STUDIES ON SHORT NYLON FIBER-RECLAIMED RUBBER/ELASTOMER COMPOSITES

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To
my Mom
who taught me
to love all that is good.
I know she is with me
always,
with her deep understanding
and endless compassion.

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CERTIFICATE

This is to Certify that the thesis entitled ***"Studies on short nylon fiber - reclaimed rubber/elastomer composites"*** is an authentic report of the original work carried out by **Miss Sreeja T.D.** under my supervision and guidance in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin - 22. No part of the work reported in this thesis has been presented for any other degree of any other institution.

Dr. Sunil K. Narayanankutty
(Supervising Teacher)

DECLARATION

I hereby declare that the thesis entitled ***"Studies on short nylon fiber – reclaimed rubber/elastomer composites"*** is the original work carried out by me under the guidance of **Dr. Sunil K. Narayanankutty,** Senior Lecturer, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin, and no part of this thesis has been presented for any other degree of any other institution

19. 5. 2001 **SREEJA T.D.**

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PREFACE

The thesis is about short nylon fiber-reclaimed rubber/elastomer composites. In this thesis an attempt has been done to partially replace virgin rubbers by reclaimed rubber, a recycled form of used rubbers. The blends are then reinforced by using nylon short fibers. Since the properties of short fiber reinforced composites are highly influenced by fiber-matrix adhesion, an attempt has been made to improve this by using a urethane bonding agent based on MDI and PEG. The composites are evaluated for their cure characteristics and mechanical properties with respect to blend ratio, fiber loading, fiber orientation and bonding agent.

The results of investigation are presented separately in different chapters as follows.

Chapter I presents a review of the literature in this field and the scope of the present investigation.

The materials used and the experimental techniques employed for the study are described in Chapter II.

In Chapter III-VIII C the results and discussion are presented.

Chapter III deals with the study of NR/reclaimed rubber blend.

Chapter IV is divided into 3 sections. Section IV (A) covers a study on the effect of fiber loading in NR compound. A detailed study of NR/reclaim blend with different amount of short nylon fiber is described in section IV (B). In section IV (C) the cure characteristics and mechanical properties of NR/WTR-short nylon fiber composites containing a urethane based bonding agent are discussed.

Chapter V is a systematic study of NBR/WTR blends.

Chapter VI (A) is an investigation on NBR/short nylon fiber composites. In Chapter VI (B) study on the reinforcement of NBR/WTR blend using short nylon fiber is given. The urethane based bonding system is used in NBR/WTR-short nylon fiber composites and the results are given in Chapter VI (C).

Chapter VII covers the optimization of SBR/WTR blends.

SBR-short nylon fiber composites are discussed in Chapter VIII (A). The effect of fiber loading on SBR/WTR blend is described in Chapter VIII (B). In Chapter VIII (C) SBR/WTR-short nylon fiber composites with a bonding agent based on MDI/PEG resin are discussed.

Conclusions of the present investigation are described in Chapter IX.

ABSTRACT

The thesis deals with the development of short nylon fiber-reclaimed rubber/elastomer composites. Three rubbers viz, natural rubber, acrylonitrile butadiene rubber and styrene butadiene rubber were selected and were partially replaced with reclaimed rubber. The blend ratio was optimized with respect to cure characteristics and mechanical properties. Reclaimed rubber replaced 40 parts of NR and SBR and 20 parts of NBR without much affecting the properties. These blends were then reinforced with short nylon fibers. The mechanical properties of the composites were studied in detail. In all the cases the tensile strength, tear strength and the abrasion resistance increased with increase in fiber content. In the case of NR/reclaimed rubber blends, the tensile strength-fiber-loading relationship was non-linear where as in the case of NBR/reclaimed rubber blends and SBR/reclaimed rubber blends the tensile strength-fiber loading relationship was linear. All the composites showed anisotropy in mechanical properties. The effect of bonding system on the composite properties was also studied with respect to cure characteristics and mechanical properties. For this, a 20 phr fiber loaded reclaimed rubber/elastomer composites were selected and the effect of MDI/PEG resin system was studied. The resin used was 5 phr and the resin ratios used were 0.67:1, 1:1, 1.5:1 and 2:1. The bonding system improved the tensile strength, tear strength and abrasion resistance. The best results are with SBR/reclaimed rubber-short nylon fiber composites. The optimized resin ratio was 1:1 MDI/PEG for all the composites.

LIST OF ABBREVIATIONS

ASTM	American society for testing and Materials
CR	Chloroprene rubber
E_L	Compression modulus in the longitudinal direction
Em	Modulus of the matrix
EPDM	Ethylene propylene diene monomer elastomer
E_T	Compression modulus in the Transverse direction
HDPE	High density polyethylene
HNBR	Hydrogenated nitrile rubber
HRH	Hexamethylenetetramine - resorcinol - hydrated silica
HS	1,2 dihydro 2,2,4-trimethyl quinoline
L	Longitudinal
L/D	Length to diameter ratio
LDPE	Low density polyethylene
MBTS	2,2'-benzothiazyl disulfide
MDI	4,4'-diphenyl methane diisocyanate
μm	Micrometer
-NCO	Isocyanate
N.m	Newton meter
NR	Natural rubber
NBR	Nitrile rubber
PE	Polyethylene
PEG	Polyethylene glycol
PET	Polyethylene terephthalate
PU	Polyurethane
RFL	Resorcinol formaldehyde latex
RH	Resorcinol hexamethylenetetramine
SBR	Styrene butadiene rubber
T	Transverse

Tan δ	Loss tangent
Tg	Glass transition temperature
Tmax – Tmin	Difference between maximum and minimum torque
TPU	Thermoplastic polyurethane
TPNR	Thermoplastic natural rubber
UTM	Universal testing machine
WRP	Waste rubber powder
WTR	Whole tyre reclaim
XNBR	Carboxylated nitrile rubber

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CHAPTER I.
INTRODUCTION

With the advent of polymeric age in the latter part of 20th century polymers and their composites have gradually replaced traditional engineering materials such as wood, metal, glass and even ceramics in many applications because of their high strength to weight ratio, high design flexibility, ease of fabrication and relatively low cost. In addition to weight savings, composites also offer many other advantages such as resistance to fatigue and corrosion, desirable thermal expansion characteristics, thermal conductivity and damping. Because the properties of the composites can be tailor-made to meet a broad spectrum of design characteristics they have found a wide variety of applications in such area as aerospace, automotive, electronics, industrial etc.

Composites are made from two or more distinct materials that when combined are better (stronger, tougher and /or more durable) than each would be separately. The mixing of the phases is not on the atomic scale. The properties of the composites are some sort of combination of the properties of its constituents. The composite consists of one or more discontinuous phases embedded in a continuous phase. The discontinuous phase is usually harder and stronger than the continuous phase and is called reinforcement or reinforcing material, where as the continuous phase is termed as the matrix. The properties of the composite are strongly influenced by the properties of their constituent materials, their distribution and the interaction among them. To provide reinforcement the discontinuous phase must be present in a substantial volume fraction (at least about 10%).[1]

1.1. Types of Composite Materials

The first distinction that can be made is between natural and artificial composite material. Examples of natural composites are human bone and wood.

Based on the form of structural constituents there are five general class of composites.[2]

1. Fiber composites composed of fibers with or without a matrix.
2. Flake composites, composed of flat flakes with or without a matrix
3. Particulate composites, composed of particles with or without a matrix
4. Filled (or skeletal) composites composed of continuous skeletal matrix filled by a second material.
5. Laminar composites composed of layer or laminar constituents.

Of all composite materials, fiber composites have evoked the most interest among engineers concerned with structural applications. Initially, most of the work was done with strong, stiff fibers of solid, circular cross section in a much weaker, more flexible matrix. The most efficient method is to combine a fibrous material of high tensile strength and high modulus of elasticity with a light weight bulk material of lower strength and lower modulus of elasticity. In nature, the most common example of this reinforcing principle is the bamboo pole. Among synthetic materials practically every type (plastic, rubber, ceramics and metal) is now being reinforced with fibers.

The important factors that contribute to the engineering performance of a fiber-matrix composite are orientation, length, shape and composition of the fiber, mechanical properties of the matrix and the integrity of the bond between fiber and matrix. The orientation of fibers in the matrix has a strong bearing on the properties of the composite. The mechanical properties in any direction are proportional to the amount of fiber by volume oriented in that direction.

The orientation of fibers in a matrix can be accomplished by using either continuous or short fibers. Although continuous fibers are more efficiently oriented they are not necessarily better. Continuous fibers are more easy to handle but more limited in design properties than short fibers. Cross sectional shape of the fibers is also an important parameter. Practically all fibers presently being used have circular cross section whether they are continuous or short. However, hexagonal, rectangular, polygonal, annular and irregular cross section appear to promise improved mechanical properties.

Both organic and inorganic fibers are available as reinforcing materials. The organic fibers such as cellulose, polypropylene and graphite fibers can be characterized, in general, as light weight, flexible, elastic and heat sensitive. Inorganic fibers such as glass, tungsten and ceramics can be generally described as very high in strength, heat resistance, rigidity and low in energy absorption and fatigue resistance.

The other major constituent in fiber composites, the matrix serves two very important functions. (1) It holds the fibrous phase in place, (2) under an applied force it deforms and distribute the stress to the high modulus fibrous constituent. The interfacial bond between fiber and matrix is an important factor influencing the mechanical properties and performance of composites. The interface is responsible for transmitting load from the matrix to the fibers, which contribute to the greater portion of the composite strength.

1.2. Short Fiber Composites

By using short fibers as reinforcement mixed into the rubber, one can impart drastic changes to the mechanical, thermal and viscoelastic properties of compounded rubber. These changes – even at low fiber concentrations – go far beyond the levels obtainable with the rubber industry's traditional reinforcement, the carbon black.

Rubber finds utility in many dynamic applications to which it is ideally suited by its low bending and torsional modulus and high resilience. The reinforcement of rubber phase by short fibers would necessarily compromise these attributes of the matrix. Too short fibers are less effective in reinforcing the low modulus materials than rigid ones. The extent to which a discontinuous fiber can approach the performance of a continuous filament or cord, depends critically upon its modulus ratio relative to that of the matrix. The continuous phase, matrix, must serve not only as a protective encapsulent or binder but also as the stress transfer medium between the applied force and the discontinuous reinforcing fibers.

Though the short fiber reinforced rubber combines the characteristics of flexible matrix and the stiffness and/or tenacity of the reinforcing fiber, short fiber reinforcement is insufficient to replace continuous cord reinforcement. However, short fibers can be incorporated directly into most of the rubbers along with other additives using standard rubber mixing equipment. The resulting product can be processed in standard rubber processing steps, economic high volume outputs are feasible. This is a significant advantage over the slow process required for the incorporation and placing of continuous fibers, cords and fabrics. Thus penalty of sacrificing noticable reinforcing strength with discontinuous fiber is counterbalanced by processing economics. In view of processing requirement it is almost mandatory to use as low a volume content of short fibers as possible and obtain improved properties. High volume content makes the compound boardy and difficult to handle in many instances. Nevertheless the improvement in mechanical properties from high volume content is important in many applications. The success of short fiber reinforcement depends on a few key requirements,[3-5] these are in descending order of importance:

- Good and uniform dispersion
- Proper fiber orientation for tension
- Appropriate placement of the fiber reinforcement
- Good fiber matrix interaction: high surface area and/or adhesion
- Proper fiber choice for thermal/chemical resistance

- Proper matrix choice for thermal/chemical resistance

Typical advantages associated with short fibers as fillers in polymer matrices include design flexibility, high low-strain modulus, anisotropy in technical properties and stiffness, good damping, ease in processing and production economy. Fibers may also improve thermochemical properties of polymer matrices to suit specific areas of applications and to reduce the cost of the fabricated articles. Moreover short fibers provide high green strength, high dimensional stability during fabrication, improved creep resistance, good ageing resistance, improved tear and impact strength and anisotropy in mechanical properties. The manufacture of complex shaped engineering articles, which is impractical from elastomers reinforced with continuous fiber can easily be accomplished with short fibers.

Foldi[6] has reported the processing advantages obtained with short fiber-rubber composites. In a review, Kun[7] presented effect of type of fiber, fiber pretreatment, compounding and processing on product performance properties. Zuev[8] studied the mechanical properties of polymeric fiber filled rubber composites and ways of effective utilization of mechanical properties of fibers in fiber filled rubber composites and compared with those of rubber compound in the absence of fibers. Advances in short fiber pre-treatment, interfacial adhesion and development of short fiber-rubber composite products were reviewed by Zhou et al.[9] Fiber reinforced plastic and rubber composite electrical insulators have been manufactured by Kadowaki et al.[10] The insulators useful as wire carriers comprise of fiber reinforced plastic cores, mono-pleat like rubber coverings attached on the cores and localized in between the rings. Campbell[11] reviewed short fiber reinforcement of rubber.

Short fibers find application in essentially all conventional rubber compounds, examples are NR, EPDM, SBR, neoprene and nitrile rubber. Various speciality elastomers like silicone rubber, fluoro elastomer, ethylene vinyl acetate, thermoplastic elastomer and polyurethane have also been found utility as composite matrices.[12 - 16]

Both natural and synthetic fibers are used as short fiber reinforcement. The generally available synthetic fibers are polyester, aramid, nylon, rayon and acrylic. It is possible to improve the properties of composites by using high performance fibers such as carbon, glass or aramid. In the case of soft rubbery composites cellulose fiber has been found to give better reinforcement than glass or carbon fibers.[17] This may be probably due to the fact that the flexibility of cellulose fibers results in less breakage during processing than that happens with the brittle glass or carbon fiber. A review of various types of short fibers highlighting their properties and shortcomings as reinforcements for polymers is given by Milewski.[18] Various natural materials which are potential reinforcements for rubber compounds are jute,[19] bagasse[20,21] and pineapple leaf fiber.[22] The use of asbestos, flax, glass and cotton fibers to reinforce various types of rubber is reviewed by Zuev et al.[23] Manceau[24] compared cellulose, glass and nylon fibers as reinforcement for SBR rubber. The use of a polyolefin based fiber as reinforcement in SBR has also been reported.[25] Boustany and Coran[26] showed improved performance of hybrid composites comprising cellulose in conjunction with a chopped textile fiber. The in situ generation of plastic reinforcing fibers within an elastomeric matrix has been disclosed in literature.[27,28] This method has been used by Coran and Patel[29] to reinforce chlorinated polyethylene with nylon fibrils.

Derringer[30] incorporated different short fibers such as rayon, nylon and glass into NR matrix to improve young's modulus of vulcanizates. Connor[31] studied the processing and properties of short fiber-elastomer composites with a variety of reinforcing fibers and concluded that composite with any desired property could be obtained by manipulating factors such as fiber type, fiber content, aspect ratio, orientation, dispersion, fiber-matrix adhesion, processing methods and properties of elastomeric matrix. Investigations have been made on the feasibility of using rubber/fiber compositions obtained from various types of waste from rubberized material and cord in the production of V-belts and tire tread compounds.[32, 33]

Goodloe et al[34,35] were the first to use short cellulose fibers in elastomer matrix and found that the tendency of the rubber to shrink was reduced in presence of short fibers. Short jute fiber reinforced NR composites have been studied by Murty et al.[19,36] Investigations have also been made on short jute fiber reinforcement of carboxylated nitrile rubber by Chakraborty et al.[37] Mukherjea[38] studied the role of interface in fiber reinforced polymer composites with special reference to natural rubber. Pre-treatment of jute fiber with polyesteramide polyols and silane coupling agent for improved dry and wet strength of jute fiber-polyester composites has been discussed.

Processing characteristics, anisotropic swelling and mechanical properties of short jute and short glass fiber reinforced SBR composites have been studied both in the presence and absence of carbon black by Murty et al.[39] It was found that jute fibers offered good reinforcement to SBR as compared to glass fiber. Bhagwan et al[40] studied the stress relaxation of short jute fiber NBR composites.

Short silk fiber reinforced CR and NR have been described by Setua et al.[41,42] Akthar[43] studied short fiber reinforcement of thermoplastic blends of NR with HDPE and LDPE. Coconut fiber reinforced rubber composites have been reported by Arumugam et al.[44] Effect of chemical treatment, aspect ratio, concentration of fiber and type of bonding system on the properties of NR-short sisal fiber composites were evaluated by Varghese et al.[45] Dynamic mechanical properties of NR reinforced with untreated and chemically treated short sisal fibers were studied and the effect of fiber-matrix interfacial adhesion on viscoelastic properties were evaluated.[46] Natural rubber-coir fiber composite was studied by Geethamma et al.[47, 48]

The advantage and consequences of reinforcing rubber compounds with Twaron, p-phenylene terephthalamide, short fiber and with p-aramid adhesive activated chopped fibers have been described.[49] The effect of short aramid fiber reinforcement on CR rubber was studied by Park et al.[50] Short aramid fiber reinforced rubber composites were prepared and the effect of fiber concentration, surface treatment and rubber type on mechanical properties of vulcanizates were detremined.[51] It was found that the optimum fiber concentration for reinforcement of butadiene/NR blend was ~10 weight percentage. The effect of surface treated short aramid fiber on CR/NBR blend was examined by Kem et al[52] and concluded that the anisotropy in tensile modulus and strength was pronounced as the fiber loading was increased. Effect of fiber loading, orientation, abrasion load and thermal ageing on the abrasion behaviour of NR reinforced with aramid short fibers were reported by Zheng et al.[53]

Mechanical properties of thermoplastic polyurethane elastomer composites reinforced with short aromatic polyamide and carbon fibers were studied by Correa et al.[54] Pervorsek et al[55] prepared short polyamide reinforced rubber compositions. Short polyester fiber-NR composites were studied by Senapati et al[56] and the effect of fiber concentration, orientation and L/D ratio on mechanical properties were examined. Ibarra et al [57] investigated the effect of different types of elastomeric matrices (NR, SBR, CR and nitrile rubber) and several levels of short polyester fiber on mechanical properties of uncured and cured compounds and on the swelling behaviour of composites in hydrocarbon solvent and concluded that the addition of fiber markedly reduced maximum swelling of the composites. Kutty et al[58] studied the reinforcement of millable PU with short Kevlar fiber.

Yoshiki[59] reviewed characteristics of short fiber reinforced NBR composites. Stress induced crystallization and dynamic properties of NR reinforced with short syndiotactic 1,2 polybutadiene fibers and with very fine nylon 6 fibers were discussed in a review.[60] Ashida[61] presented a review on the type of short fibers, adhesives used for short fibers, the preparation and performance properties of rubber-short fiber composites.

Effect of processing parameters on the mechanical properties of short Kevlar aramid fiber-thermoplastic PU composite was reported by Kutty et al.[62] They reported that the strength, storage and loss moduli of composites increased while tan δ_{max} was reduced progressively with fiber loading. For short nylon fiber SBR composites the storage modulus and loss modulus increased with fiber content[63] and there appeared a relaxation peak in the tan δ spectra at 120 ^{0}C when the interface between SBR and nylon short fibers had good adhesion. Roy et al[64] reported the mechanical and dynamic mechanical properties of short carbon fiber filled styrene-isoprene-styrene block thermoplastic elastomer composites and showed that tan δ values at the Tg region decreased on filler incorporation, but at room temperature, the values increased with filler loading.

Incorporation of short poly (p-phenylene terephthalamide) in butyl rubber, NR, neoprene rubber and EPDM rubber compounds resulted in improved tensile strength, modulus, 'on-end' abrasion, thermal stability and in 30-60% lower energy loss after shock loads compared to reference compounds.[65] The surface characteristics and the length distribution of waste short fibers from reclaimed rubber were investigated by Zhang et al.[66] The mechanical properties of waste short fiber-rubber composites and the influence of surface treatment of waste short fiber have also been investigated.

Acrylic fiber reinforced rubber has been prepared by Moyama et al.[67] Mechanical properties of composite materials consisting of short carbon fiber and thermoplastic elastomer have been studied by Ibarra et al[68] and concluded that oxidative treatment of carbon fibers exerted a beneficial influence on the properties of material reinforced with such fibers. Short fiber containing pneumatic tyres having good balance of abrasion and ice/snow–skid resistance were prepared by Midorikawa et al.[69] Development of sealing materials of jute fiber reinforced cork and butadiene acrylonitrile rubber was described by Xie et al.[70] Kikuchi[71] used nylon short fibers with 0.2-0.3 μm diameter and 100-200 μm length to reinforce NR and found that tyres made from it showed reduced weight and rolling resistance. Spherical vibrational dampers having low expansion at high temperature and good dimensional stability and shape maintenance were prepared by mixing rubbers with short fibers in their length direction.[72]

1.3. Reclaimed Rubber and Its Elastomer Blends

Recycling of the used materials has been given wider attention by the environmentalists. The used rubber products and worn out tyres can also be processed and recycled to prepare reclaimed rubber which can be reused without any damage to the environment. Reclaimed rubber is the type of degraded rubber with unique properties. Reclaiming process imparts the necessary degree of plasticity to vulcanized rubber and there by enabling it to be blended with natural or synthetic rubber.[73] Reclaimed rubber, unlike virgin rubber, is used in compounds to reduce the compound cost and also to improve the processing characteristics. It is cheaper than virgin rubber. It mixes faster than virgin rubber because all the fillers of the original product are already incorporated and the power consumed for mixing is less. The three dimensional nature of the rubber fragments and the reduced nerve of the reclaim imparts rate and gauge stability to the calendered and extruded stocks. But the mechanical properties of reclaimed rubber are very inferior to those of the virgin rubber due to the degradation of rubber during reclaiming. Hence it is added in small percentage to virgin rubbers.

Grant Crane et al[74] reported that scrap rubber vulcanizates can be depolymerized to give a product known as 'Depolymerized Scrap Rubber (DSR) which can be used as a rubber compounding ingredient and to extend fuel oil to yield a fuel which could be utilized in conventional boilers. Burgogne et al[75] reported that mechanically ground scrap rubber having a broad spectrum of particle size could act as a cheap filler having approximately the same effect on the properties as soft kaolin clay. According to Bleyie[76] as particle size of ground rubber decreases, mixing behaviour and mechanical properties of vulcanizates are improved. Swor et al[73] showed that the utilization of dry rubber reclaim in SBR improved the cure rate of SBR vulcanizates. Kazarnowicz et al[77] found that blends of reclaim or ground vulcanized waste with NR had processing as well as economic advantages. Accepta et al[78] showed that reclaimed rubber in the form of cryoground rubber could be bonded in a two-roll mill and compounded with common rubber ingredients. They developed a process to improve the quality of scrap rubber powder recovered from old tyres.[79] Phadke et al[80] reported that physical properties of reclaimed rubber vulcanizates were inferior to those of the control vulcanizate. The poor physical properties and processing characteristics could be improved by blending with fresh rubber. However high proportion of reclaimed rubber increased the stiffness and caused brittle failure. The addition of cryoground rubber caused changes in curing characteristics and showed detrimental effects on most of the vulcanizate properties.[81] Higher dose of curatives and addition of reinforcing carbon black made up the losses in physical properties. Reclaimed rubber could partially replace butyl rubber in the manufacture of inner tubes for tyres.[82] The presence of reclaimed rubber increased the thermal permanent strain and hardness. Magryta[83] studied the processing and mechanical properties of rubber vulcanizates containing reclaimed rubber and concluded that the addition of reclaimed rubber resulted in some deterioration of mechanical properties but improved thermo-oxidative stability and decreased price of vulcanizate. Waste rubber powder (WRP)/SBR/black compound has been studied by Zhao et al.[84] Addition of WRP ≤ 20 phr with a grain size ≤ 160 μm did not significantly affect the compound properties. The presence of waste rubber powder in SBR resulted in improvement in its tear strength and elongation at break.[85] Modification of the rubber powder improved the mechanical properties of rubber compounds. Decrease in scorch time and maximum rheometer torque were observed when ground vulcanizates were added to SBR compounds.[86] It has been reported that 20% of reclaimed rubber could be used in place of NR in the blend without greatly affecting mechanical properties of the products.[87] The use of reclaimed rubber in powder form gave rubber blends with better mechanical properties. The presence of NR latex modifiers improved mechanical properties and thermal stability of NR/reclaimed rubber blends. Cure and physical properties of EPDM vulcanizates containing ground rubber were studied with respect to particle size and amount of ground rubber by Seo et al.[88] The mechanical properties of rubber blends containing post consumer recycled polymer and NR, bromobutyl rubber, isobutylene rubber or EPR were examined by Theodore et al.[89] Gibala et al[90] studied the effect of black filled SBR ground vulcanizates on the tensile and trouser tear strength of rubber compounds. They reported that the compound exhibited reduced tensile strength and enhanced tear strength.

1.4. Nylon Fiber

Nylon was the first synthetic fiber to be commercialized (1939). It is a polyamide fiber derived from a diamine and a dicarboxylic acid. Because a variety of diamines and dicarboxylic acids can be produced there are very large number of polyamide materials available to prepare nylon fibers. The most common versions are nylon 6,6 and nylon 6. Nylon 6,6 which is widely used as fiber is made from adipic acid and hexamethylene diamine. The commercial production of nylon 6 begins with caprolactam. Fibers are produced commercially in various parts of the world but nylon 6,6 has been preferred in non-American markets, nylon 6 is more popular in Europe and elsewhere. The polyamide is melt spun and drawn after cooling to give the desired properties for each intended use. The fiber has outstanding durability and excellent physical properties. The features are:

- Exceptional strength
- Elasticity
- Abrasion resistance

- Lusture
- Washability
- Resistance to damage from oil and many chemicals
- Resilience
- Colourability
- 4-4.5% moisture regain
- Smooth, soft, long lasting fibers from filament yarn
- Light weight and warm fabrics from spun yarn

Like polyester fiber, nylon has high melting point which conveys good high temperature performance. The fiber is more water sensitive than polyester. Its toughness makes it a major fiber of choice in carpets. Because of excellent tear strength it is used as a blending fiber in some cases. In certain applications the performance of nylon fiber is hard to beat. Because of its high cost it is used in specialized applications where its performance can justify the cost. Nylon fibers are used for the manufacture of splittable-pie fibers. Non-wovens developed from nylon are used in automobile products, athletic wear and conveyor belts.

1.5. Short Nylon Fiber – Elastomer Composites

Short nylon fiber-elastomer composites have been a subject of a number of investigations. Brokenbrow et al[91] reported the preparation of a composite with good mechanical properties by incorporating nylon fibers in a low molecular weight non-terminally reactive liquid SBR and subsequently cross-linking it. O' Connor[31] studied the processing and properties of short fiber-elastomer composites with a variety of fibers (cellulose, nylon, glass, carbon and aramid). Effect of short nylon fibers on the mechanical properties of NR vulcanizates has been reported by Senapati et al.[92] Dynamic viscoelastic properties of nylon short fiber reinforced composites were studied by Chen et al.[63] They reported that the storage modulus and loss modulus increased with fiber loading. Short nylon fiber reinforced SBR compounds for V-belts applications were reported by King et al.[93] Ye et al[94] incorporated short nylon fibers into SBR and BR matrices and reported that the vulcanization time increased with fiber content. Factors affecting the elastic modulus of short nylon fiber-SBR rubber composites were studied by Li et al.[95] Short nylon fiber and vinylon fiber reinforced nitrile rubber and SBR were studied by Zhou et al.[96] They introduced an effective interfacial thickness concept based on Halpin-Tsai equation to characterize the fiber rubber interfaces. Zhou et al[97] studied the effect of fiber pre-treatment on properties of short nylon fiber-NBR composites. The effect of short fiber pretreatment on interfacial adhesion of nylon short fiber reinforced rubber composite was studied by Zhou et al[98] using equilibrium method. Zhang et al[99] studied the influence of fiber content, pre-treatment and temperature on the rheological properties of short nylon fiber-rubber composites. The reinforcement and orientation behavior of short nylon fibers in NR, SBR and CR were studied with emphasis on the determination of ideal aspect ratio for fibers by Bhattacharya.[100] Mechanical properties of nylon short fiber reinforced SBR/NR composites were studied in detail by Ma et al.[101] Zhang et al[102] studied the influence of loading level of nylon fiber in NR and polyester fiber in CR and proposed a model to calculate the structure of interfacial layer. The rheological and electrical properties of NR-white filler mixtures, reinforced with short nylon 6 fiber, were studied with respect to filler loading by Saad and Younan.[103] Kikuchi[71] reported that tyres from nylon short fiber having 0.2-0.3 μm diameter and 100-200 μm length in proper direction and NR showed reduction in cost and rolling resistance.

1.6. Mechanics of Short Fiber Composites

In a polymer composite the fibers are stiffer than the matrix and the proportion of the load that they support is greater than their volume fraction. The overall elastic properties of a composite are relatively easy to compute from the elastic properties of the components when the fibers are continuous and parallel.[104] For a perfectly aligned and properly bonded unidirectional composite the rule of mixture is applicable and is given by

$$\sigma_{cu} = \sigma_f V_f + \sigma_m V_m \quad 1.1$$

where,

σ_{cu} = ultimate composite strength, σ_f = ultimate fiber strength, σ_m = matrix strength at the maximum fiber strength, V_f = volume fraction of fiber and V_m = volume fraction of matrix.

In an aligned fiber composite loaded in transverse direction, most of the deflection takes place in the soft polymer phase and the fibers do not affect the strength properties significantly.

The analysis of mechanics of short fiber composites is much more difficult than for continuous aligned fiber composites. In composites, loads are not directly applied on the fibers, but are applied to the matrix material and transferred to the fibers through the fiber ends and also through the cylindrical surface of the fiber nearer the ends. When the length of a fiber is much greater than the length over which the transfer of stress takes place, the end effects can be neglected and the fibers may be considered to be continuous. The stress on a continuous fiber can thus be assumed constant over its entire length. In the case of short fiber composites the end effect can not be neglected and the composite properties are a function of fiber length. Some corrections in the values of σ_f or V_f in equation 1.1 will be needed to account for the fact that a portion of the end of each finite length fiber is stressed at less than the maximum fiber stress. The adjustment depends on the length of the fibers over which the load gets transferred from the matrix.

The most widely used model describing the effect of loading in aligned short fiber composites is the shear lag model proposed by Cox.[105] Rosen[106] discussed the effect of fiber length on tensile properties and used the shear lag analysis to explain the mechanism of stress transfer. The average longitudinal stress on an aligned short fiber composite can be obtained by the rule of mixtures give by

$$\sigma_c = \sigma_f V_f + \sigma_m V_m \qquad 1.2$$

where,

σ_f is the average fiber stress and is a function of fiber length, σ_m is the matrix stress, V_f and V_m are the volume fractions of the fiber and the matrix respectively.

When the fibers are smaller than a critical length, the maximum fiber stress is less than the average fiber strength so that fibers will not fracture and the composite failure occurs when the matrix or interface fails. When the fiber length is greater than the critical length the fibers can be stressed to their average strength and fiber failure initiates when the maximum fiber stress is equal to the ultimate strength of the fibers. As the fiber length become very large compared to load transfer length the average fiber stress approaches the maximum fiber stress and the behaviour of short fiber composite approaches that of continuous fiber composites.

Abrate[107] reviewed the mechanics of short fiber composites and examined the factors affecting the mechanical properties. Based on the shear lag model and characteristics of short fiber-rubber composite, Liqun et al[108] put forward a new mixture law and predicted the longitudinal tensile strength of short fiber rubber composites. Fukuda et al[109] described a mechanism of load transfer from matrix to fiber and predicted the young's modulus of short fiber composites. An analysis was done by Fukuda[110] for predicting the stress–strain relation and strength of unidirectional short fiber composites. The classical shear lag model was modified to take into account the effect of load transfer at the fiber ends as well as plasticity of matrix material. Theories on the strength of short fiber rubber composites were reviewed by Kondo et al.[111]

Derringer[112] postulated certain empirical equations relating volume fraction and aspect ratio of the fibers to the tensile strength, modulus and elongation at break. The variation of physical properties of the composites with the direction of fiber orientation was reported by Moghe.[113] The effect of fiber length and orientation distribution on the strength of short fiber composite was examined[114] and a general theory was formulated in terms of fiber length, orientation distribution function as well as the composite geometrical and physical properties.

The ultimate composite strength is given by

$$\sigma_{cu} = \sigma_{fu} V_f F (L/Lc) C_0 + \sigma_m (1 - V_f) \qquad 1.3$$

where,

σ_{cu} = the ultimate composite strength, σ_{fu} = ultimate fiber strength, V_f = volume fraction of fiber, σ_m = matrix strength at maximum fiber stress, L = length of the fiber, Lc = critical fiber length and C_0 is the orientation parameter.

Longitudinal and transverse moduli of the aligned short fiber composites given by Halpin Tsai equation are,

$$E_L/E_m = \frac{1 + 2l/d\, \eta_L V_f}{1 - \eta_L V_f} \qquad 1.4$$

and

$$E_T/E_m = \frac{1 + 2\, \eta_T V_f}{1 - \eta_T V_f} \qquad 1.5$$

where,

$$\eta_L = \frac{E_f/E_m - 1}{E_f/E_m + 2\, l/d} \qquad 1.6$$

$$\eta_T = \frac{E_f/E_m - 1}{E_f/E_m + 2} \qquad 1.7$$

E_L and E_T are the longitudinal and transverse moduli of an aligned short fiber composite having the same aspect ratio and fiber volume fraction as the composite under consideration. The Halpin-Tsai equation predicts that the transverse modulus of an aligned short fiber composite is not influenced by the fiber aspect ratio l/d.

The modulus of composites containing fibers that are randomly oriented in a plane is given by

$$E_{random} = 3/8\ E_L + 5/8\ E_T \qquad 1.8$$

Dzyura[115] proposed the following expression for composite strength

$$\sigma_c = \sigma_f V_f\ (1 - Li/2L)\ K + \sigma_m\ V_m \qquad 1.9$$

where,

σ_c = composite strength, σ_f = strength of the fiber, V_f = volume fraction of fiber, σ_m = strength of the matrix at its maximum attainable deformation, L = length of the fiber, K = coefficient of fiber orientation which depends on a number of factors such as method of processing, fiber concentration, type of fiber rubber composition etc., Li = ineffective length of the fiber and is calculated on the condition that the force required for breaking the fiber is equal to the maximum shear force on the rubber-fiber boundary,

$$Li = \sigma_f d/2\Gamma \qquad 1.10$$

where,

d = diameter of the fiber and Γ = maximum shear stress on the boundary.

The influence of the matrix on the value of σ_c was reported to be dependent on its stretching resistance at the maximum composite deformation, σ_m, and not on the matrix strength, σ'_m. For composites with a higher σ'_m/σ_m ratio (e.g. NR) there existed a minimum in the tensile strength-fiber concentration curve. For composites with maximum σ'_m/σ_m ratio approaching unity (e.g. SBR), the minimum was not observed. The lower the value of σ'_m/σ_m ratio the higher was the increase in relative strength σ_c as compared to σ_m'. Kern et al[116] presented a review dealing with different models of continuum theory for the prediction of mechanical properties of the composites.

1.7. Mechanical Properties

The mechanical properties of short fiber composites are intermediate between those containing continuous filaments or cords and particulate filled materials. Rubber reinforcement is manifested as an increase in tensile strength and modulus and a decrease in elongation and swelling in comparison to the matrix rubber.[11,19] Improvements in mechanical properties in presence of short cellulose fiber,[117,118] silk fiber,[43,119] vinal fiber,[120] nylon fiber[121-124] and aramid[15,125-127] have been reported. Coran[128] developed a general relationship between fiber loading, tensile strength and elongation at break. The relationship between tensile strength and fiber loading varied from rubber to rubber. For strain crystallizing rubbers such as NR and CR, the tensile strength drops initially up to a certain volume fraction of fibers, then it increases gradually with fiber loading.[56,92] For non-crystallizing rubbers such as NBR and SBR the presence of a small quantity of fiber enhances the strength.[57] Murty[19] reported that the strength minimum occur at low fiber concentrations because when the matrix is not restrained by enough fibers high matrix strain result at relatively low composite stresses. Once enough fibers are present to constrain the matrix the addition of more fibers increases the strength of the composite beyond that of the matrix alone. With excessive fiber loadings imperfections occur. The use of longer fibers move the position of the strength minimum to lower fiber concentrations, but also reduces elongation. When tested in transverse direction, strength considerably below the matrix strength may occur. Improvements in fiber-matrix bonding can improve the low transverse composite strengths.[128] The theoretical impact of orientation of individual fibers on composite strength was reported by Schafffers.[129] Abrate[107] found that fibers did not break at all except when their loading was insufficient to restrain the matrix in which case large stresses could develop at low strain. Fukuda and Chou[114] described the effect of fiber length and orientation on strength by a stochastic theory. Factors affecting the elastic modulus of short nylon fiber-SBR rubber composites were studied by Li et al[95] and an empirical relation was derived on Halpin-Tsai equation for the prediction of elastic modulus of the composite. Liqun et al[108] studied the law of tensile strength of short fiber reinforced rubber composites among a wide range of fiber volume and length. Zuev[8] reviewed with 55 references on mechanical properties of polymeric fiber filled rubber composites and ways of effective utilization of mechanical properties of fibers in rubber.

Generally the tear strength of short fiber reinforced polymer composites should improve to a greater extent when the fibers are oriented perpendicular to the direction of propagation of tear in the polymer matrix than when oriented parallel to it. This has been demonstrated by several workers for short nylon 6 and PET fiber filled natural and synthetic rubber compounds.[56,93,130] It has been reported that low fiber concentrations can elevate the tear strength of the composite above that of the matrix. However at higher concentrations, strain amplification between closely packed fibers promotes tearing parallel to the fiber direction thereby reducing tear strength.[3,107] Murty et al[19] reported that with imperfect fiber orientation or random fiber alignment, tear strength would increase as the fibers are bridging the tear. An excellent treatise was published by Kainradl and Handler[131] dealing with the tear strength measurements of vulcanized rubber, including the effects of specimen shape, prenotching of the sample and the thickness of the test piece. Manufacture of tear resistant short fiber reinforced conveyor belts has been reported by Hasegawa et al.[132]

1.8. Factors Affecting the Properties of the Composites

1.8.1. Type and Aspect Ratio of Fiber

Aspect ratio is a major parameter that controls the fiber dispersion, fiber-matrix adhesion and optimum performance of short fiber composites. If the aspect ratio is lower than the critical aspect ratio insufficient stress will be transferred and the reinforcement will be insufficient. The fibers should be neither too long to entangle with one another and cause dispersion problems nor too short to offer insufficient stress transfer and give poor reinforcement. It is generally agreed that the aspect ratio of 150 or more is sufficient for good load transfer between fiber and matrix. Since most commercially available synthetic fibers are produced with a given set of diameter, variation in aspect ratio can be most conveniently obtained through varying the fiber length. Considerable fiber breakage occurred during mixing of fibers with high aspect ratio (as high as 500) resulting in reduction in aspect ratio.[133] O'Connor[31] studied the extent of fiber breakage after both processing and vulcanization and concluded that fiber breakage and distribution of fiber length occur in the uncured stock during processing and not during curing. Fiber breakage was reported in a number of other cases.[36,37] For certain type of fibers like glass and carbon the fiber breakage was such that the resulting aspect ratio was too low to give good performance as reinforcement for rubber.[3,134] Chakraborty et al[37] have observed that an aspect ratio of 40 gave optimum reinforcement in XNBR reinforced with short jute fiber. Murty and De[36,39] reported that for jute fiber filled rubbers good reinforcement could be obtained with aspect ratio of 15 and 32 for NR and SBR respectively.

Short fibers were broken during the milling process with CR so that the maximum of the length distribution shifted from 6mm to 1.5-2 mm with short nylon, cotton and rayon fibers of diameter less than 19 μm.[135] Noguchi et al[136] reported that short PET fibers did not break up during the milling process and they were well dispersed, but carbon fibers did break up during milling, the fiber length being reduced to about 150 μm. An excellent treatment on the importance of aspect ratio especially with respect to the modulus of the matrix is given by Abrate.[107] Senapati et al[56,92] reported that fiber breakage with synthetic fibers like nylon 6 and PET during mixing into a rubber on a two roll mixing mill was negligible. A moderate breakage of short jute fibers during mixing with NR-PE thermoplastic elastomer in a Brabender plasticorder was reported by Akthar et al.[137] Significant breakage of short kevlar fibers during mixing in Brabender plasticorder in TPU matrix was reported by Kutty et al.[62,138] The effect of fiber aspect ratio on mechanical properties of reclaimed rubber composites was studied by Zhanxun et al.[139] Varghese et al[45] reported that an aspect ratio in the range of 20-60 was sufficient for reinforcement for NR-short sisal fiber composites. Nagatami et al[140] reported that PET fibers in hydrogenated styrene-isoprene-block copolymer, resisted folding and scission during mixing and the fiber length remained unchanged. The incorporation of carbon fiber in styrene isoprene block copolymer and NR-TPE (TPNR) resulted in 30 fold reduction in aspect ratio as a result of fiber scission during the milling process.[64,141] Reduction of fiber breakage of carbon fibers in CR was achieved by cement mixing method.[142] The reinforcement and orientation behaviour of short nylon fibers in NR, SBR and CR were studied with emphasis on the determination of ideal aspect ratio for fibers.[100] Ibarra et al[68] reported the drastic reduction of the aspect ratio of carbon fibers during blending in Gummix cylinder mixer. A series of short fiber reinforced SBR composites were studied by Prasanthakumar et al[143] with sisal fibers of different lengths and a fiber length of 6 mm was found to be optimum. The effect of fiber breakage and length on melt viscosity of sisal fiber-SBR composite was also reported.[144] Correa[54] reported that there was a reduction in fiber length after incorporation of short carbon and Twaron fibers to thermoplastic PU.

1.8.2. Fiber Dispersion

The primary requirement for obtaining high performance composite is good dispersion of fibers in the matrix. Good dispersion implies there will be no clumps of fibers in the finished products. The fiber will be separated from each other during the mixing operation and surrounded by the matrix. The factors that affect fiber dispersion in polymer matrices are fiber-fiber interaction, fiber length and the nature of the fibers. It is mostly influenced by the amount of fiber.[145] Fibers which break up during the mixing process can be incorporated at much higher levels (up to 50 phr) with ease but the resultant composite will, be less effective.[6] According to Derringer,[112] commercially available fibers such as nylon, rayon, polyester, acrylic flock must be cut into smaller lengths of approximately 0.4 mm for better dispersion. The uniformity of fiber dispersion is best for glass, carbon and cellulose fibers. Aramid and nylon fibers tend to clump together and do not disperse easily.[31] A pre-treatment of fibers is necessary to reduce the interaction between fiber and to increase interaction between fiber and rubber. The pre-treatments include making dispersions and formation of a soft film on the surface. Leo and Johanson[146] described pre dispersions of chopped polyester, glass and rayon fibers in neoprene latex for better mixing in to CR or SBR rubber. It has been reported that cellulose pulp may be dispersed directly into a concentrated rubber masterbatch or into a final compound, if it is sufficiently wetted to reduce fiber to fiber hydrogen bonding.[147] Intensive mixing has been done with cellulose fibers in an elastomer matrix.[148,149] Effect of shear rate, ram pressure, fill factor, power input and mixing time on fiber dispersion were studied. Derringer[30] recommended that organic fibers be first incorporated into a concentrated masterbatch where high shear force can be established between the aggregates. These can later be broken down to the desired compound formulation in order to optimise dispersion. The various equipments do not produce composites with same degree of uniformity and dispersion. Goettler[150] and Coran[151] compared the mixing efficiency of various methods and found milling to be the best based on the properties measured though it is a slow operation. Shen and Rains[149] investigated the effect of fiber dispersion on modulus and strength. They have stated a dimensionless dispersion number N_R, which is a function of rotor length, rotor diameter, rotor tip clearance, mixing chamber volume, rotor speed and mixing time, can be a reliable scale up parameter for short fiber mixing in polymers.

1.8.3. Fiber Orientation

The preferential orientation of fibers in the matrix is the key to the development of anisotropy in the matrix. During processing of rubber composites, the fibers tend to orient along the flow direction causing mechanical properties to vary in different directions.[113] Thus by changing or suitably controlling the flow direction optimum properties can be generated for a given product. The dependence of composite properties on fiber orientation and alignment is also well documented.[112,113] Milling and calendering are perhaps the most commonly used processing methods in which fibers tend to orient along the mill direction. A large shear flow during milling forces fibers to orient along mill direction.[152] For a continuous flow through a fixed mill opening, all the possible fiber orientation are achieved during the first pass. Flow pattern is not expected to change during subsequent mill passes. Boustany and Coran[153] reported that a high degree of fiber orientation could be achieved by repetitive folding and passing through a two-roll mill. Akthar et al[43] found a small nip gap and single pass in the mill to be the best. A rubber mill was used by Foldi[6] to orient various organic filaments into several types of rubber stock. Senapati et al[56] reported that two passes through tight nip gave optimum mechanical properties for short PET/NR composites. The effect of mill opening and the friction ratio of the mill and temperature of the rolls on the orientation of short kevlar fibers in TPU matrix has been described by Kutty et al.[62] It was observed that the lower the nip gap, the higher the anisotropy in tensile strength, implying greater orientation of fibers. McNally[154] has reviewed in detail the orientation of short fibers in polymer matrices.

Campbell[11] reported that when rubber matrix containing dispersed fibers is made to flow in a non-turbulent manner, the fibers are turned and aligned in the direction of the matrix flow. Goettler et al[150] described the fiber orientation under different type of flow, i.e. convergent, divergent, shear and elongational and reported that fibers aligned in the direction of flow when the flow was convergent type and perpendicular to the flow direction in a divergent flow. Two passes of short nylon 6 and PET reinforced NR composites through nip of a small mill is sufficient to orient most of the fibers in the mill direction.[56,92] Goettler and Lambright[155] developed a technique for controlling fiber orientation in extrusion by the use of an expanding mandrel die. In calendering the fiber orientation occurs preferentially in the machine direction. Calendering can achieve about the same level of fiber orientation in the machine direction as conventional extrusion.[150]

1.8.4. Fiber Matrix Adhesion

In a fiber reinforced composite the fibers carry the bulk of the applied load, the matrix serves to hold the fiber to space them, to transfer the load to individual fibers and to protect them from mechanical and chemical damage. Interfacial bonding is known to play an important role in composites. Loads are to be transferred across the fiber-matrix interface and this process affect many properties of the composite in addition to its strength and modulus. The load transfer is dependent on fiber to polymer adhesion and the fiber aspect ratio. The adhesion between low modulus polymer and high modulus fiber prevents the independent deformation of the polymer at the interface.

The improvement in reinforcement obtained by enhancing fiber-matrix adhesion through the incorporation of a bonding system has been widely studied in the case of rubber vulcanizates.[156-158] Derringer[112] evaluated the HRH system with various fibers in nitrile and natural rubber and good adhesion was obtained. He concluded that the HRH system was not effective with polyester fibers in any elastomeric matrix. Foldi[6] applied RFL dip on nylon fiber in NR-SBR matrix and found the reinforcing ability actually reduced. O'Connor[31] compared the HRH system with RH and hexa methoxy methyl melamine (HMMM) alone in various short fiber natural fiber composites. Kondo[159] reviewed the selection of adhesives for bonding short fiber reinforcements in SBR and NR compounds. Adhesion to textile fibers could be achieved with HRH system compounded into the rubber stock or by fiber treatment with either isocyanate based resins or RFL dips.[160] It has been reported that the presence of tri-component bonding system (HRH) is essential for the promotion of adhesion between fiber and rubber matrix.[19,37,41,42,161-163] Some researchers have found that the replacement of silica by carbon black in the tri-component bonding system leads to essentially similar adhesion level.[3,164] Effect of pretreatment of fiber with polyester amide polyols and silane coupling agents on the dry and the wet strength of jute fiber–polyester composite has been studied. The mechanism of action of coupling agents to improve the fiber-matrix interface properties has been studied by Mukherjea et al.[38] The role played by the HRH system in short fiber filled NR/PE blend was reported by Akthar et al.[43] Arumugam et al[44] reported that HRH system was effective in improving the adhesion between coconut fiber and rubber matrix.

Kutty and Nando[165] have reported that chemically treated polyester cord-NR vulcanizates exhibit lower Goodrich heat build up than untreated PET cord-NR composites. Also NR matrix compounded with HRH dry bonding agent gave lower heat generation than even chemically treated fiber-rubber composites owing to better interfacial adhesion between fiber and matrix. HRH bonding material was effective for short fiber reinforced butadiene rubber also.[94] Ashida,[61] in a review has mentioned about adhesives used for short fibers. Short vinal fibers pretreated with silane coupling agents gave good adhesion with CR.[120] The effect of surface treatment of nylon short fiber with RFL bonding agent was analysed for NR and EPDM rubbers.[166] Owing to surface treatment, there was some improvement in mechanical properties. It was more pronounced in the case of NR than EPDM. A two-component system of resorcinol and hexamethylene tetramine was found to be better than tri-component HRH system for NR-short sisal fiber composites.[45] Acetylation of sisal fiber improved the properties of the composite. The effect of addition of HRH system/RH system on the properties of short polyester fiber-reclaimed rubber composites has been reported.[139] The interfacial adhesion between nylon and vinylon short fiber reinforcements treated by different methods and nitrile rubber and SBR matrix was studied by Zhou et al.[96,167]

To improve adhesion between fibers and NR polyallyl acrylate was grafted on cellulose fibers by Yano et al.[168] Ibarra[169] used 1,4 carboxyl benzene sulfonyl diazide as adhesive agent for PET-SBR composites and obtained enhanced properties. A strong bond between PET fiber and isoprene-styrene block copolymer or butadiene-styrene block copolymer was obtained by surface treatment of the block copolymer with isocyanate in PhMe solution.[170] The effect of fiber-matrix interfacial adhesion on viscoelastic properties of short sisal fiber NR composites was evaluated by Siby et al.[46] The interfacial adhesion of short nylon fiber-rubber composite was strengthened by pretreating the fiber by coagulating a mix of coupling agent or adhesive, fiber and NBR/SBR latex.[98] The effect of two component system (resorcinol and hexa) on NR-short sisal fiber composite was studied in detail.[171] Interfacial adhesion between coir fiber and NR was improved by treating the fiber with alkali and NR solution and by incorporating HRH/RH system.[47,48]

Suhara et al[172] reported that in presence of HRH bonding system the water liberated during resin formation caused hydrolysis of urethane linkages and hence HRH system could not be used as interfacial bonding agent for polyurethane-short polyester fiber composite. Effect of urethane based bonding agent on the cure and mechanical properties of short fiber-PU elastomer composites has been reported.[173,174] Improvement of interfacial adhesion of ploy (m-phenylene isophthalamide) short fiber-thermoplastic elastomer composite was achieved with N-alkylation of fiber surface.[175]

1.9. Applications

Elastomers reinforced with continuous fibers are well known, but this type of composites are limited mainly to applications in tyre, belts and hoses. The manufacture of articles of complex shape can not be easily accomplished with a continuous fiber reinforced elastomer. On the other hand the preparation of intricate shaped products is possible with short fibers as reinforcements. Processing of the short fiber composites can be done by the well known extrusion and transfer moulding techniques used in the rubber industry. By adjusting parameters like fiber aspect ratio, adhesion etc. short fiber composites can replace continuous cord, as they offer flexibility in both design and processing besides imparting advantages in properties. The main application areas for short fiber composites are in hose, belting, solid tyres and pneumatic tyre components. Short fiber reinforcements in the production of hoses, V-belts, tyre tread, spindle drive wheel and complex shaped mechanical goods have been studied by many workers.[155,176-178]

An important application that utilizes the full reinforcing potential of short fibers in a load–bearing application is as a replacement for continuous cord in rubber hose. The major advantages associated with short fiber reinforcement are easy processing, economy and higher production rate. These find applications in the automotive industry[179] as well as for general purpose utility hoses. Using specially developed extrusion dies Goettler et al[155] have aligned the fibers into a predominantly circumferential dispersion within the tube wall to provide the necessary burst strength. Iddon[180] discussed an optimum screw design and extruder head construction for hose manufacturing. Schroden et al[181] developed a high-tech hose for a high-tech car turbo engine.

Power transmission belts, more precisely V-belts, are probably the earliest practical application of rubber-fiber composites. A V-belt running over pulleys is subjected to very severe stresses when bent and flexed at a frequency of thousands of cycles per minute. Tensile stresses resulting from static tensioning and load transmission are supported by the textile reinforcing cord. The compressive sidewall pressures are supported mainly by the base rubber. The ideal material for this part of the V-belt must exhibit high modulus in the transverse direction and low modulus coupled with high flexibility in the axial direction. Such complex properties can best be achieved in an anisotropic rubber-short fiber composite. The desired transverse orientation of fibers in the base rubber can be achieved by constructing the raw V-belt from compounded sheet that was first calendered to orient the fibers and then rolled up in the 90^0 direction. Rogers[182] and Yagnyatinskaya et al[183] discussed the use of short cellulose fiber along with polyester fibers as reinforcements for V-belt compounds. Tear resistant short fiber reinforced conveyor belts were manufactured by Arata et al.[184] The use of CR reinforced with aramid short fiber for transmission belts have been discussed by Ichithani et al.[185]

In tyre, chafing resistance could be improved by adding short fibers to the surface of the fabric. The apex of radial tyre has been successfully reinforced with short fibers to give it more stiffness or rather greater bending resistance. The other areas that have been identified for short fiber composite compounds in tyres are tread, belt overlay, tire inner liner and bead wrap. The use of short fibers in tire treads to improve wear characteristics has received much attention.[186,187] A reduction in crack propagation rate is obtained with the addition of 1% cellulose fibers to the tread compound.[186] Improvement in modulus and cut/crack resistance of urethane rubber was obtained with the inclusion of chopped organic fibers.[188,189] Another application of short fibers in tyres involves the circumferential reinforcement of the tread to improve strength against the centrifugal forces developed according to Dubetz.[190] Marzocchi et al[191] claimed improved tyre stability when a random short glass fiber mat was incorporated under the tread. Arnhem et al[192] reported that a small amount of short fibers in the tread of a truck tyre reduced the rolling resistance considerably. Very little has been reported on the use of short fiber reinforcement in exterior panel of automobiles.

The use of fiber reinforcement in dock fenders and methods to fabricate them have been discussed by Goettler et al.[193] Sheet roofing can benefit greatly from short fiber reinforcement. Seals and gaskets are potentially large markets for short fiber reinforcement. What short fiber reinforcement offers to seals and gaskets is excellent creep resistance, especially at elevated temperatures.

Chopped nylon fibers were used to improve the wear of crepe shoe soles.[194] The application of cotton or other cellulosic reinforced thermoplastic polyisoprene as sheeting in shoe constructions was given by Georgieva et al.[195] Additional applications claimed are[196] hard roll covers, oil well packings, bearings and bushes. De and co workers[197,198] investigated the potential of using carbon fibers in neoprene to shield against electromagnetic interference (EMI) and found that 30-40 phr carbon fiber loading was sufficient to make the composite a potential EMI shielding material in the electronic industry.

1.10. Scope and Objectives of the Present Work

The utilization of reclaimed rubber in rubber industry is widely practiced to reduce the compound cost and to conserve the raw material and energy. Reclaimed rubber is an effective and versatile source of hydrocarbon. It frequently improves processability and the final properties of the product. The presence of reclaim in the recipe enhances working properties in all primary processing operations. Moulding properties are often improved by the presence of reclaim in a compound. Reclaim stocks possess low thermoplasticity and are less affected by continuous milling than natural rubber stocks. For low cost applications the use of reclaim will permit a significant reduction in antioxidant. These advantages make reclaim to substitute virgin material in rubber compound. However, there has been no systematic approach to study the various blend parameters and their effect on the blend properties. The variables that have bearing on the blend properties are the characteristics of the rubber used, the blend ratio, the compounding ingredients and processing conditions.

NR being a general purpose rubber used in a wide range of applications, it is important to know the characteristics of its blend with reclaimed rubber. The hydrocarbon content of the reclaim being 50 parts, every part of the NR replaced is compensated by two parts of the reclaimed rubber. It will be highly useful to know how the blend properties vary with blend composition.

Though the use of reclaim in a rubber compound is sure way of reducing cost, being a low molecular weight material, the presence of the reclaim in a self reinforcing material such as NR is expected to reduce the properties. It then becomes imperative to further compensate for this by using another cheap material. It will be a good idea if short fibers can be used for this purpose. Short fibers available as scrap from the fiber industry can impart improved anisotropic mechanical properties.

The properties of short fiber containing composites depend critically on fiber content, orientation and fiber-matrix interface bond strength. The detailed study of the effect of these parameters in the composite properties will be highly informative. For improved performance of a short fiber composite at a constant fiber loading, a strong fiber-matrix bond is very important. A strong interfacial bond can effectively transfer the load from the matrix to the fiber and hence can improve the overall performance of the composite. The interfacial bond is usually strengthened by using bonding agents. The knowledge of the bonding agent type, composition and optimum concentration is very much needed for proper design of short fiber composites.

The service requirements of the elastomers in different areas of application are so wide that NR alone can not meet all of them. Of the many synthetic rubbers being used for various application, SBR and NBR are two widely used rubbers-each from a non polar and a polar group, respectively. It will be highly useful to know the optimum conditions for use of reclaim and short fibers in these matrices as well. It calls for a study in the case of these two elastomers as in the case of NR.

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CHAPTER II.
EXPERIMENTAL TECHNIQUES

The materials used, the methods of sample preparation and the experimental techniques adopted in the present investigations are given in this Chapter.

2.1. Materials

Natural rubber (ISNR-5) was supplied by the Rubber Research Institute of India, Kottayam, India. The Indian standard specifications for this grade of rubber are given below.

Mooney Viscosity [ML (1+4) at 100 °C]	82.00
Dirt content, % by mass, max	0.05
Volatile matter, % by mass, max.	1.00
Nitrogen, % by mass, max.	0.70
Ash, % by mass, max.	0.60
Initial plasticity, min.	30.00
Plasticity Retention Index (PRI) min.	60.00

Acrylonitrile butadiene rubber (NBR) was provided by Apar Polymers Ltd., India. The sample used was N553 grade with 33% acrylonitrile content.

Mooney viscosity [ML (1+4) at 100 °C]	45

Styrene butadiene rubber (SBR synaprene-1502) was obtained from Synthetics and Chemicals Ltd., Bareilly.

Styrene content, % by mass	23.5
Mooney viscosity [ML (1+4) at 100 °C]	52

Reclaimed rubber (Whole Tyre Reclaim (WTR)) was procured from Kerala Rubber and Reclaims, Mamala, India. The characteristics of reclaim used are given below.

Mooney viscosity [ML (1+4)]	18
Acetone extract (%)	13 - 15
Carbon content (%)	38 – 39

Short nylon fiber, Nylon (N-6) fibers obtained from SRF Ltd., Chennai was chopped to approximately 6mm. Specifications of nylon fiber are given below.

Breaking strength	28.3 kg - 31.5 kg
Elongation at break	27.5% - 36.5%
Twist	S 392 - 374
Denier	3656g - 3886g

2.2. Chemicals

Zinc oxide supplied by M/s. Meta Zinc Ltd., Bombay, India has the following specifications.

Specific gravity	5.5
Zinc oxide content	98%
Acidity	0.4% max.
Heat loss (2hrs. at 100 °C)	0.5% max.

Stearic acid used in the study was procured from Godrej Soaps Pvt. Ltd., Bombay, India. It has the following specifications.

Melting point	50 - 69 °C
Acid number	185 - 210
Iodine number	9.5 max.
Specific gravity	0.85 ± 0.01
Ash content	0.1% max.

Commercial grade **Vulcanox HS (1,2,-dihydro-2,2,4-trimethyl quinoline, polymerized)** with a specific gravity of 1.1 was obtained from Bayer India, Ltd., Bombay.

Dibenzothiazyl disulfide (MBTS) with a specific gravity of 1.34 and melting point 165 °C was supplied by Bayer India Ltd., Bombay.

Tetramethyl thiuram disulfide (TMTD) with a specific gravity of 1.42 and melting point 140 °C was procured from NOCIL Bombay, India.

Sulfur was supplied by Standard Chemicals Company, Pvt. Ltd., Chennai. The specifications of the sample are

Specific gravity	2.05
Acidity	0.01% max.
Ash	0.01% max.
Solubility in CS_2	98%

4,4'- diphenyl methane diisocyanate (MDI) was obtained from BASF South Korea. The characteristics of MDI are

Appearance	Brown colored liquid
Viscosity, cps/25 °C	185 ± 35
NCO content, wt%	31.0 ± 0.5
Hydrolyzable chlorides, %	0.1 - 0.3

Polyethylene glycol (PEG) with a molecular weight 4000 was obtained from Manali Petrochemicals, Chennai.

Solvent **toluene** used was analytical grade.

2.3. Processing

2.3.1. Mixing

The mixing was done as per ASTM D 3182 (1989) on a two roll laboratory size mixing mill (150 x 330 mm). Once a smooth band was formed on the roll, the ingredients were added in the following order: reclaimed rubber, fibers, MDI, PEG, activators, accelerators and finally sulfur. After complete mixing the stock was passed six times through the tight nip and finally sheeted out at a fixed nip gap so as to orient the fibers preferentially in one direction.

2.3.2. Cure Characteristics

Cure characteristics were determined by using Goettfert Elastograph Model 67.85 at 150 °C. The machine has two directly heated, opposed biconical dies that are designed to achieve a constant shear gradient over the entire sample chamber. The specimen was kept in the lower die which was oscillating through a small deformation angle (± 0.2^0) at a frequency of 50 oscillations per minute. The torque transducer on the upper die senses the force being transmitted through rubber. A typical cure curve is shown in figure 2.1.

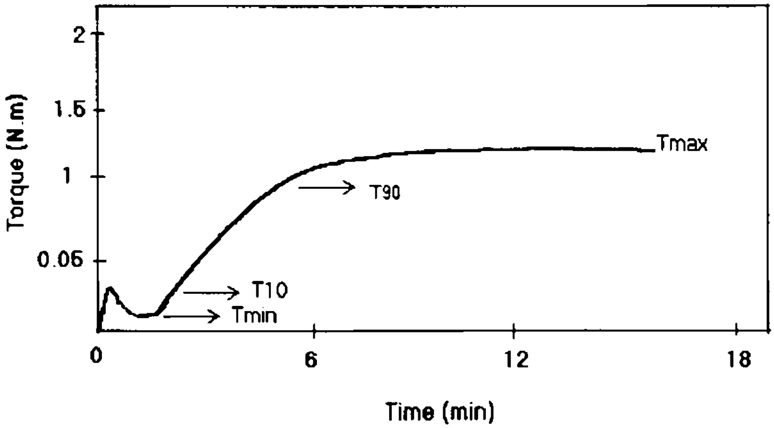

Figure 2.1. A typical cure curve.

The following data can be obtained from the cure curve.

Minimum torque (Tmin): It is the lowest torque shown by the mix at the test temperature before the onset of cure.

Maximum torque (Tmax): It is the torque recorded when curing of the mix is completed.

Scorch time (T_{10}): It is taken as the time for 10% rise in torque from the minimum torque.

The optimum cure time T_{90} corresponds to the time to achieve 90% of maximum cure.

2.3.3. Vulcanisation

Test specimens marked with the mill grain direction were vulcanized at 150 ± 2 °C and at a pressure of $180 kg/cm^2$ in an electrically heated hydraulic press to their respective cure times. For thicker samples sufficient extra cure time was given to obtain satisfactory mouldings. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cold dark place for 24 hours and were used for subsequent property measurements.

2.4. Fiber Breakage

The extent of fiber breakage during mixing on a two roll mill was determined by dissolving out the matrix in toluene followed by separation and drying. Fiber length was measured by using a travelling microscope. A batch size of approximately 100 fibers was taken and the distribution of fiber length was reported.

2.5. Fiber Orientation

The matrix was dissolved out from the compounded stock using a solvent and the fiber orientation was observed using an optical microscope.

2.6. Physical Properties

The vulcanizates were tested for different mechanical properties according to the relevant ASTM standards. Tensile strength, tear strength, elongation at break, heat build up and abrasion resistance were tested using samples where the fibers were oriented along and across the sample length. Schematic representation of fiber orientation in different test samples is given in figure 2.2. For ageing samples were kept in an air oven for 48 hours at 70 ^{0}C (ASTM 573 – 88). The properties were measured 24 hours after the completion of ageing.

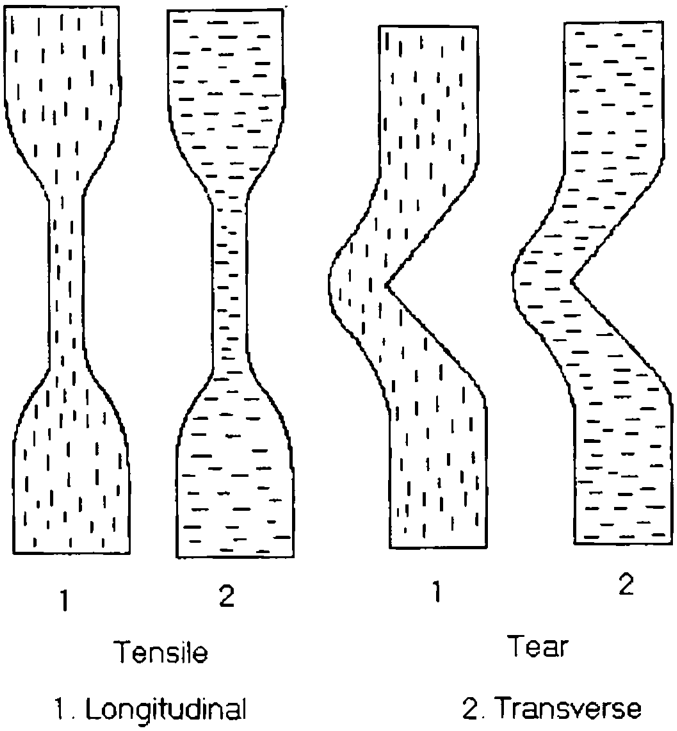

Figure 2.2. Schematic representation of fiber orientation.

2.6.1. Tensile Strength and Elongation at Break

These tests were carried out using Zwick Universal Testing Machine Model 1445 according to ASTM D 412 (die E). Samples were punched out from the moulded sheets both along and across the grain direction. The grip separation speed was 500 mm/min.

2.6.2. *Tear Strength*

The tear test was done on Zwick Universal Testing Machine Model 1445 according to ASTM D 624 (die C). The samples were punched from the moulded sheets along and across the grain direction. The test speed was 500 mm/min.

2.6.3. *Abrasion Resistance*

Abrasion resistance of the samples was measured using a DIN abrader based on DIN 53516, both in the longitudinal and transverse directions. Samples having a diameter of 12 ± 0.2 mm and a thickness of 16 - 20 mm was placed on a rotating holder and a load of 10 N was applied. A pre-run was given for conditioning the sample and the sample weight was taken. Weight after the test was also noted. The difference in weight is the weight loss of the test piece after its travel through 40 m on a standard abrasive surface. The results were expressed as volume loss per hour.

2.6.4. *Rebound Resilience*

Rebound resilience was determined by vertical rebound method according to ASTM D 2832 - 88. In this method a plunger suspended from a given height (400 ± 1mm) above the specimen was released and the rebound height was measured. The resilience scale was marked in 100 equally spaced divisions and hence the rebound height is equal to the resilience (%).

2.6.5. *Heat Build Up*

Heat build up test was carried out using Goodrich Flexometer as per ASTM D 623 - 78 method A. The samples were 25 mm in height 19 mm in diameter. The oven temperature was kept constant at 50 ^{0}C. The stroke was adjusted to 4.45 mm and the load to 10.05 kg/cm^{2}. The samples were preconditioned at the test temperature in the oven for 20 minutes prior to the test. The heat development at the base of the sample was sensed by a thermocouple and relayed to a digital temperature indicator. The temperature rise (ΔT °C) at the end of the specific time intervel (20 minutes) was taken as the heat build up.

2.6.6. Compression Set

Compression set at constant strain was measured according to ASTM D 395 – 86 method B. Samples with 6.25 mm thickness and 18 mm diameter were compressed to constant strain (25%) and kept for 22 hours in an air oven at 70 ^{0}C. At the end of the test period the test specimens were taken out, cooled to room temperature for 30 minutes and the final thickness was measured. The compression set in percemtage was calculated as follows.

$$\text{Compression set (\%)} = \frac{Ti - Tf}{Ti - Ts} \times 100 \qquad 2.1$$

where,

Ti and Tf are the initial and the final thickness of the specimen and Ts is the thickness of the space bar used.

2.6.7. Density

Density of the samples was measured as per ISO 2781 method A. Weight of the sample in air and water was taken. Density of the sample was calculated as

$$\text{Density} = \frac{W_1}{W_2} \times D \qquad 2.2$$

where,

W_1 = weight of the sample in air
W_2 = loss of weight in water
D = density of water, (1 g/cm^3)

2.6.8. *Gel Content*

Gel content was determined as per ASTM D 3616 – 88. In this method about 0.39 to 0.41g ± 0.1 mg of compounded stock was punched out and allowed to swell in a solvent of 100 ml for 20 hours. The solution was filtered and 25 ml of the liquid was dried to constant mass. Gel content was calculated as follows:

$$A \times 4 = B$$

$$\text{Gel, \%} = \frac{C - B}{C} \times 100 \qquad 2.3$$

where,

A = mass of the dried sol, 25 ml volume
B = mass of the total dried sol
C = mass of the original sample

CHAPTER III.

NR - WTR BLENDS*

A versatile elastomer with many dramatic properties, natural rubber finds applications in wide range of areas such as tyres, belts, bushes etc. A combination of high tensile strength and high elongations along with low cost makes it an ideal choice for many engineering applications.

Usually natural rubber is compounded with fillers to improve properties and/or to reduce cost. Reclaimed rubber is one such method which can be blended with virgin natural rubber as a source of hydrocarbon and reinforcing filler. The use of reclaimed rubber in NR reduces the cost, conserves the raw material and energy. Though the molecular weight of reclaimed rubber is lower than the virgin rubber, the presence of reinforcing filler and oil can be expected to contribute to improved processability and mechanical properties.

This Chapter deals with a systematic study of the effect of blending reclaimed rubber with virgin natural rubber. The reclaimed rubber (Whole Tyre Reclaim) is used for replacing up to 40 parts of the virgin natural rubber and the blend cure characteristics and the mechanical properties are studied in detail.

Formulation of the mixes is given in Table III.1. Sample preparation and the various test methods employed are given detail in Chapter 2.

3.1. Cure Characteristics

The variation of minimum torque with reclaim content is shown in figure 3.1. The minimum torque, a measure of the stock viscosity,

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*Results of this Chapter have been published in Polym. Plast. Tech. Engg., 39(3) (2000) 501.

Table III.1. Formulation of the mixes

Ingredient	Mix No.				
	A	B	C	D	E
NR	100	90	80	70	60
Reclaim	-	20	40	60	80

Zinc oxide - 4 phr, Stearic acid - 2 phr, HS - 1 phr, MBTS - 0. 5 phr, TMTD - 1. 8 phr & Sulfur - 0. 3 phr are common to all mixes.

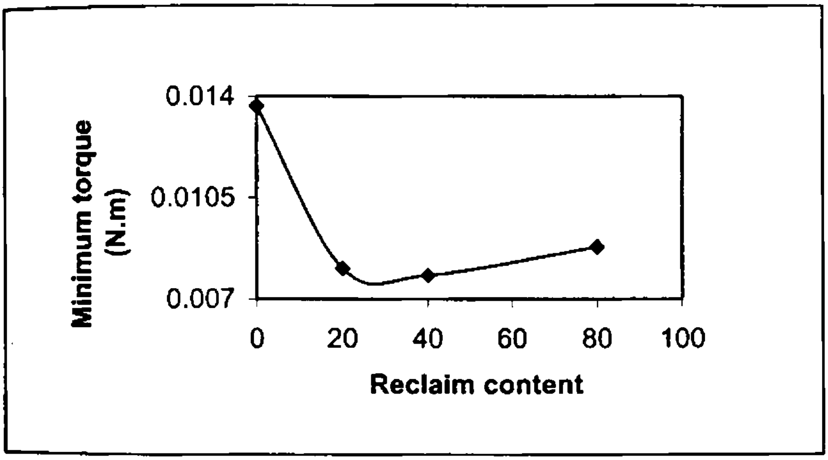

Figure 3.1. Variation of minimum torque with reclaim loading.

shows a major reduction at 20 parts of reclaim loading, beyond which the torque shows a marginal increase. At all reclaim loading the minimum torque value is lower than that of the gum compound indicating an improved processability of the blends. The higher oil content of the reclaimed rubber explains the initial reduction of torque values. However at higher reclaim loading the effect of filler present in the reclaim seems to offset the increased plasticity. The acetone extractable fraction and filler content of the reclaim used are given in Chapter 2. The acetone extractable fraction indicates the oil content of the reclaim.

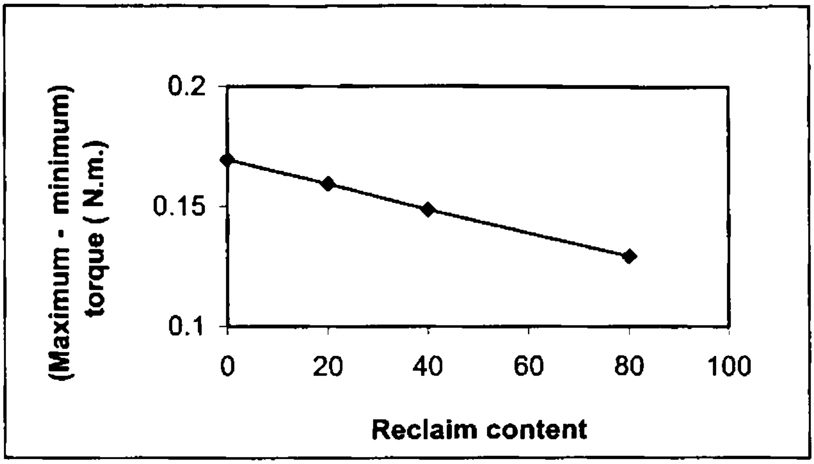

Figure 3.2. Variation of (maximum – minimum) torque with reclaim loading.

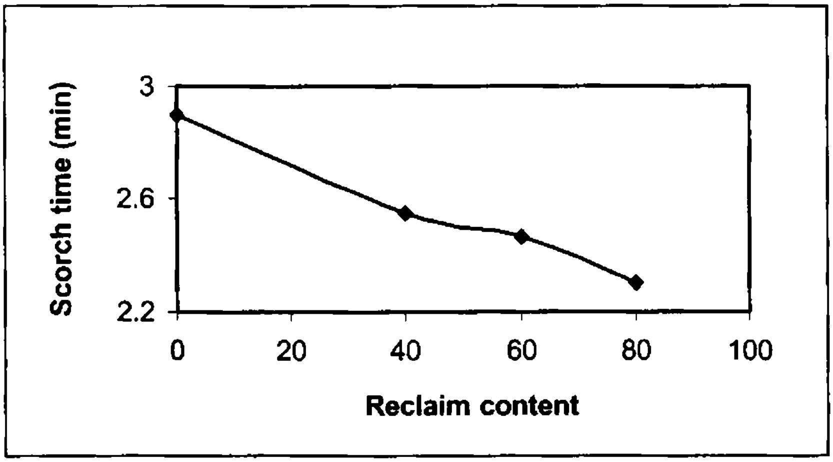

Figure 3.3. Variation of scorch time with reclaim loading.

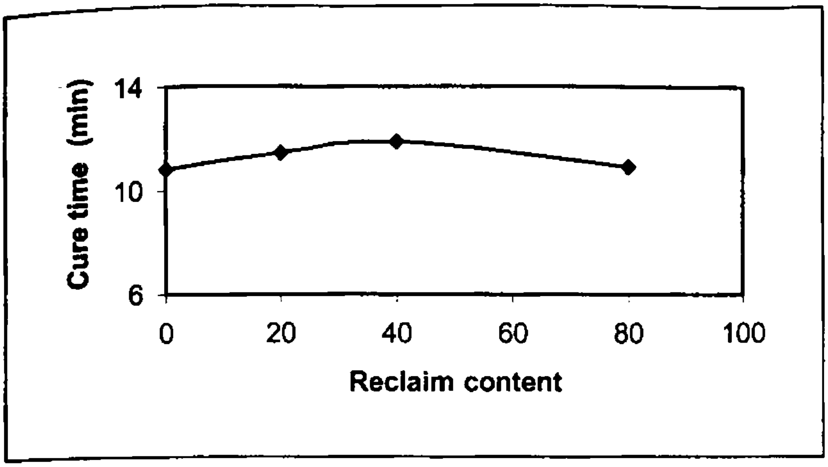

Figure 3.4. Variation of cure time with reclaim loading.

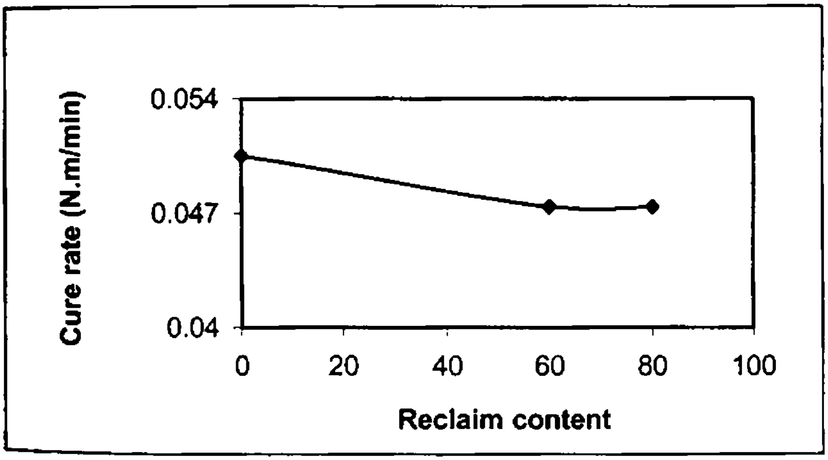

Figure 3.5. Variation of cure rate with reclaim loading.

The (maximum – minimum) torque values show a linear reduction with increase in reclaim loading (figure 3.2.). Though the reclaim contains carbon black as filler, the excess oil present in the reclaim seems to reduce the higher expected value of (maximum –

minimum) torque.

While the scorch time shows a reduction from 2.9 minutes to 2.3 minutes with increase in reclaim loading,[1] the cure time shows a minor maximum at 40 parts (figure 3.3. & 3.4.). The decrease in scorch time with increase in reclaim content can be attributed to the crosslink precursors or unreacted curatives in reclaimed rubber. The reduced scorch safety with increased cure time indicates a lower rate of cure, as is evident from figure 3.5, which is a plot of cure rate versus the reclaim loading.

3.2. Mechanical Properties

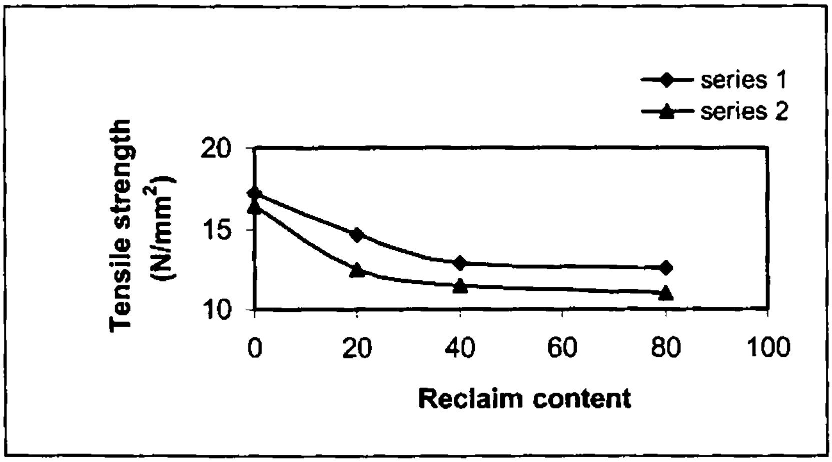

Figure 3.6. Variation of tensile strength with reclaim loading. (series 1. - unaged, series 2. - aged)

The variation of tensile strength with the addition of reclaimed rubber is shown in figure 3.6. The lowering of tensile strength with the addition of reclaimed rubber is due to the lower molecular weight of the reclaimed rubber.[2] The high shear and temperature during the reclamation process severely breaks down the molecular chains to shorter segments. Incorporating more of this low molecular weight fraction results in progressive reduction in the tensile strength. The reclaim contains about 38% of carbon black. However this does not seem to improve the tensile strength of the blends with a relatively weaker matrix.

The series 2 in figure 3.6 is the post-ageing tensile strength of the blends. All the mixes except the gum compound show lower tensile strength values after ageing indicating a higher level of degradation (the scission of cross links or scission of a fraction of rubber chain at points between cross links can occur) in the case of mixes containing reclaimed rubber. There is about 15% reduction after ageing for mixes containing 20 parts and above of the reclaim. For the gum compound the tensile strength before and after ageing are very close to each other.

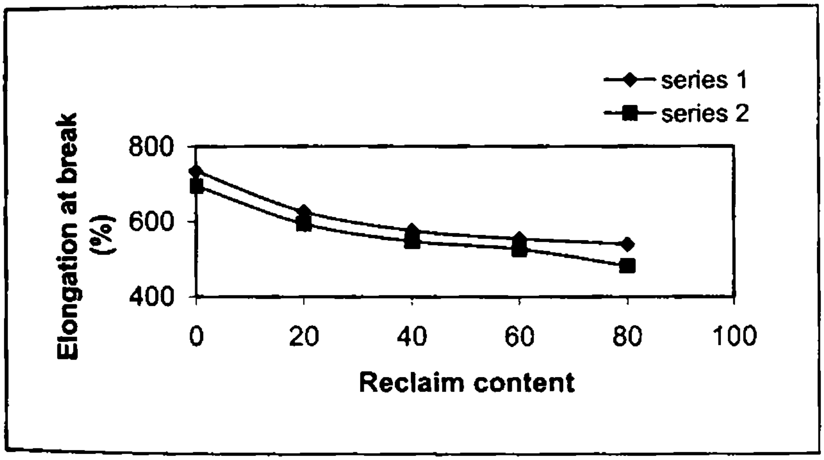

Figure 3.7. Variation of elongation at break with reclaim loading. (series 1. - unaged, series 2. - aged)

Figure 3.7 shows variation of elongation at break with reclaim loading. The elongation at break values decrease with increase in reclaim loading. There is a gradual reduction from 735% at 0 parts to 540% at 80 parts reclaim loading. The lower molecular weight of reclaimed rubber and the presence of reinforcing filler in it which may inhibit molecular orientations causes the sample to fail at lower elongation as is also evident from the lower tensile strength of the blends. There is a uniform drop in the elongation at break values of the blends after ageing as shown by series 2 in figure 3.7.

The variation of tear strength with increasing reclaim loading is shown in figure 3.8. The tear strength is improved from 23 N/mm to 27 N/mm with 20 parts reclaim loading beyond which the improvement seems to be marginal. The improved tear strength can partly be attributed to the presence of reinforcing black in the blend. However at higher reclaim loading the effect is not apparent because of the lower molecular weight of the reclaimed rubber. The series 2 represent the post-ageing tear strength values, which is very close to unaged values.

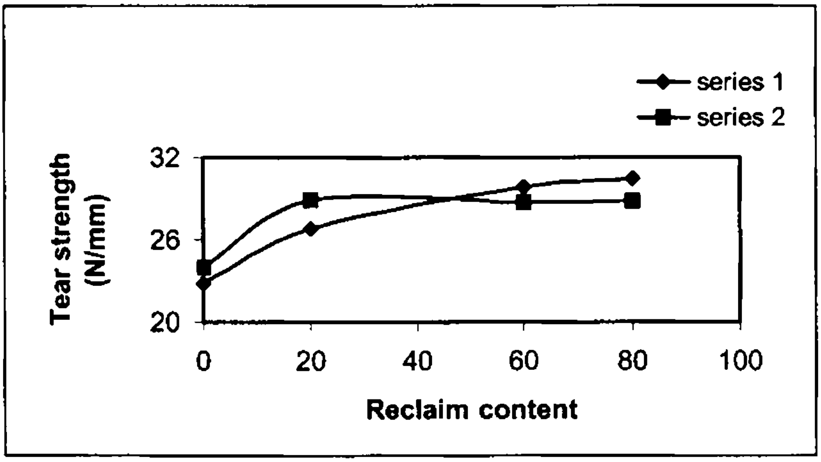

Figure 3.8. Variation of tear strength with reclaim loading. (series 1. - unaged, series 2. - aged)

Under a tear test condition propagation of crack through the bulk is a critical step. The reinforcing fillers can arrest or deflect the crack front resulting in better tear strength values where as in a tensile strength test sample failure is initiated at the filler-matrix interface simultaneously at multiple points. This, coupled with the lower
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molecular weight of reclaimed rubber results in lower tensile strength.

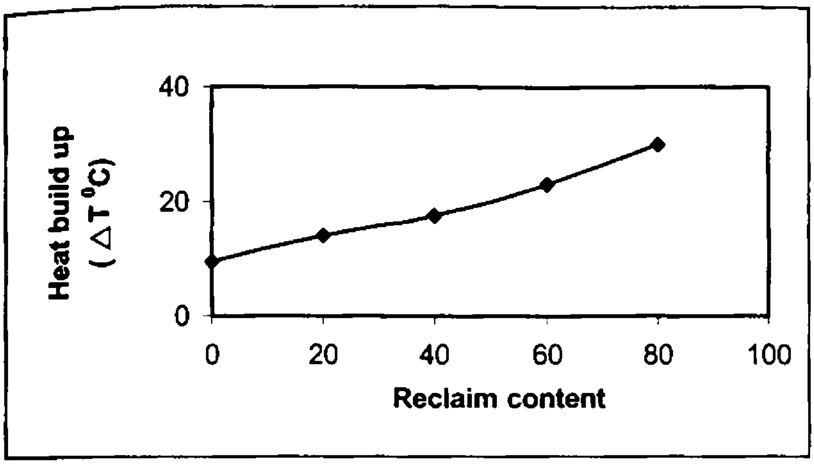

Figure 3.9. Variation of heat build up with reclaim loading.

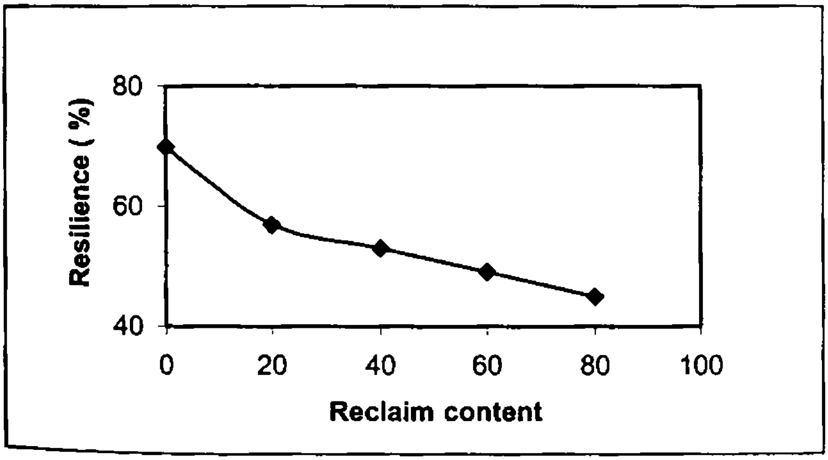

Figure 3.10. Variation of resilience with reclaim loading.

Figure 3.9 shows the heat generation values of the mixes. There is almost a linear increase in the heat build up values with increase in reclaim content. The maximum heat generated during the 20 minutes test time is increased from 9.5 ^{0}C at 0 parts to 30 ^{0}C at 80 parts of reclaim loading. The increased hysteresis loss can be attributed to increasing filler content of different blends. This is also accompanied by a corresponding reduction of the resilience values (figure 3.10.).

After an initial quick reduction at 20 parts reclaim loading the resilience decreases almost linearly at higher reclaim loading. There is about 36% reduction in resilience at 80 parts reclaim loading. Reduced tensile strength and resilience coupled with higher hysteresis indicate a stiffer matrix in the case of the blends. However because of the low molecular weight of the reclaim blends fail to support higher load.

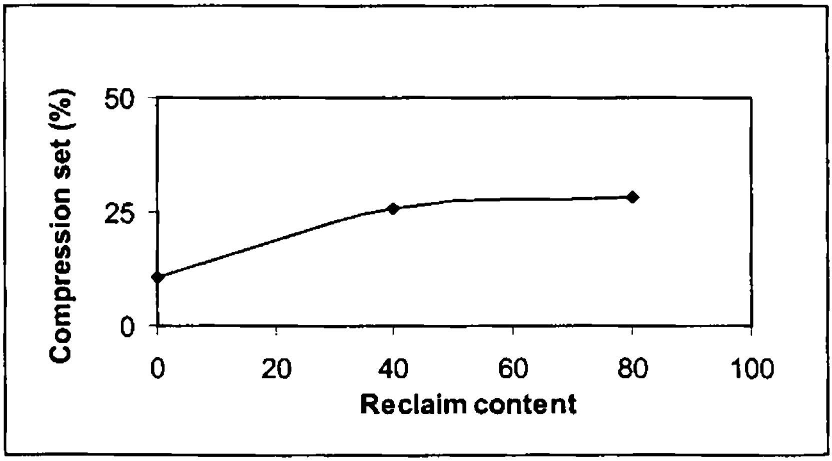

Figure 3.11. Variation of compression set with reclaim loading.

The variation of compression set at constant strain is shown in figure 3.11. The compression set increases with increase in reclaim loading. This is in agreement with the observed reduced resilience and increased hysteresis loss.

Figure 3.12 gives the abrasion loss of the blends containing different amounts of reclaimed rubber. There is a marginal increase in the abrasion resistance of the blends at high level of reclaim loading. The weaker matrix of the blends might have offset the expected improvement in the abrasion resistance of the blends.

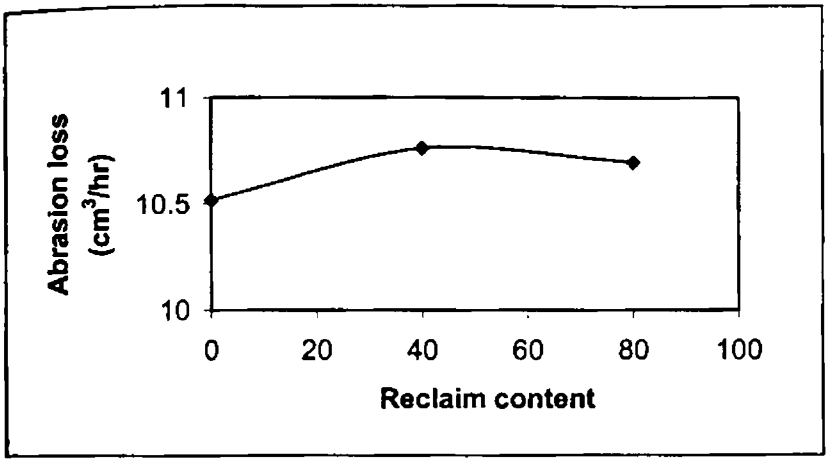

Figure 3.12. Variation of abrasion loss with reclaim loading.

3.3. References

1. Phadke A.A., Bhattacharya A.K., Chakraborty S.K. and De S.K., Rubber Chem. Technol., **56** (1983) 726.
2. Phadke A.A., Chakraborty S.K. and De S.K., Rubber Chem. Technol., **57** (1984) 19.

CHAPTER IV. A.

NR - SHORT NYLON FIBER COMPOSITES*

This Chapter deals with the incorporation of NR using short nylon fibers.

Traditionally carbon black has been used in the rubber industry as an effective reinforcing agent for NR. However, the tensile improvements obtainable through higher loadings of carbon black are offset both by increasing processing difficulties and by the deterioration of other properties also. However at higher loadings of carbon black, the improvements in tensile properties are offset by processing difficulties and the deterioration of the mechanical properties. In addition the incorporation of carbon black in the rubber products add to its cost. Short fibers can impart many desirable properties to rubber articles up to now unobtainable with traditional reinforcements. Short fibers are waste products from textile industries. Thus the method is a cost effective and environmentally acceptable approach to tackle the solid waste problem also.

Short fiber reinforced rubber composites have got much attention because of processing advantages and improved mechanical properties. The composite properties depend on fiber concentration, dispersion, fiber-matrix adhesion, and aspect ratio of fiber in addition to the nature of the matrix. A systematic study of the cure characteristics and the mechanical properties of natural rubber containing different levels of short nylon fibers are discussed in this Chapter.

Table IV.A.1 gives formulation of the mixes. The details of preparation of the mixes, cure characteristics determination, moulding and testing are given in Chapter 2.

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*Results of this Chapter have been accepted for publication in J. Elastomers Plast.

Table IV.A.1. Formulation of the mixes

Ingredient	Mix No			
	A	B	C	D
NR	100	100	100	100
Short nylon fiber	0	10	20	30

Zinc oxide - 4 phr, Stearic acid - 2 phr, HS - 1 phr, MBTS - 0.5 phr, TMTD - 1.8 phr & Sulfur - 0.3 phr are common to all mixes.

4.A.1. Fiber Breakage

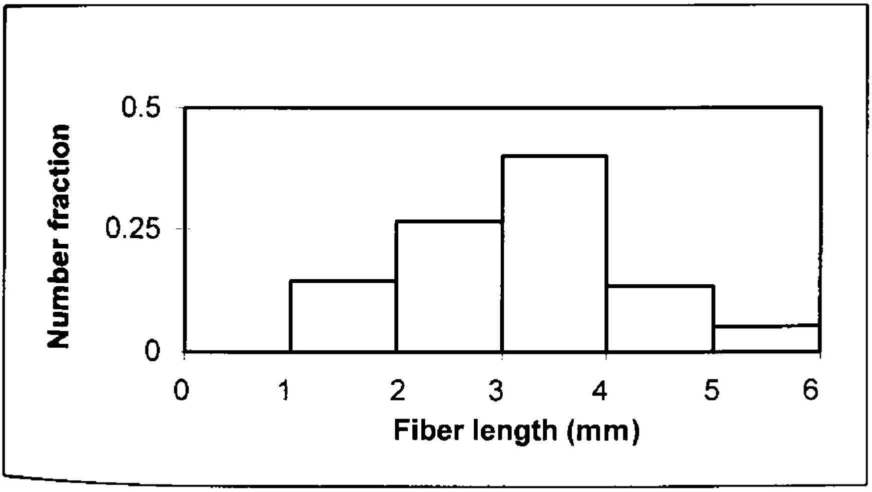

Figure 4.A.1. Variation of fiber length with number fraction of fiber.

Figure 4.A.1 shows the length distribution of the fiber extracted from the compounded stock. The average fiber length is reduced

from the original 6mm to about 3mm. This shows that there is a good amount of fiber breakage taking place during the mixing process on the two-roll mill.

4.A.2. Fiber Orientation

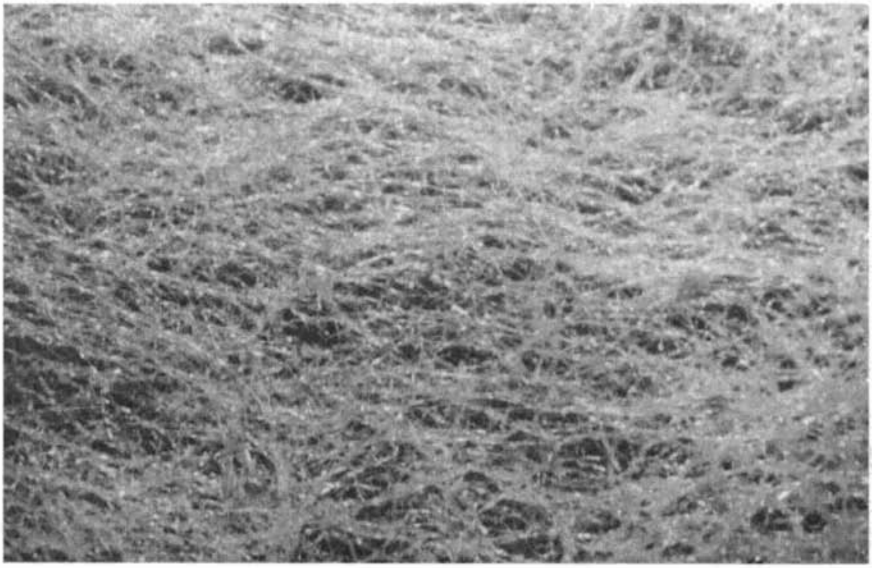

Figure 4.A.2. The spatial distribution of fibers in the composite.

The spatial distribution of fibers in the composite after sheeting through tight nip is shown in figure 4.A.2. The photograph was taken after dissolving out the matrix material in a solvent. The photograph shows that exposed fibers oriented preferentially in one direction. ie. the direction of milling. The flow pattern at the nip region forces the fibers to orient along the flow direction.

4.A.3. Cure Characteristics

Figure 4.A.3 gives variation of minimum torque with fiber loading. The minimum torque values show an almost linear increase with

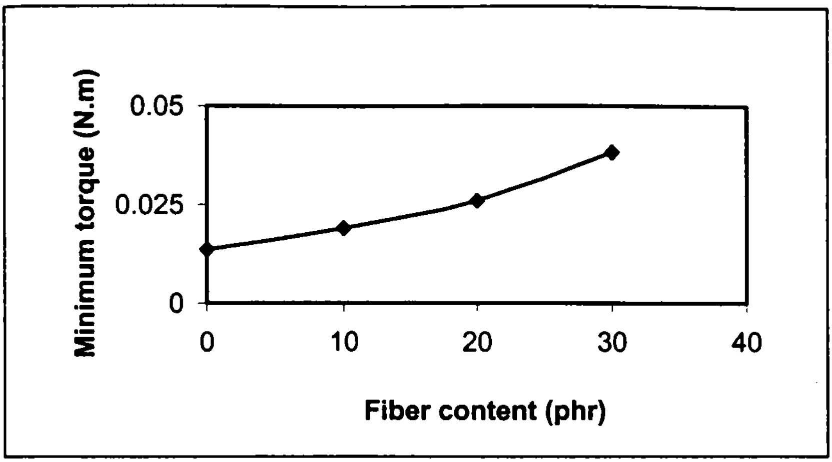

Figure 4.A.3. Variation of minimum torque with fiber loading.

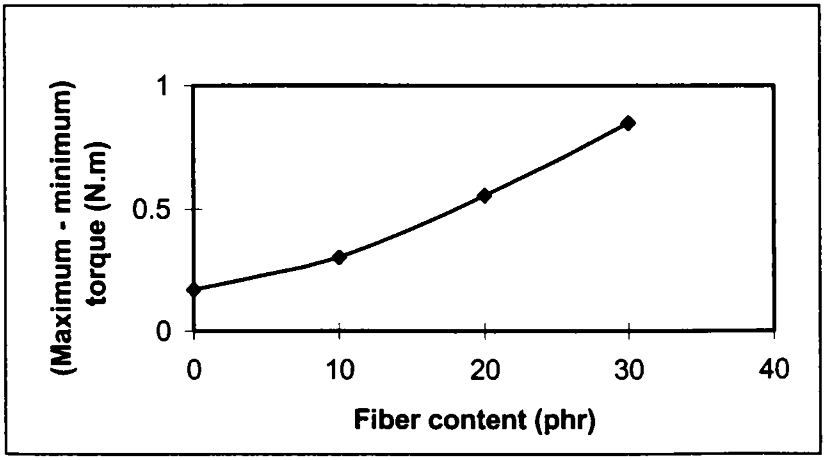

Figure 4.A.4. Variation of (maximum – minimum) torque with fiber loading.

increase in fiber content indicating a progressive loss in the processability of the composite. The torque values change from

0.01367 N.m at 0 phr to 0.0383 N.m at 30 phr.

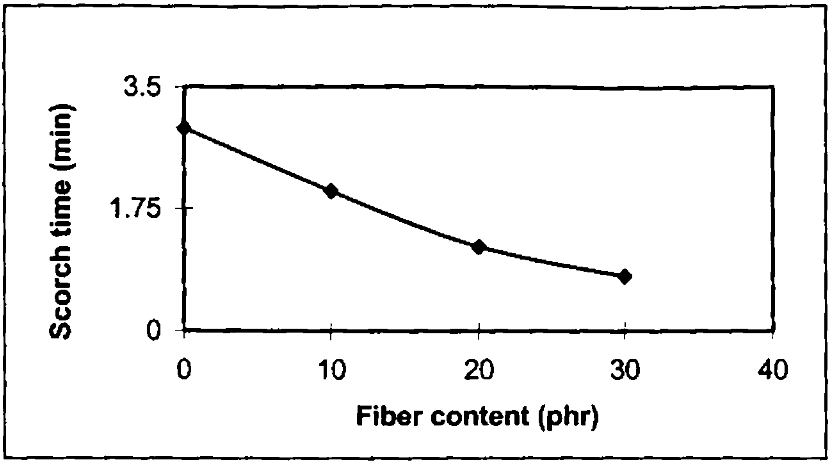

Figure 4.A.5. Variation of scorch time with fiber loading.

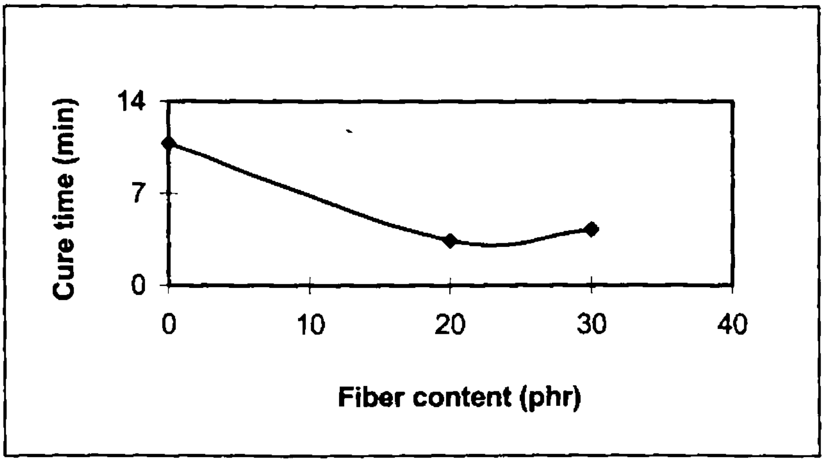

Figure 4.A.6. Variation of cure time with fiber loading.

Figure 4.A.4 shows (maximum – minimum) torque values of the

composites containing different amounts of short fiber. The linearly increasing torque values indicate a progressively more restrained matrix. The torque values change from 0.16943 N.m at 0 phr to 0.8457 N.m at 30 phr.

Figure 4.A.5 and 4.A.6 show the scorch time and the cure time of the short fiber composites. Both the scorch time and cure time are found to be lowered in presence of short fibers. The reduced cure time is also accompanied by the increased cure rate (figure 4.A.7).

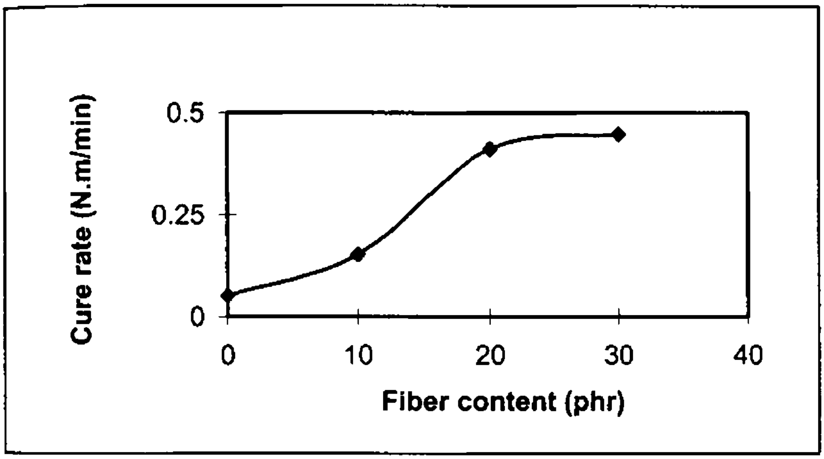

Figure 4.A.7. Variation of cure rate with fiber loading.

4.A.4. Mechanical Properties

Figure 4.A.8 shows variation of tensile strength with fiber loading. The tensile strength in longitudinal direction shows a minimum at 10 phr of fiber loading beyond which it increases. At low fiber concentrations the matrix is not restrained by the fibers, and highly localized strains occur in the matrix at low stresses, causing either the fiber to break or debond before the failure of entire composite. The matrix is diluted by the holes resulting from the broken or

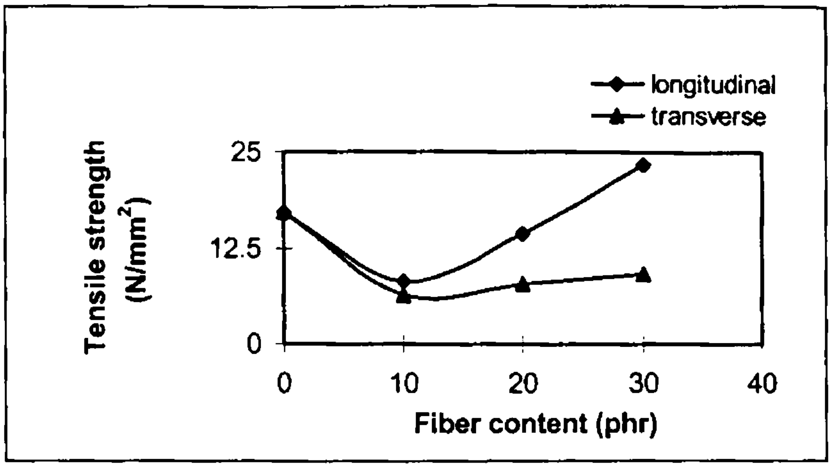

Figure 4.A.8. Variation of tensile strength with fiber loading.

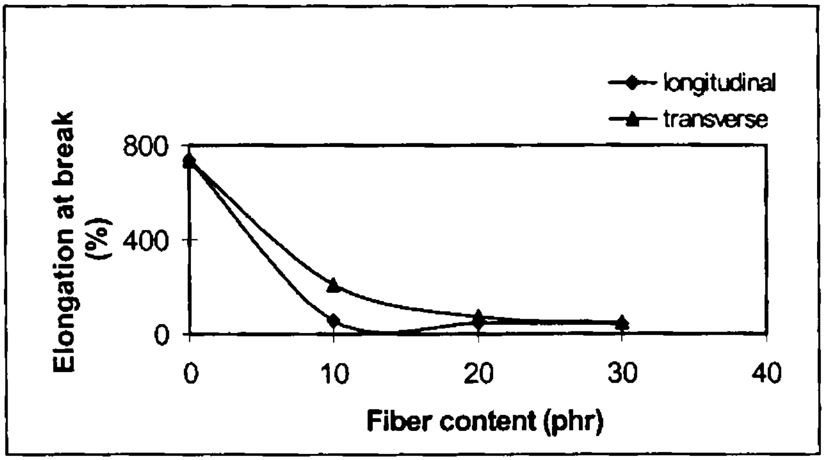

Figure 4.A.9. Variation of elongation at break with fiber loading.

debonded fibers. As fiber concentration increases matrix is restrained and effective functioning of fibers as reinforcing agents can take place resulting in higher tensile strength. In the transverse direction the tensile strength is lower than the gum compound at all fiber loading. The growing crack can easily pass through the fiber-matrix interfaces facilitating easy failure of the sample. Similar results have been reported by Connor, Derringer, Murty et al and Kutty et al.[1-4]

Figure 4.A.9 shows the variation of elongation at break with fiber loading. The elongation at break of the composite samples, are significantly lower than that of the gum compound. There is a drastic drop at 10 phr of fiber loading beyond which the values tend to stabilize, in both the orientations of fibers. The inability of the matrix to support higher strains arises partially from the premature fiber pull out or fiber breakage.

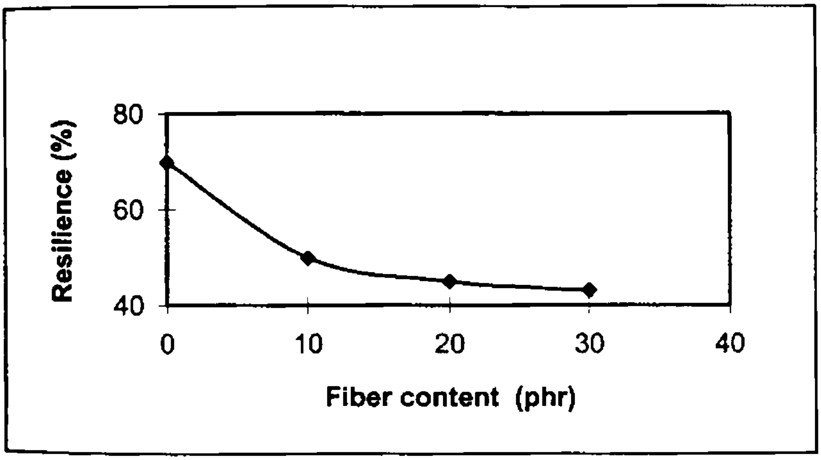

Figure 4.A.10. Variation of resilience with fiber loading.

A continuous decrease in resilience is observed with the increase in fiber concentration in all the mixes (figure 4.A.10.). As more energy is dissipated at the fiber matrix interface the resilience is reduced with the increase in interface area (fiber concentration).

Compression set shows an increase with fiber concentration (figure

4.A.11.). This is consistent with the observed lower resilience values.

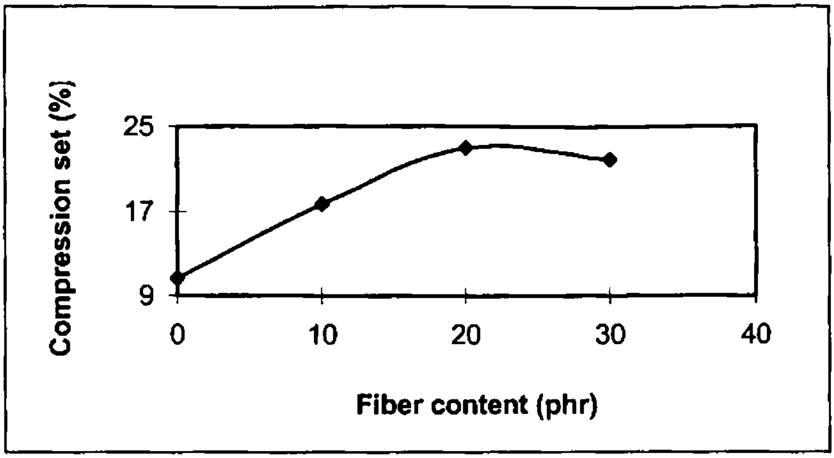

Figure 4.A.11. Variation of compression set with fiber loading.

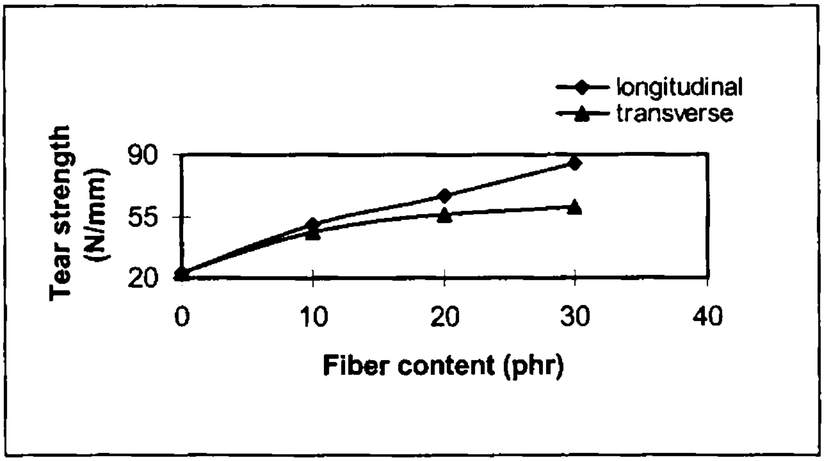

Figure 4.A.12. Variation of tear strength with fiber loading.

The variation of tear strength of the composites is shown in figure

4.A.12. Tear strength in longitudinal direction increases with the increase of fiber concentration. In the transverse direction the effect is less pronounced. The higher tear strength of the samples with longitudinally oriented fibers is due to the obstruction of tear path by longitudinally oriented fibers. This does not take place in composites with transverse fiber orientation.

Heat build up values in both the directions increase with the increase of fiber loading in the composites (figure 4.A.13.). However samples with transversely oriented fibers register lower heat build up values. The vulcanizates, which are stiffer in the direction of stress experience higher stress for a given strain and generate more heat since the dissipation of energy depends upon both stress and strain amplitudes. The stiffness of composites with longitudinally oriented fibers is higher than the stiffness of the composites with transversely aligned fibers, in the direction of stress. Thus heat build up is less for composites with transversely oriented fibers. Similar results have been reported by Das.[5]

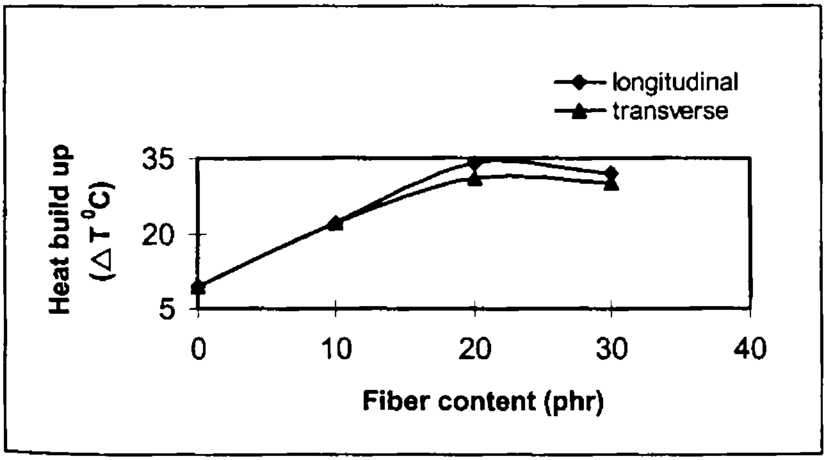

Figure 4.A.13. Variation of heat build up with fiber loading.

The abrasion loss of the fiber filled samples are lower than that of the gum compound (figure 4.A.14.). This is because of more restrained matrix of composite. Samples with transversely oriented fibers show higher abrasion loss than the samples with fibers oriented along the direction of abrasion. This is because of the fact that fibers when are oriented perpendicular to the direction of abrasion get debonded and separated from the matrix more easily than the samples with longitudinally oriented fibers.

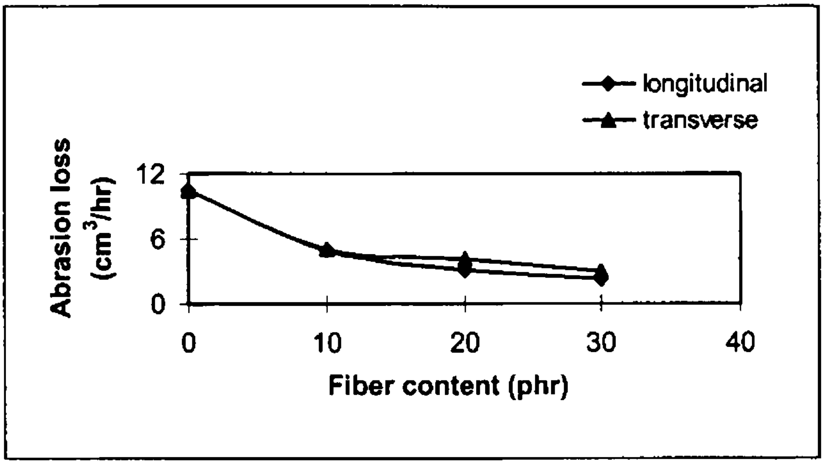

Figure 4.A.14. Variation of abrasion loss with fiber loading.

4.A.5. Ageing Resistance

Table IV.A.2 shows the percentage retention in tensile strength of the mixes after ageing. Mix A containing no fiber shows a marginal drop in tensile strength after ageing. All other mixes containing different levels of fiber show a marginal improvement in the strength properties. The percentage retention values seem to be function of fiber orientation also, the retention being higher in the longitudinal direction compared to the transverse direction.

Table IV.A.3 shows percentage retention values of elongation at break after ageing. All the mixes show more or less comparable retention values.

Table IV.A.2. Tensile properties of the mixes before and after ageing

Mix No.	Orientation	Tensile strength (N/mm^2)		Percentage retention
		Before ageing	After ageing	
A		17.2	16.5	96
B	L	8.2	10.8	131
	T	6.4	6.4	100
C	L	14.5	16.4	113
	T	7.8	8.4	107
D	L	23.4	24.7	106
	T	9.2	10.6	115

L - Longitudinal orientation T - Transverse orientation

Table IV.A.3. Elongation at break values of the mixes before and after ageing

Mix No.	Orientation	Elongation at break (%)		Percentage retention
		Before ageing	After ageing	
A		735	695	95
B	L	59	46	79
	T	212	205	97
C	L	48	46	97
	T	75	73	98
D	L	40	38	95
	T	48	44	93

L - Longitudinal orientation T - Transverse orientation

The percentage retention values of tear strength given in Table IV. A.4 show marginal increase in the tear strength values after ageing. Retention in tear strength of the samples with transversely oriented fibers are better compared to samples with longitudinally oriented fibers at all fiber loadings. During ageing even though the matrix becomes weaker, the fiber-matrix interface may have improved interaction. As the tear in samples with transversely oriented fibers propagates through the fiber-matrix interface an improved interfacial interaction results in higher tear strength values.

Table IV.A.4. Tear properties of the mixes before and after ageing

Mix No.	Orientation	Tear strength (N/mm)		Percentage retention
		Before ageing	After ageing	
A		22.8	24.0	105
B	L	50.4	54.2	108
	T	46.1	56.4	122
C	L	66.7	67.7	101
	T	56.1	66.1	118
D	L	85.2	92.6	109
	T	60.6	69.5	115

L - Longitudinal orientation T - Transverse orientation

4.A.6. References

1. O' Connor J.E., Rubber Chem. Technol., **50** (1977) 945.
2. Derringer G.C., J. Elastoplast., **3** (1971) 230.
3. Murty V.M. and De S.K., Rubber Chem. Technol., **55** (1982) 287.
4. Kutty S.K.N. and Nando G.B., Plast. Rub. Comp. Proces. Appl., **14(2)** (1990) 109.
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CHAPTER IV.B.

NR/WTR - SHORT NYLON FIBER COMPOSITES*

Short fiber reinforced rubber compounds have gained importance due to processing advantages and improved mechanical properties. A small amount of properly chosen short fibers can supplant a large quantity of reinforcing black or other particulate fillers. Short fibers can improve thermomechanical properties of the composites and reduce the cost of fabrication. In the present chapter the results of investigations on short nylon fiber reinforcement of NR/WTR blend is described. An 80/40 of NR/WTR blend was selected from previous study (Chapter III) and the fiber loading varied from 0 - 30 phr.

The formulation of the mixes is given in Table IV.B.1 and the experimental details are given in Chapter 2.

Table IV.B.1. Formulation of the mixes

Ingredient (Parts by weight)	Mix No.			
	A	B	C	D
NR	80	80	80	80
WTR	40	40	40	40
Nylon short fiber	0	10	20	30

Zinc oxide - 4 phr, Stearic acid - 2 phr, - HS - 1 phr, MBTS - 0. 5 phr, TMTD - 1. 8 phr & Sulfur - 0. 3 phr are common to all mixes

4.B.1. Cure Characteristics

The variation of minimum torque with fiber loading is shown in

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*Results of this Chapter have been communicated for publication in J. Mater. Sci.

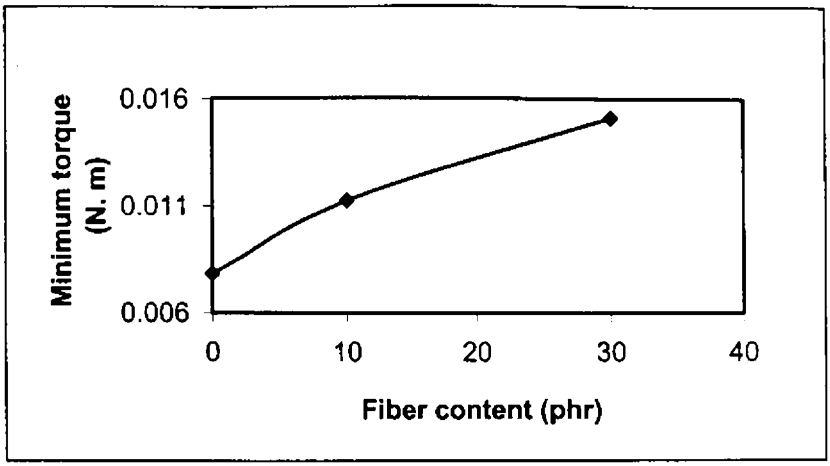

Figure 4. B.1. Variation of minimum torque with fiber loading.

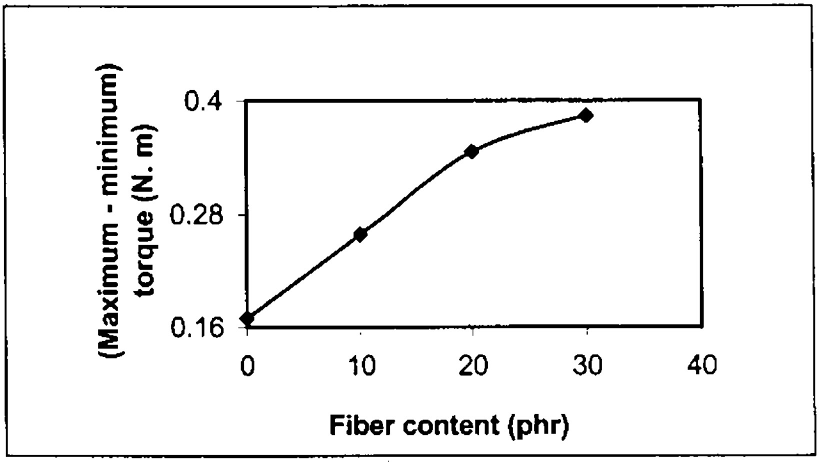

Figure 4.B.2. Variation of (maximum – minimum) torque with fiber loading.

figure 4.B.1. The minimum torque shows an increase with fiber concentration, indicating that the processability of the composite is adversely affected by the introduction of fibers.

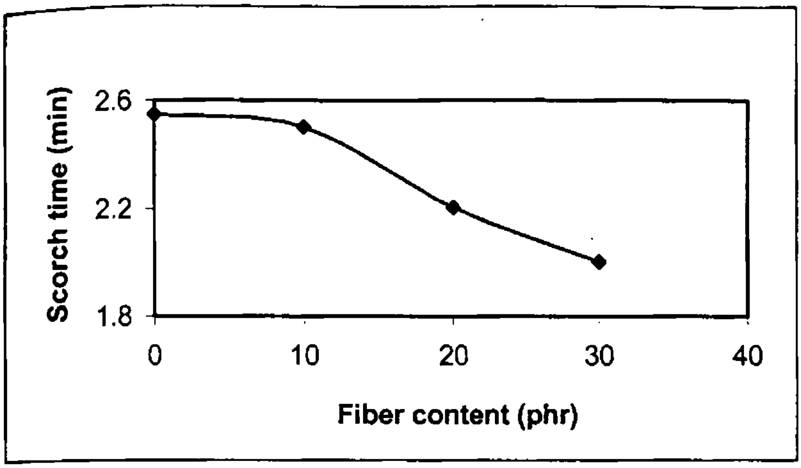

Figure 4.B.3. Variation of scorch time with fiber loading.

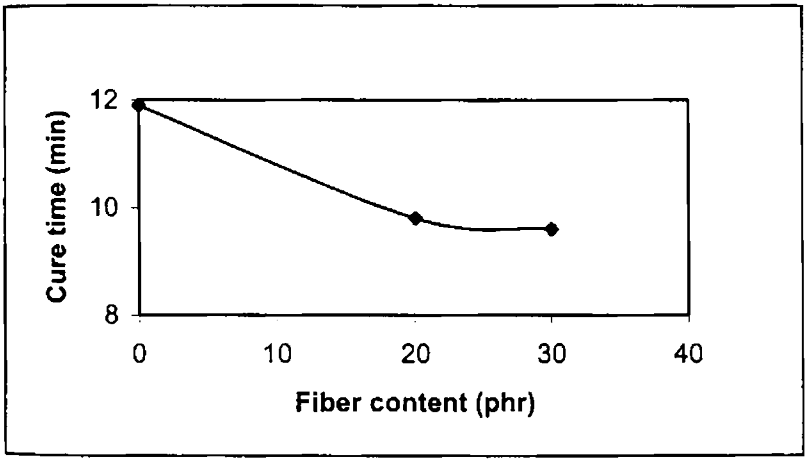

Figure 4.B.4. Variation of cure time with fiber loading.

Figure 4.B.2 shows the variation of (maximum- minimum) torque with fiber loading. The (maximum- minimum) torque shows a linear increase with a minor leveling off at 30 phr, indicating a

more restrained matrix in the case of composites, with increase in fiber content.

Scorch time shows a marginal reduction from 2.5 minutes at 0 phr to 2 minutes at 30 phr (figure 4.B.3.). The cure time is reduced from 11.9 minutes at 0 phr to 9.6 minutes at 30 phr (figure 4.B.4).

The reduced cure time is indicative of increased cure rate as is evident from figure 4.B.5. The cure rate shows a corresponding increase from 0.047 N.m./minute at 0 phr to 0.12 N.m./minute at 30 phr.

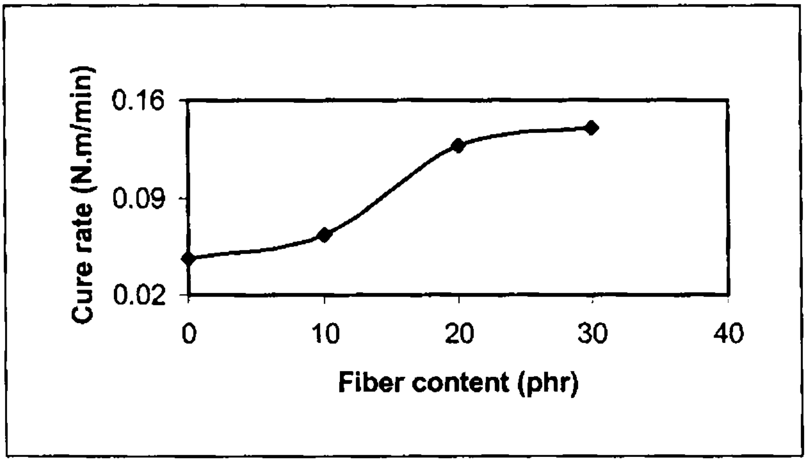

Figure 4.B.5. Variation of cure rate with fiber loading.

4.B.2. Mechanical Properties

The variation of tensile strength with fiber concentration is given in figure 4.B.6. The tensile strength in the longitudinal direction decreases up to 10 phr fiber loading and then gradually increases. At 10 phr the reinforcing effect is insufficient to compensate the dilution effect brought about by the fibers and hence the tensile strength is lower. Since the number of fibers is very small, uniform

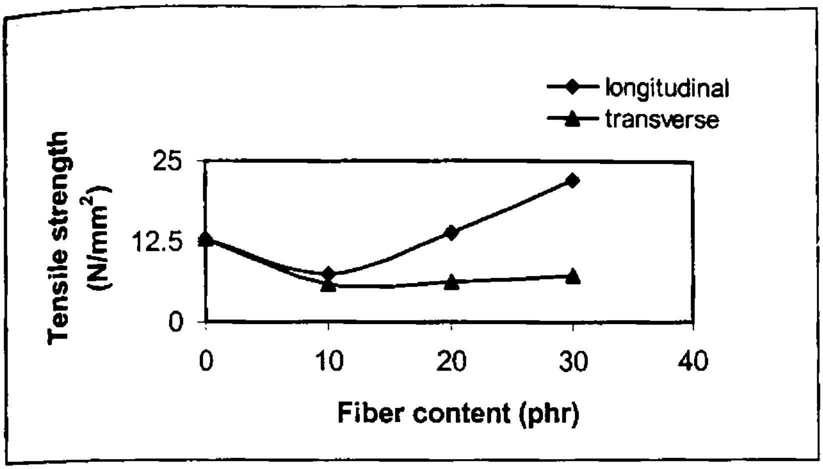

Figure 4.B.6. Variation of tensile strength with fiber loading.

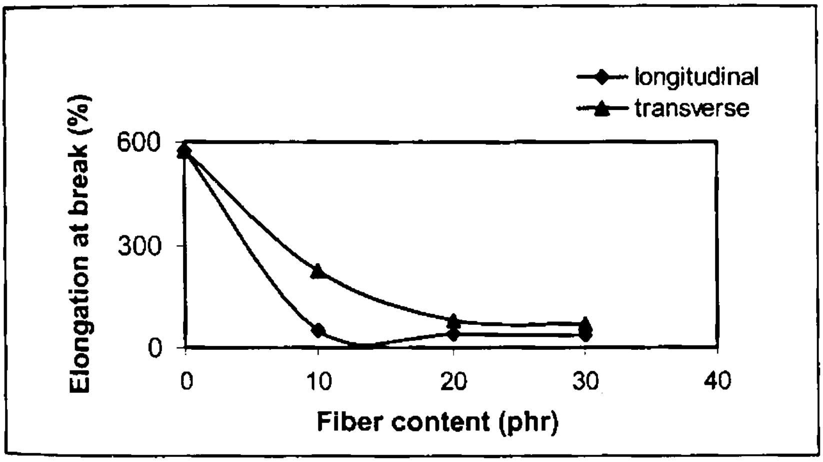

Figure 4.B.7. Variation of elongation at break with fiber loading.

transmission of stress in the matrix does not take place, resulting in localized stress at fiber-matrix interface leading to poor reinforcement. At higher fiber concentrations there are more fibers to hinder the fracture front, and the stress is more evenly distributed. Hence the tensile strength increases with fiber concentration beyond 10 phr. In the transverse direction the tensile strength drops with fiber content up to 10 phr, beyond that it remains somewhat constant. The fibers oriented parallel to the growing front is insufficient in arresting the crack or taking up the load. These observations are similar to the results with other fibers reported by other workers.[1-3]

The elongation at break undergoes a sharp fall on the introduction of fibers figure 4.B.7. But with further fiber loading, the decrease is very small. Elongation at break values of the samples with transversely oriented fibers are higher than that of the samples with longitudinally oriented fibers. The fibers inhibit the orientation of molecular chains and hence the ultimate elongation decreases substantially on introduction of fibers.

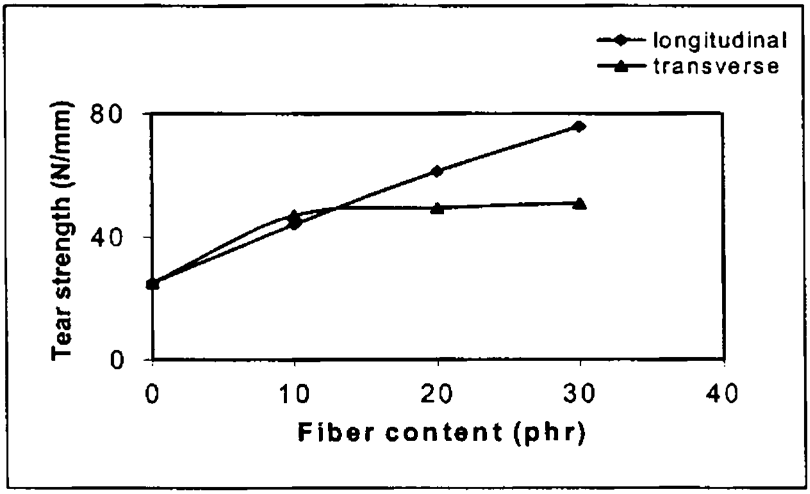

Figure 4.B.8. Variation of tear strength with fiber loading.

The variation of tear strength of the composites with fiber concentration is given in figure 4.B.8. Tear strength shows a continuous increase with increase in fiber content, both in longitudinal and transverse orientation of fibers. As fiber concentration increases there is more and more hindrance to the propagation of crack front. At any given fiber loading, mixes with longitudinal fiber orientation show higher tear strength than mixes with transverse fiber orientation. In the transverse direction fibers are parallel to the crack front, offer less resistance to propagation of tear, and hence the lower tear values than in the longitudinal direction. Similar results have been reported by De and coworkers and by Prasantha Kumar et al.[4-7]

Heat build up shows an increase with increase in fiber concentration as in figure 4.B.9. Heat build up in transverse direction is higher than that in longitudinal direction. In samples with longitudinally oriented fibers, buckling of fibers lead to absorption of greater part of applied stress in stress-strain cycle. There is thus less residual energy to dissipate as heat. In transverse direction, buckling of fibers does not occur, and less amount of applied stress is absorbed leading to generation of more heat.

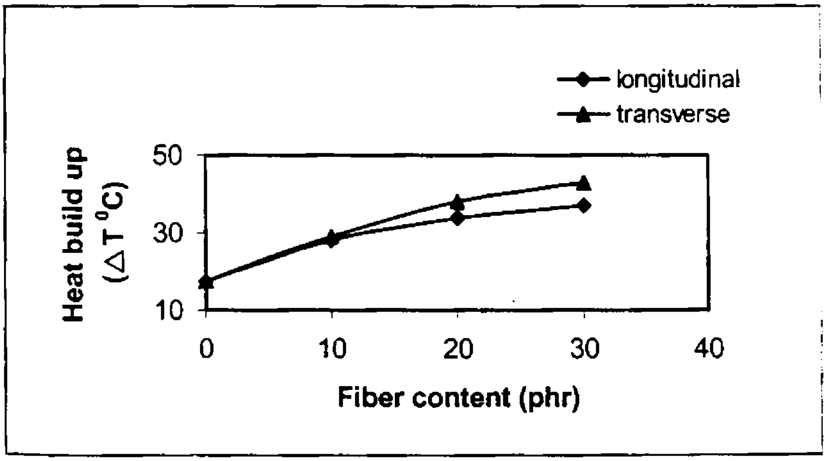

Figure 4.B.9. Variation of heat build up with fiber loading.

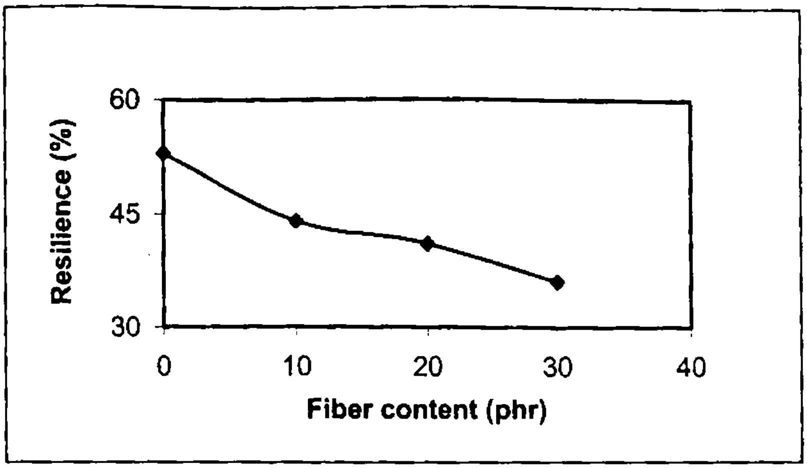

Figure 4.B.10. Variation of resilience with fiber loading.

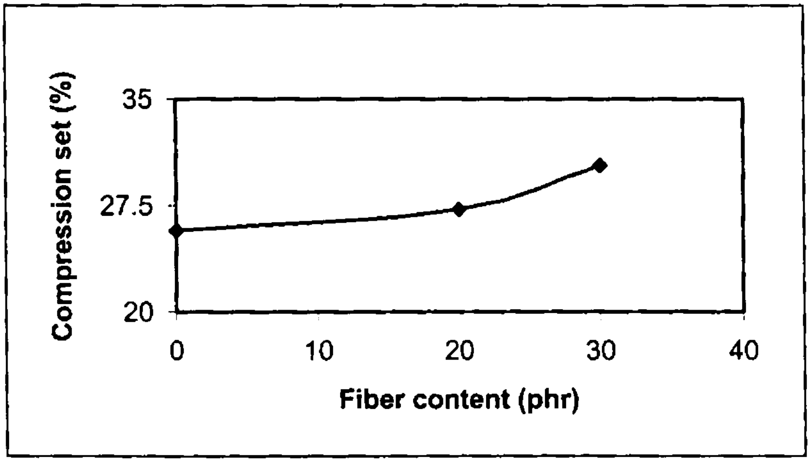

Figure 4.B.11. Variation of compression set with fiber loading.

Rebound resilience, an indication of material elasticity, decreases with fiber content (figure 4.B.10.). This may be attributed to the change of energy loss at the fiber-matrix interface. Higher the fiber loading higher is the interface area and hence higher is the loss of energy.

The compression set values increase with the fiber concentration, as shown in figure 4.B.11. This is in agreement with the decreased resilience values.

Abrasion resistance registers an improvement with increase in fiber content in both longitudinal and transverse orientation of fibers (figure 4.B.12). At higher fiber concentration the loss is marginally higher in the transverse direction than in the longitudinal direction. In transverse direction the fibers get debonded and separated from the matrix more easily than in the longitudinal direction resulting in higher abrasion loss in that direction.

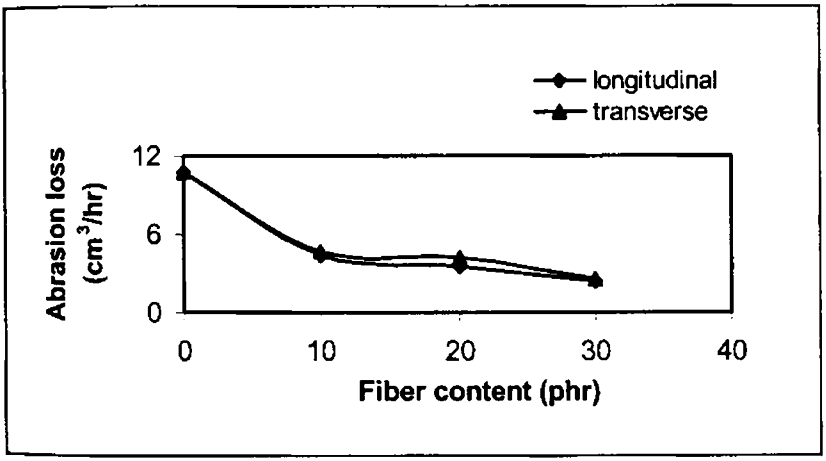

Figure 4.B.12. Variation of abrasion loss with fiber loading.

4.B.3. Ageing Resistance

Table IV.B.2 shows the retention of tensile properties of the composites before and after ageing. In all the cases the retention of tensile strength is found to be better for composites than the blend. The presence of reclaim rubber in the blend makes it more

Table IV.B.2. Tensile strength of the mixes before and after ageing

Mix No	Fiber orientation	Tensile strength (N/mm^2)		Percentage retention
		Before ageing	After ageing	
A		12.9	11.5	89
B	L	7.4	8.8	117
	T	6.0	6.2	104
C	L	13.8	14.7	107
	T	6.2	6.3	103
D	L	22.2	25.8	117
	T	7.3	9.3	128

L - Longitudinal orientation T - Transverse orientation

Table IV.B.3. Elongation at break values of the mixes before and after ageing

Mix No	Fiber orientation	Elongation at break (%)		Percentage retention
		Before ageing	After ageing	
A		576	548	95
B	L	50	46	91
	T	226	222	98
C	L	40	39	97
	T	79	74	94
D	L	38	36	95
	T	70	42	60

L - Longitudinal orientation T - Transverse orientation

prone to degradation, as it mainly consists of natural rubber. Moreover the unreacted reclaiming agents added during reclamation process also may contribute to reduced stability at elevated temperature. The presence of fibers reduces the chances of oxidative degradation reaction by making the matrix rigid and restrained. Hence the composites show marginally higher tensile values after ageing. This is also supported by the lower elongation at break values of the fiber filled samples.

Elongation at break is not much affected by ageing (Table IV.B.3.).

Table IV.B.4 shows retention values of tear strength after ageing. The tear strength shows a marginal increase after ageing. During ageing eventhough the matrix becomes weaker, the improved fiber - matrix interaction results in higher tear strength values.

Table IV.B.4. Tear strength of the mixes before and after ageing

Mix No	Fiber orientation	Tear strength (N/mm)		Percentage retention
		Before ageing	After ageing	
A		24.9	25.3	102
B	L	44.1	46.6	106
	T	47.0	53.4	114
C	L	61.3	71.8	117
	T	49.3	53.6	109
D	L	75.8	85.8	113
	T	50.9	56.7	111

L - Longitudinal orientation T - Transverse orientation

4.B.4. References

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CHAPTER IV.C.

NR/WTR - SHORT NYLON FIBER COMPOSITE WITH BONDING AGENT*

The fiber-matrix interfacial bond is known to play an important role in composites since this interface has a decisive impact on the service properties of the composite. A chemical bonding agent can be used to improve the interfacial bond. Recently, the usage of a urethane resin as bonding agent for short nylon fiber-elastomer composite has been reported[1]. This resin is used in this part of the study as a fiber-matrix interfacial modifier for NR/WTR-short nylon fiber composite. The optimization of the resin composition is done with respect to cure characteristics and mechanical properties. An 80/40 blend of NR/WTR reinforced with 20 phr nylon fiber has been selected for the study (Chapter IV.B.). The amount of resin used was 5 phr and the MDI/PEG ratios used were 0.67:1, 1:1, 1.5:1 and 2:1.

Formulation of the mixes is given in Table IV.C.1. The preparation of the samples and the experimental techniques are explained in Chapter 2.

4.C.1. Cure Characteristics

Figure 4.C.1. shows the variation of minimum torque with MDI/PEG ratio. Minimum torque increases significantly in the MDI-PEG ratio range 0.5-1 beyond which it is almost constant. Increased minimum torque indicates increased stock viscosity implying a marginal loss in the processability of the composite. It may be arising from a low level of urethane resin formation during the processing stage. It is further confirmed by estimating the gel content of the compounded stock before vulcanisation (Table IV.C. 2.). It follows a pattern similar to those of minimum torque values.

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*Results of this Chapter have been accepted for publication in Polym. Plast. Tech. Engg.

Table IV.C.1. Formulation of the mixes

Ingredient (parts by weight)	Mix No.					
	A	B	C	D	E	F
NR	80	80	80	80	80	80
WTR	40	40	40	40	40	40
Nylon short fiber	20	20	20	20	20	20
MDI	0	2	2.5	3	3.33	0
PEG	0	3	2.5	2	1.67	5

Zinc oxide – 4 phr, stearic acid - 2 phr, HS - 1 phr, MBTS - 0.5 phr, TMTD - 1.8 phr and sulfur - 0.3 phr are common to all mixes

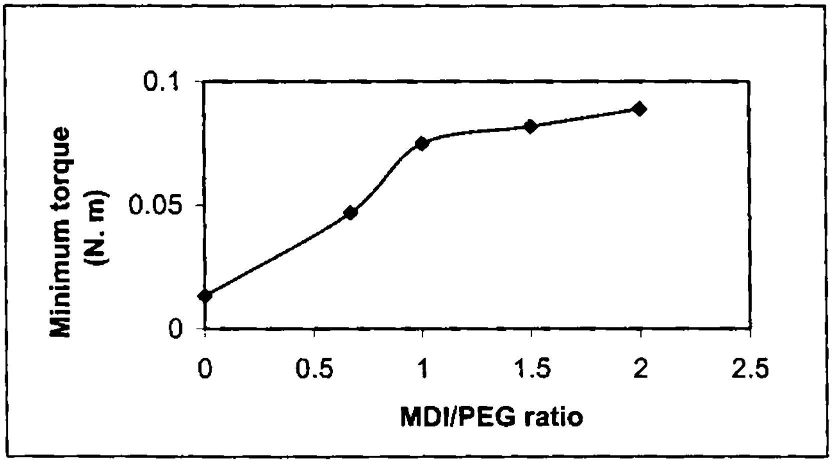

Figure 4.C.1. Variation of minimum torque with MDI/PEG ratio.

The gel content increases sharply up to a MDI/PEG ratio of 1:1 and then tends to stabilize. Beyond the optimum ratio of 1:1 further increase does not seem to contribute to the level of resin formation.

Figure 4.C.2 shows the variation of maximum torque with MDI/PEG ratio. The maximum torque shows a reduction on

introduction of bonding agent but with further increase in isocyanate concentration the values increase. The initial reduction can be attributed to the less effective utilisation of monomer functionalities of the bonding agents. The increased values with further increase in MDI point to a more restrained matrix.

Table IV.C.2. Gel content of the mixes

Mix No.	Gel content (%)
A	31
B	49
C	50
D	51
E	56

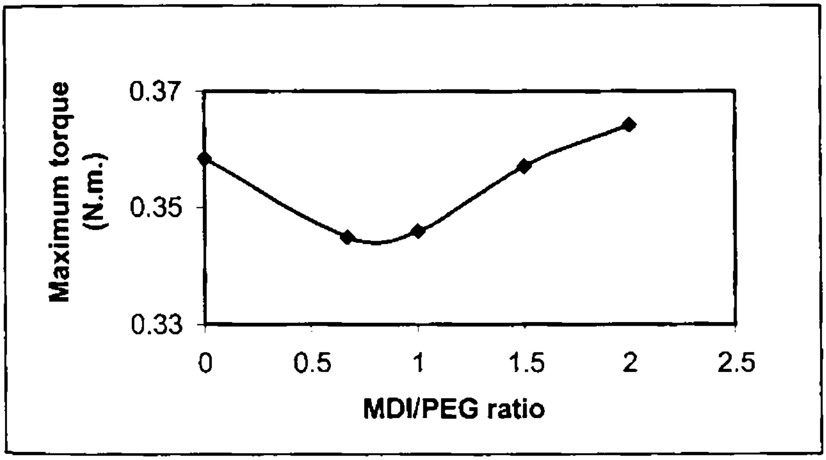

Figure 4.C.2. Variation of maximum torque with MDI/PEG ratio.

The scorch time (figure 4.C.3.) shows a reduction from 2.2 minutes to 1.1 minutes at lower MDI/PEG ratios, where as the cure time (figure 4.C.4.) decreases from 9.8 to 3.6 minutes with MDI/PEG ratio up to 1. With further increase in the MDI/PEG ratio, both

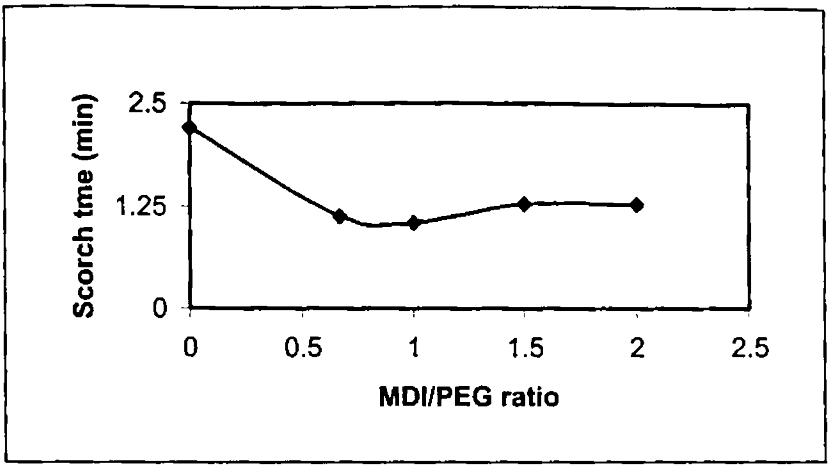

Figure 4.C.3. Variation of scorch time with MDI/PEG ratio.

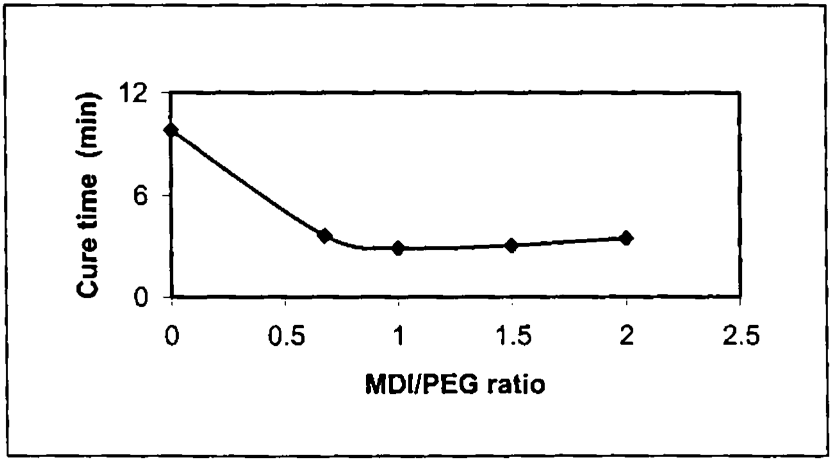

Figure 4.C.4. Variation of cure time with MDI/PEG ratio.

scorch time and cure time are found to stabilize. There is a corresponding increase in cure rate values (figure 4.C.5.). It indicates that the excess free diol groups present at lower

MDI/PEG ratio is accelerating the sulfur cure reaction. The cure time and cure rate of the mixes A & F are given Table IV.C.3. The increased cure rate in the presence of polyethylene glycol confirms that diol groups improve the sulfur cross linking reaction.

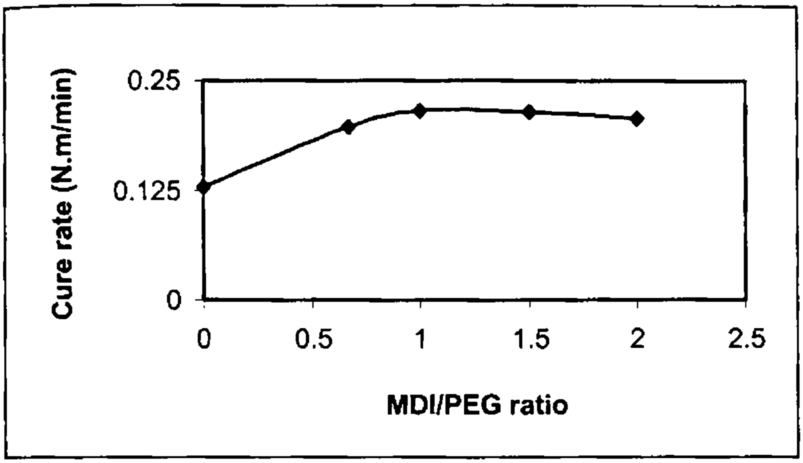

Figure 4.C.5. Variation of cure rate with MDI/PEG ratio.

Table IV.C.3. Cure time and cure rate of mix A & F

Mix No.	cure time (min)	cure rate (N.m/min)
A	9.8	0.1278
F	7.5	0.1292

4.C.2. Mechanical Properties

Figure 4.C.6. shows the variation of tensile strength with isocyanate concentration. Tensile strength in longitudinal direction shows an improvement with increase in MDI/PEG ratio with a marginal reduction at lower MDI concentration. Similar trend is

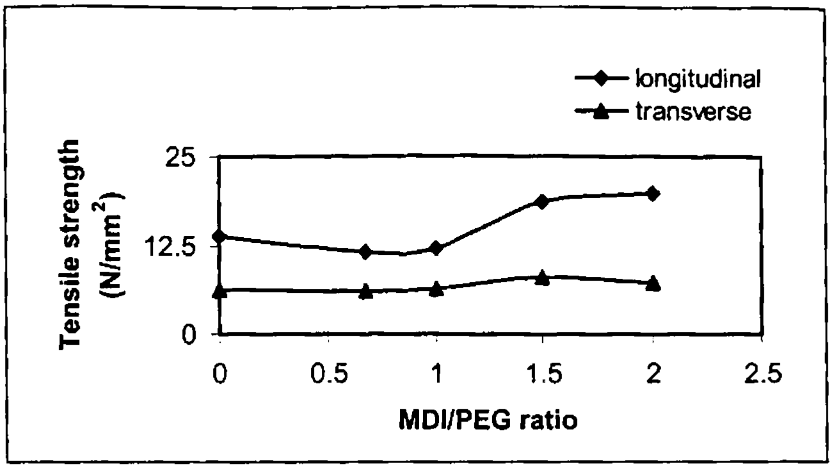

Figure 4.C.6. Variation of tensile strength with MDI/PEG ratio.

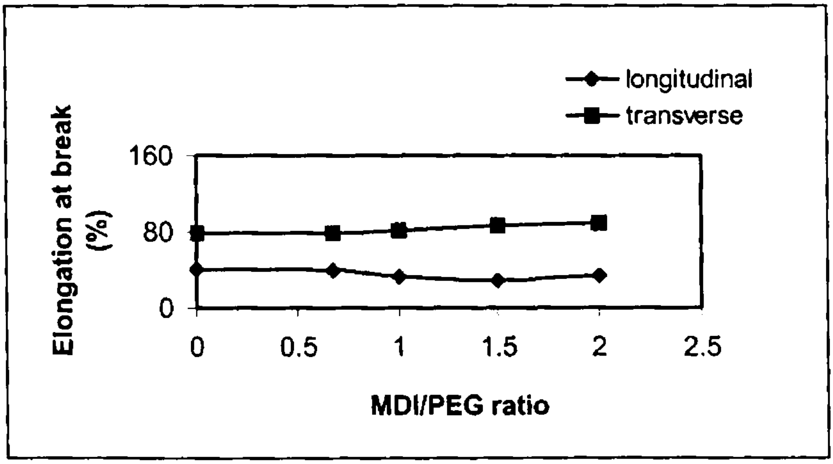

Figure 4.C.7. Variation of elongation at break with MDI/PEG ratio.

seen in transverse direction also, but the effect is less pronounced. The improvement in tensile strength can be attributed to better interfacial bonding, in the presence of urethane resin. Improved interfacial bonding facilitates better load transfer to the reinforcing member and hence better tensile strength.

Figure 4.C.7 shows the variation of elongation at break values with MDI concentration. In the longitudinal direction the elongation at break values decrease with isocyanate concentration, showing a better fiber matrix adhesion in presence of bonding agent. The improved interfacial bond inhibits molecular orientations causing the sample to fail at lower elongations. However in the transverse direction the elongation at break values remain almost constant. This is because, in the transverse orientation, the fibers are less efficient to restrain the matrix and the load is primarily borne by the matrix. Hence improved interfacial bond also does not affect the ultimate elongation significantly.

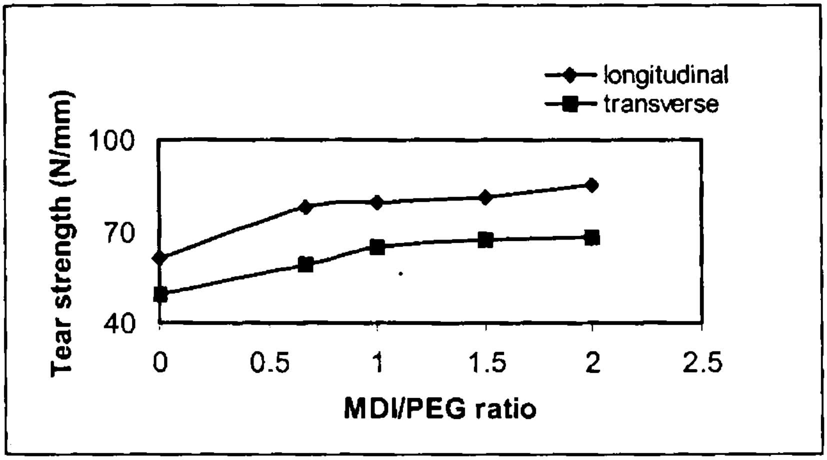

Figure 4.C.8. Variation of tear strength with MDI/PEG ratio.

The variation of tear strength in presence of urethane resin is shown in figure 4.C.8. Both in the longitudinal and in the transverse directions, the tear strength increases with isocyanate concentration, further confirming a better fiber matrix adhesion in presence of urethane resin. Beyond MDI/PEG ratio of 1:1, further increase does not bring about any advantage.

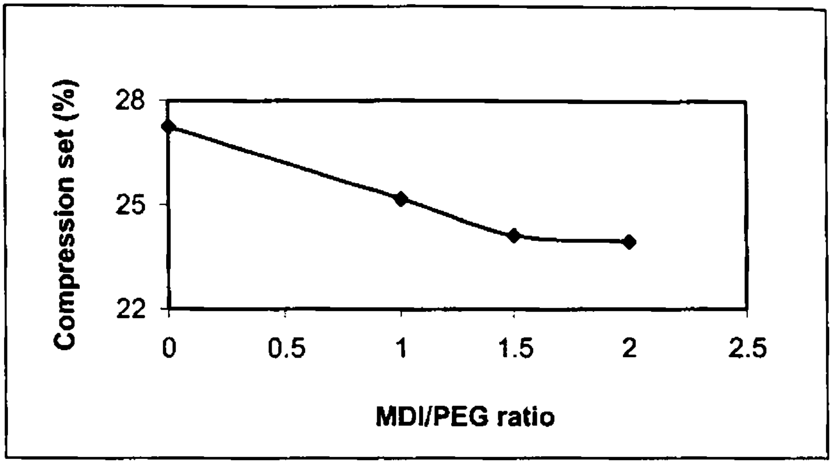

Figure 4.C.9. Variation of compression set with MDI/PEG ratio.

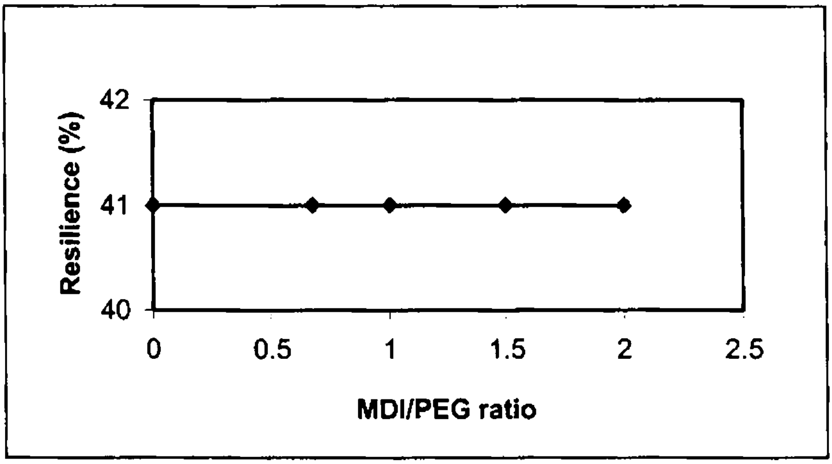

Figure 4.C.10. Variation of resilience with MDI/PEG ratio.

Compression set shows a reduction with increase in isocyanate concentration (figure 4.C.9.). The set decrease by 11% in presence of bonding agent. The interfacial bond formed may prevent the molecular chains from slipping under constant load, thus resulting in lower compression set values.

The resilience values (figure 4.C.10.) remain constant in presence of urethane resin. The resilience test relates to the elasticity of the matrix at very low strain levels. The constant resilience values indicate that the elasticity of the composite at very low extensions is not affected by the presence of bonding agent. Basically it means there is less chance for the load to be transferred to the fibers since the strain level is very small. Hence the improved interfacial bond has no significant effect on the resilience values.

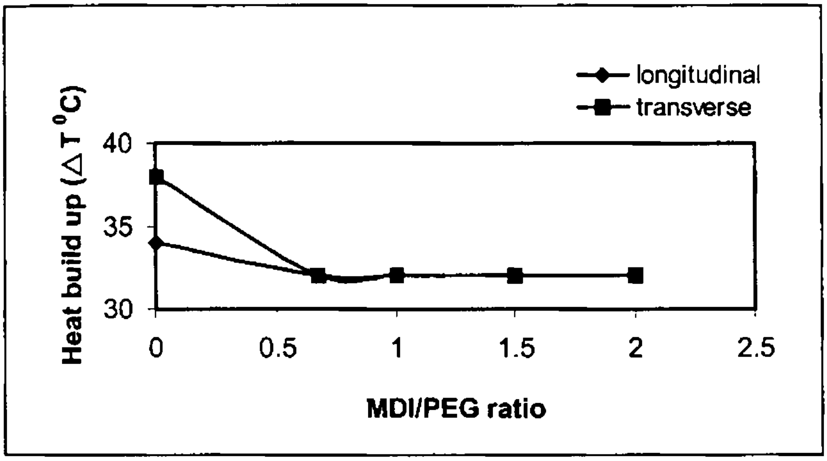

Figure 4.C.11. Variation of heat build up with MDI/PEG ratio.

The heat build up values of the composites in presence of bonding agent is shown in figure 4.C.11. The heat build up decreases on the introduction of bonding agent in both the orientations of fibers. A strong interfacial bond reduces the chances for energy loss at the fiber-matrix interface and hence results in lower heat build up values.

Abrasion loss in both directions decreases with increase in isocyanate concentration (figure 4.C.12.). During abrasion test the matrix as well as the reinforcing fiber are worn out by the abrading surface. A stiffer matrix has lower abrasion loss. In this case the presence of the bonding agent renders the matrix more stiff and lowers the abrasion loss. Similar results have been reported by Ibarra.[2] The almost constant values of abrasion loss for mixes D and E indicates that the optimum MDI/PEG ratio is 1:1.

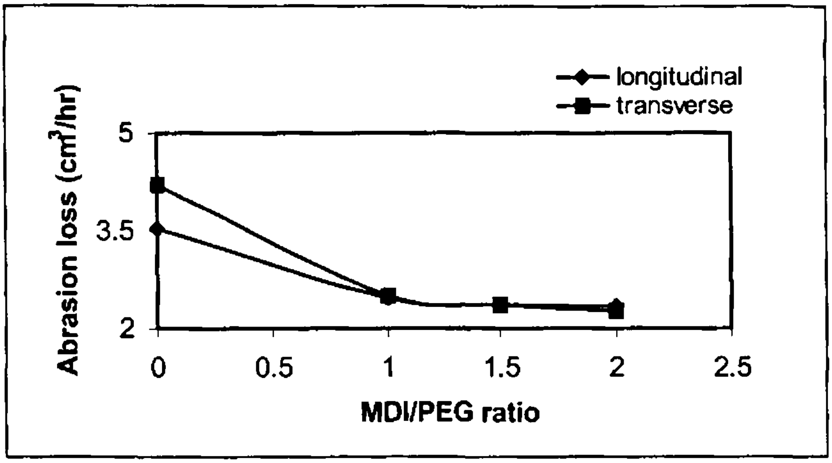

Figure 4.C.12. Variation of abrasion loss with MDI/PEG ratio.

4.C.3. Ageing Resistance

Table IV.C.4 and IV.C.5 show the retention tensile and tear strengths of the composites before and after ageing. The retention of tensile and tear properties are close to 100%. This shows that the bonding agent is not affecting the respond of the composite to ageing at elevated temperature.

Table IV.C.4. Tensile properties of the composites before and after ageing

Mix No.	Fiber orientation	Tensile strength (N/mm^2)		Percentage retention
		Before ageing	After ageing	
A	L	13.8	14.7	106
	T	6.2	6.3	103
B	L	11.5	12.8	111
	T	6.0	6.8	113
C	L	12.1	12.6	103
	T	6.3	7.4	118
D	L	18.6	13.4	72
	T	8.0	7.8	98
E	L	19.9	15.4	77
	T	7.4	8.4	114

L - longitudinal orientation T - transverse orientation

Table IV.C.5. Tear properties of the composites before and after ageing

Mix No.	Fiber orientation	Tear strength (N/mm)		Percentage retention
		Before ageing	After ageing	
A	L	61.3	71.8	117
	T	49.3	53.6	109
B	L	78.1	72.6	93
	T	59.0	55.3	94
C	L	79.7	86.7	109
	T	60.6	67.4	111
D	L	81.2	83.4	103
	T	67.2	68.3	102
E	L	96.3	98.3	102
	T	68.0	67.1	99

L - longitudinal orientation T - transverse orientation

4.C.4. References

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2. Ibarra L., Kaustschuk Gummi Kunststoffe, **48** (12/95) 860.

CHAPTER V.

NBR - WTR BLENDS[*]

NBR, a general purpose synthetic rubber known for its oil resistance is very widely used in such applications as oil delivery hoses, gaskets, etc. A low gum strength rubber with poor mechanical properties NBR is usually compounded with reinforcing fillers. In this chapter the results of a systematic study on the partial substitution of NBR with WTR are discussed.

The formulation of the mixes is given in Table V.1. The details of sample preparation, cure characteristics determination, moulding and determination of mechanical properties are given in Chapter 2.

Table V.1. Formulation of the mixes

Ingredient	Mix No.				
	A	B	C	D	E
NBR	100	90	80	70	60
Reclaim	-	20	40	60	80

Zinc oxide - 4 phr, Stearic acid - 2 phr, HS - 1 phr, MBTS - 0. 5 phr, TMTD - 1. 8 phr & Sulfur - 0. 3 phr are common to all mixes

5.1. Cure Characteristics

The minimum torque values (figure 5.1.) show an increase at 20 parts of reclaim loading, beyond which it decreases. The initial increase can be attributed to the filler content of the reclaimed rubber. The reclaim contains about 39% of carbon black in addition to the plasticising oil. At higher reclaim loading the effect of plasticiser present in the reclaim becomes more predominant and the minimum torque values decrease.

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[*] Results of this Chapter have been communicated for publication in J. Elastomers Plast.

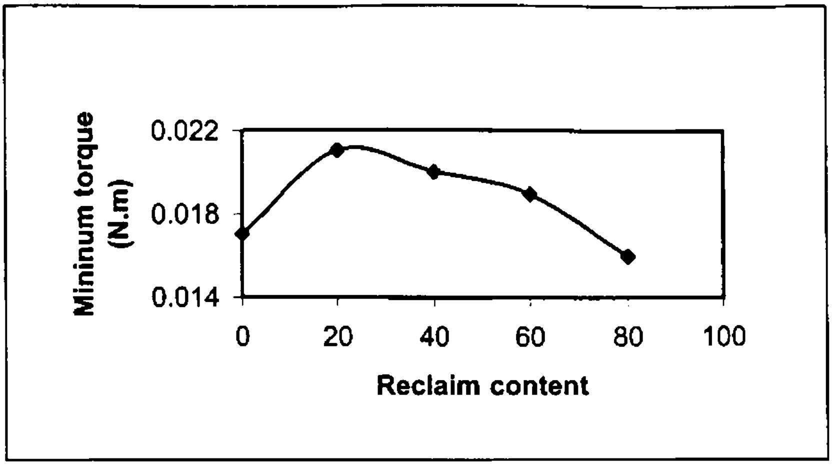

Figure 5.1. Variation of minimum torque with reclaim loading.

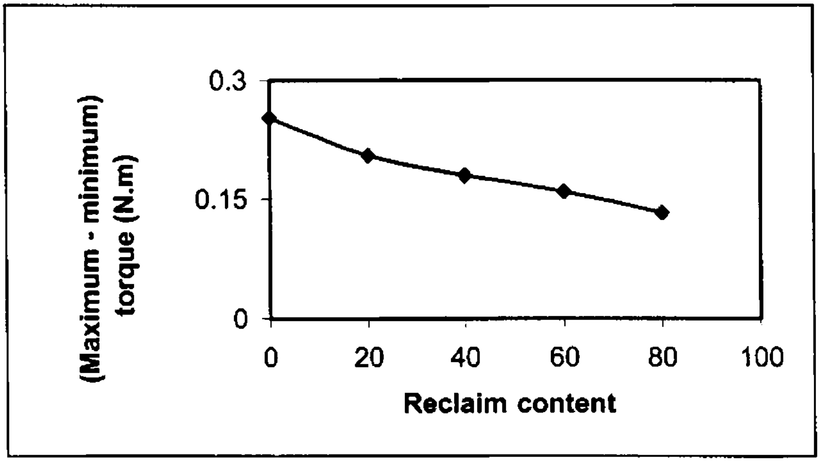

Figure 5.2. Variation of (maximum – minimum) torque with reclaim loading.

The (maximum – minimum) torque values show a linear decrease with increase in reclaim content (figure 5.2.), which can be

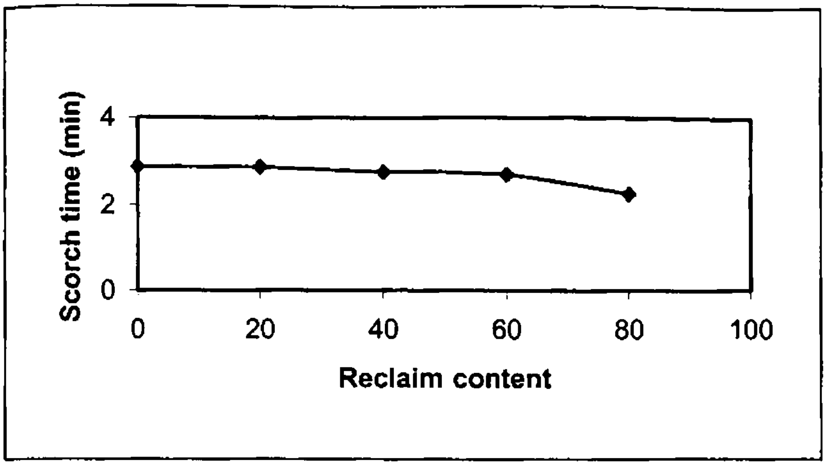

Figure 5.3. Variation of scorch time with reclaim loading.

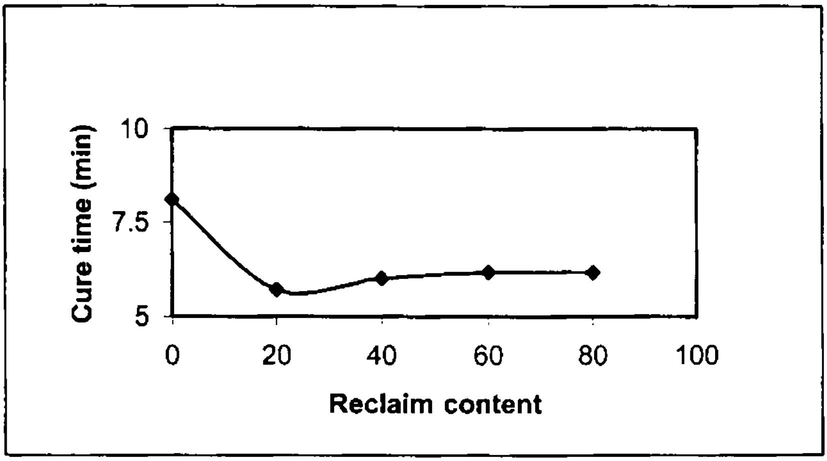

Figure 5.4. Variation of cure time with reclaim loading.

attributed to the excess oil present in the reclaim. There is about 13% oil in the reclaim, as indicated by the acetone extract (Chapter 2). The lower molecular weight of the reclaimed rubber also contributes to the lower (maximum – minimum) torque values.

Variation of scorch time with reclaim content is shown in figure 5.3. The scorch time is more or less constant with only a marginal reduction at very high reclaim content. However the cure time is drastically reduced even at 20 parts of reclaim loading (figure 5.4.). For mixes C-E, the cure time values are almost constant. The consistently lower cure times of the blends, compared to the gum compound can be attributed to the presence of unreacted curatives present in the reclaim. However there is no corresponding increase in the cure rate (figure 5.5.). This may be attributed to the fact that as reclaim content in the blend increases, there is a corresponding reduction in the reactive sites for cross linking as the reclaimed rubber is partially crosslinked.

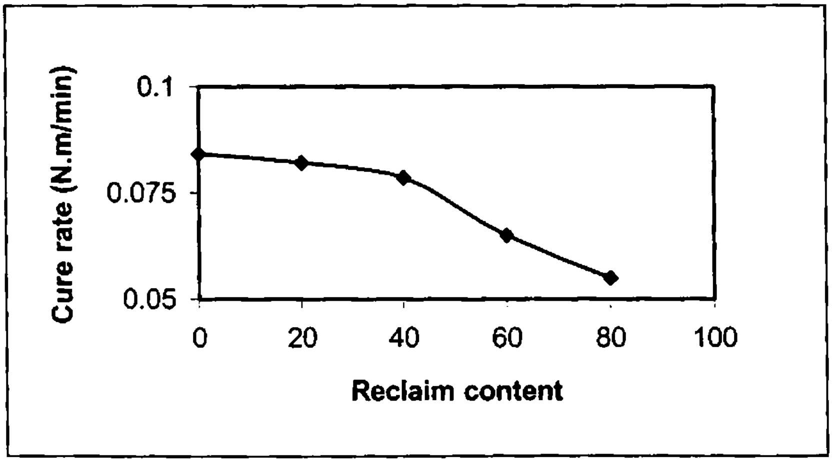

Figure 5.5. Variation of cure rate with reclaim loading.

5.2. Mechanical Properties

The variation of tensile strength with the addition of reclaimed rubber is shown in figure 5.6. The tensile strength shows an almost linear increase with increasing reclaim content. This is in contrast

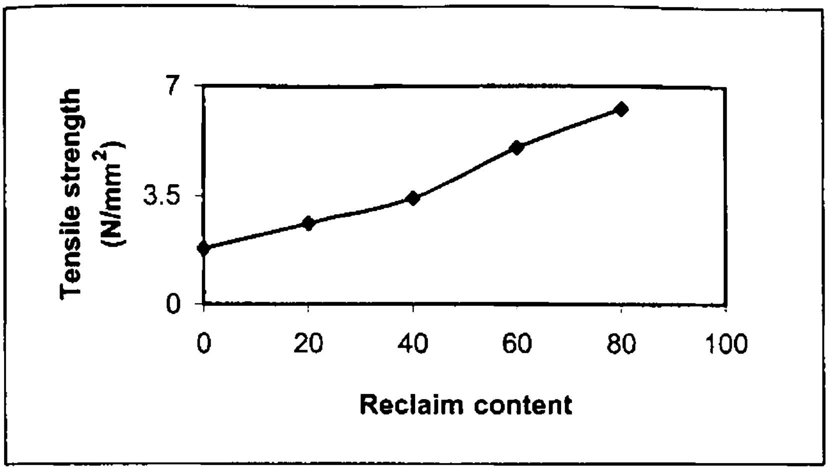

Figure 5.6. Variation of tensile strength with reclaim loading.

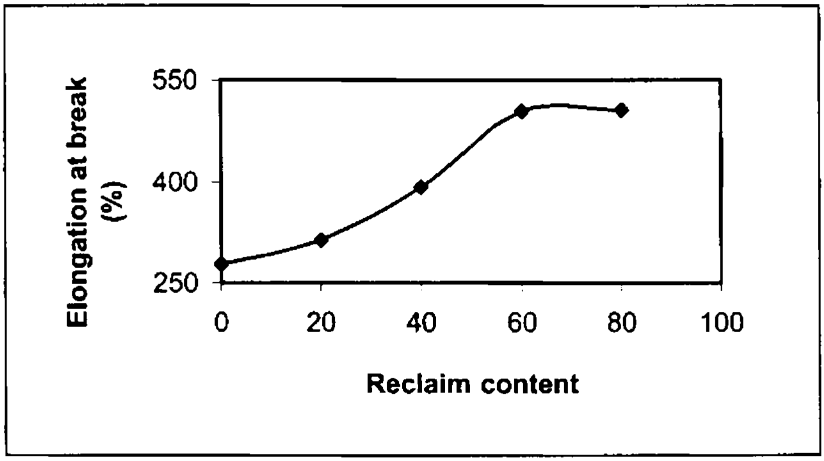

Figure 5.7. Variation of elongation at break with reclaim loading.

to the results obtained in the case of NR-reclaimed rubber blends (Chapter III). The difference can be attributed to the non-crystallizing nature of the NBR, which gives it poor gum strength.

The presence of reinforcing filler in the reclaim rubber can contribute to the tensile strength of NBR. In the case of NR-reclaim blend, the low gum strength reclaim causes more of dilution of the NR matrix than reinforcement.

The elongation at break values (figure 5.7.) show an increase from 278% at 0 parts to 506% at 80 parts of reclaim content. The increase in reclaim content can be attributed to the increasing amount of oil in the case of blends.

The tear strength values remain somewhat constant at all reclaim loading (figure 5.8.). The expected increase in tear strength values due to the presence of reinforcing black might have been offset by the lower molecular weight of reclaimed rubber.

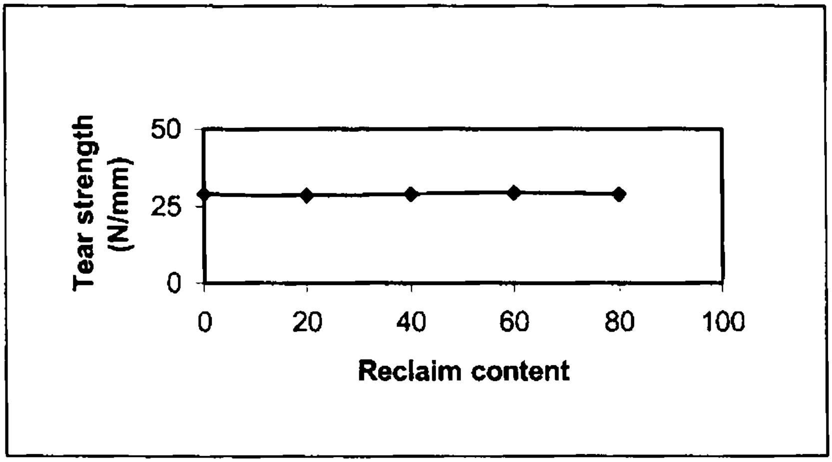

Figure 5.8. Variation of tear strength with reclaim loading.

Figure 5.9 shows the heat generation values of the mixes. There is a gradual increase in heat build up values in the case of blends. Higher the concentration of filler, higher is the chances of energy dissipation as heat. The energy dissipation can be through loss at filler – matrix interface, friction between the chains and breakdown of filler structure. This will be manifested as lower resilience values. As given in figure 5.10, the resilience values show a linear decrease with increasing reclaim content.

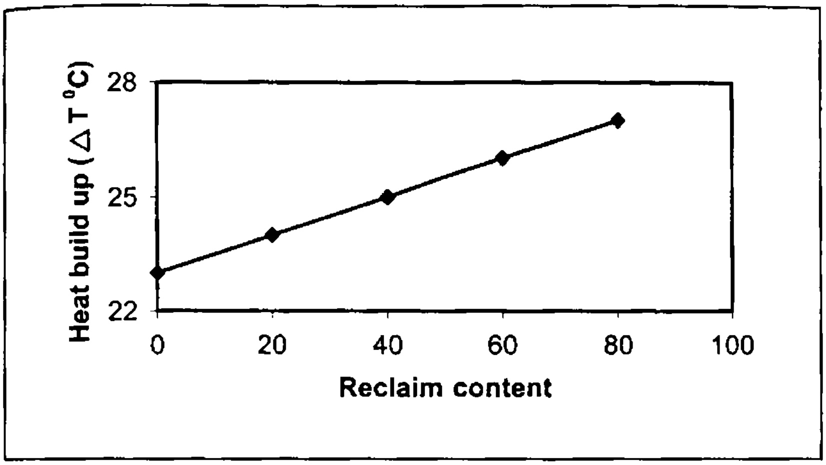

Figure 5.9. Variation of heat build up with reclaim loading.

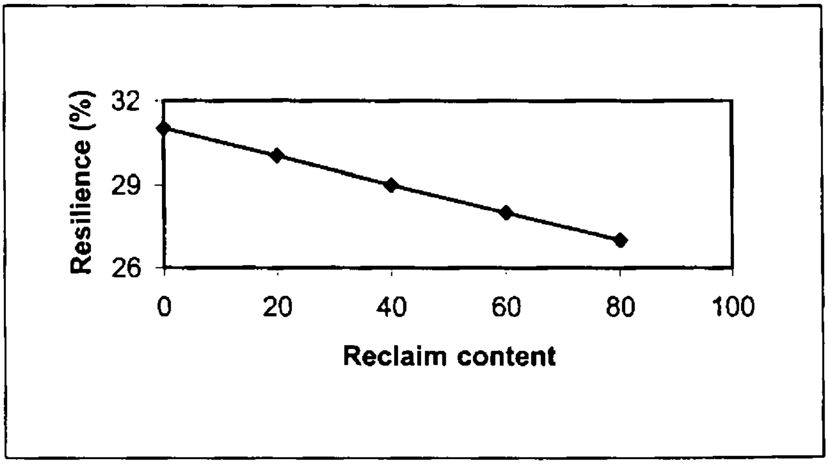

Figure 5.10. Variation of resilience with reclaim loading.

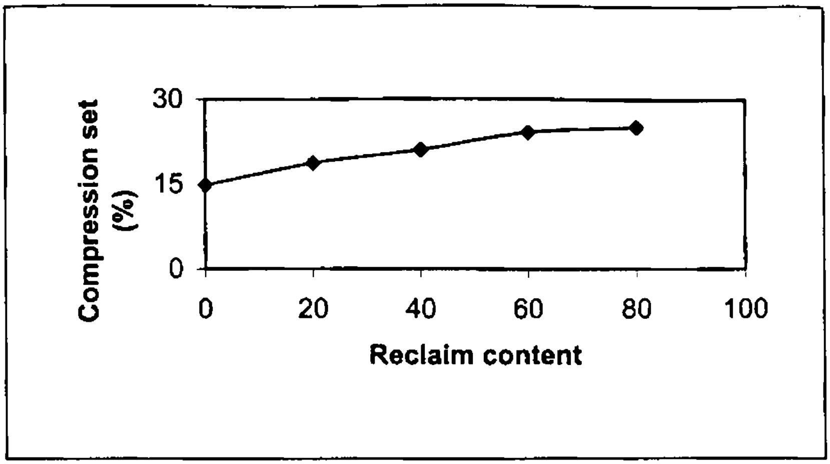

Figure 5.11. Variation of compression set with reclaim loading.

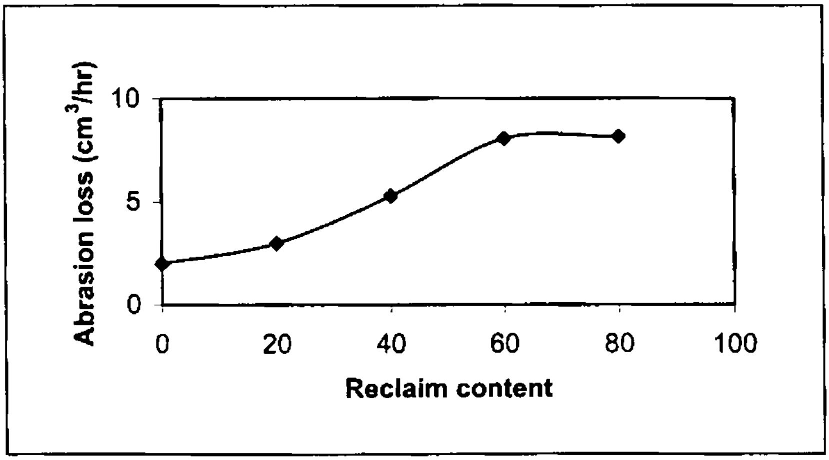

Figure 5.12. Variation of abrasion loss with reclaim loading.

Figure 5.11 shows variation of compression set at constant strain. The compression set increase with increase in reclaim loading. This is in agreement with the observed reduced resilience and increased hysteresis loss. Similar results have been reported by

Phadke et al.[1]

Figure 5.12 gives the abrasion loss of the blends containing different amounts of reclaimed rubber. The abrasion loss shows an increase with increase in reclaim content. The abrasion is a phenomenon involving tear and hysteresis. Even though the tear resistance is almost constant, the hysteresis is increasing. This, combined with relatively lower molecular weight of the reclaimed rubber, results in increased abrasion loss. Similar results have been reported in the case of NR/reclaimed rubber blends.[2]

5.3. Ageing Resistance

Table V.2. Tensile properties of the mixes before and after ageing

Mix No	Tensile strength (N/mm^2)		Percentage retention
	Before ageing	After ageing	
A	1.8	2.2	120
B	2.6	2.3	89
C	2.6	2.5	92
D	5.0	4.7	94
E	6.3	5.7	91

Table V.2 gives the tensile properties of mixes before and after ageing. All mixes except the gum compound shows lower tensile strength values after ageing. The percentage retention in the case of the gum compound (mix A) is 120%. This shows that the state of cure is improved while ageing. However in the presence of reclaimed rubber in the blends there is some extent of degradation. This may be attributed to the fact that the reclaim mainly consists of natural rubber and it is more prone to degradation under elevated temperature.

Table V.3. Tear properties of the mixes before and after ageing

Mix No	Tear strength (N/mm)		Percentage retention
	Before ageing	After ageing	
A	28.9	21.5	74
B	28.5	21.0	74
C	28.7	21.5	75
D	29.2	22.8	78
E	28.8	24.4	85

Table V.4. Elongation at break values of the mixes before and after ageing

Mix No	Elongation at break (%)		Percentage retention
	Before ageing	After ageing	
A	278	292	105
B	312	285	91
C	391	324	83
D	504	451	90
E	506	490	97

Tear strength values before and after ageing is shown in Table. V.3. The aged values are found to be lower than that of the unaged one at all cases. This may be arising out of the fact that the tear strength is better when the compound is slightly under cured.

The elongation at break values of the blends after ageing is lower than that of the unaged samples (Table V.4.).

5.4. References

1. Phadke A.A., Chakraborty S.K. and De S.K., Rubber Chem. Technol., **57** (1984) 19.
2. Phadke A.A., Bhattacharya A.K., Chakraborty S.K. and De S.K., Rubber Chem. Technol., **56** (1983) 726.

CHAPTER VI.A.

NBR - SHORT NYLON FIBER COMPOSITES*

In this chapter cure characteristics and mechanical properties of short nylon fiber-NBR composites are discussed. The fiber concentration varies from 0-30 phr.

The formulation of the mixes is given in Table VI.A. The methods of sample preparation and the experimental techniques employed are described in Chapter 2.

Table VI.A1. Formulation of the mixes

Ingredient	Mix No			
	A	B	C	D
NBR	100	100	100	100
Short nylon fiber	0	10	20	30

Zinc oxide – 4 phr, Stearic acid – 2 phr, HS – 1 phr, MBTS - 0.5 phr, TMTD - 1.8 phr & Sulfur - 0.3 phr are common to all mixes

6.A.1. Cure Characteristics

The variation of minimum torque with fiber loading is shown in figure 6.A.1. The minimum torque increases linearly with increase in fiber concentration, indicating that the processability of the composite is adversely affected by the introduction of fibers.

Figure 6.A.2 shows the variation of (maximum – minimum) torque values of the composites. The (maximum – minimum) torque values increase from 0.253 N.m. at 0 phr to 0.489 N.m at 30 phr fiber, indicating a more restrained matrix in the case of composites.

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*Results of this Chapter have been communicated for publication in J. Elastomers Plast.

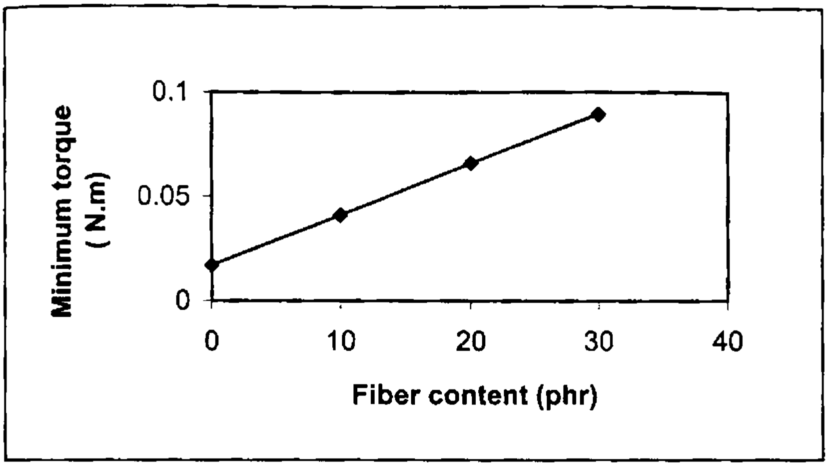

Figure 6.A.1. Variation of minimum torque with fiber loading.

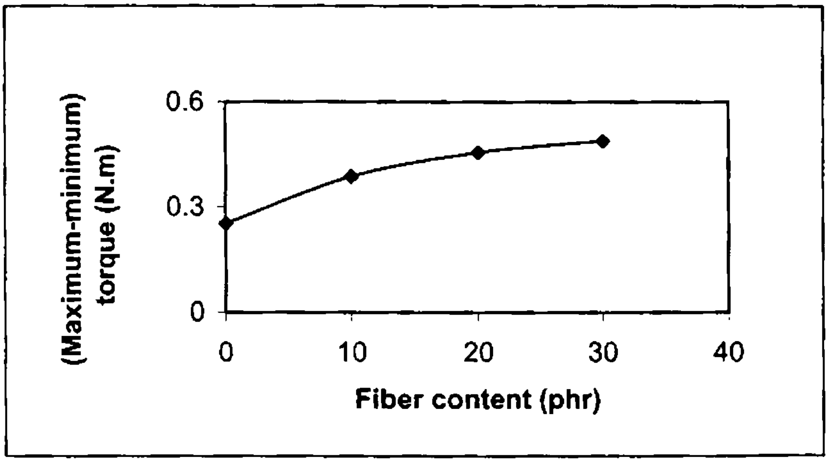

Figure 6.A.2. Variation of (maximum – minimum) torque with fiber loading.

Scorch time shows a reduction from 2.85 minutes at 0 phr to 2.1 minutes at 30 phr (figure 6.A.3.). Cure time is reduced from 8

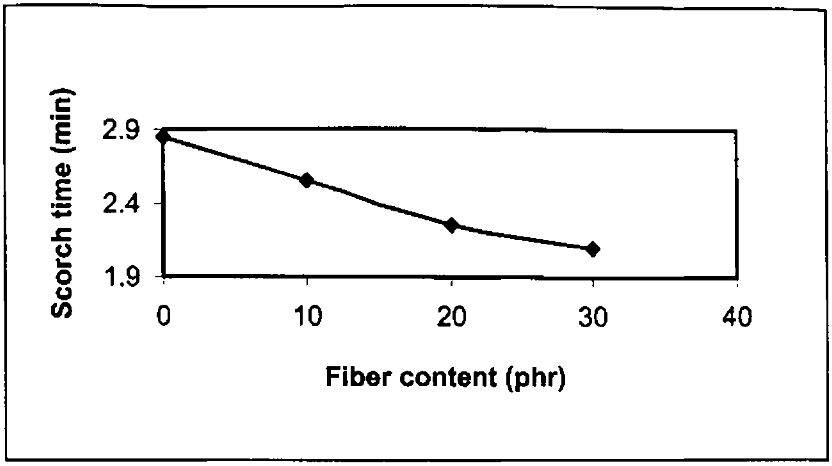

Figure 6.A.3. Variation of scorch time with fiber loading.

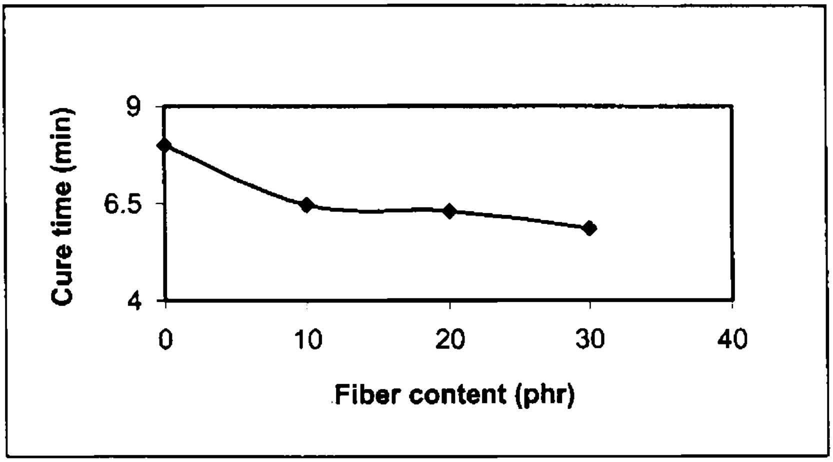

Figure 6.A.4. Variation of cure time with fiber loading.

minutes at 0 phr to 5.85 minutes at 30 phr (figure 6.A.4.). The reduced cure time is accompanied by the increased cure rate values (figure 6.A.5.). The cure rate values increase from 0.0842

N.m/minute at 0 phr to 0.2256 N.m/minute at 30 phr. That both the scorch time and cure time are reduced indicates that the presence of short nylon fibers is accelerating the cure reaction. This may be attributed to the possible generation of amines from nylon fibers by degradation at the curing temperature.

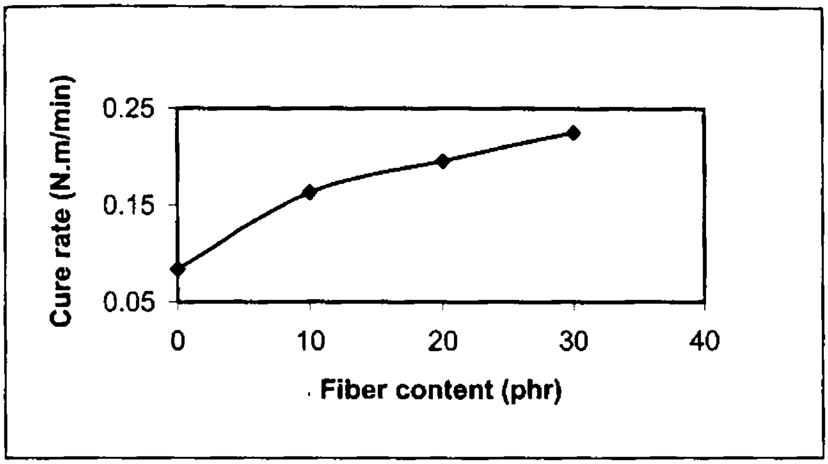

Figure 6.A.5. Variation of cure rate with fiber loading.

6.A.2. Mechanical Properties

Figure 6.A.6 shows the variation of tensile strength of NBR with different fiber content. The tensile strength is found to increase linearly with increase in fiber loading. This is in contrast to the pattern observed for short nylon fiber-NR composites (Chapter IV.A), where the tensile strength-fiber loading relationship was non-linear with a minimum at lower fiber concentrations. This arises mainly from the fact that NR matrix has a high gum strength arising out of strain induced crystallization where as NBR has relatively lower gum strength. In a matrix with very high gum strength, the presence of low levels of fillers causes a dilution effect rather than a reinforcing effect. This is not applicable in the case of NBR and hence the variation is linear. At any given fiber loading, mixes with longitudinal fiber orientation show higher

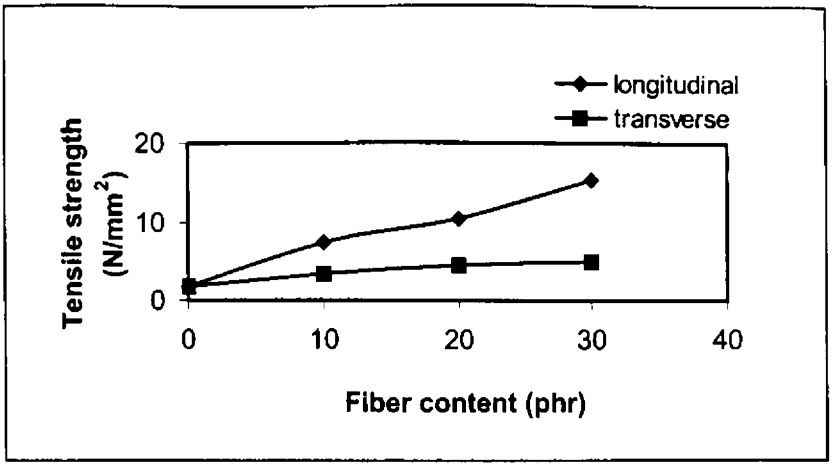

Figure 6.A.6. Variation of tensile strength with fiber loading.

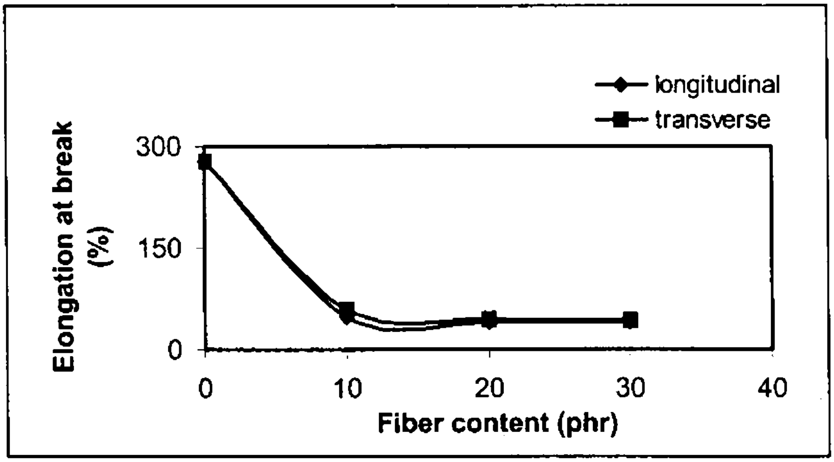

Figure 6.A.7. Variation of elongation at break with fiber loading.

tensile strength than mixes with transversely oriented fibers. The growing crack can easily pass through the fiber matrix interfaces when the fibers are oriented transversely facilitating easy failure of the sample, resulting in lower tensile strength. Similar results have been obtained in the case of SBR-short jute fiber composites.[1]

The ultimate elongation shows a sharp fall on the introduction of fibers (figure 6.A.7.). But with further increase, the values tend to stabilize. In the presence of short fibers, the matrix is more restrained and the failure is initiated at multiple points, resulting in lower ultimate elongation values. Similar results have been obtained with NR-short jute fiber composites.[2]

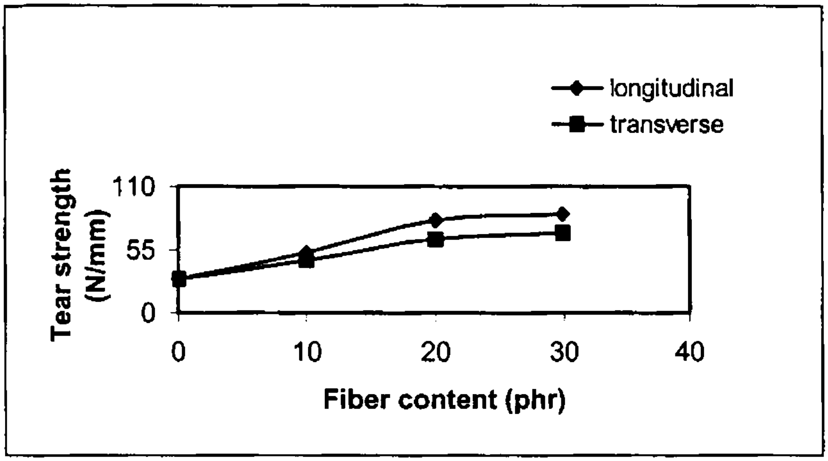

Figure 6. A.8. Variation of tear strength with fiber loading.

Tear strength is found to increase with fiber content in both the orientations of fibers (figure 6.A.8.). As fiber concentration increases, there is more and more hindrance to the propagating tear by the fibers and hence the improvement in tear strength. The tear strength values are higher in the longitudinal direction at all fiber loadings. In the case of transversely oriented fibers, most of them being parallel to the propagating crack front, offer less resistance to propagating tear and hence lower tear strength values. This is similar to the results reported earlier.[3,4]

The heat build up values of the composites are given in figure

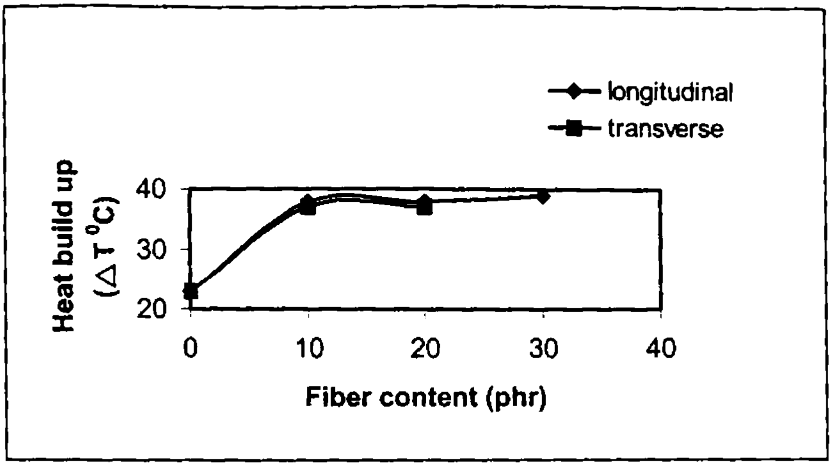

Figure 6.A.9. Variation of heat build up with fiber loading.

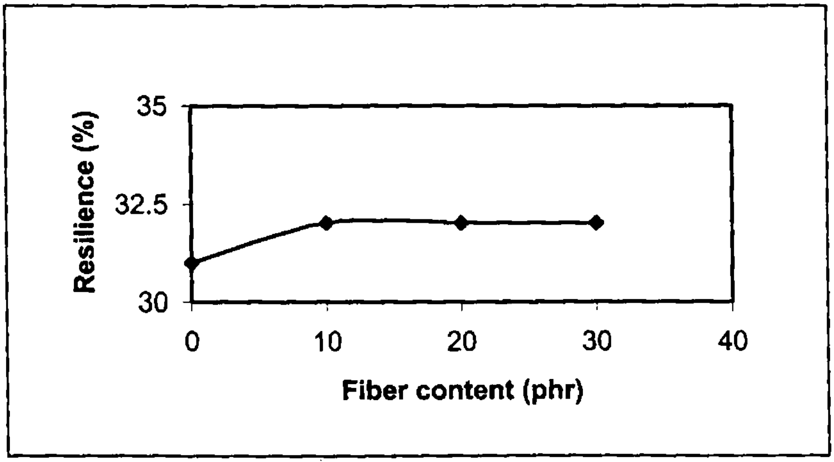

Figure 6.A.10. Variation of resilience with fiber loading.

6.A.9. The heat build up values in both the orientations of fibers increase with fiber content. At all fiber loadings, the heat build up is higher for the longitudinally oriented fiber samples than the samples with fibers oriented transversely. The higher heat generation in the longitudinally oriented fiber samples can be attributed to higher stiffness of the samples in that direction. In the case of 30 phr fiber loaded sample, fibers oriented transversely to the direction of strain, the crack generated inside could grow fast along the fiber-matrix interface as the matrix was soft. This resulted in the premature failure of the sample at 30 phr.

Resilience shows a marginal improvement on introduction of fibers (figure 6.A.10.). But with further increase in fiber loading, it remains unchanged. This may be attributed to the relatively lower elasticity of the gum compound. The acrylonitrile part of the NBR contributes to the lower resilience of NBR. The short fibers restrain the matrix and the resilience is improved marginally.

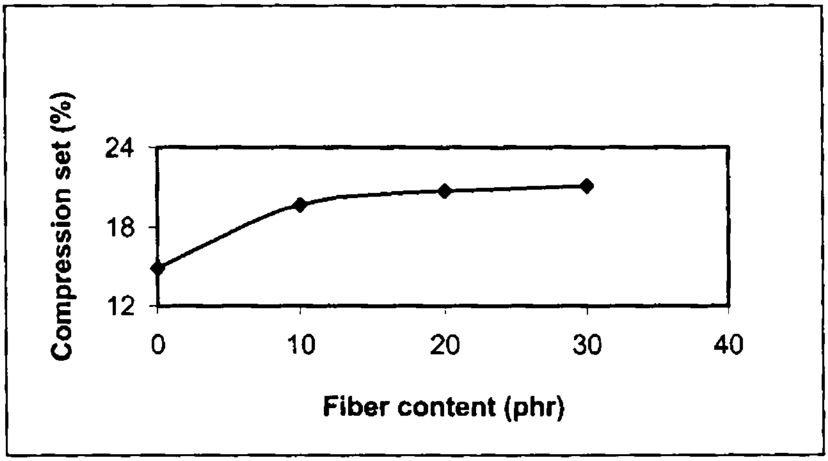

Figure 6.A.11. Variation of compression set with fiber loading.

Compression set increased with increase in fiber concentration (figure 6.A.11.). This trend is in contrast to the pattern observed in the case of resilience. This is because, the compression set test is conducted at elevated temperature where as the resilience is a room temperature test.

The abrasion resistance registers an improvement with increasing fiber loading (figure 6.A.12.). This is due to the more restrained matrix in the case of composite. Abrasion loss is found to be higher in the case of transversely oriented specimens. In transverse direction the fibers get debonded and separated from the matrix more easily than in samples with transversely oriented fibers while being abraded through the abrader surface.

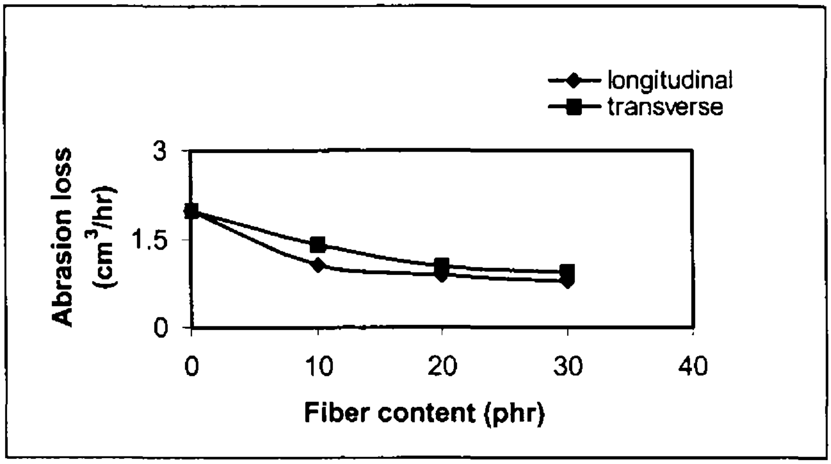

Figure 6.A.12. Variation of abrasion loss with fiber loading.

6.A.3. Ageing Resistance

The percentage retention of tensile properties of the composites is given in Table VI.A.2. All the compounds show more than 100% retention after ageing. This means that the property has improved on ageing. This can be attributed to a post curing effect as the cure pattern of NBR is a marching cure. The fiber filled mixes (mixes B-D) show retention values higher than that of the gum compound. This indicates an improvement in the fiber matrix interfacial bond during the ageing.

The elongation at break values of all the mixes are affected only marginally by ageing (Table VI.A.3.).

Table VI.A.2. Tensile properties of the mixes before and after ageing

Mix No	Orientation	Tensile strength (N/mm^2)		Percentage retention
		Before ageing	After ageing	
A		1.8	2.2	120
B	L	7.3	11.2	154
	T	3.3	3.8	114
C	L	10.4	12.8	123
	T	4.5	6.0	135
D	L	14.3	16.4	117
	T	5.0	6.2	123

L - Longitudinal orientation T - Transverse orientation

Table VI.A.3. Elongation at break values of the mixes before and after ageing

Mix No	Orientation	Elongation at break (%)		Percentage retention
		Before ageing	After ageing	
A		278.0	292.0	105
B	L	49.0	52.4	107
	T	58.8	61.9	105
C	L	41.6	41.3	99
	T	43.9	37.4	85
D	L	40.1	43.2	108
	T	41.8	41.3	99

L - Longitudinal orientation T - Transverse orientation

The tear resistance of the gum compound (mix A) is reduced while that of all the fiber filled mixes (mixes B-D) is improved by ageing at elevated temperature (Table VI.A.4.). This is because, the tear resistance of an elastomer is better when the matrix is slightly under cured. Since ageing leads to further curing in the case of NBR, the tear resistance of mix A is lowered after ageing. For the fiber filled samples, since the fibers compensate for such losses with interfacial bonding that is improved during ageing, the retention values are better.

Table VI.A.4. Tear properties of the mixes before and after ageing.

Mix No	Orientation	Tear strength (N/mm)		Percentage retention
		Before ageing	After ageing	
A		28.9	21.5	74
B	L	52.2	71.3	136
	T	45.3	48.2	107
C	L	80.3	87.2	108
	T	64.3	66.8	104
D	L	86.6	92.1	106
	T	70.2	75.2	107

L - Longitudinal orientation T - Transverse orientation

6.A.4. References

1. Murty V.M. and De S.K., J. Appl. Polym. Sci., **29** (1984) 1355.
2. Murty V.M. and De S.K., Rubber Chem. Technol., **55** (1982) 287.
3. Senapati A.K., Kutty S.K.N., Pradhan B. and Nando G.B., Int. J. Polym. Mater., **12** (1989) 203.
4. Akthar S., De P.P. and De S.K., J. Appl. Polym. Sci., **32** (1986) 5123.

CHAPTER VI.B.

NBR/WTR - SHORT NYLON FIBER COMPOSITES*

In this chapter the effect of short nylon fibers on NBR/WTR blend is given. A 90:20 blend of NBR:WTR was selected (Chapter V) and the effect of fiber loading on the cure characteristics and mechanical properties of the composite was investigated. The fiber loading was varied from 0-30 phr. The anisotropy in mechanical properties have also been studied.

The formulation of the mixes is given in Table VI.B. Sample preparation and the determination of cure characteristics and mechanical properties are given in Chapter 2.

Table VI.B. 1. Formulation of the mixes

Ingredient	Mix No.			
	A	B	C	D
NBR	90	90	90	90
WTR	20	20	20	20
Nylon short fibers	0	10	20	30

Zinc oxide - 4 phr, Stearic acid - 2 phr, - HS - 1 phr, MBTS - 0. 5 phr, TMTD - 1. 8 phr & Sulfur - 0. 3 phr are common to all mixes

6.B.1. Cure Characteristics

Figure 6.B.1 shows the variation of minimum torque with fiber loading. The minimum torque increases from 0.021 N.m. at 0 phr

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*Results of this Chapter have been accepted for publication in Int. J. Polym. Mater.

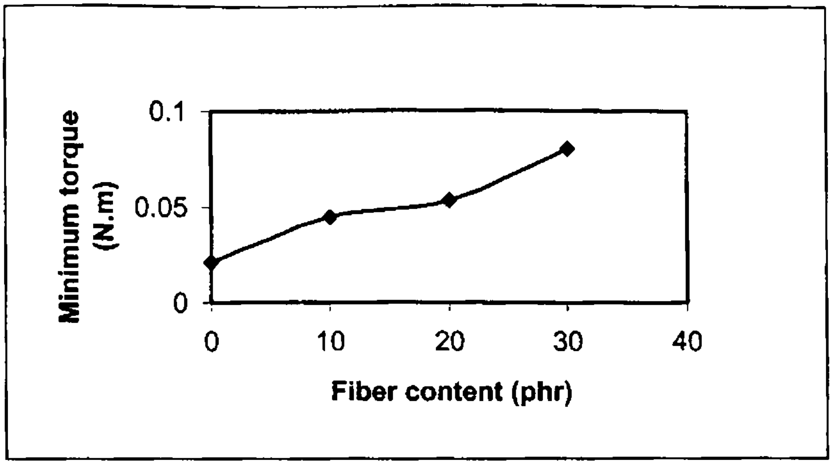

Figure 6.B.1. Variation of minimum torque with fiber loading.

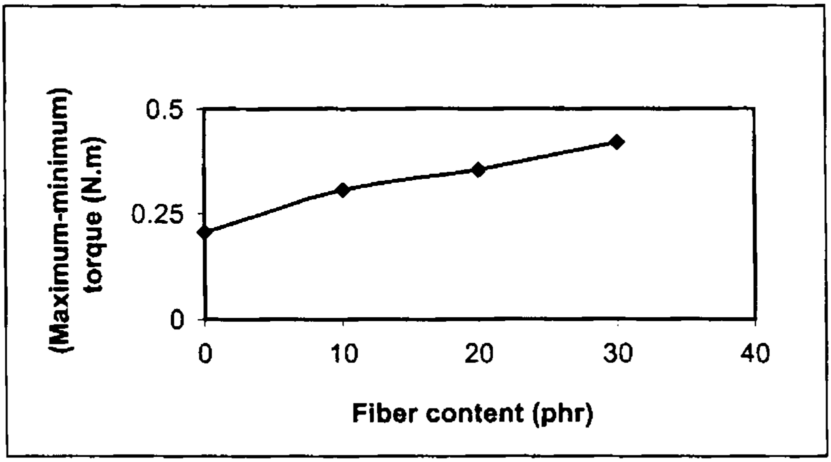

Figure 6.B.2. Variation of (maximum – minimum) torque with fiber loading.

to 0.08 N.m. at 30 phr fiber loading indicating a loss in processability of the composite on the introduction of fibers.

Minimum torque is related to the processability of the compound. Increasing minimum torque with increasing fiber content indicates that the fiber restricts the free flow of chains.

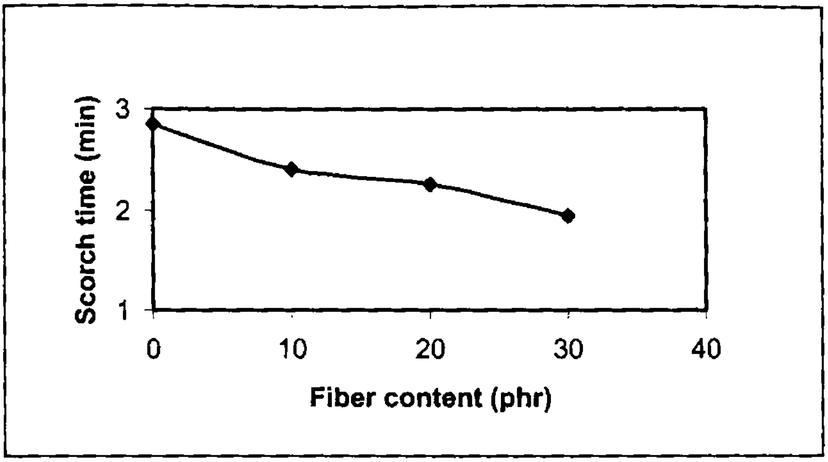

Figure 6.B.3. Variation of scorch time with fiber loading.

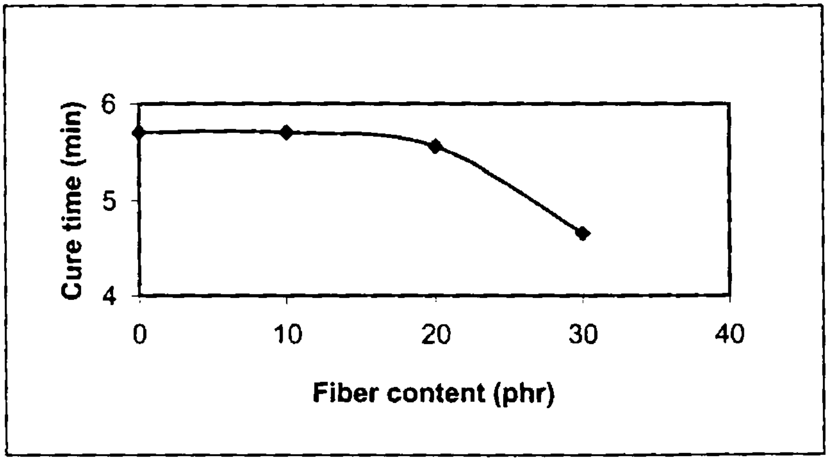

Figure 6.B.4. Variation of cure time with fiber loading.

(Maximum – minimum) torque values of the composites are given in figure 6.B.2. (Maximum – minimum) torque values increase from 0.2057 N.m. at 0 phr to 0.42 N.m. at 30 phr fiber loading indicating a more restrained matrix in the case of composites, with increase in fiber content.

Scorch time showed a reduction from 2.85 minutes at 0 phr fiber to 2.4 minutes at 30 phr fiber loading (figure 6.B.3). Cure time is reduced from 5.75 minutes at 0 phr fiber to 4.65 minutes at 30 phr fiber (figure 6.B.4.). The reduced cure time is accompanied by the increased cure rate values (figure 6.B.5.). The cure rate values increase from 0.0821 N.m/minute at 0 phr to 0.23 N.m/minute at 30 phr. This suggests that the cure reaction is accelerated by the presence of short nylon fibers. Nylon is prone to degradation at the elevated temperature and one of the degradation product is amine and amines are known cure boosters.

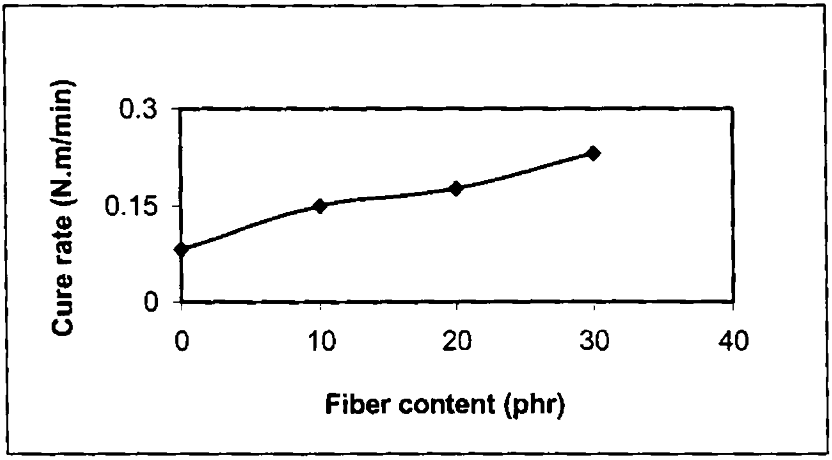

Figure 6.B.5. Variation of cure rate with fiber loading.

6.B.2. Mechanical Properties

Figure 6.B.6 shows the variation of tensile strength of the composites with varying amount of fiber. The tensile strength in

both directions increases with increase in fiber content. This is in contrast to the pattern obtained for short nylon fiber-NR/WTR composites (Chapter IV.B.), where the tensile strength-fiber loading relationship is non-linear with a minimum at lower fiber concentrations. This arise mainly from the fact that NR matrix has high gum strength arising out of strain induced crystallization where as NBR has a relatively lower gum strength. In the former case at lower fiber loadings, the dilution effect due to physical presence of short fibers contributes to the initial reduction in tensile strength. The tensile strength in all cases is higher in the longitudinal direction. In longitudinal direction the fibers will hinder the growing crack front and hence the higher tensile strength values. As fiber concentration increases there are more and more fibers to hinder the crack front and the tensile strength increases. Similar results have been reported in the case of SBR-short jute fiber composites.[1]

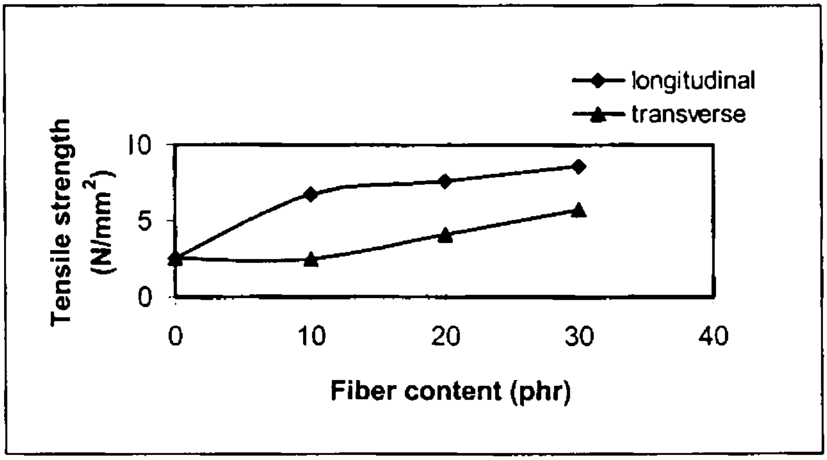

Figure 6.B.6. Variation of tensile strength with fiber loading.

The elongation at break values of the composites are given in figure 6.B.7. The elongation at break values show a sharp fall on introduction of fibers but with further increase in fiber content the

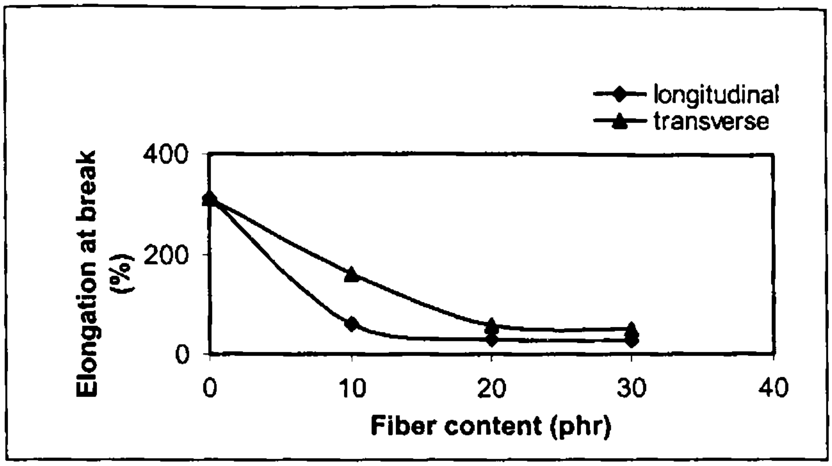

Figure 6.B.7. Variation of elongation at break with fiber loading.

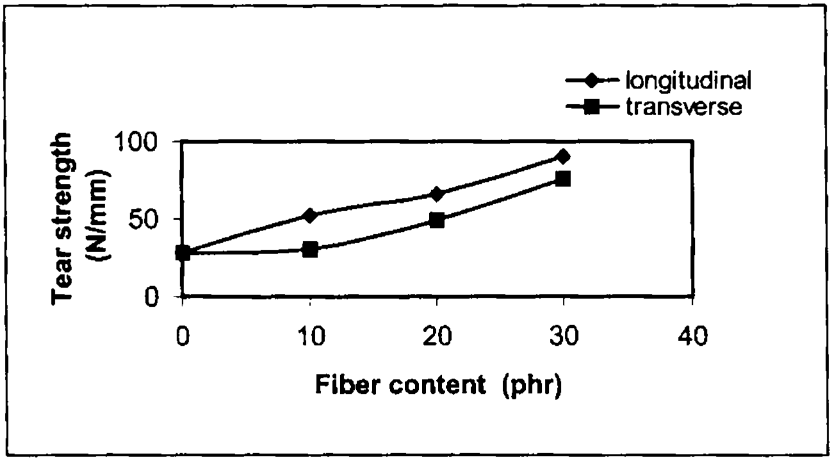

Figure 6.B.8. Variation of tear strength with fiber loading.

reduction is small. The presence of large amount of fiber tips initiate failure at low strains resulting in lower ultimate elongation values. The elongation at break values are higher in the transverse direction, where the load is primarily supported by the matrix. Similar results have been reported by Murty et al.[2]

Tear strength in both direction increases with fiber content as shown in figure 6.B.8. As fiber concentration increases there is more and more hindrance to the propagating crack front and hence the tear strength increases. The tear strength values are found to be higher in longitudinal direction. The lower values of tear strength in transverse direction is due to the inability of fibers aligned parallel to the crack propagation to block the advancing crack front. Similar results are obtained with polyester-NR composites.[3]

Resilience shows an improvement on introduction of fibers but with further fiber loading it remains unchanged (figure 6.B.9.). A lower value of resilience indicates a more viscous matrix where energy dissipation is higher by way of polymer chain slippage and interfacial bond breakage. The 20 parts of reclaimed rubber in the matrix facilitates this type of loss as it contains plasticiser and filler. The short nylon fibers are able to restrain the blend matrix, rendering it more elastic.

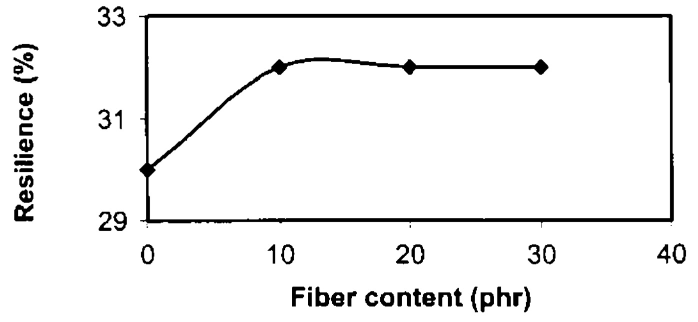

Figure 6.B.9. Variation of resilience with fiber loading.

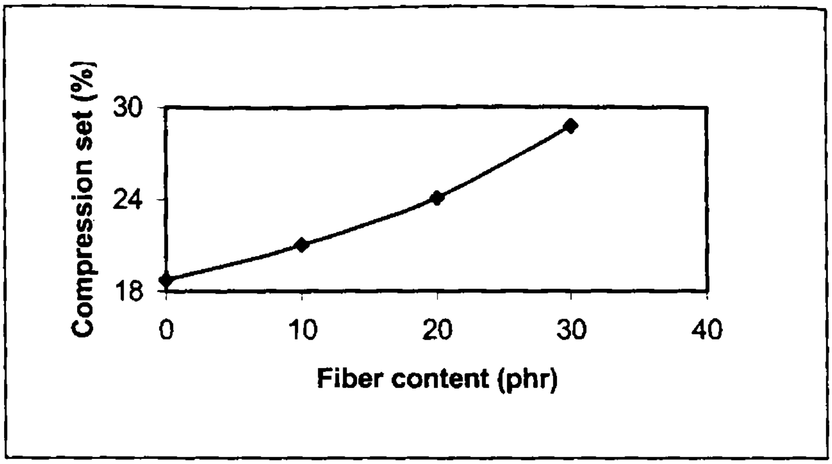

Figure 6.B.10. Variation of compression set with fiber loading.

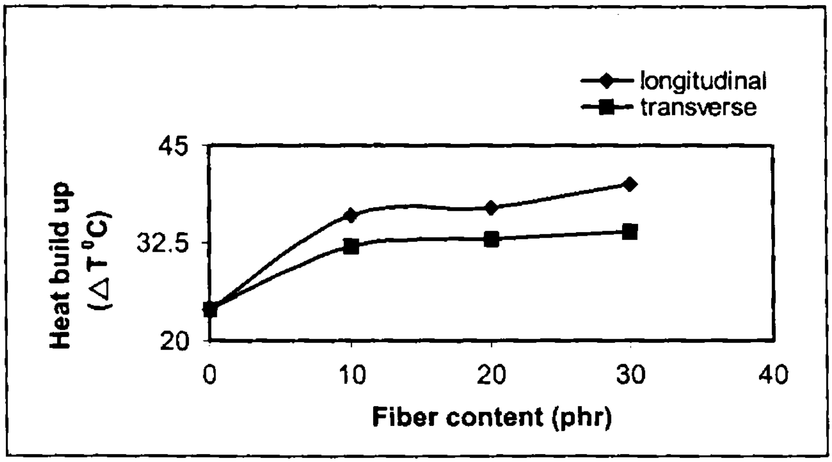

Figure 6.B.11. Variation of heat build up with fiber loading.

Variation of compression set with fiber content is shown in figure 6.B.10. Compression set increased from 18.7% at 0 phr to 28.7% at 30 phr. This trend is in contrast to the pattern observed in the case of resilience. This is because the compression set test is conducted at elevated temperature where as the resilience is a room temperature test.

The heat build up values of the composites are given in figure 6.B.11. The heat build up increases with increase in the amount of fiber in the composite in both the orientations of fibers. However, vulcanizates with longitudinally oriented fibers register higher hysteresis loss. Vulcanizates which are stiffer in the direction of stress experience higher stress for a given strain and generate more heat since the dissipation of energy depends upon both the stress and strain amplitudes. The stiffness of the composites with longitudinally oriented fibers is higher than the stiffness of the composites with transversely oriented fibers. Thus the heat build up is higher in longitudinal direction.

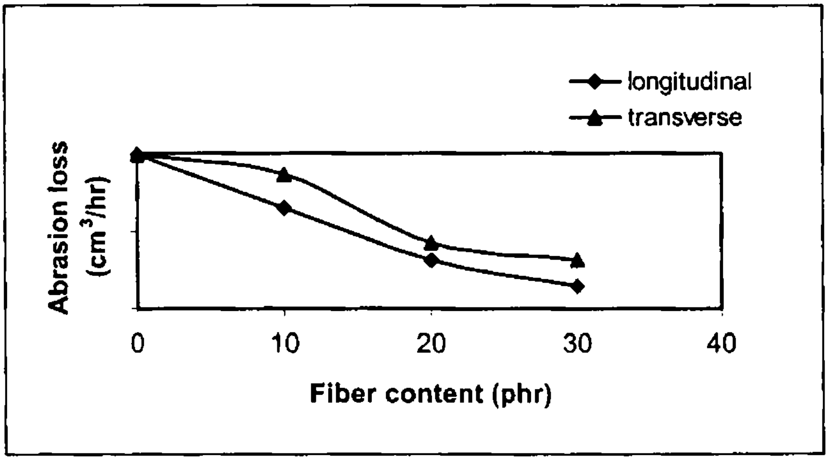

Figure 6.B.12. Variation of abrasion loss with fiber loading.

The abrasion loss of the composites is given in figure 6.B.12. The abrasion resistance of the composites increases with the amount of fiber in the composite indicates a more restrained matrix with increasing fiber content. The abrasion loss in the transverse direction is higher than that in the longitudinal direction. In transverse direction the fibers get debonded and separated from the matrix more easily than in the longitudinal direction causing higher abrasion loss in that direction.

6.B.3. Ageing Resistance

Table VI.B.2. Tensile properties of the mixes before and after ageing

Mix No	Fiber orientation	Tensile strength (N/mm^2)		Percentage retention
		Before ageing	After ageing	
A		2.6	2.3	89
B	L	6.7	8.0	119
	T	2.8	3.6	129
C	L	7.7	8.8	115
	T	4.5	4.8	108
D	L	8.6	11.8	137
	T	5.7	6.6	116

L - Longitudinal orientation T - Transverse orientation

Table VI.B.2. shows the retention of tensile properties of the composites before and after ageing. In all the cases retention of tensile strength of the composites (mixes B-D) is found to be better than that of the blend (mix A). The presence of reclaim rubber in the blend makes it more prone to degradation, as it mainly consists of natural rubber. Moreover the unreacted reclaiming agents added during reclamation process also may contribute to reduced stability at elevated temperature. The presence of fibers reduce the chances of oxidative degradation reaction by making the matrix rigid and restrained. Hence the composites show marginally higher tensile values after ageing.

Table VI.B.3. Tear properties of the mixes before and after ageing

Mix No	Fiber orientation	Tear strength (N/mm)		Percentage retention
		Before ageing	After ageing	
A		28.5	21.0	74
B	L	52.1	71.3	137
	T	30.7	31.6	103
C	L	66.3	87.2	132
	T	49.0	49.6	101
D	L	90.4	92.0	102
	T	76.0	79.0	104

L - Longitudinal orientation T - Transverse orientation

Table VI.B.4. Elongation at break values of the mixes before and after ageing

Mix No	Fiber orientation	Elongation at break (%)		Percentage retention
		Before ageing	After ageing	
A		312.0	285.0	91
B	L	61.4	65.3	106
	T	160.3	164.4	103
C	L	30.0	35.1	117
	T	57.3	95.4	166
D	L	28.8	52.2	181
	T	50.3	55.2	110

L - Longitudinal orientation T - Transverse orientation

The tear resistance of the gum compound (mix A) is reduced while that of all the fiber filled mixes (mixes B-D) are improved by ageing at elevated temperature (Table VI.B.3.). This is because, the tear resistance of an elastomer is better when the matrix is slightly under cured. Since ageing leads to further cure in the case of NBR, the tear resistance of mix A is lower after ageing. For the fiber filled samples, since the fibers compensate for such losses with interfacial bonding that is improved during ageing, the retention values are better.

The retention of elongation at break values of the composites is given in Table VI.B.4. The elongation at break values of the composites after ageing is found to be better than that of before ageing. The retention value for the blend is found to be reduced by ageing.

6.B.4. References

1. Murty V.M. and De S.K., J. Appl. Polym. Sci., **29** (1984) 1355.
2. Murty V.M. and De S.K., Rubber Chem. Technol., **55** (1982) 287.
3. Senapati A.K., Kutty S.K.N., Pradhan B. and Nando G.B., Int. J. Polym. Mater., **12** (1989) 203.

CHAPTER VI.C.

NBR/WTR - SHORT NYLON FIBER COMPOSITE WITH BONDING AGENT*

The fiber-matrix interfacial bond has a decisive role in deciding the properties of short fiber elastomer composites. In this chapter the MDI/PEG system is tried for a 90/20/20 NBR/WTR-short nylon fiber composite. The amount of resin used was 5 phr and the MDI/PEG ratios used were 0.67:1, 1:1, 1.5:1 and 2:1.

The formulation of the mixes is given in Table VI.C.1. The method of sample preparation and the experimental techniques adopted are explained in Chapter 2.

Table VI.C.1. Formulation of the mixes

Ingredient (parts by weight)	Mix No.				
	A	B	C	D	E
NBR	90	90	90	90	90
WTR	20	20	20	20	20
Nylon short fiber	20	20	20	20	20
MDI	0	2	2.5	3	3.33
PEG	0	3	2.5	2	1.67

Zinc oxide - 4 phr, stearic acid - 2 phr, HS - 1 phr, MBTS - 0.5 phr, TMTD - 1.8 phr and Sulfur - 0.3 phr are common to all mixes

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*Results of this Chapter have been accepted for publication in Advances in Polymer Technology.

6.C.1. Cure Characteristics

The minimum torque values of the composites increases with increase in isocyanate concentration with a marginal reduction at higher isocyanate concentration (figure 6.C.1). The increased minimum torque indicates a marginal loss in the processability of the composites. The increase in stock viscosity is arising from a low level of urethane resin formation during the processing stage. Similar results have been obtained in the case of NR/WTR/short nylon fiber composites with urethane based bonding agent (Chapter IV.C.).

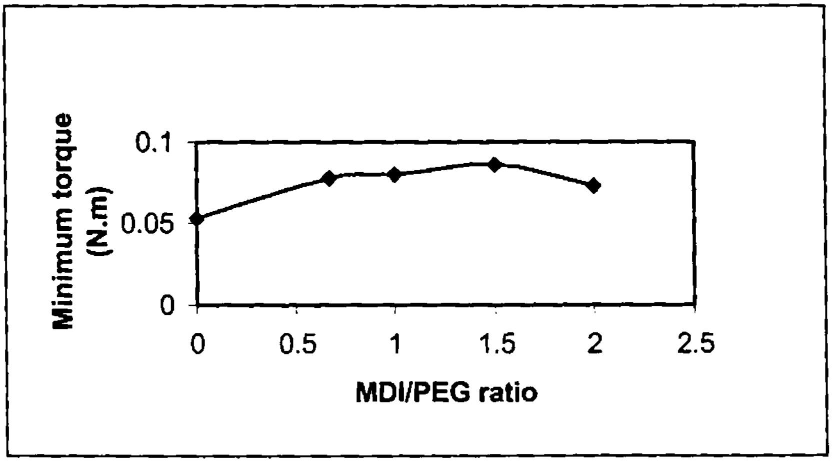

Figure 6.C.1. Variation of minimum torque with MDI/PEG ratio.

A plot of (maximum – minimum) torque values with isocyanate concentration is given in figure 6.C.2. The (maximum – minimum) torque values increase with increase in isocyanate concentration with a marginal reduction at higher MDI/PEG ratio. This indicates a more restrained matrix arising from better fiber matrix bonding in presence of urethane resin. The reduction at higher isocyanate concentration can be attributed to less effective utilization of monomer functionalities.

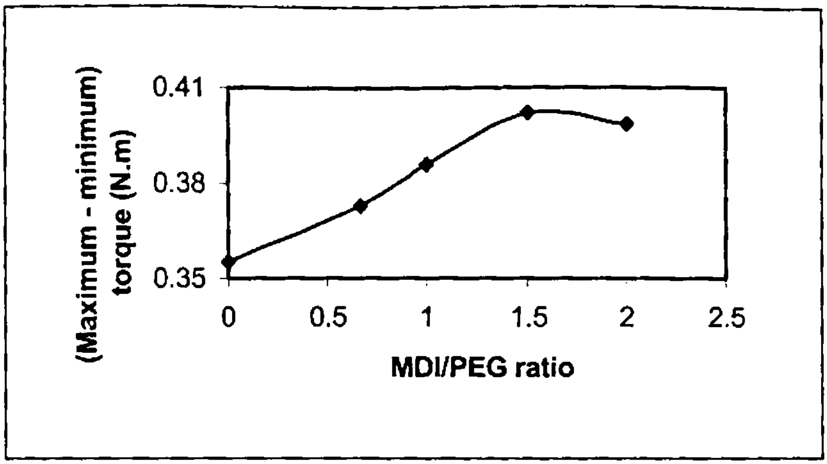

Figure 6.C.2. Variation of (maximum – minimum) torque with MDI/PEG ratio.

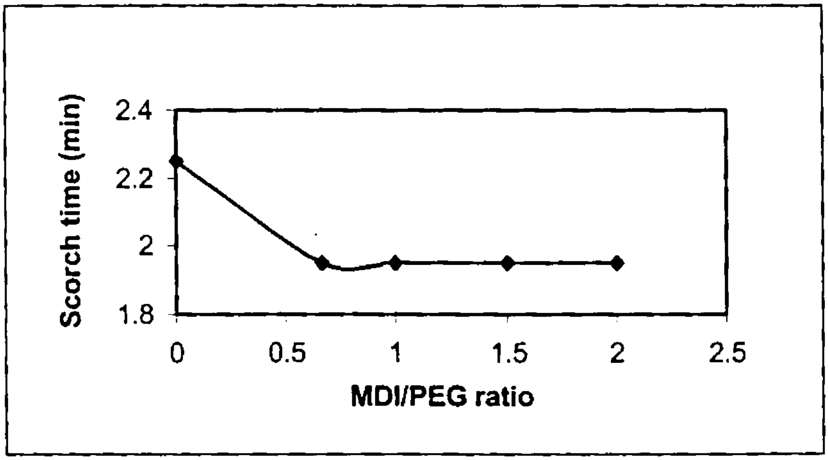

Figure 6.C.3. Variation of scorch time with MDI/PEG ratio.

Scorch time shows a reduction from 2.25 minutes to 1.95 minutes on introduction of bonding agent (figure 6.C.3.). The cure time

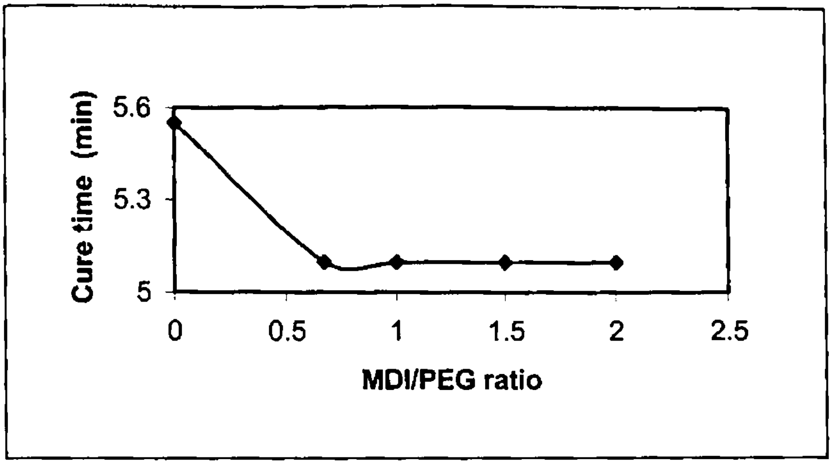

Figure 6.C.4. Variation of cure time with MDI/PEG ratio.

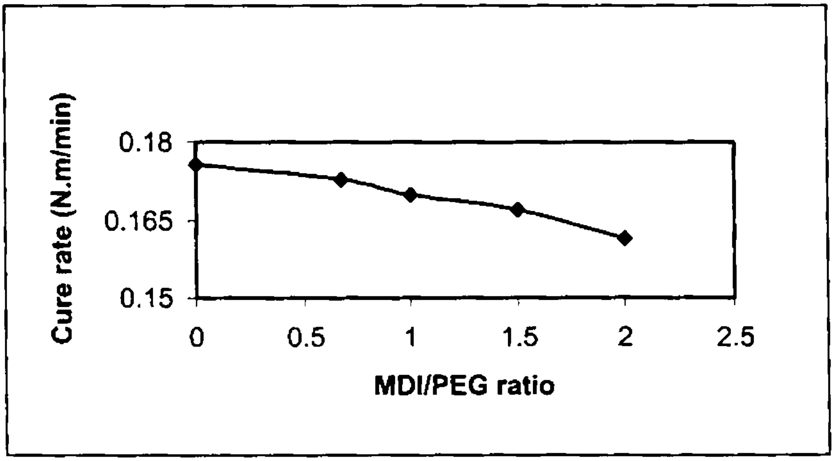

Figure 6.C.5. Variation of cure rate with MDI/PEG ratio.

is decreased from 5.55 minutes to 5.1 minutes in presence of urethane resin (figure 6.C.4.). With further increase in MDI/PEG ratio both the scorch time and the cure time tend to stabilize. The cure rate values are found to decrease with increase in MDI/PEG ratio (figure 6.C.5.). Beyond the optimum MDI/PEG ratio of 0.67:1, the presence of isocyanate group is interfering with the sulfur crosslinking reaction.

6.C.2. Mechanical Properties

A plot of variation of tensile strength with MDI/PEG ratio is shown in figure 6.C.6. The tensile strength in both the orientations of fibers increases with isocyanate concentration. The interfacial bond formed facilitates better load transfer to the fibers and results in higher tensile values. At any MDI/PEG ratio the tensile strength is higher in the longitudinal direction. In longitudinal direction the fibers are more effective in restraining the matrix and hence better tensile values in that direction.

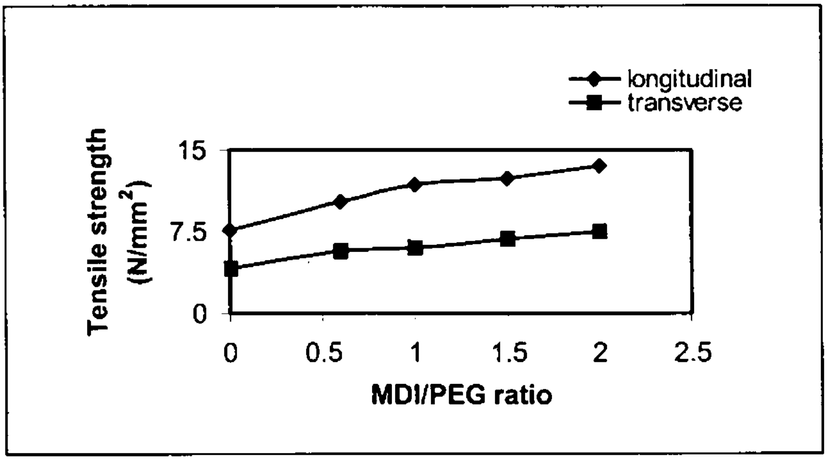

Figure 6.C.6. Variation of tensile strength with MDI/PEG ratio.

Elongation at break values of the composite with different MDI/PEG ratio are shown in figure 6.C.7. The elongation at break values are not much affected by the bonding agent. In all cases the elongation values are higher in the transverse direction.

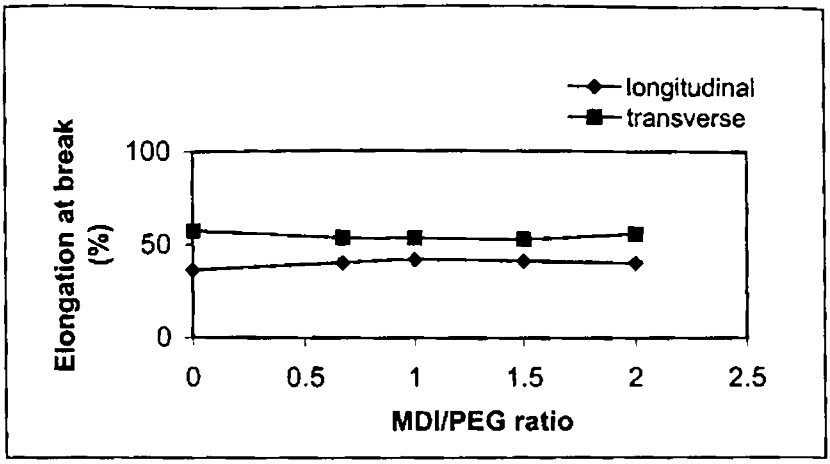

Figure 6.C.7. Variation of elongation at break with MDI/PEG ratio.

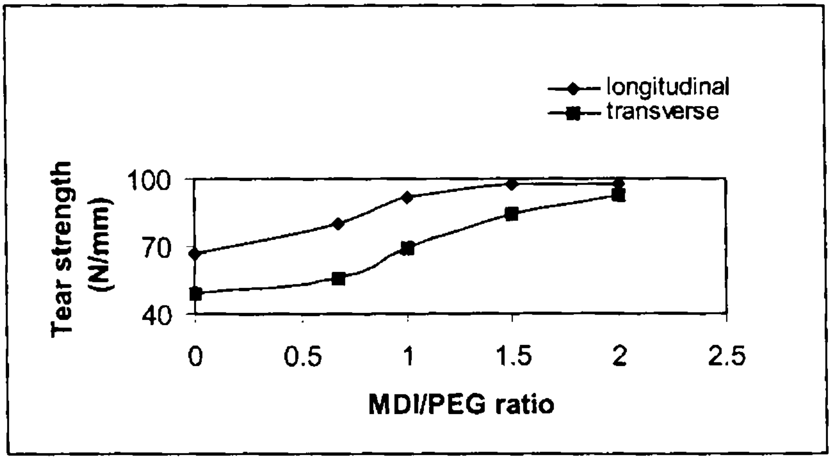

Figure 6.C.8. Variation of tear strength with MDI/PEG ratio.

The tear strength in both the orientations of fibers shows an improvement with MDI/PEG ratio (figure 6.C.8.). The improvement in tear strength further confirms a better fiber matrix bonding in presence of urethane resin. The tear strength values are higher in longitudinal direction in all cases. The growing crack easily passes through the fiber matrix interface when the fibers are in transverse direction and the improvement in interfacial strength is less prominent in this case. Similar results have been reported by Suhara et al.[1]

The resilience values (figure 6.C.9.) remain constant in presence of urethane resin. The resilience test relates to the elasticity of the matrix at very low strain levels. The constant resilience values indicate that the elasticity of the composite at very low extensions is not affected by the presence of bonding agent as there is less chance for the load to be transferred to the fibers at low strain levels.

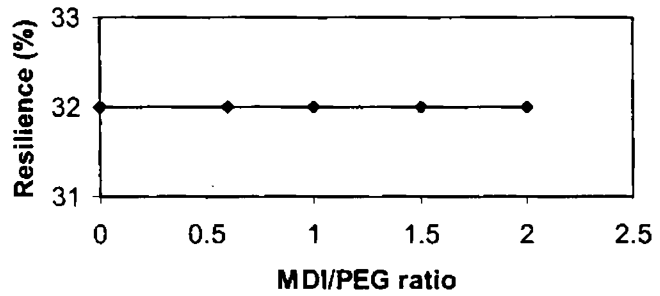

Figure 6.C.9. Variation of resilience with MDI/PEG ratio.

The compression set increases with increase in isocyanate concentration (figure 6.C.10.). The increased compression set indicates an increased viscous nature of the matrix, especially at higher MDI/PEG ratio. The elevated test temperature renders the matrix more viscous and increases the flow under stress.

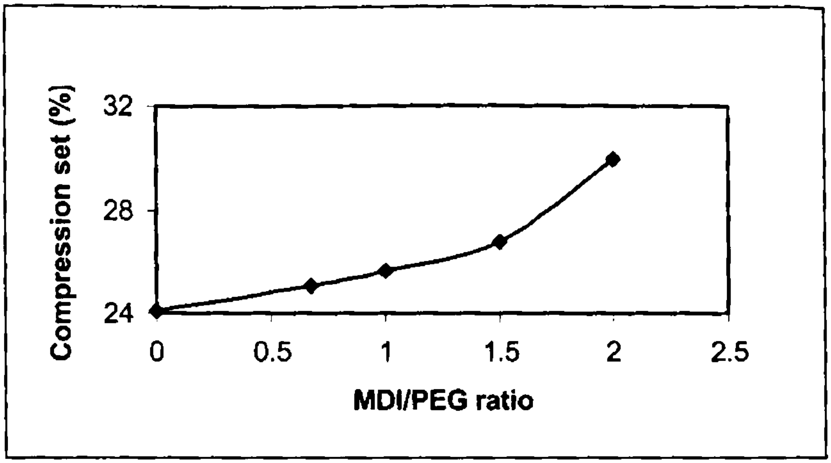

Figure 6.C.10. Variation of compression set with MDI/PEG ratio.

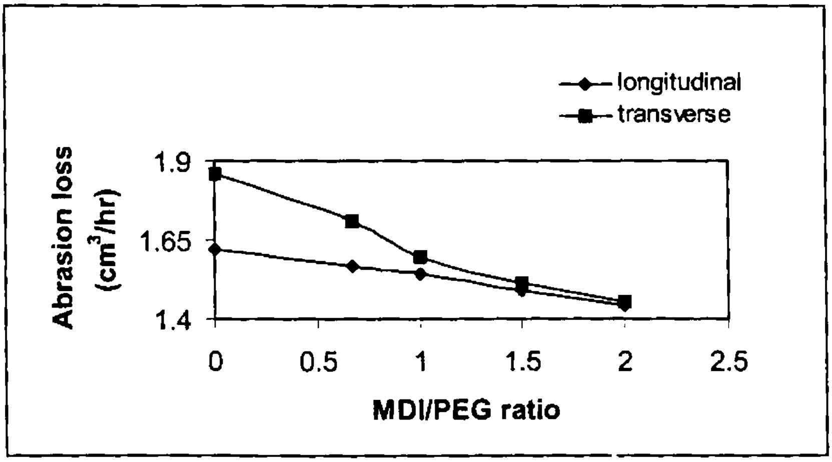

Figure 6.C.11. Variation of abrasion loss with MDI/PEG ratio.

The abrasion loss of the composite in presence of bonding agent is shown in figure 6.C.11. Abrasion loss shows a reduction with increase in isocyanate concentration. The interfacial bond formed makes the matrix more stiff and resist the debonding of fiber from the matrix resulting in higher abrasion resistance. The abrasion resistance is higher in the longitudinal direction in all cases. Similar results have been reported earlier.[2]

6.C.3. Ageing Resistance

Table VI.C.2. Tensile properties of the mixes before and after ageing

Mix No.	Fiber orientation	Tensile strength (N/mm^2)		Percentage retention
		Before ageing	After ageing	
A	L	7.7	8.9	115
	T	4.5	4.8	108
B	L	10.3	11.4	111
	T	5.6	6.0	106
C	L	11.8	13.2	112
	T	6.0	6.0	101
D	L	12.4	13.9	113
	T	6.8	7.9	116
E	L	13.5	15.1	112
	T	7.5	7.8	105

L - longitudinal orientation T - transverse orientation

Table VI.C.2. shows the retention of tensile properties of the composites before and after ageing. There is minor improvement in the tensile strength of all the mixes after ageing. This improved strength values indicates an improved fiber-matrix interfacial bond coupled with increased state of cure after ageing.

The tear properties of the composites are given in Table VI.C.3. The retention values are around 100% at lower MDI/PEG ratio.

Table VI.C.3. Tear properties of the mixes before and after ageing

Mix No.	Fiber orientation	Tear strength (N/mm)		Percentage retention
		Before ageing	After ageing	
A	L	66.3	87.2	132
	T	49.0	49.6	100
B	L	80.0	72.6	91
	T	56.0	55.3	99
C	L	91.5	91.9	100
	T	69.3	67.4	97
D	L	97.1	70.4	73
	T	84.2	45.3	54
E	L	97.5	74.3	76
	T	92.2	37.1	40

L - longitudinal orientation T - transverse orientation

However at higher isocyanate concentration the retention values are found to be reduced. Higher level of MDI in the matrix leaves many free isocyanate group which may be contributing to the low retention of the tear strength during ageing. Since the micromechanism of failure under tensile and tear conditions are different the test results are not parallel with respect to the isocyanate concentration.

The percentage retention of the elongation at break values is found to be less than 100 in the presence of bonding agent (Table VI.C.4.). The lower values of retention is exhibited by mixes containing higher isocyanate concentration. This suggests a possible acceleration of the ageing process by the free isocyanate groups.

Table VI.C.4. Elongation at break values of the mixes before and after ageing

Mix No.	Fiber orientation	Elongation at break (%)		Percentage retention
		Before ageing	After ageing	
A	L	30.2	35.1	117
	T	57.3	95.4	166
B	L	40.3	42.7	107
	T	53.5	55.9	105
C	L	41.9	41.4	99
	T	53.5	64.6	121
D	L	41.3	39.2	95
	T	53.0	44.1	83
E	L	40.3	42.5	106
	T	56.0	37.0	66

L - longitudinal orientation T - transverse orientation

6.C.4. References

1. Suhara F., Kutty S.K.N. and Nando G.B., Polym. Plast. Technol. Eng, **37(2)** (1998) 241.
2. Ibarra L., Kaustschuk Gummi Kunststoffe, **48** (12/95) 860.

CHAPTER VII.

SBR – WTR BLENDS*

In this study reclaimed rubber is blended with a general purpose synthetic rubber, SBR. SBR is more uniform in quality than NR. It is being widely used in products such as tyres and belts. It retains its plasticity during mastication while the plasticity decreases for NR during processing. The general balance of properties that can be obtained with SBR is a little below that obtainable with natural rubber. SBR possesses better abrasion resistance than NR while the resilience is inferior to that of NR. SBR is a non-crystallizing matrix. The major drawback of SBR is its very poor gum strength. Blending with reclaimed rubber can reduce cost and improve its mechanical properties. This chapter is a systematic study on the SBR/WTR blends with respect to cure characteristics and mechanical properties

Formulation of the mixes is given in Table VII.1. The preparation of the samples and the experimental techniques employed are explained in Chapter 2.

Table VII.1. Formulation of the mixes

Ingredient	Mix No.				
	A	B	C	D	E
SBR	100	90	80	70	60
Reclaim	-	20	40	60	80

Zinc oxide - 4 phr, Stearic acid - 2 phr, HS - 1 phr, MBTS - 0. 5 phr, TMTD - 1. 8 phr & Sulfur - 0. 3 phr are common to all mixes.

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* Results of this Chapter have been accepted for publication in Int. J. Polym. Mater.

7.1. Cure Characteristics

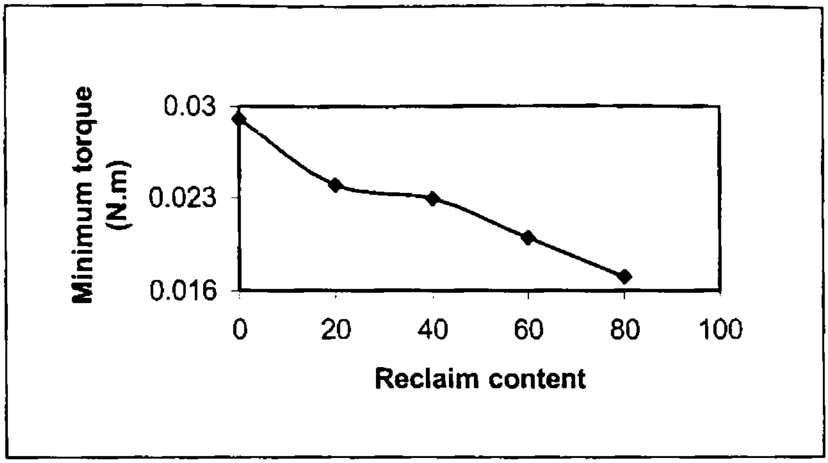

Figure 7.1. Variation of minimum torque with reclaim loading.

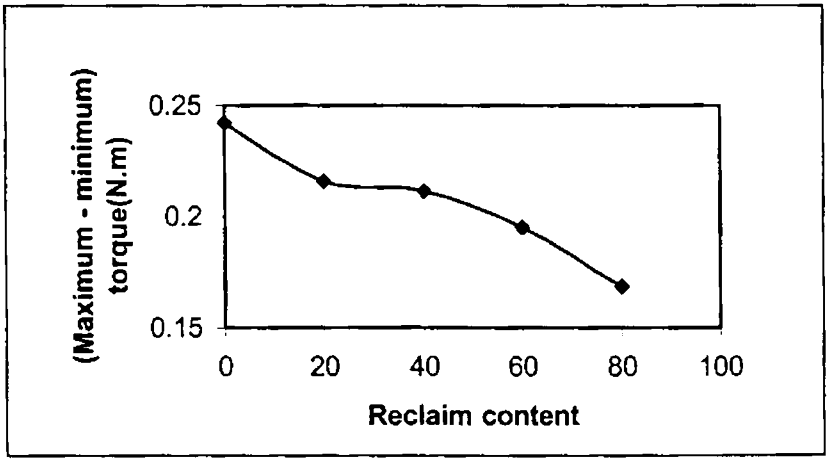

Figure 7.2. Vriation of (maximum - minimum) torque with reclaim loading.

The minimum torque values of the blends are given in figure 7.1. The minimum torque values show a reduction from 0.029 N.m at 0 parts to 0.017 N.m. at 80 parts of reclaim content. The decreased minimum torque values indicate improved processability in the case of blends. The presence of oil in the reclaimed rubber explains the decreased minimum torque values of the blends. The acetone extractable fraction of the reclaim, which is an indication of oil content of the reclaim, is 13% (Chapter II).

The (maximum- minimum) torque values show a reduction from 0.2424 N.m. at 0 parts to 0.1687 N.m. at 80 parts of reclaim loading (figure 7.2.). The decrease in (maximum – minimum) torque values with increase in reclaim loading is due to the higher oil content present in the reclaimed rubber. The oil content of the reclaim is about 13%. The low molecular weight of the reclaimed rubber also contributes to the lower (maximum – minimum) torque values.

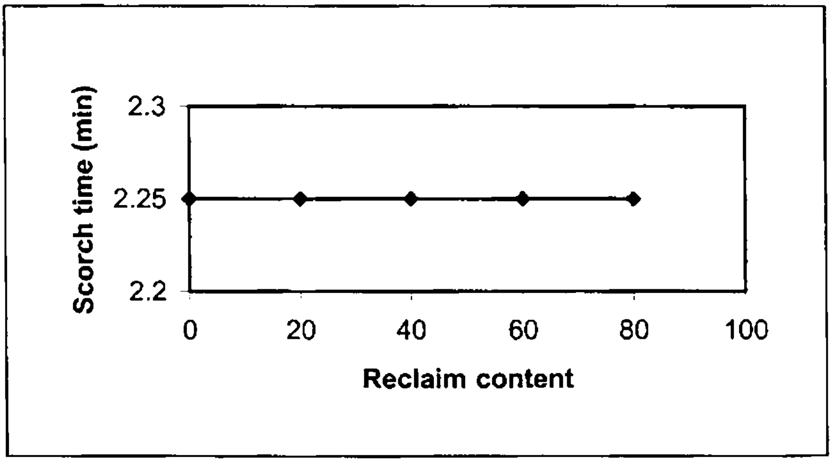

Figure 7.3. Variation of scorch time with reclaim loading.

The scorch time is not affected by the addition of reclaimed rubber (figure 7.3.). The cure time shows a drop in the 20 – 40

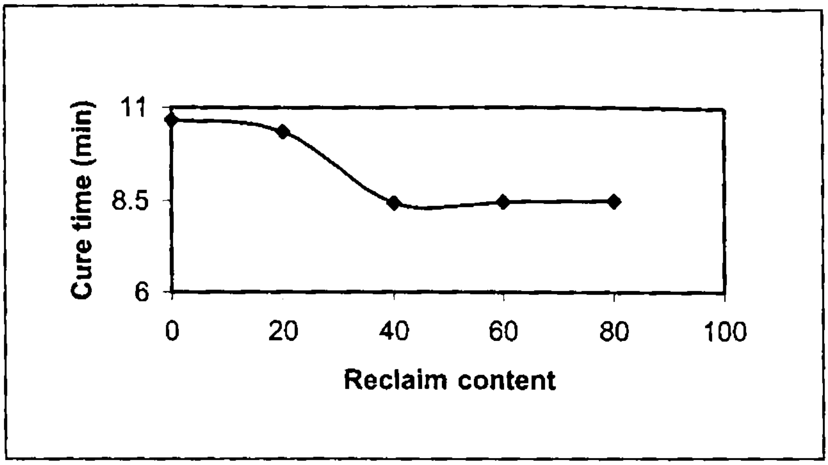

Figure 7.4. Variation of cure time with reclaim loading.

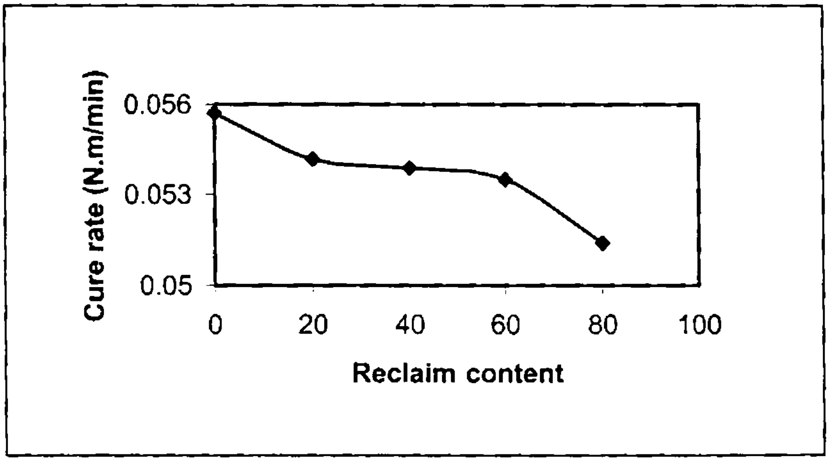

Figure 7.5. Variation of cure rate with reclaim loading.

parts of reclaim loading (figure 7.4.) and remains constant for mixes C-E. The reduced cure time may be attributed to the presence of accelerator relics present in the reclaimed rubber.

However its effect becomes insignificant at higher reclaim loading as the number of available reactive sites for crosslinking becomes less when the reclaim content in the blend becomes higher. This is also reflected in the cure rate values, which are lower for the blends (figure 7.5.). The partially crosslinked state of the reclaimed rubber limits its further crosslinkability.

7.2. Mechanical Properties

The variation of tensile strength with the addition of reclaimed rubber is shown in figure 7.6. The tensile strength shows an increase from 1.9 N/mm^2 at 0 parts to 5.07 N/mm^2 at 80 parts of reclaimed rubber. This is in contrast to the results reported in the case of NR-reclaimed rubber blends (Chapter III). The difference can be attributed to the non-crystallizing nature of the SBR, which gives it poor gum strength. The presence of reinforcing filler in the reclaim rubber can contribute to the higher tensile strength of the blend. In the case of NR-reclaim blend, the low gum strength reclaim cause more of dilution of the NR matrix than reinforcement.

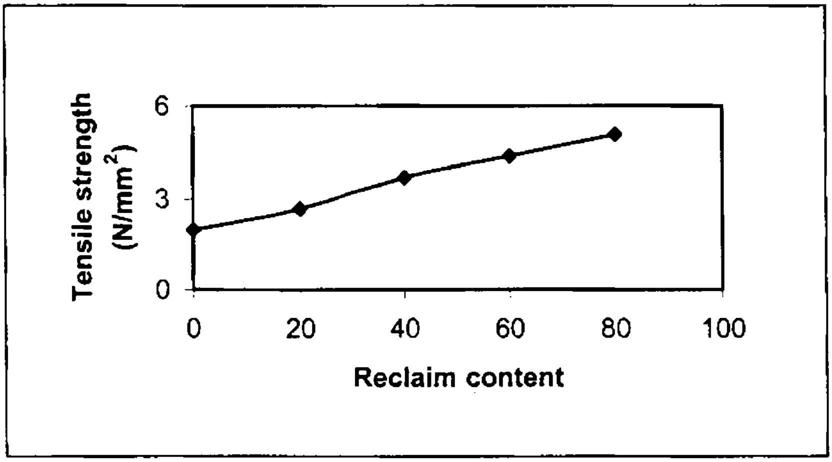

Figure 7.6. Variation of tensile strength with reclaim loading.

The elongation at break values of the blends are given in figure 7.7. The elongation at break shows an increase with increase in reclaim content which can be attributed to the higher oil content in the case of reclaimed rubber.

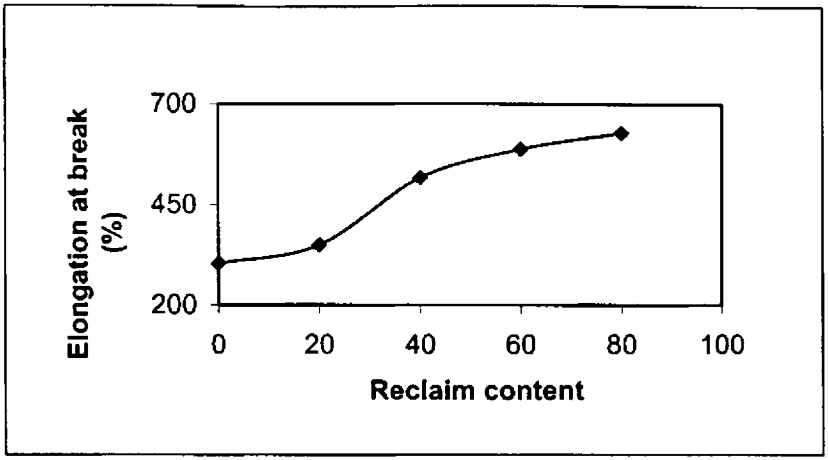

Figure 7.7. Variation of elongation at break with reclaim loading.

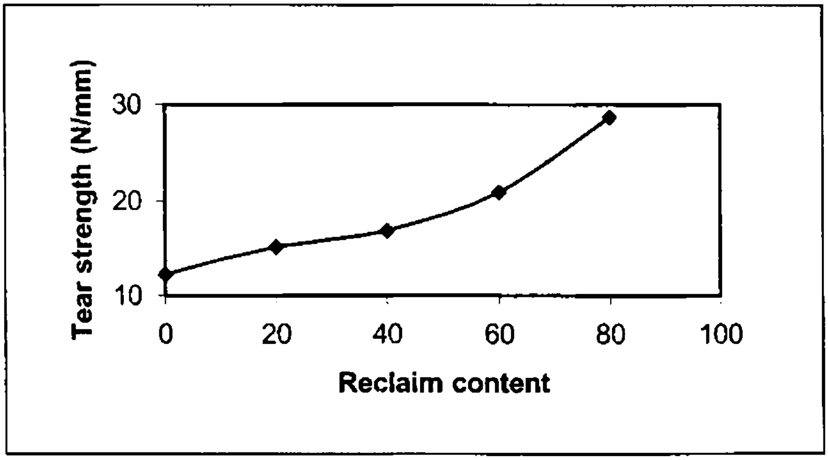

Figure 7.8. Variation of tear strength with reclaim loading.

A plot of tear strength versus reclaim content is shown in figure 7.8. The increase in tear strength with reclaim content can be attributed to the presence of reinforcing black in the case of blends.

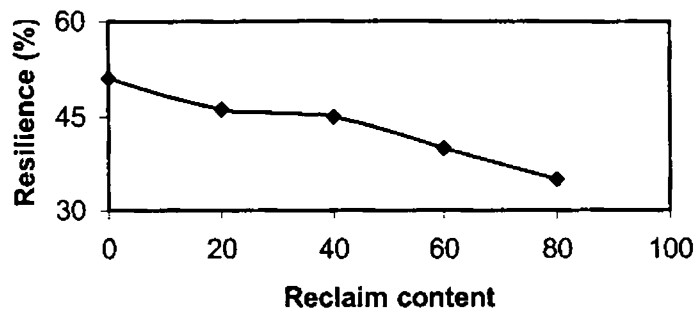

Figure 7.9. Variation of resilience with reclaim loading.

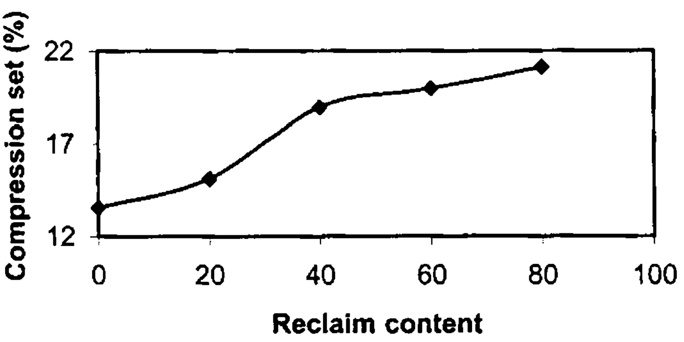

Figure 7.10. Variation of compression set with reclaim loading.

Resilience, a measure of material elasticity, is found to decrease with increase in reclaim content (figure 7.9.). The resilience decreases from 51% at 0 parts to 35% at 80 parts of reclaimed rubber. Higher the concentration of filler and plasticiser, higher is the chances of energy dissipation. The energy dissipation can be through loss at filler-matrix interface, friction between the chains and breakdown of filler structure. This is manifested as lower resilience values.

The variation of compression set at constant strain is shown in figure 7.10. The compression set increases with increase in reclaim loading, which is in agreement with the observed reduced resilience. The increased compression set arises from the flowability of the compound under load at elevated temperature. The relatively lower molecular weight of the reclaimed rubber renders the blend more plastic. Similar results have been reported by Phadke et al.[1]

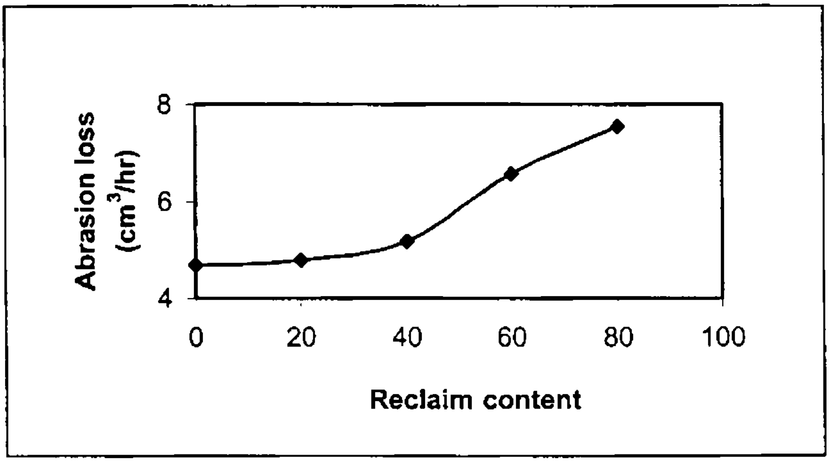

Figure 7.11. Variation of abrasion loss with reclaim loading.

Figure 7.11 gives the abrasion loss of the blends containing different amounts of reclaimed rubber. The abrasion loss is small at lower reclaim loading but the loss is higher at higher reclaim loading. This may be attributed to the relatively lower molecular weight of the reclaimed rubber. The higher hysteresis loss as indicated by lower resilience of the blend may also be contributing to the increased abrasion loss. Similar results have been reported in the case of NR/reclaimed rubber blends.[2]

7.3. Ageing Resistance

Table VII.2. Tensile properties of the mixes before and after ageing

Mix No	Tensile strength (N/mm^2)		Percentage retention
	Before ageing	After ageing	
A	2.0	2.2	112
B	2.6	2.9	108
C	3.7	3.8	104
D	4.4	5.0	115
E	5.1	5.8	115

Table VII.3. Tear properties of the mixes before and after ageing

Mix No	Tear strength (N/mm)		Percentage retention
	Before ageing	After ageing	
A	12.2	10.8	89
B	15.1	15.2	100
C	16.7	18.9	113
D	20.8	21.8	105
E	28.7	31.3	109

The retention values of tensile strength after ageing are shown in Table VII.2. All mixes show retention marginally above 100%. This indicates a nominal level of post curing taking place during ageing. This is to be expected because of the marching cure pattern of SBR.

The tear strength values before and after ageing are shown in Table VII.3. All retention values are close to 100%.

The aged values of elongation at break are found to be lower than that of the unaged one at all reclaim loading (Table VII.4.). This is in agreement with improved tensile strength values.

Table VII.4. Elongation at break values of the mixes before and after ageing

Mix No	Elongation at break (%)		Percentage retention
	Before ageing	After ageing	
A	304	261	86
B	349	345	99
C	517	391	76
D	588	496	84
E	629	525	84

7.4. References

1. Phadke A.A., Chakraborty S.K. and De S.K., Rubber Chem. Technol., **57** (1984) 19.
2. Phadke A.A., Bhattacharya A.K., Chakraborty S.K. and De S.K., Rubber Chem. Technol., **56** (1983) 726.

CHAPTER VIII.A.

SBR – SHORT NYLON FIBER COMPOSITES*

In this chapter the effect of short nylon fiber on a general purpose synthetic rubber, SBR, is described. The fiber loading was varied from 0-30 phr.

Formulation of the mixes used is given in Table VIII.A.1. The details of sample preparation, cure characteristics determination, moulding and determination of mechanical properties are described in Chapter 2.

Table VIII.A.1. Formulation of the mixes

Ingredient	Mix No			
	A	B	C	D
SBR	100	100	100	100
short nylon fiber	0	10	20	30

Zinc oxide – 4 phr, Stearic acid – 2 phr, HS - 1 phr, MBTS - 0.5 phr, TMTD - 1.8 phr & Sulfur - 0.3 phr are common to all mixes.

8.A.1. Cure Characteristics

A plot of minimum torque versus fiber content is shown in figure 8.A.1. The minimum torque shows an increase from 0.029 N.m. at 0 phr to 0.083 N.m. at 30 phr of fiber indicating a loss in the processability of the composite. The presence of fibers restrict the flow of matrix and results in higher minimum torque values.

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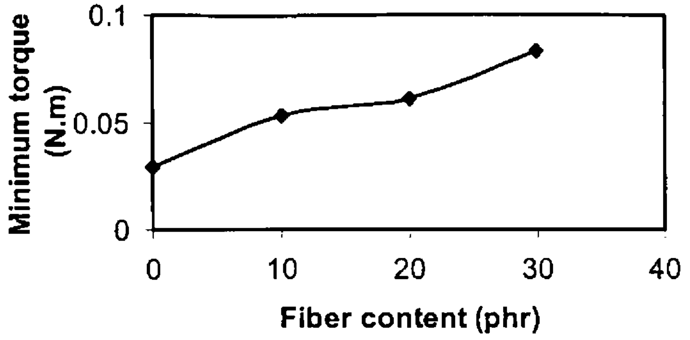
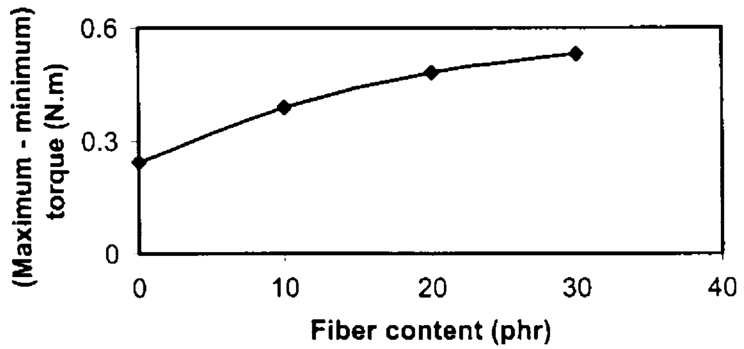
*Results of this Chapter have been accepted for publication in Int. J. Polym. Mater.



'igure 8.A.1. *Variation of minimum torque with fiber loading.*



'igure 8.A.2. *Variation of (maximum – minimum) torque with fiber oading.*

Maximum – minimum) torque values show an increase with fiber oading as shown in figure 8.A.2. The increase in (maximum –

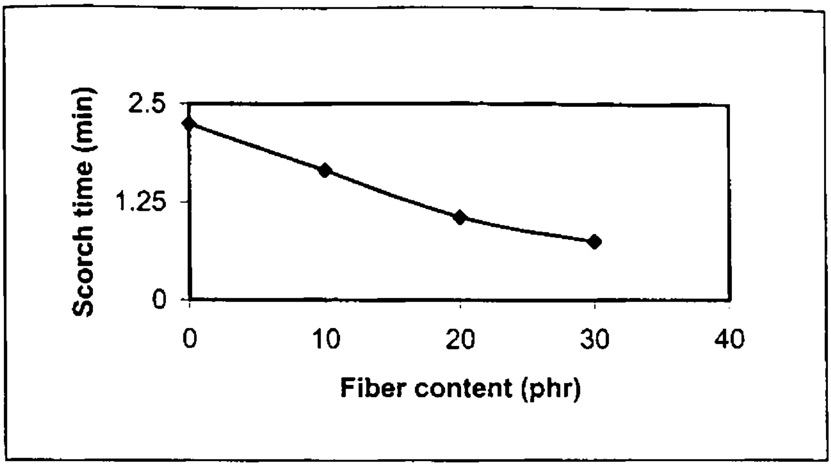


Figure 8.A.3. Variation of scorch time with fiber loading.

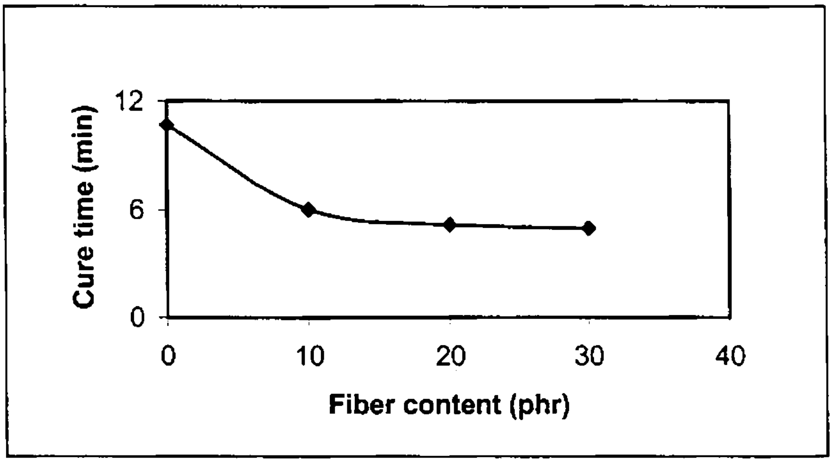


Figure 8.A.4. Variation of cure time with fiber loading.

minimum) torque arises from the more restrained matrix in the case of composites in presence of short fibers. Similar results have been obtained in the case of NBR- short nylon fiber composites

(Chapter VI.A.).

A plot showing the variation of scorch time with various amount of fiber is shown in figure 8.A.3. The scorch time is decreased from 2.25 minutes at 0 phr to 0.75 minutes at 30 phr fiber. There is a reduction in cure time also with fiber content as shown in figure 8.A.4. These results indicate that the cure reaction is being accelerated in the presence of short fibers. The cure rate increases from 0.0557 N.m/minute at 0 phr to 0.2442 N.m/min. at 30 phr fiber (figure 8.A.5.). This may be attributed to the possible degradation of the nylon fibers at the curing temperature. The amine functionality of the degradation products can accelerate the cure reaction. Similar results have been obtained in the case of NBR-short nylon fiber composites (Chapter VI.A.).

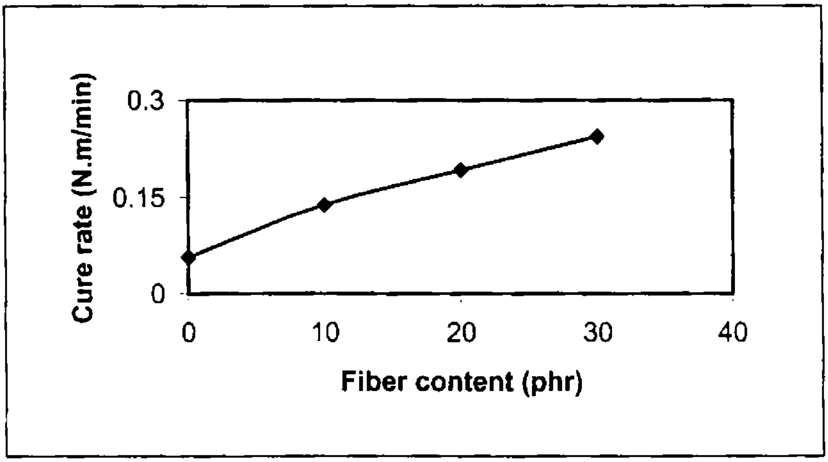


Figure 8.A.5. Variation of cure rate with fiber loading.

8.A.2. Mechanical Properties

The variation of tensile strength with fiber content is shown in figure 8.A.6. The tensile strength in both the orientations of fibers (longitudinal and transverse) increases with fiber concentration. This is in agreement with the results obtained in the case of short nylon fiber-NBR composites, as both SBR and NBR are low gum strength matrices (Chapter VI.A.) which do not undergo strain induced crystallization. At any given fiber loading the tensile strength values are higher in the longitudinal direction. In longitudinal direction the fibers are more effective in hindering the growing crack front and this results in higher tensile strength in that direction. As fiber concentration increases there are more and more fibers to hinder the crack front and tensile strength increases with fiber concentration. Similar results have been obtained in the case of SBR-short jute fiber composites.[1]

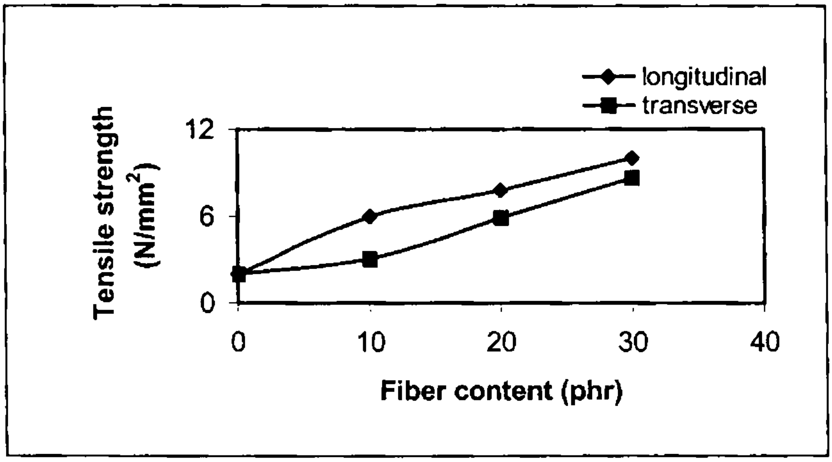


Figure 8.A.6. Variation of tensile strength with fiber loading.

The ultimate elongation shows a sharp fall on the introduction of fibers (figure 8.A.7.), but with further increase the values tend to stabilize. In the presence of short fibers, the matrix is more restrained and the failure is initiated at multiple points, resulting in lower ultimate elongation values. At all fiber loading the elongation at break values are higher in the transverse direction. Similar results have been reported earlier.[2-4]

The variation of tear strength with fiber concentration of the

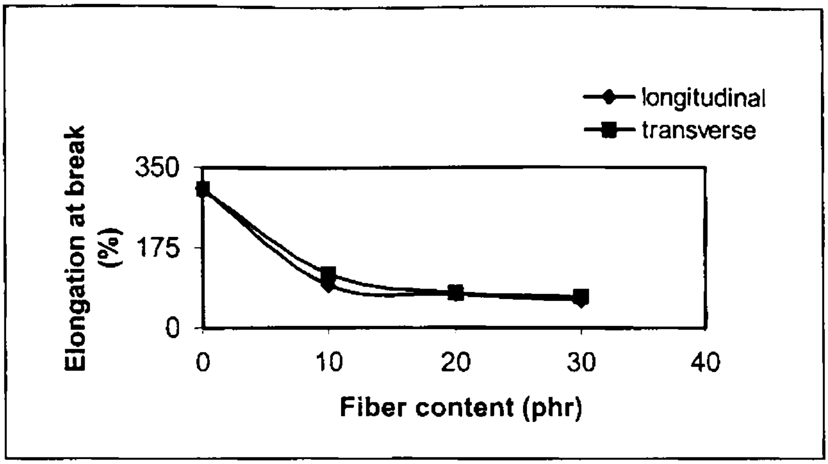


Figure 8.A.7. Variation of elongation at break with fiber loading.

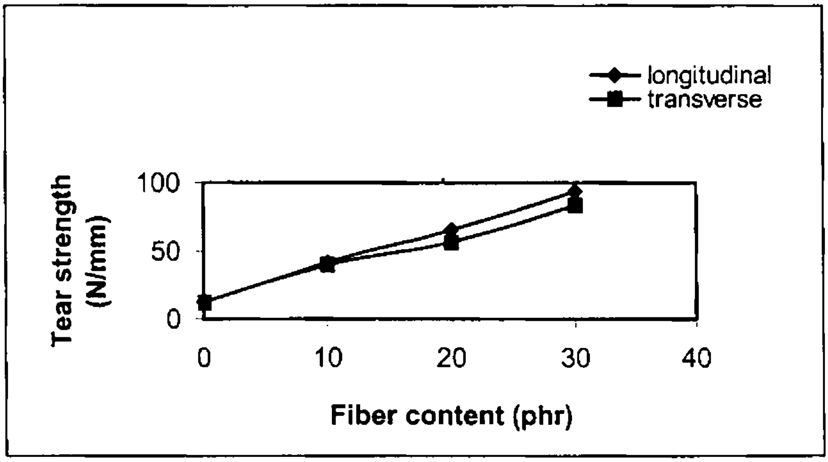


Figure 8.A.8. Variation of tear strength with fiber loading.

composites is given in figure 8.A.8. Tear strength shows a continuous increase with increase in fiber content, both in longitudinal and transverse orientations of fibers. As fiber concentration increases there is more and more hindrance to the crack propagation. At any given fiber loading, mixes with longitudinal fiber orientation show higher tear strength than mixes with transverse fiber orientation. In the transverse direction fibers are parallel to the crack front, hence offers less resistance to propagation of tear, thus the lower tear values than the longitudinal direction. Similar results have been reported earlier.[5]

Resilience shows a reduction from 51% to 41% on introduction of fibers (figure 8.A.9.). With further increase in fiber amount it remains unchanged. The dissipation of energy at fiber-matrix interface results in lower resilience value in the case of composite.

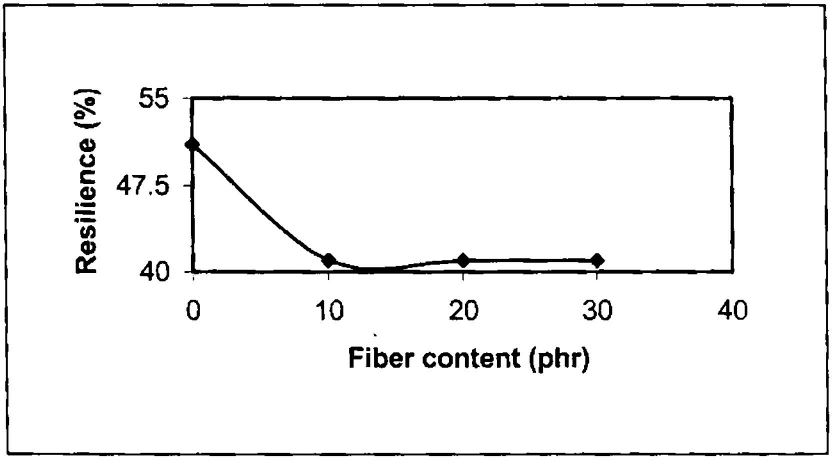


Figure 8.A.9. Variation of resilience with fiber loading.

Figure 8.A.10 is a plot of compression set versus fiber content. There is a linear increase in compression set values with increase in fiber concentration. This is in agreement with the decreased resilience values.

Abrasion resistance registers an improvement with increase in fiber content in both longitudinal and transverse orientations of fibers (figure 8.A.11.). At any fiber concentration the loss is greater in

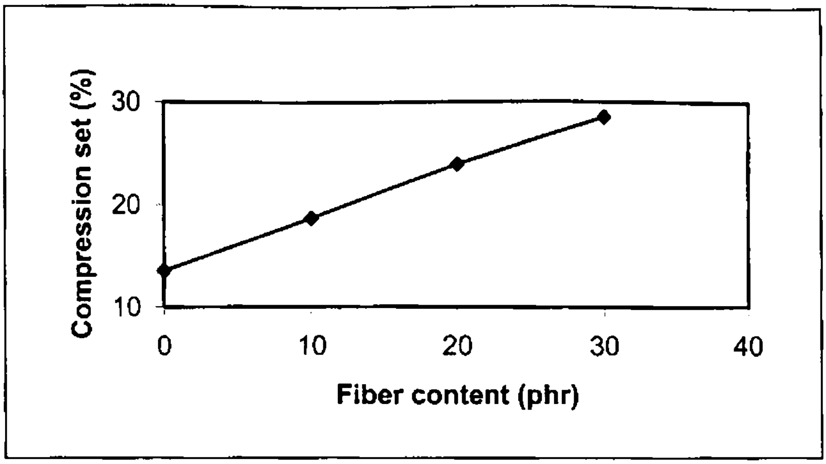


Figure 8.A.10. Variation of compression set with fiber loading.

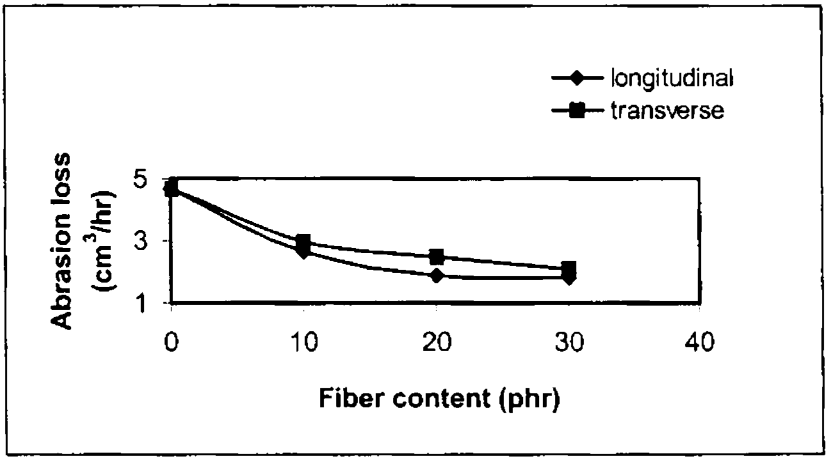


Figure 8.A.11. Variation of abrasion loss with fiber loading.

the transverse direction than in the longitudinal direction. The fibers get debonded and separated from the matrix more easily when the fibers are arranged transversely resulting in higher abrasion loss in that direction.

8.A.3. Ageing Resistance

Table VIII.A.2. Tensile properties of the mixes before and after ageing

Mix No	Orientation	Tensile strength (N/mm^2)		Percentage retention
		Before ageing	After ageing	
A		2.0	2.2	113
B	L	7.0	10.4	150
	T	3.0	5.3	140
C	L	7.8	11.1	142
	T	5.9	8.6	147
D	L	10.1	13.5	134
	T	8.6	10.1	117

L - Longitudinal orientation T - Transverse orientation

Table VIII.A.2 shows the retention of tensile properties of the composites before and after ageing. In all cases the retention of tensile strength is found to be better for the composites. This may be arising out of improved fiber matrix interfacial bond during the ageing. The direction of fiber orientation does not seem to have much influence on the retention values.

The tear resistance of the gum compound (mix A) is reduced while that of all the fiber filled mixes (mixes B - D) are improved by ageing at elevated temperature (Table VIII.A.3). This is because, the tear resistance of an elastomer is better when the matrix is slightly under cured. Since ageing leads to further cure in the case of SBR, the tear resistance of mix A is lower after ageing. For the fiber filled samples, since the fibers compensate for such losses with interfacial bonding that is improved during ageing, the retention values are better.

Table VIII.A.3. Tear properties of the mixes before and after ageing

Mix No	Orientation	Tear strength (N/mm)		Percentage retention
		Before ageing	After ageing	
A		12.2	10.8	89
B	L	41.4	44.3	107
	T	39.3	40.9	104
C	L	64.8	73.5	113
	T	55.7	65.4	118
D	L	93.5	94.3	101
	T	83.2	88.1	106

L - Longitudinal orientation T - Transverse orientation

Table VIII.A 4. Elongation at break values of the mixes before and after ageing

Mix No	Orientation	Elongation at break (%)		Percentage retention
		Before ageing	After ageing	
A		304	261	86
B	L	92	94	102
	T	118	128	108
C	L	74	78	105
	T	77	85	111
D	L	61	71	117
	T	68	75	112

L - Longitudinal orientation T - Transverse orientation

The percentage retention values of elongation at break is shown in Table VIII.A.4. The retention values of the composites are almost similar.

8.A.4. References

1. Murty V.M. and De S.K., J. Appl. Polym. Sci., **29** (1984) 1355.
2. Chakraborty S.K., Setua D.K. and De S.K., Rubber Chem. Technol., **55** (1982) 1286.
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4. Akthar S., De P.P. and De S.K., J. Appl. Polym. Sci., **32** (1986) 5123.
5. Senapati A.K., Kutty S.K.N., Pradhan B. and Nando G.B., Int. J. Polym. Mater., **12** (1989) 203.

CHAPTER VIII.B.

SBR/WTR - SHORT NYLON FIBER COMPOSITES*

From the previous chapter (Chapter VII) it is clear that the reclaimed rubber can partly replace SBR with improvement in most of its mechanical properties. The abrasion resistance of such blends was found to be inferior. In this chapter an attempt has been made to further improve the properties of the composite by incorporating short nylon fibers. An 80:40 blend of styrene butadiene rubber-reclaimed rubber was selected from previous study (Chapter VII) and the fiber loading was varied from 0 to 30 phr.

Table VIII.B.1 gives the formulation of the mixes. The details of sample preparation and experimental techniques are described in Chapter 2.

Table VIII.B.1. Formulation of the mixes

Ingredient	Mix No.			
	A	B	C	D
SBR	80	80	80	80
WTR	40	40	40	40
Nylon short fibers	0	10	20	30

Zinc oxide - 4 phr, Stearic acid - 2 phr, -HS - 1 phr, MBTS - 0. 5 phr, TMTD - 1. 8 phr & Sulfur - 0. 3 phr are common to all mixes.

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*Results of this Chapter have been communicated for publication Advances in Polymer Technology.

8.B.1. Cure Characteristics

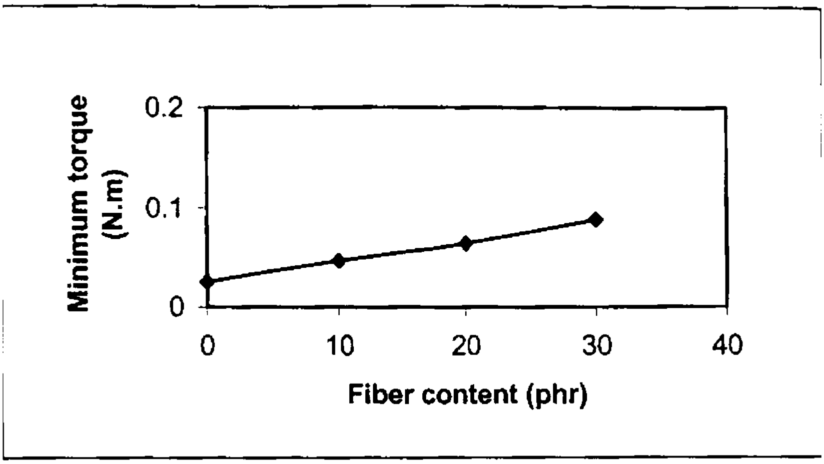

Figure 8.B.1. Variation of minimum torque with fiber loading.

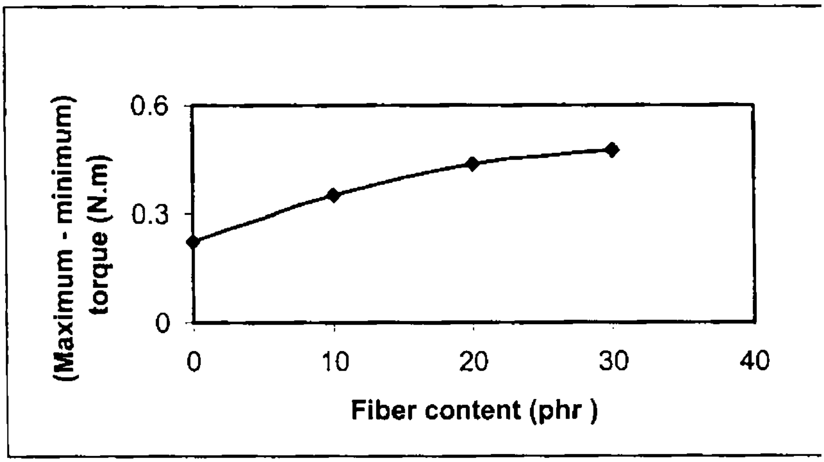

Figure 8.B.2. Variation of (maximum – minimum) torque with fiber loading.

Figure 8.B.1 gives variation of minimum torque with fiber loading. The minimum torque values show an almost linear increase with increase in fiber content indicating a progressive loss in the processability of the composite. The torque values change from 0.023 N.m at 0 phr to 0.088 N.m at 30 phr.

Figure 8.B.2 shows the variation of (maximum- minimum) torque values of the composites. (Maximum- minimum) torque shows a linear increase, indicating a more restrained matrix in the case of composites, with increase in fiber content. The torque values increased from 0.2122 N.m. at 0 phr to 0.4762 N.m. at 30 phr.

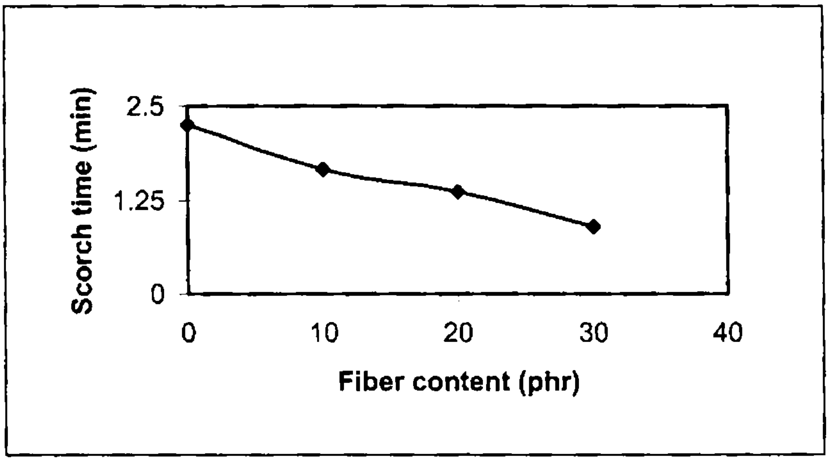

Figure 8.B.3. Variation of scorch time with fiber loading.

Plots of scorch time and cure time with fiber content are shown in figure 8.B.3 and 8.B.4, respectively. Both scorch time and cure time are found to be lowered in the presence of short fibers. The reduced cure time is also accompanied by increased cure rate values (figure 8.B.5.). Reduction in scorch time and cure time indicates that short nylon fibers are accelerating the cure reaction. This may be attributed to the possibility of generation of amines from nylon fibers by degradation at the curing temperature. Similar bservations have also been discussed in chapters IV.B and VI.B.

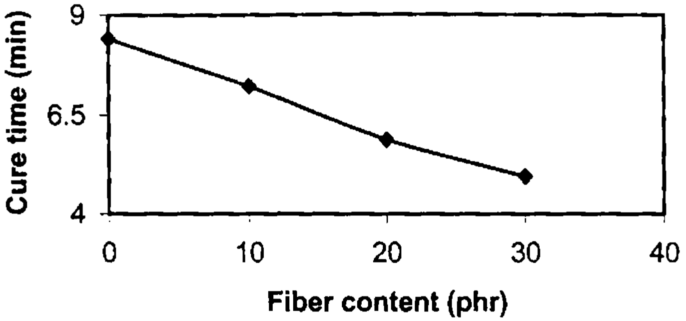

Figure 8.B.4. Variation of cure time with fiber loading.

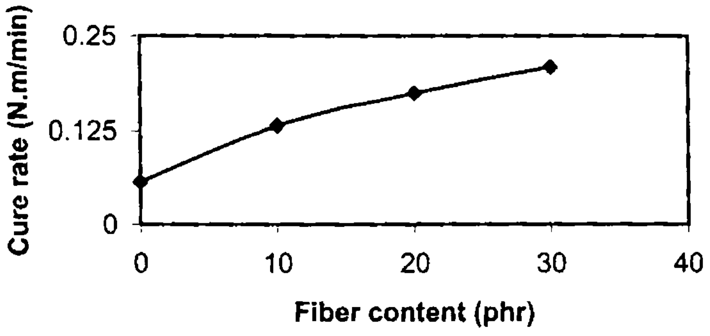

Figure 8.B.5. Variation of cure rate with fiber loading.

8.B.2. Mechanical Properties

Figure 8.B.6 is a graph of tensile strength versus fiber content. The tensile strength increases with fiber content in both the orientations of fibers. The tensile strength increases linearly with increase in fiber loading. This is in contrast to the pattern obtained for short nylon fiber-NR/WTR composites, where the tensile strength - fiber relationship is non-linear with a minimum at lower fiber concentrations (Chapter IV.B.), owing to strain induced crystallizing nature of NR. At all fiber loading the tensile strength values are higher in the longitudinal direction. In transverse direction the growing crack can easily pass through the fiber-matrix interfaces facilitating easy failure of the sample. Similar results have been reported by Murty et al.[1]

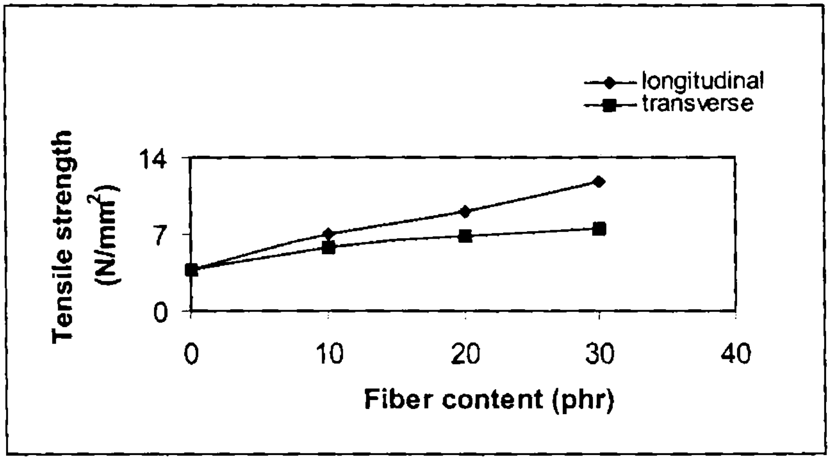

Figure 8.B.6. Variation of tensile strength with fiber loading.

The elongation at break undergoes a sharp fall on the introduction of 10 phr of fibers (figure 8.B.7.). But with further fiber loading, the ultimate elongation remains almost constant. Elongation at break values of the samples with transversely oriented fibers are higher than that of the samples with longitudinally oriented fibers.

The fibers inhibit the orientation and flow of molecular chains and hence the ultimate elongation decreases substantially on introduction of fibers. Similar results have been reported by many workers.[2-4]

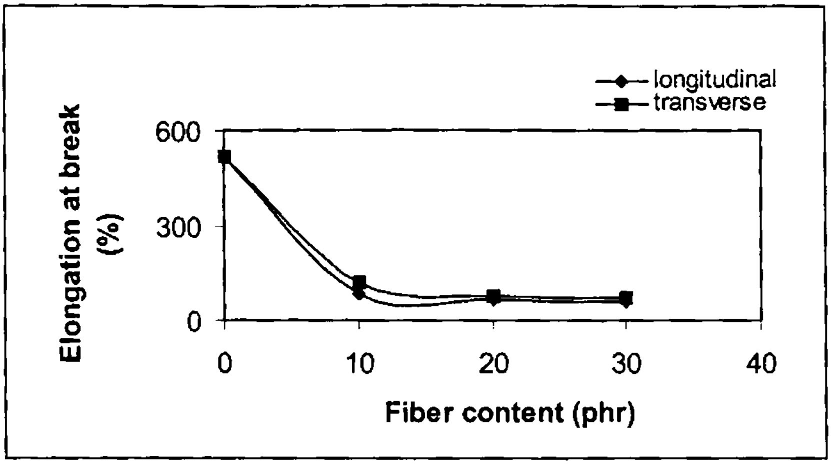

Figure 8.B.7. Variation of elongation at break with fiber loading.

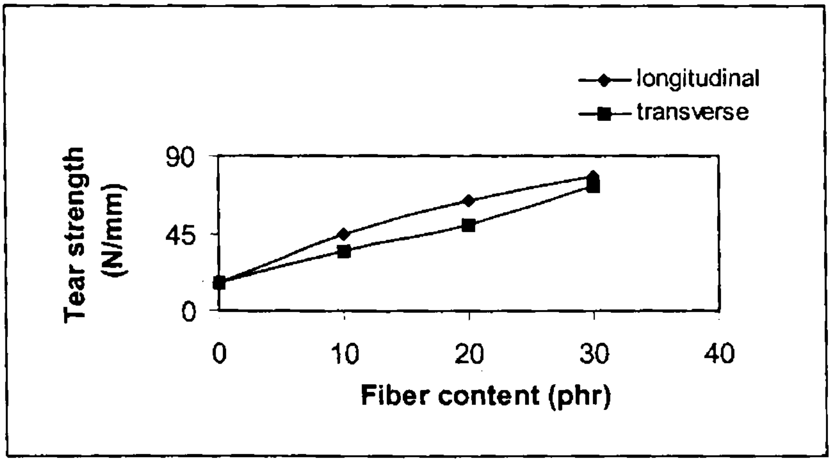

Figure 8.B.8. Variation of tear strength with fiber loading.

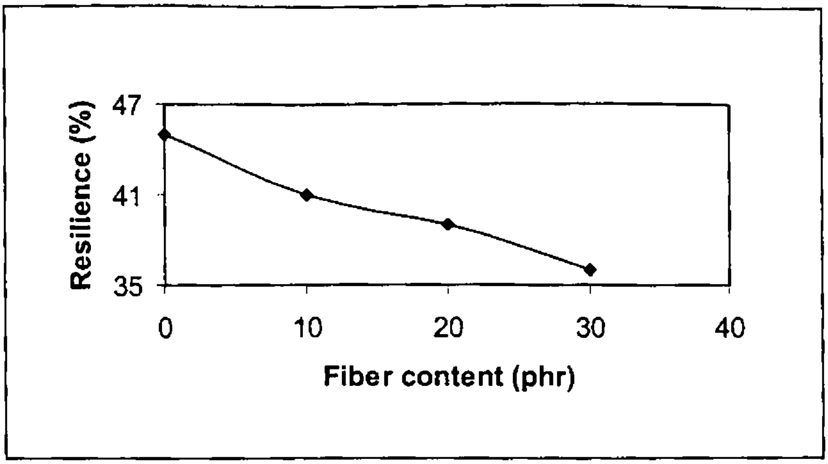

Figure 8.B.9. Variation of resilience with fiber loading.

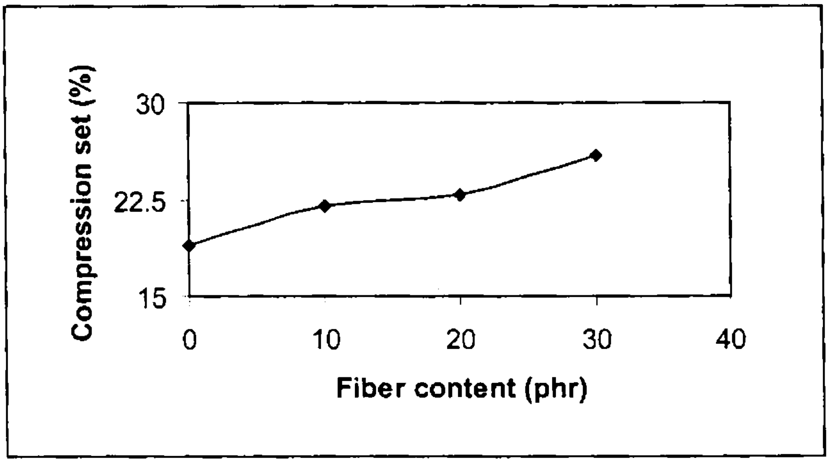

Figure 8.B.10. Variation of compression set with fiber loading.

Tear strength increases with fiber content in both the orientations of fibers (figure 8.B.8). As fiber concentration increases, there is more and more hindrance to the propagating tear by the fibers and nce the improvement in tear strength. The tear strength values higher in the longitudinal direction. In the case of transversely ented fibers, most of them being parallel to the propagating ack front, offers less resistance to propagating tear and hence wer tear strength values. Similar results have been reported by napati et al.[5]

esilience shows a reduction from 45% at 0 phr to 36% at 30 phr fiber (figure 8.B.9.). The dissipation of energy takes place rough fiber matrix interface and as fiber concentration increases ergy loss also increases and results in reduction in resilience alues.

plot of compression set versus fiber content is shown in figure .B.10. There is a linear increase in compression set values with ncrease in fiber concentration. This is in agreement with the ecreased resilience values.

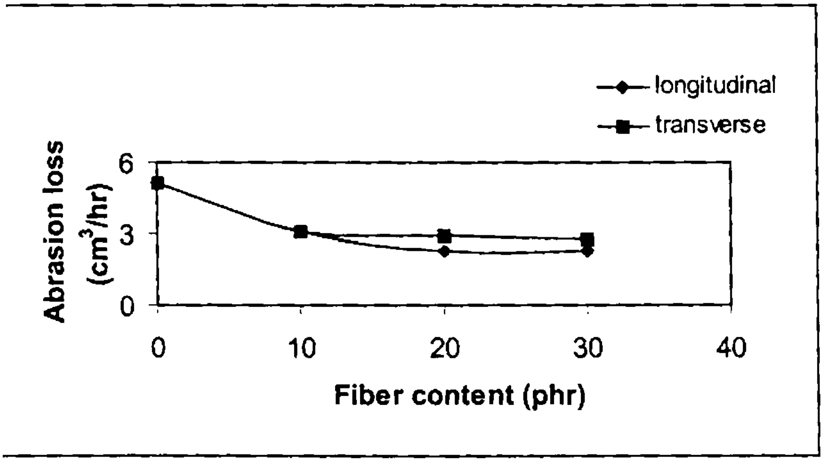

Figure 8.B.11. Variation of abrasion loss with fiber loading.

The abrasion loss of the fiber filled samples, are lower than that of the blend (figure 8.B.11.) This is because of more restrained matrix of composite. Samples with transversely oriented fibers show higher abrasion loss than the samples with fibers oriented along the direction of abrasion. This is because fibers get debonded and separated from the matrix more easily in samples with transversely oriented fibers.

8.B.3. Ageing Resistance

TableVIII.B.2. Tensile properties of the mixes before and after ageing

Mix No	Fiber orientation	Tensile strength (N/mm^2)		Percentage retention
		Before ageing	After ageing	
A		3.7	3.8	104
B	L	7.0	8.2	118
	T	5.8	6.3	190
C	L	9.0	9.7	107
	T	6.8	7.8	115
D	L	11.8	12.3	105
	T	7.5	8.0	107

L - Longitudinal orientation T - Transverse orientation

Table VIII B.2. shows the retention of tensile properties of the composites before and after ageing. In all cases the retention of tensile strength is found to be better for the composites. This may be attributed to marginal increase in state of cure of the composite, apart from improved fiber-matrix interfacial bond.

The retention of tear properties is shown in Table VIII.B.3. All mixes shows retention values above 100 indicating better fiber-matrix interfacial bond strength.

The elongation at break values of the composites before and after ageing is shown in Table VIII.B.4. All mixes except the gum compound shows retention values above 100%.

Table VIII.B.3. Tear properties of the mixes before and after ageing

Mix No	Fiber orientation	Tear strength (N/mm)		Percentage retention
		Before ageing	After ageing	
A		16.7	22.9	137
B	L	44.2	58.4	132
	T	35.1	50.1	143
C	L	63.7	72.4	114
	T	50.2	53.8	107
D	L	77.9	84.6	109
	T	72.8	89.6	123

L - Longitudinal orientation T - Transverse orientation

Table VIII.B.4. Elongation at break values of the mixes before and after ageing

Mix No	Fiber orientation	Tear strength (N/mm)		Percentage retention
		Before ageing	After ageing	
A		516.6	390.6	76
B	L	82.7	86.2	104
	T	117.4	182.8	156
C	L	72.4	82.4	114
	T	74.7	90.8	122
D	L	67.8	77.0	114
	T	71.8	84.8	118

L - Longitudinal orientation T - Transverse orientation

8.B.4. References

1. Murty V.M. and De S.K., J. Appl. Polym. Sci., **29** (1984) 1355.
2. Chakraborty S.K., Setua D.K. and De S.K., Rubber Chem. Technol., **55** (1982) 1286.
3. Murty V.M. and De S.K., Rubber Chem. Technol., **55** (1982) 287.
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5. Senapati A.K., Kutty S.K.N., Pradhan B. and Nando G.B., Int. J. Polym. Mater., **12** (1989) 203.

CHAPTER VIII.C.

NBR/WTR - SHORT NYLON FIBER COMPOSITE WITH BONDING AGENT*

The MDI/PEG resin was found to be a better interfacial bonding agent for NR/WTR-short nylon fiber composites (Chapter IV.C.) and also for NBR/WTR-short nylon fiber composites (Chapter VI.C.). In this chapter the effectiveness of this bonding system is evaluated for SBR/WTR-short nylon fiber composites. An 80/40/20 SBR/WTR-short nylon fiber composite was selected (Chapter VIII.B.). The amount of resin used was 5 phr and the MDI/PEG ratios used were 0.67:1, 1:1, 1.5:1 and 2:1.

The formulation of the mixes is given in Table VIII.C.1. The methods of sample preparation and the experimental techniques employed are given in Chapter 2.

Table VIII.C.1. Formulation of the mixes

Ingredient (parts by weight)	Mix No.				
	A	B	C	D	E
SBR	80	80	80	80	80
WTR	40	40	40	40	40
Nylon short fiber	20	20	20	20	20
MDI	0	2	2.5	3	3.33
PEG	0	3	2.5	2	1.67

Zinc oxide - 4 phr, stearic acid - 2 phr, HS - 1 phr, MBTS - 0.5 phr, TMTD - 1.8 phr and Sulfur - 0.3 phr are common to all mixes

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*Results of this Chapter have been communicated for publication in J. Mater. Sci.

8.C.1. Cure Characteristics

The variation of minimum torque with MDI/PEG ratio is shown in figure 8.C.1. The minimum torque shows an increase up to MDI/PEG ratio of 1.5:1. With further increase in isocyanate concentration the minimum torque value decreases. The initial improvement can be attributed to the low level of urethane resin formation in the processing stage. Due to the increase in stock viscosity as indicated by minimum torque values, the processability of the composite is reduced in presence of bonding agent. Similar results have been obtained in the case of NR/WTR-short nylon fiber composites (Chapter IV.C.) and also for NBR/WTR-short nylon fiber composites (Chapter VI.C.). However beyond a ratio of 1.5, further increase in the MDI concentration does not bring about corresponding increase in resin formation; rather the free isocyanate group is inhibiting the resin formation. It may be attributed to the possibility of formation of allophenate linkage by the reaction between the isocyanate groups.

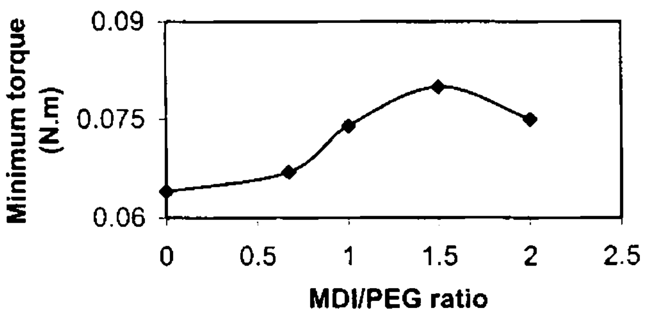

Figure 8.C.1. Variation of minimum torque with MDI/PEG ratio.

The maximum torque values show a reduction at lower MDI/PEG

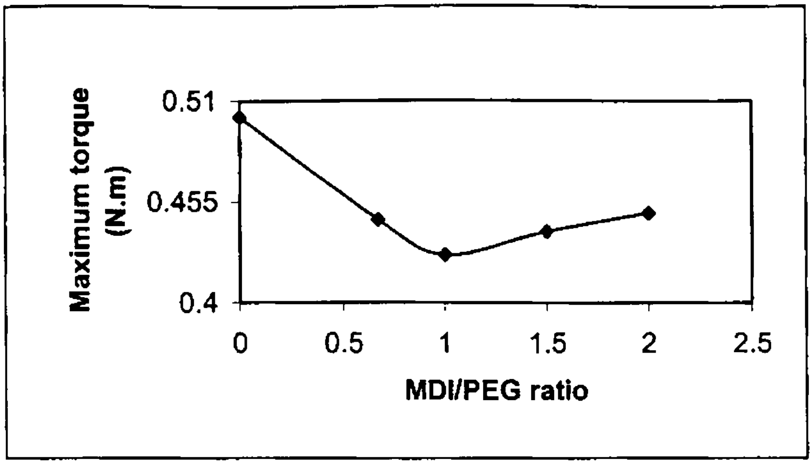

Figure 8.C.2. Variation of maximum torque with MDI/PEG ratio.

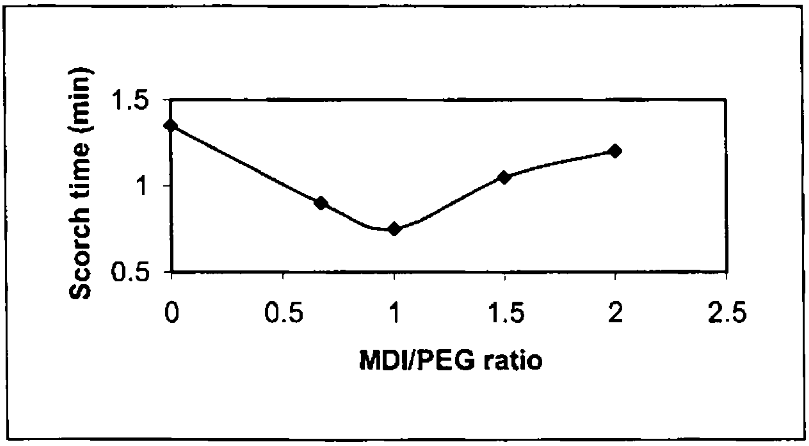

Figure 8.C.3. Variation of scorch time with MDI/PEG ratio.

ratio, with further increase in isocyanate concentration the torque values increase (figure 8.C.2.). The initial reduction arise from less effective utilisation of monomer functionalities of the bonding agent. With further increase in isocyanate concentration the matrix become more restrained and the torque increases.

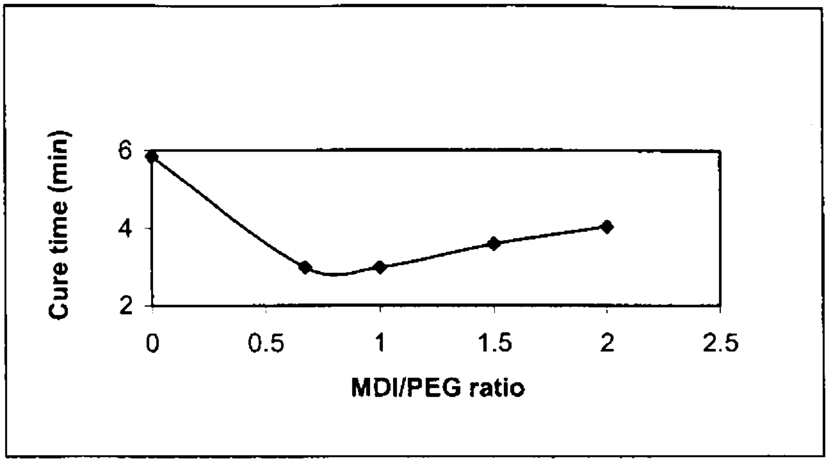

Figure 8.C.4. Variation of cure time with MDI/PEG ratio.

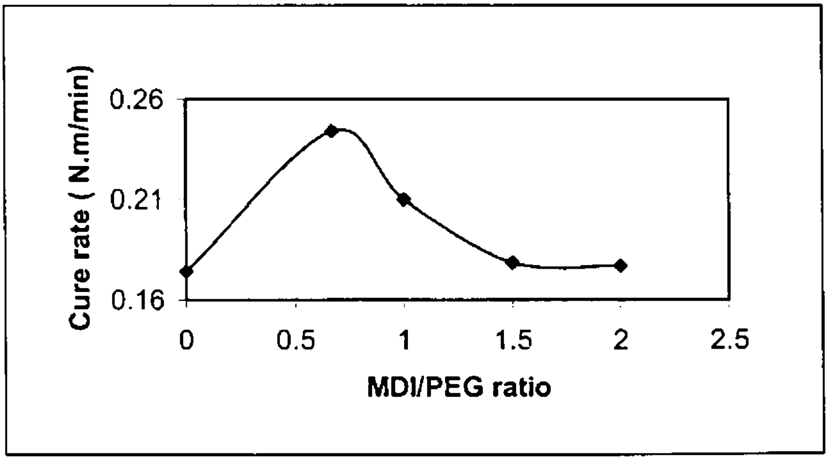

Figure 8.C.5. Variation of cure rate with MDI/PEG ratio.

The scorch time plotted against MDI/PEG ratio is given in figure 8.C.3. The scorch time shows a reduction at lower MDI/PEG ratio and with further increase in MDI content the scorch time increases. Similar trend is seen in the case of cure time also (figure 8.C.4.). There is a corresponding increase in cure rate values at lower MDI/PEG ratio (figure 8.C.5.). The excess free diol groups present at lower MDI/PEG ratio accelerate the sulfur crosslinking reaction result in higher cure rate values. Similar results have been reported in previous chapters (Chapter IV.C. &VI.C).

8.C.2. Mechanical Properties

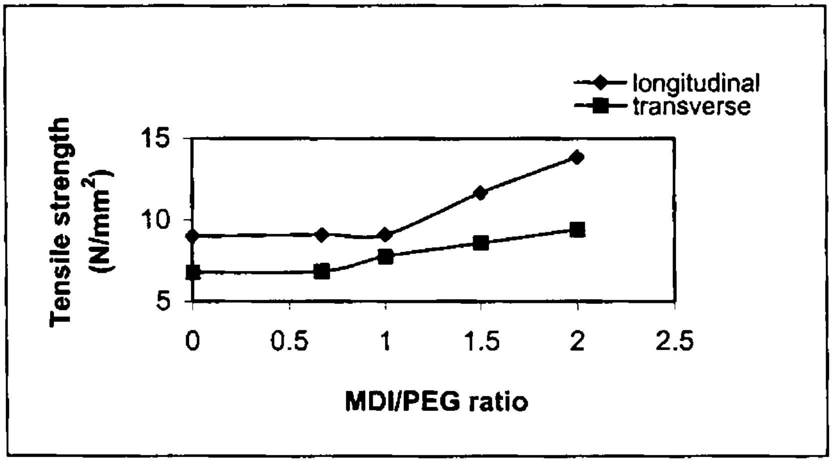

Figure 8.C.6. Variation of tensile strength with MDI/PEG ratio.

The tensile strength in both the orientations of fibers increase with isocyanate concentration. In all cases the tensile strength is higher in the longitudinal direction. The improved interfacial bond may facilitate better load transfer from matrix to fibers resulting in higher tensile strength. In transverse direction the fibers are less effective in restraining the matrix and hence lower tensile strength values in this direction.

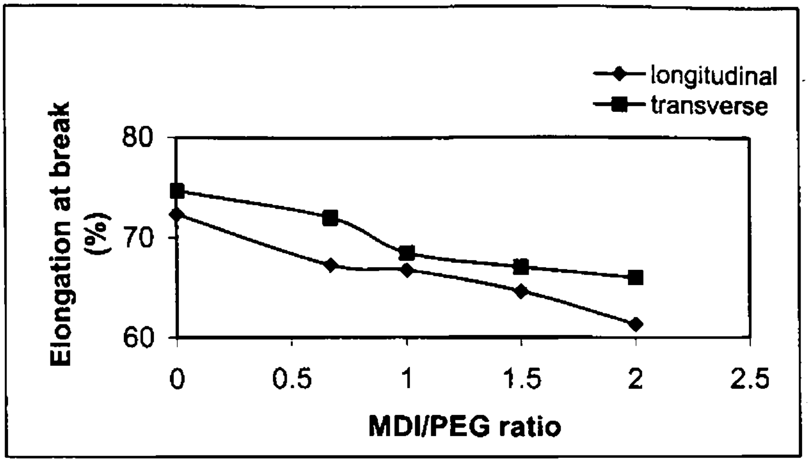

Figure 8.C.7. Variation of elongation at break with MDI/PEG ratio.

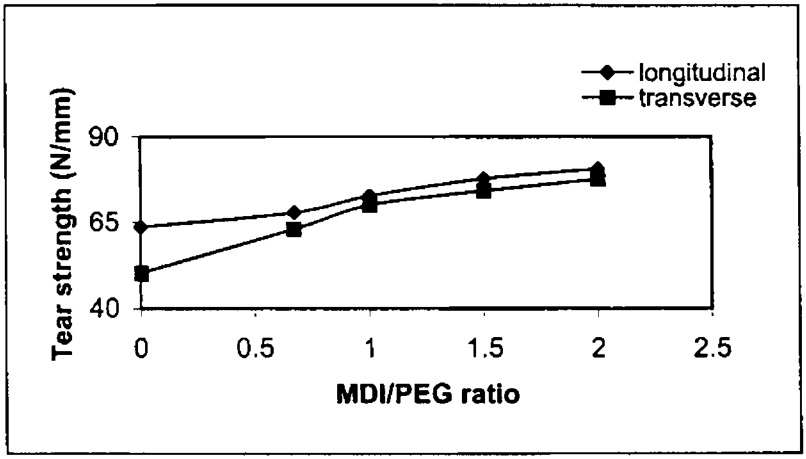

Figure 8.C.8. Variation of tear strength with MDI/PEG ratio.

With increase in MDI concentration the elongation at break values decrease (figure 8.C.7.). The elongation at break values are higher

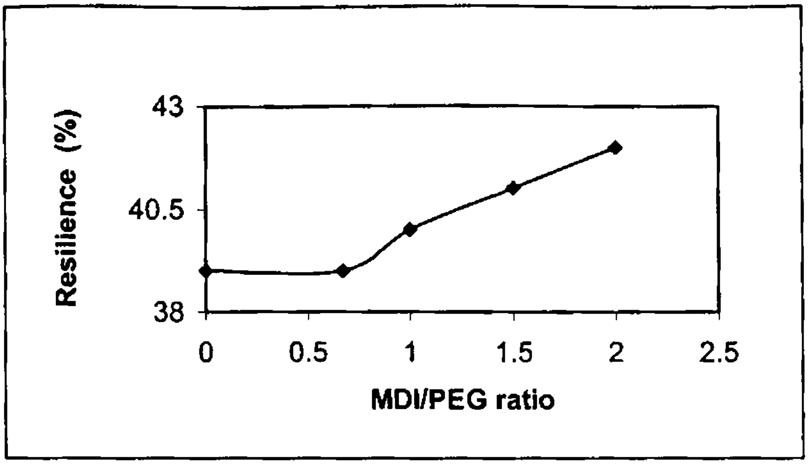

Figure 8.C.9. Variation of resilience with MDI/PEG ratio.

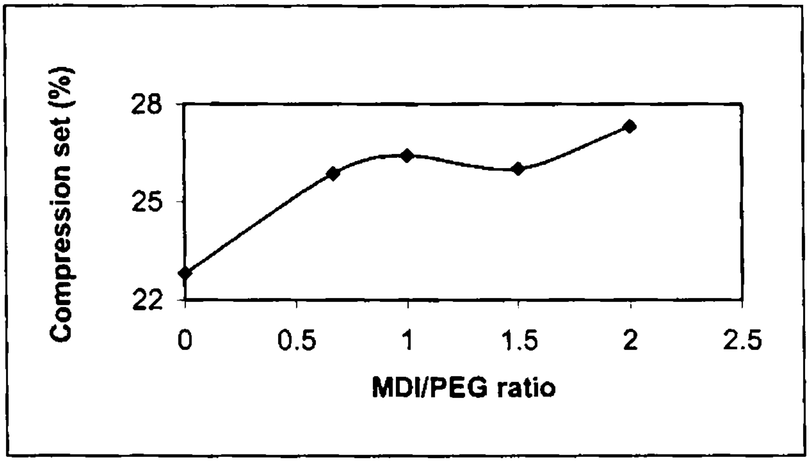

Figure 8.C.10. Variation of compression set with MDI/PEG ratio.

in the transverse direction. This also indicates a stiffer matrix, arising from the improved interfacial adhesion.

The tear strength shows an improvement with increase in the MDI/PEG ratio in both the orientations of fibers (figure 8.C.8.). Due to the improved interfacial bond the crack propagation is hindered more effectively and the tear strength increases. Similar results have been reported earlier.[1]

Resilience shows an increase with isocyanate concentration (figure 8.C.9.) indicates that in presence of urethane resin the elasticity of the composite is improved, which may be attributed to improved interfacial adhesion.

The compression set increases with isocyanate concentration (figure 8.C.10.). The increased compression set indicates an increased viscous nature of the matrix. The elevated test temperature renders the matrix more viscous and increases the flow under stress.

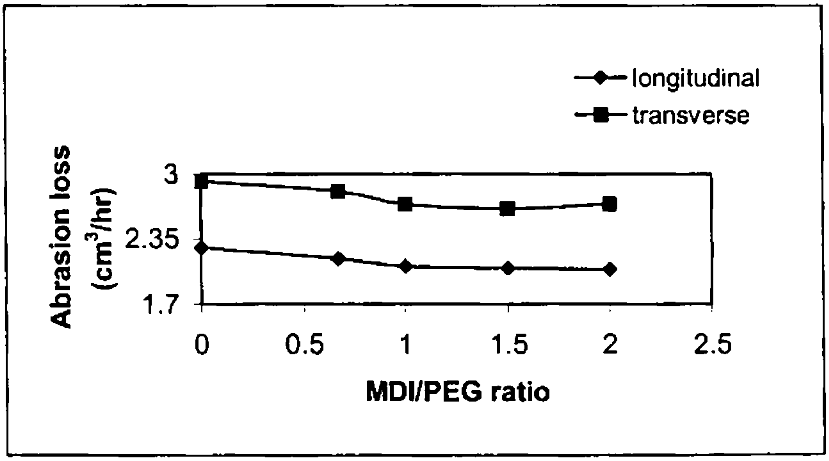

Figure 8.C.11. Variation of abrasion loss with MDI/PEG ratio.

Abrasion loss shows a reduction with increasing isocyanate concentration in both the orientations of fibers (figure 8.C.11.).

The improved interfacial bond makes the matrix more stiff resulting in lower abrasion loss. Similar results have been reported earlier.[2]

8.C.3. References

1. Suhara F., Kutty S.K.N. and Nando G.B., Polym. Plast. Technol. Eng, **37(2)** (1998) 241.
2. Ibarra L., Kaustschuk Gummi Kunststoffe, **48** (12/95) 860.

CHAPTER IX.

CONCLUSIONS

Whole Tyre Reclaim (WTR) can be successfully used to replace partially the virgin rubber in the case of NR, SBR and NBR. Short nylon fibers can be used to reinforce these blends. The properties of elastomer/WTR-short nylon fiber composites are different with respect to WTR content and short fiber loading. The effect of a urethane based fiber-matrix interfacial bonding agent on the performance of these composites is also found to be matrix dependent.

In short, the conclusions can be summarised as:

The replacement of natural rubber by reclaimed rubber improves its processability and tear resistance. The reclaimed rubber can replace up to 40 parts of NR without much affecting its tensile strength, resilience and abrasion resistance.

The presence of reinforcing nylon fibers in an 80/40 NR/WTR blend improves most of its mechanical properties. The tensile strength, tear strength, and abrasion resistance improve with increase in fiber content. The tensile strength-fiber content relationship is non - linear with a dip at 10 phr fiber. Anisotropy in mechanical properties are also exhibited by the composites. The tensile strength, tear strength and abrasion resistance are higher in the samples with longitudinal fiber orientation.

The urethane based resin system can improve the properties of a 20 phr fiber loaded 80/40 NR/WTR blend. The composite shows anisotropy in mechanical properties. The tensile strength, tear strength and abrasion resistance are improved in presence of bonding agent. The hysteresis loss and elastic properties are improved by the presence of bonding agent. The optimum properties are obtained with MDI/PEG ratio of 1:1.

In a non-crystallizing polar NBR matrix, the replacement by reclaimed rubber causes strengthening of the matrix. The tensile strength and elongation at break are improved in presence of reclaimed rubber. Reclaimed rubber can replace up to 20 parts of NBR without much affecting its properties.

In a 90/20 NBR/WTR blend the presence of reinforcing fibers improves its tensile strength, tear strength, resilience and abrasion resistance. Anisotropy in mechanical properties is also observed. The tensile strength-fiber loading relationship is linear.

The urethane resin system in a 90/20/20 NBR/WTR/short nylon fiber composite further improves its properties. The resin system increases tensile strength, tear strength and abrasion resistance. The optimum MDI/PEG ratio is 1:1.

Reclaimed rubber replaces up to 40 parts of SBR with improvement in its most properties. As in the case of NBR/WTR blends reclaimed rubber act as reinforcing filler in this case, resulting in improvement in tensile strength and tear strength.

An 80/40 SBR/WTR blend with different amounts of short fibers shows improvement in properties with increase in fiber content. The tensile strength, tear strength and abrasion resistance increase with fiber content. The anisotropy in mechanical properties is also shown by the composites.

In an 80/40/20 SBR/WTR-short nylon fiber composite the MDI/PEFG resin system acts as interfacial bonding agent. The tensile strength, tear strength and resilience are improved and the optimum resin ratio is 1:1.

LIST OF PUBLICATIONS

1. *"Cure characteristics and mechanical properties of natural rubber/reclaimed rubber blends,"* Polym. Plast. Technol. Eng., 39(3) (2000) 501.

2. *"Cure characteristics and mechanical properties of natural rubber-short nylon fiber composites,"* J. Elastomers Plast. (in press).

3. *"Cure characteristics and mechanical properties of short nylon fiber reinforced natural rubber/reclaimed rubber blends,"* J. Mater. Sci. (communicated).

4. *"Effect of urethane based bonding agent on the cure characteristics and mechanical properties of natural rubber/whole tyre reclaim-short nylon fiber composite,"* Polym. Plast. Technol. Engg. (accepted).

5. *"Studies on acrylonitrile butadiene rubber-reclaimed rubber blends,"* J. Elastomers Plast. (communicated).

6. *"Studies on acrylonitrile butadiene rubber-short nylon fiber composites,"* J. Elastomers Plast. (communicated).

7. *"Cure characteristics and mechanical properties of short nylon fiber reinforced acrylonitrile butadiene rubber-reclaimed rubber blends,"* Int. J. Polym. Mater. (in press)

8. *"NBR/reclaimed rubber/nylon fiber composite,"* Advances in Polymer Technology (in press).

9. *"Styrene butadiene rubber/reclaimed rubber blends,"* Int. J. Polym. Mater. (in press).

10. *"Styrene butadiene rubber-short nylon fiber composites,"* Int. J. Polym. Mater. (in press).

11. ***"Effect of short nylon fiber reinforcement on styrene butadiene rubber/reclaimed rubber blends,"*** Advances in Polymer Technology (communicated).

12. ***"Effect of urethane based bonding agent on the cure characteristics and mechanical properties of styrene butadiene rubber-whole tyre reclaim-short nylon fiber composite,"*** J. Mater. Sci. (communicated).