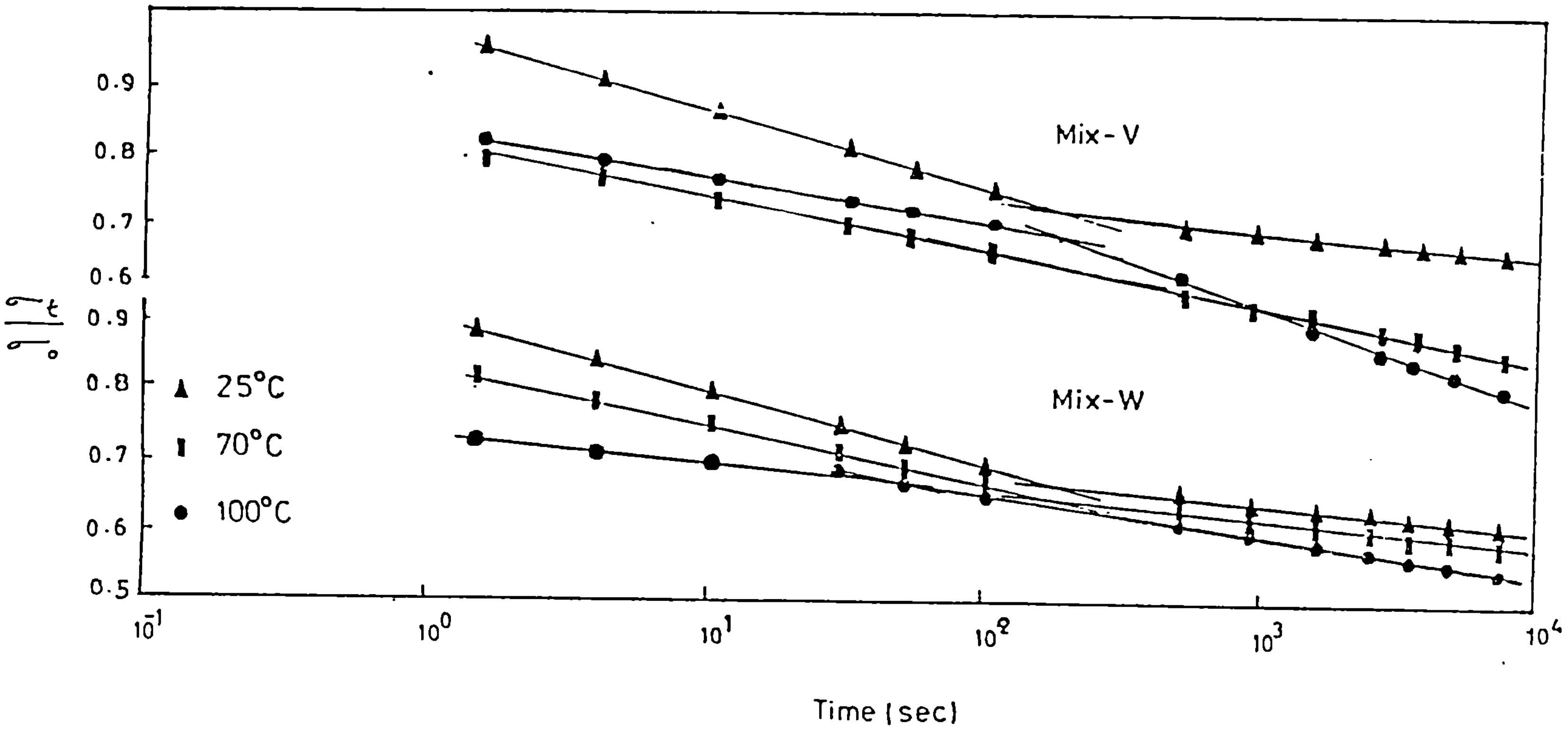

Figure VI.7. Stress relaxation curves of mixes V and W at 30% elongatioon (After ageing).

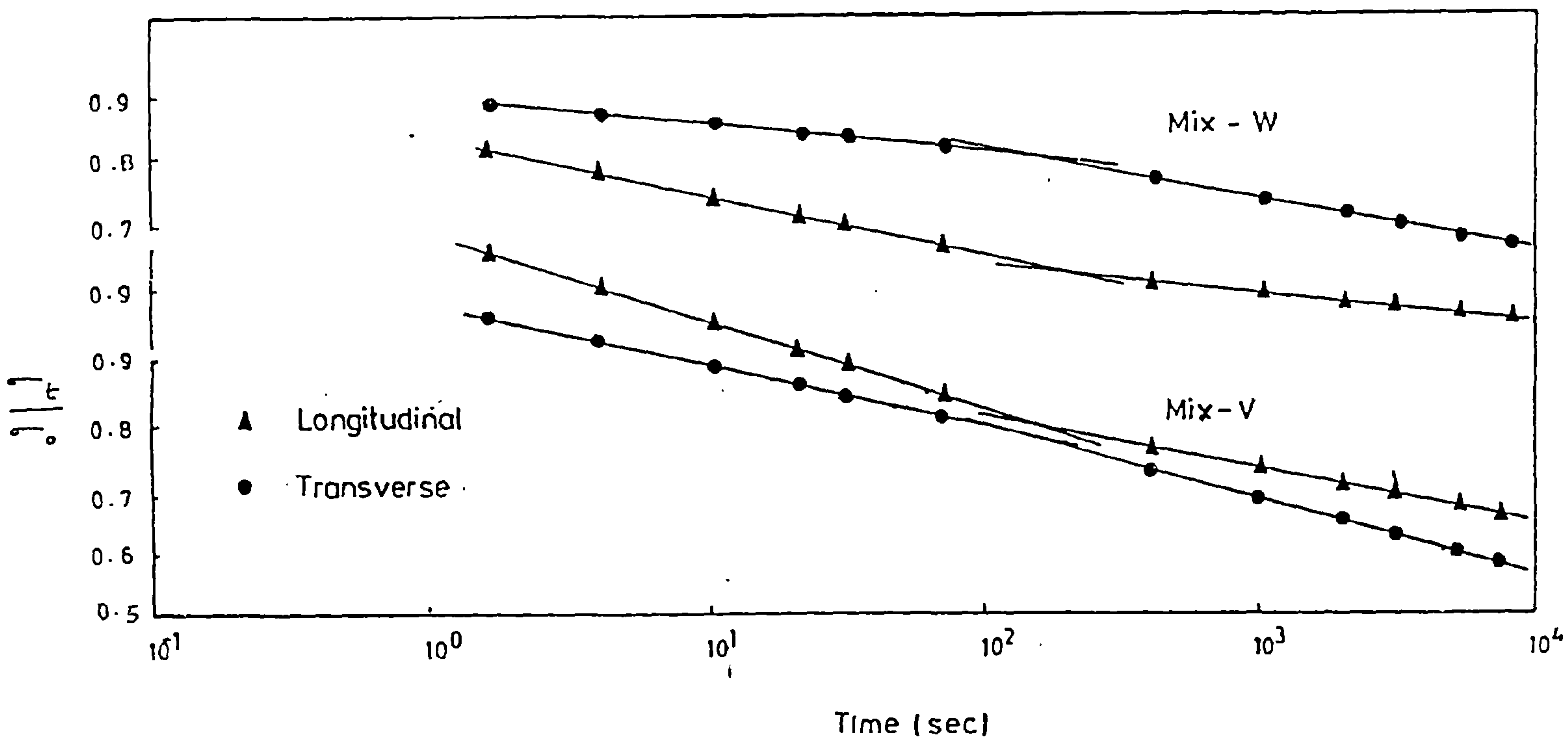

**Figure VI.8.** The effect of fibre orientation on stress relaxation at 30% strain level of mixes V and W.

# CHAPTER VII

# EQUILIBRIUM SWELLING BEHAVIOUR OF SHORT SISAL FIBRE-NATURAL RUBBER COMPOSITES

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The results of the above study have been communicated to Rubber Chemistry and Technology.

Swelling of rubber vulcanizates in a wide range of liquids has been studied by Whitby and co-workers[1]. Vulcanized rubber differs from raw rubber essentially in that it possesses a structure which cannot be broken down completely by any solvent, the material therefore swells but cannot be dispersed. The sorption and transport of organic solvents by polymer membranes have been studied extensively by Aminabhavi and co-workers[2,3]. They also investigated the diffusion characteristics of polyurethane membranes in normal alkanes and observed that the diffusion mechanism followed the Fickian trend and the kinetics of sorption was of first order. The swelling of vulcanized rubber in various liquids has been investigated by Gee[4]. He found that the entropy of swelling of vulcanized rubber is independent of the nature of swelling liquid. Kraus[5] determined the degree of cure in filler reinforced vulcanizates by the swelling method. In order to understand the correlation between molecular structure and intermolecular attraction, Saloman and Van Amerongen[6] have made a comparison of swelling equilibria of different polymers under the influence of polar and polarizable groups which were introduced in solvents and polymers having different molecular structures. They concluded that the strength of interaction depends on the mutual attraction of both components. Coran and co-workers[7] have studied the solvent swelling of unidirectional rubber-fibre composite. From their studies it was concluded that fibres restrict the amount of swelling in unidirectional fibre composite. The adhesion between rubber and short glass and asbestos fibres has been studied by Das[8] using restricted swelling measurement. It has been demonstrated that with improved adhesion between short fibre and rubber the factor $\frac{V_I - V_F}{V_I}$ decreases, where $V_I$ and $V_F$ are the volume fraction of rubber in dry and swollen samples, respectively.

Numerous techniques such as H-block, strip adhesion, U, T and many others, both static and dynamic in nature, have been used to measure adhesion between fibres and rubber. While most of these give a good relative indication of adhesion, the time dependent nature of the viscoelastic materials sometimes overshadows the real effect. Equilibrium swelling is another technique which has been used to assess rubber-fibre adhesion since, fibres, if bonded, are supposed to restrict the swelling of elastomers[8]. Hence, in this work restricted equilibrium swelling is tried as a means to measure the degree of adhesion.

## VII.1. Effect of bonding agent

Formulations of mixes are given in Table VII.1. The room temperature sorption curves obtained by plotting mole percentage uptake ($Q_t$) of the liquid by 100g of the polymer versus square root of time ($\sqrt{t}$) for pentane, hexane, heptane and octane are given in Figures VII.1, 2, 3 and 4, respectively. Since all the liquids followed the same diffusion pattern as evident from diffusion curves, the discussion is limited only to that of hexane (Figure VII.2). The sorption curves of composites with bonding agent is represented by continuous line and the discontinuous curves represent the composites without bonding agent. The gum compound takes up the maximum amount of solvent at equilibrium, since there is no restriction for the penetrant to enter into the polymer.

Though the volume loading of fibre is the same, the amount of solvent sorbed by a composite at equilibrium swelling is less for the composite containing bonding agent compared to composite without bonding agent (Figure VII.5). Another interesting factor which can be seen from sorption curves of the composites in hexane is the different initial rates of diffusion for different composites. The initial rates of diffusion is fast for composites without bonding agent compared to those containing the bonding agent. This is because of the fact that in unbonded fibre-rubber composites, the solvent can penetrate into the polymer along the thickness direction and also through the weak interfaces parallel and perpendicular to the fibre orientation. The weak interface allows easy entrance of the penetrant and these interfaces act as solvent pockets at equilibrium. But in the case of composites which contained the bonding agent the interface is strong and the liquid can penetrate into the polymer only through the space in between two fibre ends in the thickness direction. As a result, the diffusion rate is slow in well bonded composites. At the same fibre loading a composite which contained no bonding agent absorbed more liquid at equilibrium swelling compared to a composite which contained the bonding agent. This may also be due to the formation of liquid pockets at the weak interface of the composite without bonding agent. This will not occur when a strong interface is formed by the bonding agent.

The restricted swelling due to improved adhesion in composites has been reported by Das[8]. He has demonstrated that with improved adhesion between short fibre and rubber the ratio $V_T = \frac{V_I - V_F}{V_I}$ decreased by more than 0.04 units where $V_I$ and $V_F$ are the volume fraction of rubber in the dry and swollen samples, respectively. A highly bonded system would exhibit high resistance to swelling. Consequently $V_F$ would have a relatively higher value and $V_T$ a relatively lower value. On the other hand, if the bonding is poor $V_F$ will be relatively lower resulting in higher $V_T$ value[6].

Table VII.2 summarises the swelling results of sisal fibre reinforced natural rubber composites. It is evident that for the fibre composites containing bonding agent (P, Q, R, S and L) have substantially lower $\frac{V_I - V_F}{V_I}$ value than those without bonding agent (Po, Qo, Ro, So and Lo). In the case of composites containing bonding agent also the magnitude of $\frac{V_I - V_F}{V_I}$ value decreases gradually as the fibre loading increases. But the magnitude of $V_T$ value is always greater in the unbonded composite compared to the bonded one for the same fibre loading.

## VII.2. Effect of fibre loading

As the fibre loading increases, the amount of liquid taken by the specimen at equilibrium swelling decreases (Figure VII.5). This is due to the increased hindrance exerted by the fibre at higher loading. As the fibre loading increases, in both cases the liquid uptake decreases gradually but the reduction is sharp in the case of bonded composites. Another interesting factor is the initial decrease in swelling rate with fibre loading.

Though the pattern of diffusion curves obtained for pentane, hexane, heptane and octane are the same, it is interesting to have a look at the equilibrium swelling of the composites in these liquids. Table VII.3 shows the amount of different solvents absorbed by mixes Q and $Q_o$, As the molecular size (chain length) increases, the liquid uptake increases and it reaches a maximum for heptane and then decreases. This type of absorption is also reported earlier by Saloman and Van Amerongen[6]. This may be due to the greater association of molecules of the lower alkanes in the liquid state.

## VII.3. Dimensional changes

Swelling is one of the techniques to measure the adhesion between short fibre and rubber, in which the fibres, if bonded, are supposed to restrict the swelling of elastomers. In a well bonded, oriented fibre-rubber composite the swelling of the composite will be anisotropic. It will swell to a greater extent in a direction perpendicular to the fibre orientation.

One surprising feature of the solvent swelling data is the significant swelling in the thickness direction. This is because the oriented fibres will prevent penetration of the liquid along the direction perpendicular to the flat surface of the specimen. Hence the penetrant can diffuse into the polymer only along the direction parallel to the fibre orientation. Hence swelling was considered to be constrained in one direction and as a result thickness of the specimen increased considerably and little change occured in the diameter (since the specimen is circular). The control sample (mix J) with no fibre also showed greater swelling in the thickness direction but the difference becomes pronounced when fibres are added.

The percentage increase in thickness of the specimen at equilibrium swelling is shown in Figure VII.6. It is observed that the change in thickness is maximum for composites containing the bonding agent and it increases marginally with fibre loading. Though the increase in thickness during swelling is shown by composite containing the bonding agent and those without the bonding agent, the effect is more noticeable in the case of composites containing bonding agent, especially at low fibre loading. At high fibre loading (>40 phr) the increase in thickness is comparable. As the fibre loading increases the number of fibres in unit volume increases and the penetrant molecule finds it more difficult to diffuse into the polymer and the entire swelling will take place in the thickness direction. In the bonded composites at low loading the penetrant can enter into the matrix both parallel and perpendicular directions of the fibre orientation. When the bonding is poor, the matrix swells both in diameter and thickness directions. As a result at low loading and also in the absence of a bonding agent, swelling in the thickness direction will be less. However, as the fibre loading increases, the swelling takes place predominantly in the thickness direction and as a result contribution in that direction increases.

The change in diameter of the specimen at equilibrium swelling against fibre loading is given in Figure VII.7. At higher loadings, in the case of bonded composites, the swelling is restricted and takes place mostly in the thickness direction and the hydrostatic pressure inside the specimen will distort the polymer as a result of which the diameter of the sample decreases below the initial diameter (ie., before swelling).

The optical photograph of the swollen samples in hexane is given in Figure VII.8. From the photograph it is clear that as the fibre loading increases, the size of the samples (diameter) decreases. At the same fibre loading the diameters of the bonded composites are lower than those of the unbonded composites. From this it is, beyond doubt, established that in highly bonded composites swelling is possible only in the thickness direction. Therefore this restricted swelling can be used to measure the bonding between fibre and rubber.

## VII.4. Effect of acetylation

The effect of chemical treatment can be understood from the equilibrium sorption curves of mixes $L_o$ and $Q_o$ given in Figure VII.9. Mix $Q_o$, which contains the treated fibre, absorbed less amount of octane compared to mix $L_o$ which contains untreated fibre. In both these systems the bonding agent is absent. In the case of composites containing bonding agent, the same trend was observed. The mix Q absorbed less amount of liquid at equilibrium than mix L. The rate of diffusion is slow when the composite contained the bonding agent. This is because of the fact that the treated fibre in presence of bonding agent created a strong interface. The optical photograph of the samples $L_o$ and $Q_o$ at equilibrium swelling in hexane is given in Figure VII.10. Since the bonding in $L_o$ is poor it swells like a gum compound compared to mix $Q_o$. This observation further confirmed that acetylation of sisal fibre improved the adhesion with natural rubber.

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Table VII.1. **Formulation of mixes containing varying amounts of fibre**

| | J | L | Lo | P | Po | Q | Qo | R | Ro | S | So |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Natural rubber | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Stearic acid | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Resorcinol | 0 | 5 | 0 | 2.5 | 0 | 5 | 0 | 7.5 | 0 | 10 | 0 |
| Hexa[1] | 0 | 3.2 | 0 | 1.6 | 0 | 3.2 | 0 | 4.8 | 0 | 6.4 | 0 |
| Sisal fibre (untreated) | 0 | 20 | 20 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sisal fibre (acetylated) | 0 | 0 | 0 | 10 | 10 | 20 | 20 | 30 | 30 | 40 | 40 |
| TDQ[2] | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| CBS[3] | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| Sulphur | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |

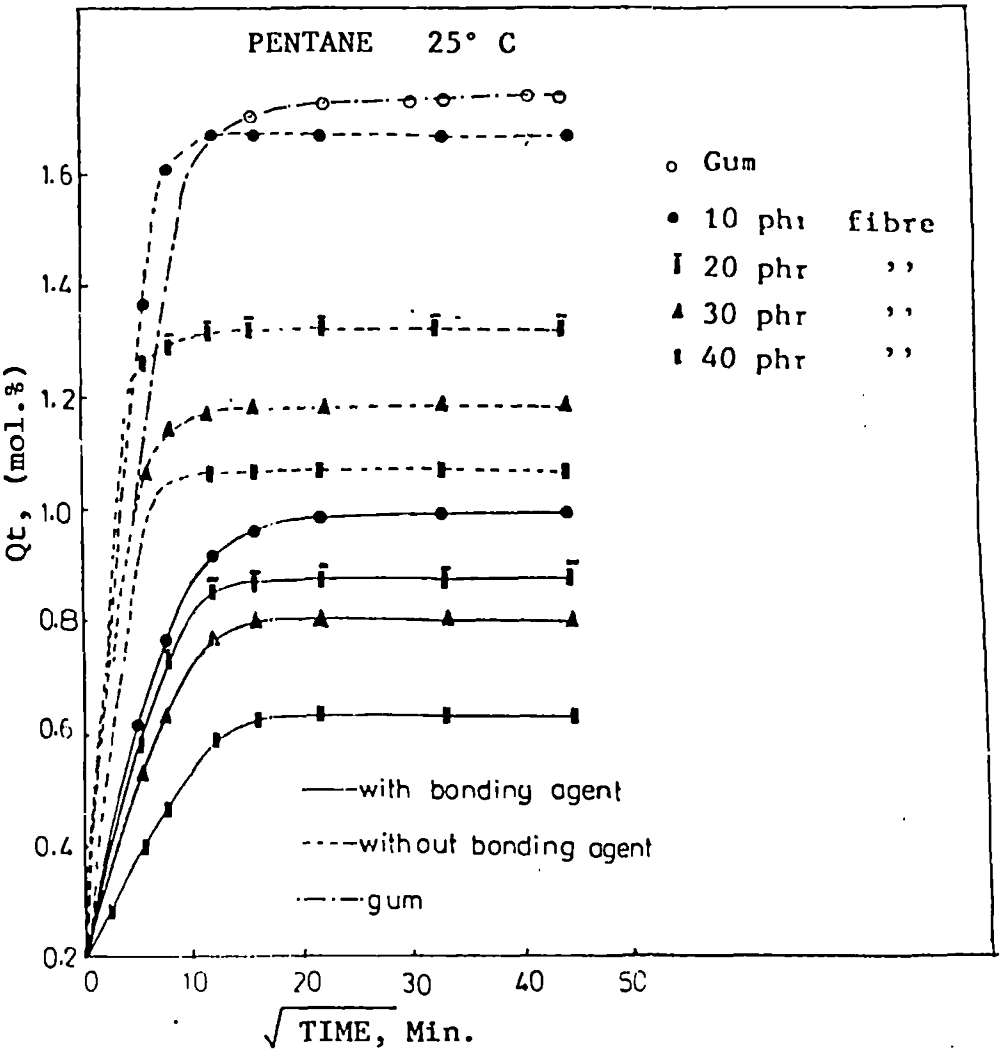
1. Hexamethylenetetramine
2. 2:2:4 trimethyl 1,2 dihydroquinoline polymerised
3. N-cyclohexyl-2-benzthiazylsulphenamide

Table VII.2. **Volume fraction of rubber in the composites at equilibrium swelling in hexane**

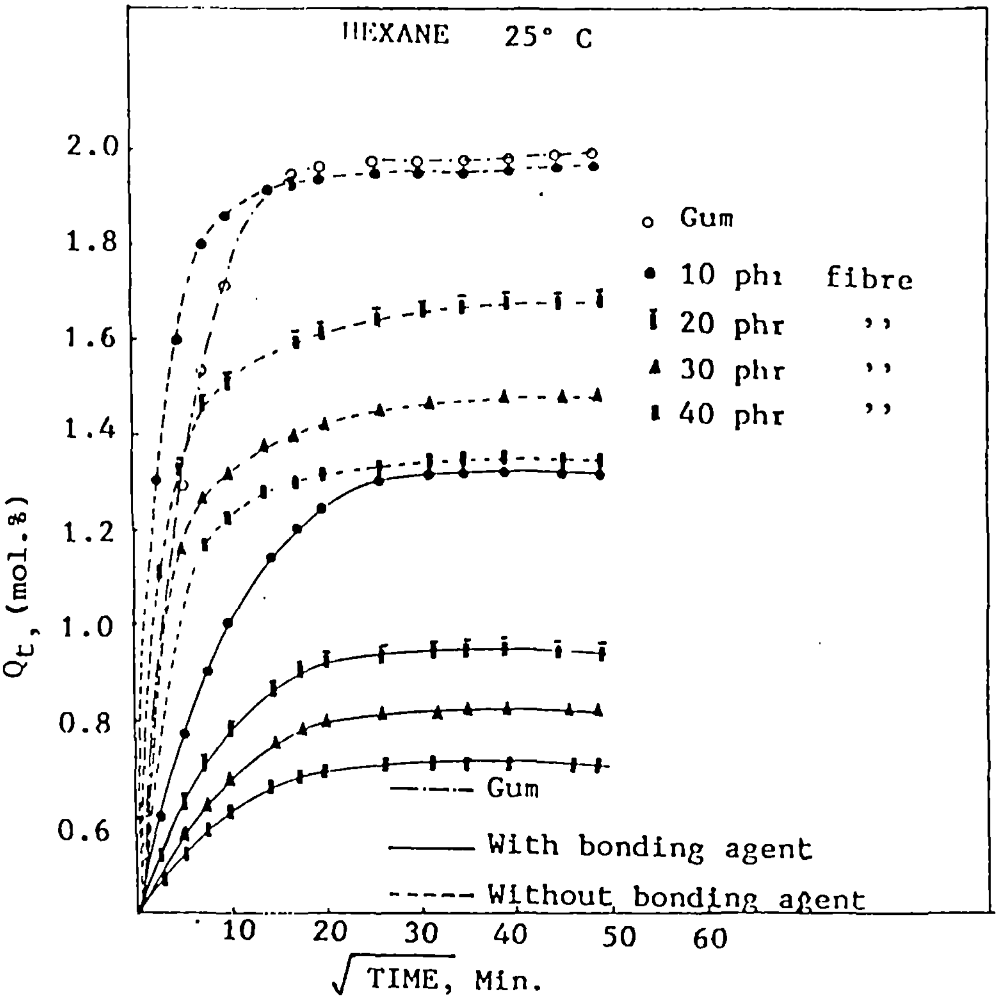
| | Volume fraction of rubber in the dry specimen ($V_I$) | Volume fraction of rubber in swollen specimen ($V_F$) | |
|---|---|---|---|
| J | 0.98 | 0.20 | 0.79 |
| P | 0.84 | 0.31 | 0.63 |
| Po | 0.83 | 0.22 | 0.73 |
| Q | 0.77 | 0.35 | |
| Qo | 0.75 | 0.31 | 0.58 |
| R | 0.72 | 0.34 | 0.52 |
| Ro | 0.76 | 0.28 | 0.63 |
| S | 0.65 | 0.33 | 0.48 |
| So | 0.71 | 0.26 | 0.63 |
| L | 0.79 | 0.32 | 0.50 |
| Lo | 0.84 | 0.24 | 0.71 |

Table VII.3. Amount of solvent absorbed by mix Q and mix $Q_0$ at equilibrium swelling

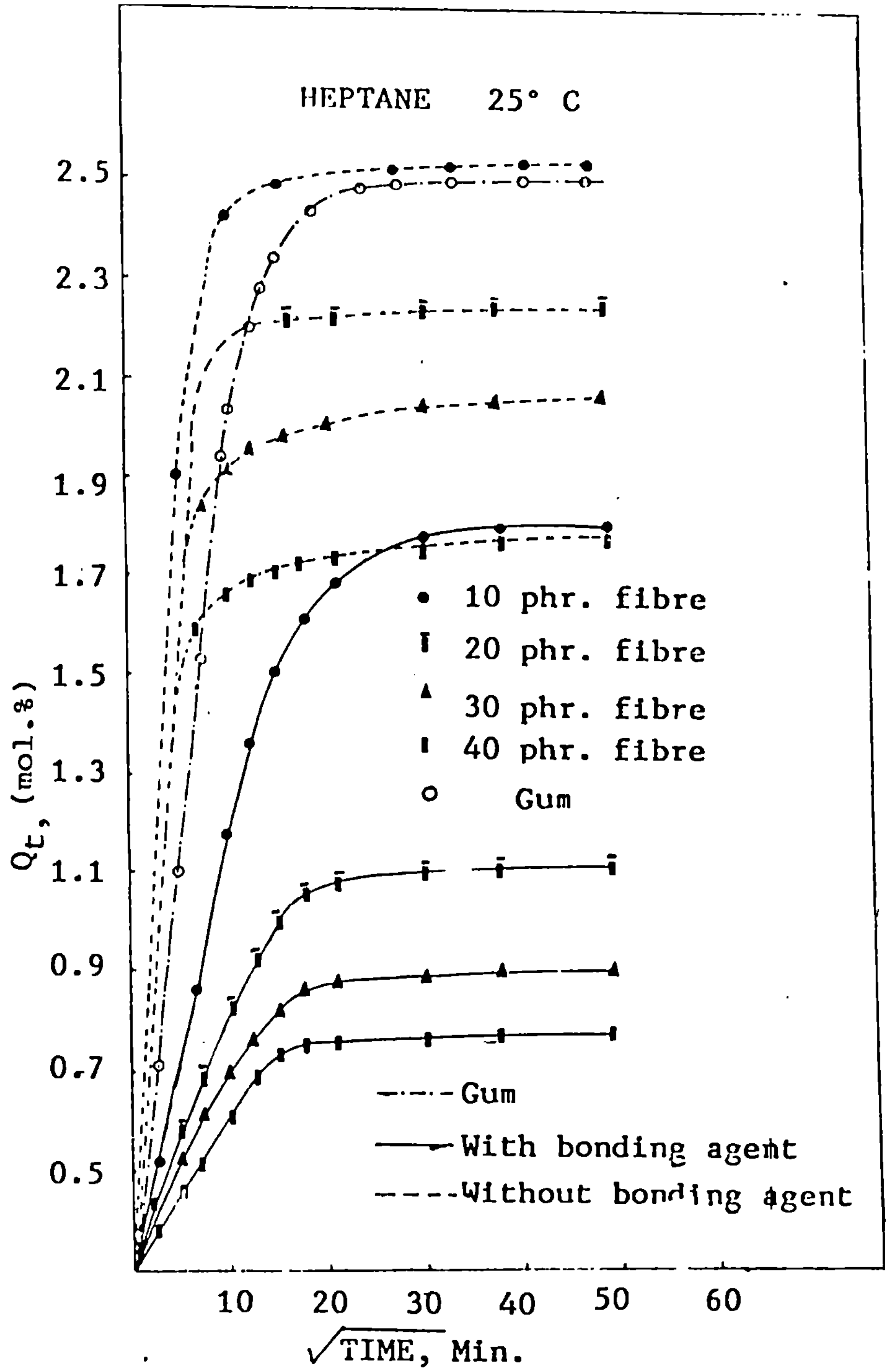
| Solvent | Bonded composite (Q) mole percentage/ 100gm of composites | mole percentage/ 100gm of composites |
|---|---|---|
| Pentane | 0.88 | 1.32 |
| Hexane | 0.95 | 1.68 |
| Heptane | 1.10 | 2.23 |
| Octane | 0.72 | 1.14 |



igure VII.1. Sorption curves of mixes J, P, Q, R, S, $P_o$, $Q_o$, $R_o$ and $S_o$ in pentane.



gure VII.2. Sorption curves of mixes J, P, Q, R, S, $P_o$, $Q_o$, $R_o$ and $S_o$ in hexane.



igure VII.3. Sorption curves of mixes J, P, Q, R, S, $P_o$, $Q_o$, $R_o$ and $S_o$ in heptane.

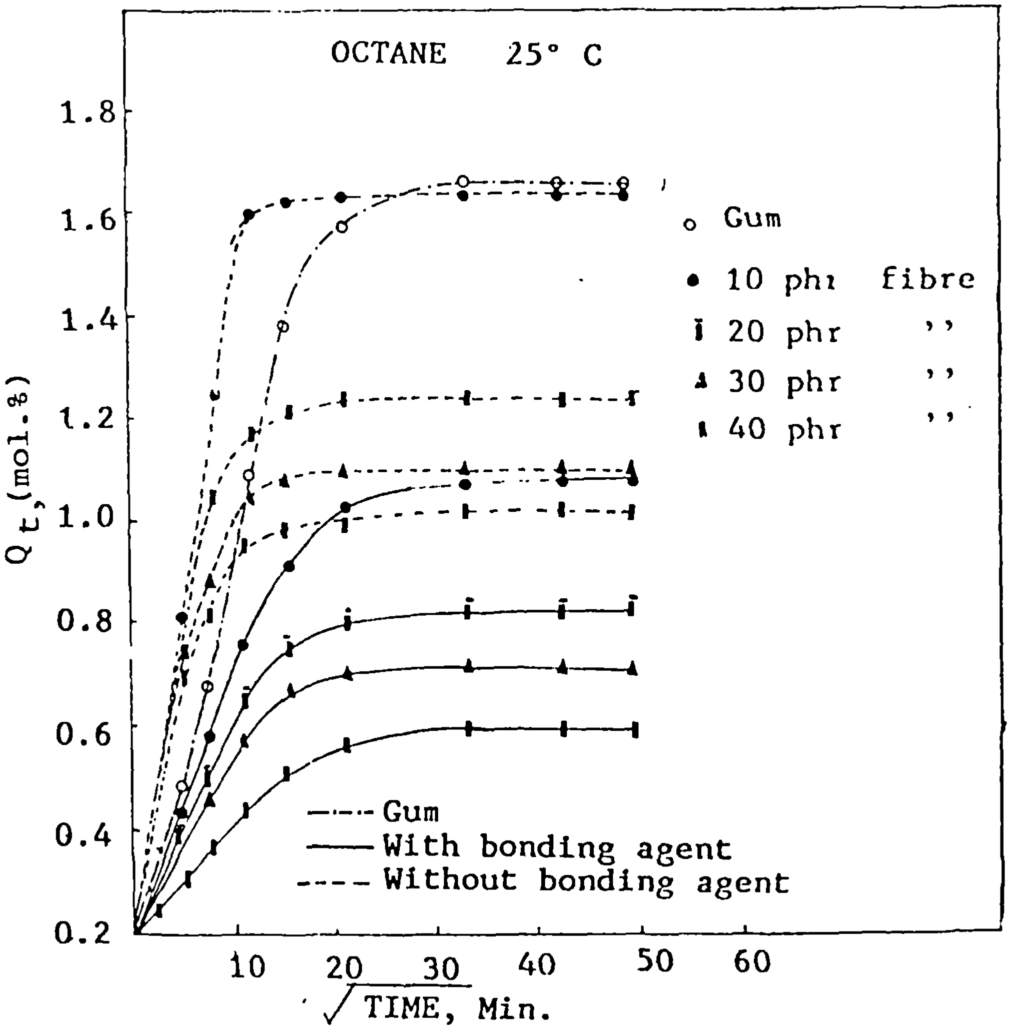


Figure VII.4. Sorption curves of mixes J, P, Q, R, S, $P_o$, $Q_o$, $R_o$ and $S_o$ in octane.

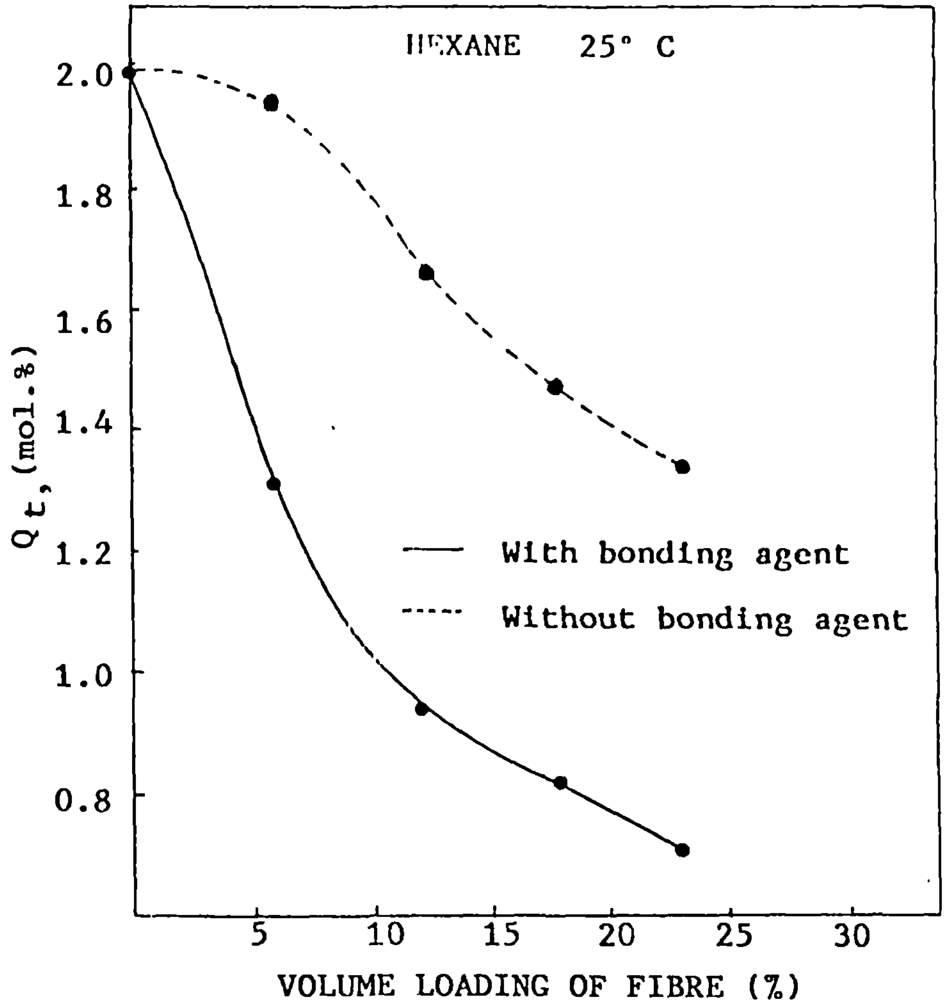


Figure VII.5. Comparison of sorption curves of NR-sisal composites with and without bonding agent, in hexane.

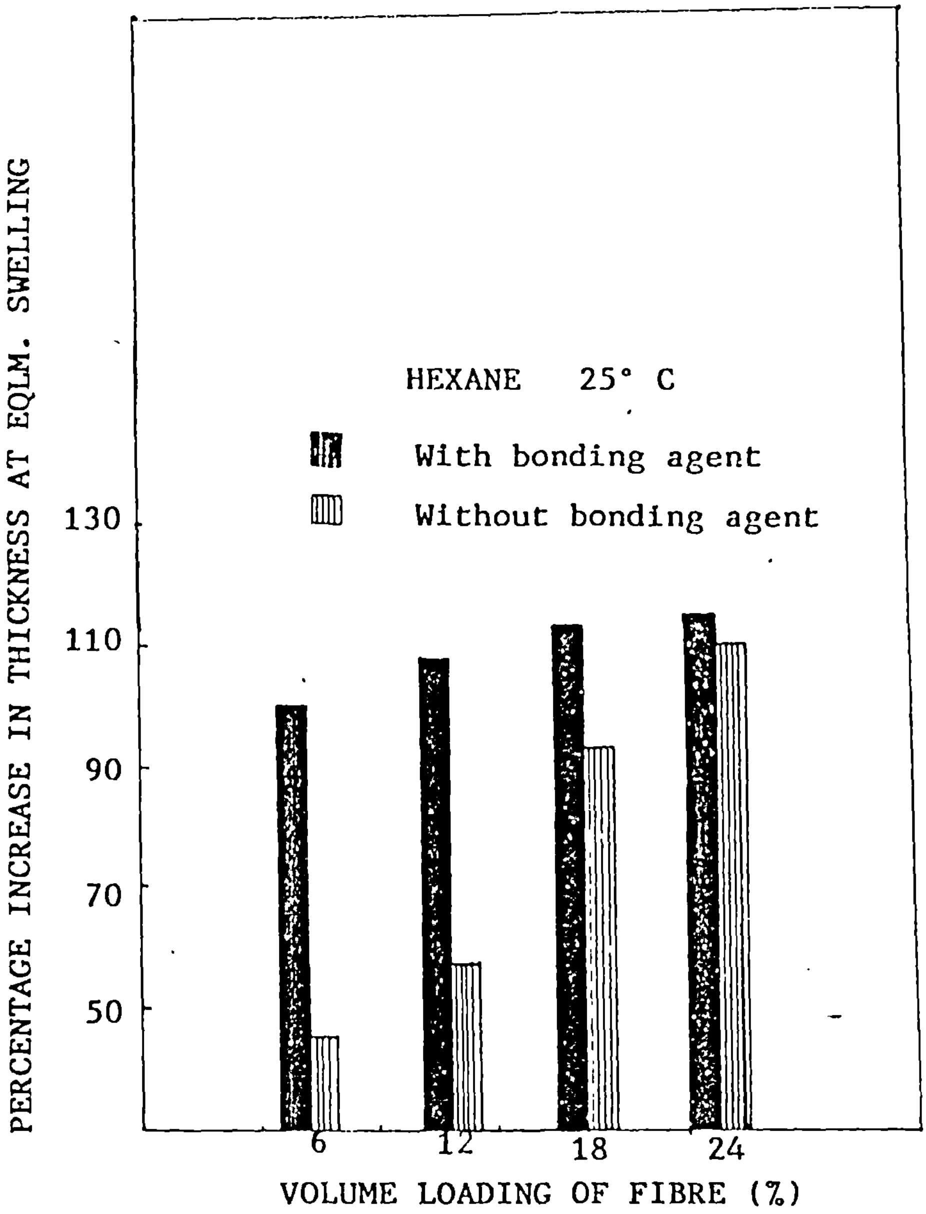


Figure VII.6. Percentage increase in "thickness" of the composites at equilibrium swelling i hexane, against fibre loading

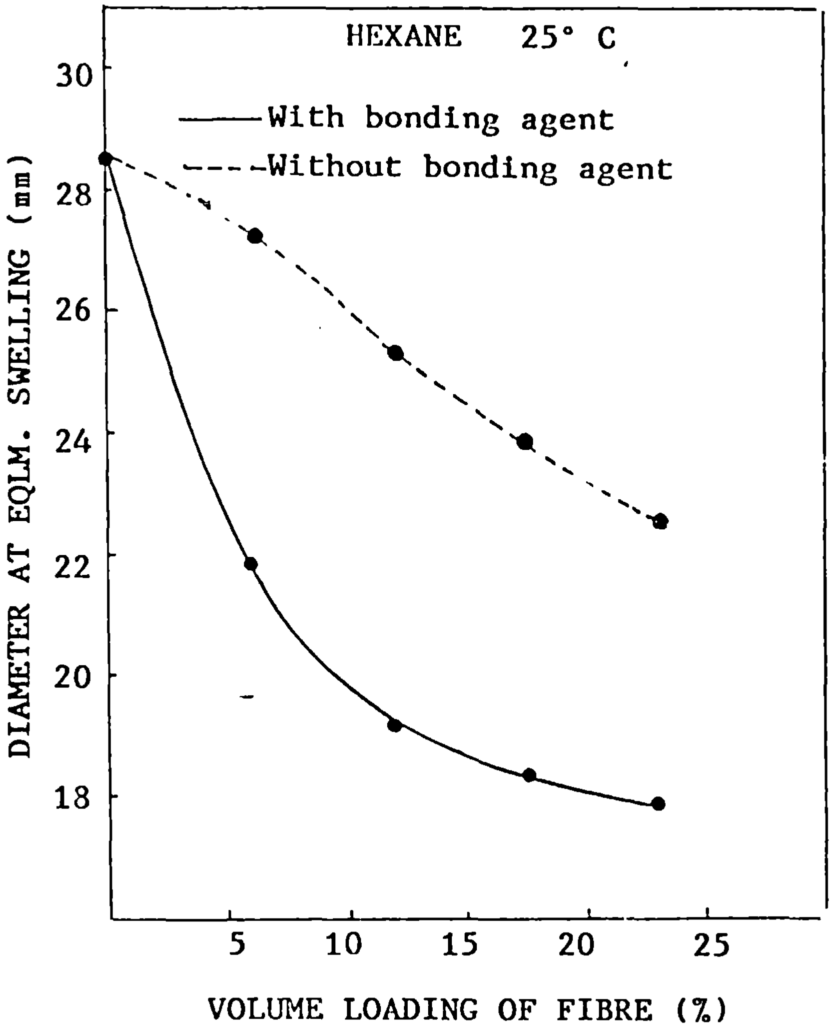


Figure VII.7. The change in diameter of the composites at equilibrium swelling in hexane against fibre loading.

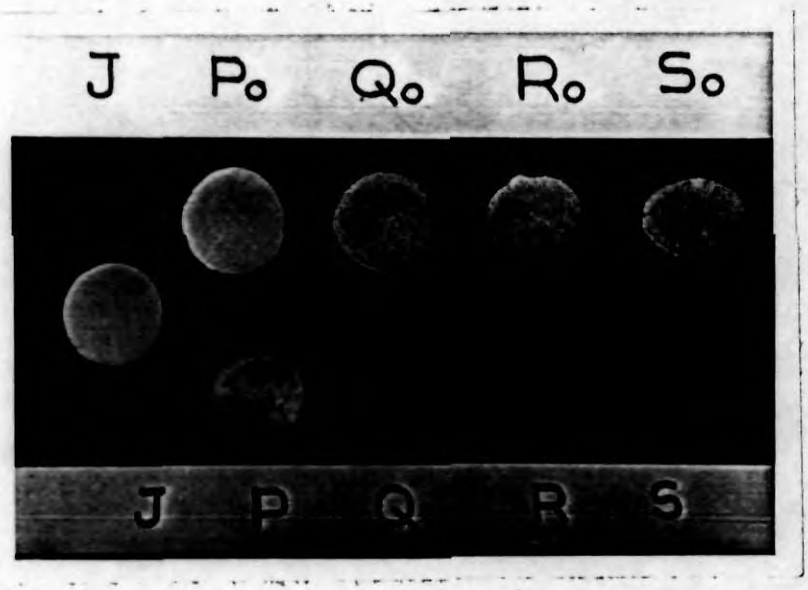


Figure VII.8. Optical photograph of the swollen samples in hexane.

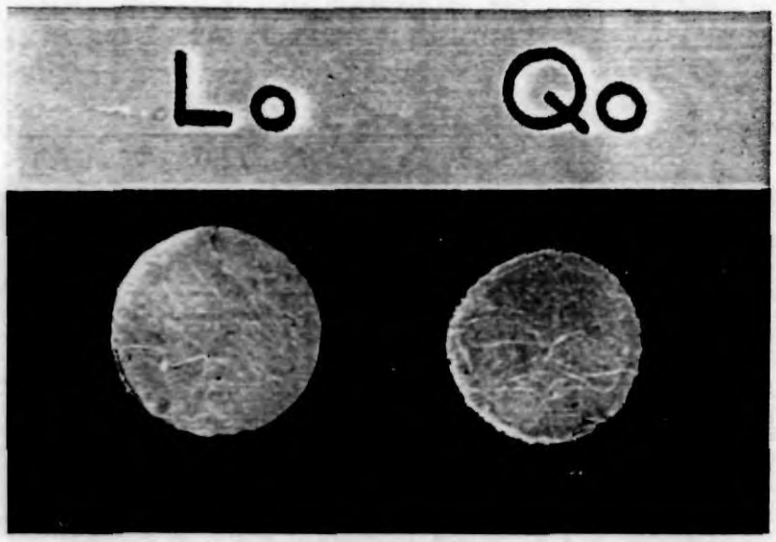


**Figure VII.10.** The optical photograph of the samples $L_o$ and $Q_o$ at equilibrium swelling in hexane.

# CHAPTER VIII

# DEGRADATION BEHAVIOUR OF SHORT SISAL FIBRE-NATURAL RUBBER COMPOSITES

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The results described in this chapter have been communicated for publication in the *Journal of Applied Polymer Science*.

Use of polymeric composites under the influence of degrading agents such as ozonized air, $\gamma$- radiation and heat has increased rapidly during the last few years[1]. Hence it is very important to study the effects of such degrading agents on the performance of composites. For NR, the resistance to ageing and ozone is poor due to the presence of reactive double bonds in the main chain. Sisal fibre possesses excellent ageing resistance. Hence the behaviour of NR-sisal fibre composites against the action of various degrading agents is worth examining. Several studies have been reported on the thermo-oxidative ageing of rubber[2] and on the protection of polymers against the action of ozone[3]. The effects of radiation on polymeric materials, their blends and composites have also been reported by several research groups.[4-8]

This chapter discusses the results of the studies on the retention of tensile strength and modulus of NR-sisal composites after exposing test samples to different degrading agents such as $\gamma$- radiation, heat and ozone. The effects of fibre loading, fibre orientation and bonding agent have been examined. The details of the experimental procedures adopted for this studies are given in chapter II.

## VIII.1. Effect of radiation

Radiation is a powerful method for crosslinking elastomers and composites. In the case of composites, bonding sites may form either at the fibre surface or on the polymer chain, which bind the two components together, improving the adhesion. The extent of crosslinking/degradation undergone by each polymer composite depends on the nature of the matrix polymer, type of fibre, presence of protective agents etc. Radiation has two major effects on the mechanical properties. It produces permanent crosslinks between carbon atoms and it reduces the crystallinity[9]. These two effects operate in opposite directions, the former increases the stiffness while the latter reduces it.

Figure VIII.1. gives the plot of percentage retention of tensile strength aganist volume loading of fibre at three different radiation doses. The continuous lines represent the composites with bonding agent and discontinuous lines represent the composites without bonding agent. At a dose rate of 5 Mrad, the retention in tensile strength remains almost constant beyond 6 volume per cent loading of fibre for both the systems (with and without bonding agent). A slight increase in retention of tensile strength may be due to the covalent bonds formed at the interface through the reactive sites created by the radiation. At a dose rate of 10 Mrad the retention in tensile strength increases continuously with fibre loading. From this it is clear that a dose rate of 10 Mrad is ideal for establishing some type of permanent bond between fibre and rubber. At a dose rate of 15 Mrad, degradation of the polymer chain is the main reaction taking place at low fibre loading. But at higher fibre loading, where enough fibre is there, the retention of tensile properties is higher. However, the actual values are lower than those for 5 and 10 Mrad radiation. In the case of transversely oriented fibre composites (Figure VIII.2.) the pattern of curves is almost the same as that of the previous one.

In Figure VIII.3. retention in modulus for 10 per cent elongation is plotted against fibre loading, for the samples having longitudinal fibre orientation. The composites which contained the bonding agent showed steady increase in modulus retention with increase in dose rate as well as with increase in volume loading. For samples which did not contain the bonding agent, the modulus retention increased with fibre loading for 10 and 15 Mrad dosages, whereas samples exposed to 5 Mrad, registered a decrease in modulus retention at lower levels of fibre loading. The better retention of the composites containing higher fibre loading may be due to the better interfacial attachment/adhesion between the fibre and rubber, which is developed due to the action of radiation.

In the transverse fibre orientation (Figure VIII.4.) the pattern of retention of modulus (10% elongation) with fibre loading is almost the same for both sets of composites (with and without bonding agent). The bonding agent incorporated composites have slightly higher retention of modulus on $\gamma$- irradiation.

## VIII.2. Effect of thermal ageing

It is well known that during thermal ageing, main chain scission, crosslink formation and crosslink breakage can take place. It is also possible that the existing crosslinks may break and a more stable type of crosslink can be formed[10]. The relative ratio and the magnitude of such reactions which take place during ageing govern the amount of change in each property. In composites, the various reactions during ageing are (1) crosslinking of rubbers (2) bonding resin formation and (3) degradation of polymer chain. All these reactions have significant effect on the performance of the composites.

The percentage retention of tensile strength after ageing for 3 and 5 days at 100°C against volume loading of fibre (longitudinal direction) is shown in Figure VIII.5. For samples aged for 3 days the retention in tensile strength increases continuously with fibre loading for both the systems (with and without bonding agent). But the increase in retention is more in the case of bonding agent incorporated composites. At moderate temperature, the bonding resin formation will predominate over polymer chain degradation which results in a higher retention of tensile strength. The tensile retention for composites in the absence of bonding agent is due to the fact that some of the groups in the treated fibre surface may be activated and form bonds with rubber. However as the ageing period is increased from 3 to 5 days the composites which did not contain the bonding agent showed lower retention of tensile strength. This indicated that the polymer degradation predominated in these composites whereas resin formation continued to take place in those composites which contained the bonding agent, during prolonged ageing.

The retention of modulus for 10 per cent elongation in the longitudinal direction is given in Figure VIII.6. In the case of bonding agent incorporated composites a continuous increase in modulus is observed with fibre loading. Though the same trend is observed in the case of composites which contained no bonding agent, the increase is only marginal. The same effect is observed in the retention of modulus in the transverse fibre orientation (Figure VIII.7.) for the composites which contained the bonding agent. For the composites which did not contain the bonding agent prolonged ageing decreased the retention of modulus as the fibre loading was increased.

### VIII.3. Effect of exposure to ozone

Unsaturated elastomers, especially those containing activated double bonds in the main chain, are severely attacked by ozone, resulting deep cracks in a direction perpendicular to the applied stress. Protection against ozone attack can be achieved by blending with any saturated elastomer or mixing with antiozonants. In the case of composites, the fibres incorporated in the mixes prevent the crack initiation and also hinder the crack propagation. Two conditions should be satisfied for the effective prevention of crack by the fibres. These are (1) the fibre orientation should be perpendicular to the direction of crack propagation (2) there should be good bonding between the fibre and the rubber.

Figure VIII.8. is a photograph of NR-sisal composites with bonding agent after being exposed to ozone for 40 h. The ozone concentration used was 50 pphm. A number of cracks perpendicular to the direction of strain are evident in the sample J (Gum). The intensity of cracks decreased with the increase in fibre loading. It has been reported by Bhagawan and De[11] that the addition of clay or carbon black increases the modulus of the compound.

Hence, for a given strain, the stress in the filled specimen is higher than that in the unfilled specimen. Similarly though greater strain is experienced in composite with high fibre loading, it is highly resistant to crack propagation. The sample without any fibre (mix-J) is severely attacked by ozone.

Figure VIII.9. is an optical photograph of the NR-sisal composites without any bonding agent after being exposed to ozonised air for 40 h. Even in the absence of bonding agent all the composites are resistant to ozone attack except the gum sample (J).

## VIII.4. Effect of acetylation

If the bonding between the fibre and rubber is sufficiently strong, the resulting composites effectively prevent the propagation of the crack created by ozone attack. $L_0$ and $Q_0$ are mixes containing 20 phr of untreated and acetylated fibre, respectively. These mixes do not contain the bonding system. The photograph of the samples after being exposed to ozonised air for 40 h is depicted in Figure VIII.10. In the case of mix $L_0$, even in the longitudinal fibre orientation, some cracks are observed. This is because of the fact that in mix $L_0$ the untreated fibre fails to form sufficiently strong bonds with rubber which in fact fails to hinder the crack propagation. This will not happen in the case of $Q_0$

where the acetylated fibre creates better bonding with rubber. The effect of acetylation on improving the fibre - rubber adhesion is also explained in chapter VII, where, the acetylated fibre incorporated mixes, restricted the swelling of the composites in solvents.

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Table VIII.1. Formulation of mixes containing varying amounts of fibre

| | J | L | Lo | P | Po | Q | Qo | R | Ro | S | So |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Natural rubber | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Stearic acid | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| Resorcinol | 0 | 5 | 0 | 2.5 | 0 | 5 | 0 | 7.5 | 0 | 10 | 0 |
| Hexa[1] | 0 | 3.2 | 0 | 1.6 | 0 | 3.2 | 0 | 4.8 | 0 | 6.4 | 0 |
| Sisal fibre (untreated) | 0 | 20 | 20 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sisal fibre (acetylated) | 0 | 0 | 0 | 10 | 10 | 20 | 20 | 30 | 30 | 40 | 40 |
| TDQ[2] | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| CBS[3] | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| Sulphur | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |

1. Hexamethylenetetramine
2. 2:2:4 trimethyl-1,2-dihydroquinoline polymerised
3. N-Cyclohexyl-2-benzthiazylsulphenamide

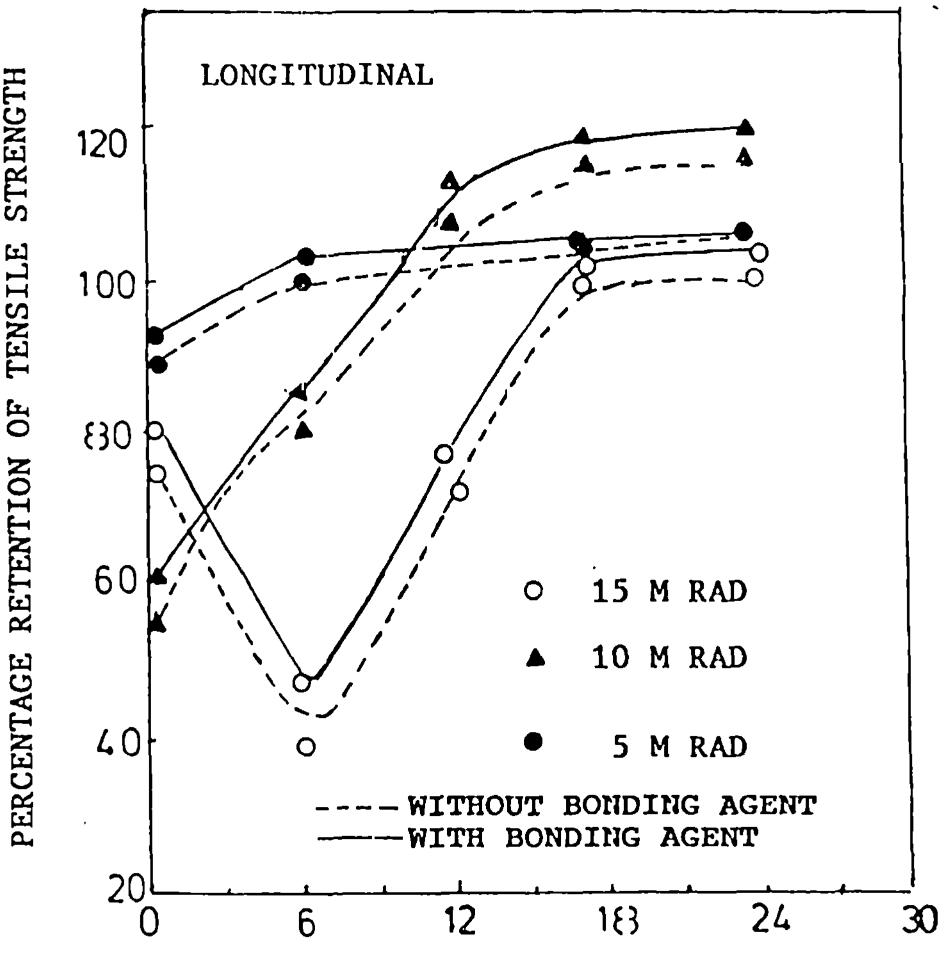

Figure VIII.1 Percentage retention of tensile strength with fibre loading at different radiation doses in the longitudinal direction.

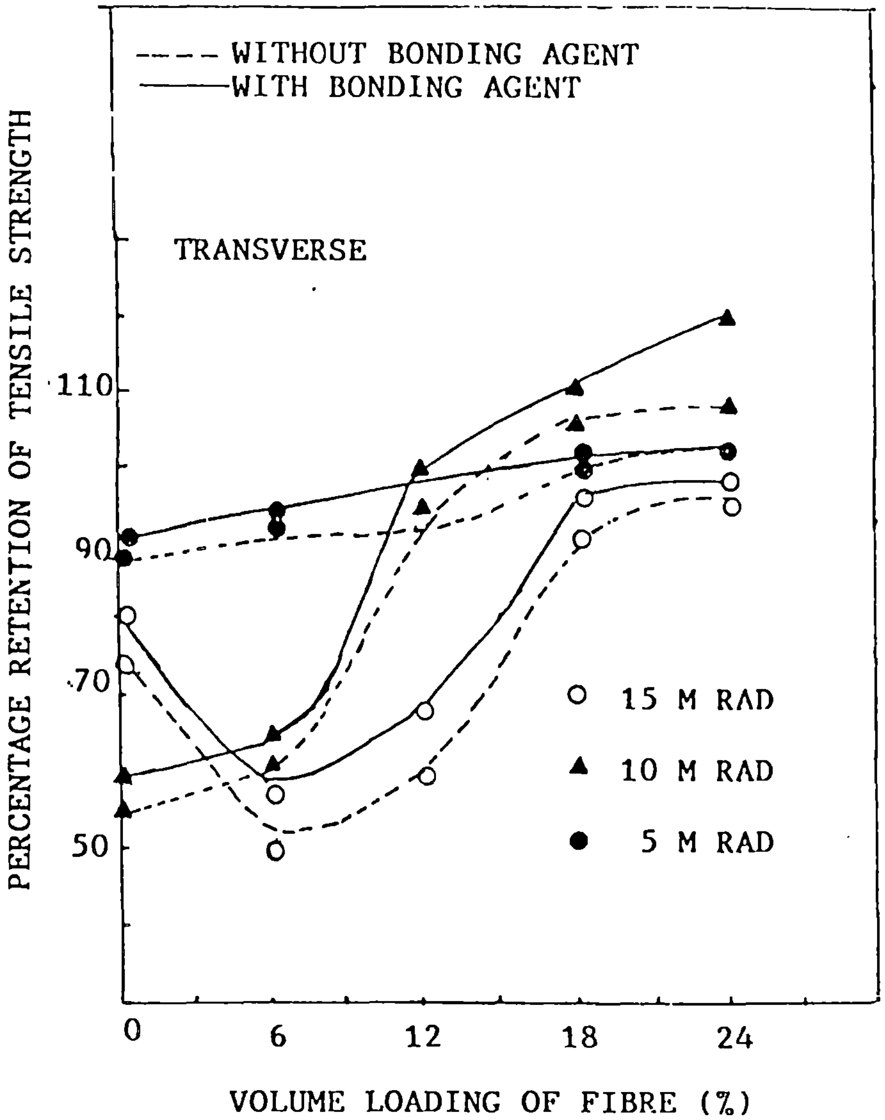

Figure VIII.2 Percentage retention of tensile strength with fibre loading at different radiation doses in the transverse direction.

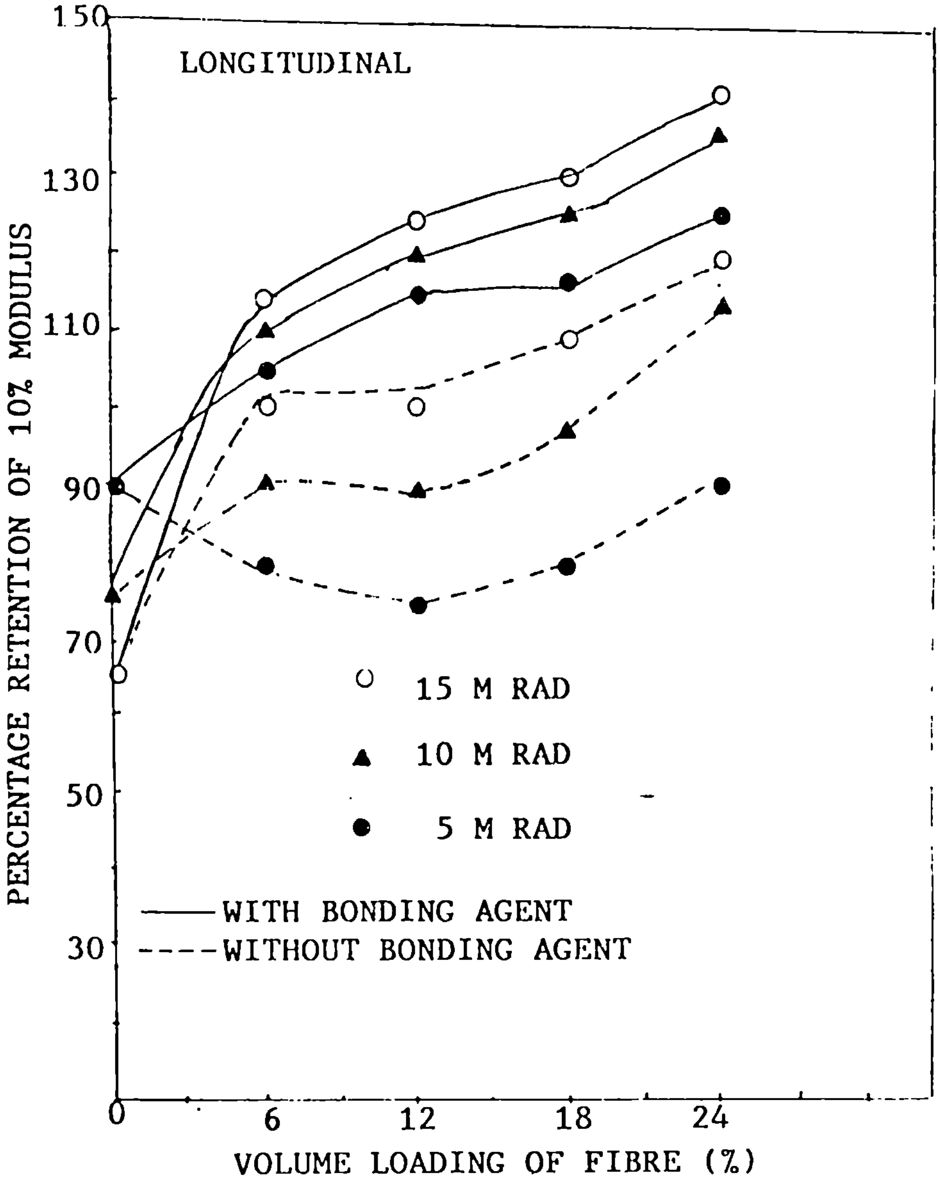

Figure VIII.3 Percentage retention of modulus for 10 per cent elongation with fibre loading at different radiation doses in the longitudinal direction.

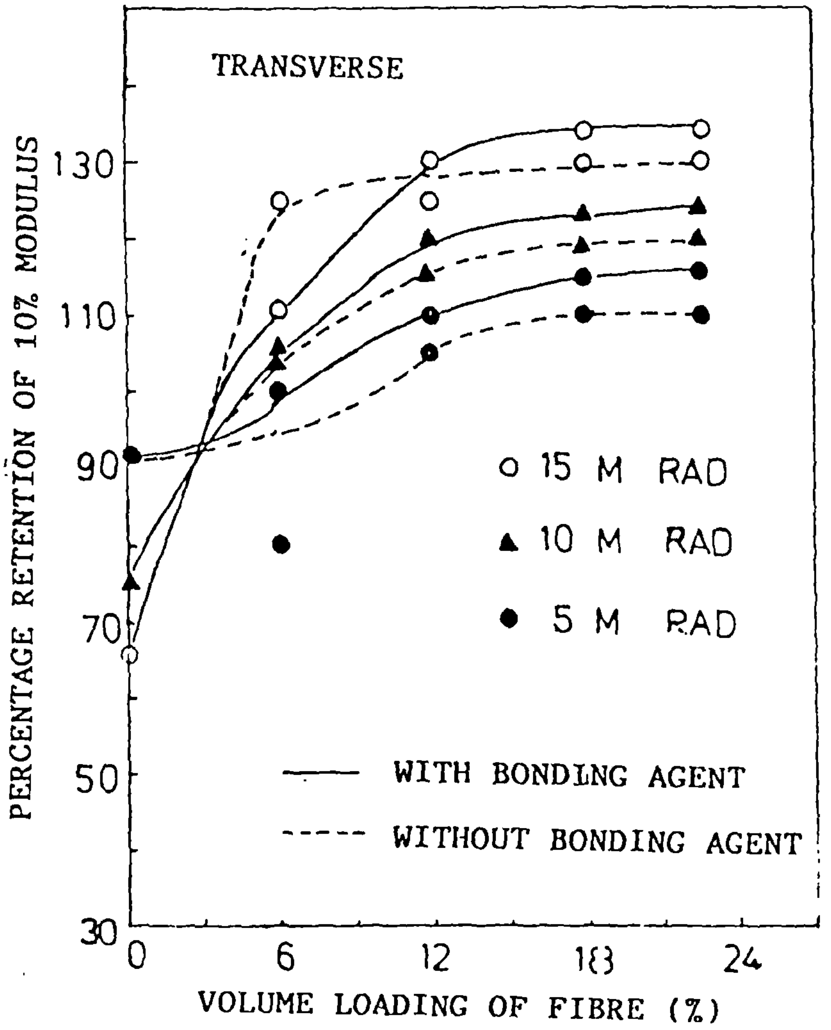

Figure VIII.4 Percentage retention of modulus for per cent elongation with fibre loading different radiation doses in t lon~~gitudin~~al direction.
Transverse

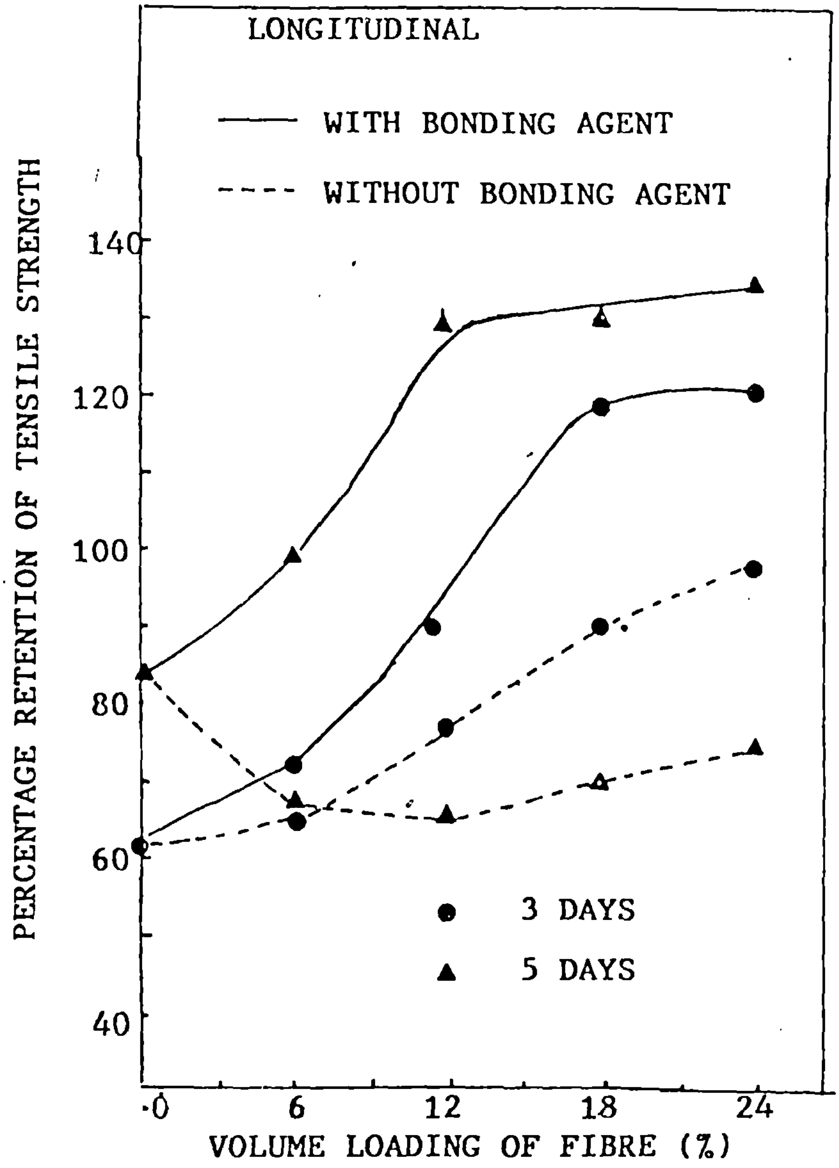

Figure VIII.5 Percentage retention of tensile strength with fibre loading after ageing the samples at 100°C for different periods in the longitudinal direction.

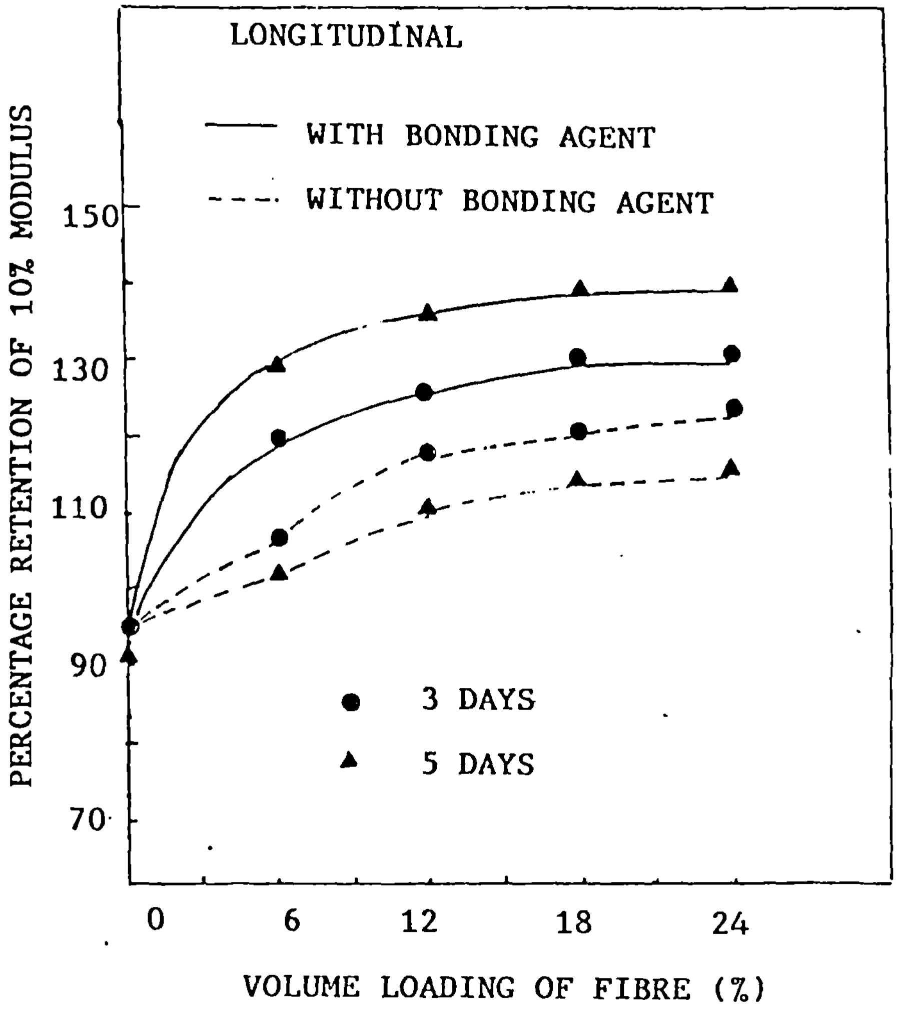

Figure VIII.6 Percentage retention of modulus for 10 per cent elongation with fibre loading after ageing the samples for different periods in the longitudinal direction.

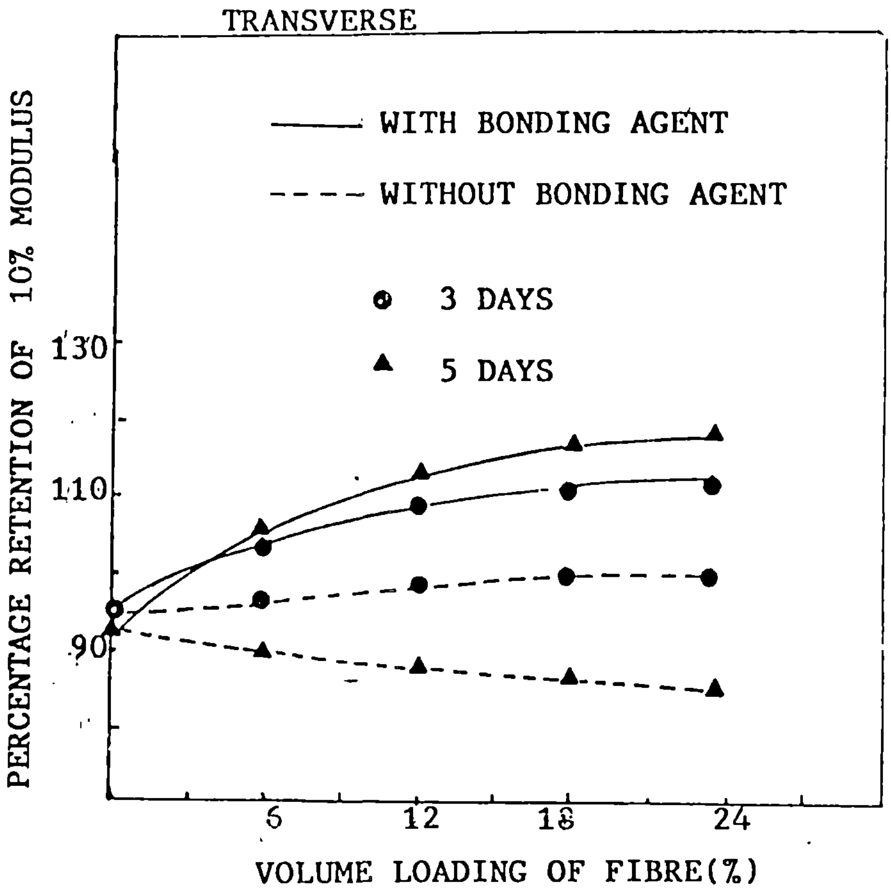

Figure VIII.7 Percentage retention of modulus for 10 per cent elongation with fibre loading after ageing the samples for different periods in the transverse direction.

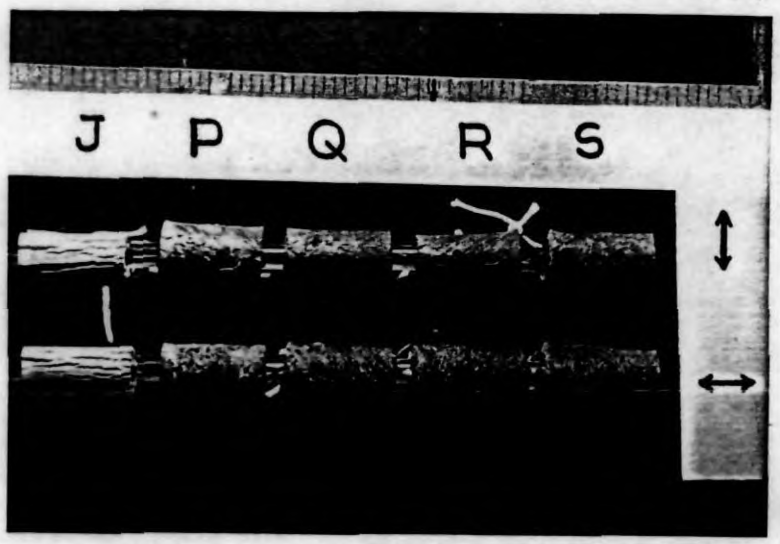

Figure VIII.8. Photograph of NR-sisal composites (with bonding agent) after exposure to ozone for 40 h.

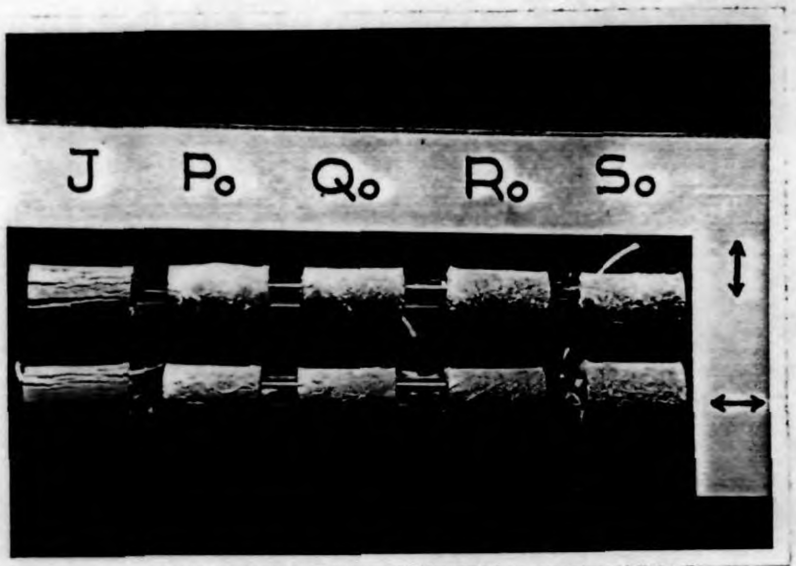

Figure VIII.9. Photograph of NR-sisal composites (without bonding agent) after exposure to ozone for 40 h.

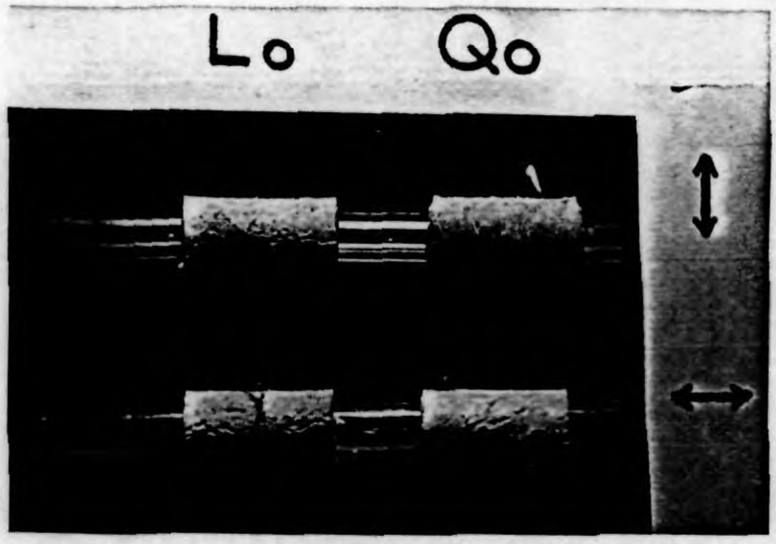

Figure VIII.10. Photograph of mixes $L_0$ & $Q_0$ after exposure to ozone for 40 h.

# SUMMARY AND CONCLUSIONS

## SUMMARY AND CONCLUSIONS

Short fibre reinforced rubber composites have gained wide importance due to their easy processing and low cost coupled with high strength. Reinforcement of elastomers with short fibres combines the rigidity of the fibre with the elasticity of the rubber. The resulting composites are used in many applications especially in hoses and V-belts. The use of short fibre presents the additional benefit that the fibre is incorporated as one of the ingredients of the recipe. The properties and performance of the composites depend mainly on (a) concentration and type of fibre (b) aspect ratio of the fibre (c) degree of dispersion of the fibre (d) adhesion of the fibre to the rubber matrix. Various fibres such as glass, rayon, nylon, asbestos , aramid and cellulose have been studied as reinforcement in both natural and synthetic rubber matrices. The composites reinforced with fibrous cellulosic fillers have gained a lot of interest in recent years.

Sisal is a natural fibre which is very cheap, easily available and renewable. The overall mechanical properties of sisal fibre is superior to other fibres. However, studies related to sisal fibre reinforced rubber composites are scanty. Therefore, a detailed investigation has been carried out on sisal fibre reinforced natural rubber composites with special reference to the effects of fibre length, fibre loading, chemical treatment of fibre and interface adhesion.

The thesis consists of eight chapters. The first chapter provides a review of the earlier work done on natural fibre reinforced polymer composites. The scope and objectives of the present study have been discussed. The advantages of short fibre reinforcement in elastomers and the different component materials used for composite preparation are also discussed in this chapter.

Chapter two gives a detailed account of the materials used and the experimental procedures adopted for the preparation of the composites and the test samples. This chapter also describes the moulding and testing procedures adopted in the investigations. The details of the equipments used are also described in this chapter.

The mechanical properties of short sisal fibre reinforced natural rubber composites are given in chapter three. The effects of acetylation, aspect ratio, concentration of fibre and bonding agent on the properties of short sisal fibre reinforced NR composites were evaluated. The results indicated that acetylation of sisal fibre improved the mechanical properties of the composites. Fibre aspect ratio in the range of 20-60 was found to be sufficient for optimum reinforcement. A minimum of 12% (v/v) loading of the acetylated fibre was found to be necessary for proper reinforcement. A two component system consisting of resorcinol and hexamethylenetetramine was found to be better than the normal tricomponent bonding system consisting of resorcinol, hexamethylenetetramine and hydrated silica. A mechanism has been proposed to illustrate the interface bonding between acetylated fibre and rubber molecule through the bondig resin.

In chapter four, the dynamic mechanical properties of natural rubber composites filled with untreated and acetylated short sisal fibres are described. By mixing short sisal fibres, the storage modulus (E') of natural rubber was improved. The effect of fibre-matrix interface adhesion on the viscoelastic properties of the composite has been evaluated and it is found that interface adhesion increases the dynamic modulus and mechanical loss. The effects of fibre orientation, fibre loading and temperature on the dynamic mechanical properties have also been investigated. With the increase in temperature, mechanical loss and storage modulus decreased sharply indicating a possible deterioration of the interfacial adhesion at higher temperatures. The storage modulus(E'), loss modulus (E") and loss factor (tan $\delta$ ) increased continuously with the increase of fibre loading.

Chapter five deals with the melt rheological behaviour of acetylated sisal fibre reinforced natural rubber composites. The results illustrate the effect of fibre concentration and shear stress/shear rate on melt viscosity and melt elasticity of the composites. Fibre undergoes severe breakdown during extrusion and as the shear rate increases, the breakdown also increases. The composites showed pseudoplastic behaviour which increased with fibre loading. Incorporation of acetylated sisal fibre into natural rubber results in an increase of its melt viscosity and a decrease of melt elasticity. The morphology of the extrudates was found to be dependant on the rate of shear.

In chapter six, the results of the studies on the stress relaxation behaviour of acetylated short sisal fibre reinforced natural rubber composites are presented. The effects of bonding agent, strain level, fibre loading, fibre orientation and temperature on the relaxation process have been studied in detail. The existence of a single relaxation pattern in the unfilled stock and a two stage relaxation mechanism for the fibre filled composite is observed. The relaxation process is influenced by the bonding agent which indicated that the process involved fibre-rubber interface. The rate of stress relaxation increased with fibre loading, whereas it decreased after ageing.

Chapter seven deals with the investigation on the solvent swelling of the composites filled with both untreated and acetylated fibre. In this study composites were subjected to swelling in a series of normal alkanes such as pentane, hexane, heptane and octane. The restriction for swelling of elastomer exerted by sisal fibre as well as the anisotropy of the swelling of the composites have been confirmed by this study. The results showed that increase of fibre content brings about a greater restriction of swelling. It is also observed that the use of bonding agent reduced swelling considerably. One important observation of this study is the swelling in the thickness direction. The control sample without fibre also showed greater swelling in the thickness direction but the difference becomes even more pronounced when the fibres are added. As the fibre loading increase the amount of liquid taken by the specimen at equilibrium swelling decreases. The chemically modified fibre incorporated composites absorbed less amount of solvent compared to composites containing untreated fibre at the same fibre loading.

The eighth chapter illustrates the degradation behaviour of short sisal fibre reinforced natural rubber composites containing acetylated and untreated fibre. The effects of fibre loading, bonding agent and acetylation of fibre on thermal ageing, $\gamma$-radiation and ozone resistance of the composites have been evaluated. It is observed that composites containing bonding agent have excellent ageing resistance. The data show that composites with higher fibre loading show better thermal ageing and $\gamma$ - radiation resistance. Fibre orientation and acetylation of fibre were also found to influence the degradation process.

# List of publications from this work

1. Studies on natural rubber-short sisal fibre composites.

   S. Varghese, B. Kuriakose, S. Thomas and A.T.Koshy, Indian J. Nat. Rubb. Res., 4(1), 55 (1991).

2. Rheological behaviour of short sisal fibre reinforced natural rubber composites.

   S. Varghese, B. Kuriakose, S. Thomas, C.K. Premaletha and A.T. Koshy, Plast. Rubb. Comp. Proc. Appl., (In press).

3. Dynamic mechanical properties of short sisal fibre reinforced natural rubber composites.

   S. Varghese, B. Kuriakose, S. Thomas and A.T. Koshy, Indian J. Nat. Rubb. Res., (In press).

4. Stress relaxation in short sisal fibre reinforced natural rubber composites.

   S. Varghese, B. Kuriakose and S. Thomas, J. Appl. Polym. Sci., (communicated)

5. Effect of adhesion on the equilibrium swelling of short sisal fibre reinforced natural rubber composites.

   S. Varghese, B. Kuriakose and S. Thomas, Rubber Chem. Technol., (communicated).

6. Studies on the effect of fibre loading and bonding agent on the degradation of short sisal fibre reinforced natural rubber composites.

   S. Varghese, B. Kuriakose and S. Thomas, J. Appl. Polym. Sci., (communicated).

7. Scanning electron microscopy studies on the tensile, tear and abrasion failure of short sisal fibre reinforced natural rubber composites.

   S. Varghese, B. Kuriakose and S. Thomas, J. Mater. Sci., (communicated).

## Papers presented in international conferences from this work

1. Dynamic mechanical properties of short sisal fibre reinforced natural rubber composites

   S. Varghese, B. Kuriakose, S. Thomas and A.T. Koshy

   Proceedings of the International natural rubber conference held at Bangalore Feb.5-8 (1992).

2. Stress relaxation in short sisal fibre reinforced natural rubber composites.

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   Proceedings of the Polymer Processing Society, eighth annual meeting (PPS-8) held in New Delhi, March 24-27, (1992).

3. Rheological behaviour of short sisal fibre reinforced natural rubber composites.

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