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.

1.1 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 10^4 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.

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 used
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 i.e., 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'**

\[
\begin{align*}
\text{OH} & \quad \text{CH}_2 \quad \text{CH}_2 \text{OH} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

\[
+ \quad \begin{align*}
\text{H} & \quad \text{C} \quad \text{R} \\
\text{R'} & \quad \text{R''}
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{C} \quad \text{R} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

B. **CHROMAN FORMATION**

\[
\begin{align*}
\text{OH} & \quad \text{CH}_2 \quad \text{CH}_2 \text{OH} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

\[
+ \quad \begin{align*}
\text{H} & \quad \text{C} \quad \text{R} \\
\text{R'} & \quad \text{R''}
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \quad \text{CH}_2 \quad \text{C} \quad \text{R} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

Possible Reactions Between
Resorcinol Resin and Unsaturated Rubbers
A. WITH CELLULOSICS

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 1.1.

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 up to 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].

1.11.2 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.

1.11.2.1 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 trigonometric 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,

\[
\frac{1}{E_{\phi}} = \frac{\sin^2 \phi}{E_T} + \frac{\cos^2 \phi}{E_L} \quad \text{..... (I.1)}
\]
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 Brabender 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($L_c$),
where, \( d \) = fibre diameter, \( \sigma_{fu} \) = ultimate fibre strength, \( \gamma \) = 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 particularly 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 mixture is applicable and is given by

\[ \sigma_{cu} = \sigma_f v_f + \sigma_m v_m \]  

\[ \text{...... (1.3)} \]

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-cry stallizing 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°, giving the lowest value at 90°.

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

\[ \sigma_{cu} = \sigma_{fu} V_f F (L_c/\bar{L}) C_o + \sigma_m (1 - V_f) \ldots \ldots (I.4) \]

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

\( \bar{L} \) = length of the fibre (average)

Dzyura[110] proposed that the strength of a rubber-fibre composite may be described by the additivity rule provided that adhesion and orientation coefficients 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

\[ \sigma_C = \sigma_f V_f (1-Li/2L) K + \sigma_m V_m \ldots \ldots (I.5) \]

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

\[ L_i = \frac{\sigma_f \cdot d}{2f} \] ...... (I.6)

where $d = \text{diameter of the fibre and } f = \text{the minimum shear stress on boundary.}$ 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 stretching 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 exists 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 $\sigma_m'$.

### 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 up to 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 \left(1 + 0.67 f C + 1.62 f^2 c^2 \right) \ldots \ldots \text{(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'Connell [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].

1.21.2. 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 chunxing 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
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 their effect on 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, γ- 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.


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.
References


91. Z. Rigbi, and N. Sabatov, Polymer, 15, 373 (1974).


<table>
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<th>Research group</th>
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