STUDIES ON SHORT NYLON-6 FIBER - ELASTOMER COMPOSITES WITH EPOXY RESIN AS BONDING AGENT

Thesis submitted to the

COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY

By

A. SEEMA

in partial fulfillment of
the requirements for the award of the degree of

DOCTOR OF PHILOSOPHY

IN THE FACULTY OF TECHNOLOGY

DEPARTMENT OF POLYMER SCIENCE AND RUBBER TECHNOLOGY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
COCHIN 682 022

SEPTEMBER 2004

To

My Beloved Parents

Dr. Sunil K. Narayanankutty
Reader

Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Cochin 682 022

1 - 09 - 2004

CERTIFICATE

This is to certify that the thesis entitled "**Studies on short Nylon-6 fiber - elastomer composites with epoxy resin as bonding agent**" is an authentic report of the original work carried out by Miss A. SEEMA under my supervision and guidance in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin - 682 022. 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-6 fiber - elastomer composites with epoxy resin as bonding agent**" is the original work carried out by me under the guidance of Dr. Sunil K. Narayanankutty, Reader, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682 022, and no part of this thesis has been presented for any other degree of any other institution.*

Seema

A. SEEMA

Cochin
01-09-2004

ACKNOWLEDGEMENT

A journey is easier when you travel together. Interdependence is certainly more valuable than independence. Many, many people have helped me not to get lost during the development of this thesis. It is a pleasant aspect that I have now the opportunity to express my gratitude for all of them.

First and foremost I want to thank my research guide, Dr. Sunil .K. Narayanankutty who was always there for me, sharing his wisdom and never ending love and affection towards me. His overly enthusiasm and integral view on research and his mission for providing 'only high-quality work and not less', has made a deep impression on me. I owe him lots of gratitude for having me shown this way of research. He not only served as my supervisor but also encouraged and challenged me through out my academic program. He guided me through out the thesis process never accepting less than my best efforts. Thank you for being my role model and mentor.

I am highly obliged to Dr. Rani Joseph, Head Department of Polymer science and Rubber Technology, for providing all the facilities and support for the completion of the work. I am grateful to Dr. K.E. Geroge and Dr. A.P. Kuriakose former Heads of the department of Polymer science and Rubber Technology for their help and encouragement to complete this piece of work. I express my heartfelt gratitude to all the teachers of the department for all their help, support, interest and valuable hints.

I am deeply indebted to Dr. S.L. Sarnot, Former Executive director of C-MET and Dr. B.K. Das, Executive Director of C-MET who gave and confirmed the permission for this PhD work and encouraged me to go ahead with my thesis. I am extremely happy to express my sincere thanks to Shri. P. Sasidharan, Director C-MET, Thrissur and Shri. I.C. Rao, Former Director for their stimulating support.

I profusely thank Shri K.R.Dayas for his keen interest and persistent support during the progress of research work. Needless to say, that I am grateful to all of my colleagues at C-MET who have been extremely eager to give all possible helps. Especially I am indebted to:

Potty and Ratheesh – who shared their experinece of research with me; Prasad – for his assistance and willingness for work arrangement.

I acknowledge my debt to the non- teaching staff of the department of Polymer Science and Rubber Technology for their wholehearted co-operation even though I can't acknowledge them individually.

I wish to thank my fellow research scholars for their help through out my period of research. My special thanks to: Honey and Ushamani - for their invaluable support and suggestions; Thomas and Rinku- who gave excellent co-operation in doing the TGA analysis; Bipin Bal and Jacob Samuel- for helping me in sample preparation; Lity, Jaya and Nisha – for being always there with helping hand.

To Dr. Sam Philip, Principal Scientist, IISC, Bangalore, I am greatly indebted. He provided me the SEM facility and patiently helped me to take SEM photomicrograph of too many samples.

I also extend my sincere thanks to Apollo tyres, Kalamassery for providing Goodrich flexometer for measuring Heat build up property.

I feel a deep sense of gratitude for my late father and mother who formed part of my vision and taught me the good things that really matter in life. The happy memory of my father still provides a persistent inspiration for my journey in this life. I am grateful to my sister and brother for rendering me the sense and the value of sister and brotherhood. I am glad to be one of them.

Last and surely not least, I want to acknowledge my wonderful friends. There were periods at my lowest point when someone would purposefully ask, "How's it going?" or "what are you finding?" serving to renew my spirit and refocus my attention and energy. In particular I want to thank: Bindu with whom I share all my feelings; Rema, Sheena and Manju – for converting hostel to homely atmosphere. They were always nice and considerate; Sindhu and Bini - who took all the pain to make my work complete. Roy deserves a special mention. He strictly monitored the thesis writing. I always enjoyed the conversation with him; his positive belief has encouraged me so many times.

A. SEEMA

Preface

The objective of this study is to explore the use of epoxy resin as interfacial bonding agent in short Nylon –6 fiber - elastomer composites. The properties of short fiber composite are greatly influenced by the fiber – matrix adhesion. The interfacial bonding agents are widely used to improve fiber – matrix adhesion. In the present study, epoxy resin is used as interfacial-bonding agent for short Nylon-6 fiber reinforced acrylonitrile butadiene rubber (NBR), Neoprene rubber (CR) and styrene butadiene rubber (SBR) composites. The composites were evaluated for their cure, mechanical, rheological and thermal properties, with and without epoxy resin bonding agent.

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

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

Chapter II gives a brief account of the experimental techniques used. It describes the different materials, and machinery and the method used for this study.

Chapter III deals with the cure and mechanical properties of the composites with and without bonding agent. Chapter III is divided into three sections.

Chapter IIIA discusses the cure and mechanical properties of short Nylon-6 fiber reinforced NBR composite with and without epoxy bonding agent. Chapter IIIB presents the cure and mechanical properties of CR-short Nylon-6 composites and the composites with epoxy resin as bonding agent. Chapter IIIC deals the cure and mechanical properties of short Nylon-6 fiber reinforced SBR composites and the same in the presence of epoxy bonding agent.

Chapter IV describes rheological characteristics of the composites and the effect of epoxy resin on the rheological properties of the composites. The results are presented in two sections.

Chapter IVA details the rheological characteristics of the short Nylon –6 reinforced NBR composite in the presence of the bonding agent. Chapter IVB gives results on the study of the rheological characteristics of the short Nylon –6 reinforced SBR composite with and without bonding agent

Chapter V gives an account on thermal degradation studies of the composite. This is presented in two sections.

Chapter VA discusses the thermal degradation of short Nylon –6 reinforced NBR composite and also the effect of epoxy resin on the thermal stability of the composites. Chapter VB deals with thermal degradation of SBR- short Nylon –6 composite.

Chapter VI is the concluding chapter of the thesis.

ABSTRACT

The thesis describes the development and evaluation of epoxy resin as interfacial bonding agent for short Nylon-6 fiber elastomer composites. Epoxy resin is well known for its adhesive property. The potential use of it as interfacial bonding agent in short fiber composite is not explored yet. Three rubbers viz., acrylonitrile butadiene rubber (NBR), Neoprene rubber (CR) and styrene butadiene rubber (SBR) were selected and different fiber loading were tried. The resin concentration was optimized for each fiber loading with respect to cure characteristics and mechanical properties. Rheological characteristics and thermal degradation of the composites containing different fiber loading and different resin concentrations were studied in detail to find the effect of epoxy resin bonding system. The mechanical properties were studied in detail. The short Nylon –6 fiber improved most of the mechanical properties of all the three rubbers. Tensile strength showed a dip at 10 phr fiber loading in the case of CR while it was continuously increased with fiber loading in the case of NBR and SBR. All the composites showed anisotropy in mechanical properties. The epoxy resin is an effective bonding agent for short Nylon –6 fiber reinforced NBR and CR composites. Epoxy resin improved tensile strength, abrasion resistance and modulus of these composites. SEM studies confirmed the improved bonding of fiber and matrix in the presence of epoxy bonding agent. Epoxy resin was not effective as bonding agent in the case of short Nylon fiber- SBR composite. From the rheological studies of the composites with and without bonding agent it was observed that all the composite exhibited pseudoplasticity, which decreased with temperature. At higher shear rates all the mixes showed plug flow. SEM pictures showed that maximum orientation of fibers occured at a shear rate, just before the onset of plug flow. The presence of fiber reduced the temperature sensitivity of the flow at a given shear rate. Die swell was reduced in the presence of fiber. Shear viscosity of the composite was increased in the presence of resin. Die swell was increased in the presence of epoxy resin for composites at all shear rates. The thermal degradation of NBR and SBR composites with and without bonding agent followed single step degradation pattern. Thermal stability of the composites was improved in the presence of bonding agent. The degradation of virgin elastomer and the composites followed first order kinetics.

CONTENTS

---

* *Detailed Contents are given at the beginning of each chapter*

Chapter I

INTRODUCTION

INTRODUCTION

Composite Materials have occurred in nature since the evolution of life. Wood and bones are naturally occurring composites. Owing to their favourable performance characteristics, composite materials have been gaining wide use in commercial, military and space applications. High strength and stiffness, high toughness and low weight are the most important characteristics of an ideal engineering material. Conventional engineering materials, metals and their alloys are strong and tough, but not light. Polymeric materials are light but lack strength. Fiber reinforced composites have all the ideal properties leading to their rapid development and successful use for many applications over the last decade. However, the potential advantages of these fiber filled polymer composites are far from being fully realized and continued growth is anticipated in their use for many years to come.

Composite material consists of two or more chemically distinct constituents or phases with a distinguishable interface between them and some of their properties are radically different from their constituents. Composite consists of a continuous phase called matrix in which a discontinuous phase is embedded. The discontinuous phase, which is harder and stronger than matrix, is called reinforcement or reinforcing material. The properties of the composites are strongly influenced by the properties of their constituent materials, their distribution and interaction among them. Composite properties may be either the sum of the properties of the distinct phases, or it may be the resultant property of the synergic action of constituent phases.

1.1 Classification of Composites

The strengthening mechanism of composites strongly depends on the geometry of the reinforcement. Based on the geometry of reinforcement the classification of the composite is shown in the Figure. 1.1.[1].

A composite whose reinforcement is a particle, by definition all the dimensions are roughly equal, is called particle reinforced composites. Particle fillers are widely used to improve the matrix properties such as to modify the thermal and electrical conductivities, improve performance at elevated temperatures, reduce friction, increase wear and abrasion resistance, improve machinabilty, increase surface hardness and reduce shrinkage. They are simply used to reduce the cost in many cases.

Fiber reinforcement composites contain reinforcements having lengths higher than cross sectional dimensions. These can be broadly classified as single layer composites and multilayer composites. Reinforcing fiber in a single layer composite may be short or long compared to its overall dimensions. Composites with long fibers are called continuous fiber reinforcement and composites in which short or staple fibers are embedded in the matrix are termed as discontinuous fiber reinforcement.

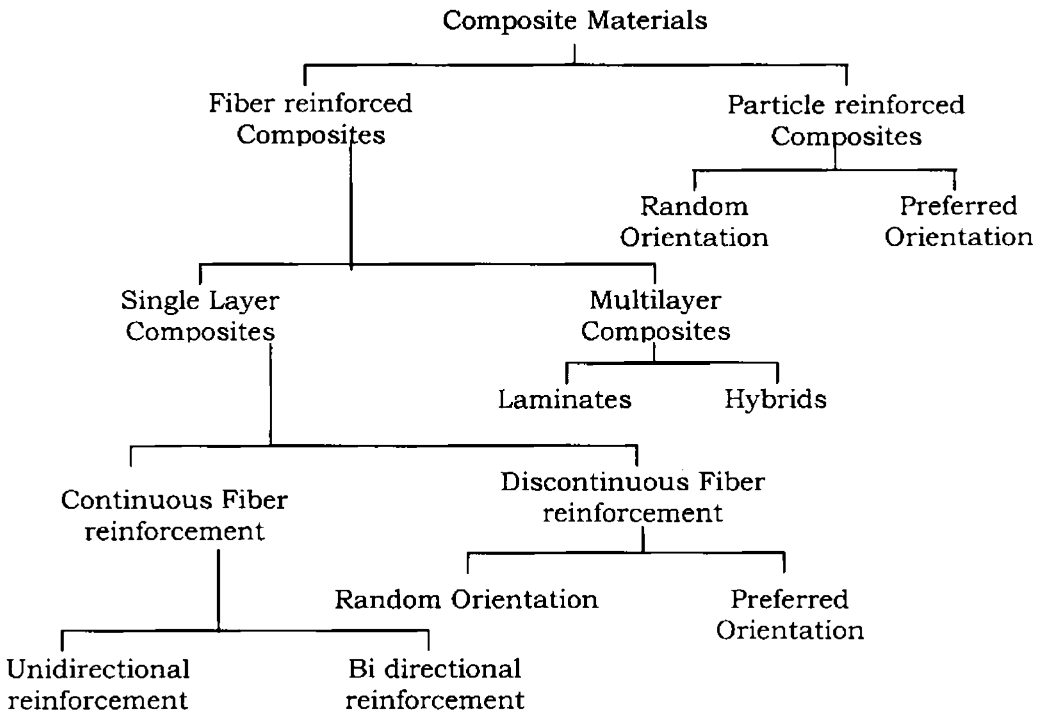

Figure. 1.1. Classification of composites

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 lightweight, 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. Natural and manmade fibers are used as reinforcement. Cellulose, jute, sisal, cotton etc. are examples of natural fiber; man made fibers include carbon, aramid, polyester, nylon, boron, glass etc. In these composites, fibers are the main load carriers and matrix holds the fibers together and it maintains the desired fiber orientations and transfers the load to the fibers. Matrix also protects the fibers against environmental attack and damage due to handling.

1.2 Short Fiber Composites

The reinforcement of a rubber with fibers would combine the elastic behavoiur of the rubber with the strength and stiffness of the reinforcing fiber. Conventionally most rubbers are reinforced with fillers of a particulate nature. 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.

The reinforcement of elastomers with short fibers has become necessary in many product applications. Composites with lower fiber content is useful for improving the hose and belt performance due to an increase in composite stiffness without a great sacrifice of the basic processablity characteristics of the compound[2]. In view of the processing requirements, even though the use of high volume content of fiber in the matrix cause difficulties during manufacture and product development, the improvement in the mechanical properties resulting from higher fiber loading is important in many applications.

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 can 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 desired anisotropy in mechanical properties. The manufacture of complex shaped engineering articles, which are impractical for formation from elastomers reinforced with continuous fiber, can easily be accomplished with short fibers.

The parameters influencing the characteristics of short fiber composites include fiber concentration, fiber aspect ratio, fiber matrix adhesion and fiber orientation[3]. Composites of good strength can be prepared from a variety of elastomers. Too short fibers are necessarily less effective in reinforcing low modulus materials for efficiency of reinforcement, i.e., the extent to which a discontinuous fiber can stimulate the performance of a continuous filament or cord depends on its modulus ratio relative to the matrix. Optimum properties of the short fiber composites depend on[4-6]

- Preservation of high aspect ratio
- Proper fiber orientation
- Maintaining better fiber matrix interface through pysico-chemical bonding
- Homogeneous dispersion
- Proper choice and appropriate orientation of fiber reinforcement

- Optimal formulation of the rubber compound to accommodate: (a) processing conditions, (b) facilitate stress transfer and (c) flexibility to preserve dynamic properties.

Zuev[7] 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. Foldi[8] has reported the processing advantages obtained with short fiber-rubber composites. In a review, Kun[9] presented effect of type of fiber, fiber pretreatment, compounding and processing on product performance properties. Advances in short fiber pretreatment, interfacial adhesion and development of short fiber-rubber composite products were reviewed by Zhou et al.[10]. Fiber reinforced plastic and rubber composite electrical insulators have been manufactured by Kadowaki et al.[11]. 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[12] reviewed short fiber reinforcement of rubber.

The advantages of short fiber – reinforced composites are high degree of dimensional stability during fabrication and extreme service environments by restricting matrix distortion, improved creep resistance, better resistance to solvent swelling, good fatigue life under high stress conditions and improved tear and impact strength by blunting and growing crack tips[13].

Both synthetic and natural fibers were used for the reinforcement of elastomers, natural as well as synthetic rubbers. 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[14]. 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[15]. Various natural materials which are potential reinforcements for rubber compounds are jute,[16] bagasse[17,18] and pineapple leaf fiber[19]. The use of asbestos, flax, glass and cotton fibers to reinforce various types of rubber is reviewed by Zuev et al.[20]. Manceau[21] 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[22]. Boustany and Coran[23] 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[24,25]. This method has been used by Coran and Patel[26] to reinforce chlorinated polyethylene with nylon fibrils.

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[27 - 31].

Derringer[32] incorporated different short fibers such as rayon, nylon and glass into NR matrix to improve young's modulus of vulcanizates. Goodloe et al[33,34] 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.[14,35] Investigations have also been made on short jute fiber reinforcement of carboxylated nitrile rubber by Chakraborty et al[36]. Mukherjea[37] 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.

Murty et al[38]studied processing characteristics, anisotropic swelling and mechanical properties of short jute and short glass fiber reinforced SBR composites both in the presence and absence of carbon black. It was found that jute fibers offered good reinforcement to SBR as compared to glass fiber. Bhagwan et al[39]studied the stress relaxation of short jute fiber NBR composites.

Cure characteristics and mechanical properties of short nylon -6 fiber nitrile rubber composite was studied by Rajesh et al.[40]. Sreeja et al[41] studied the short Nylon-6 fiber reinforced natural rubber reclaimed blends and found that most of the mechanical properties of NBR were improved by the presence of nylon fibers. Short silk fiber reinforced CR and NR have been described by Setua et al.[42,43]. Akthar[44] 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.[45]. 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.[46]. 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[47]. Natural rubber-coir fiber composite was studied by Geethamma et al.[48, 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 determined[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 composite materials consisting of short carbon fiber and thermoplastic elastomer have been studied by Ibarra et al[54] and concluded that oxidative treatment of carbon fibers exerted a beneficial influence on the properties of material reinforced with such fibers. Acrylic fiber reinforced rubber has been prepared by Moyama et al.[55]. Short fiber containing pneumatic tyres having good balance of abrasion and ice/snow-skid resistance were prepared by Midorikawa et al.[56]. Development of sealing materials of jute fiber reinforced cork and butadiene acrylonitrile rubber was described by Xie et al.[57]. Kikuchi[58] 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.[59].

Effect of processing parameters on the mechanical properties of short Kevlar aramid fiber-thermoplastic PU composite were reported by Kutty et al.[60]. 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[61] and there appeared a relaxation peak in the tan δ spectra at 120 °C when the interface between SBR and nylon short fibers had good adhesion. Roy et al[62] 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[63]. The surface characteristics and the length distribution of waste short fibers from reclaimed rubber were investigated by Zhang et al.[64]. The mechanical properties of waste short fiber-rubber composites and the influence of surface treatment of waste short fiber have also been investigated.

Mechanical properties of thermoplastic polyurethane elastomer composites reinforced with short aromatic polyamide and carbon fibers were studied by Correa et al.[65]. Pervorsek et al[66] prepared short polyamide reinforced rubber compositions. Short polyester fiber-NR composites were studied by Senapati et al[67] and the effect of fiber concentration, orientation and L/D ratio on mechanical properties were examined. Ibarra et al [68] 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[69] studied the reinforcement of millable PU with short Kevlar fiber.

Short fiber reinforced NBR composites was studied by Yoshiki[70]. 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[71]. Ashida[72] presented a review on the type of short fibers, adhesives used for short fibers, the preparation and performance properties of rubber-short fiber composites.

1.3. Nylon Fiber

The aliphatic polyamides or Nylons were the first fully synthetic fibers to achieve commercial success (1939). Nylon is a condensation polymer of a diamine and a dicarboxylic acid. Because a variety of diamines and dicarboxylic acids can be produced, there are very large numbers 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 main features are exceptional strength, high elastic recovery, abrasion resistance, lusture, washability, resistance to damage from oil and many chemicals, high resilience, colourability, relatively insensitive to moisture, smooth, soft and long lasting fibers from filament yarn, light weight and warm fabrics from spun yarn. The typical physical properties of Nylon fibers are given below (Table 1.1).

Table 1.1 Typical physical properties of Nylon fibers

Property	Continuous filament	Staple
Tenacity at break, N/tex, 65% Rh, 21°C	0.40 - 0.71	0.35 - 0.44
Extension at break, % 65% Rh, 21°C	15 - 30	30 - 45
Elastic Modulus, N/tex, 65% Rh, 21°C	3.5	3.5
Moisture regain at 65% Rh, %	4.0 - 4.5	4.0 - 4.5
Specific Gravity	1.14	1.14
Approx. volumetric swelling in water, %	2 - 10	2 - 10

Like polyester fiber, nylon has high melting point which conveys good high temperature performance. 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.

1.4. Short Nylon Fiber – Elastomer Composites

Many researchers have carried out various studies on short nylon fiber reinforced elastomers. Senapati et al.[73]. studied the effect of short nylon fibers on the mechanical properties of NR vulcanizates. Brokenbrow et al.[74] 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. Sreeja et al. [75-77] studied short Nylon –6 reinforced NR, NBR SBR composites and found that short Nylon –6 is enhancing the mechanical properties of these rubbers. O' Connor[3] reported the processing and properties of short fiber-elastomer composites with a variety of fibers (cellulose, nylon, glass, carbon and aramid). Dynamic viscoelastic properties of nylon short fiber reinforced composites were studied by Chen et al.[61]. 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.[78]. Ye et al.[79] 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.[80]. Short nylon fiber and vinylon fiber reinforced nitrile rubber and SBR were studied by Zhou et al.[81]. They introduced an effective interfacial thickness concept based on Halpin-Tsai equation to characterize the fiber rubber interfaces. Zhou et al.[82] 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.[83] using equilibrium method. Saad and Younan.[84] studied the rheological and electrical properties of NR-white filler mixtures, reinforced with short nylon-6 fiber with respect to filler loading. Kikuchi[58] 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. Zhang et al.[85] 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[86]. Mechanical properties of nylon short fiber reinforced SBR/NR composites were studied in detail by Ma et al.[87]. Zhang et al.[88] 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. Rajesh et al.[40] studied cure and mechanical properties of short Nylon fiber NBR composites. The influences of fiber length, loading and rubber crossliking systems on the properties of the composites were analyzed.

1.5. Mechanism of Stress Transfer in Short Fiber Composites

Different theories were proposed for the stress transfer in polymer composites. 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[89]. For a perfectly aligned and properly bonded unidirectional continuous fiber 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.

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 cannot 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[90]. Rosen[91] 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 given 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.

A critical fiber length is required to obtain the transfer of maximum load from the matrix to the fiber. 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 becomes 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.

Based on the shear lag model and characteristics of short fiber-rubber composite, Liqun et al.[92] put forward a new mixture law and predicted the longitudinal tensile strength of short fiber rubber composites. Abrate[93] reviewed the mechanics of short fiber composites and examined the factors affecting the mechanical properties. Fukuda et al[94] 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[95] 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.

The variation of physical properties of the composites with the direction of fiber orientation was reported by Moghe[96]. Derringer[97] postulated certain empirical equations relating volume fraction and aspect ratio of the fibers to the tensile strength, modulus and elongation at break. The effect of fiber length and orientation distribution on the strength of short fiber composite was examined[98] 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

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

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,

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

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

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. E_f and E_m are the modulus of fiber and matrix respectively. 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[99] 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.[100] presented a review dealing with different models of continuum theory for the prediction of mechanical properties of the composites.

1.6. Properties of the Composites

1.6.1. Mechanical properties

Mechanical properties are the major criteria in selecting a composite for a particular application or end use. The mechanical properties of short fiber composites are intermediate between those containing continuous filaments or cords and particulate filled materials. Reinforcement of rubber with short fiber enhanced tensile strength and modulus and reduced elongation and swelling of the rubber matrix[12,16]. Short fibers such as cellulose fiber,[101,102] silk fiber,[44,103] vinal fiber,[104] nylon fiber [75-77, 105-108] and aramid[30, 109-111] are used for improving the mechanical properties of the elastomers. The variation of tensile strength and elongation at break with fiber content was studied by Coran et al.[112]. 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[67,73]. For non-crystallizing rubbers such as NBR and SBR the presence of a small quantity of fiber enhances the strength[68]. Murty[16] 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[112]. The theoretical impact of orientation of individual fibers on composite strength was reported by Schafffers[113]. Abrate[93] 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[98] 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.[80] and an empirical relation was derived on Halpin-Tsai equation for the prediction of elastic modulus of the composite. Liqun et al.[92] studied the law of tensile strength of short fiber reinforced rubber composites among a wide range of fiber volume and length. Zuev[7] 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.

Short fiber improves the tear strength of the polymer composites to a greater extent when the fibers are oriented perpendicular to the direction of propagation of tear in the polymer matrix than when they oriented parallel to it. This has been demonstrated by several workers for short nylon-6 and PET fiber filled natural and synthetic rubber compounds[67,75-77,78,114]. 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[4, 93]. Murty et al.[16] 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[115] 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.[116].

1.6.2. Rheological Characteristics

As many of processing steps such as mixing, milling, extrusion, calendaring and moulding in the modern polymer industry involve flow of the polymer; an understanding of the rheological characteristics of the composite is essential. The rheological behaviour of polymer melts provides the choice of processing conditions and influences the morphology and mechanical properties of the final product. The need for rheological studies and its importance in selection of processing conditions were pointed out by Brydson[117]. White and Tokita [118-120] established a correlation between rheology and processing. Crowson et al.[121-122] reported the rheology of short glass fiber reinforced thermoplastics and found that fibers orient along the flow direction in the convergent flow and perpendicular to the flow direction in the divergent flow. Several studies on the reheological characteristics of short fiber reinforced polymer melts were reported [123-127]. Murty et al.[128] studied the rheology of short jute fiber filled natural rubber composites. A lot of studies were done on the dependence of the die swell on the L/D (length to diameter) ratio of the capillary [129-131]. Flow characteristics of thermosets compound filled with PET fiber have been reported by Owen and WhyBrew[132]. Gupta and co workers [133] reported the flow properties of PP- EPDM blend filled with short glass fibers. The rheological characteristics of the short carbon fiber filled thermoplastic blends of NR and HDPE have been reported by Roy et al. [134]. Rheological properties of Nylon polyester short fiber filled rubber were studied by Zhang et al. [135]. A Chinese review with 45 references deals with the dependence of rheological properties of short fiber reinforced composites on the short fibers and matrix, the amount and length of the short fiber, temperature and shear rate in the flow field[136]. Kutty et al.[137] reported the rheological characteristics of short fiber reinforced thermoplastic polyurethane. Rheological behaviour of short sisal fiber reinforced natural rubber composite was studied by Vargehse et al.[138]. Rheological properties of short polyester fiber polyurethane elastomer composite with and without bonding agent was reported by Suhara et al. [139-140].

1.6.3. Thermal Properties

Thermal stability of short fiber rubber composites by thermogravimertic analysis was studied by many researchers. Ronaldo et al.[141] studied the influence of short fibers on the thermal resistance of the matrix, Tg and kinetic parameters of the degradation reaction of thermoplastic polyurethane and found that thermal resistance of aramid fiber reinforced composite was greater than those of carbon fiber reinforced composites. The degradation characteristics of Kevlar fiber reinforced thermoplastics were reported by Kutty et al[142]. Younan et al.[143] studied the thermal stability of natural rubber polyester short fiber composites. Suhara et al.[144] studied thermal degradation of short polyester fiber - polyurethane elastomer composite and found that incorporation of short fiber enhanced the thermal stability of the elastomer. Rajeev et al.[145] studied thermal degradation of short melamine fiber reinforced EPDM, maleated EPDM and nitrile rubber composite with and without bonding agent and found that the presence of melamine fiber in the vulcanizates reduces the rate of decomposition and the effect is pronounced in the presence of the dry bonding system.

1.7. Fracture Analysis by Scanning Electron Microscopy

Scanning electron microscope is a versatile technique for the determination of fiber orientation, fiber distribution, fiber matrix adhesion and fracture mechanism of fiber reinforced composites. Fiber breakage and dispersion of glass fiber reinforced rubber composite was studied using phase microscopy by Derringer[32]. He also made use of SEM to characterize the dispersion and fracture of various NR composites filled with Nylon, Rayon, Polyester and acrylic fibers[97]. Moghe[2] used SEM to analyse the distribution of fiber length due to buckling and crimping under large deformations during processing of aramid fiber in PU elastomer composites. SEM was used to study the properties of short glass fiber filled rubber composites with and without silica by Murty et al.[146-147]. They also studied the effect of bonding agents on the fiber pull out on the fracture surface of the jute fiber filled composites. With the help of SEM Boustany and Arnold[148] studied the extent of breakage of the glass and Santowebr fibers in the elastomer matrices. Different fracture surfaces of the short fiber composites were explained using SEM by many researchers[36, 149-151]. With the help of SEM Kutty et al.[152] explained the tear and wear properties of short Kevlar fiber reinforced TPU composites and failure mode of the composite.

1.8. Parameters Affecting The Properties Of The Composites

Fiber aspect ratio, fiber orientation, fiber dispersion and fiber matrix - adhesion are the major factors which affect the properties of the short fiber reinforced composites.

1.8.1. Type and Aspect Ratio of Fiber

The aspect ratio of fibers is a major parameter that controls the fiber dispersion, fiber matrix adhesion, and optimum performance of short fiber polymer composites. An aspect ratio in the range of 100 – 200 is essential for high performance fiber rubber composites for good mechanical properties. For synthetic fibers an aspect ratio of 100 – 500 is easily attained as they are available in the diameter range of 10 – 30 μm. Considerable fiber breakage occurred during mixing of fibers with high aspect ratio (as high as 500) resulting in reduction in aspect ratio[153]. O'Connor[3] 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. 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[4,154]. Chakraborty et al.[36] have observed that an aspect ratio of 40 gave optimum reinforcement in XNBR reinforced with short jute fiber. Murty and De[35,38] reported that for jute fiber filled rubbers good reinforcement could be obtained with aspect ratio of 15 and 32 for NR and SBR respectively.

Correa et al [65] reported that there was a reduction in fiber length after the incorporation of short carbon and Twaron fibers to thermoplastic PU. Noguchi et al.[155] 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. 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[156]. An excellent treatment on the importance of aspect ratio especially with respect to the modulus of the matrix is given by Abrate[93]. Senapati et al.[67,73] 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. Akthar et al.[157] reported that a moderate breakage of short jute fibers occurs during mixing with NR-PE thermoplastic elastomer in a Brabender plasticorder. Significant breakage of short kevlar fibers during mixing in Brabender plasticorder in TPU matrix was reported by Kutty et al.[60,151]. The effect of fiber aspect ratio on mechanical properties of reclaimed rubber composites was studied by Zhanxun et al.[158]. Varghese et al.[46] reported that an aspect ratio in the range of 20-60 was sufficient for reinforcement for NR-short sisal fiber composites. Nagatami et al.[159] 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[62,160]. Reduction of fiber breakage of carbon fibers in CR was achieved by cement mixing method[161]. 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[86]. Ibarra et al.[54] 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.[162] 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[163].

1.8.2. Fiber Dispersion

One of the major factor which affects the high performance of the composite is good dispersion of fibers in the matrix. Good dispersion implies there will be no clumps of fibers in the finished products, ie., 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.[164] 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.[8] According to Derringer,[97] 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[3]. 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[165] 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.[166-168] Effect of shear rate, ram pressure, fill factor, power input and mixing time on fiber dispersion were studied. The effect of fiber dispersion on modulus and strength was studied by Shen and Rains[168]. 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. Derringer[32] 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[124] and Coran[169] 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.

1.8.3. Fiber Orientation

The properties of short fiber polymer composites are strongly dependent on the fiber orientation distribution. 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[96]. Enormous benefits would be possible, if methods could be developed for exercising tight control over the fiber orientation in moldings made from short fiber polymer composites. The dependence of composite properties on fiber orientation and alignment is also well documented[96,97]. 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[2]. 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. A high degree of fiber orientation could be achieved by repetitive folding and passing through a two-roll mill as reported by Boustany and Coran[170]. Akthar et al.[44] found a small nip gap and single pass in the mill to be the best. A rubber mill was used by Foldi[8] to orient various organic filaments into several types of rubber stock. Senapati et al.[67] 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.[60] It was observed that the lower the nip gap, the higher the anisotropy in tensile strength, implying greater orientation of fibers. The orientation of short fibers in polymer matrices has reviewed in detail by McNally[171].

Goettler and Lambright[172] developed a technique for controlling fiber orientation in extrusion by the use of an expanding mandrel die. During 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[124]. Campbell[12] 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.[124] 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[67,73].

1.8.4. Fiber Matrix Adhesion

Interfacial bond is known to play an important role in composites since it is through this interface the load is transferred to the fiber. 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. Different techniques have been employed to achieve a strong interfacial bond between fiber and matrix. These include HRH systems, RFL dips, fiber surface grafting and use of coupling agents.

Studies on the interfacial adhesion with short different fibers and matrices have been carried out earlier [173-175]. 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[176-178]. Kondo has reviewed the selection of adhesives for bonding short fiber reinforcements in SBR and NR compounds[179]. Derringer[97] 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[8] applied RFL dip on nylon fiber in NR-SBR matrix and found the reinforcing ability actually reduced. O'Connor[3] compared the HRH system with RH and hexa methoxy methyl melamine (HMMM) alone in various short fiber natural fiber composites. 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[180]. 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[16,36,42,44,181-183]. Some researchers have found that the replacement of silica by carbon black in the tri-component bonding system leads to essentially similar adhesion level[4,184]. 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.[37] The role played by the HRH system in short fiber filled NR/PE blend was reported by

Akthar et al.[44]. Arumugam et al.[45] reported that HRH system was effective in improving the adhesion between coconut fiber and rubber matrix.

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.[81,82]. Kutty and Nando[185] 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[79]. Ashida,[72] in a review has mentioned about adhesives used for short fibers. Short vinyl fibers pretreated with silane coupling agents gave good adhesion with CR[104]. The effect of surface treatment of nylon short fiber with RFL bonding agent was analysed for NR and EPDM rubbers[186]. 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[46]. 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[158].

To improve adhesion between fibers and NR polyallyl acrylate was grafted on cellulose fibers by Yano et al.[187]. Ibarra[188] 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[189]. The effect of fiber-matrix interfacial adhesion on viscoelastic properties of short sisal fiber NR composites was evaluated by Siby et al.[47]. 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[83]. The effect of two component system (resorcinol and hexa) on NR-short sisal fiber composite was studied in detail[190]. Interfacial adhesion between coir fiber and NR was improved by treating the fiber with alkali and NR solution and by incorporating HRH/RH system[48,49].

Suhara et al.[191] reported that in the 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[192,175]. Improvement of interfacial adhesion of poly (m-phenylene isophthalamide) short fiber-thermoplastic elastomer composite was achieved with N-alkylation of fiber surface[193]. Sreeja et al.[174,194] reported the urethane based bonding agent for short Nylon-6 reinforced NBR ad SBR rubber composites. Rajeev et al.[195] studied the effect of dry bonding system in improving the adhesion between fiber and matrix of short melamine fiber –nitrile rubber composite.

1.9. Applications

Unlike continuous fiber, short fiber can process similar way to the matrix. The manufacture of articles of complex shape cannot 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[172,196-198].

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[199] as well as for general purpose utility hoses. Using specially developed extrusion dies Goettler et al.[172] have aligned the fibers into a predominantly circumferential dispersion within the tube wall to provide the necessary burst strength. Iddon[200] discussed an optimum screw design and extruder head construction for hose manufacturing. Schroden et al.[201] 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[202] and Yagnyatinskaya et al.[203] 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.[204]. The use of CR reinforced with aramid short fiber for transmission belts have been discussed by Ichithani et al.[205].

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[206,207]. A reduction in crack propagation rate is obtained with the addition of 1% cellulose fibers to the tread compound.[206] Improvement in modulus and cut/crack resistance of urethane rubber was obtained with the inclusion of chopped organic fibers[208,209]. 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[210] Marzocchi et al.[211] claimed improved tyre stability when a random short glass fiber mat was incorporated under the tread. Arnhem et al.[212] 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.[213]. 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[214]. The application of cotton or other cellulosic reinforced thermoplastic polyisoprene as sheeting in shoe constructions was given by Georgieva et al.[215]. Additional applications claimed are[216] hard roll covers, oil well packings, bearings and bushes. De and co workers [217,218] 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 of the Work

The use of short fibers as reinforcing agents in elastomers opens up a new avenue for the utilization of waste fibers, available in plenty from fiber and textile industries. Short fibers as reinforcement in rubber offers substantial improvements in the mechanical, thermal and viscoelastic properties of the 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.

Although the ultimate properties of the short fiber reinforcement depend mainly on the fiber orientation, fiber loading and aspect ratio, the adhesion between the fiber and the matrix plays a very important role. Load is applied directly to the matrix rather than to the fiber. For high performance, load must be transferred effectively to the fibers, which demands a strong fiber – matrix interface. The various methods used to improve the interfacial bonding includes usage of adhesive systems, external bonding agents, coupling agent, pretreatment of fiber, grafting of fiber and modifying the polymer to provide functional groups that can bond to the fiber or to the surface coating. The use of wet bonding system based on resorcinol, formaldehyde and latex and dry bonding system based on Hexamethylene tetraamine, resorcinol and silica have been explored extensively. The use of a polar resin such as Polyurethane or Epoxy as an interfacial-bonding agent is a relatively new area. Though, recently, Polyurethane has been used to improve composite properties, the use of Epoxy resin in short fiber- rubber composites has not been studied systematically.

Epoxy resin is well known for its adhesive properties. Development of epoxy based bonding agent for short fiber reinforced synthetic rubber composites will be highly useful for the rubber industry. Wide ranges of synthetic rubbers are used for various applications. NBR and CR are the most commonly used special purpose rubbers. SBR is a general purpose rubber with wide range of applications. The short Nylon fiber is a promising reinforcing agent for these rubbers since they have good strength and cheap. The present work focuses on the development of an Epoxy based bonding agent for short Nylon-6 fiber reinforced NBR, CR and SBR composites and evaluation of the resulting composite with respect to the processability and important technological properties.

Cure characteristics of the composites with and without bonding agent provide information on the effect of bonding agent on the crossliking of the composite. Mechanical properties of the composite are the determining factor in selecting a composite for specific applications or end use. A detailed study on the effect of fiber concentration, fiber dispersion, fiber orientation and fiber – matrix adhesion on the mechanical properties of the composite have been carried out.

Tensile fracture surface has been examined under scanning electron microscope for a thorough understanding of the micro mechanism of failure. These studies reveal the various failure modes and fiber orientation in the matrix.

Rheological studies give an idea on the processing characteristics of a composite material. Shear viscosity, an important parameter that influences the processability of the composite and the die swell of the extrudate products are dependent on processing parameters like shear rate, temperature and the filler loading. It is very important to have knowledge on the effect of epoxy resin on the shear viscosity, activation energy of flow and die swell of the composite. Also included are the changes in these properties in the presence of bonding agent with shear rate, temperature and fiber content. SEM has been used to investigate the fiber orientation in the extrudates at different shear rates and temperatures.

A knowledge of the degradation characteristics of the composite is important in many applications. The thermal stability of elastomer may be influenced by the presence of the short fibers and bonding agent. Thermogravimerty has been used to study the thermal degradation behaviour of the composite.

1.11. REFERENCES

1. Bhagwan D. Agarwal and Larence J. Broutman., Analysis and Performance of Fiber Composites., Jhon Wiely Publications., 1980
2. Moghe. S.R., Rubber Chemisrty and technology., **49** (1976)1160.
3. O' Connor J.E., Rubber Chem. Technol., **50** (1977) 945.
4. Goettler L.A. and Shen K.S., Rubber Chem. Technol., **56** (1983) 619.
5. Foldi A. P., Reinforcement of Rubber Compounds With Short Individual Fibers: Theory and Practice. Paper presented at the ACS Rubber Division Meeting, New York City, April 1986.
6. Foldi A.P., Rubber Compounds Reinforced with Short Individual Fibers: A New Kind of Composite. Paper Presented at the International Rubber Conference, Sydney, Australia, October 1988.
7. Zuev, Yu.S., Kauch Rezina, **12** (1991) 30.
8. Foldi A.P., Rubber Chem. Technol., **49** (1976) 379.
9. Kun Byung Kyu, Park Chen Young and Shen Kwi Sook, Komu Hakhoechi, **26** (3) (1991) 246.
10. Zhou Yanhao, Zhang Liqun, Li Chen, Wu Weidong, Chen Tao and Li Donghong, Hecheng Xiangjiao Gongye, **21**(1) (1998) 1.
11. Kadowaki, Kazunori Kilajima Mitsuhiro and Tan Michio, Jpn. Kokai Tokkyo Koho JP 09,320,368 (97,320,368) 12 Dec. 1997.

12. Campbell J.M., Prog. Rubber Technol., **41** (1978) 43.
13. Coran A.Y., Boustany K. and Hamned P. Rubbr Chemistry and Technology., **47** (1974) 396.
14. Murty V.M. and De S.K., Polym. Eng. Revs., **4** (1984) 313.
15. Milewski J.W., Plastics Compounding, May/June (1982) 53.
16. Murty V.M. and De S. K., Rubber Chem. Technol., **55** (1982) 287.
17. Usmani A.M., Salyer I.O., Ball G.L.III and Schewndeman J.L., American Chem. Soc. Div. Org., Coatings and Plastics Chem. Papers, **45** (1981) 466.
18. Usmani A.M., Salyer I.O., Ball G.L.III and Schewndeman J.L., J. Elast. Plast., **13** (1981) 46.
19. Bhattacharya T.B., Biswas A.K. and Chatterjee J., Plast. Rub. Comp. Proces. Appl., **6** (1986) 119.
20. Zeuv Y.S., Karpovich T.I. and Bukhina M.F., Kauch Rezina, No.6 (1978) 28.
21. Manceau F., Rev. Gen. Caoulch Plast., **56** (592) (1974) 95.
22. Blanc D. and Evrand G., The Reinforcement of Elastomers by Polyolefin Fibrils, 5th Conf. Envr. Plast. Caoutch, **2** (1978) D15.
23. Boustany K. and Coran A.Y., (to Monasanto Co.) US 3,709,845 (Jan. 9, 1973).
24. Anon, Res. Disel., **177** (1979) 19.
25. Duhbar J.A. and Pope G.A., Chem. Abstracts, **90** (1979) 88581 g.
26. Coran A.Y. and Patel R., Rubber Chem. Technol., **56** (1983) 210.
27. Warick E.L., Pierce O.R., Polmanteer K.E. and Saam J.C., Rubber Chem. Technol., **52** (1979) 437.
28. Novikova L.A., Kolensnikovu N.N. and Tolstukhina F.S., Kauch Rezina, No. 6 (1978) 19.
29. Felterman M.Q., J. Elastomers Plast., **9** (1977) 226.
30. Kane R.P., J. Elastomers Plast., **9** (4) (1977) 416.
31. Sheelerz J.W., J. Elastomers Plast., **9** (3) (1977) 267.
32. Derringer G.C., Rubber World, **165** (1971) 45
33. Goodloe P.M., Mc Murtie D.H. and van Nostrand R.J., Rubber Age, **67** (1950) 687.
34. Goodloe P.M., Reiling T.L. and Mc Murtie, Rubber Age, **61** (1947) 697.
35. Murty V.M. and De S.K., J. Appl. Polym. Sci., **27** (1982) 4611.

36. Chakraborty S.K., Setua D.K. and De S.K., Rubber Chem. Technol., **55** (1982) 1286.
37. Mukherjea R.N., Pal S.K. and Sanyal S.K., J. Polym. Mater. **1** (1984) 69.
38. Murty V.M. and De S.K., J. Appl. Polym. Sci., **29** (1984) 1355.
39. Bhagwan S.S., Tripathy D.K. and De S.K., J. Appl. Polym. Sci., **33** (1987) 1623.
40. Rajesh C.,Uniikrishnan G., Purushothaman E., Sabu Thomas, J. Appl. Polym. Sci., **92** (2004) 1023.
41. Srjeea T.D, Kutty S.K.N., Polym. Plast. Technol. Eng., **42** (2), (2003), 239.
42. Setua D.K. and Dutta B., J. Appl. Polym. Sci., **29** (1984) 3097.
43. Setua D.K. and De S.K., Rubber Chem. Technol., **56** (1983) 808.
44. Akthar S., De P.P. and De S.K., J. Appl. Polym. Sci., **32** (1986) 5123.
45. Arumugam N., Tamere Selvy K. and Venkata Rao K., J. Appl. Polym. Sci., **37**(1989) 2645.
46. Varghese Siby, Kuriakose Baby, Thomas Sabu and Koshy Alex T., Indian J. Nat. Rubber Res., **4**(1) (1991) 55.
47. Varghese Siby, Kuriakose Baby, Thomas Sabu and Koshy Alex T., Indian J. Nat. Rubber Res., **5** (1- 2) (1992) 18.
48. Geethamma V.G., Reethamma J. and Thomas Sabu, J. Appl. Polym. Sci., **55**(4) (1995) 583.
49. Geethamma V.G., Thomas M.K., Lakshminarayanan R. and Thomas Sabu., Polymer, **39** (1998) 6.
50. Park Chen and Kem Byung Kyu, Pollimo, **13** (10) (1989) 882.
51. Park Chen Young and Kem Byung Kyu, Pollimo, **14** (3) (1989) 197.
52. Kem Byung Kyu, Kang Chang Kee and Shin Gui Sook, Pollimo, **15**(6) (1991) 742.
53. Zheng Yuansuo, Song Yue Xian Zhang Wen, Wang Youdav and Jin Zhihao, Xiang Jiaotong Daxue Xuebao, **32**(10) (1998) 88.
54. Ibarra L., Macias A. and Palma E., Kulchunk Gummi Kunstst. **48** (3/95) 180.
55. Moyama Tomoko and Nakkahara Akihiro, Eur. Pat. Appl., JP 511,838,04 Nov. 1992.
56. Midorikawa Shingo, Kondo Takanori and Harada Masaaki, Jpn. Kokai Tokkyo Koho, JP 06, 328, 905 (94, 328, 905) 29 Nov. 1994.

57. Xie Sujiang, Lu Renliang and Zhou Hujun, Runhera Yu Mifeng, **3** (1995) 14.
58. Kikuchi, Naohike, Rubber World, **214**(3) (1996) 31.
59. Yokobori Shizno and Ondo Kenji, Jpn. Kokai Tokkyo, JP 07 24 960 (95,24,960) 27 Jan. 1995.
60. Kutty S.K.N. and Nando G.B., Plast. Rub. Comp., **19**(2) (1993) 105.
61. Li Chen, Liu Bo and Zhou Yanhao, Fuhe Cailiao Xuebao, **6**(4) (1989) 79.
62. Roy D., Bhowmick A.K. and De S.K., J. Appl. Polym. Sci., **49**(2) (1993) 263.
63. Van der Pol J.F., Rubber World, **210** (3) (1994) 32.
64. Zhang Liqun, Liu Li, Geng Haiping, Chen Sang and Zhou Yanhao, Xiangjiao Gongye, **42** (9) (1995) 515.
65. Correa R.A., Nunes R.C.R. and Filho W.Z.F., Polym. Compos,. **19**(2) (1998) 152.
66. Pervorsek Dusan Ciril, Kwon Young Doo, Berringer Charles W. and Rowan, Hugh Harvey PCT Int. Appl. No. 90,04,617, 3 May 1990.
67. Senapati A.K., Kutty S.K.N., Pradhan B. and Nando G.B., Int. J. Polym. Mater., **12** (1989) 203.
68. Ibarra L. and Chamorro Celia, J. Appl. Polym. Sci., **43** (10) (1991) 1805.
69. Kutty S.K.N. and Nando G.B., Plast. Rub. Comp. Proces. Appl., **14**(2) (1990) 109.
70. Ono Yoshiki and Tamino Kichiya, Nippon Gomu Kyokaishi, **65**(9) (1992) 497.
71. Yamamotos, Compos. Polym. **1**(5) (1998) 371.
72. Ashida M., Nippon Gomu Kyokaishi, **63** (11) (1990) 694
73. Senapati A.K., Nando G.B. and Pradhan B., Int. J. Polym. Mater., **12** (1988) 73.
74. Brokenbrow B.E., Sims D. and Stokoe A.G., Rubber J., **151**(10) (1969) 61.
75. Sreeja, T.D.; Kutty S.K.N. J. Elastomers and Plastics, **34** (2) (2002) 157.
76. Sreeja T.D., Kutty S.K.N, J. Elastomers and Plastics, **33** (3) (2001) 225
77. Sreeja T.D., Kutty S.K.N. Int. J. Polym. Mater., **52** (3) (2003) 239.
78. King Chang Kee, Shin Gui Sook and Kim Byung Kyu, Pollimo, **14**(5) (1990) 456.
79. Ye L., Pan J. and Li D., Jixie Gong Cheng Xuebao, **26** (4) (1990) 68.

80. Li Chen and Zhou Yanhao, Fuhe Cailiao Xuebao, **7** (4) (1990) 53.
81. Zhou Yanhao, Chen Tao Wu Weidong, Li Chen, Li Donghong and Zhang Liquin, Heecheng Xiangjiao Gongye, **15**(6) (1992) 329.
82. Zhou Yanhao, Chen Tao, Li Chen and Li Donghong, Heching Xiangjiao Gongye, **15** (2) (1992) 294.
83. Zhou Y.H., Chen T., Wu W.D., Li C., Li D.H. and Zhang L.Q., Macromol. Rep., **A 30** (Suppl.5) (1993) 365.
84. Saad A.L.G. and Younan A.F., Polym. Degrd. Stab., **50** (2) (1995) 133.
85. Zhang Liqun, Zhou Yanhao, Zhang Yuding Geng Haiping and Qui Huanyu, Xiangjiao Gongye, **41**(12) (1994) 708.
86. Bhattacharya J.K., Rubber India, **46** (9) (1994) 13,36.
87. Ma Peiyu, Zhao Jan, Tang Jiansheng and Dai Guihua, Guofenzi Cailiao Kexue Yu Gongcheng, **10** (6) (1994) 55.
88. Zhang Liqun, Zhou Yanhao Li Donghong and Li Chen, Xiangjiao Gongye, **41**(5) (1994) 267.
89. Piggott M.R., Load Bearing Fiber Composites, Pergamon, Oxford (1980).
90. Cox H.L., Br. J. Appl. Phys., **3** (1952) 72.
91. Rosen B.W., Fiber Composite Materials, American Chemical Society for Metals, Metal Park, Ohio, (1965).
92. Liqun Zhang Riguan Jin, Haiping Geng and Song Chen Yanhao Zhou, Fuhe Cailiao Xeubau, **15** (4) (1998) 89.
93. Abrate S., Rubber Chem. Technol., **59** (1986) 384.
94. Fukuda H. and Kawala K., Fiber Sci. Tech., **7** (1974) 207.
95. Fukuda H. and Chou T.W., Fiber Sci. Tech., **15** (1981) 243.
96. Moghe S. R., Rubber Chem. Technol., **47** (1974) 1074.
97. Derringer G.C,. J. Elastoplast., **3** (1971) 230.
98. Fukuda H. and Chou T.W., J. Mater. Sci., **17** (1982) 1003.
99. Dzyura E.A., Int. J. Polym. Mater., **8** (1980) 165.
100. Kern Heinrich and Janezak Jolanta, Materials Wiss Werkstofftech, **23** (2) (1992) 54.
101. Podesva M., Karel Vas and Milos Krajear, Czech CS **237** (1987) 729.
102. Westerlind B., Hirose S., Yanno S. Halekayama H. and Rigdahl M., Int. J.
103. Polym. Mater., **11**(4) (1987) 333.

104. Setua D.K., Kautsch. Gummi Kunstst., **37** (11) (1984) 962.
105. Hata Katsuhiko, Jpn. Kokai Tokkyo Koho JP 02, 292, 336(90,292,336) (Cl. CO 855/24) 03 Dec. 1990 Appl. 89/109, 89529 Apr. 1980 5 pp.
106. Chung T.Y., Moon C.K., Cho H.H. and J.K. Loe, Pollimo, **143** (1990) 203.
107. Oda K., Fuji Y. and Takeshi T., Japan Kokai Tokkyo Koho, JP 02,251 550 (1990).
108. Kita M. and Kono M., Japan Kokai Tokkyo Koho, JP 02,258,867 (1990).
109. Luo D. and Liang Z., Heechang Xiangjiao Gongye, **14** (1) (1991) 46.
110. Anderopoulos A.G. , Konstantinidou A.V. and Pet sales H. J., J. Appl. Polym. Sci., **38** (11) (1990) 2073.
111. Foldi A.P., Mater. Res. Conf. Proc., **85** (32) (1987) 427.
112. Hata K., Japan Kokai Tokkyo Koho JP 02,292,328 (1990).
113. Coran A.Y., Boustany K. and Hamed P., Rubber Chem. Technol., **47** (1974) 396.
114. Schaffers W.J., Text. Res. J., **47** (1977) 502.
115. Rueda L.I. and Gamarro A.C., J. Appl. Polym. Sci., **37** (1989) 197.
116. Kainradl P. and Handler F., Rubber Chem. Technol., **33** (1960) 1938.
117. Hasegawa Arata, Koga Toshiaki, Mizuno Takahido, Takashima Hidesuke, Matsuo Yasunori and Ookawa Husoshi, Jpn. Kokai Tokkyo Koho, JP 08 55,512 (9655,512), (Cl. F21 V 31/00), 27 Feb 1991 App 941219,358, (10 Aug.1994) 4pp.
118. Brydson J.A., Flow Properties of Polymer Melts, 2nd ed; George Godwin, London 1981.
119. White, J.L., Rubb. Chem. Technol., **42** (1969) 257.
120. White J.L., Tokita N. J. Appl. Polym. Sci., **11** (1967) 321.
121. White J.L., Rubb.Chem. Technol., **50** (1977) 163.
122. Crowson, J., Flokes, M.J., Bright P.F., Poly. Eng. Sci., **20** (1980) 925.
123. Crowson, J., & Flokes, M.J., Poly. Eng. Sci., **20** (1980) 934
124. Goettler L.A., Lambright A.J., Leib R.I., Dimauro P.J., Rubb. Chem. Technol., **54** (1981) 277.
125. Goettler L.A., Leib R.I., Lambright A., J. Rubb.Chem.Technol., (1979) **52** 838.
126. Chan Y., White J.L., Oyanagi Y., J. Rheol. **22** (1978) 507.
127. Setua.D.K., Int. J. Polym. Mater, **11** (1985) 67.

128. Kuruvilla Joseph, Kuriakose B., Premalatha C.K.. Sabu Thomas, Pavithran C., Plast. Rub. Compos. Process Appl., **21** (1994) 237.

129. Murty, V.M., Gupta, B.R., De, S.K., Plast. Rub. Proc. Appl., **5** (1985) 307.

130. Arai, T., Aoyama, H., Trans. Soc. Rheol., **7** (1963) 333.

131. Rogers, M.G., J. Appl. Polym. Sci., **14** (1970) 1679.

132. Han, C.D., Charles, M., Philippoff, W. Trans. Soc. Rheol.,**14** (1970) 393.

133. Owen M.J and Whybrew K., Plastics and Rubber **1** (1976) 231.

134. Gupta A.K., Kumar Krishna P. and Ratnam B.R., J. Appl. Polym. Sci., **42** (1991) 2595.

135. Roy, D., Bhattacharya A.K. and Gupta B.R., J. Elastoplast., **25** (1) (1993) 46.

136. Zhang Liquin., Zhou Yanhao., Zhang Yudong., Geng Haiping and Ouin Huanyu., Xiangjiao Gongye., **41** (2) (1994) 708.

137. Zhang Liquin., Zhou Yanhao., Wu Weidong., Geng Haiping and Ouin Huanyu., Hencheng Xiangjiao Gongye., **19** (1) (1996) 5 (Chin).

138. Kutty S.K.N, De, P.P& Nando, G.B.. Plast. Rub. Compos. Process Appl., **15** (1991) 23.

139. Vargehse, S. Kuriakose,B., Thomas, S., Premalatha, C.K& Koshy, A.T., Plast. Rub. Compos. Process Appl., **20** (1993). 93

140. Suhara, F., Kutty S.K.N, & Nando, G.B., Polym. - Plast.Technol.Eng.,**36** (1997) 399

141. Suhara, F., Kutty S.k.N, Nando, G.B. & Bhattacharya, A.K. Polym. - Plast.Technol.Eng.,**37** (1998) 57.

142. Correa Ronaldo A., Nunes Regina C.R., Lourenco Vera L., Polym Degrad Stab **52** (3) (1996) 245.

143. Kutty S.K.N., Chaki T.K., Nando G.B., Polym Degrad Stab., **38** (1992)187.

144. Younan A.F, Ismail M.N, Khalaf A.I., Polym Degrad Stab., **48** (1) (1995) 103.

145. Suhara F, Kutty S.K.N, Nando G.B., Polym Degrad Stab., **61**(1) (1998) 9.

146. Rajeev R.S, De S.K, Bhowmick A.K, John Baby. Polym Degrad Stab., **79** (3) (2003) 449.

147. Muty V.M., Bhowmick A.K., De, S.K ., J. Mater. Sci., **17** (1982) 709.

148. Muty V.M., De, S.K., Bhagwan S.S., Sivaramakrishna, Athithan S.K., J. Appl. Polm. Sci., **28** (1983) 348.

149. Boustany K. Arnold R. L., J. Elastoplast., **8** (1976) 160.
150. Andries J.c., Rhee C.K., Smith R.W., ross D.B., Diem H.E., Rubber Chemistry and Technology., **52** (1979) 823.
151. White J.R., Thomas E.L., Rubber Chemistry and Technology., **57** (1984) 457.
152. Kutty S.K.N., Nando G.B., J. Appl. Polym. Sci., **43** (1991) 1913.
153. Kutty S.K.N., Nando G.B., Int. J. Polym. Mater., **17** (1992) 235.
154. Stickney P.B. and Falb R.D., Rubber Chem. Technol., **37** (1964) 1299.
155. Ashida M., Nippon Gomu Kyokaishi, **56** (1983) 768.
156. Noguchi T., Ashida M. and Mashimo S., Nippon Gomu Kyokaishi, 12 (1984) 829; Int. Polym. Sci. Technol., **12**(7) (1985) (7/67).
157. Noguchi T. et al., Nippon Gomu Kyokaishi, **57** (1984) 171; Int. Polym. Sci. Technol., **10** (1984) 44.
158. Akthar S., Bhowmick A.K. De P.P. and De S.K., J. Mater. Sci., **21** (1986) 4179.
159. Zhanxun, Fu Shenjin Wang Kexin and Xu Shuzhen, Heching Xiangjiao Gongye, **14** (5) (1991) 323.
160. Nagatami A. et al, Nippon Gomu Kyokaishi, **66** (1993) 741.
161. Roy D., Bhowmik A.K. and De S.K., Polym. Eng. Sci., **32** (1992) 971.
162. Jana P.P., Plast. Rub. Comp. Proces. Appl., **20** (1993) 107.
163. Prasantha Kumar R. and Thomas Sabu, Bull. Mater. Sci., **18** (8) (1995) 1021.
164. Prasantha Kumar R., RamaMurty K., Schit S.C. and Thomas Sabu, Macromol..... New Front , Proc. IUPAC Int. Symp. Adv. Polym. Sci. Technol., **2** (1998) 793.
165. Tyrone L. Vigo and Barbara Jikingzip, Composite Applications, The Role of matrix fiber and Interface, pp.133.
166. Leo T.J. and Johanson A.M., US patent, 4,263,184 (to Wyrough and Loser Inc.) April 21, 1989.
167. Goettler L.A. , US Patent 4,248,743, Feb 3, 1981.
168. Anthocne G., Arnold R.L., Rains R.K. and Shen K.S., reinforcement of rubber Compounds with Discontinuous Cellulose Fiber, International Rubber Conference, Brighton, England (1977).
169. Shen K.S. and Rains R.K., Rubber Chem. Technol, **52** (1979) 764.

170. Coran A.Y., Hamed P. and Goettler L.A., Rubber Chem. Technol., **49** (1976) 1167.
171. Boustany K. and Coran A.Y., (to Monasanto Co) US 3,697, 364, (Oct 10,1972).
172. McNally D.L., Polym. Plast. Technol. Eng., **8** (1977) 101.
173. Goettler L.A. and Lambright A.J., US Patent 4,056, 591 (to Monasanto Co.) Nov.1 1977.
174. Zhou Y. H., Chen T., Wu W. D., Li D. H., Li C, and Zhang L.Q. Macromol. Re., 1993 A 30 (suppl.5)
175. Sreeja T.D.and Kutty S.K.N. Prog. In Rubber Plast. & Recyling Technol. **18** (4) 2002, 283.
176. Suhara F., Kutty S. K. N. and Nando G. B. Polym. Plast. Technol. Eng, **37** (2) (1998) 241.
177. Lee L.H., J. Polym. Sci., **5** (1967) 751.
178. Dunnom D.D., Rubber Age, **100** (1968) 49.
179. Hewitt N.L., Rubber Age, **104** (1972) 59.
180. Kondo A., Selchaku, **22** (5) (1978) 13.
181. Dzyura E.A. and Serebro A.L., Kauch Rezina, **7** (1978) 32.
182. Creasy J.R. and Wagner M.P., Rubber Age, **100** (10) (1968) 72.
183. Morita E., Rubber Chem. Technol., **53** (1980) 795.
184. Setua D. K. and De S. K., J. Mater. Sci., **19** (1984) 983.
185. Manas-Zloczorver I., Nir A. and Tadmor Z., Rubber Chem. Technol., **57** (1984) 583.
186. Kutty S.K.N. and Nando G.B., Kautschuk Gummi Kunststoffe, **43** (1990) 189.
187. Chung T.Y., Moon C.K., Cho H.H., Lee J.K. and Lee J.O., Pollimo, **14**(3) (1990) 203.
188. Yano Shoichiro, Stenberg and Bingth Flink, Per. Nihon Reoroji Gakkarshi, **20** (3) (1992) 132.
189. Ibarra L., J. Appl. Polym. Sci., **49** (9) (1993) 1593.
190. Ashida M. and Guo Wuyun, J. Appl. Polym. Sci., **49** (4) (1993) 573.
191. Varghese Siby, Kuriakose Baby, Thomas Sabu and Koshi T. Alex, J. Adhes. Sci. Technol., **8** (3) (1994) 235.
192. Suhara F., Kutty S.K.N. and Nando G.B., Plast. Rub. Comp. Proces. Appl., **24** (1995) 37.

193. Suhara F., Kutty S.K.N. and Nando G.B., Int. J. Polym. Mater. **38** (1997) 205.
194. Chantaratcharoen Anongnuch, Sirisinha Chakrit, Amorn Sukchai Taweechai, Buclek Limcharoen Sauvarop and Meesiri Wiriya, J. Appl. Polym. Sci., **74** (10) (1999) 2414.
195. Sreeja T.D., Kutty S.K.N Advances in Polymer Technology, 20 (4) (2001) 281.
196. Rajeev,R.S; Anil.K.Bhowmick; De, S.K; Bandyopadhyay, S. Short melamine fiber filled nitrile rubber composites. J. Appl. Polym. Sci. 2003, **90** (2), 544.
197. Beatly J.R. and Hamed P., Paper Presented at the ACS Meeting, Rubber Div., Montreal, Quebee, Canada, May 1978.
198. Patent to Bridge Stone Co. Chem. Abstr., 96 219182f (1982).
199. Anonymous, Gummi Asbest. Kunst, Int. Polym. Sci. Technol., **10** (2) (1983) 35.
200. Anon, High Strength Automotive Hose Reinforced with Short Fibers, Design Eng. 24 May 1980.
201. Iddon M. I., Recent Developments in the Extrusion of Curved Hoses with Special Emphasis on the Implication of Scroll Design, Paper Presented at the Scandinavian Rubber Conference, Ronneby, Sweden, May 8, 1980.
202. Schroden Thomas and Keuper Dieter, Kaust. Gummi Kunstst., **44**(9) (1991) 878.
203. Rogers J.W., Rubber World, **183**(6) (1981) 27.
204. Yagnyatinskaya S.M., Goldberg B.B., Dubinker E.M. and Pozdnyakova LV., Kauch Rezina, **32**(7) (1973) 28.
205. Hasegawa Arata, Koga Toshiaki, Mizuno Takahido Takashima Hidesuke, Matsuo Yasunori and Ookawa Hiroshi, Jpn. Kokai Tokkyo Koho, JP 08 55,512 (9655,512) 27 (1996).
206. Ichitani Ru, Tachibana Firoyuki and Kerada Mitsumori, Jpn. Kokai Tokkyo Koho, JP 05, 262,919 (93,262,916) 12, (1993).
207. Beatly J.R. and Hamed P, Elastomers, **110** (8) (1978) 27.
208. Anon, Product Eng., **39** (18) (1968) 107.
209. Inoue S., Nishi T., Shibala S., Malsunaga T. and Kaneko Y., (to Bridgestone Tire Co.) US 3, 968,182 (July 6, 1976).

210. Martin F.S., (to United States Rubber Co.) US 2,751,363 (1956).
211. Dubetz A. et al., (to The Firestone Tire and Rubber Co.) US 3, 05, 389 (1962).
212. Marzoechi A. et al. (to Owens Corning Fiber glass Corp.) US 3,315,722 (1967).
213. Rijpkema B., Arnhem Kautschuk Gummi Kunststoffe, 47, Jahrgang Nr. 10/94.
214. Goettler L.A. and Swiderski Z, in Composite Applications, The Role of Matrix, Fiber and Interface, Eds. Vigo T.L. and Kinzip B.J., VCH Publishers, New York, (1992) 333.
215. Anon, Plast. Rubbers, Textiles **1**(3) (1970) 115
216. Georgieva V.S. and Vinogradva G.C., Kozh-Obuvn Prom-st, **22**(4) (1980) 45.
217. When Your Elastomeric Application Calls for Reinforcement......., Company Publication H-20485 (10/89) Du Pont Co., Willington, DE 19898.
218. Jana P.B., Mallick A.K. and De S.K., Composites, **22** (1989) 451. Jana P.B., Chaudhari S., Pal A.K. and De S.K., Polym. Eng. Sci. **32** (1992) 448.

Chapter II

EXPERIMENTAL TECHNIQUES

This chapter deals with the description of the materials used, the methods of sample preparation and the experimental techniques adopted in the present investigations.

2.1. Materials

Acrylonitrile Butadiene Rubber (NBR) was supplied by M/s Apar Polymers Ltd., India. The sample used was N553 grade with 33% acrylonitrile content.

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

Chloroprene Rubber (CR) (Neoprene rubber) W type used in this study was manufactured by M/s Du Pont, USA.

Mooney viscosity [ML (1+4) at 100°C]	47

Styrene Butadiene Rubber (SBR synaprene-1502) was obtained from M/s Synthetics and Chemicals Ltd., Bareilly.

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

Short Nylon Fiber (Nylon-6) fibers obtained from M/s 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	3656 - 3886

2.2. Chemicals

Zinc oxide supplied by M/s. Meta Zinc Ltd., Mumbai, India had the following specifications.

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

Stearic acid used in the study was procured from M/s Godrej Soaps Pvt. Ltd., Mumbai, India. It had the following specifications.

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

Dibenzothiazyldisulfide (MBTS) with a specific gravity of 1.34 and melting point 165°C was supplied by M/s Bayer India Ltd, Mumbai.

Tetramethylthiuramdisulfide (TMTD) with a specific gravity of 1.42 and melting point 140°C was procured from NOCIL, Mumbai, India.

N-Cyclohexyl-2-benzthiazylsulphenamide(CBS) used in the study was Santocure CBS, supplied by M/s Polyolefins Industries, Mumbai.

Sulphur was supplied by M/s Standard Chemicals Company, Pvt. Ltd., Chennai. The specifications of the sample were:

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

Ethylenethiourea (NA 22), accelerator used in the chloroprene vulcanization was obtained from M/s Akrochem Corporation, USA.

Magnesium oxide, MgO (light weight) used in the study was calcinated lightweight magnesia with a specific gravity 3.6, supplied by M/s Merck India Ltd., Mumbai, India.

Epoxy Resin (LAPOX, A31) and Hardener (LAPOX K30) was obtained from M/s Cibatul Limited, Gujarat, India.

Resin : Hardener Ratio	1:0.5
Curing Temperature	150°C
Hardener	Amine type
Weight per Epoxy equivalent	260

2.3. Processing

2.3.1. Compounding

The mixing was done as per ASTM D 3184 (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: fibers, activators, resin- hardener mixture, accelerators and finally sulphur. 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. For NBR sulphur was added first since solubility of sulphur in NBR is poor.

2.3.2. Cure Characteristics

Cure characteristics at 150°C were determined by using Goettfert Elastograph Model 67.85. 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°) at a frequency of 50 oscillations per minute. The torque transducer on the upper die senses the force being transmitted through the rubber. A typical cure curve is shown in figure 2.1.

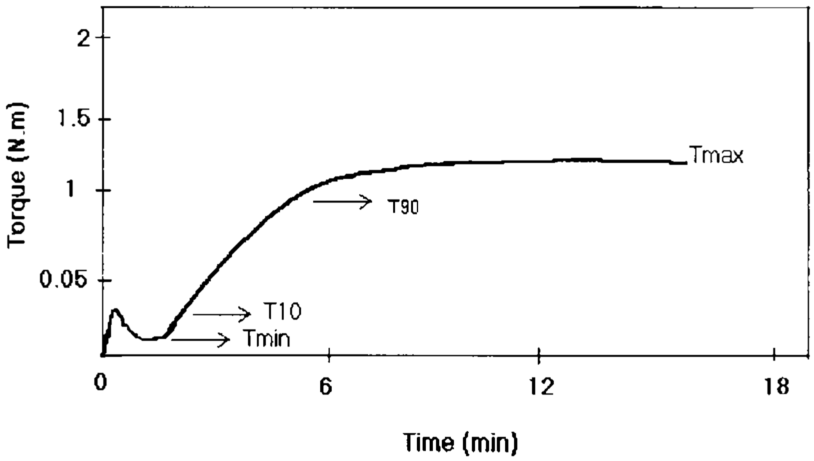

Figure 2.1. A typical cure curve

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 maximum torque recorded when curing of the mix is completed.

(Maximum – Minimum) torque : It is the difference between maximum torque and minimum torque during vulcanization. It represents improvement in the degree of crosslinking on vulcanization, i.e. it is a measure of final cross link density of the vulcanizate.

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 which was calculated using the formula

Torque at optimum cure = $0.9\,(T_{max} - T_{min}) + T_{min}$

where T_{max} and T_{min} are the maximum and minimum torques, respectively.

Cure rate: Cure rate is the rate at which crosslinking and development of stiffness of the compound occur after the scorch point. The slope of the steepest portion of the cure curve is taken as the cure rate.

2.3.3. Vulcanization

Test specimens marked with the mill grain direction were vulcanized at 150 ± 2°C and at a pressure of 180kg/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. Physical Properties

The vulcanizates were tested for different mechanical properties according to the relevant ASTM standards. Mechanical properties like tensile strength, tear strength, elongation at break, heat build up and abrasion resistance were tested using samples with the fibers oriented along (Longitudinal direction) and across (Transverse direction) the sample length. Schematic representation of fiber orientation in different test samples is given in figure 2.2. For ageing studies, the samples were kept in an air oven for 48 hours at 100°C (ASTM 573 – 88). The properties were measured after 24 hours on the completion of ageing.

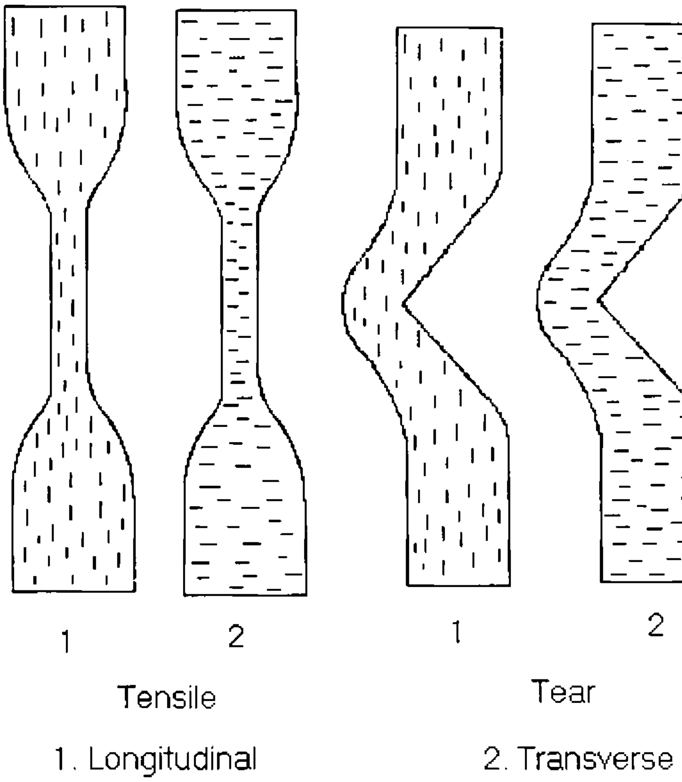

Figure 2.2. Schematic representation of fiber orientation

2.4.1. Tensile Strength, Modulus and Elongation at Break

Tensile properties were measured using Shimadzu Universal Testing Machine Model AG-I 50 KN according to ASTM D 412. Samples were punched out from the moulded sheets both along and across the grain direction with a dumb-bell die (die E). The grip separation speed was 500 mm/min. The ultimate strength, modulus at different elongations and ultimate elongation were noted.

2.4.2. Tear Strength

The tear strength was determined using Shimadzu Universal Testing Machine Model AG-I 50 KN according to ASTM D 624 (die C). The samples were punched from the moulded sheets along and across the direction of fiber orientation. The test speed was 500 mm/min.

2.4.3. Hardness

The hardness of the sample (Shore A) was determined using Zwick 3114 hardness tester according to ASTM D 2240 - 86. Samples having dimensions of 12 mm diameter and minimum 6 mm thickness were used. A load of 12.5 N was applied and the readings were taken 10 seconds after the indentor had made a firm contact with the specimen.

2.4.4. 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.

$$V = \frac{\Delta M \times 27.27}{\rho}$$

where V= Abrasion loss in cm^3/hr, Δ M = mass loss and ρ = density of the sample.

2.4.5. 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 (%).

2.4.6. Heat Build Up

Heat build up was tested using Goodrich Flexometer as per ASTM D 623 - 78 method A. The samples were 25 mm in height and 19 mm in diameter. The oven temperature was kept constant at 50°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 interval was taken as the heat build up. For fiber filled samples, where the test could not be completed to the standard test time of 20 minutes, due to premature sample failure, the value before the blown out were taken.

2.4.7. 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°C. At the end of the test period the test specimens were taken out, kept at room temperature for 30 minutes and the final thickness was measured. The compression set in percentage was calculated as follows.

$$\text{Compression set (\%)} = \frac{T_i - T_f}{T_i - T_s} \times 100 \qquad 2.1$$

where T_i and T_f are the initial and the final thickness of the specimen respectively and T_s is the thickness of the space bar used.

2.4.8. 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/cc)

2.5. RHEOLOGY

The mixes were prepared as per ASTM D 3182 (1989) on a laboratory size two roll mixing mill. The compounding temperature was kept below 90°C by passing water through the mill rolls.

Rheological studies were carried out using a capillary rheometer attached to a Shimadzu Universal Testing Machine model AG-I 50 KN. A capillary of L/D 10 and an angle of entry 90° was used. The measurements were carried out at various shear rates ranging from1.6 to 831.2 s^{-1}. The temperature difference between different zones was kept minimum. Small strips of composites were placed inside the barrel and warmed for a minute. Then they were forced down with a plunger attached to the moving crosshead. The height of the melt in the barrel before extrusion was kept constant in all runs. The experiments were carried out at six different shear rates obtained by moving the cross head at pre – selected speeds (1 to 500mm/min). The force corresponding to different plunger speeds was recorded. The true shear stress was calculated as[1]

$$\tau_w = \frac{PR}{2L}$$

where τ_w is the shear stress of the wall, P is the pressure drop, L is the length of the capillary and R is the radius of the capillary.

Apparent shear rate, shear rate at wall and viscosity were calculated using the following equations

$$\gamma_a = \frac{32Q}{\pi d_c^3}$$

$$\gamma_w = \frac{(3n'+1)\gamma_a}{4n'}$$

$$\eta = \frac{\tau_w}{\gamma_w}$$

where, γ_a is the apparent shear rate (s^{-1}); Q is the volumetric flow rate ($mm^3\ s^{-1}$); d_c is the diameter of the capillary (mm); γ_w is the shear rate at wall (s^{-1}) ; n' is the flow behaviour index, and η is the shear viscosity (Pa.s)

n' was calculated by linear regression from log (τ_w) and log (γ_a). The extrudates emerging from the capillary were collected with the utmost care to avoid any further deformation and the diameters were measured after a relaxation period of 24 hrs. The die swell was calculated as the ratio of the diameter of the extrudate to that of the capillary (d_e/d_c).

Relative Viscosity (η_r) was calculated by using the following equation

$$\eta_r = \frac{\eta_b}{\eta_0}$$

where η_b is the viscosity of the mixes with bonding agent and η_0 is the viscosity of the mixes without bonding agent.

Relative Die swell ratio (D_r) was calculated by using the following equation

$$D_r = \frac{D_b}{D_0}$$

where D_b is the die swell ratio of the mixes with bonding agent and D_0 is the die swell ratio of the mixes without bonding agent.

Relative Activation energy was calculated by using the following equation

$$A_r = \frac{A_b}{A_0}$$

where A_b is the activation energy of the mixes with bonding agent and A_0 is the activation energy of the mixes without bonding agent.

2.6. Thermal Analysis

Thermogravimetric analyses of the gum and composites were carried out on Universal V3 2B TA Instrument with a heating rate of 10°C/min under nitrogen atmosphere. The following characteristics were determined from the thermogravimetric curves: the temperature of onset of degradation, the temperature at peak rate of decomposition, the peak rate of degradation and the weight of residue remaining at 600°C. Using Freeman - Carroll equation, the order of the degradation reaction of the composite was calculated.

2.7. Scanning Electron Microscopy (SEM)

Scanning electron microscopic studies were carried out using SEM Model No S 360, Cambridge Instruments, U.K. To study the failure mode, the surfaces were carefully cut from the failed test specimens without touching the fracture surface and were sputter coated with gold. The orientation of the samples was kept constant in a particular mode of failure.

Chapter III

CURE CHARACTERISTICS AND MECHANICAL PROPERTIES

Section A. Part I
NBR-short Nylon-6 fiber composites

- 3.A.1.1. Cure characteristics
- 3.A.1.2. Mechanical properties
- 3.A.1.3. Ageing resistance

Section A. Part II
NBR-short Nylon-6 fiber composites with epoxy resin as bonding agent

- 3.A.2.1. Cure characteristics
- 3.A.2.2. Mechanical properties
- 3.A.2.3. Ageing resistance

Section B. Part I
CR-short Nylon-6 fiber composites

- 3.B.1.1. Cure characteristics
- 3.B.1.2. Mechanical properties
- 3.B.1.3. Ageing resistance

Section B. Part II
CR-short Nylon-6 fiber composites with epoxy resin as bonding agent

- 3.B.2.1. Cure characteristics
- 3.B.2.2. Mechanical properties
- 3.B.2.3. Ageing resistance

Section C. Part I
SBR-short Nylon-6 fiber composites

- 3.C.1.1. Cure characteristics
- 3.C.1.2. Mechanical properties
- 3.C.1.3. Ageing resistance

Section C. Part II
SBR-short Nylon-6 fiber composites with epoxy resin as bonding agent

- 3.C.2.1. Cure characteristics
- 3.C.2.2. Mechanical properties
- 3.C.2.3. Ageing resistance

SECTION A. PART (I)

NBR-SHORT NYLON-6 FIBER COMPOSITES

Nitrile rubber is a speciality synthetic rubber, having excellent oil and gasoline resistance due to the presence of polar acrylonitrile group. It is widely used in oil delivery hoses, gaskets, diaphragms, sealants etc. Because of its low gum strength and poor mechanical properties, NBR is usually reinforced with black fillers. Short Nylon fibers with good strength make an excellent reinforcing material for NBR. Nylon short fiber is also a waste product of textile industries and hence the method is cost effective and environment friendly.

The properties of short fiber containing composites depend critically on fiber content, orientation, aspect ratio and fiber- matrix interface bond strength. In this section, the results of investigations on short Nylon fiber - NBR composite are described.

Table 3.A.1.1 gives formulation of the mixes. The details of preparation of the mixes, determination of cure characteristics, moulding and testing are given in Chapter 2.

Table 3.A.1.1. Formulation of the mixes

Ingredients	Mix No.			
	A	B	C	D
CR	100	100	100	100
Short Nylon fiber	0	10	20	30

Zinc oxide - 4 phr, Stearic acid - 2 phr, MBTS - 1 phr, TMTD - 1.8 phr & Sulphur- 0.7 phr are common to all mixes.

3.A.1.1 Cure Characteristics

A plot of minimum torque versus fiber loading is shown in Figure 3.A.1.1. Minimum torque increases linearly with fiber content, indicating that processability of the composite is adversely affected. The presence of fibers restricts the flow of the matrix causing higher minimum torque.

(Maximum- Minimum) torque increases linearly with fiber concentration, indicating the formation of more restrained matrix in the case of composites (Figure 3.A.1.2.).

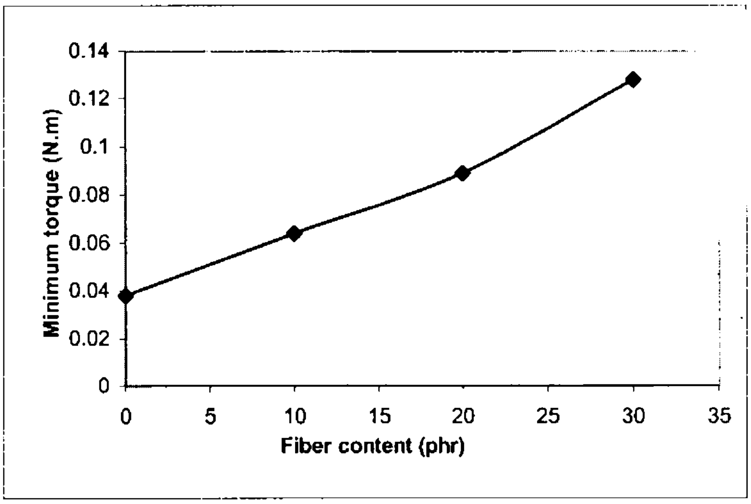

Figure 3.A.1.1. Variation of minimum torque with fiber concentration

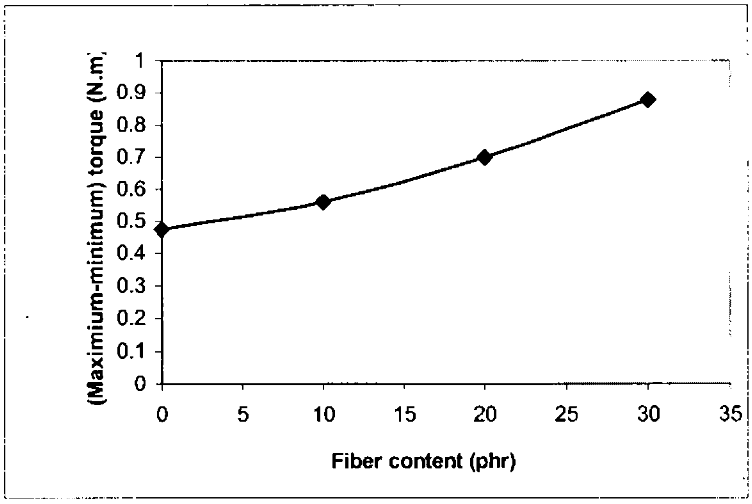

Figure 3.A.1.2. Variation of (maximum-minimum) torque with fiber concentration

Scorch time decreases from 2.9 min at 0 phr fiber loading to 1.7 min at 30 phr fiber concentration (Figure 3.A.1.3.). Cure time is reduced as fiber concentration increases (Figure 3.A.1.4.) and cure rate is increased with fiber content (Figure 3.A.1.5.). These results show that Nylon-6 fibers are accelerating cure reaction. Similar results have been reported earlier[1].

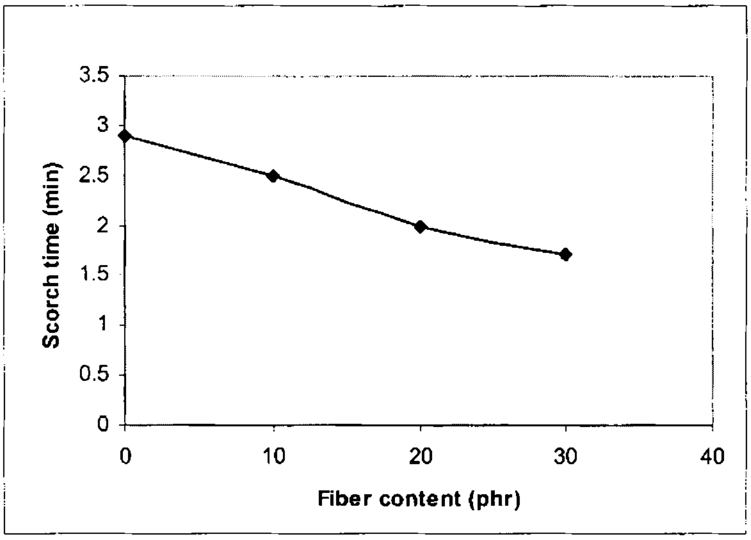

Figure 3.A.1.3. Variation of scorch time with fiber concentration

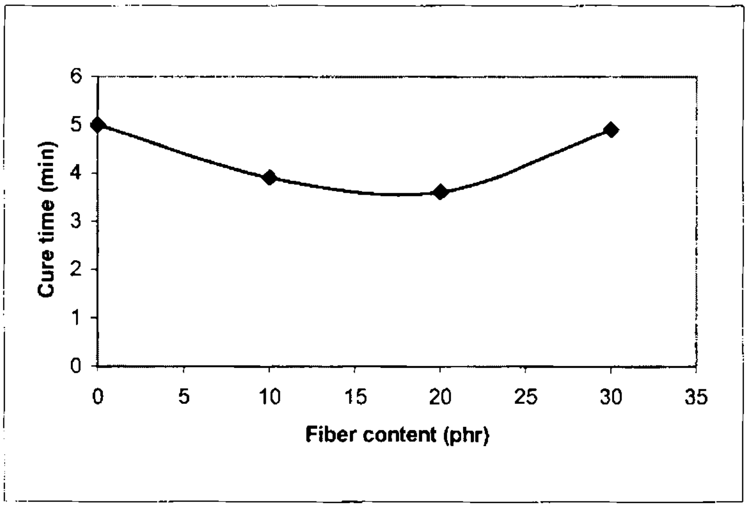

Figure 3.A.1.4. Variation of cure time with fiber concentration

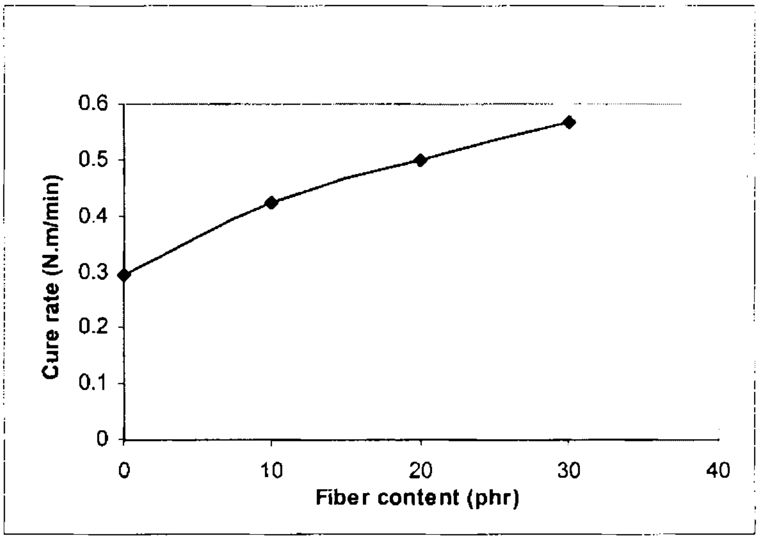

Figure 3.A.1.5. Variation of cure rate with fiber concentration

3.A.1.2 Mechanical Properties

The variation of tensile strength with fiber content is shown in Figure 3.A.1.6. The tensile strength in longitudinal orientation of fibers increases with fiber concentration. More restrained matrix is formed in the presence of fibers thereby increasing the tensile strength. At any fiber loading the tensile strength in longitudinal direction is higher than that in transverse direction. The growing crack can easily pass through the fiber matrix interfaces when the fibers are oriented transversely, resulting in easy failure of the sample under tension, resulting in lower tensile strength values. In the transverse orientation of fibers the tensile strength is not much improved with fiber concentration.

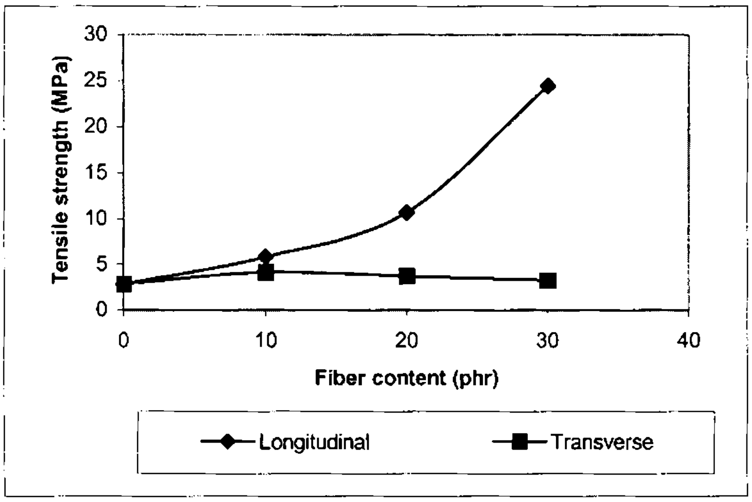

Figure 3.A.1.6. Variation of tensile strength with fiber concentration

Modulus at 20% elongation increases with fiber concentration in longitudinal direction of fibers (Figure 3.A.1.7.) while in transverse orientation of fibers it remains more or less constant.

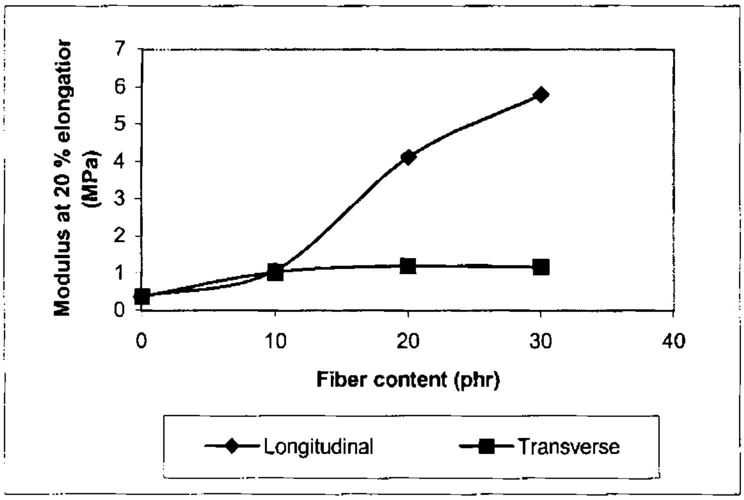

Figure 3.A.1.7. Variation of modulus with fiber concentration

Variation of elongation of break with fiber concentration is shown in Figure 3.A.1.8. Elongation at break at longitudinal direction shows a drastic decrease at 10 phr of fiber loading and remains more or less constant with further increase in fiber concentration. Similar trend was observed in transverse direction also. At any fiber loading, elongation at break is more in transverse direction than in longitudinal direction. This is in agreement with earlier reports[2-3].

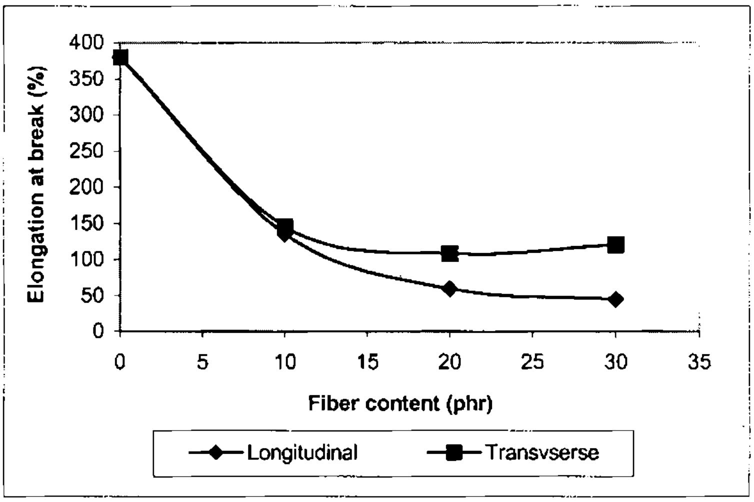

Figure 3.A.1.8. Variation of elongation at break with fiber concentration

Tear strength increases with fiber concentration in both longitudinal and transverse orientations of fibers (Figure 3.A.1.9.). As fiber concentration increases, there is more and more hindrance to the propagating tear by the fibers and hence improvement in tear strength. The tear strength in longitudinal orientation of fiber is higher than to the transverse direction and the effect is more prominent at higher fiber loading. In the case of transversely oriented fibers, most of them being parallel to the propagating crack front, they offer less resistance to propagating tear and hence lower tear strength values. Similar results were reported in the case of short polyester fiber – NR composites[4].

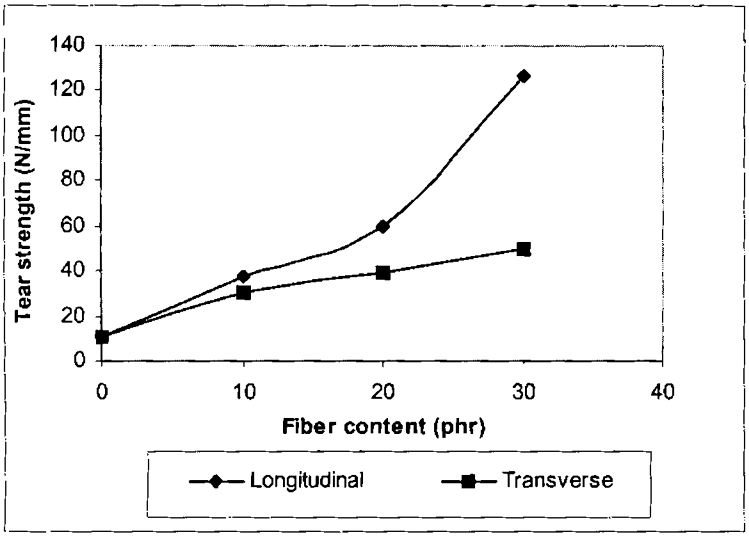

Figure 3.A.1.9. Variation of tear strength with fiber concentration

Hardness increases with fiber concentration (Figure 3.A.1.10.). Resilience, a measure of elasticity of the matrix, decreases with increase in fiber concentration (Figure 3.A.1.11.). 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[5].

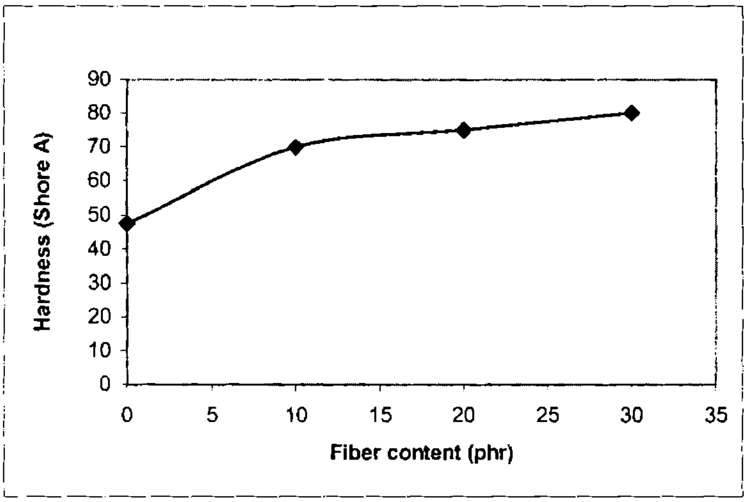

Figure 3.A.1.10. Variation of hardness with fiber concentration

Compression set shows an increase with fiber concentration (Figure 3.A.1.12.). This is consistent with the observed lower resilience values of the composite.

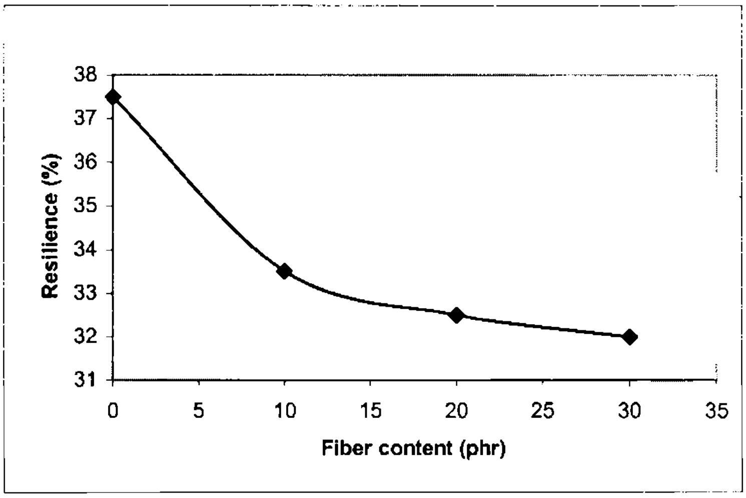

Figure 3.A.1.11. Variation of resilience with fiber concentration

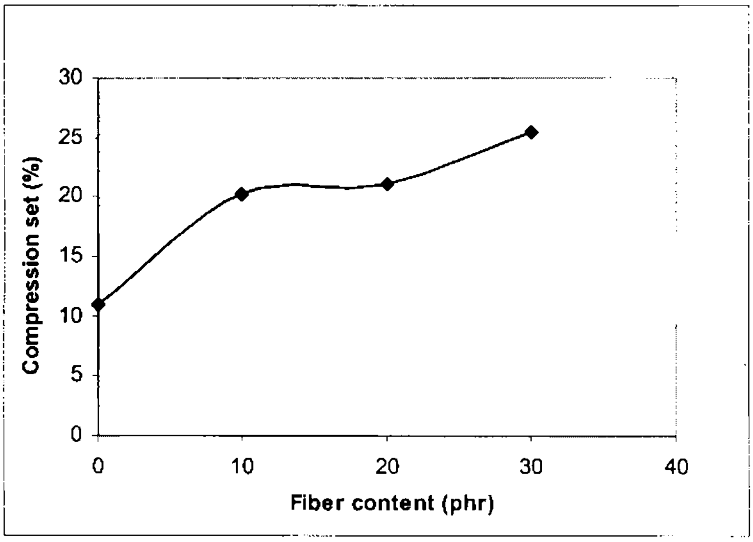

Figure 3.A.1.12. Variation of compression set with fiber concentration

The variation of abrasion resistance with fiber concentration is shown in (Figure 3.A.1.13.). The abrasion loss in longitudinal direction decreases with fiber concentration, indicating the formation of more restrained matrix in the case of composite. In the transverse direction the abrasion loss remains more or less constant with fiber content. At any fiber loading abrasion loss is more in transverse orientation of fibers. In transverse direction the fibers get debonded and separated from the matrix more easily during abrasion.

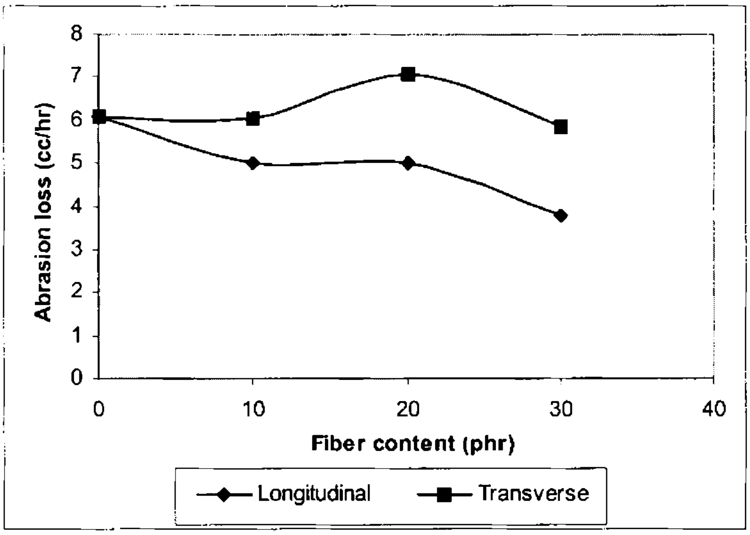

Figure 3.A.1.13. Variation of abrasion loss with fiber concentration

Heat build up increases with fiber content in both orientations of fibers (Figure 3.A.1.14.). The higher generation of heat lead to the premature failure of 30 phr fiber loaded sample. Heat build in transverse direction is higher than that in longitudinal orientation of fiber. 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. Similar results were reported in the case of short Nylon reinforced NR/WTR composites[6].

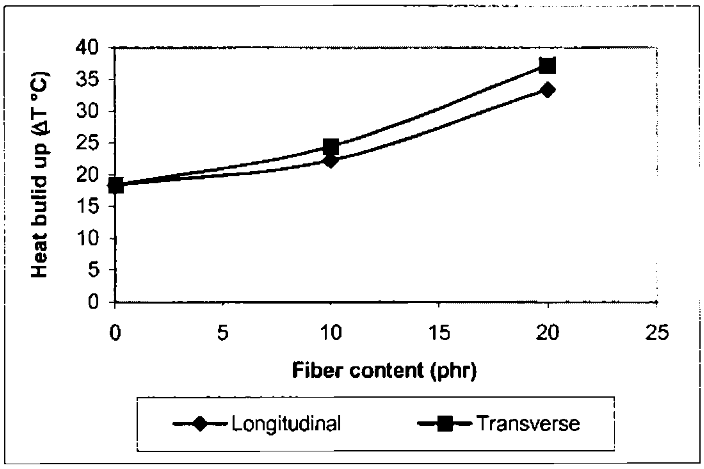

Figure 3.A.1.14. Variation of heat build up with fiber concentration

3.A.1.3 Ageing Resistance

Percentage retention in tensile strength with fiber concentration is shown in Figure 3.A.1.15. All the compounds show more than 100% retention after ageing. This indicates that the tensile strength is improved on ageing. This can be attributed to a post curing effect, as the cure pattern of NBR is a marching cure. The retention in tensile strength increases as fiber concentration increases in both transverse and longitudinal directions.

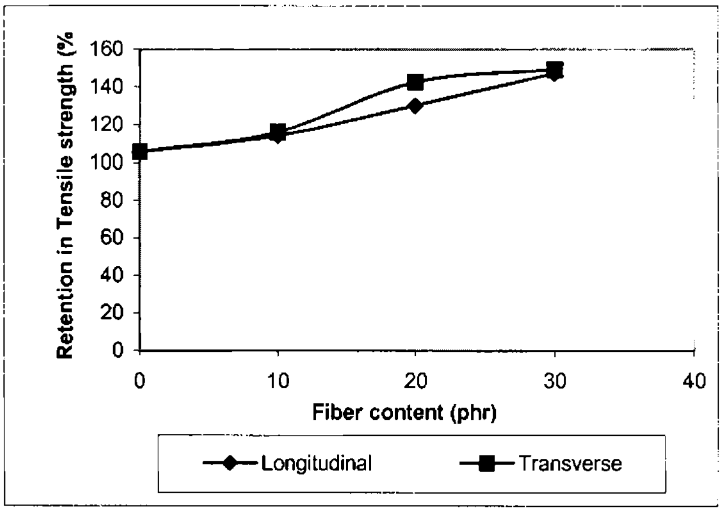

Figure 3.A.1.15. Variation of percentage retention in tensile strength with fiber concentration

REFERENCES

1. Sreeja T.D. and Kutty S.K.N., Int. J. Polym. Mater., **52** (3) (2003) 239.
2. Suhara F., Kutty S. K. N. and Nando G. B., Polym. Plast. Technol. Eng., **37** (2) (1998) 241.
3. Murty V.M. and De S.K., Rubber Chem. Technol., **55** (1982) 287.
4. Senapati A.K., Kutty S.K.N., Pradhan B. and Nando G.B., Int. J. Polym. Mater., **12** (1989) 203.
5. Sreeja T.D. and Kutty S.K.N., J. Elastomers and Plastics, **33** (3) (2001) 225.
6. Sreeja. T.D. and Kutty S.K.N. Polym. Plast. Technol. Eng., **42** (2) (2003) 239.

SECTION A. PART (II)
NBR-SHORT NYLON-6 FIBER COMPOSITES WITH EPOXY RESIN AS BONDING AGENT

Properties of short fiber - elastomer composites critically depend upon the interfacial bonding between fiber and the matrix. External bonding agents are widely used to improve fiber - matrix interface. Kondo reviewed the selection of adhesives for bonding short fiber styrene - butadiene rubber and natural rubber[1]. The effect of urethane resin based bonding agent on short polyester fiber reinforced polyurethane rubber composite was studied by Suhara et al[2]. Rajeev et al. studied the effect of dry bonding system in improved adhesion between fiber and matrix of short melamine fiber -nitrile rubber composite[3]. Epoxy is well known for its adhesive nature and its potential as bonding agent in short fiber composites has not been explored yet.

This section contains the results of studies on the effect of epoxy based bonding agent on the cure and mechanical properties of short Nylon- 6 fiber reinforced NBR composite. Resin concentration is varied from 0 to 5 phr and the fiber concentration from 0 to 30 phr.

Formulation of the test mixes are given in the Table 3.A.2.1. Sample preparation and the various test methods are detailed in chapter II.

Table 3.A.2.1. Formulation of mixes

Ingredients	Mix No.											
	A	B	C	D	E	F	G	H	I	J	K	L
NBR	100	100	100	100	100	100	100	100	100	100	100	100
Nylon	0	10	20	30	0	10	20	30	0	10	20	30
Resin*	0	0	0	0	3	3	3	3	5	5	5	5

* Epoxy resin formed by 1:0.5 equivalent combination of epoxy resin and amine type hardener; (Zinc Oxide - 4 phr; Stearic acid -2 phr; Sulhur - 0.7phr; MBTS - 1phr; TMTD -1.8 phr are common to all mixes)

3.A.2.1 Cure Characteristics

The variation of minimum torque with resin concentration at various fiber loading is shown in the Figure 3.A.2.1. The minimum torque shows only a marginal increase with increasing resin concentration for all fiber loading (0-30 phr). This indicates that the processability of the composite is not much affected by the incorporation of the resin. Similar results have been reported earlier in the case of short polyester fiber – polyurethane elastomer composite with urethane bonding agent[4].

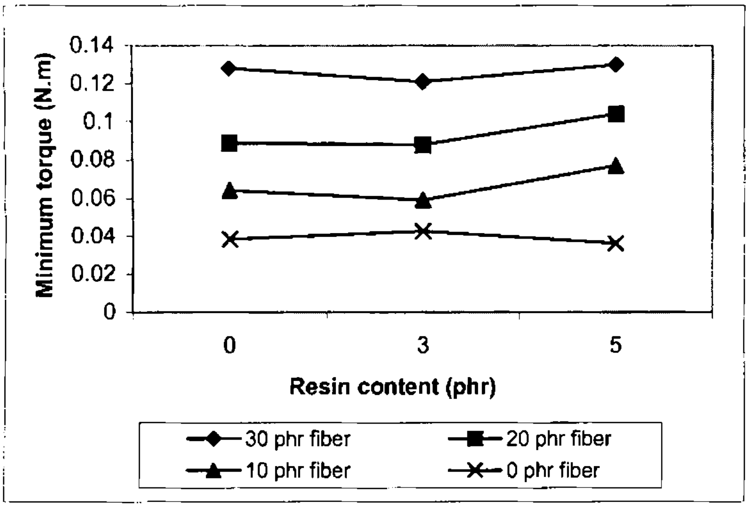

Figure 3.A.2.1.Variation of minimum torque with resin concentration

On introduction of the resin, the (Maximum –Minimum) torque increases for all fiber loadings (Figure 3.A.2.2.). This may be due to the better interaction of fiber and matrix in the presence of epoxy resin. At 5 phr resin loading there is a minor decrease in the (Maximum –Minimum) torque values.

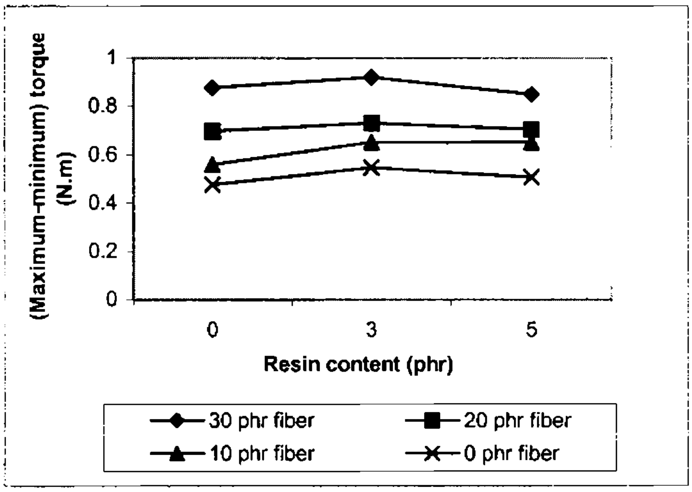

Figure 3.A.2.2. Variation of (maximum – minimum) torque with resin concentration

Figure 3.A.2.3.shows the variation of scorch time with resin content at different fiber loadings. Scorch time decreases sharply when resin is introduced for all fiber concentration and further increase in resin concentration causes only a slight decrease. Scorch time decreases from 2.9 to 1.7 s when fiber concentration was increased from 0 to 30 phr in the absence of resin. But in the presence of 5 phr resin content, all fiber concentration have almost same scorch time (0.8 s).

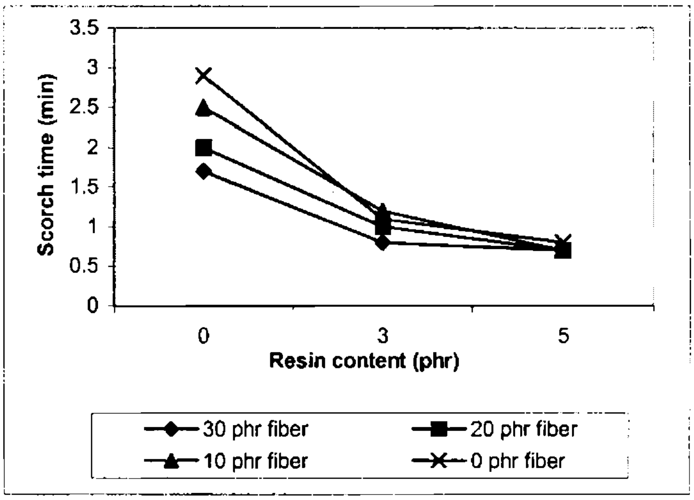

Figure 3.A.2.3. Variation of scorch time with resin concentration

In the case of gum compound there is a drastic reduction in the cure time on the introduction of the resin and on further increase, the cure time levels off (Figure 3.A.2.4.). This indicates that resin is interacting with the curatives and accelerating the cure reaction. There is also a corresponding rise in the cure rate (Figure 3.A.2.5.). In the case of composites, the cure time is increased at higher resin content, the effect being more prominent at higher fiber loading.

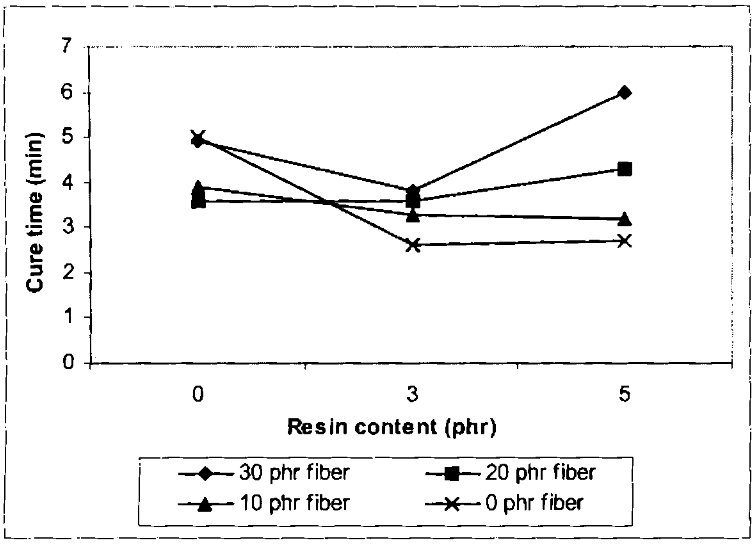

Figure 3.A.2.4. Variation of cure time with resin concentration

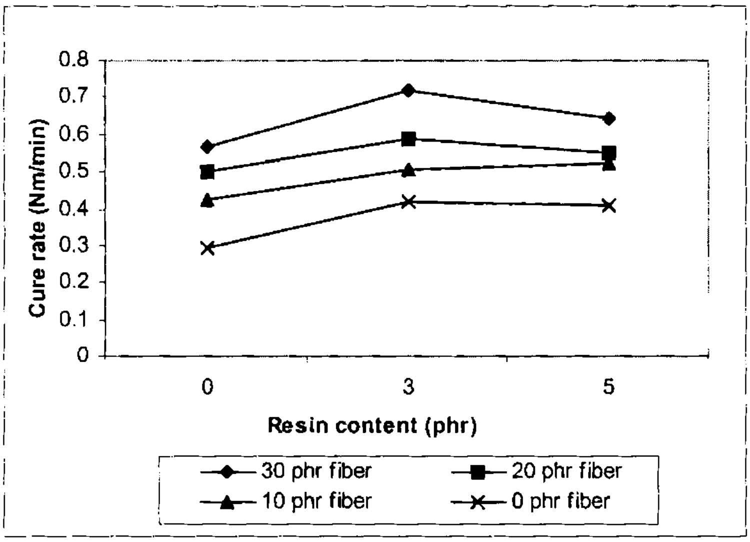

Figure 3.A.2.5. Variation of cure rate with resin concentration

3.A.2.2. Mechanical Properties

The variation of tensile strength with resin concentration at various fiber loading in longitudinal and transverse orientations of fiber is shown in Figure 3.A.2.6a. and Figure 3.A.2.6b., respectively. It is found that in the case of 30 phr fiber loaded composite, a resin concentration of 5phr (mix I) gives maximum tensile strength. A similar trend is shown by the 10 phr fiber loading also. This indicates that the epoxy resin is an effective interfacial bonding agent for this composite. There is marginal reduction in tensile strength for 20 phr fiber loaded composite.

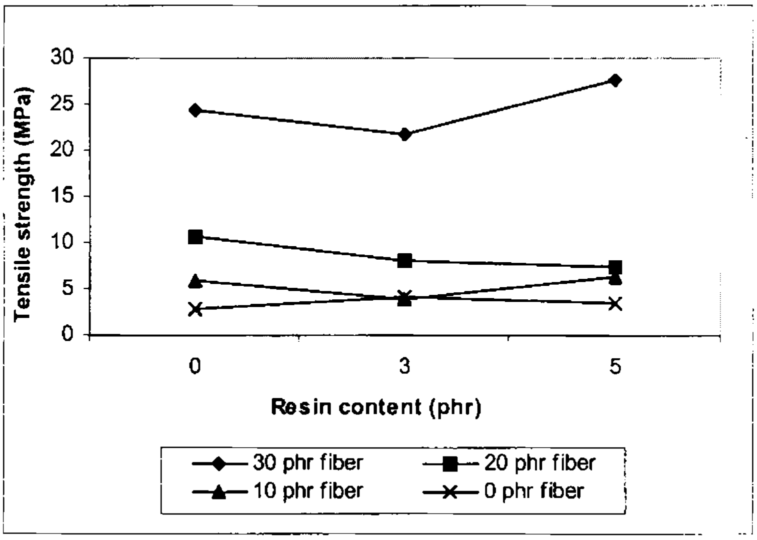

Figure 3.A.2.6a. Variation of tensile strength (Longitudinal) with resin concentration

In all the cases tensile strength in longitudinal direction is more than in transverse direction (Figure 3.A.2.6b.). In the transverse direction the fibers are less effective in restraining the matrix.

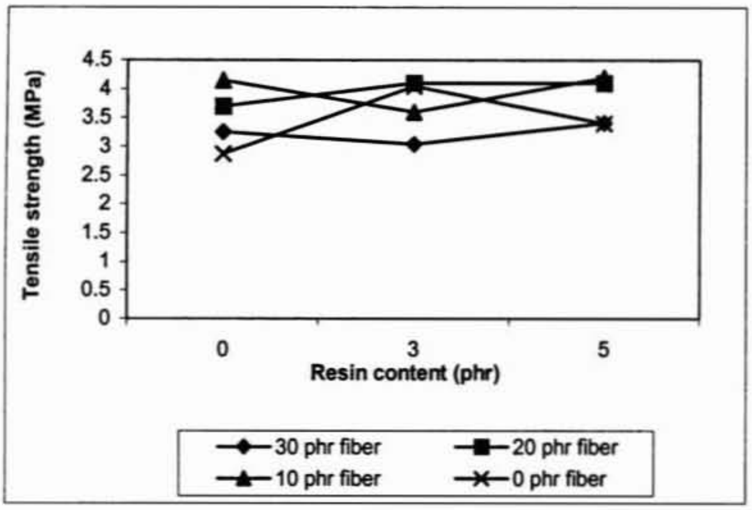

Figure 3.A.2.6b. Variation of tensile strength (Transverse) with resin concentration

Figure 3.A.2.6c. shows the SEM photomicrograph of the tensile fracture surface of gum vulcanizate. The fracture surface is smooth with no crack propagation lines. This pattern is typical of weak matrices.

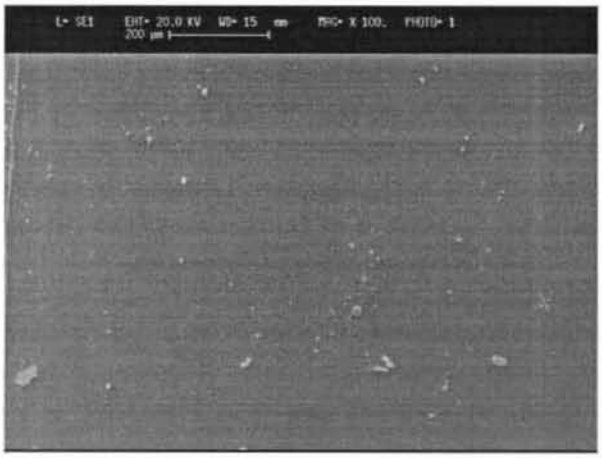

Figure 3.A.2.6c. SEM photomicrograph of tensile fracture surface of mix A (original magnification x100; marker 200µ)

Figures 3.A.2.6d. & 3.A.2.6e. show the SEM photomicrographs of tensile surface of the 10 phr fiber loaded sample containing 5 phr epoxy resin as bonding agent (Mix J) in longitudinal orientation of fibers and Figure 3.A.2.6f.& Figure 3.A.2.6g. are that of the 10 phr fiber loaded compound without resin (Mix B).

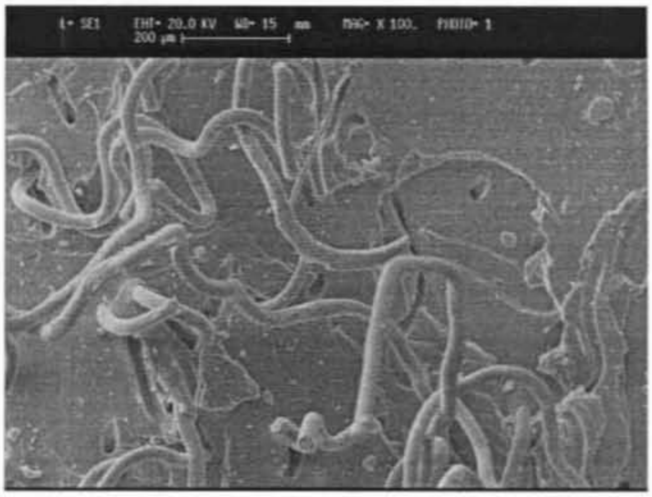

Figure 3.A.2.6d. SEM photomicrograph of tensile fracture surface of mix J with fibers oriented in longitudinal direction (original magnification x100; marker 200µ)

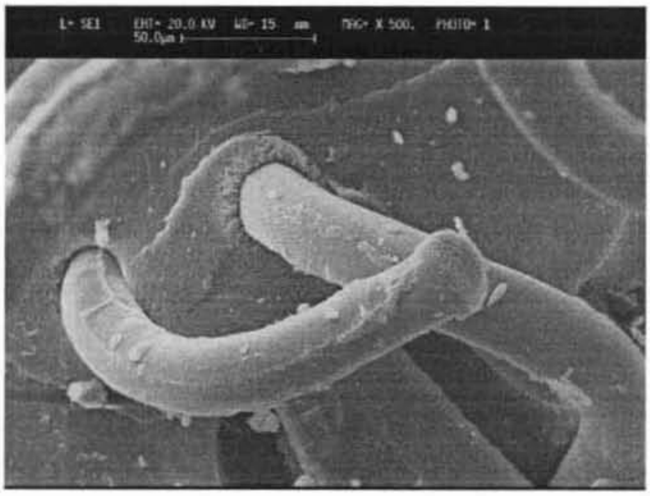

Figure 3.A.2.6e. SEM photomicrograph of tensile fracture surface of mix J with fibers oriented in longitudinal direction (original magnification x500; marker 50µ)

Large number of fiber ends and fiber pulled out holes are visible in the case of Mix J. The fibers are seen to be more firmly adhered to the matrix. It can also be observed that the fibers protruding out in the case of Mix J are not clean. Some portion of matrix is sticking to the surface of the fiber. But in the case of mix D the fiber surface is smooth, clean and matrix is less mutilated. This suggest better fiber – matrix interfacial bonding in the presence of resin and supports the higher tensile strength of Mix J compared to that of mix B.

Figure 3.A.2.6f. SEM photomicrograph of tensile fracture surface of mix B with fibers oriented in longitudinal direction (original magnification x100; marker 200µ)

The tensile fracture surface of mix L with fibers in the transverse direction is shown in Figure 3.A.2.6h. The fibers oriented in the horizontal plane are clearly visible in the figure. The channels formed by the fiber removal during fracture can be seen in the figure. This indicates that the fracture occurs by interface failure.

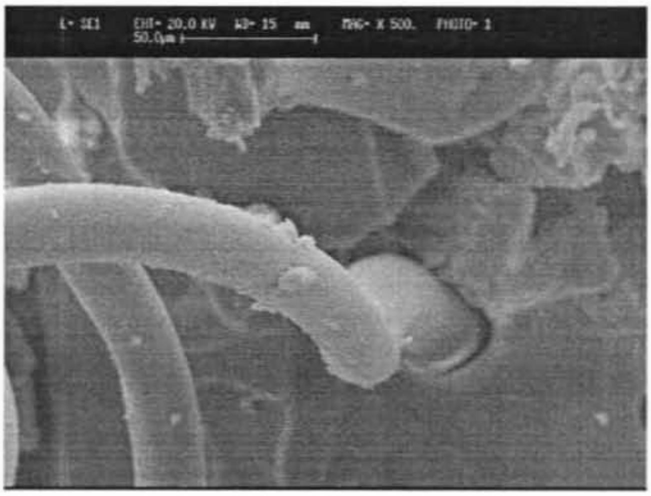

Figure 3.A.2.6g. SEM photomicrograph of tensile fracture surface of mix B with fibers oriented in longitudinal direction (original magnification x500; marker 50μ)

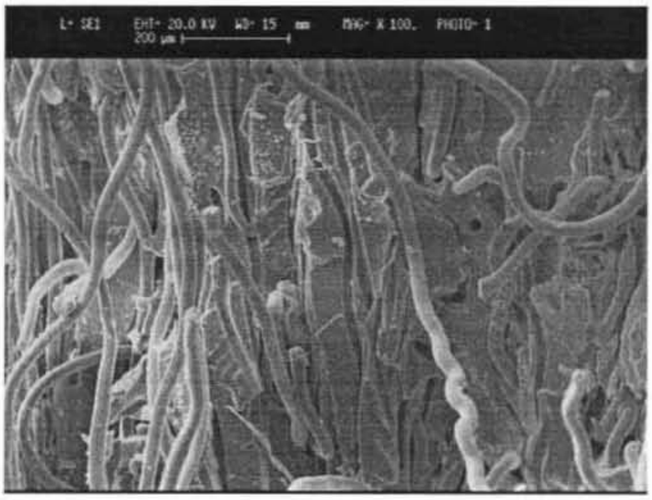

Figure 3.A.2.6h. SEM photomicrograph of tensile fracture surface of mix L with fibers oriented in transverse direction (original magnification x100; marker 200μ)

Modulus at 20% elongation in longitudinal orientation of fiber increases as resin concentration increases for 30 phr fiber loading, indicating better restraining of the matrix by the improved fiber - matrix interfacial bond in the presence of resin (Figure 3:A.2.7a.).

For 0 to 20 phr fiber loading the modulus remains more or less constant with resin concentration. Modulus in the transverse direction does not show much variation with resin content for all fiber concentrations (Figure 3.A.2.7b.).

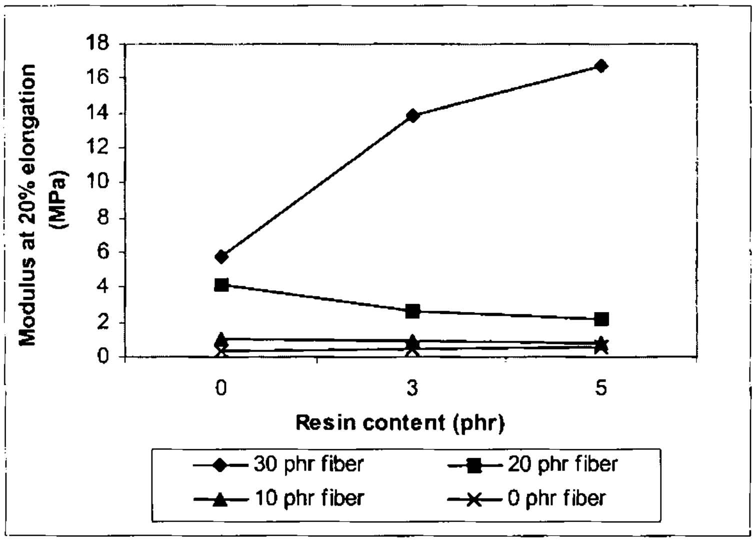

Figure 3.A.2.7a.Variation of modulus (Longitudinal) with resin concentration.

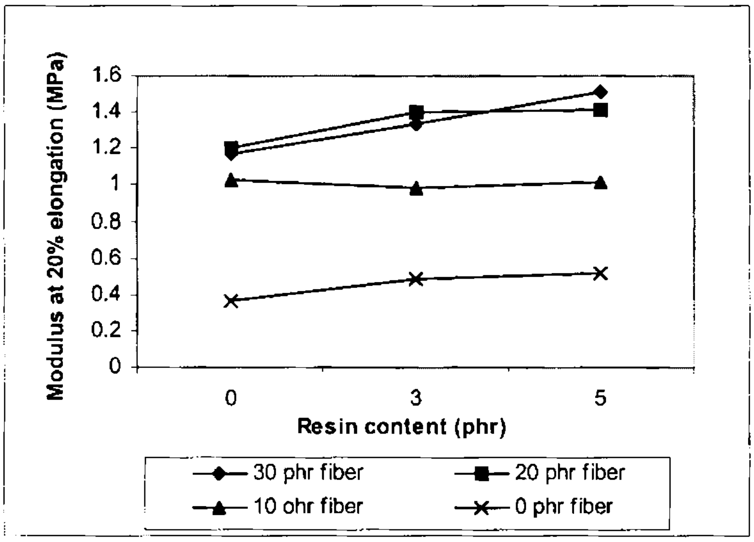

Figure 3.A.2.7b. Variation of modulus (Transverse) with resin concentration

The variation of elongation at break (EB) with resin concentration in longitudinal and transverse orientations of fiber is shown in the Figure 3.A.2.8a & Figure 3.A.2.8b., respectively. In the case of composite, the EB is marginally increased at higher resin loading. As the fiber concentration increases, the effect of resin loading on elongation at break becomes insignificant and the EB remains constant at all the resin loading. This may be attributed partly to the plasticizing effect of resin in the composites. At lower fiber loading the resin is in excess at 5 phr level.

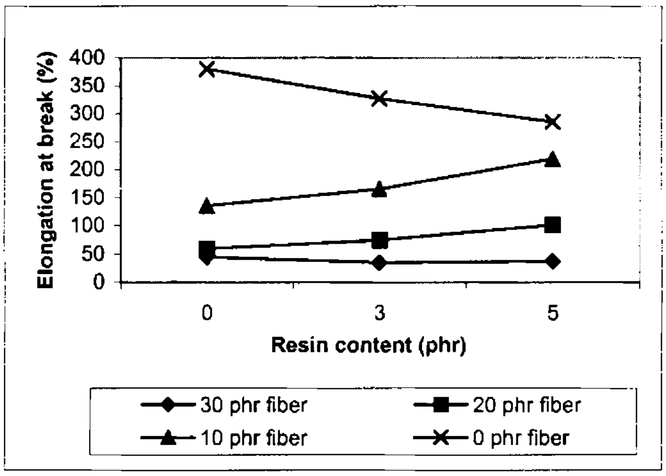

Figure 3.A.2.8a. Variation of elongation at break (Longitudinal) with resin concentration

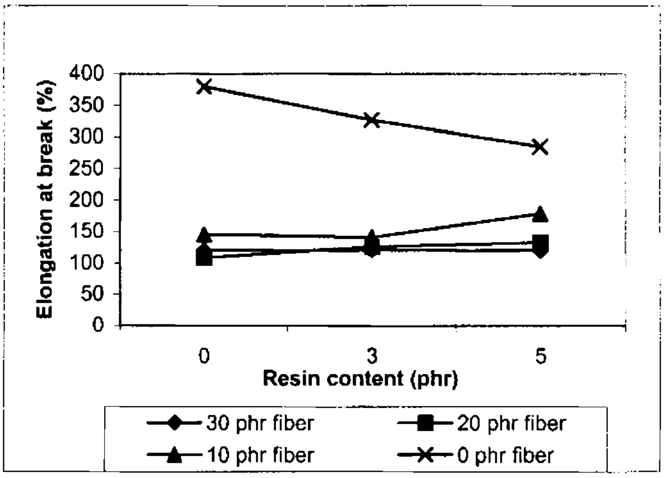

Figure 3.A.2.8b. Variation of elongation at break (Transverse) with resin concentration

Variation of tear strength with resin concentration in both longitudinal and transverse directions is shown in Figure 3.A.2.9a. and Figure 3.A.2.9b., respectively. Tear resistance decreases when resin is introduced to 30 phr fiber loaded composite and on further rise in resin concentration, the tear resistance remains unchanged. Tear strength is not much affected by the addition of resin in the case of composites having fiber loading 0 to 20 phr.

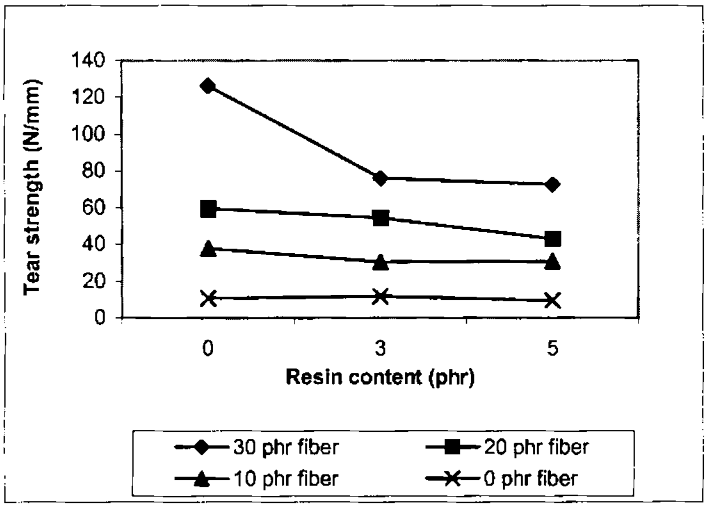

Figure 3.A.2.9a. Variation of tear strength (Longitudinal) with resin concentration

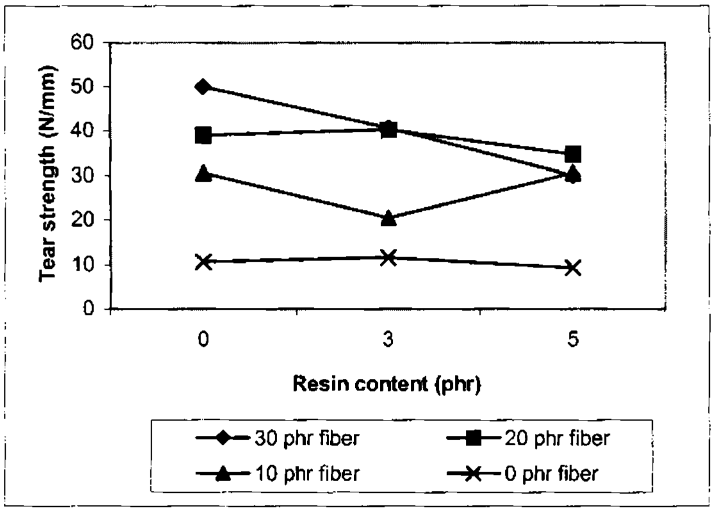

Figure 3.A.2.9b. Variation of tear strength (Transverse) with resin concentration

Hardness improves marginally with resin concentration for composites with different fiber loadings (Figure 3.A.2.10.). It remains more or less constant in the case of gum compound.

Resilience, an indication of material elasticity, shows a marginal decrease with resin concentration for all fiber loading (Figure 3.A.2.11.). Resilience decreases as fiber concentration increases. The dissipation of energy at fiber - matrix interface results in lower resilience value in the case of composite. The compression set values increase with resin concentration for all fiber concentration (Figure 3.A.2.12.). This is in agreement with decreased resilience values.

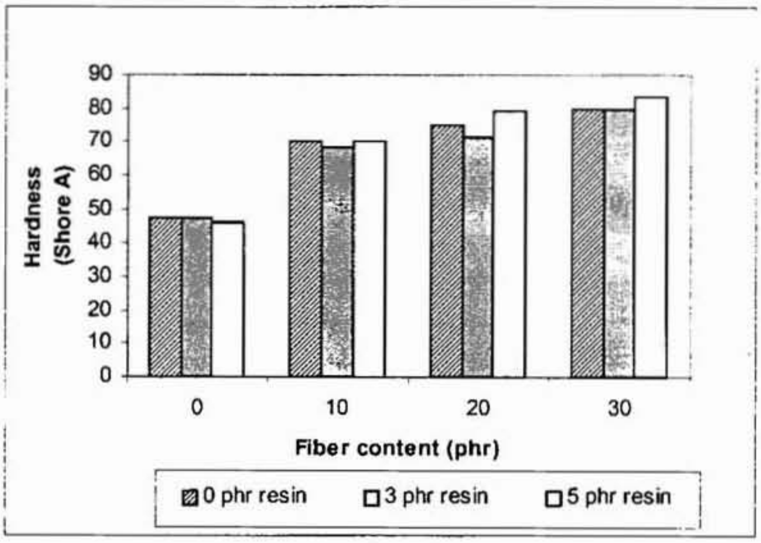

Figure 3.A.2.10. Variation of hardness with resin concentration

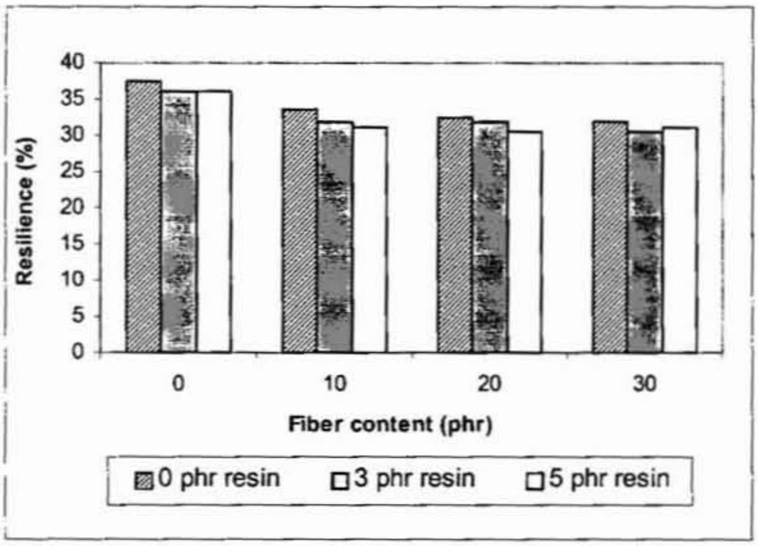

Figure 3.A.2.11. Variation of resilience with resin concentration

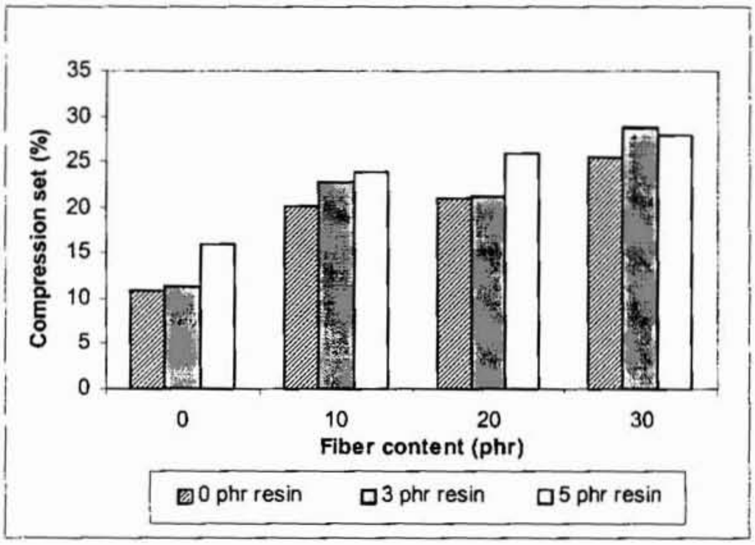

Figure 3.A.2.2. Variation of compression set with resin concentration

Figures 3.A.2.13a. & 3.A.2.13b. show the variation of abrasion loss with resin concentration in longitudinal and transverse orientations of fiber, respectively. Abrasion resistance is improved in the presence of resin. Up to 3 phr resin loading abrasion loss decreases in both longitudinal and transverse directions for all fiber concentrations, indicating the formation of a good interfacial bonding between fiber and matrix, which resist the debonding of fiber.

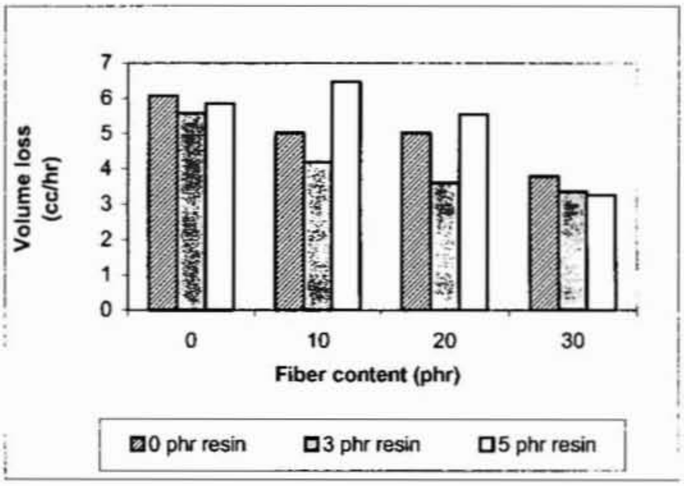

Figure 3.A.2.13a. Variation of abrasion loss (Longitudinal) with resin concentration

But further increase in resin content shows an increase in abrasion loss at lower fiber concentrations (0 to 20 phr) in both transverse and longitudinal directions while at 30 phr fiber loading abrasion loss decreases with resin concentrations. At lower fiber loading resin is excess at 5 phr level.

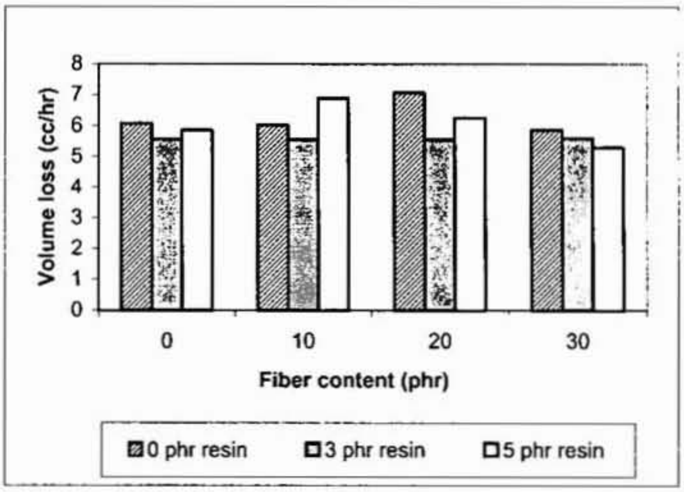

Figure 3.A.2.13b. Variation of abrasion loss (Transverse) with resin concentration

The variation of heat build up with resin concentration for various fiber loading in longitudinal and transverse directions is shown in the Figure 3.A.2.14a.and Figure 3.A.2.14b., respectively. Heat build decreases with resin content in both longitudinal and transverse directions in the case of gum compound.

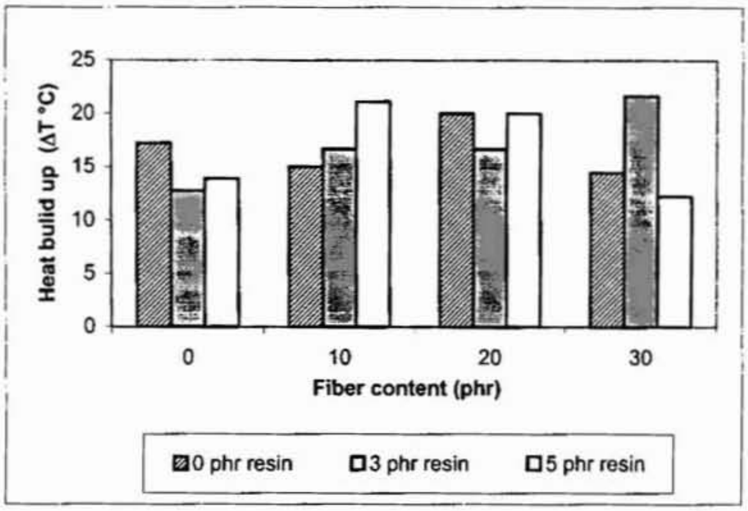

Figure 3.A.2.14a. Variation of heat build up (Longitudinal) with resin concentration.

Heat build up registers an increase when resin is introduced in the case of composites. Heat build up in the transverse direction is higher than that in the longitudinal direction for composites. In samples with longitudinally oriented fibers, buckling of fibers lead to absorption of great part of applied stress in the stress –strain cycle. There is thus, less residual energy to dissipate as heat. In the transverse direction buckling of fibers does not occur, and hence heat generation is higher.

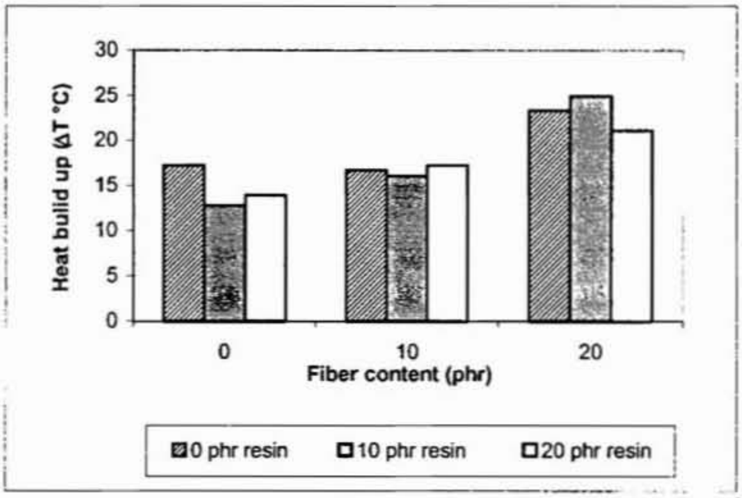

Figure 3.A.2.14b. Variation of heat build up (Transverse) with resin concentration

3.A.2.3 Ageing Resistance

Percentage retention in tensile strength decreases as resin content increases in the case of 30 phr fiber loaded composite in longitudinal direction (Figure 3.A.2.15a.). This may be due to weakening of the interfacial bonds during ageing.

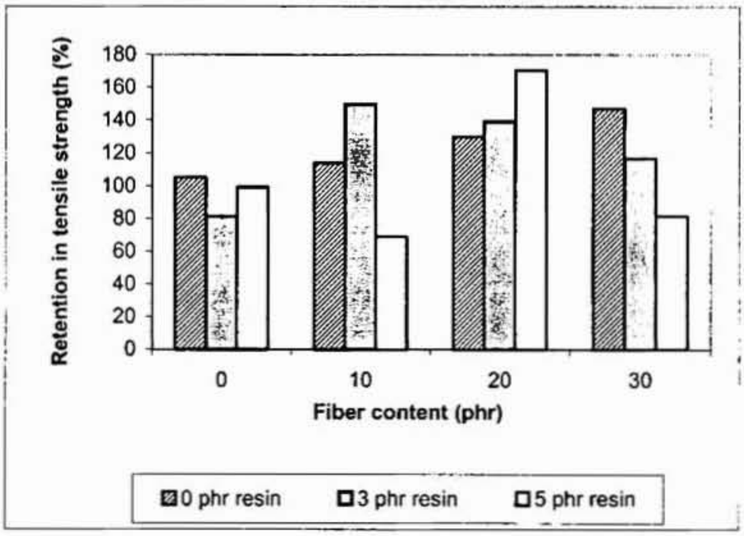

Figure 3.A.2.15a. Variation of percentage retention in tensile strength (Longitudinal) with fiber loading

In the transverse direction the percentage retention in tensile strength is higher (Figure 3.A.2.15b.). In longitudinal direction the stress is taken up by the fiber through fiber matrix interface. So if the interface get weakened, the effective load transfer is not possible. But in the case of transverse direction the matrix takes up the stress.

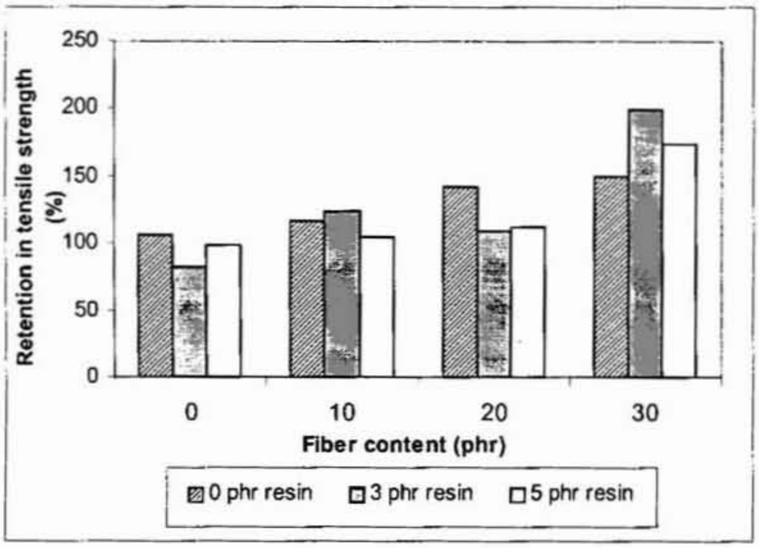

Figure 3.A.2.15b. Variation of percentage retention in tensile strength (Transverse) with fiber loading

REFERENCES

1. Kondo A., Setchaku, **22** (5) (1978) 135.
2. Suhara F., Kutty S. K. N. and Nando G. B. Polym. Plast. Technol. Eng, **37** (2) (1998) 241.
3. Rajeev R.S., Anil.K.Bhowmick, De S.K. and Bandyopadhyay S. J. Appl. Polym. Sci.,**90** (2) (2003) 544.
4. Suhara F., Kutty S. K. N., Nando G. B. Inter. J. of Polym. Materials. **38** (1997) 205.

SECTION B. PART (I)

CR-SHORT NYLON-6 FIBER COMPOSITES

Chloroprene rubber is a highly versatile synthetic rubber. Being polar, CR has better resistance to mineral and vegetable oils and fats. It also has excellent flame, weather and ozone resistance. In contrast to most synthetic rubbers, unfilled chloroprene exhibit high tensile strength. Short fibers can impart many desirable properties to rubber articles, up to now unobtainable with traditional reinforcements. Short fibers can improve thermomechanical properties of the composites and reduce the cost of fabrication.

A systematic study of the cure characteristics and the mechanical properties of chloroprene rubber containing different levels of short nylon fibers are discussed in this section.

Table 3.B.1.1. gives formulation of the mixes. The details of preparation of the mixes, determination of cure characteristics, moulding and testing are given in Chapter 2.

Table 3.B.1.1. Formulation of the mixes

Ingredients	Mix No.			
	A	B	C	D
CR	100	100	100	100
Short Nylon fiber	0	10	20	30

Zinc oxide - 5 phr, Stearic acid - 1 phr, MgO - 4 phr & Ethylene thiourea - 0.5 phr are common to all mixes.

3.B.1.1. Cure Characteristics

Figure 3.B.1.1 shows the variation of minimum torque with fiber loading. The minimum torque increases with fiber concentration indicating that the processability of the composite is affected in the presence of fibers.

The (maximum – minimum) Torque values increases from 0.285 N.m at 0 phr to 0.607 N.m at 30 phr fiber, indicating a more restrained matrix in the case of composites (Figure 3.B.1.2.)

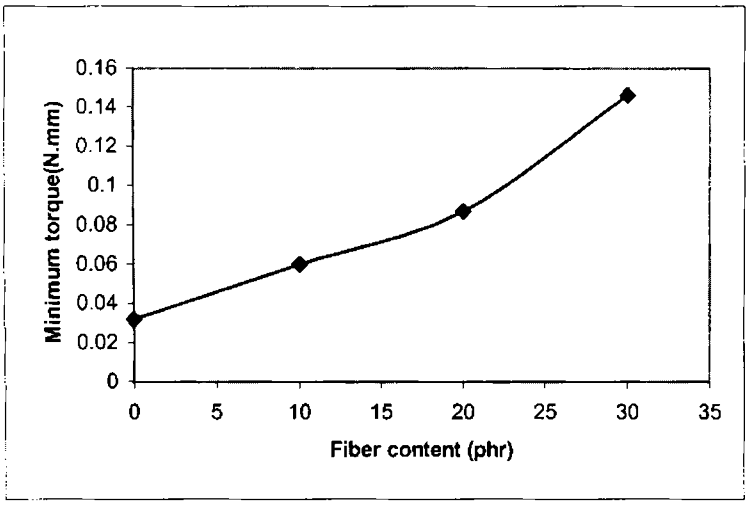

Figure 3.B.1.1. Variation of minimum torque with fiber concentration

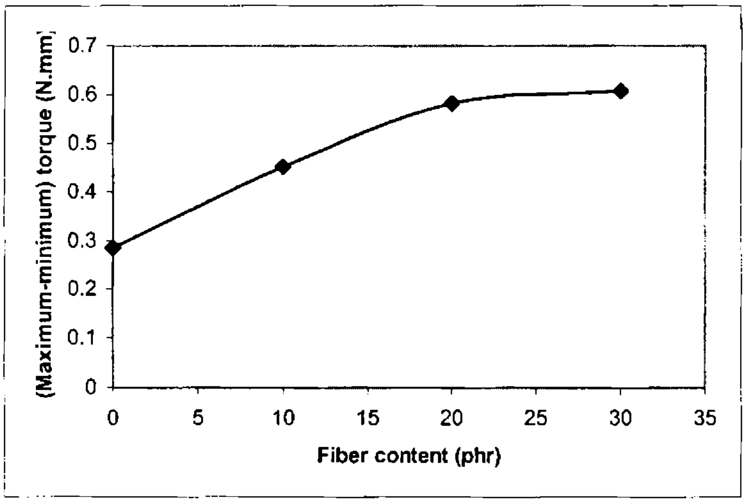

Figure 3.B.1.2. Variation of (maximum – minimum) torque with fiber concentration

Variation of scorch time with fiber concentration is shown in the Figure 3.B.1.3. Scorch time reduces marginally from 1.9 to 1.8 min on introduction of fiber, thereafter it remains constant with fiber content. Scorch safety is not much affected by the presence of fibers. Cure time is marginally increased with fiber concentration (Figure 3.B.1.4.) Cure rate increases marginally on introduction of fiber, afterwards it remains more or less constant

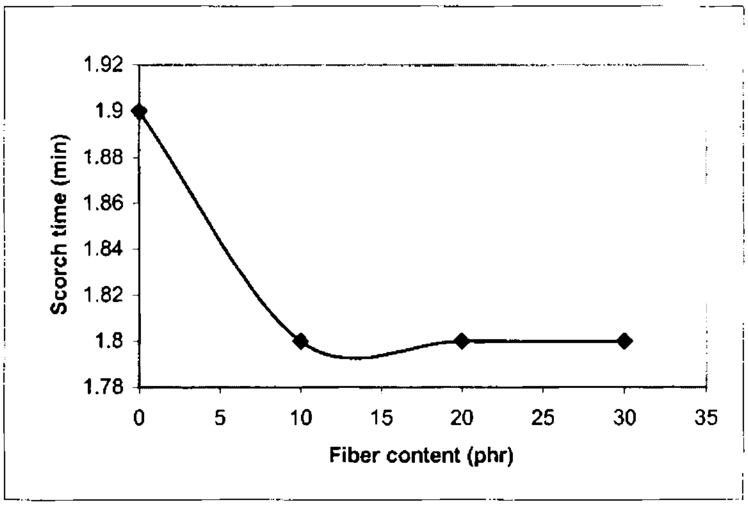

Figure 3.B.1.3. Variation of scorch time with fiber concentration

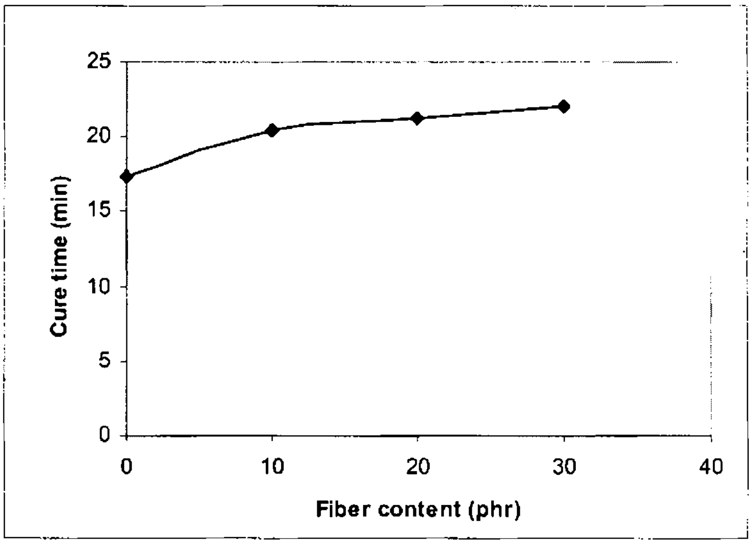

Figure 3.B.1.4. Variation of cure time with fiber concentration

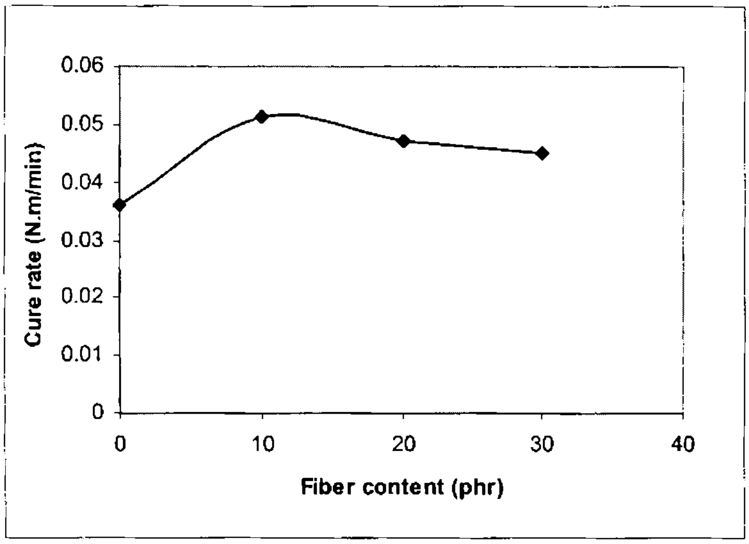

Figure 3.B.1.5. Variation of cure rate with fiber concentration

3.B.1.2. Mechanical Properties

The variation of tensile strength with fiber concentration is given in Figure 3.B.1.6. The tensile strength in the longitudinal direction shows a minimum value at 10 phr fiber loading, beyond which it increases with fiber content. At 10 phr, the reinforcing effect of fiber is insufficient to compensate for the dilution effect brought by the fibers and hence tensile strength decreases. 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 drops with fiber concentration upto 10 phr and it increases marginally thereafter. This is due to the weakening of the rubber matrix by the presence of transversely oriented fiber. Similar results have been reported before[1-4].

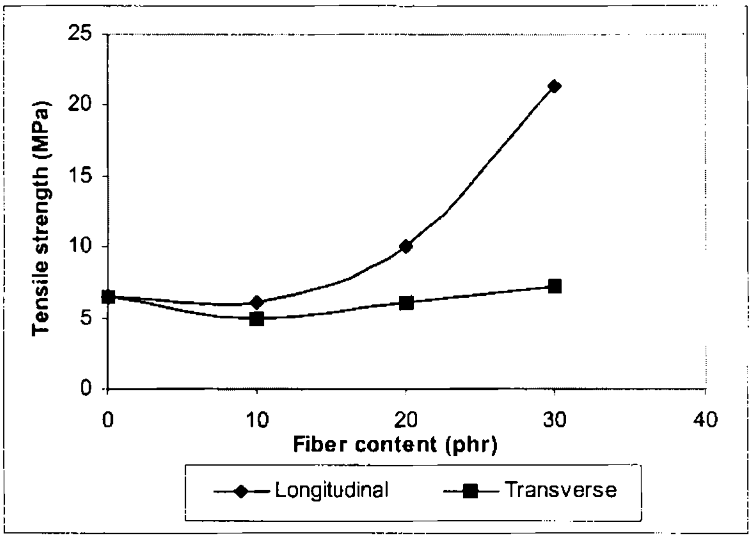

Figure 3.B.1.6. Variation of tensile strength with fiber concentration

Figure 3.B.1.7. shows the variation of modulus at 50% elongation with fiber concentration in longitudinal and transverse orientations of fibers. The modulus at 50% elongation increases with fiber concentration in both longitudinal and transverse directions of fibers indicating formation of more restrained matrix in the presence of fibers. Modulus is higher for longitudinal direction of fiber at all fiber loading.

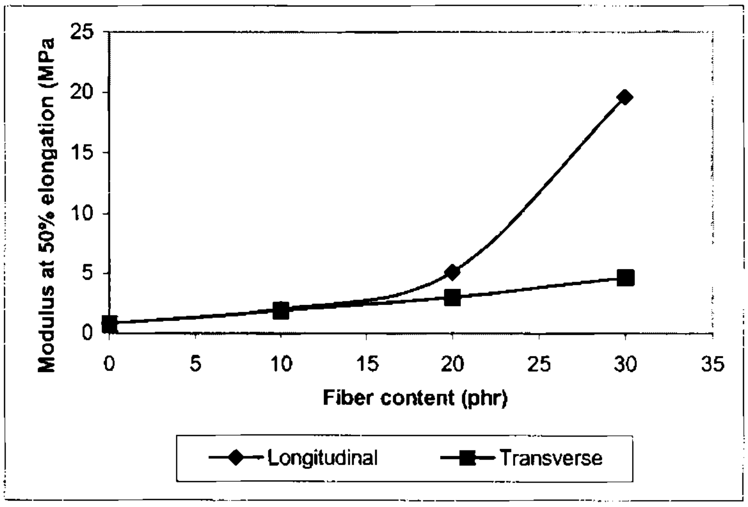

Figure 3.B.1.7. Variation of modulus with fiber concentration

The elongation of break decreases sharply on introduction of fiber and with further increase in fiber concentration it remains more or less constant (Figure 3.B.1.8.). The fibers inhibit the orientation of molecular chains, and, hence, the ultimate elongation decreases drastically on introduction of fibers[3].

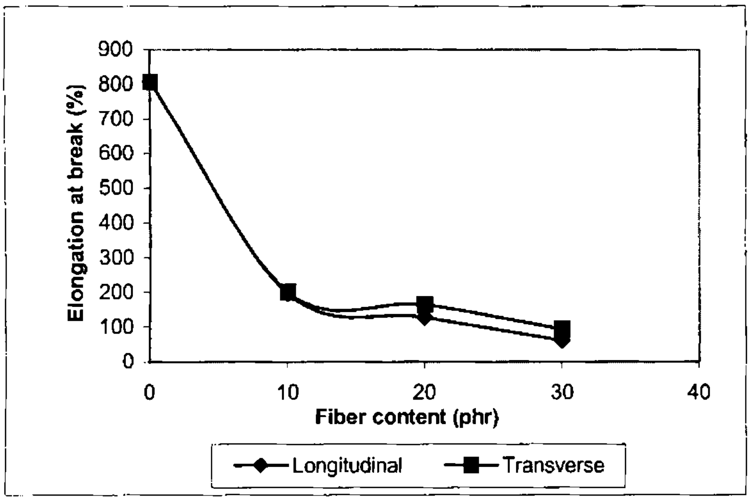

Figure 3.B.1.8. Variation of elongation at break with fiber concentration

The variation of tear strength with fiber concentration of the composites is given in Figure 3.B.1.9. Tear strength increases with fiber concentration in both longitudinal and transverse directions of fibers. The fibers hinder the propagation of crack front, thereby increasing the tear resistance. At any given fiber loading, the mixes with longitudinal fiber orientation show higher tear strength than mixes with transverse direction. Fibers are oriented parallel to the crack front in the transverse direction and hence offer less resistance to the propagation of crack, resulting in lower tear strength when compared to longitudinal orientation of fibers.

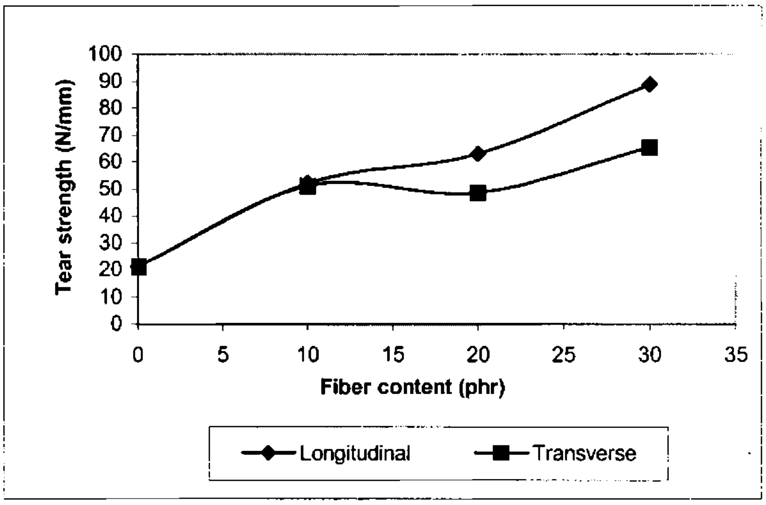

Figure 3.B.1.9. Variation of tear strength with fiber concentration

Hardness remains more or less constant with fiber concentration (Figure 3.B.1.10.). Rebound resilience increases with fiber concentration (Figure 3.B.1.11.). The short fibers restrain the matrix and the resilience is improved in the case of composite.

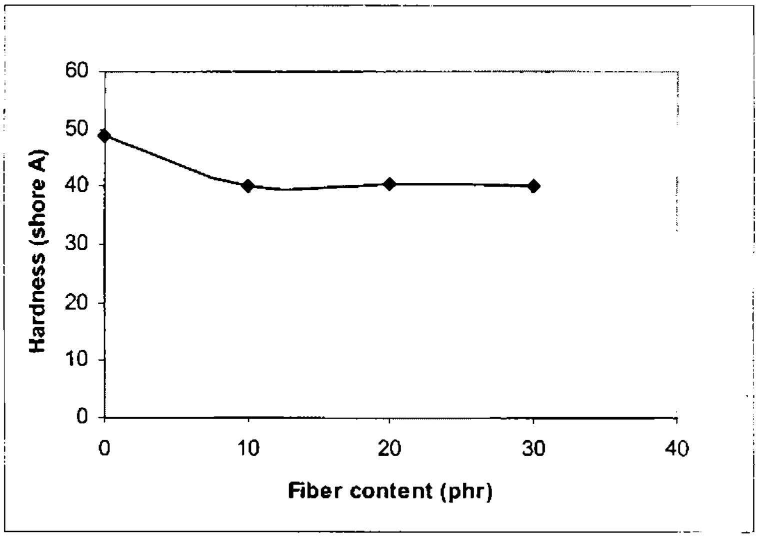

Figure 3.B.1.10. Variation of hardness with fiber concentration

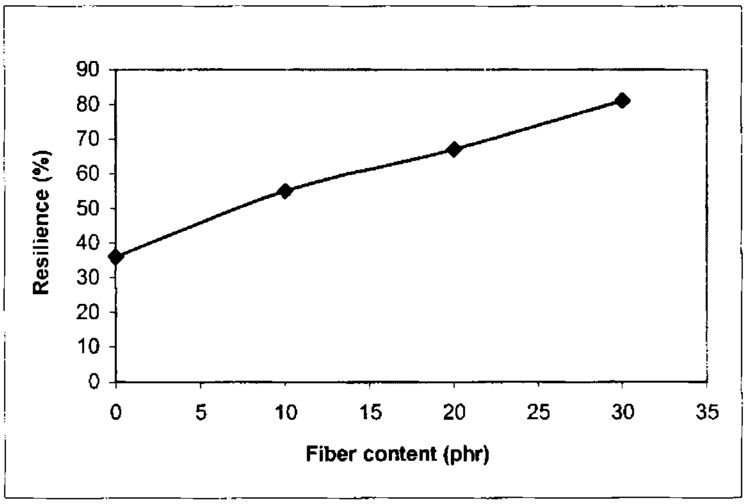

Figure 3.B.1.11. Variation of resilience with fiber concentration

The compression set is increased when fiber is introduced to the matrix; afterwards it remains more or less constant (Figure 3.B.1.12.). 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. Similar results have been reported earlier[5].

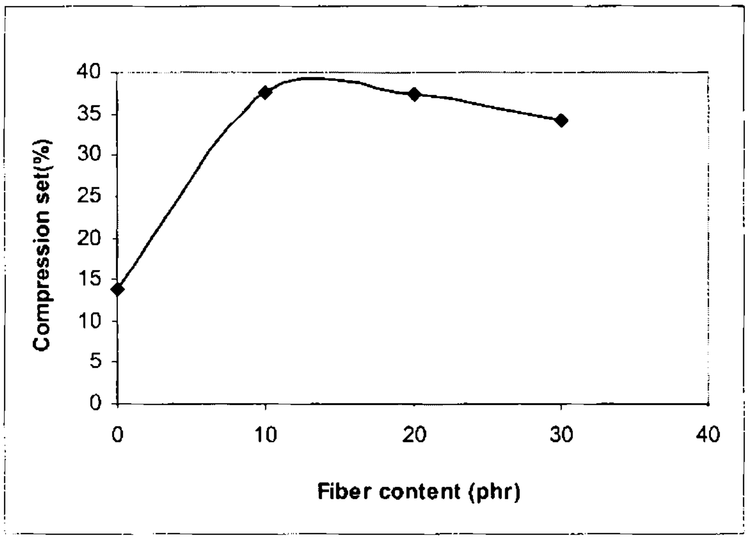

Figure 3.B.1.12. Variation of compression set with fiber concentration

Abrasion loss of the fiber filled samples are lower than that of the gum compound (Figure 3.B.1.13.). This again confirms the formation of more restrained matrix in the presence of fibers. Samples with transversely oriented fibers show higher abrasion loss than the samples with fibers oriented along the direction of abrasion. This is because the fibers are more easily debonded when oriented perpendicular to the direction of abrasion.

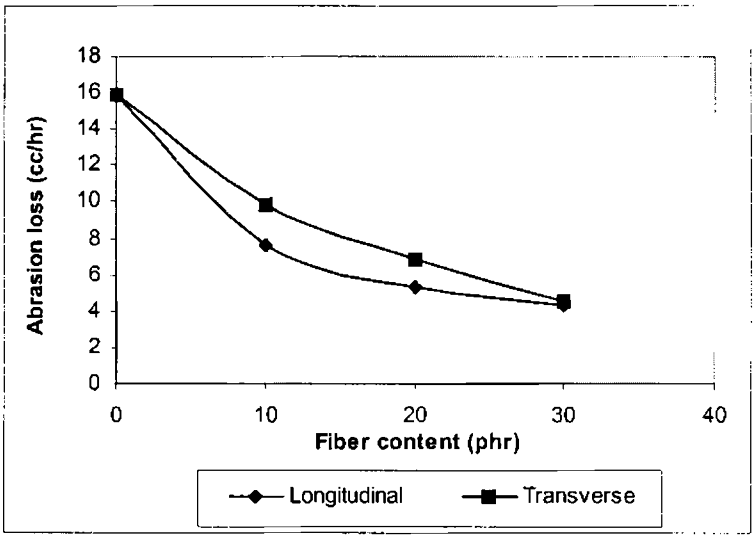

Figure 3.B.1.13. Variation of abrasion loss with fiber concentration

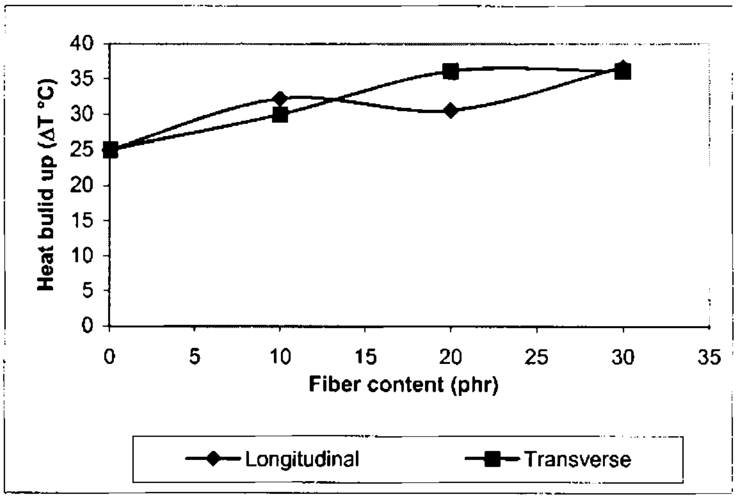

Figure 3.B.1.14. Variation of heat build up with fiber concentration

Heat build up shows an increase with increase in fiber concentration in both longitudinal and transverse direction (Figure 3.B.1.14.). Heat build up is not much influenced by the orientation of fiber.

3.B.1.3. Ageing Resistance

Percentage retention in tensile strength with fiber concentration is shown in Figure 3.B.1.15. The tensile strength of gum compound is deteriorated to 60% of its original value after ageing. All the composites show more than 100% retention in tensile strength.

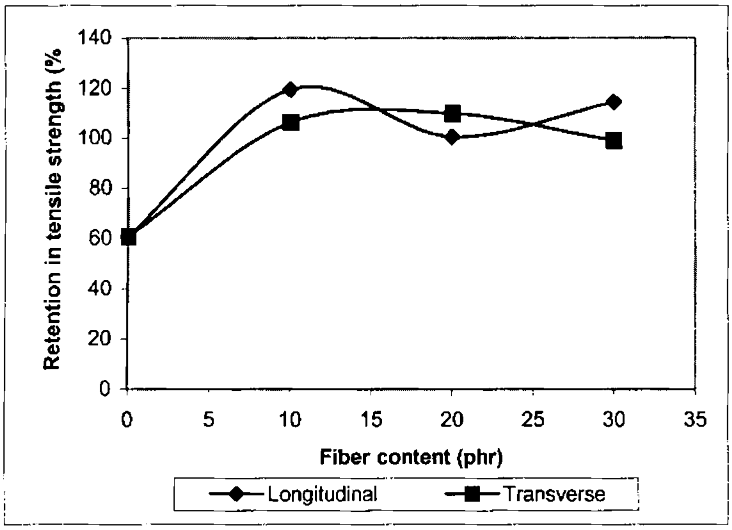

Figure 3.B.1.15. Variation of percentage retention in tensile strength with fiber concentration

The retention in tensile strength is improved substantially on introduction of fibers and further increase in fiber concentration it remains more or less constant. This is due to the better fiber matrix interface formation after ageing. The retention in tensile strength is found to be higher for longitudinal orientation of fibers.

REFERENCES

1. Murty V.M. and De S.K., Rubber Chem. Technol., **55** (1982) 287.
2. Kutty S.K.N. and Nando G.B., Plast. Rub. Comp. Proces. Appl., **14** (2) (1990) 109.
3. Sreeja, T.D.; Kutty S.K.N. J. Elastomers and Plastics, **33** (3) (2001) 225.
4. Sreeja, T.D.; Kutty S.K.N. Polym. Plast. Technol. Eng, **42** (2) (2003) 239.
5. Sreeja, T.D.; Kutty S.K.N. J. Elastomers and Plastics, **34** (2) (2002) 157.

SECTION B. PART (II)
CR-SHORT NYLON-6 FIBER COMPOSITES WITH EPOXY RESIN AS BONDING AGENT

Interfacial bond is known to play an important role in short fiber composites since this interface is critical in transferring the load from the matrix to the fiber. Several methods are used to improve fiber matrix adhesion. Rajeev et al. studied the effect of dry bonding system in improving adhesion between fiber and matrix of short melamine fiber –nitrile rubber composite[1]. This section discusses the results of investigation of epoxy resin as bonding agent for chloroprene -short Nylon fiber composites. Resin concentration was varied from 0 to 5 phr for all fiber concentration.

Formulation of the test mixes are given in the Table 3.B.2.1. Method of preparation and procedure adopted for the determination of cure characteristics and mechanical properties of the mixes are given in the chapter II.

Table 3.B.2.1. Formulation of the mixes

Ingredients	Mix No.											
	A	B	C	D	E	F	G	H	I	J	K	L
CR	100	100	100	100	100	100	100	100	100	100	100	100
Nylon	0	10	20	30	0	10	20	30	0	10	20	30
Resin*	0	0	0	0	3	3	3	3	5	5	5	5

* Epoxy resin formed by 1:0.5 equivalent combination of epoxy resin and amine type hardener. (Zinc Oxide-5phr; Stearic acid-1phr; Magnesium oxide-4phr Ethylene thiourea-0.5phr are common to all mixes)

3.B.2.1 Cure Characteristics

The variation of minimum torque with resin content for various fiber loading and gum vulcanizate is given in the Figure 3.B.2.1. With increasing resin content minimum torque increases, indicating a more restrained matrix. In the absence of resin, the minimum torque is increased from 0.0317 N.m to 0.1406 N.m when the fiber loading is increased from 0 to 30 phr. While in the presence of 5 phr resin, the corresponding improvement is from 0.0273 N.m to 0.206 N.m indicating a better fiber matrix interaction in the presence of resin.

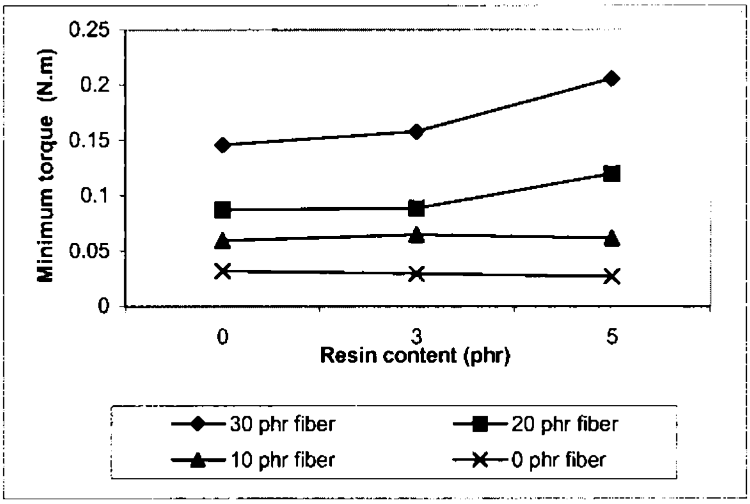

Figure 3.B.2.1. Variation of minimum torque with resin concentration

(Maximum – minimum) torque for various fiber loading and resin content is plotted in the Figure 3.B.2.2. On introduction of resin, ΔTm decreases for all fiber loading but on further increase in resin to 5 phr, an increase in torque is observed for higher fiber loading. The reduction of (Maximum – minimum) torque in the case of gum compound in the presence of resin indicates the adverse effect it has on the cure reaction. The lower ΔTm values indicate low level of cross links formed. However, with increasing fiber loading the (Maximum – minimum) torque is found to be increased, the effect being more prominent at higher resin content. This may be arising from the combined effect of improved fiber matrix bonding and the probable contribution to the state of cure in the presence of fibers. Similar result in the case of short nylon fiber reinforced SBR -WTR composite with urethane based bonding agent has been reported by Sreeja & Kutty[2].

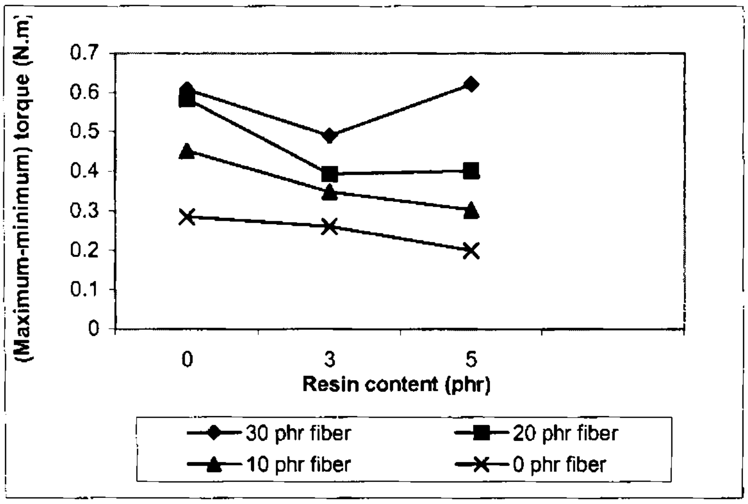

Figure 3.B.2.2. Variation of (maximum – minimum) torque with resin concentration

Scorch time increases with resin content in the case of gum compound (Figure 3.B.2.3.). In the case of fiber - containing mixes, the scorch time decreases with resin content, the effect being more pronounced at higher fiber loading. At any resin loading, the scorch time is lower in the presence of nylon fibers. The early start of the cure reaction, as indicated by the lower scorch time, points to positive contribution of the nylon fibers to the cure reaction. Similar results in the case of short Nylon fiber - NBR rubber composite have been reported earlier[3].

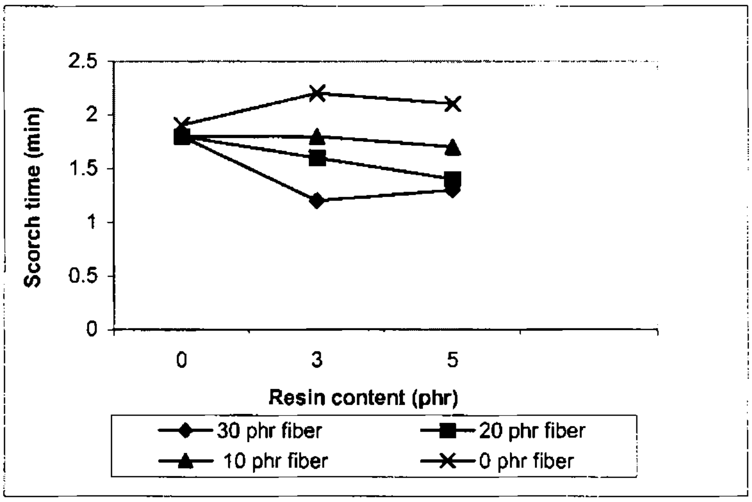

Figure 3.B.2.3. Variation of scorch time with resin concentration

Cure time increases with resin content and stabilizes around 3 phr (Figure 3.B.2.4.). At 5 phr of resin all the mixes show the same cure time. The increased cure time is also reflected as reduced cure rate (Figure 3.B.2.5.). The contribution of fibers to the cure is also evident from the figure. All the mixes containing short fibers show higher cure rate at all resin loadings.

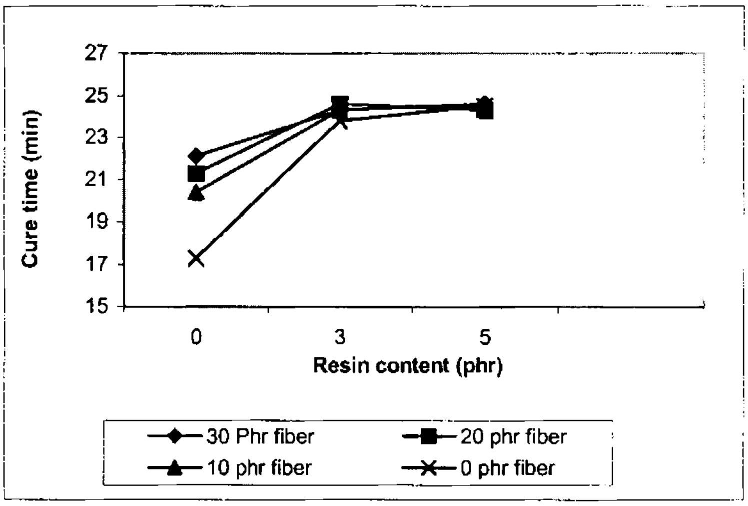

Figure 3.B.2.4. Variation of cure time with resin concentration

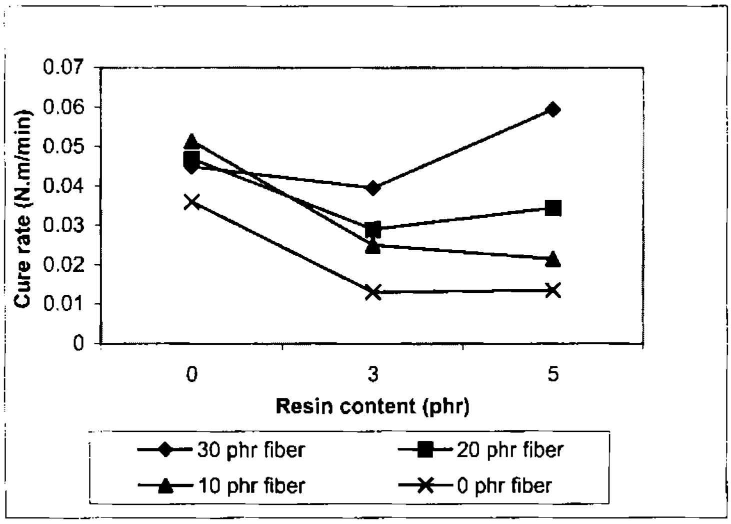

Figure 3.B.2.5. Variation of cure rate with resin concentration

3.B.2.2. Mechanical Properties

Variation of tensile strength with resin concentration for composite containing different fiber loadings is given in Figure 3.B.2.6a. & Figure 3.B.2.6b. Tensile strength increases with increasing resin content for all mixes, the effect being more significant at higher fiber loading (Figure 3.B.2.6a.). In the case of gum compound the tensile strength changes from 6.51 to 7.96 Mpa only in the presence of 5 phr resin, where as the change is from 21.28 to 37.32 Mpa in the case of mix containing 30 phr of fiber. It shows that optimum concentration of the resin required for improved strength is a function of the fiber loading. The improved strength in the presence of bonding agent indicates that the resin improves the fiber -matrix interfacial bond, there by permitting better transfer of load to the fibers. In the transverse orientation of the fibers, the tensile strength shows only marginal increase with increasing resin loading (Figure 3.B.2.6b.). The effect of increasing the fiber content at any resin loading is not as apparent as in the case of longitudinal orientation. This is because, in the transverse orientation, the load is primarily supported by the matrix. Hence in this case, all the composites show almost the same pattern as the gum compound.

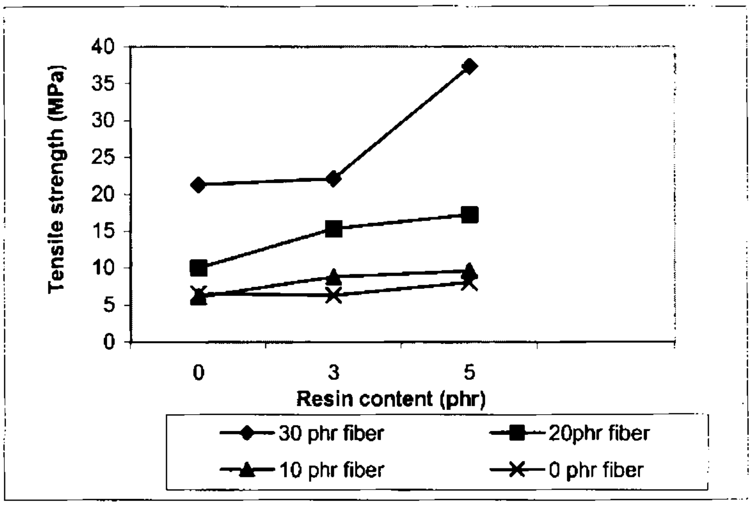

Figure 3.B.2.6a. Variation of tensile strength (Longitudinal) with resin concentration.

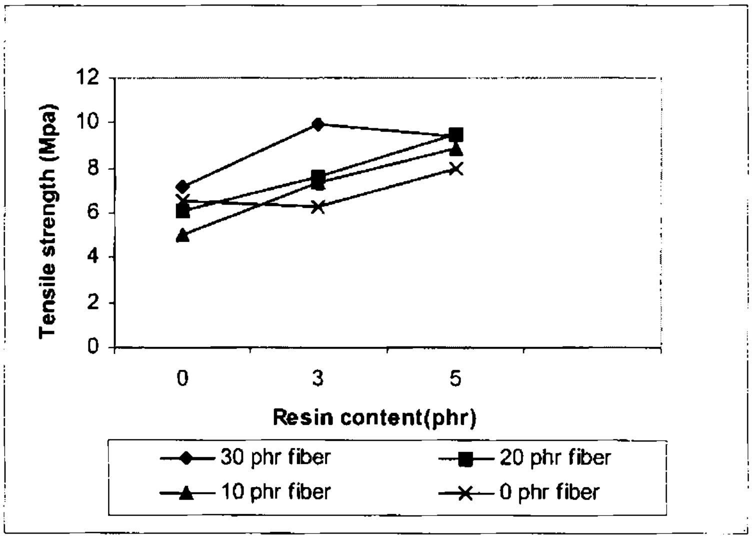

Figure 3.B.2.6b.Variation of tensile strength (Transverse) with resin concentration

The SEM photomicrographs of the tensile fracture surface of the 30 phr fiber loaded sample containing 5 phr epoxy resin as bonding agent (Mix L) in longitudinal direction is shown in Figure 3.B.2.6c. and Figure 3.B.2.6d. Figure 3.B.2.6e. and Figure 3.B.2.6f. show the SEM photomicrographs of the tensile fracture surface of the 30 phr fiber loaded sample with out resin (Mix D). It can be clearly seen from the figures that the matrix is more mutilated in the case of mix L indicating that the matrix is more strained during tensile fracture compared to mix D. It can also be observed that the fibers protruding out in mix L are not smooth and some portion of matrix is sticking to the surface of the fiber.

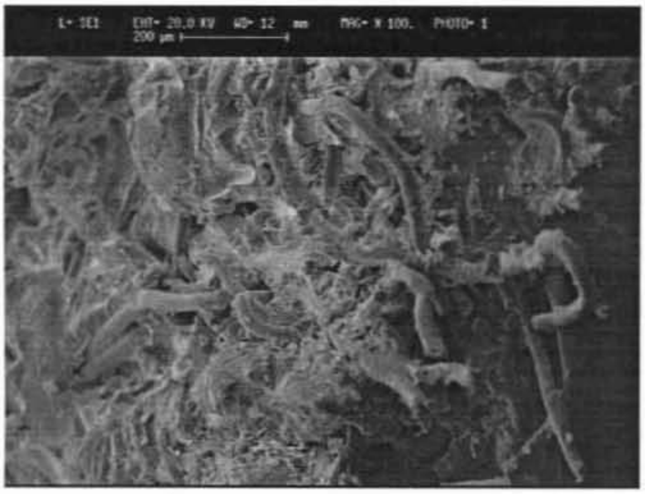

Figure 3.B.2.6c. SEM photomicrograph of tensile fracture surface of mix L with fibers oriented in longitudinal direction (original magnification x100; marker 200μ)

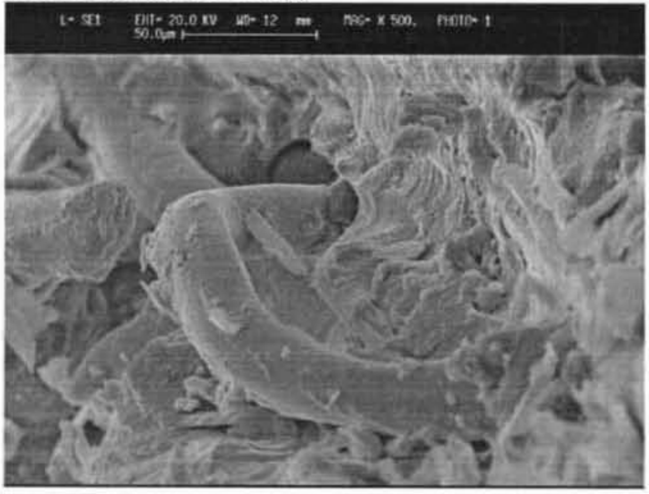

Figure 3.B.2.6d. SEM photomicrograph of tensile fracture surface of mix L with fibers oriented in longitudinal direction (original magnification x500; marker 50μ)

But in the case of mix D the surface is smooth, clean and matrix is less mutilated. These suggest a stronger fiber -matrix interfacial bonding in the presence of resin and support the higher tensile strength of mix L compared to mix D.

Figure 3.B.2.6e. SEM photomicrograph of tensile fracture surface of mix D with fibers oriented in longitudinal direction (original magnification x100; marker 200µ)

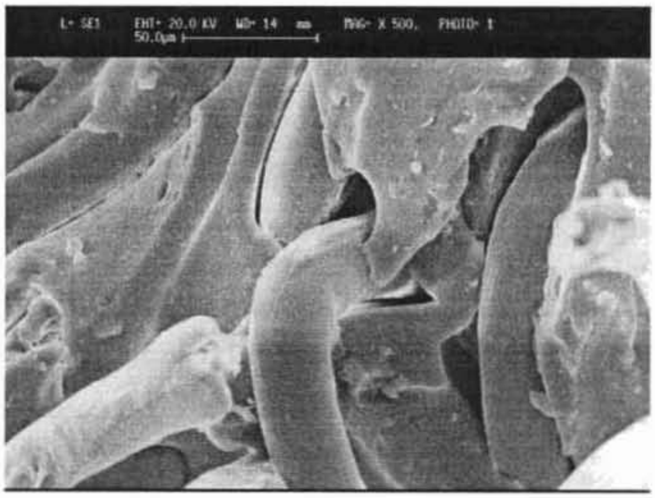

Figure 3.B.2.6f. SEM photomicrograph of tensile fracture surface of mix D with fibers oriented in longitudinal direction (original magnification x500; marker 50µ)

The tensile fracture surface of mix L with fibers in the transverse direction is shown in Figure 3.B.2.6g. The fibers oriented in the horizontal plane are clearly visible in the figure. The channels formed by the fiber removal during fracture can be seen in the figure while in longitudinal direction (Figure 3.B.2.6c.) holes are formed due to fiber pull out. This indicated that in transverse direction fiber - matrix interface failure is causing the tensile fracture.

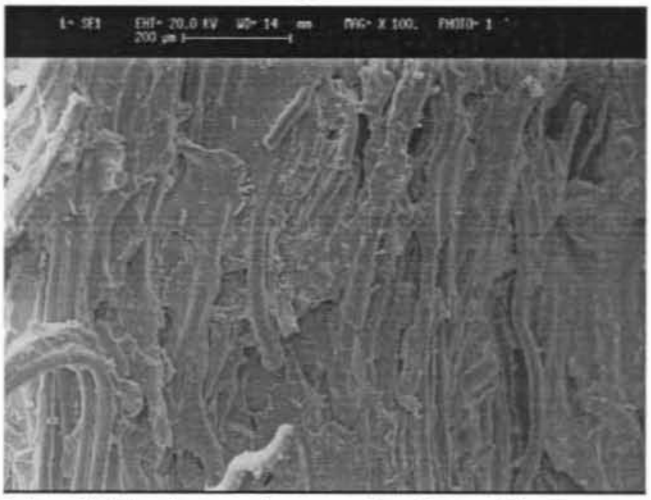

Figure 3.B.2.6g. SEM photomicrograph of tensile fracture surface of mix L with fibers oriented in transverse direction (original magnification x100; marker 200μ)

Variation of elongation at break with resin content is shown in Figure 3.B.2.7a. and Figure 3.B.2.7b. Elongation at break of the gum compound decreases with increase in resin loading whereas it is marginally increased in the case of fiber – filled samples. In all the cases, the composite shows significantly low elongation at break values compared to the gum compound. Similar behaviour is also observed in the transverse orientation of fibers.

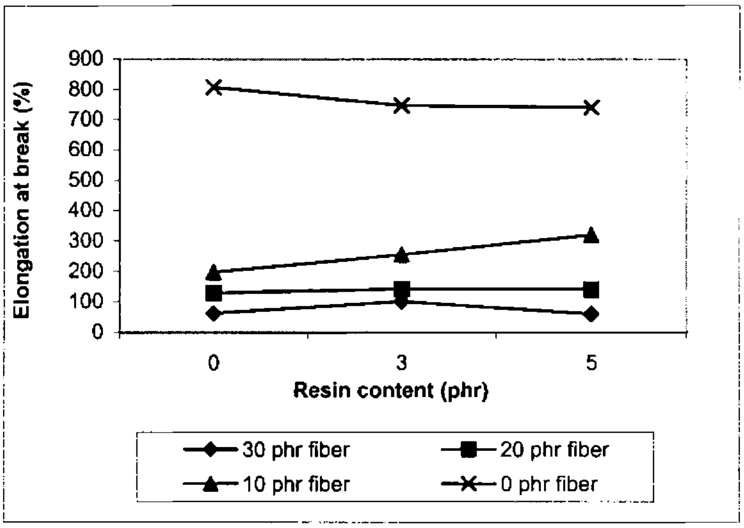

Figure 3.B.2.7a. Variation of elongation at break (Longitudinal) with resin concentration

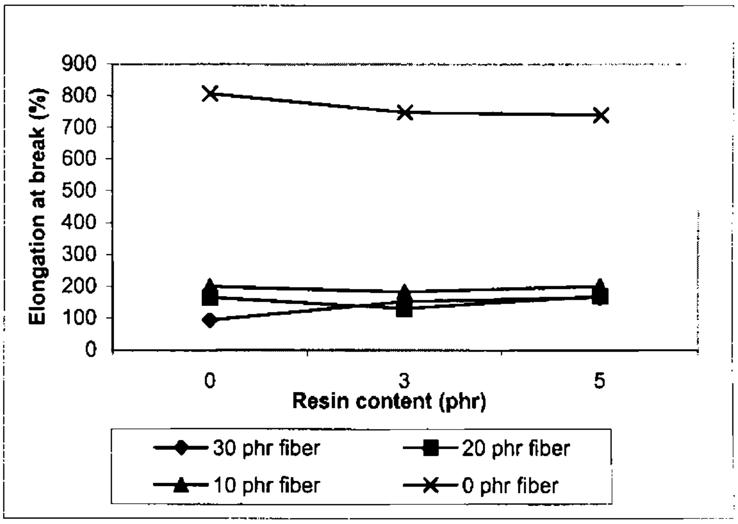

Figure 3.B.2.7b. Variation of elongation at break (Transverse) with resin concentration

Modulus at 50% elongation at various resin ratios for composites containing different fiber loading is shown in the Figure 3.B.2.8a. and Figure 3.B.2.8b. Modulus at 50% elongation (E50) shows no significant changes with increasing resin content at lower fiber loadings. In the case of mix containing 30 phr fiber there is marked increase in E50 when the resin loading is 5 phr.

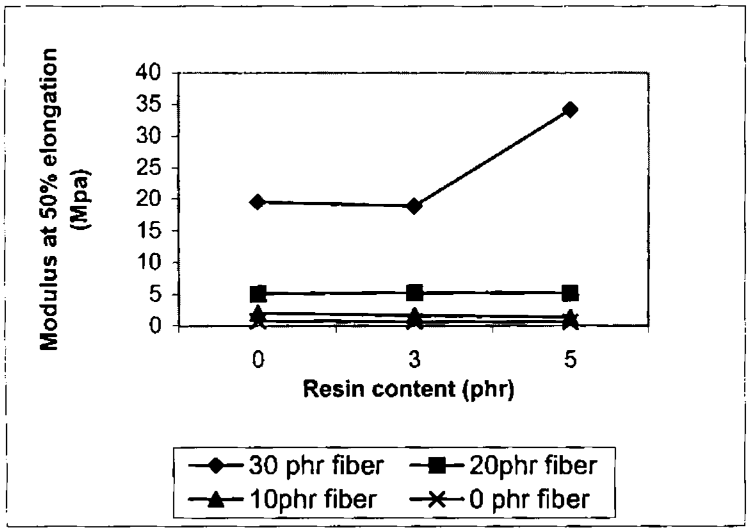

Figure 3.B.2.8a. Variation of modulus (Longitudinal) with resin concentration

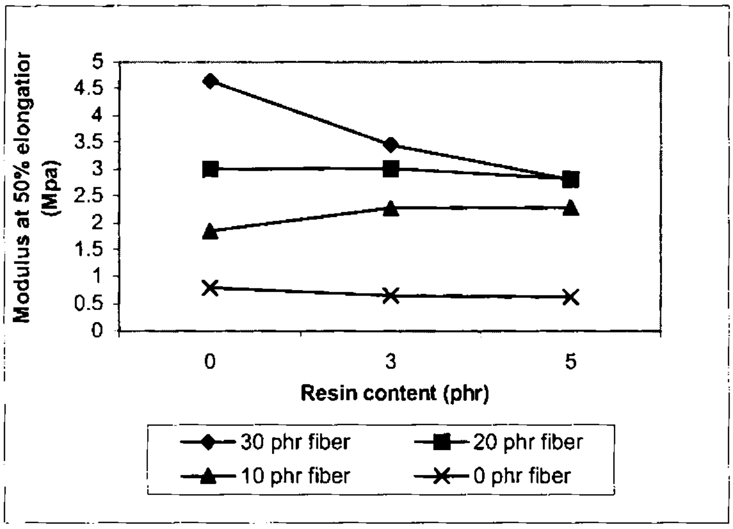

Figure 3.B.2.8b. Variation of modulus (Transverse) with resin concentration

In the transverse orientation of fibers again the modulus (E50) is more or less constant with increasing resin content (Figure

3.B.2.8b) except for 30 phr fiber loading where a marginal decrease is observed. At all fiber loading, E50 in the transverse orientation of fibers is lower than that of the longitudinal orientation. At all resin loading the E50 is increased with fiber loading

The variation of tear strength of the composite with different fiber loading and with different resin concentration is shown in the Figure 3.B.2.9a and Figure 3.B.2.9b. Tear strength increases as resin concentration increases for all the composite with different fiber loading in both longitudinal and transverse directions. Tear strength is not affected by the presence of resin in the case of gum compound in both longitudinal and transverse direction. The tear strength increases as fiber content increases. The rise in tear strength of composite with increase in resin content is more prominent as fiber concentration increases, especially in the longitudinal orientation of fiber. This again confirms a better bonding between fiber and matrix in the presence of resin.

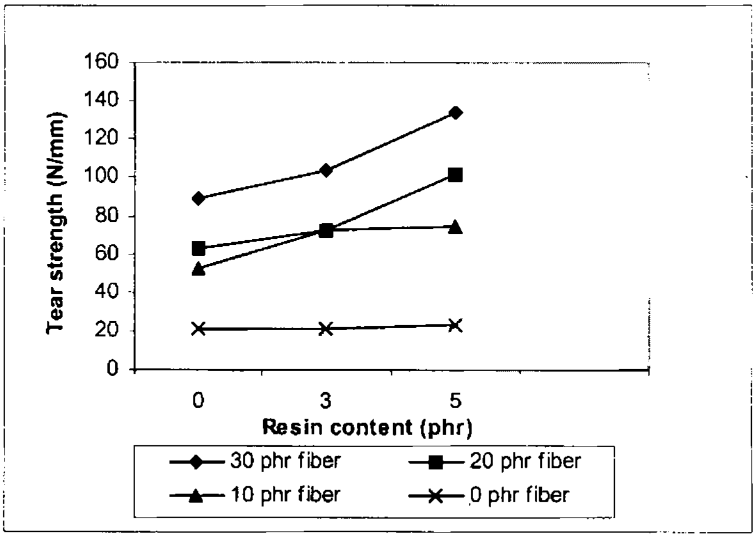

Figure 3.B.2.9a. Variation of tear strength (Longitudinal) with resin concentration.

The tear strength in the longitudinal direction is higher than the tear strength in transverse direction. In the transverse direction fibers are parallel to the crack front and hence the crack propagation cannot be arrested effectively resulting in lower tear strength when compared to longitudinal direction.

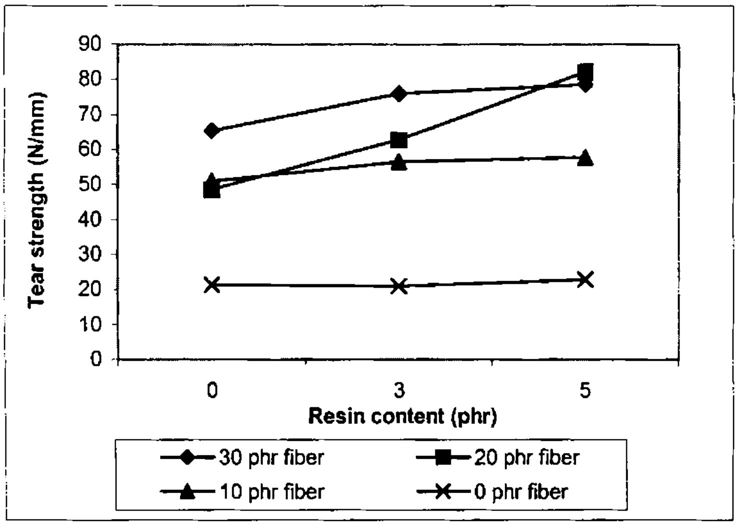

Figure 3.B.2.9b. Variation of tear strength (Transverse) with resin concentration

The variation of hardness with increase in resin concentration for different fiber loading of the composite is shown in Figure 3.B.2.10. Hardness is only marginally affected by the presence of resin.

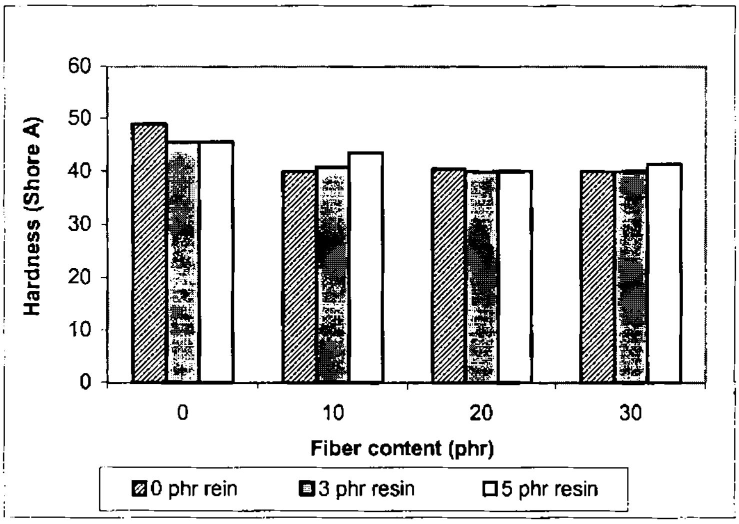

Figure 3.B.2.10. Variation of hardness with resin concentration

Resilience increases with fiber loading (Figure 3.B.2.11.). Resilience increases with resin content at lower fiber loading. At 30 phr fiber, however there is a marginal reduction in the resilience with resin loading. Compression set is higher for samples containing resin. The resin softens under elevated test temperatures and permits irreversible flow of the matrix under load (Figure 3.B.2.12).

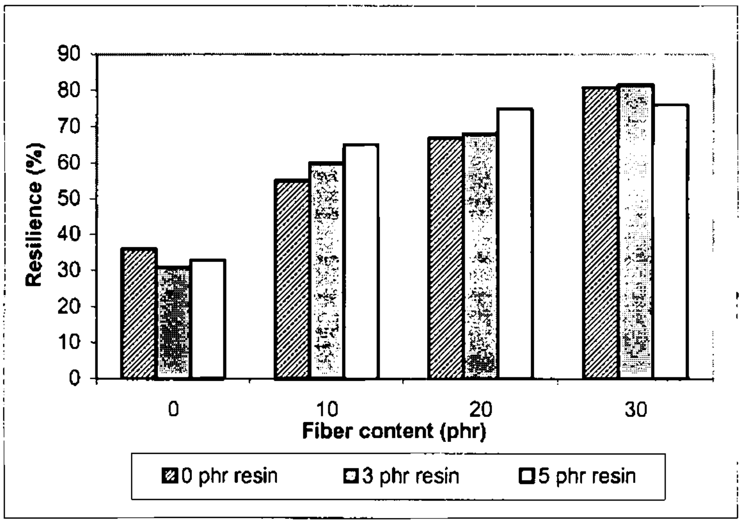

Figure 3.B.2.11. Variation of resilience with resin concentration

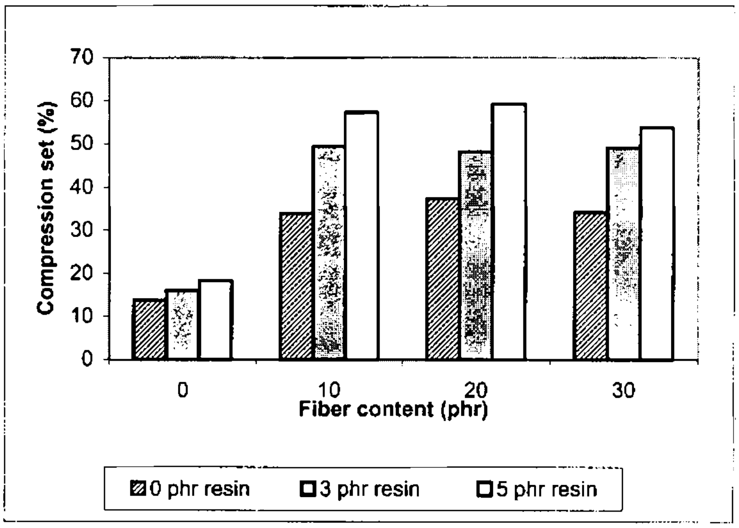

Figure 3.B.2.12. Variation of compression set with resin concentration

Variation of abrasion loss with resin concentration for different fiber loading of the composite and gum compound is shown in Figure 3.B.2.13a. and Figure 3.B.2.13b. Abrasion resistance is improved with an increase in fiber concentration in both longitudinal and transverse directions.

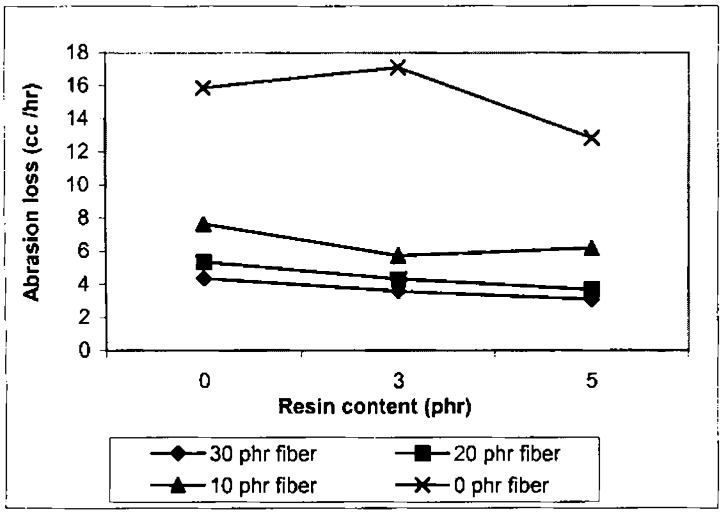

Figure 3.B.2.13a. Variation of abrasion loss (Longitudinal) with resin concentration

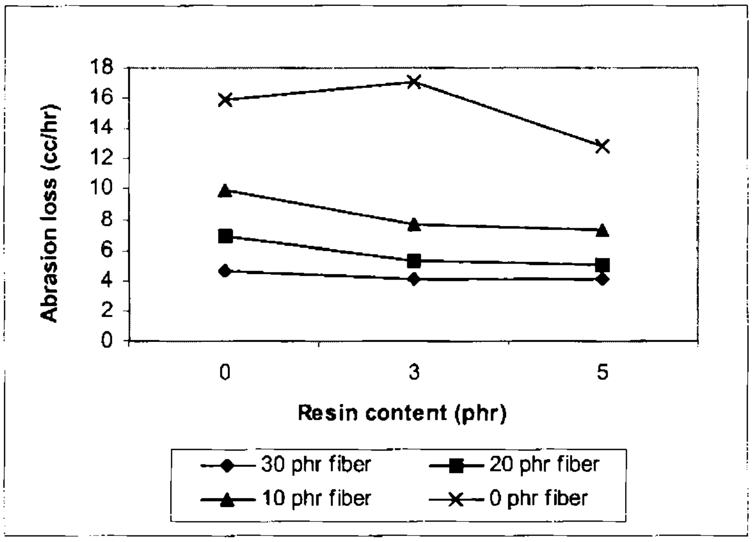

Figure 3.B.2.13b. Variation of abrasion loss (Transverse) with resin concentration.

Abrasion loss decreases as resin concentration increases for all fiber loadings of the composite in both longitudinal and transverse directions. This again confirms a strong bonding between the fiber and matrix. At any fiber and resin concentration the loss in transverse orientation is higher than loss in longitudinal orientation of fibers.

Heat build up increases as resin concentration increases for all fiber loadings and the gum compound (Figure 3.B.2.14a & Figure 3.B.2.14b) in both longitudinal and transverse directions. In the absence of resin all fiber loading have almost same heat build up in both transverse and longitudinal directions. But as resin content increases, the rise in heat build up as fiber concentration increases from 0 to 30 phr, incresaes. Buckling of fibers lead to absorption of a greater part of applied stress in the stress-strain cycle and hence less residual energy to dissipate as heat. In the presence of resin, the buckling of the fibers will be less due to good bonding of the fiber and matrix, as a result less amount of applied stress is absorbed leading to more heat build up.

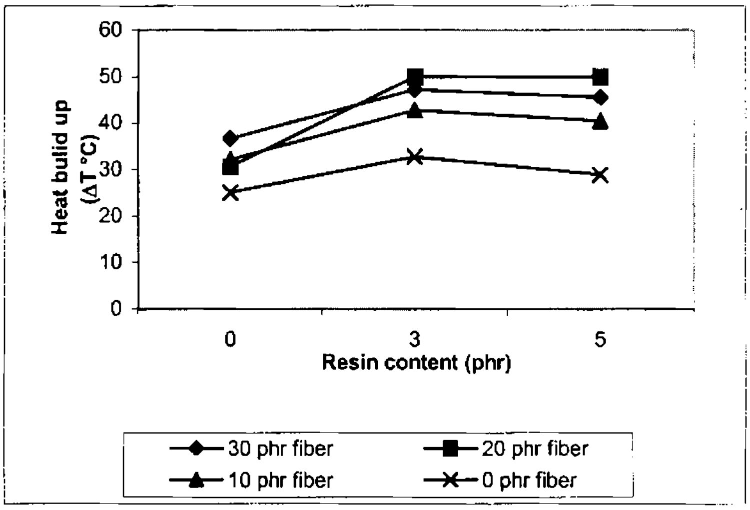

Figure 3.B.2.14a. Variation of heat build up (Longitudinal) with resin concentration

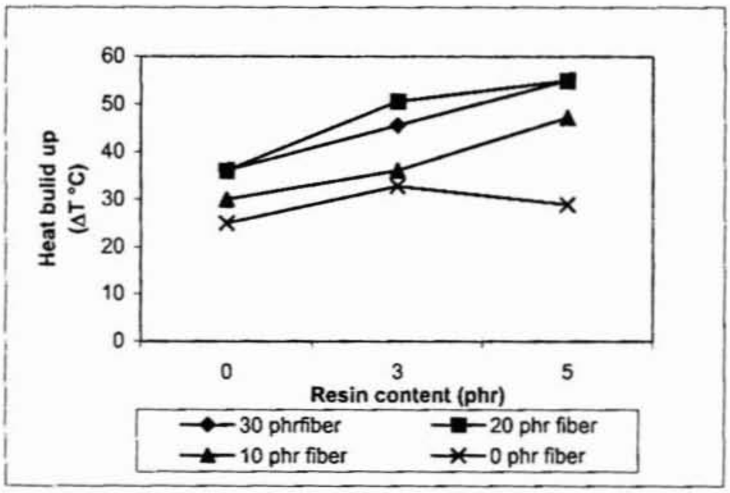

Figure 3.B.2.14b. Variation of heat build up (Transverse) with resin concentration.

3.B.2.3. Ageing Resistance

The ageing resistance of the mixes was studied and the percentage retention of properties after ageing for 48 hrs at 70°C is given in the Figure 3.B.2.15a & Figure 3.B.2.15b. The percentage retention in tensile strength both in longitudinal and traverse directions increases as fiber is introduced to the matrix.

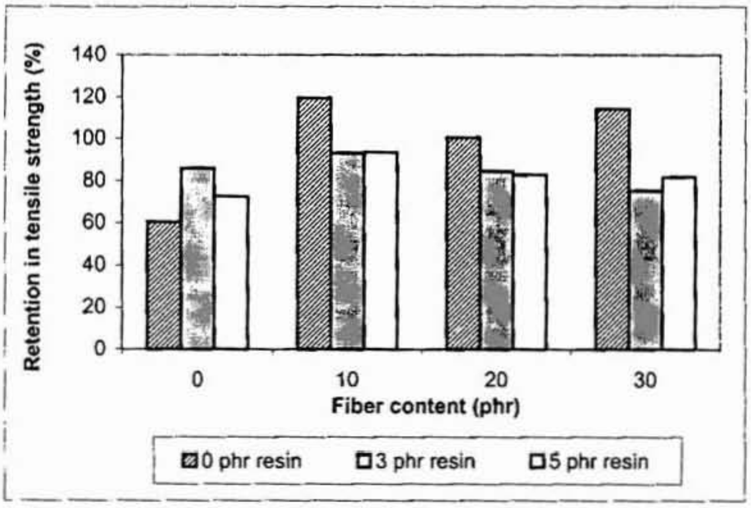

Figure 3.B.2.15a. Variation of percentage retention in tensile strength (Longitudinal) with fiber loading

The retention of tensile strength of composite decreases sharply as the resin content increases to 3 phr and levels off on further increase to 5 phr. But in the gum compound there is a rise in percentage retention in the presence of resin. This indicates that interfacial bonding between fiber and matrix is weakening to some extent on ageing.

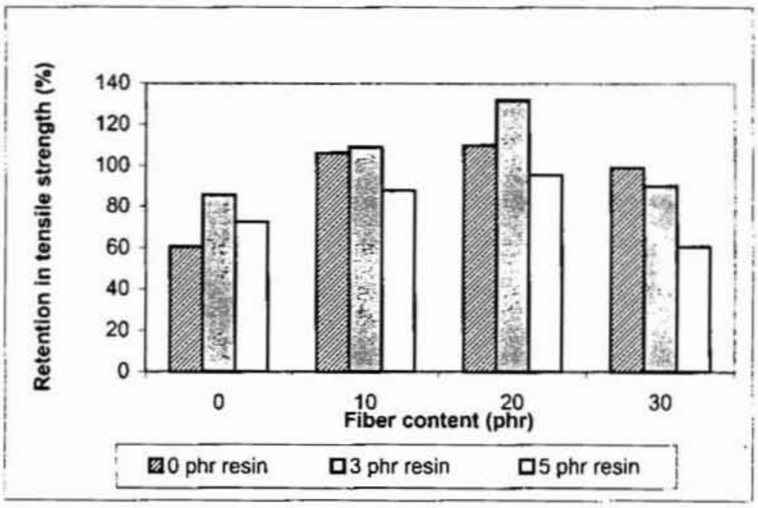

Figure 3.B.2.15b. Variation of percentage retention in tensile strength (Transverse) with fiber loading

References

1. Rajeev R.S., Anil.K.Bhowmick, De S.K. and Bandyopadhyay S. J. Appl. Polym. Sci.,**90** (2) (2003) 544.

2. Sreeja T.D., Kutty S.K.N. Prog. In Rubber Plast. & Recyling Technol. **18** (4) (2002) 1.

3. Sreeja, T.D.; Kutty S.K.N. J. Elastomers and Plastics **34** (2) (2002) 157.

SECTION C. PART (I)

SBR-SHORT NYLON-6 FIBER COMPOSITES

SBR, a general purpose synthetic rubber is widely used in products such as tyres and belts, is much superior to NR with respect to ageing and ozone resistance. However cuts and cracks are faster in SBR than in NR. SBR is also characterized by relatively high hysteresis and poor resilience. The abrasion resistance of SBR is as good as that of natural rubber or slightly better. The major draw back of SBR is its poor gum strength. Reinforcing SBR with short Nylon fibers will improve its mechanical properties.

In the present section, the variation of cure and mechanical properties of short Nylon -6 fiber - Styrene butadiene rubber composite with fiber concentration and orientation is described. Fiber content is varied from 0 to 30 phr.

Table 3.B.1.1 gives formulation of the mixes. The details of sample preparation and experimental techniques are described in Chapter 2.

Table 3.B.1.1. Formulation of the mixes

Ingredients	Mix No.			
	A	B	C	D
SBR	100	100	100	100
Short Nylon fiber	0	10	20	30

Zinc oxide - 5 phr, Stearic acid – 1.5 phr, CBS – 0.8 phr, TMTD – 0.2 & Suplhur - 2 phr are common to all mixes.

3.C.1.1. Cure Characteristics

The variation of minimum torque with fiber content is shown in Figure 3.C.1.1. The minimum torque increases with fiber concentration upto 20 phr fiber loading and then almost levels off on further increase in fiber concentration. The processability of the composite is affected in the presence of fibers.

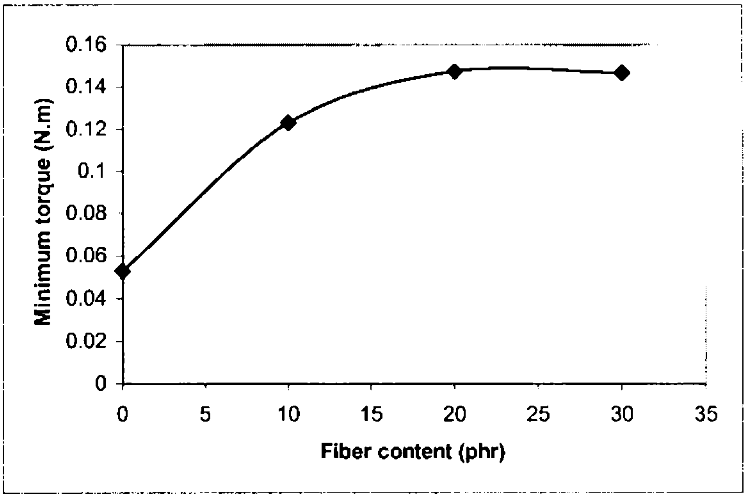

Figure 3.C.1.1. Variation of minimum torque with fiber concentration

The (maximum – minimum) torque values increase from 0.486 N.m at 0 phr to 0.833 N.m at 30 phr fiber, indicating a more restrained matrix in the case of composites (Figure 3.C.1.2.). Similar results have been obtained in the case of NBR short Nylon -6 and CR short Nylon -6 composites (Sections 3.A.I. & 3.B.I., respectively)

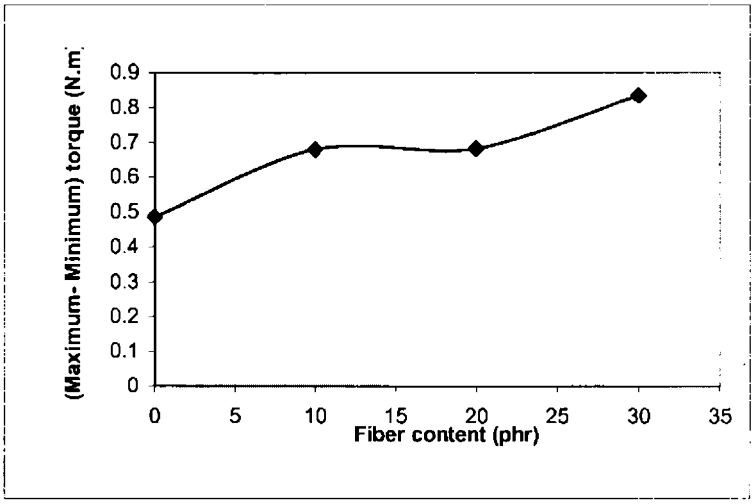

Figure 3.C.1.2. Variation of (maximum – minimum) torque with fiber concentration

Variation of scorch time with fiber concentration is shown in the Figure 3.C.1.3. Scorch time decreases with fiber concentration. There is a reduction in cure time with fiber concentration as shown in Figure 3.C.1.4.

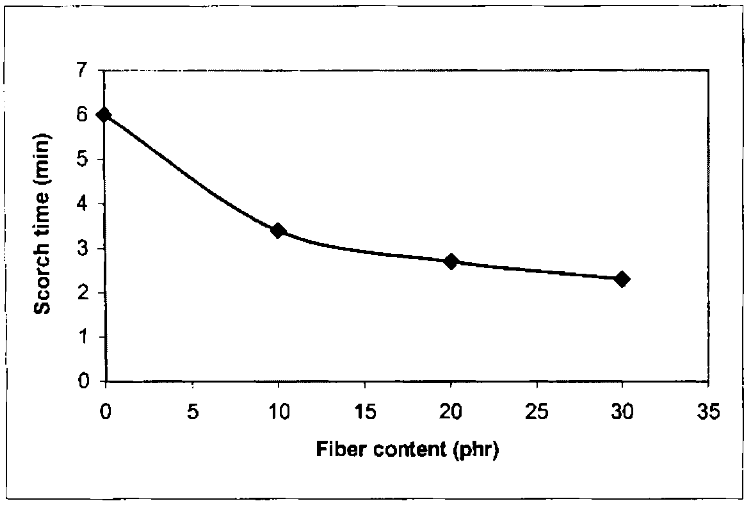

Figure 3.C.1.3. Variation of scorch time with fiber concentration

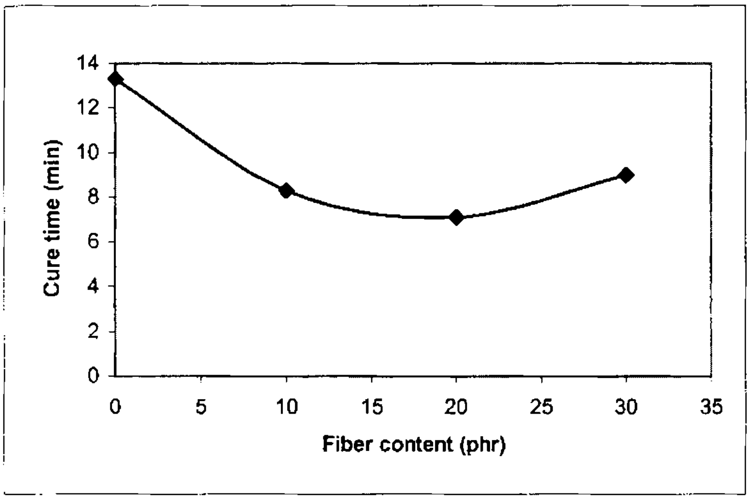

Figure 3.C.1. 4. Variation of cure time with fiber concentration

Cure rate increases as fiber concentration increases (Figure 3.C.1.5.). 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 reported in the case of Nylon –6 reinforced NBR composites[1].

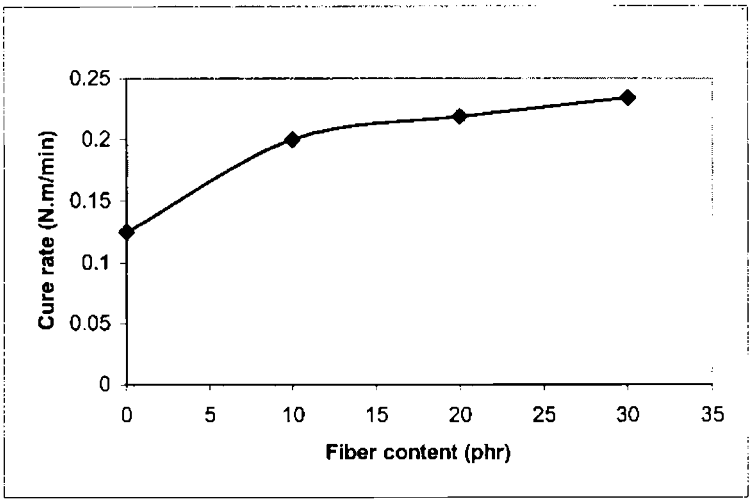

Figure 3.C.1.5. Variation of cure rate with fiber concentration

3.C.1.2. Mechanical Properties

The variation of tensile strength with fiber content is shown in Figure 3.C.1.6. The tensile strength in longitudinal direction increases as fiber concentration increases. Similar results were obtained in the case of Nylon –6 reinforced NBR composites also (Section 3.A.I.I). SBR and NBR are low gum strength matrices, which do not undergo strain induced crystallization; hence no dilution effect is observed as in the case of CR – short Nylon –6 composite (Section 3.B.I.). Tensile strength remains more or less constant with fiber concentration in the transverse orientation of fibers. Tensile strength in longitudinal direction is higher than that in transverse direction. In longitudinal direction the fibers are aligned in the direction of stress applied, so more effective in hindering the growing crack front and hence higher tensile strength in that direction. This is in agreement with earlier results obtained in the case of SBR – short jute fiber composite[2].

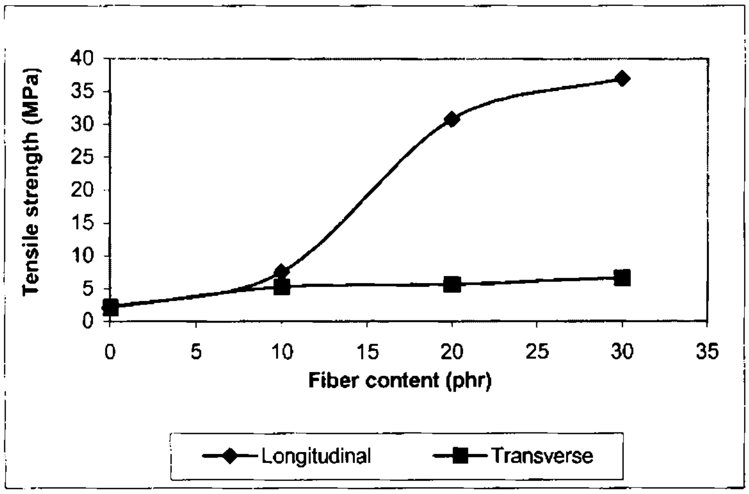

Figure 3.C.1.6. Variation of tensile strength with fiber concentration

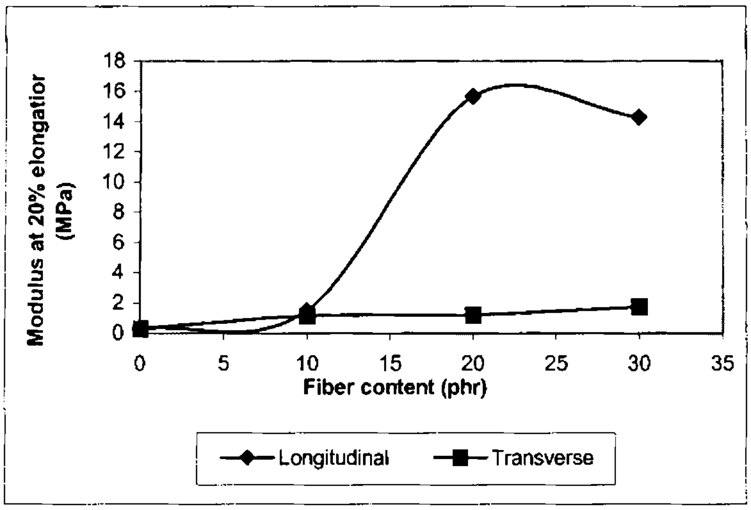

Figure 3.C.1.7. Variation of modulus with fiber concentration

Modulus at 20% elongation in longitudinal direction increases with fiber concentration upto 20 phr fiber loading and remains almost constant on further increase in fiber concentration to 30 phr fiber (Figure 3.C.1.7.). Modulus at 20% elongation remains more or less constant with fiber content in the transverse direction of fibers.

The variation of ultimate elongation with fiber concentration is shown in Figure 3.C.1.8. There is sharp reduction in ultimate elongation on introduction of fibers and the values tend to stabilize on further increase in fiber concentration. In the case of composites, the matrix is more restrained and the failure is initiated at multiple points, resulting in lower elongation at break values. At any fiber loading, ultimate elongation values are higher in the transverse direction. Similar results have been reported earlier[3-4].

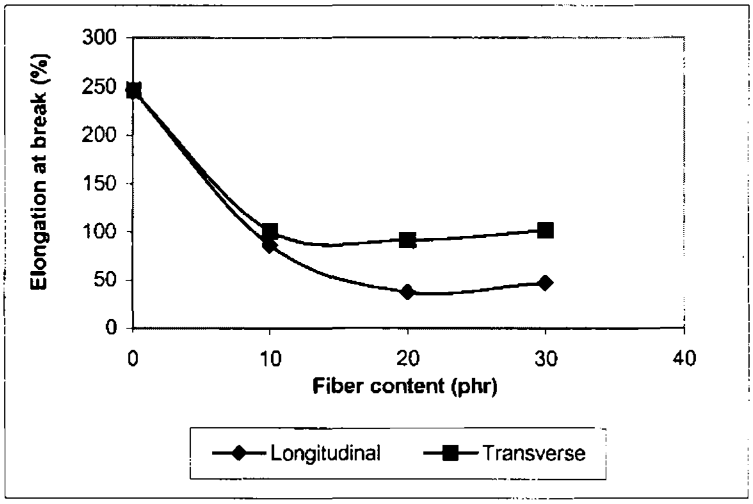

Figure 3.C.1.8. Variation of elongation at break with fiber concentration

Tear strength in longitudinal direction increases with fiber concentration (Figure 3.C.1.9.). As fiber concentration increases, there will be more hindrance to crack propagation. There is a marginal increase in tear strength with fiber content in transverse direction. At any fiber loading tear strength in longitudinal direction is more than that in the transverse direction. In transverse direction fibers are parallel to the crack front and offers less resistance to the propagation of tear.

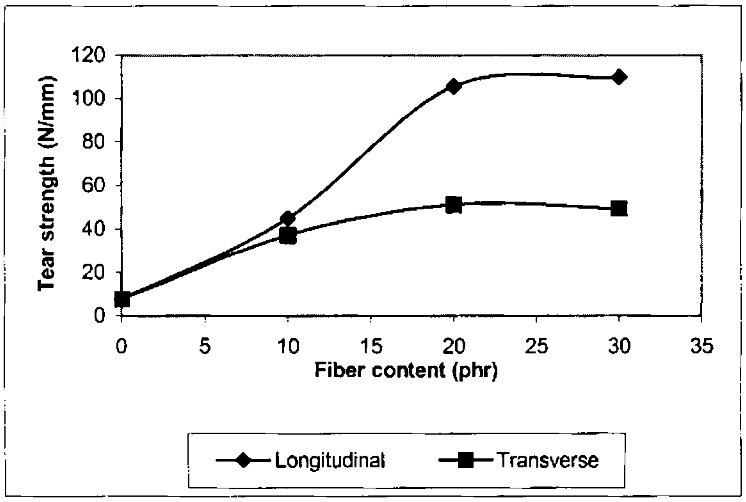

Figure 3.C.1.9. Variation of tear strength with fiber concentration

Hardness decreases on introduction of fiber and levels off on further increase in fiber concentration (Figure 3.C.1.10.). Resilience increases when fiber is introduced to the matrix and tends to stabilize on further increase in fiber concentration (Figure 3.C.1.11.) Similar results were reported earlier[1].

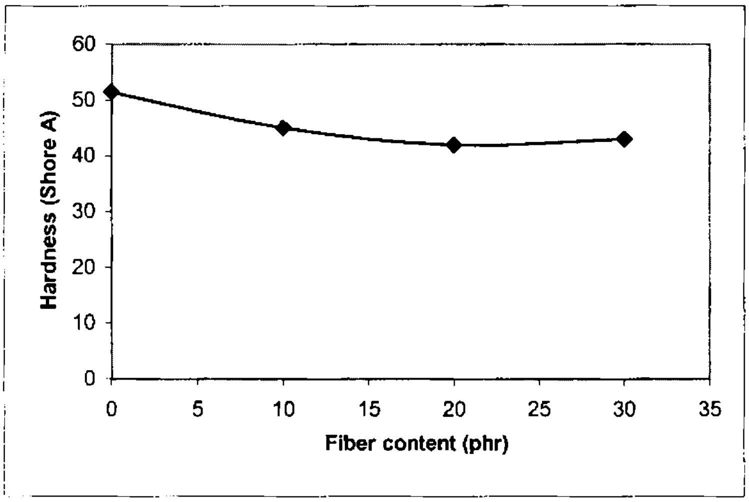

Figure 3.C.1.10. Variation of hardness with fiber concentration

Compression set decreases with fiber concentration (Figure 3.C.1.12.). This is in agreement with the increased resilience values.

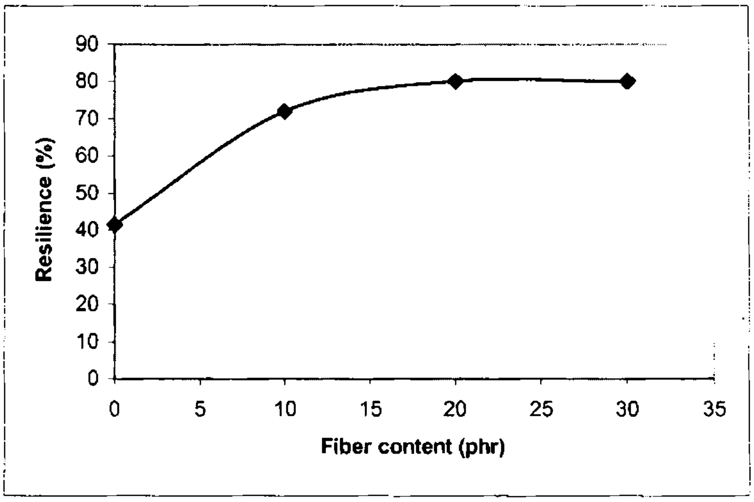

Figure 3.C.1.11. Variation of resilience with fiber concentration

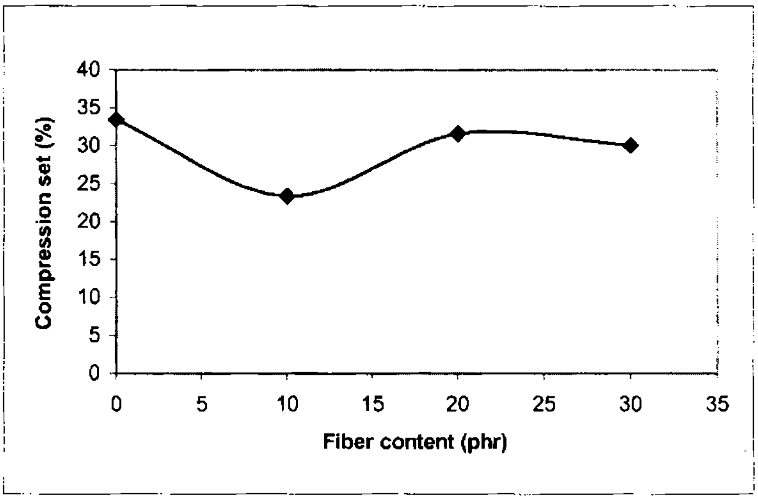

Figure 3.C.1.12. Variation of compression set with fiber concentration

Abrasion resistance increases as fiber concentration increases in both longitudinal and transverse orientations of fibers, indicating the formation of more restrained matrix in the case of composites (Figure 3.C.1.13.). At any fiber concentration the loss is higher in transverse direction than in longitudinal orientations of fibers. The fibers are easily debonded from the matrix when they are arranged transversely and hence higher loss in that direction.

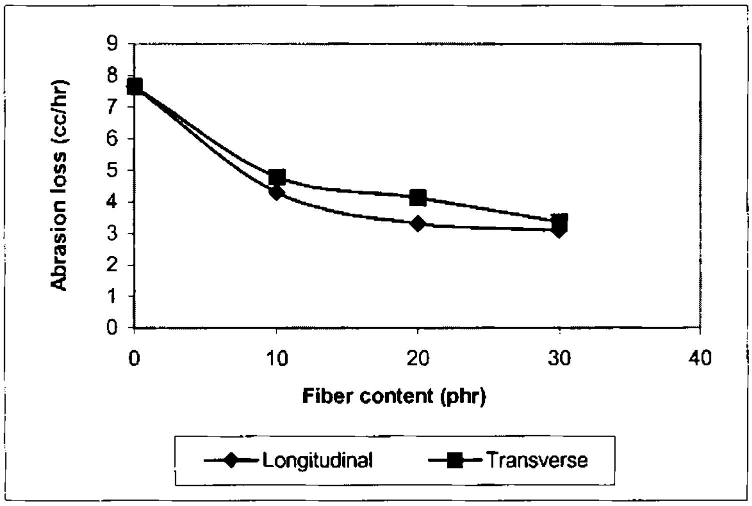

Figure 3.C.1.13. Variation of abrasion loss with fiber concentration

Heat build up increases as fiber concentration increases in both longitudinal and transverse direction. Samples with transversely oriented fibers have less heat build up when compared to sample with longitudinal oriented fiber. 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 Sreeja et al and Das[5-6].

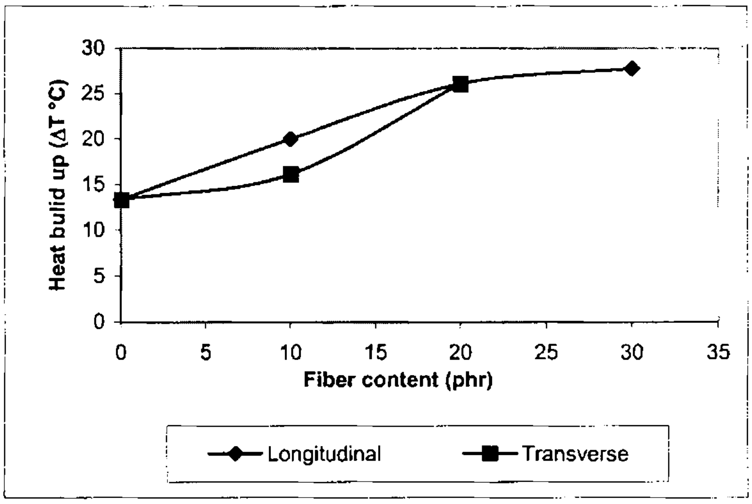

Figure 3.C.1.14. Variation of heat build up with fiber concentration

3.C.1.3. Ageing Resistance

All the mixes show a drop in tensile strength after ageing in both longitudinal and transverse directions. Composites register less retention in tensile strength compared to the gum compound. Retention in tensile strength is not much influenced by orientation of fibers.

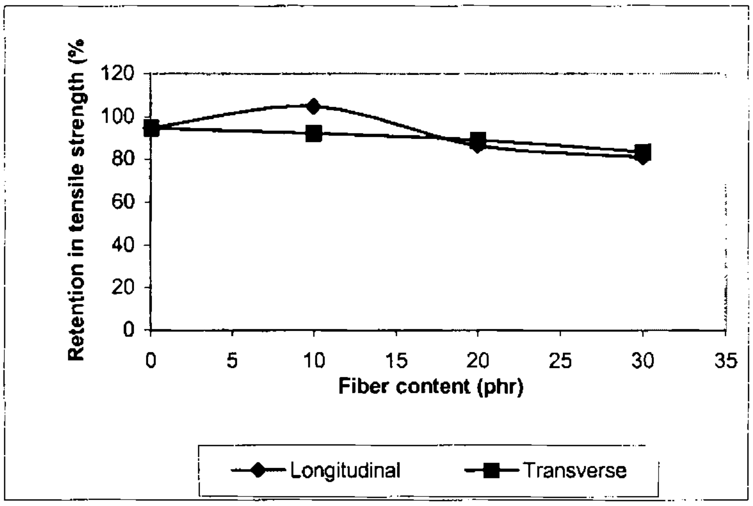

Figure 3.C.1.15. Variation of percentage retention in tensile strength with fiber concentration

REFERENCES

1. Sreeja, T.D.; Kutty S.K.N. J. Elastomers and Plastics, **34** (2) (2002) 157.
2. Murty V.M. and De S.K., J. Appl. Polym. Sci., **29** (1984) 1355.
3. Chakraborty S.K., Setua D.K. and De S.K., Rubber Chem. Technol., **55** (1982) 1286.
4. Akthar S., De P.P. and De S.K., J. Appl. Polym. Sci., **32** (1986) 5123.
5. Sreeja T.D., Kutty S.K.N, J. Elastomers and Plastics, **33** (3) (2001) 225.
6. Das B., J. Appl. Polym. Sci., **17** (1973) 1091.

SECTION C. PART (II)
SBR-SHORT NYLON-6 FIBER COMPOSITES WITH EPOXY RESIN AS BONDING AGENT

Although the ultimate properties of the short fiber reinforcement depend mainly on the fiber orientation, fiber loading and aspect ratio, the adhesion between the fiber and the matrix plays a very important role. External bonding agents are used to improve fiber matrix interface in short fiber composite. In this section the investigation of epoxy resin as bonding agent for short Nylon –6 reinforced SBR composite is reported.

Formulation of the test mixes are given in the Table 3.C.2.1. Method of preparation, procedure adopted for the determination of cure characteristics and mechanical properties of the mixes are given in chapter II.

Table 3.C.2.1. Formulation of the mixes

Ingredients	Mix No.											
	A	B	C	D	E	F	G	H	I	J	K	L
SBR	100	100	100	100	100	100	100	100	100	100	100	100
Nylon	0	10	20	30	0	10	20	30	0	10	20	30
Resin*	0	0	0	0	3	3	3	3	5	5	5	5

* Epoxy resin formed by 1:0.5 equivalent combination of epoxy resin and amine type hardener; (Zinc oxide - 5 phr, Stearic acid – 1.5 phr, CBS – 0.8 phr, TMTD – 0.2 phr & Suplhur - 2 phr are common to all mixes).

3.C.2.1 Cure Characteristics

Minimum torque decreases marginally as the resin concentration increases for all fiber concentration of the composite, the effect being more pronounced at lower fiber loading (Figure 3.C.2.1.). The processability of the gum and composites is not much affected in the presence of resin. At all resin concentrations, as fiber content increases minimum torque increases.

The variation of (maximum – minimum) torque (ΔT) is shown in Figure 3.C.2.2. A sharp fall in ΔT is observed on introduction of resin. But further increase in resin concentration causes only marginal reduction in ΔT. The epoxy resin is showing a plasticizing effect on the matrix rather than a bonding action in SBR.

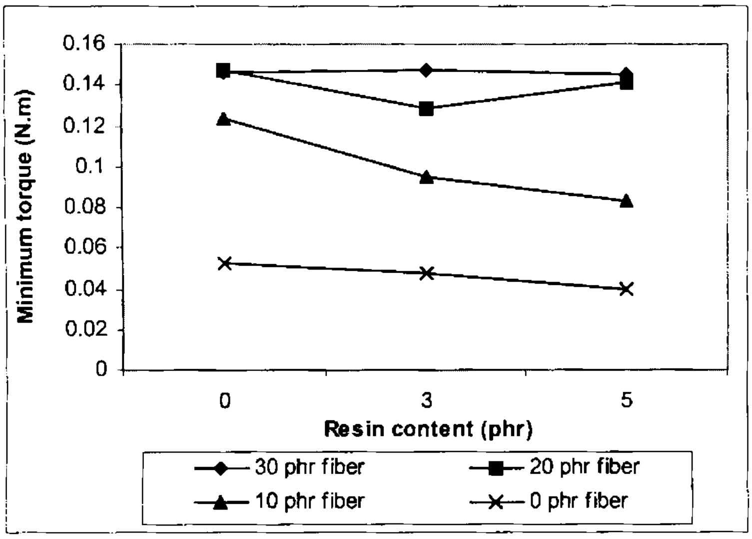

Figure 3.C.2.1. Variation of minimum torque with resin concentration

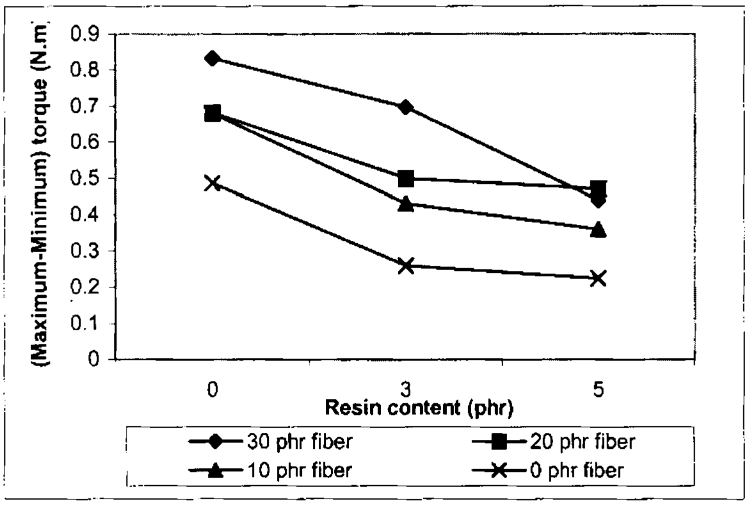

Figure 3.C.2.2. Variation of (maximum – minimum) torque with resin concentration

Scorch time decreases sharply on introduction of resin to the gum compound. Further increase in resin concentration causes only marginal decrease in scorch time (Figure 3.C.2.3). Composites also follow similar trend as that of gum compound; but reduction in scorch time is less in the case of composites when compared to the gum compound. At higher resin concentration all the mixes show more or less similar scorch time.

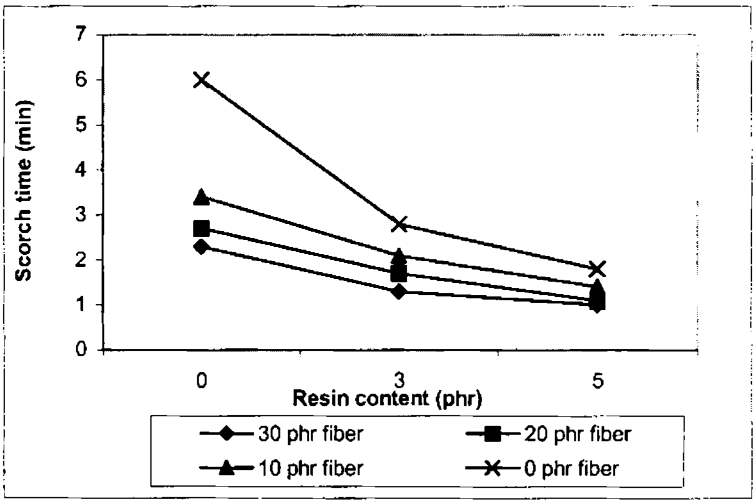

Figure 3.C.2.3. Variation of scorch time with resin concentration

Cure time increases with resin concentration for all fiber - containing mixes. In the case of gum compound introduction of resin causes a reduction in cure time and further increase in resin causes an increase in cure time (Figure 3.C.2.4). Resin is interacting with the curatives and retarding the cure reaction, which is confirmed by the reduction in the cure rate in presence of resin (Figure 3.C.2.5).

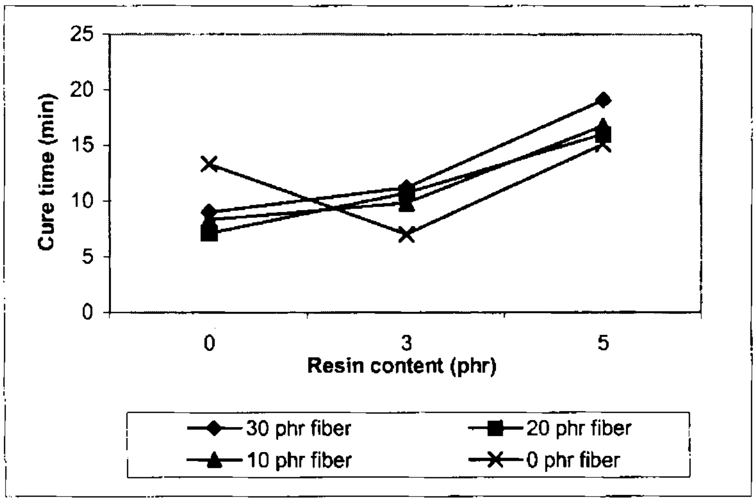

Figure 3.C.2.4. Variation of cure time with resin concentration

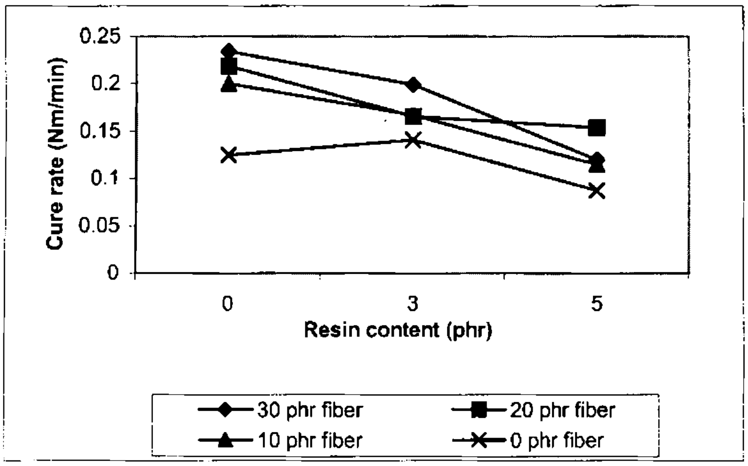

Figure 3.C.2.5. Variation of cure rate with resin concentration

3.C.2.2. Mechanical Properties

The variation of tensile strength with resin concentration in longitudinal and transverse orientations of fiber is shown in the Figures 3.C.2.6a. and 3.C.2.6b., respectively. Tensile strength of the gum compound increases with resin concentration, indicating the formation of more restrained matrix in the presence of resin. There is a reduction in tensile strength with resin concentration for composites in both longitudinal and transverse directions. Epoxy resin being polar in nature, has strong adhesion to the nylon fiber but cannot bind to the non polar SBR matrix. Hence it weakens fiber matrix interface leading to lower tensile strength.

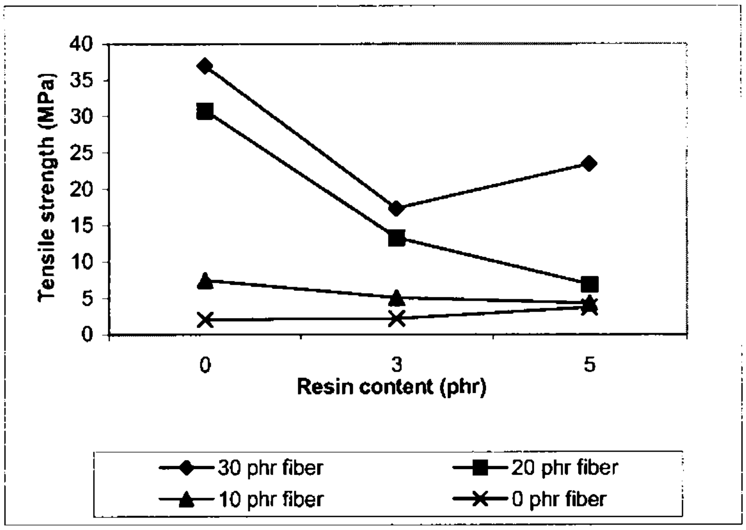

Figure 3.C.2.6a. Variation of tensile strength (Longitudinal) with resin concentration

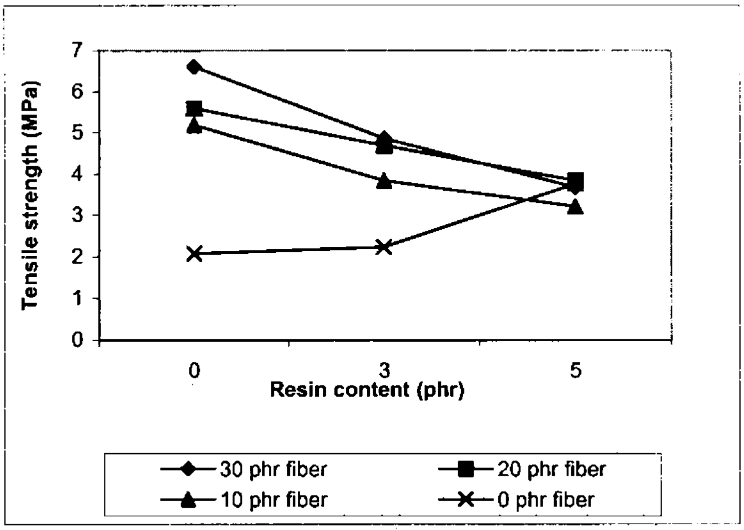

Figure 3.C.2.6b. Variation of tensile strength (Transverse) with resin concentration

Figures 3.C.2.6c. & 3.C.2.6d. show the SEM photomicrographs of tensile surface of the 30 phr fiber loaded sample containing 5 phr epoxy resin as bonding agent (Mix L) in longitudinal direction of fiber orientation. Figures 3.C.2.6e. & 3.C.2.6f. are the SEM of 30 phr fiber loaded compound with out resin (Mix D).

Figure 3.C.2.6c. SEM photomicrograph of tensile fracture surface of mix L with fibers oriented in longitudinal direction (original magnification x100; marker 200μ)

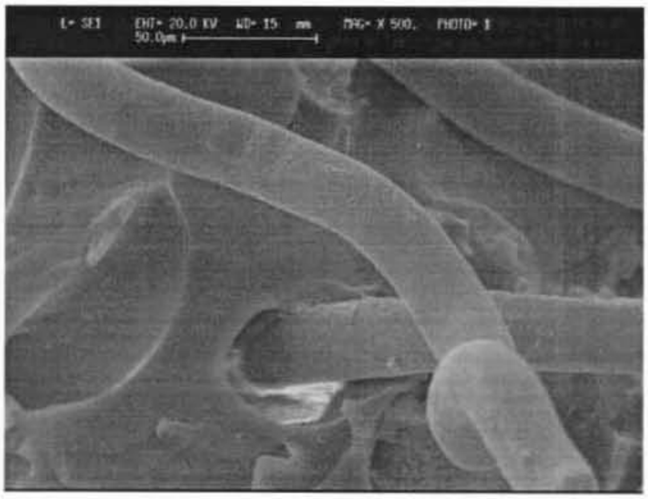

Figure 3.C.2.6d. SEM photomicrograph of tensile fracture surface of mix L with fibers oriented in longitudinal direction (original magnification x 500; marker 50μ)

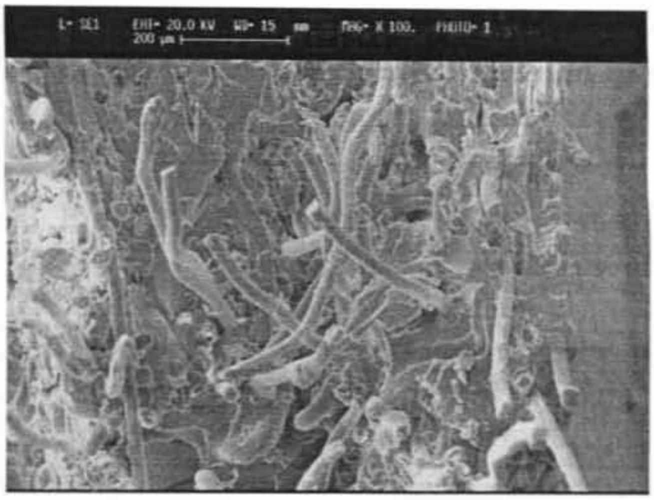

Figure 3.C.2.6e. SEM photomicrograph of tensile fracture surface of mix D with fibers oriented in longitudinal direction (original magnification x100; marker 200µ)

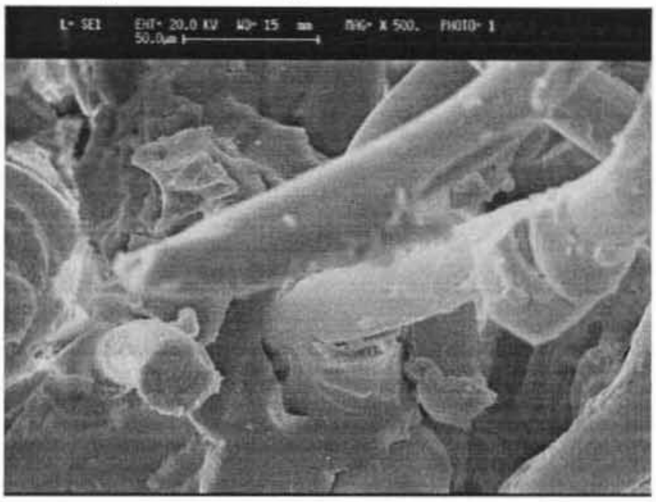

Figure 3.C.2.6f. SEM photomicrograph of tensile fracture surface of mix D with fibers oriented in longitudinal direction (original magnification x500; marker 50µ)

It can be seen from the figures that there are more fiber ends protruding and fiber pulled out holes in the case of mix D and fibers are more firmly adhere to the matrix. It can also be observed that the fibers protruding out in mix D are not clean and smooth. Some portion of matrix is sticking to the surface of the fiber. But in the case of mix L the fiber surface are relatively smooth, clean and matrix is less mutilated. These suggests that the fiber - matrix interface is weakened in the presence of resin, which is reflected in the lower tensile strength of mix L compared to mix D.

The tensile fracture surface of mix D with fibers in the transverse direction is shown in Figure 3.C.2.6g. The fibers oriented in the horizontal plane are clearly visible in the figure. The channels formed by the fiber removal during fracture can be seen in the figure. This indicates that in transverse orientation of fibers, matrix - fiber interface failure is initiating the tensile fracture.

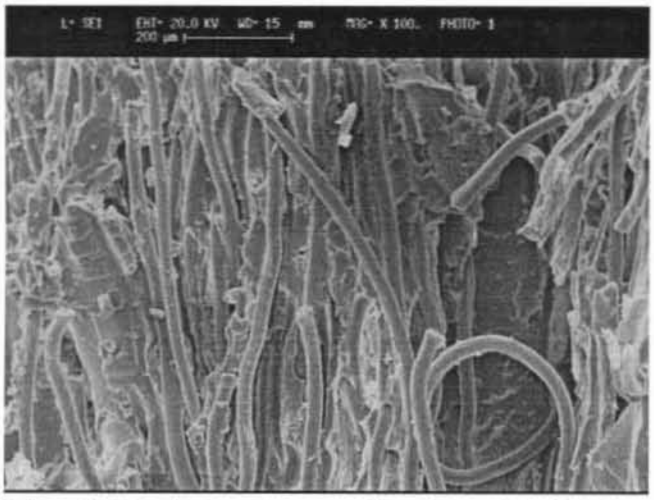

Figure 3.C.2.6g. SEM photomicrograph of tensile fracture surface of mix L with fibers oriented in transverse direction (original magnification x100; marker 200μ)

The variation of modulus at 20 % elongation with resin concentration in longitudinal and transverse orientations of fiber is shown in Figures 3.C.2.7a. and 3.C.2.7b., respectively. In the case of gum compound modulus increases marginally with resin concentration. Modulus at 20 % elongation in longitudinal orientation of fiber decreases with resin concentration for composites (Figure 3.C.2.7a.). Modulus at 20 % elongation in transverse orientation of fiber remains almost constant when resin is introduced; but further rise in resin content modulus decreases marginally.

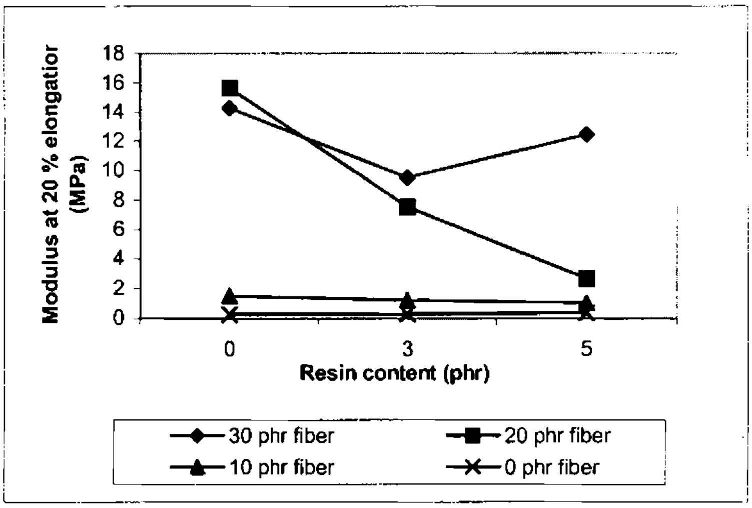

Figure 3.C.2.7a. Variation of modulus (Longitudinal) with resin concentration

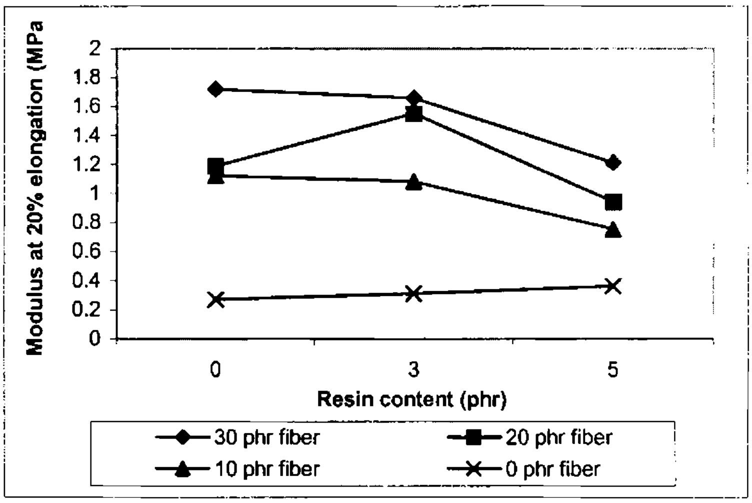

Figure 3.C.2.7b. Variation of modulus (Transverse) with resin concentration

Elongation at break increases with resin concentration for fiber loading from 0 to 20 phr in longitudinal direction (Figure 3.C.2.8a.). In the case of 30 phr fiber loaded composite EB remains more or less constant. EB increases with resin content for all fiber concentrations in the transverse orientation of fiber (Figure 3.C.2.8b.).

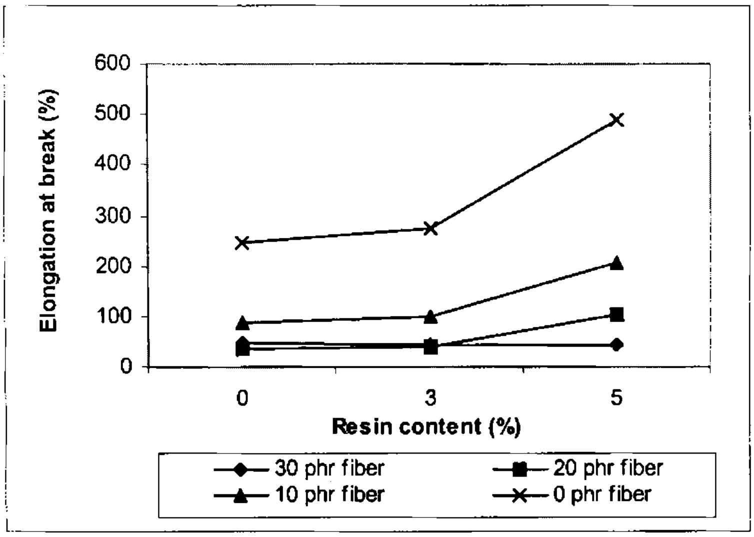

Figure 3.C.2.8a. Variation of elongation at break (Longitudinal) with resin concentration.

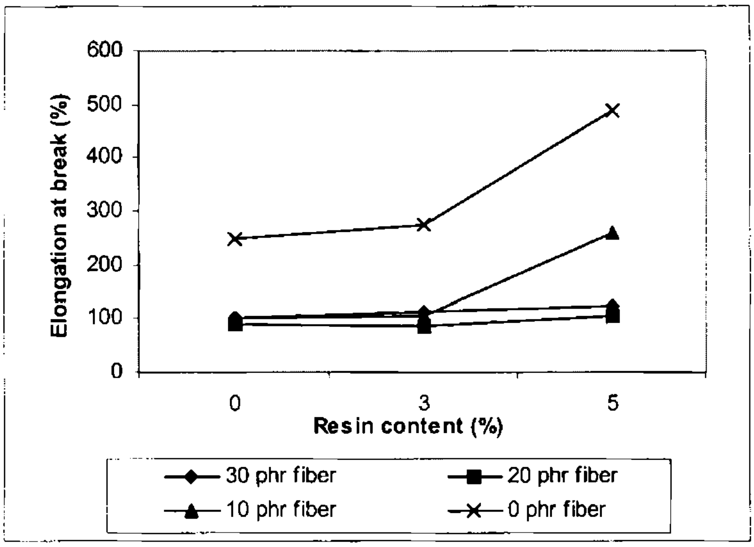

Figure 3.C.2.8b. Variation of elongation at break (Transverse) with resin concentration

Variation of tear resistance with resin concentration at various fiber loading in the longitudinal and transverse directions is shown in the Figures 3.C.2.9a. and 3.C.2.9b., respectively. Tear resistance increases with resin concentration for gum compound, indicating the formation of more restrained matrix in the presence of resin.

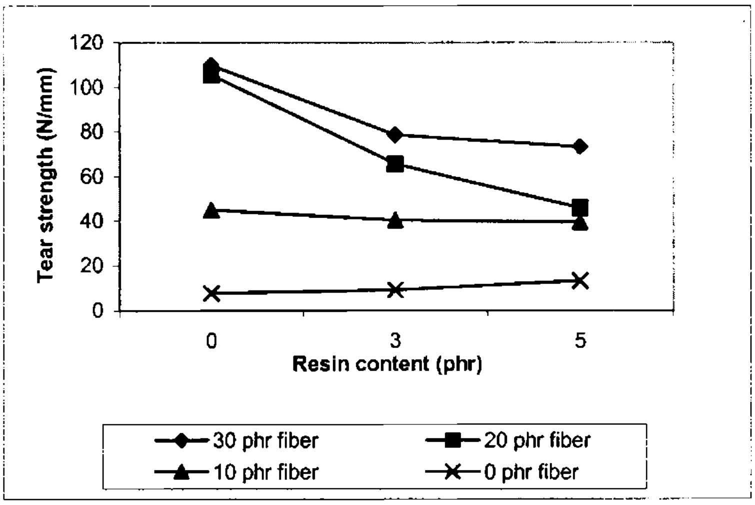

Figure 3.C.2.9a. Variation of tear strength (Longitudinal) with resin concentration

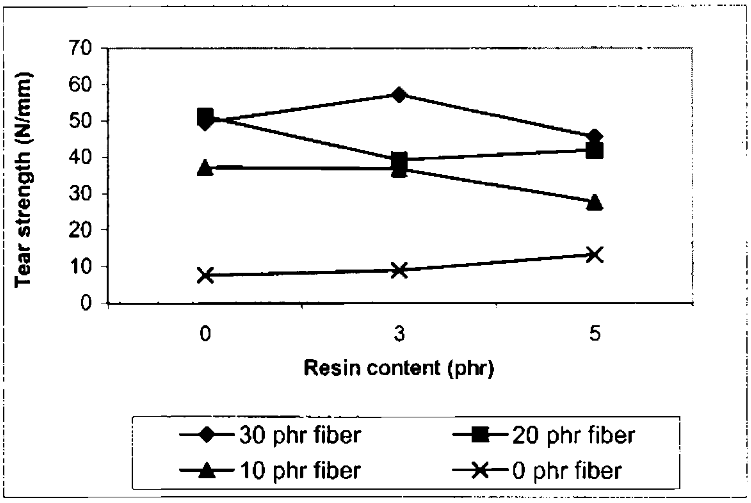

Figure 3.C.2.9b. Variation of tear strength (Transverse) with resin concentration

Tear resistance decreases as resin concentration increases for composites, the effect being more pronounced at higher fiber loading. This shows that the fiber matrix interface is weakened in the presence of resin.

There is not much variation in hardness with resin concentration for all composites with different fiber loading (Figure 3.C.2.10.). Resilience shows a slight decrease with resin concentration for all composites (Figure 3.C.2.11.).

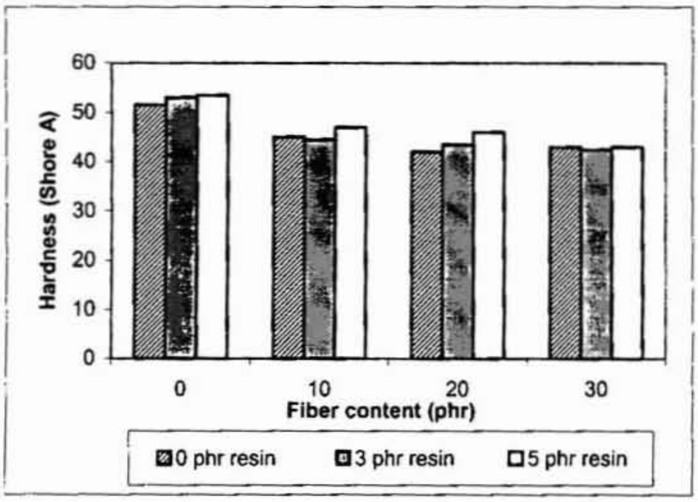

Figure 3.C.2.10. Variation of hardness with resin concentration

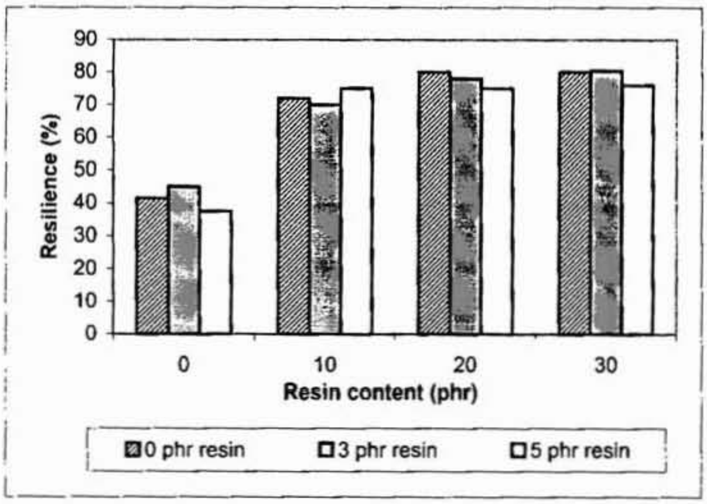

Figure 3.C.2.11. Variation of resilience with resin concentration

Compression set increases with resin concentration for all composites (Figure 3.C.2.12.). This is in agreement with the decreased value of resilience.

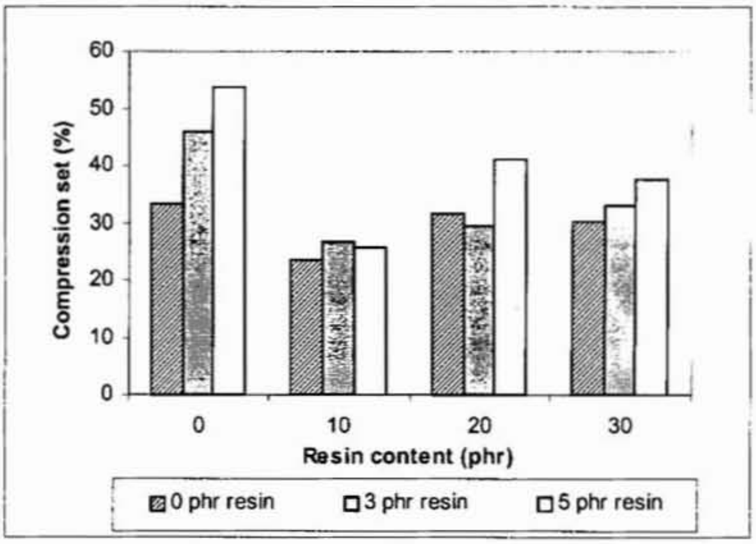

Figure 3.C.2.12. Variation of compression set with resin concentration

Variation of abrasion resistance with resin concentration at various fiber loading in the longitudinal and transverse directions is shown in the Figures 3.C.2.13a. and 3.C.2.13b. respectively. In the case of gum compound abrasion loss registers considerable reduction with increase in resin concentration. Abrasion loss in longitudinal orientation of fiber is showing a marginal rise with resin concentration for all fiber loading. In transverse orientation of fiber, the abrasion loss shows slight decrease at 3 phr resin concentration for lower fiber loadings (10 to 20 phr) (Figure 3.C.2.13a.). But on further increase in resin concentration shows a sharp rise in abrasion loss for fiber concentration. This shows that epoxy resin is weakening the fiber matrix bonding.

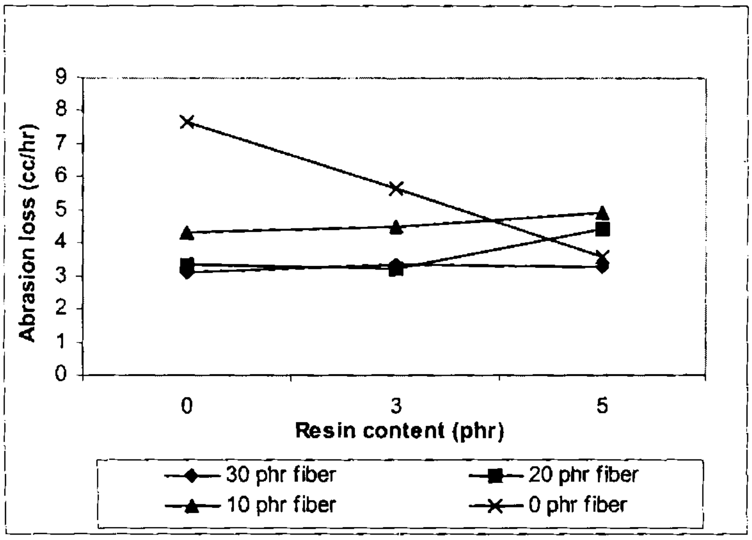

Figure 3.C.2.13a. Variation of abrasion loss (Longitudinal) with resin concentration

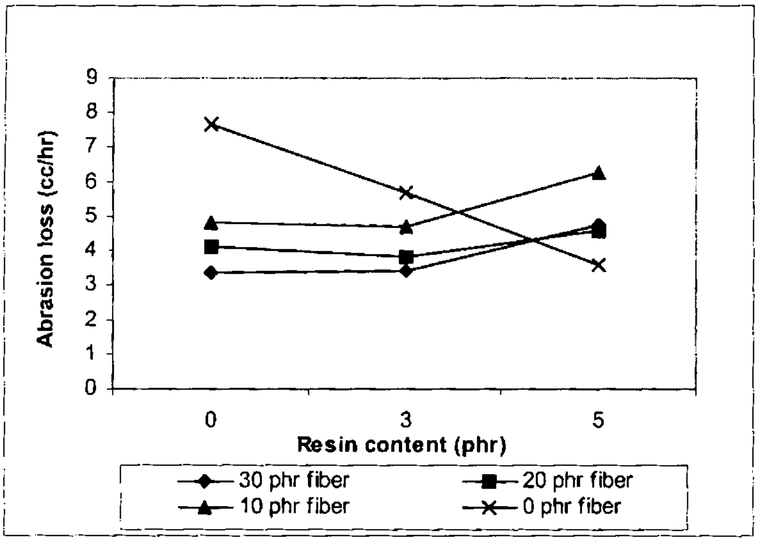

Figure 3.C.2.13b. Variation of abrasion loss (Transverse) with resin concentration.

Heat build up in the longitudinal direction increases with resin concentration for all the mixes, the effect being more prominent at higher fiber loading (Figure 3.C.2.14a.). In the transverse orientation, the heat build up increases on introduction of resin after wards it remains more or less constant (Figure 3.C.2.14 b.).

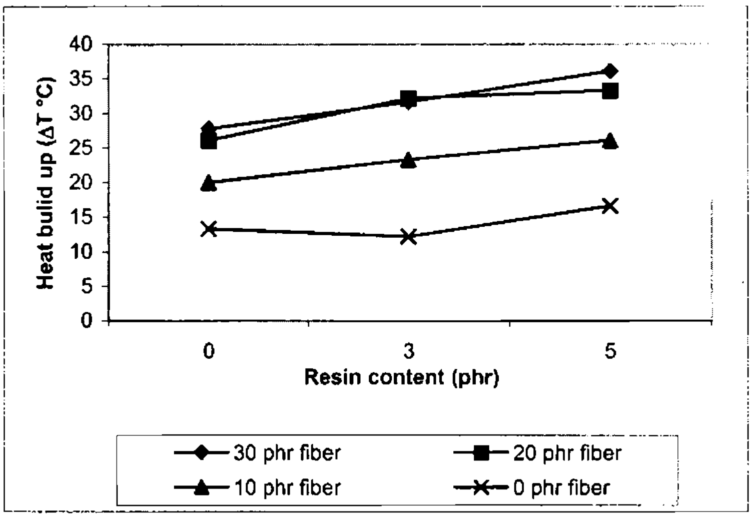

Figure 3.C.2.14a. Variation of heat build up (Longitudinal) with resin concentration

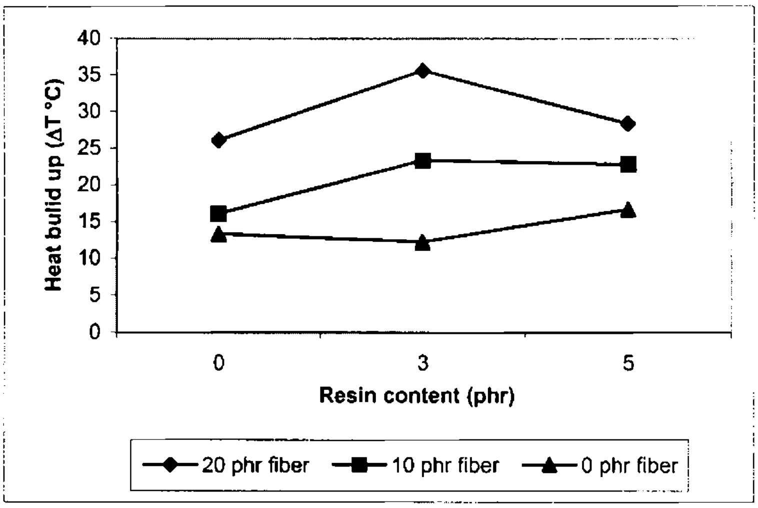

Figure 3.C.2.14b. Variation of heat build up (Transverse) with resin concentration.

3.C.2.3. Ageing Resistance

Percentage retention in tensile strength after ageing at 70°C is more with resin than without resin. In longitudinal direction, the percentage retention in tensile strength increases up to 3 phr resin concentration and shows a decreasing tendency at higher resin concentration (Figure 3.C.2.15a.). In transverse direction percentage retention increases as resin concentration increases for all composites (Figure 3.C.2.15b.).

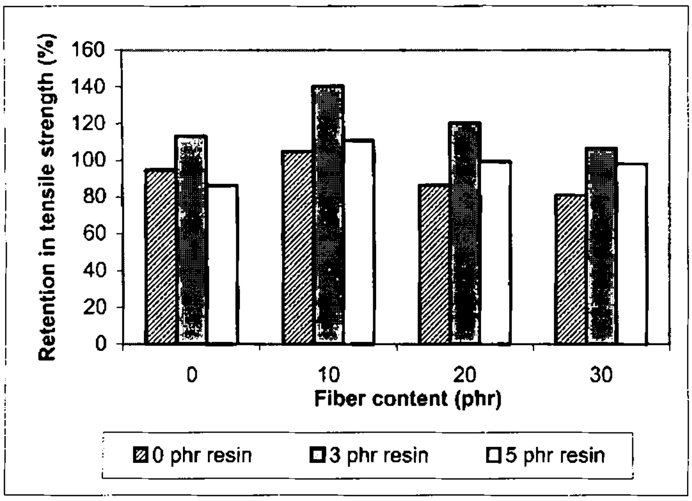

Figure 3.C.2.15a. Variation of percentage retention in tensile strength (Longitudinal) with fiber loading

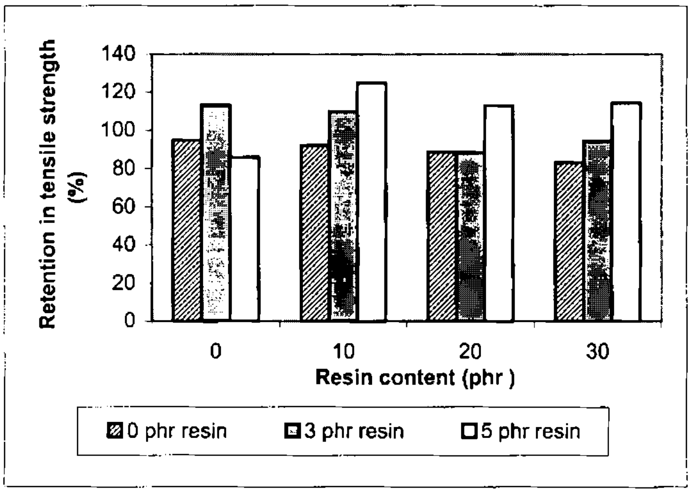

Figure 3.C.2.15b. Variation of percentage retention in tensile strength (Transverse) with fiber loading

Chapter IV

RHEOLOGICAL STUDIES

Section A. Part I

NBR- short Nylon-6 fiber composites

4.A.1.1. Effect of shear rate and shear stress
4.A.1.2. Effect of fiber content
4.A.1.3. Effect of temperature
4.A.1.4. Activation energies
4.A.1.5. Flow behaviour index
4.A.1.6. Die swell

Section A. Part II

NBR-short Nylon-6 fiber composites with epoxy resin as bonding agent

4.A.2.1. Effect of shear rate and shear stress
4.A.2.2. Effect of fiber content
4.A.2.3. Effect of temperature
4.A.2.4. Activation energies
4.A.2.5. Flow behaviour index
4.A.2.6. Die swell
4.A.2.7. Effect of bonding agent

Section B. Part I

SBR - short Nylon-6 fiber composites

4.B.1.1. Effect of shear rate and shear stress
4.B.1.2. Effect of fiber content
4.B.1.3. Effect of temperature
4.B.1.4. Activation energies
4.B.1.5. Flow behaviour index
4.B.1.6. Die swell

Section B. Part II

SBR- short Nylon-6 fiber composites with epoxy resin as bonding agent

4.B.2.1. Effect of shear rate and shear stress
4.B.2.2. Effect of fiber content
4.B.2.3. Effect of temperature
4.B.2.4. Activation energies
4.B.2.5. Flow behaviour index
4.B.2.6. Die swell
4.B.2.7. Effect of bonding agent

SECTION A. PART (I)
NBR- SHORT NYLON-6 FIBER COMPOSITES

Since many of the processing steps in modern polymer industry such as milling, extrusion, calendering and moulding involve flow of polymer; an understanding of the rheological characteristics of the composite is essential. The rheological behaviour of polymer melts prescribes the choice of processing conditions and influences the morphology and mechanical properties of the final product. The need for rheological studies and its importance in selection of processing conditions were pointed out by Brydson[1]. Several studies on the rheological characteristics of short fiber reinforced polymer melts were reported[2-4]. This section deals with the rheological characteristics of short Nylon fiber reinforced acrylonitrile butadiene rubber with respect to the effect of shear rate, fiber concentration and temperature on shear viscosity and die swell.

Formulation of mixes is given in Table 4.A.1.1. These mixes were prepared as per ASTM D 3182 (1989) on a laboratory size two roll mixing mill.

Table 4.A.1.1 Composition of mixes (parts by weight)

Ingredients	Mix No.			
	A	B	C	D
NBR	100	100	100	100
Nylon	0	10	20	30
ZnO	4	4	4	4
Stearic acid	2	2	2	2

Rheological studies were carried out using a capillary rheometer attached to a Shimadzu Universal Testing Machine Model AG-I 50 KN. A capillary of L/D 10 and an angle of entry 90° was used. The measurements were carried out at various shear rates ranging from 1.6 to 831.2 s^{-1}. Detailed description of experimental techniques are given in chapter II.

4.A.1.1. Effect of Shear Rate and Shear Stress

Figures 4.A.1.1- 4.A.1.3 show the variation of viscosity with shear rate of all the mixes at 80, 90 and 100 °C, respectively. In all the cases it is seen that the viscosity decrease almost linearly with shear rate in the shear rate range studied, indicating a pseudoplastic behaviour of the composite.

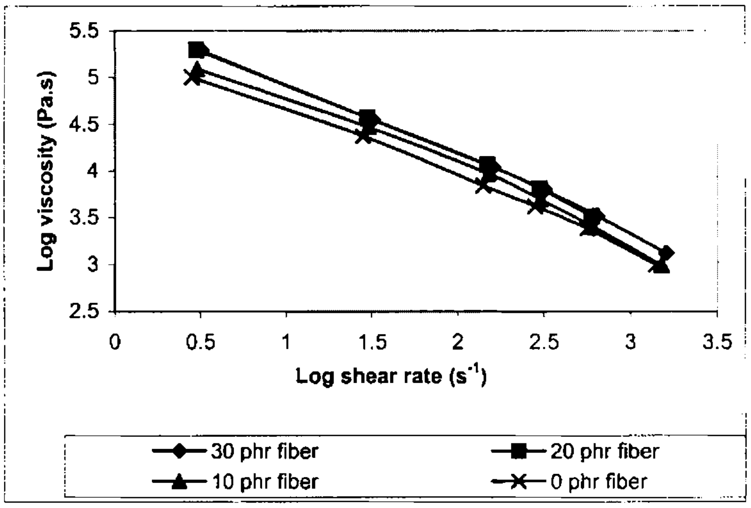

Figure 4.A.1.1. Shear viscosity versus shear rate at 80°C

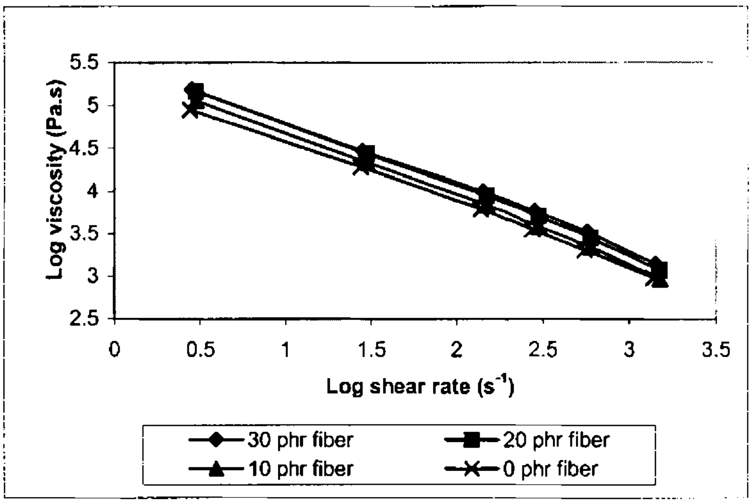

Figure 4.A.1.2. Shear viscosity versus shear rate at 90°C

The reduction in viscosity with increasing shear rate may be arising from the molecular alignment during flow through the capillary. The fact that the pattern is also observed in the case of fiber filled mixes indicates that the fibers, while restricting the free flow of the melt, also get aligned in the direction of flow.

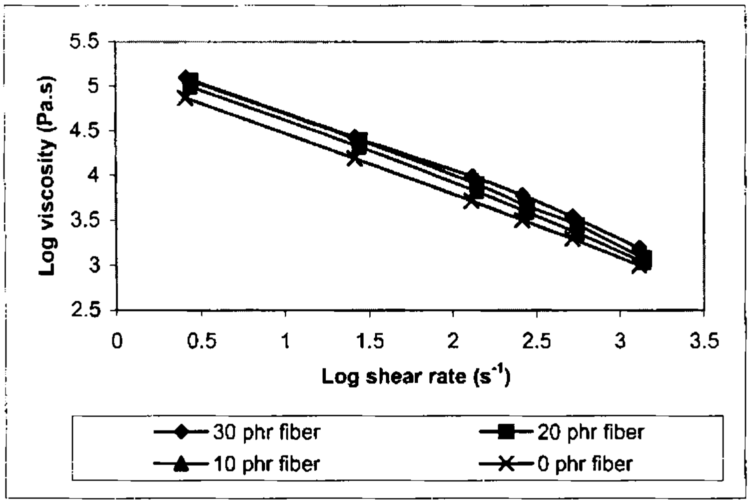

Figure 4.A.1.3. Shear viscosity versus shear rate at 100°C

This is evident from SEM photomicrograph of extrudates of mix D. The Figures 4.A.1.4a and 4.A.1.4b show the fractured surfaces of extrudates of mix D at shear rates 1 s^{-1} and 100 s^{-1}, respectively at 100°C. Higher level of orientation at higher shear rate is evident from figure 4.A.1.4b. The cut ends of the fibers oriented along the flow direction is clearly seen in the figure. Similar results in the case of short polyester fiber polyurethane elastomer composite have been reported by Suhara et al[5-6].

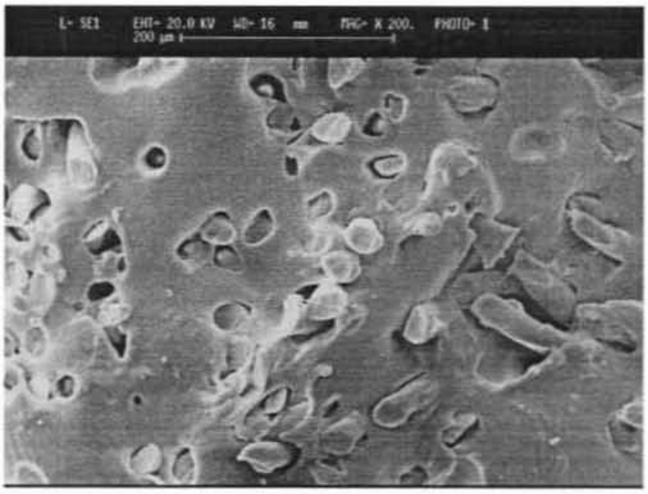

Figure 4.A.1.4a. SEM photomicrograph of the broken surface of the extrudate of mix D; Shear rate 1s^{-1} and temperature 100°C (original magnification x200; marker 200μ)

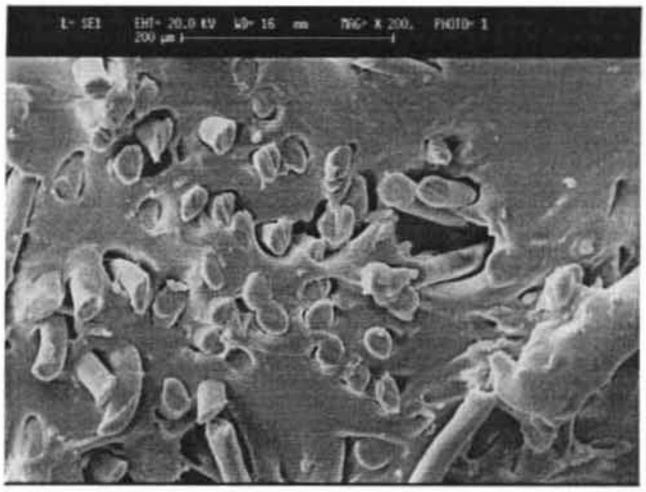

Figure 4.A.1.4b. SEM photomicrograph of the broken surface of the extrudate of mix D; Shear rate 100s^{-1} and temperature 100°C (original magnification x200; marker 200μ)

Plots of shear viscosity versus shear stress also show similar patterns but with marked difference at higher shear stresses. (Figures 4.A.1.5 – 4.A.1.7). All the plots show significant drop in viscosity at shear stress beyond1 MPa.

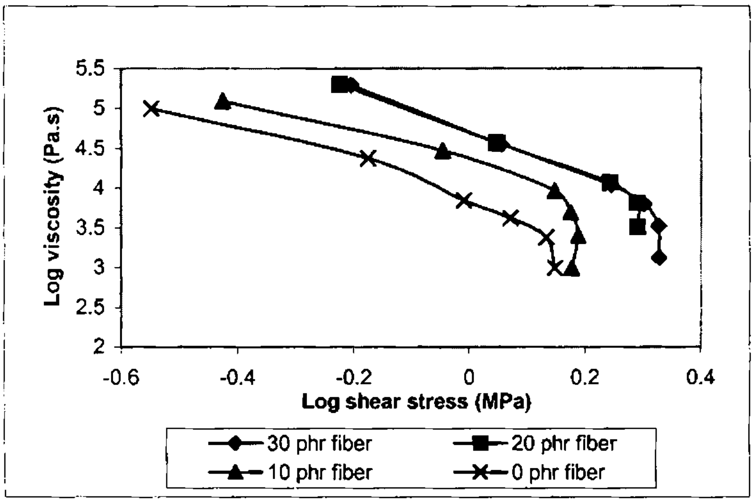

Figure 4.A.1.5. Shear viscosity versus shear stress at 80°C

The point at which the sudden drop occurs is shifted to higher shear stress values in the case of fiber filled samples. For the gum compound it occurs at 1.35 MPa at 80°C whereas for the 30 phr fiber filled sample the corresponding value is 2 MPa at 80°C. The sudden drop at higher shear stress values also indicates probable plug flow at higher rates of flow.

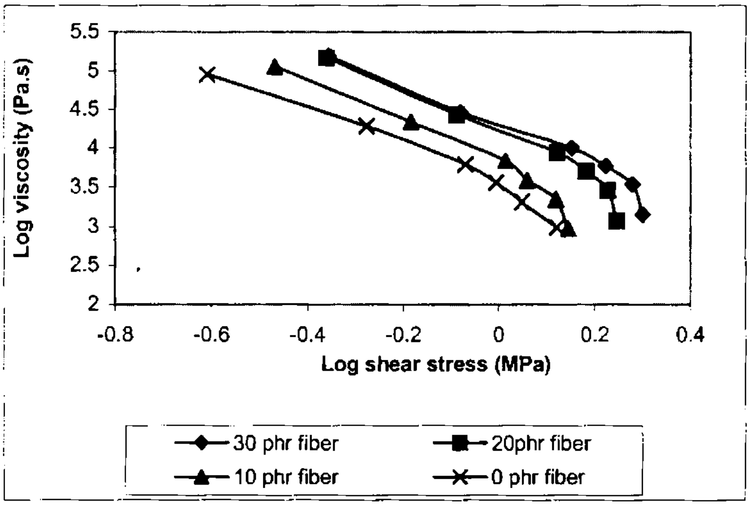

Figure 4.A.1.6. Shear viscosity versus shear stress at 90°C

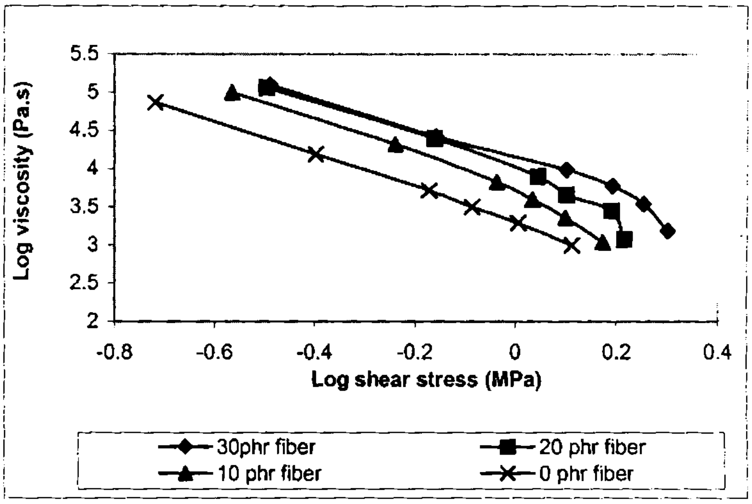

Figure 4.A.1.7. Shear viscosity versus shear stress at 100°C

The point of inflection is plotted against the corresponding fiber loading in Figures 4.A.1.8a and 4.A.1.8b at 80 and 90 °C, respectively. It is observed that there is a linear relationship between the onset of plug flow and the fiber content at both the temperatures. This is because with increasing fiber content the melt viscosity is increased. With high melt viscosity the material slips at the wall and the stress is relieved. Figure 4.A.1.9a is the SEM photomicrograph of mix D at 80°C at a shear rate of 1s^{-1} and Figure 4.A.1.9b is the SEM of mix D at the drop shear rate, viz.500 s^{-1} at 80°C. Scanning Electron Micrograph of the extrudate at the plug flow region (Fig. 4.A.1.9b) shows that there is relatively lower fiber orientation compared to the extrudate of the lower shear stress region (Fig. 4.A.1.9a). The extent of drop is reduced with increasing temperature. This may be because the chance of plug flow is lower when the sample becomes softer at elevated temperature. This is also evident from the fact that the gum compound with relatively lower viscosity shows no evidence of plug flow at 90 and 100 °C.

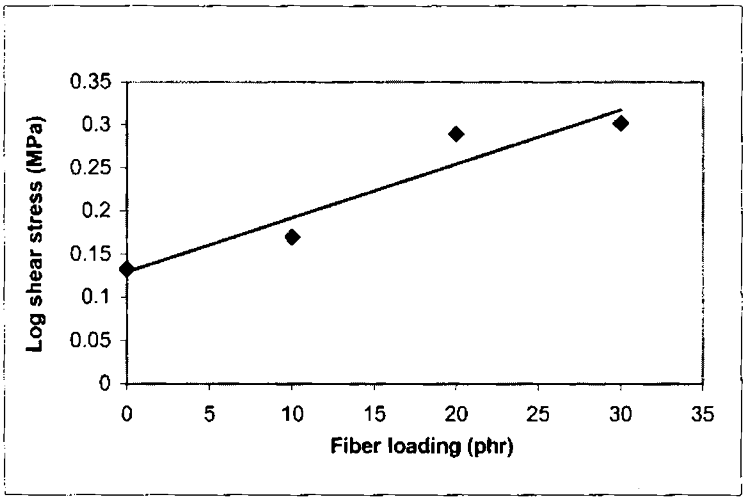

Figure 4.A.1.8a. Variation of shear stress at the point of inflection with fiber loading at 80°C

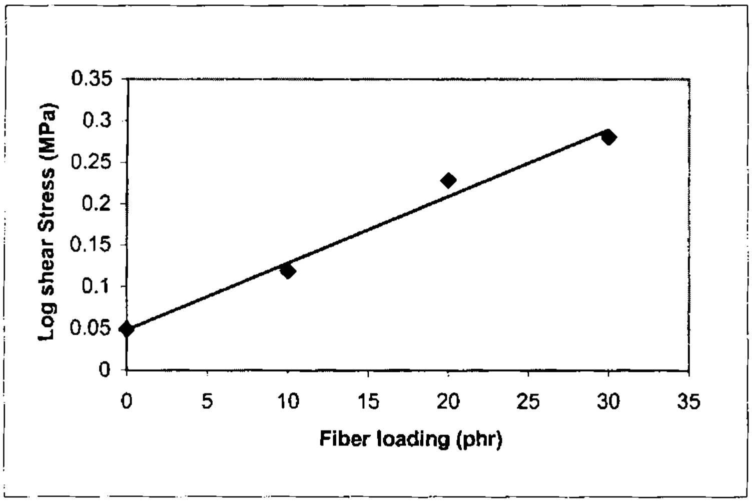

Figure 4.A.1.8b. Variation of shear stress at the point of inflection with fiber loading at 90°C

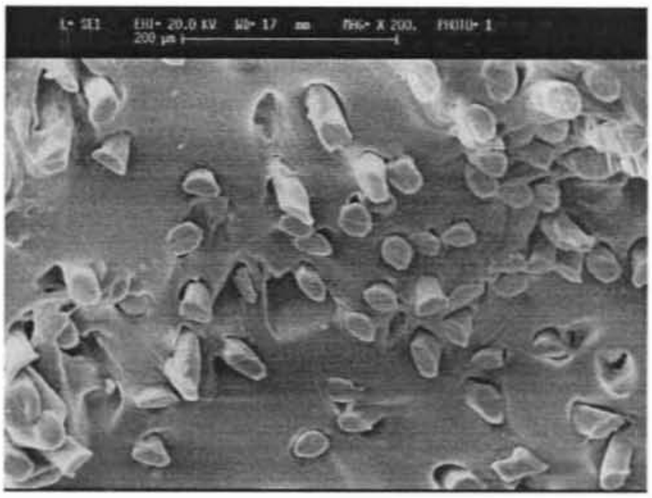

Figure 4.A.1.9a. SEM photomicrograph of the broken surface of the extrudate of mix D; Shear rate 1s^{-1} and temperature 80°C (original magnification x200; marker 200μ)

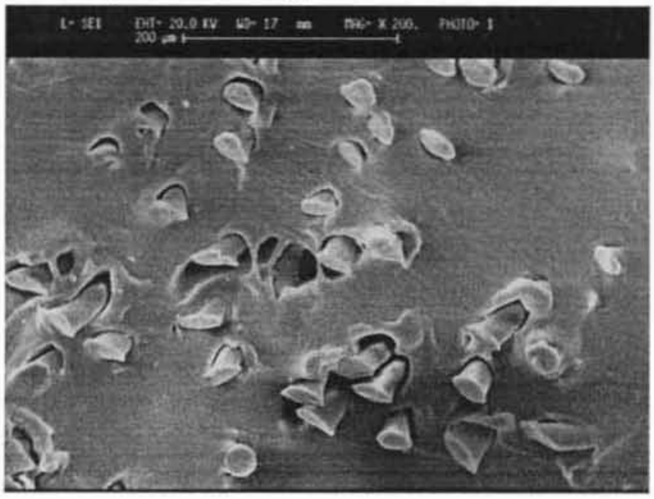

Figure 4.A.1.9b. SEM photomicrograph of the broken surface of the extrudate of mix D; Shear rate 500s^{-1} and temperature 80°C (original magnification x200; marker 200μ)

4.A.1.2. Effect of Fiber Content

From Figures 4.A.1.1- 4.A.1.3, it can be seen that viscosity is increased when fiber is introduced to the matrix at all temperatures. The presence of fiber restricts the molecular mobility under shear, resulting in higher viscosity. Viscosity increases as fiber concentration increases up to 20 phr fiber loading. Further increase to 30 phr fiber concentration there is not much increase in viscosity especially at lower temperatures and lower shear rates. As the shear rate increases, the increase in viscosity with fiber concentration decreases and at higher shear rate of 831.2 s^{-1} all the mixes are showing almost same viscosity. This means the effect of fiber on shear viscosity is prominent at lower shear rates only. This is in agreement with the earlier observations[7-8].

4.A.1.3. Effect of Temperature

Figures 4.A.1.10 & 4.A.1.11 show the variation of shear viscosity with shear rate for mixes A & D, respectively at various temperatures. As the temperature increases the viscosity decreases for both the mixes at all the shear rates studied. The effect of temperature on the viscosity is found to be dependent on the shear rate. In the case of gum compound, at lower shear rates, the viscosity drops from 5.003 Pa.s to 4.907 Pa.s as the temperature is changed from 80 to 100 °C while at higher shear rate all the viscosity values tend to merge to a common point. This trend seems to be more pronounced in the case of fiber filled sample. The changed temperature sensitivity of the composite is also reflected in the activation energy values calculated (Table 4.A.1.2).

In the case of gum compound the log viscosity decreases from 5.003 to 4.907 Pa.s at a lower shear rate of 1.6 s^{-1} (Fig. 4.A.1.10). But as the shear rate increases the drop in viscosity with temperature decreases and shows almost constant values at a shear rate of 831.2 s^{-1} at all temperatures. In the case of 30 phr fiber loading (Fig. 4.A.1.11) the log viscosity decreases from 5.288 to 5.096 Pa.s at a lower shear rate of 1.6 s^{-1}. But as the shear rate increases, the drop in viscosity with temperature decreases more in the mix D.

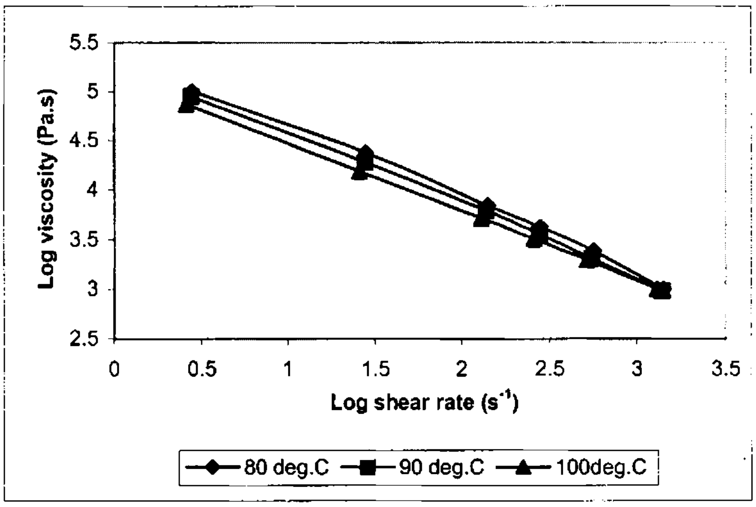

Figure 4.A.1.10. Shear viscosity versus shear rate for Mix A

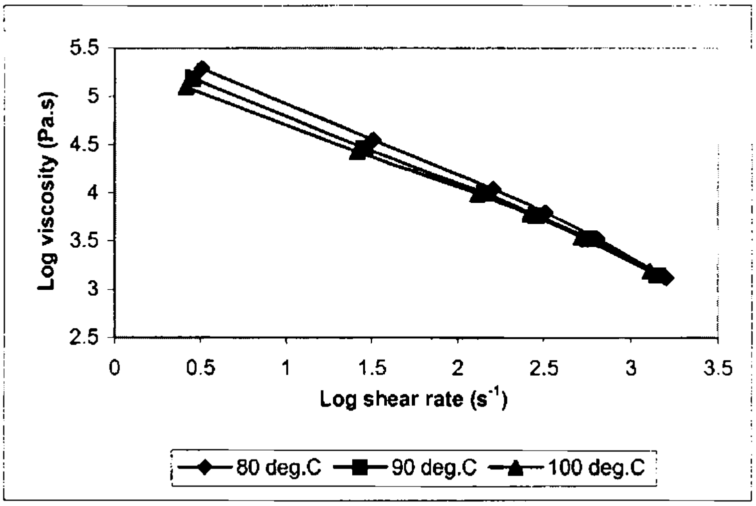

Figure 4.A.1.11. Shear viscosity versus shear rate for Mix D

4.A.1.4. Activation Energies

The activation energies of mixes A to D are given in the Table 4.A.1.2. Activation energies were calculated from the Arrhenius plots of viscosity and temperatures at different shear rates. The activation energy of flow is reduced in the presence of fibers. The higher temperature sensitivity of flow of rubber matrix is reduced in the presence of fibers especially at higher fiber loading. Similar results have been reported earlier[7]. The activation energy of all the melts decreases as shear rate increases. This indicates that the temperature sensitivity of the gum and composite melts are also shear dependent and the sensitivity is less at higher shear rates.

Table 4.A.1.2. Activation energies of flow of mixes A-D (Kcal/mol)

Mixes	Shear rates (s^{-1})		
	16.6	83.1	166.2
A	6.0	4.2	4.0
B	4.6	4.3	3.0
C	5.4	5.0	4.7
D	3.7	1.5	0.51

4.A.1.5. Flow Behaviour Index

Fig. 4.A.1.12 shows flow behaviour indices of mixes A to D at different temperatures. It is found that for all the mixes flow behaviour increases as temperature increases indicating that the melt becomes more Newtonian in nature as the temperature is increased.

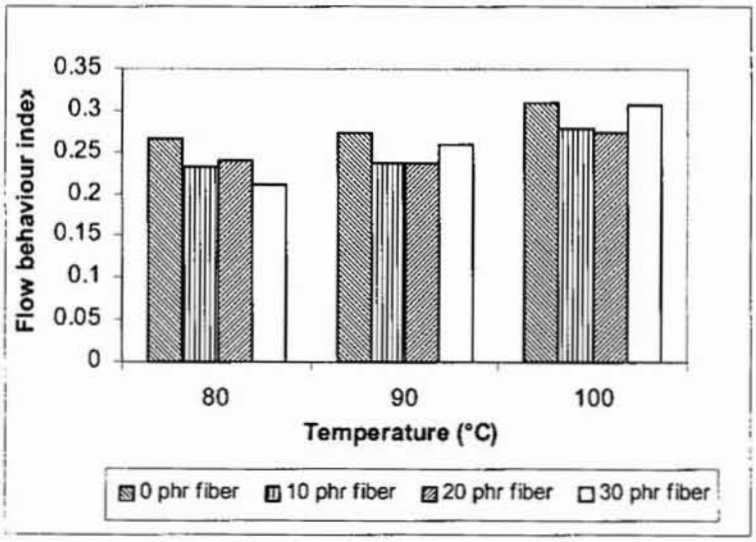

Figure 4.A.1.12. Flow behaviour index versus temperature

Introduction of the fiber reduces Newtonian behaviour as indicated by the lower n' values. But at higher fiber loading and higher temperatures, the n' value of composite melts approaches to that of gum compound.

4.A.1.6. Die Swell

Table 4.A.1.3 gives the die swell ratio of the gum and fiber filled mixes at different temperatures and shear rates. In the case of gum compound there is not much variation in die swell with shear rate. But as temperature increases the die swell ratio is found to decrease. The swelling of polymer melts on emerging from extrusion is due to the recovery of the elastic deformation occurred during flow. At higher temperature the stored- up elastic energy is less, which results in lower relaxation after extrusion. Die swell shows a sharp fall by the addition of fiber and the die swell ratio less than 1 at higher fiber loading. The reduction in the die swell in the presence of fiber has been reported earlier[3,7,8]. The reduction in die swell with fiber loading may be due to the irreversible orientation of the fibers in the matrix.

Table 4.A.1.3. Die swell ratios of mixes A-D at different temperatures

Mix	Temperature (°C)	Shear rates (s^{-1})					
		1.6	16.6	83.1	166.2	332.5	831.2
A	90	1.428	1.357	1.428	1.571	1.428	1.714
	100	1.212	1.428	1.381	1.428	1.428	1.571
B	90	1.061	1.061	1.061	1.061	1.212	1.212
	100	1.214	1.428	1.381	1.428	1.428	1.571
C	90	1.093	0.937	1.041	1.015	1.094	0.989
	100	0.882	0.882	1.029	1.029	1.029	1.029
D	90	0.968	0.860	0.968	0.968	1.129	1.129
	100	0.9559	0.882	1.029	1.029	0.980	0.931

REFERENCES.

1. Brydson J.A., Flow Properties of Polymer Melts, 2nd ed., George Godwin, 1981. 18.
2. Setua D.K., Int. J. Polym. Mater., **11** (1985) 67.
3. Murty V.M., Gupta B.R. and De S.K., Plast. Rub. Proc. Appl., **5** (1985) 307.
4. Vargehse S., Kuriakose B., Thomas S., Premalatha C.K. and Koshy A.T., Plast. Rub. Compos. Process Appl., **20** (1993) 93.
5. Suhara F., Kutty S.K.N and Nando G.B., Polym. Plast.Technol.Eng., **36** (1997) 399.
6. Suhara F., Kutty S.K.N, & Nando G.B. and Bhattacharya A.K Polym. Plast.Technol.Eng., **37** (1998) 57.
7. Kutty S.K.N., De P.P and Nando G.B., Plast. Rub. Compos. Process Appl., **15** (1991) 23.
8. Chan Y., White J.L. and Oyanagi Y., J. Rheol. **22** (1978) 507

SECTION A. PART (II)

NBR - SHORT NYLON-6 FIBER COMPOSITES WITH EPOXY RESIN AS BONDING AGENT

A thorough knowledge of the flow characteristics of the polymer melt is essential as processing in most cases involves flow of the material. The effect of interfacial bond on the rheological characteristics was studied by many workers[1-3].

This section describes the studies on the shear viscosity and die swell of short Nylon fiber reinforced Acrylonitrile Butadiene rubber containing epoxy resin as bonding agent with respect to shear rate, temperature and fiber concentration.

Formulation of mixes is given in Table 4.A.2.1. Detailed description of experimental techniques adopted for the study is given in chapter II.

Table 4.A.2.1. Composition of mixes (parts by weight)

Ingredients	Mix No.							
	A	B	C	D	A_0	B_0	C_0	D_0
NBR	100	100	100	100	100	100	100	100
Nylon	0	10	20	30	0	10	20	30
Epoxy resin*	3	3	3	3	0	0	0	0
ZnO	4	4	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2	2	2

*Epoxy resin formed by 1:0.5 equivalent combination of epoxy resin and amine based hardener.

4.A.2.1. Effect of Shear Rate and Shear Stress

The variation shear viscosity with shear rate for the mixes A-D at 80, 90 and 100 °C is shown in figures 4.A.2.1. - 4.A.2.3., respectively. In all the cases it is seen that the viscosity decreases almost linearly with shear rate in the shear rate range studied, indicating a pseudoplastic behaviour of the composite containing bonding agent. The reduction in viscosity with increasing shear rate may be arising from the molecular alignment during flow through the capillary. Fiber-filled mixes also show similar pattern as that of gum compound indicates that the fibers, while restricting the free flow of the melt, also get aligned in the direction of flow. These results are similar to NBR - short Nylon 6 composite without bonding agent (Section 4.A.1.1).

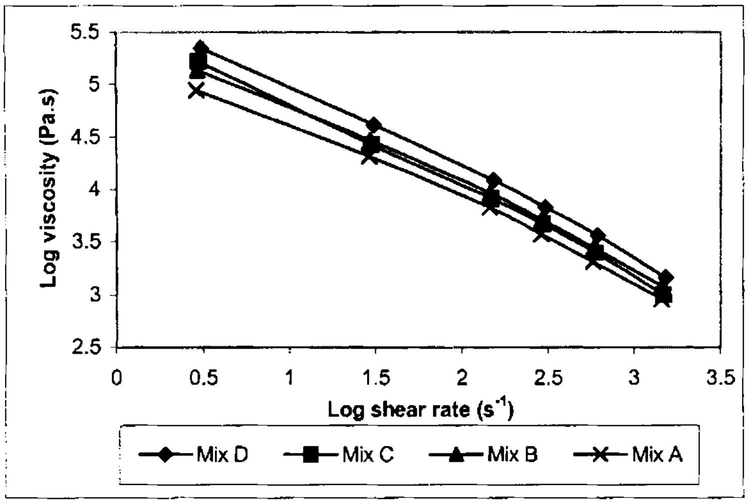

Figure 4.A.2.1. Shear viscosity versus shear rate at 80°C

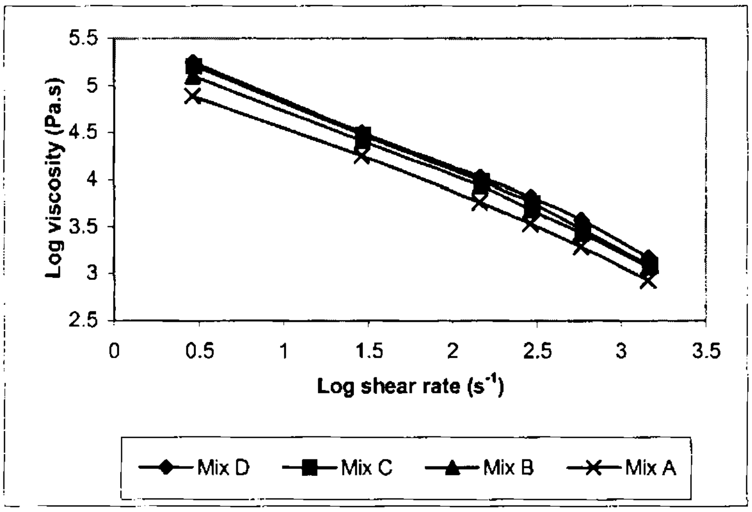

Figure 4.A.2.2. Shear viscosity versus shear rate at 90°C

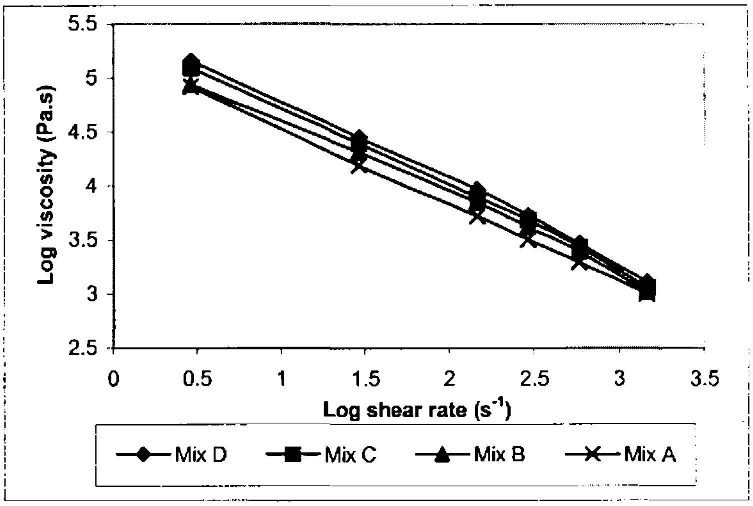

Figure 4.A.2.3. Shear viscosity versus shear rate at 100°C

Plots of shear viscosity versus shear stress of mixes A-D also show similar patterns but with marked difference at higher shear stresses (Figures. 4.A.2.4. – 4.A.2.6.).

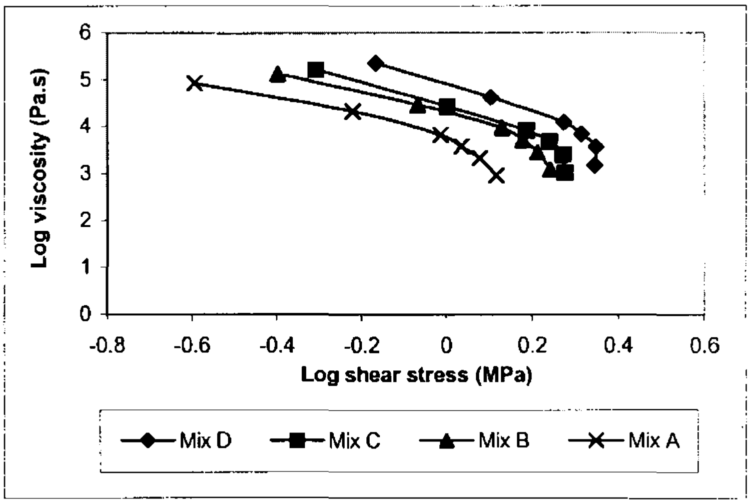

Figure 4.A.2.4. Shear viscosity versus shear stress at 80°C

All the plots show significant drop in viscosity at shear stress beyond 1 MPa. The point at which the sudden drop occurs is shifted to higher shear stress values in the case of fiber filled samples. For the gum compound it occurs at 1.08 MPa at 80 °C whereas for the 30 phr fiber filled sample the corresponding values is 2.06 MPa at the same temperature. The sudden drop at higher shear stress values also indicates probable plug flow at higher rates of flow.

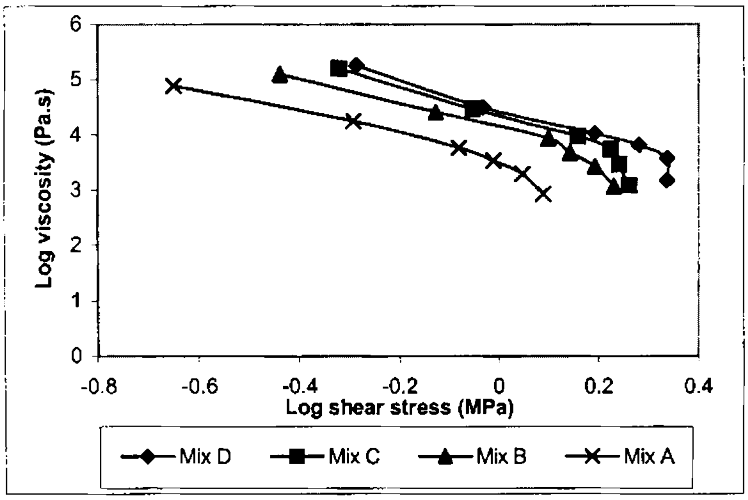

Figure 4.A.2.5. Shear viscosity versus shear stress at 90°C

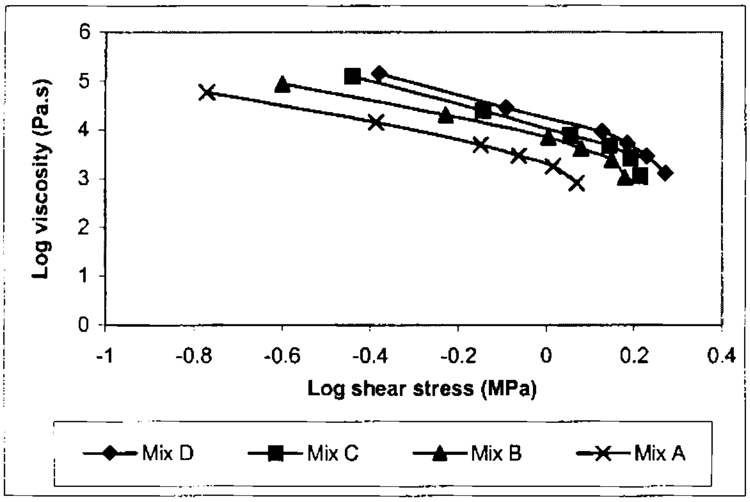

Figure 4.A.2.6. Shear viscosity versus shear stress at 100°C

The point of inflection is plotted against the corresponding fiber loading in Figures 4.A.2.7a and 4.A.2.7b at 80 and 90 °C, respectively. It is observed that there is a linear relationship between the onset of plug flow and the fiber content at both the temperatures. This is because with increasing fiber content the melt viscosity is increased. With high melt viscosity the material slips at the wall and the stress is relieved. The extent of drop is reduced with increasing temperature. This may be because the chance of plug flow is lower when the sample becomes softer at elevated temperature. This is also evident from the fact that the gum compound, with relatively lower viscosity, shows no evidence of plug flow at 90 and 100°C.

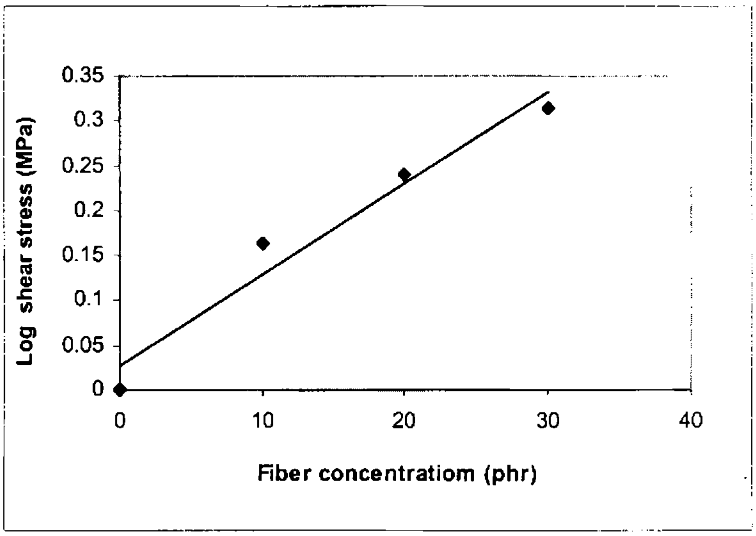

Figure 4.A.2.7a. Variation of shear stress at the point of inflection with fiber loading at 80°C

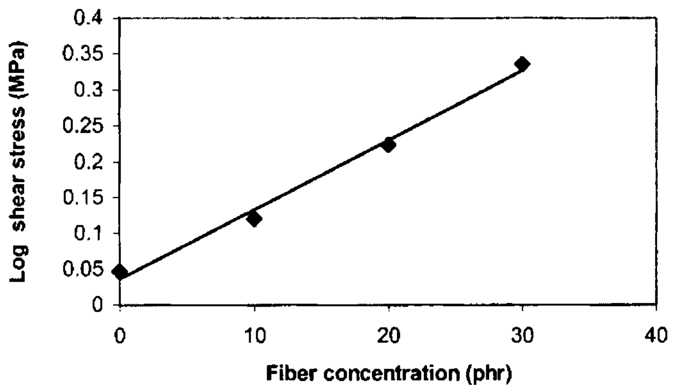

Figure 4.A.2.7b. Variation of shear stress at the point of inflection with fiber loading at 90°C

4.A.2.2. Effect of Fiber Content

Viscosity increases with increase in fiber concentration at all shear rates (Figures 4.A.2.1. - 4.A.2.3.). The presence of fiber restricts the molecular mobility under shear, resulting in higher viscosity. The increase in viscosity on introduction of fiber is temperature dependent and is more at higher temperatures. Rise in viscosity with fiber concentration decreases at higher shear rates. This means the effect of fiber on shear viscosity is prominent at lower shear rates only. This is in agreement with the earlier observations[4-5]. All fiber- containing mixes have more or less equal viscosity at higher shear rates and is higher than gum compound. This indicates that a good fiber matrix interaction is taking place in the presence of a bonding agent.

4.A.2.3. Effect of Temperature

Figures. 4.A.2.8. and 4.A.2.9. show the variation of shear viscosity with shear rate for mixes A & D at various temperatures and shear rates. The effect of temperature on the viscosity is found to be dependent on the shear rate. In the case of gum compound, at lower shear rates, the log viscosity drops from 4.94 Pa.s to 4.76 Pa.s as the temperature is changed from 80 to 100 °C while at higher shear rate all the viscosity values tend to merge to a common point. Similar trends are shown by the fiber filled sample. The changed temperature sensitivity of the composite is also reflected in the activation energy values calculated (Table4.A.2.2.).

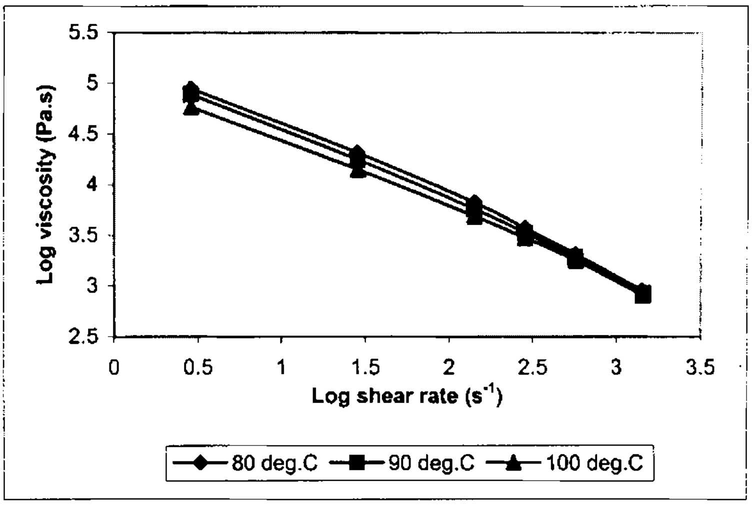

Figure 4.A.2.1.8. Shear viscosity versus shear rate for Mix A

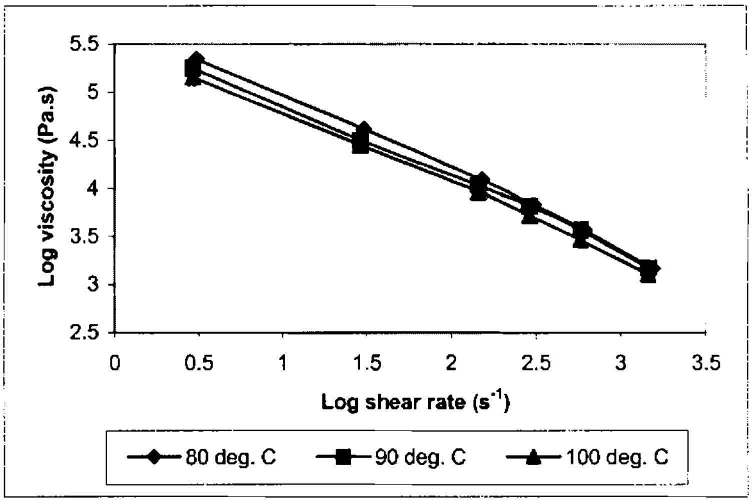

Figure 4.A.2.9. Shear Viscosity Versus Shear rate for Mix D

4.A.2.4. Activation Energies

The activation energies of various mixes were calculated from the Arrhenius plots of viscosity and temperatures at different shear rates and given in the Table 4.A.2.2. The activation energy of the melt flow is not much affected by the presence of fibers. Similar trend was reported in the case of short polyester fiber- polyurethane elastomer composite[3,6]. The activation energy of the unfilled compound and composites containing 3 phr resin decreases as shear rate increases. This indicates that the temperature sensitivity of the mixes are shear rate dependent and the sensitivity is lesser at higher shear rates.

Table 4.A.2.2. Activation energies of flow of various mixes (Kcal/mol)

Mixes	Shear rates (s^{-1})			
	1.6	16.6	83.1	166.2
A	5.32	4.99	4.08	2.95
B	5.87	4.60	3.52	2.76
D	5.68	5.12	3.7	3.21

4.A.2.5. Flow Behaviour Index

It is found that for the all mixes (A to D) the flow behaviour index increases as temperature increases (Fig. 4.A.2.10).

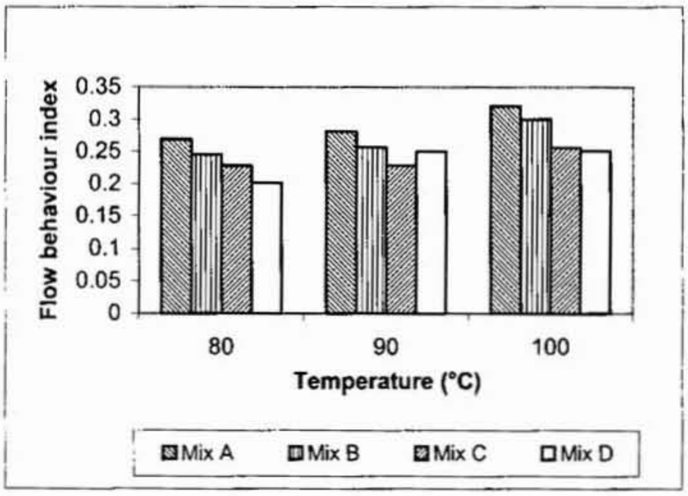

Figure 4.A.2.10. Flow behaviour index versus Temperature

This indicates that the melt becomes more Newtonian in nature as the temperature increases. The Newtonian behaviour of the melt reduces with fiber concentration, as indicated by the reduction in n' values.

4.A.2.6. Die Swell

Table 4.A.2.3. gives the die swell ratio, (d_e/d_c) of the gum and fiber filled mixes at different temperatures and shear rates. The die swell of the gum compound remains more or less constant with the shear rates and temperatures. Die swell decreases sharply by the addition of fiber. The reduction in the die swell with fiber have been reported earlier[4-5]. The reduction in die swell with fiber loading may be due to the lower elastic deformation of the matrix constrained by the fibers. In the case of fiber filled mixes the effect of shear rates and temperature on the die swell is marginal.

Table 4.A.2.3. Die swell ratios of various mixes at different temperatures

Mix	Temperature °C	Shear Rate s^{-1}					
		1.6	16.6	83.1	166.2	332.5	831.2
A	80	1.351	1.351	1.442	1.396	1.622	1.892
	90	1.486	1.351	1.622	1.442	1.486	1.666
	100	1.316	1.579	1.579	1.579	1.579	1.579
B	80	1.026	1.026	1.154	1.240	1.282	1.282
	90	1.143	1.214	1.286	1.286	1.286	1.286
	100	1.163	1.046	1.163	1.201	1.201	1.163
C	80	1.026	1.026	1.026	1.090	1.026	1.026
	90	1.111	1.111	1.111	1.111	1.204	1.157
	100	1.052	1.052	1.184	1.184	1.227	1.184
D	80	1.149	1.216	1.081	1.081	1.081	1.081
	90	1.052	1.184	1.316	1.272	1.184	1.053
	100	1.125	1.125	1.084	1.125	1.125	1.125

4.A.2.7. Effect of Bonding Agent

The effect of bonding agent has been quantified in terms of relative viscosity, defined as the ratio of the viscosity of the mixes with bonding agent to the viscosity of the mixes without bonding agent. Table 4.A.2.4. gives the relative viscosity of mixes at different shear rates and temperatures. Relative viscosity of the gum compound is less than 1 at all shear rates and all temperatures. This indicates that the viscosity is reduced in the presence of the bonding agent. The resin is acting as plasticizer in the gum compound. In the case of fiber filled samples, the relative viscosity is higher than one, indicating a higher melt viscosity of the composites resulting from a better fiber – matrix interaction in the presence of bonding agent

Table. 4.A.2.4. Relative viscosities at different temperatures for various fiber loadings

Temperature (°C)	Fiber loading (phr)	Shear rate (s^{-1})					
		1.6	16.6	83.1	166.2	332.5	831.2
90	0	0.874	0.928	0.938	0.949	0.955	0.888
	10	1.110	1.183	1.260	1.257	1.228	1.265
	20	1.110	1.097	1.099	1.111	1.041	1.043
	30	1.157	1.095	1.074	1.119	1.115	1.065
100	0	0.792	0.917	0.942	0.942	0.914	0.812
	10	0.879	0.978	1.051	1.057	1.071	0.967
	20	1.082	0.992	0.978	1.049	0.957	0.948
	30	1.149	1.045	0.947	0.877	0.843	0.835

The relative activation energies of the mixes as a function of the shear rate are given in Figure 4.A.2.11. For mixes A to C, A_r remains almost close to one at all shear rates. At higher fiber loading (mix D) the A_r is found to be sensitive to shear rate. Higher A_r values of mix D at higher shear rate indicates, a critical role that strong fiber – matrix interface, has on the shear flow of the composite. At higher fiber loading there is more of fiber -matrix interface, which is strengthened in the presence of bonding agent.

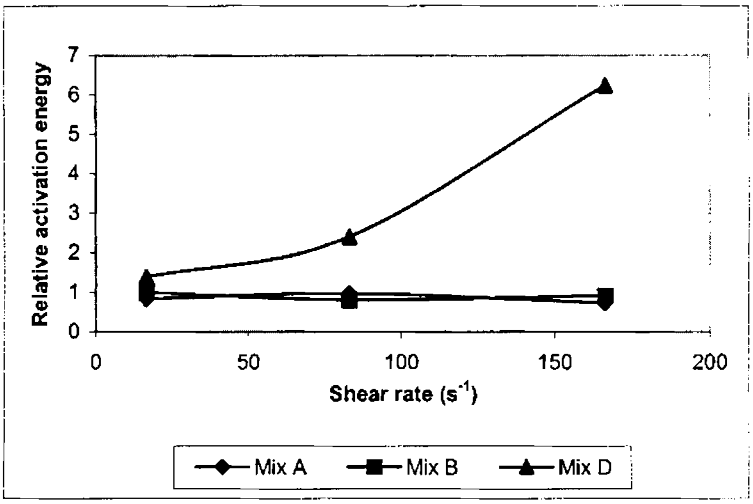

Figure 4.A.2.11. Relative activation energy versus shear rate

The die swell of the composites with and without bonding agent is quantified as Relative die swell (D_r) is given in table 4.A.2.5. In general all the mixes show D_r values marginally higher than one. Higher die swell is associated with more elastic deformation during flow. This is in agreement with the view that the fiber –matrix bond is strengthened in the presence of epoxy bonding agent.

Table. 4.A.2.5. Relative die swell ratios at different temperatures

Temperature (°C)	Mix	Shear rate (s^{-1})					
		1.6	16.6	83.1	166.2	332.5	831.2
90	A	1.04	0.996	1.135	0.917	1.040	0.972
	B	1.077	1.145	1.212	1.212	1.061	1.061
	C	1.016	1.185	1.068	1.094	1.101	1.170
	D	1.088	1.377	1.360	1.315	1.049	0.932
100	A	1.084	1.105	1.143	1.105	1.105	1.004
	B	0.957	0.732	0.843	0.841	0.841	0.74
	C	1.193	1.193	1.150	1.150	1.192	1.150
	D	1.177	1.275	1.053	1.093	1.147	1.210

REFERENCES.

1. Vargehse S., Kuriakose B., Thomas S., Premalatha C.K. and Koshy A.T., Plast. Rub. Compos. Process Appl., **20** (1993) 93.
2. Geethamma V.G., Ramanamurty K., Janardhan R. and Sabu Thomas., Inter. J. Polym. Mater., **32** (1996) 147.
3. Suhara F., Kutty S.K.N, & Nando G.B. and Bhattacharya A.K Polym. Plast.Technol.Eng., **37** (1998) 57.
4. Kutty S.K.N., De P.P and Nando G.B., Plast. Rub. Compos. Process Appl., **15** (1991) 23.
5. Chan Y., White J.L. and Oyanagi Y., J. Rheol. **22** (1978) 507.
6. Suhara F., Kutty S.K.N. and Nando G.B., Polym. Plast. Technol.Eng., **36** (1997) 399.

SECTION. B. PART (I)
SBR - SHORT NYLON-6 FIBER COMPOSITES

During processing, a rubber compound is subjected to various forms of shear such as mixing, calendering and extrusion. White and Tokita established a correlation between rheology and processing[1-2]. Murty et.al., studied the rheology of short jute fiber filled natural rubber composites[3]. Rheological studies give an idea on the processing characteristics of short fiber composite material.

This section deals the study of the rheological behaviour of short Nylon fiber reinforced styrene butadiene rubber. The effect of shear rate, fiber concentration and temperature on shear viscosity and die swell was studied.

Formulation of mixes is given in Table 4.B.1.1. The experimental details were described in chapter II.

Table 4.B.1.1 Composition of mixes (parts by weight)

Ingredients	Mix No.			
	A	B	C	D
SBR	100	100	100	100
Nylon	0	10	20	30
ZnO	5	5	5	5
Stearic acid	1.5	1.5	1.5	1.5

4.B.1.1. Effect of Shear Rate and Shear Stress

Figures 4.B.1.1. to 4.B.1.3. show the variation of viscosity with shear rate of all the mixes at 80, 90 and 100 °C, respectively. The viscosity decreases almost linearly with shear rate for all the mixes in the shear rate range studied, indicating a pseudoplastic behaviour for the composite. The reduction in viscosity with increasing shear rate may be arising from the molecular alignment during flow through the capillary. The fact that the pattern is also observed in the case of fiber filled mixes indicates that the fibers, while restricting the free flow of the melt, also get aligned in the direction of flow. This is evident from SEM photomicrograph of extrudates of mix D. The Figures 4.B.1.4a. and 4.B.1.4b. show the SEM photomicrograph of cut surfaces of extrudates of mix D at shear rates 1 and100 s^{-1}, respectively at 100°C. Higher level of orientation at higher shear rate is evident from Figure 4.B.1.4b. The cut ends of the fibers oriented along the flow direction is clearly seen in the figure. Similar results in the case of short Kevlar fiber reinforced thermoplastic polyurethane composite have been reported by Kutty et al.[4].

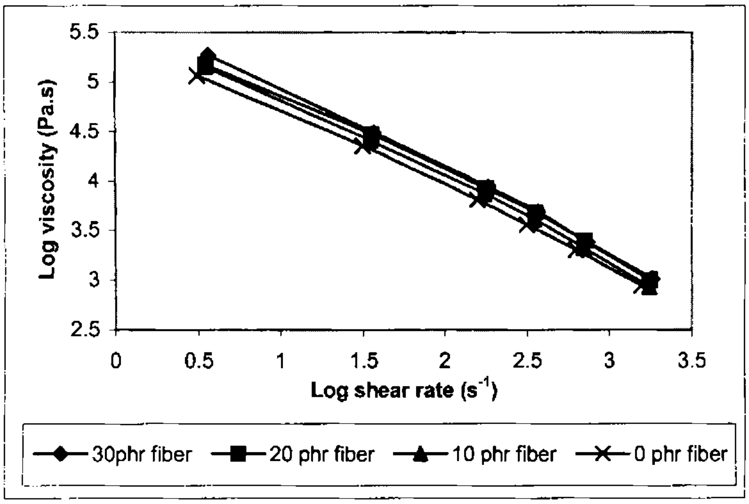

Figure 4.B.1.1. Shear viscosity versus shear rate at 80°C

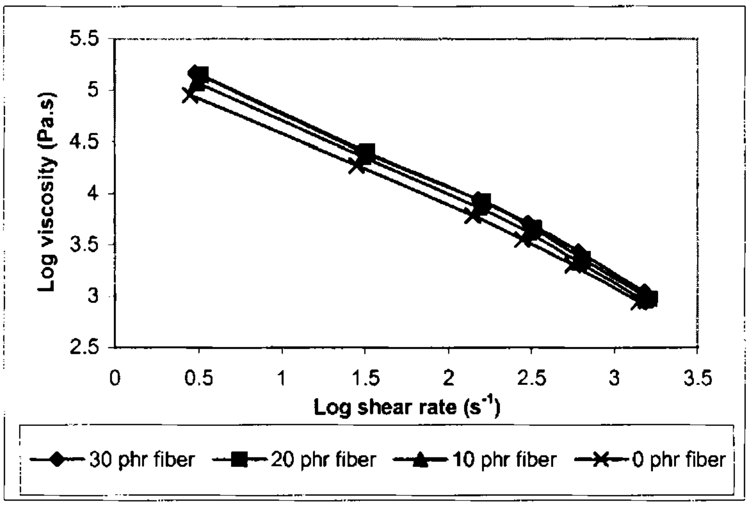

Figure 4.B.1.2. Shear viscosity versus shear rate at 90°C

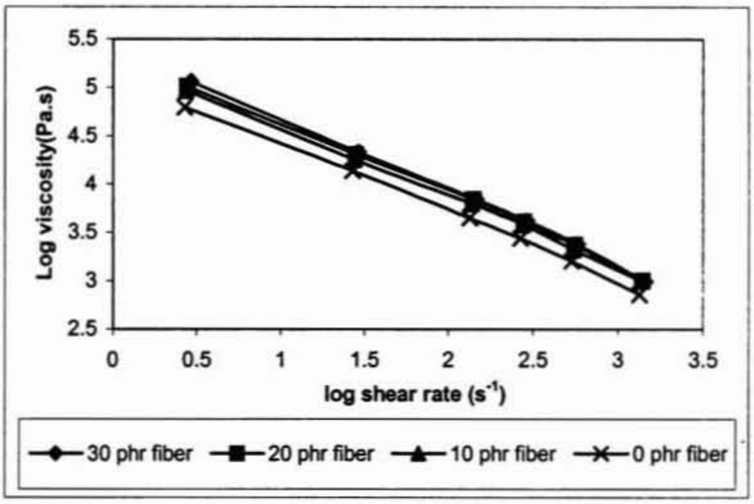

Figure 4.B.1.3. Shear viscosity versus shear rate at 100°C

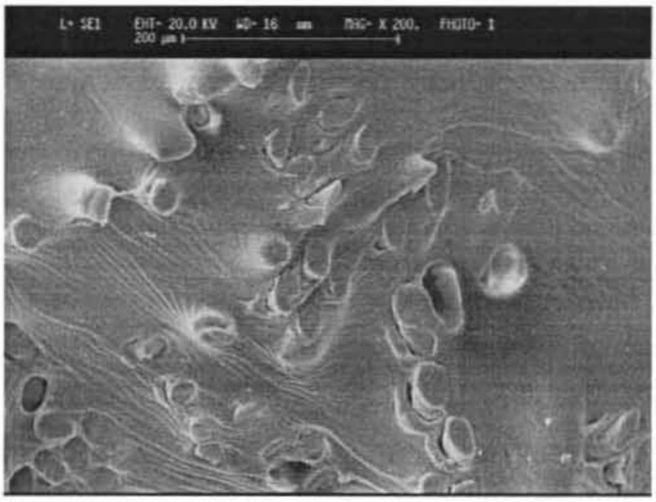

Figure 4.B.1.4a. SEM photomicrograph of the cut surface of the extrudate of mix D; Shear rate $1s^{-1}$ and temperature 100°C (original magnification x200; marker 200µ)

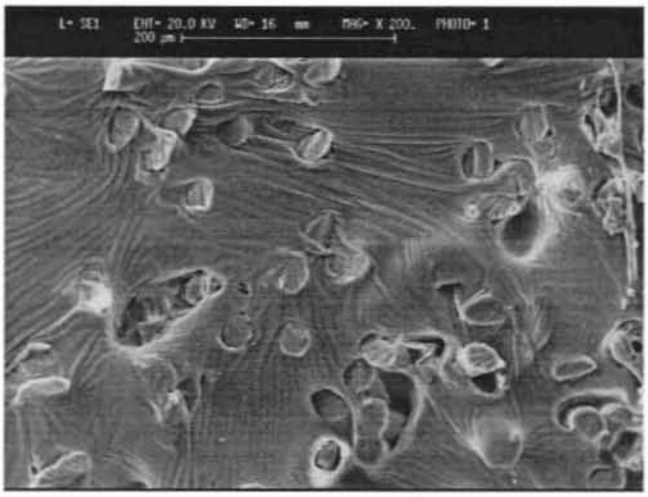

Figure 4.B.1.4b. SEM photomicrograph of the cut surface of the extrudate of mix D; Shear rate 100s^{-1} and temperature 100°C (original magnification x200; marker 200μ)

Plots of shear viscosity versus shear stress also show similar patterns but with marked difference at higher shear stresses. (Figures 4.B.1.5. – 4.B.1.7.).

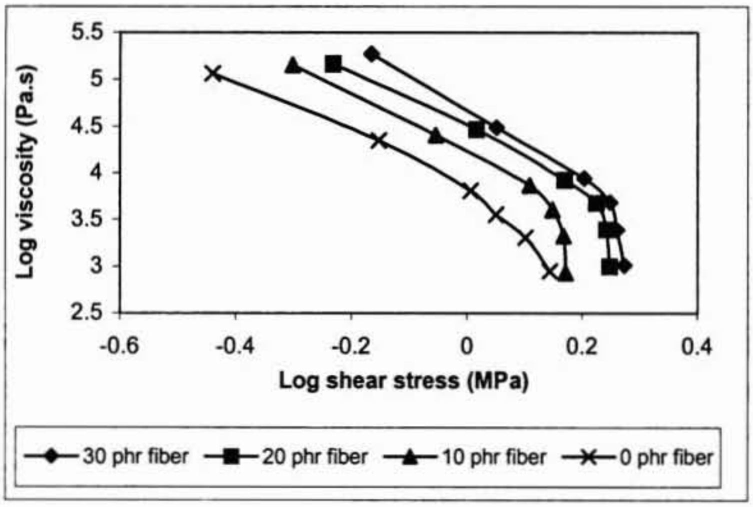

Figure 4.B.1.5. Shear viscosity versus shear stress at 80°C

All the plots show significant drop in viscosity at shear stress beyond 1 MPa. The point at which the sudden drop occurs is shifted to higher shear stress values in the case of fiber filled samples. For the gum compound it occurs at 1.08 MPa at 80°C whereas for the 30 phr fiber filled sample the corresponding values is 1.77 MPa at 80°C. The sudden drop at higher shear stress values is due to the plug flow at the higher rates of flow.

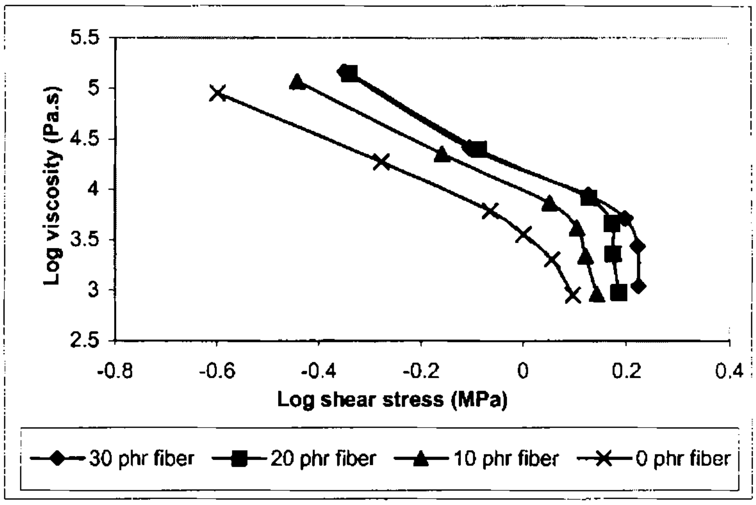

Figure 4.B.1.6.Shear viscosity versus shear stress at 90°C

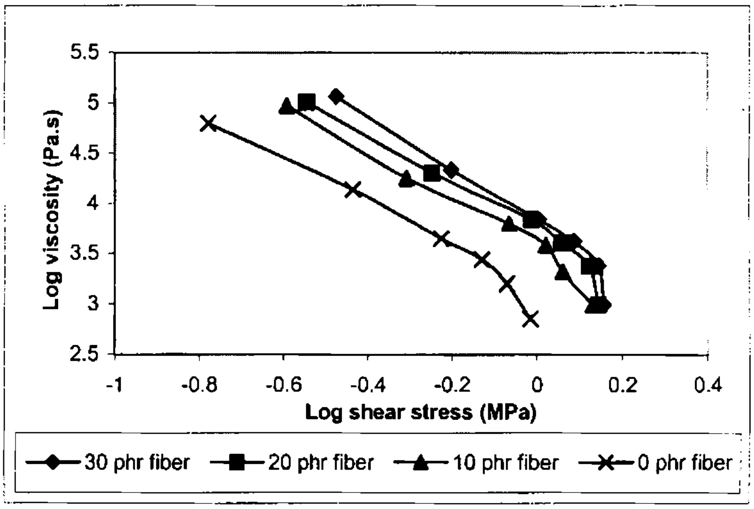

Figure 4.B.1.7. Shear viscosity versus shear stress at 100°C

The point of inflection is plotted against the corresponding fiber loading in Figures 4.A.1.8a., 4.A.1.8b. and 4.A.1.8c. at 80, 90 and 100°C, respectively. It is observed that there is a linear relationship between the onset of plug flow and the fiber content at all the temperatures. This is because with increasing fiber content the melt viscosity is increased. With high melt viscosity the material slips at the wall and the stress is relieved.

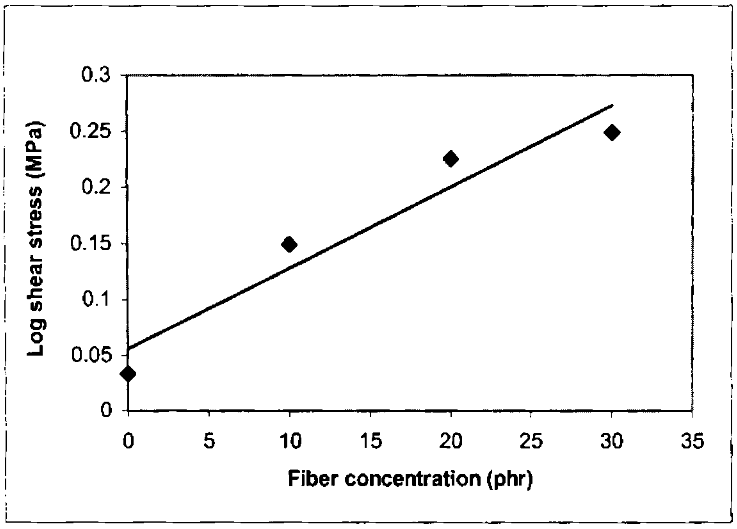

Figure 4.B.1.8a. Variation of shear stress at the point of inflection with fiber loading at 80°C

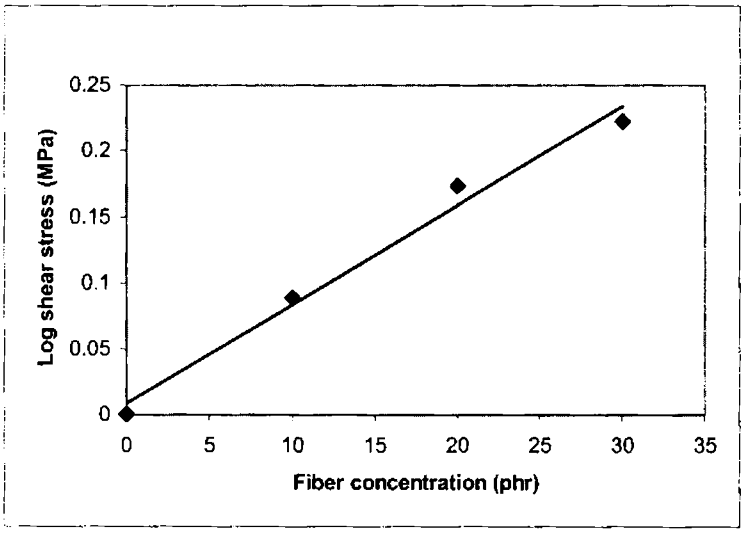

Figure 4.B.1.8b. Variation of shear stress at the point of inflection with fiber loading at 90°C

Figures 4.B.1.9a. – 4.B.1.9c. show the SEM photomicrographs of mix D at shear rates 1s^{-1}, 100s^{-1}, 500 s^{-1}, respectively at a temperature of 80°C. Scanning Electron Micrograph of the extrudate at the plug flow region (Figure 4.B.1.9c.) shows that there is less fiber orientation compared to the extrudate of the lower shear stress regions (Figures 4.B.1.9a. & 4.B.1. 9b.).

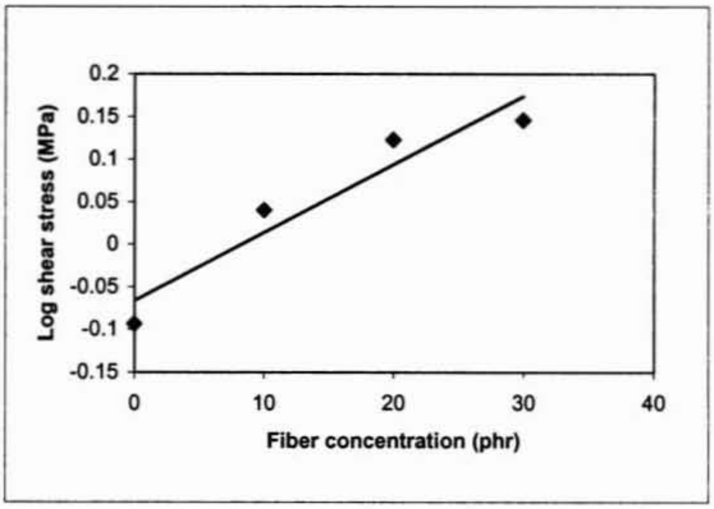

Figure 4.B.1.8c. Variation of shear stress at the point of inflection with fiber loading at 100°C

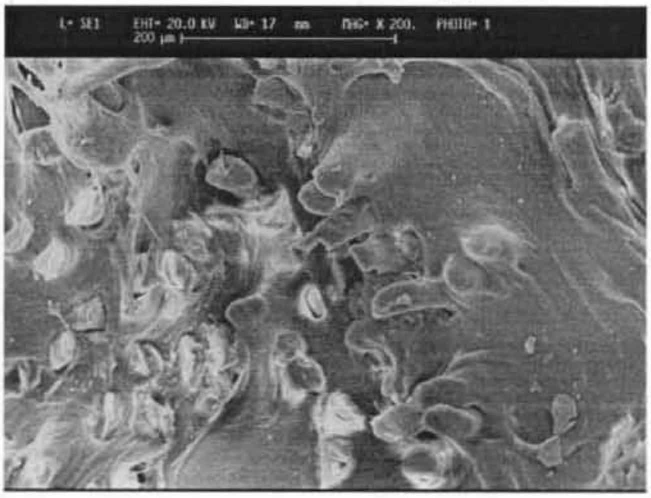

Figure 4.B.1.9a. SEM photomicrograph of the cut surface of the extrudate of mix D; Shear rate 1s^{-1} and temperature 80°C (original magnification x200; marker 200µ)

The maximum fiber orientation is at the shear rate just above the drop (Figures 4.B.1.9b.). This also suggests the occurrence of plug flow at higher shear stress values. At higher temperature the extent of drop is found to be reduced. This may be due to the lower plug flow when the sample becomes softer at elevated temperature.

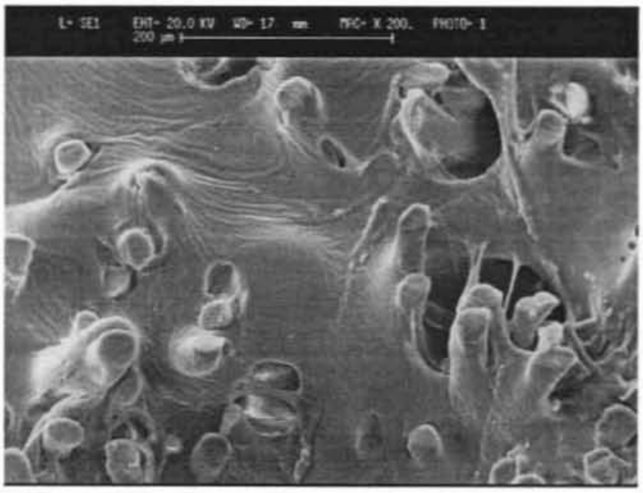

Figure 4.B.1.9b. SEM photomicrograph of the cut surface of the extrudate of mix D; Shear rate 100s^{-1} and temperature 80°C (original magnification x200; marker 200µ)

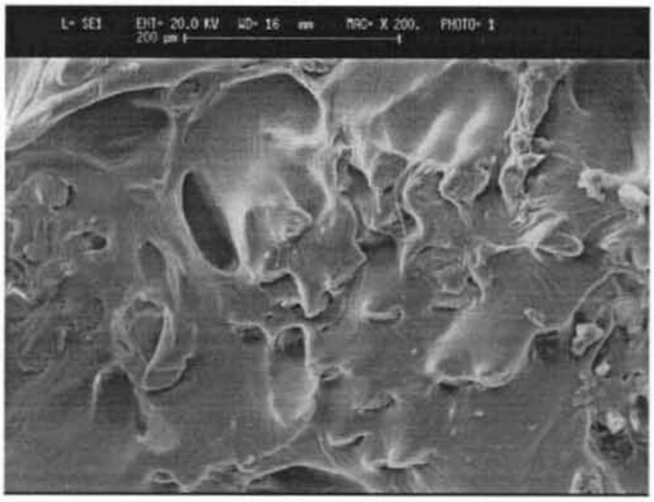

Figure 4.B.1.9c. SEM photomicrograph of the cut surface of the extrudate of mix D; Shear rate 500s^{-1} and temperature 80°C (original magnification x200; marker 200µ)

4.B.1.2. Effect of Fiber Content

From Figures 4.B.1.1. - 4.B.1.3. it can be seen that viscosity is increased when fiber is introduced to the matrix at all temperatures. The presence of fiber restricts the molecular mobility under shear, resulting in higher viscosity. With further increase in fiber concentration there is not much increase in viscosity. As the shear rate increases, the increase in viscosity with fiber concentration decreases and at a shear rate of 831.2s^{-1} all the mixes show almost same viscosity. This means the effect of fiber on shear viscosity is prominent at lower shear rates only. This is in agreement with the earlier observations [4-5].

4.B.1.3. Effect of Temperature

Figures 4.B.1.10. - 4.B.1.11. show the variation of shear viscosity with shear rate for mixes A & D, respectively at various temperatures. As the temperature increases the viscosity decreases for both the mixes at all the shear rates studied. The effect of temperature on viscosity is found to be dependant on the shear rate. In the case of gum compound, at lower shear rates, the viscosity drops from 5.063 to 4.795 Pa.s as the temperature is changed from 80°C to 100°C while at higher shear rate the decrease in viscosity with temperature is reduced and viscosity values tend to merge to a common point. A similar tend is also shown by the fiber filled samples. The changed temperature sensitivity of the composite is also reflected in the activation energy values calculated (Table 4.B.2.2).

In the case of 30 phr fiber loading (Figure. 4.B.1.11.) the log viscosity decreases from 5.27 to 5.06 Pa.s at a lower shear rate of 1.6 s^{-1}. But as the shear rate increases, the drop in viscosity with temperature decreases more in the mix D compared to mix A.

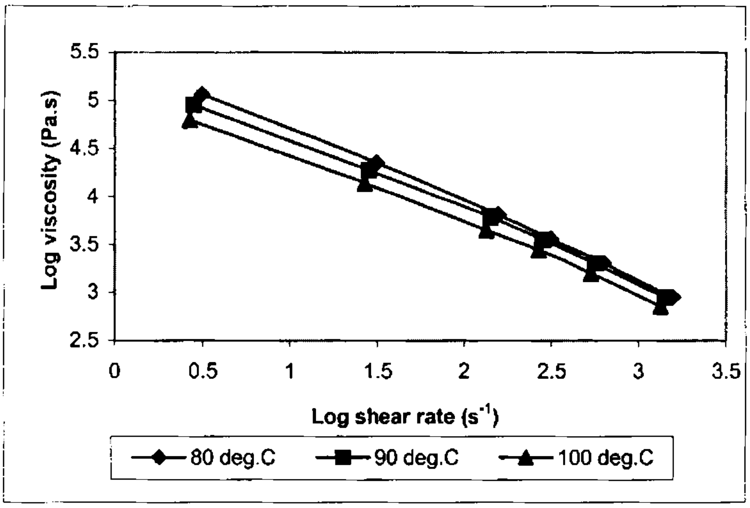

Figure 4.B.1.10. Shear viscosity versus shear rate for Mix A

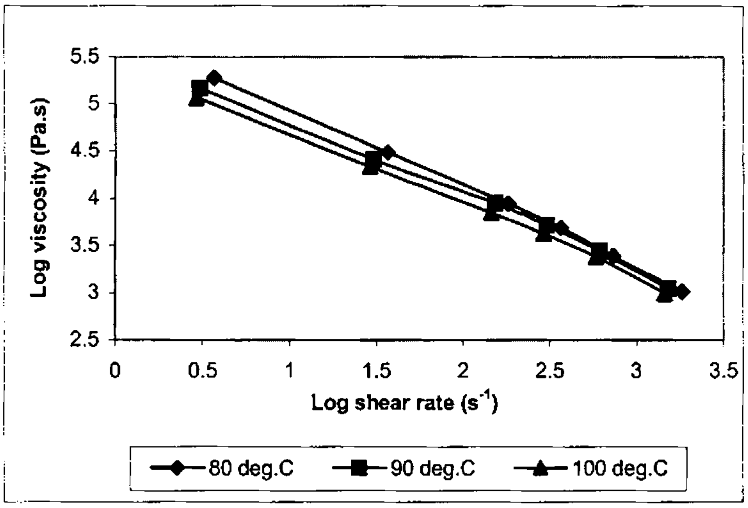

Figure 4.B.1.11. Shear viscosity versus shear rate for Mix D

4.B.1.4. Activation Energies

The activation energies of mixes A to D were calculated from the Arrhenius plots of viscosity and temperatures at different shear rates and given in the Table 4.B.2.2. The activation energy of flow, an indication of the temperature sensitivity of the melts, is reduced in the presence of fibers. This indicates that higher temperature sensitivity of flow of rubber matrix is reduced in the presence of fibers. Similar trends were reported earlier[4]. The activation energy of all the melts decreases as shear rate increases. This indicates that the temperature sensitivity of the gum and composite melts are also shear dependent and the sensitivity is lower at higher shear rates.

Table 4.B.1.2. Activation energies of flow of mixes A-D (Kcal/mol)

Mixes	Shear rates (s^{-1})			
	1.6	16.6	83.1	166.2
A	2.04	1.62	1.23	0.84
B	1.41	1.13	0.52	0.16
C	1.39	1.41	0.78	0.66
D	1.48	1.05	0.62	0.34

4.B.1.5. Flow Behaviour Index

Figure. 4.B.1.12. shows flow behaviour indices of mixes A to D at different temperatures. It is found that for the all mixes flow behaviour increases as temperature increases indicating that the melt becomes more Newtonian in nature as the temperature is increased.

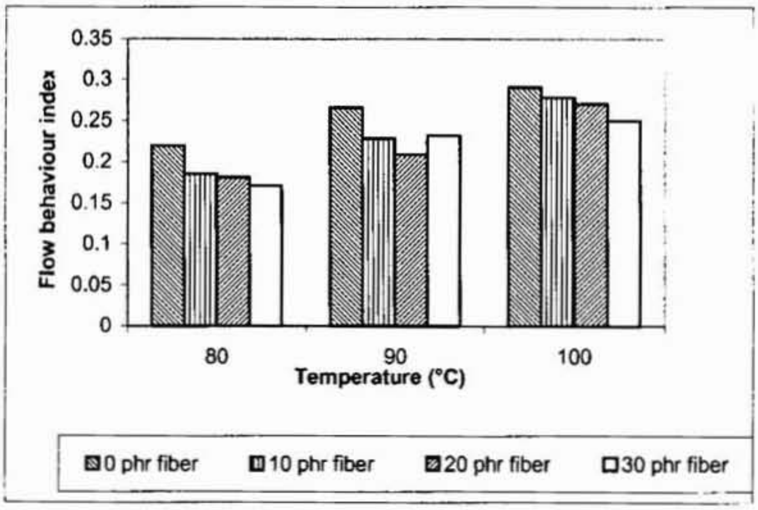

Figure 4.B.1.12. Flow behaviour index versus temperature

Incorporation of fiber reduces Newtonian behaviour as indicated by the reduction in n' values. As fiber concentration increases the deviation from Newtonian behaviour increases.

4.B.1.6. Die Swell

Table 4.B.2.3. gives the die swell ratio, (d_e/d_c) of the gum and fiber filled mixes at different temperatures and shear rates. The die swell of the gum compound remains almost unaffected by shear rate and temperature. Die swell decreases sharply by the addition of fiber and the die swell ratio is less than 1 at higher fiber loading. The reduction in the die swell in the presence of fibers has been reported earlier[3-5]. The reduction in die swell with fiber loading may be due to the orientation of the fibers in the matrix. Die swell of the higher fiber loaded composites (Mixes C & D) decreases with temperatures, especially at lower shear rates and at higher shear rates the die swell remains more or less constant with temperature.

Table 4.B.1.3. Die swell ratios of mixes A-D at different temperatures

Mix	Temperature (°C)	Shear rates (s^{-1})					
		1.6	16.6	83.1	166.2	332.5	831.2
A	80	1.28	1.22	1.22	1.22	1.62	1.76
	90	1.25	1.25	1.25	1.29	1.34	1.57
	100	--	--	1.30	1.46	1.77	1.58
B	80	1.03	1.03	1.03	1.03	1.18	1.32
	90	0.946	0.946	1.01	1.08	1.08	1.35
	100	1.14	1.22	1.52	1.39	1.48	1.13
C	80	0.972	0.972	1.06	0.972	0.972	1.065
	90	0.921	0.921	0.964	0.964	1.05	1.05
	100	0.897	0.897	1.15	1.41	1.28	1.15
D	80	0.986	0.986	0.939	0.891	0.891	0.915
	90	0.921	0.921	1.05	1.05	0.921	1.05
	100	0.812	0.875	1.08	1.21	1.08	1.00

REFERENCES.

1. White J.L., Rubb. Chem. Technol., **42** (1969) 257.
2. White J.L. and Tokita N., J. Appl. Polym. Sci.,**11** (1967) 321.
3. Murty V.M., Gupta B.R. and De S.K., Plast. Rub. Proc. Appl., **5** (1985) 307.
4. Kutty S.K.N., De P.P and Nando G.B., Plast. Rub. Compos. Process Appl., **15** (1991) 23.
5. Chan Y., White J.L. and Oyanagi Y., J. Rheol. **22** (1978) 507.

SECTION B. PART (II)
SBR- SHORT NYLON-6 FIBER COMPOSITES WITH EPOXY RESIN AS BONDING AGENT

The rheological behaviour of polymer melts provides choice of processing conditions and influences the morphology and mechanical properties of the final product. In this section the rheology of short Nylon-6 fiber reinforced styrene butadiene rubber containing an epoxy resin bonding agent is described. The fiber loading was varied from 0 to 30 phr.

Formulation of mixes is given in Table 4.B.2.1. Detailed description of experimental techniques adopted for the study is given in chapter II.

Table 4.B.2.1. Composition of mixes (parts by weight)

Ingredients	Mix No.							
	A	B	C	D	A_0	B_0	C_0	D_0
NBR	100	100	100	100	100	100	100	100
Nylon	0	10	20	30	0	10	20	30
Epoxy resin*	3	3	3	3	0	0	0	0
ZnO	5	5	5	5	5	5	5	5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

* Epoxy resin formed by 1:0.5 equivalent combination of epoxy resin and amine based hardener respectively

4.B.2.1. Effect of Shear Rate and Shear Stress

The variation in shear viscosity with shear rate of the mixes A-D at 80, 90 and 100 °C is shown in the Figures 4.B.2.1. - 4.B.2.3., respectively. In all the cases it is seen that the viscosity decreases almost linearly with shear rate in the shear rate range studied, indicating a pseudoplastic behaviour of the composite with epoxy as bonding agent. The reduction in viscosity with increasing shear rate may be arising from the molecular alignment during flow through the capillary. Similar pattern is also observed in the case of fiber filled mixes. This indicates that the fibers, while restricting the free flow of the melt, also get aligned in the direction of flow. Similar results in the case of short polyester fiber polyurethane elastomer composite have been reported by Suhara et al.[1-2].

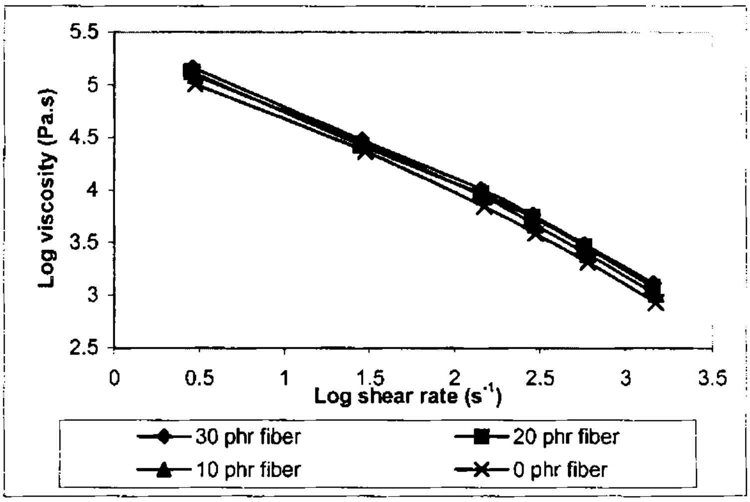

Figure 4.B.2.1. Shear viscosity versus shear rate at 80°C

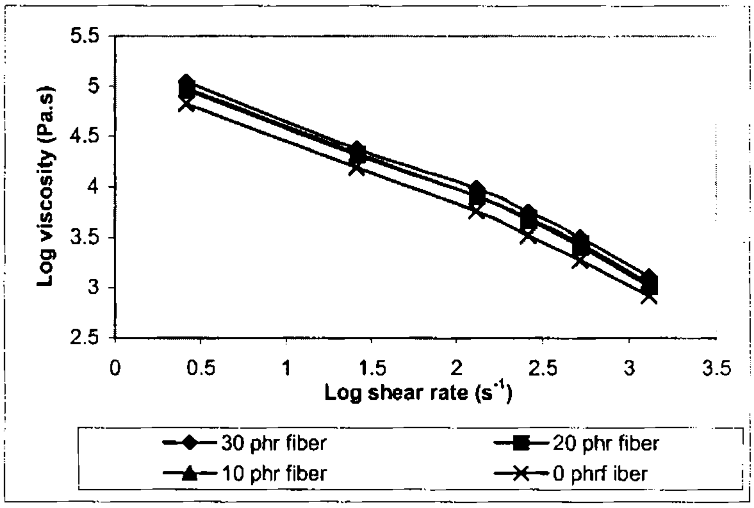

Figure 4.B.2.2. Shear viscosity versus shear rate at 90°C

Figures 4.B.2.4. - 4.B.2.6., show the variation of shear viscosity with shear stress for mixes A-D. Plots of shear viscosity versus shear stress also show similar patterns; but with marked difference at higher shear stresses. All the plots show significant drop in viscosity at shear stress beyond 1 Mpa. As the fiber concentration increases, the point at which the sudden drop occurs is shifted to higher shear stress values. For the gum compound it occurs at 1.13 MPa at 80 °C whereas for the 30 phr fiber filled sample the corresponding values is 1.67 MPa at the same temperature. The sudden drop at higher shear stress values also indicates probable plug flow at higher rates of flow. The point of inflection is plotted against the corresponding fiber loading in Figures 4.B.2.7a and 4.B.2.7b at 80 and 90 °C, respectively.

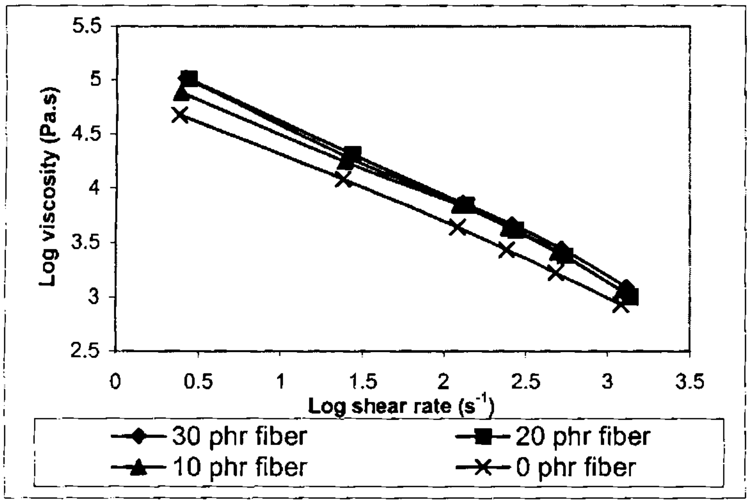

Figure 4.B.2.3. Shear viscosity versus shear rate at 100°C

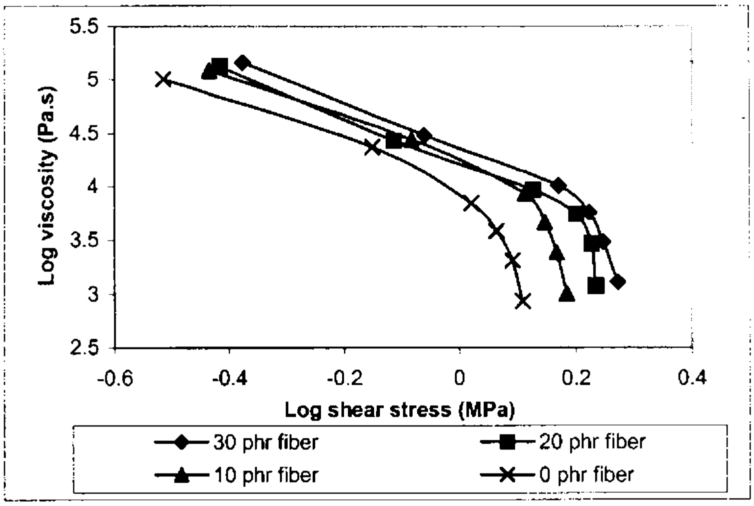

Figure 4.B.2.4. Shear viscosity versus shear stress at 80°C

It is observed that there is a linear relationship between the onset of plug flow and the fiber content at both the temperatures. This is because with increasing fiber content the melt viscosity is increased. With high melt viscosity the material slips at the wall and the stress is relieved.

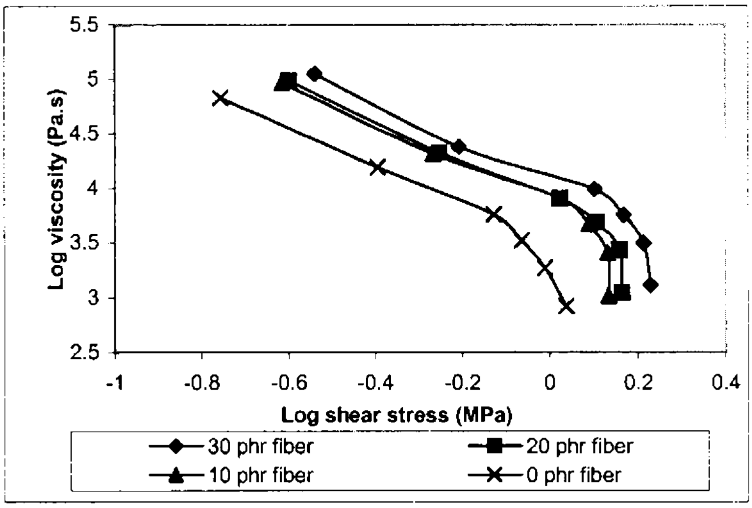

Figure 4.B.2.5. Shear viscosity versus shear stress at 90°C

The extent of drop is reduced with increasing temperature. This may be because the chance of plug flow is lower when the sample becomes softer at elevated temperature. This is also evident from the fact that the gum compound, with relatively lower viscosity, shows no evidence of plug flow at 100 °C.

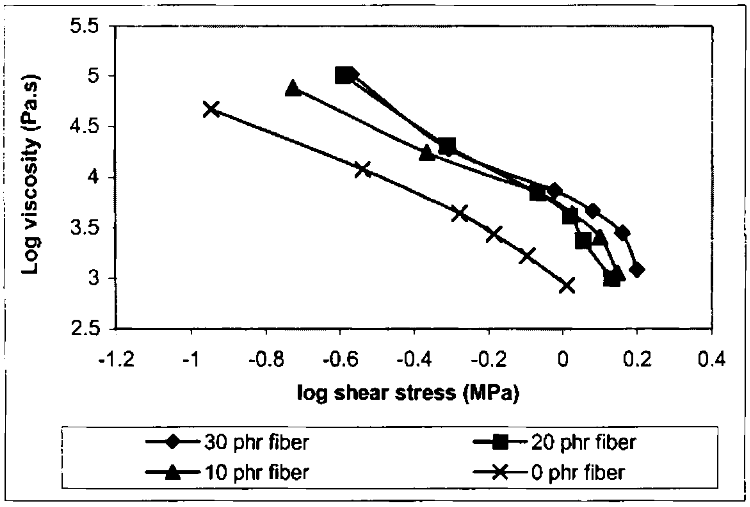

Figure 4.B.2.6. Shear viscosity versus shear stress at 100°C

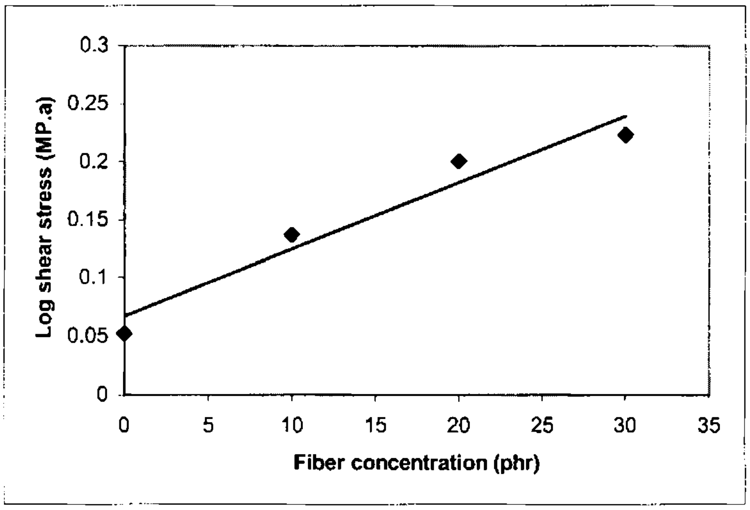

Figure 4.B.2.7a. Variation of shear stress at the point of inflection with fiber loading at 80°C

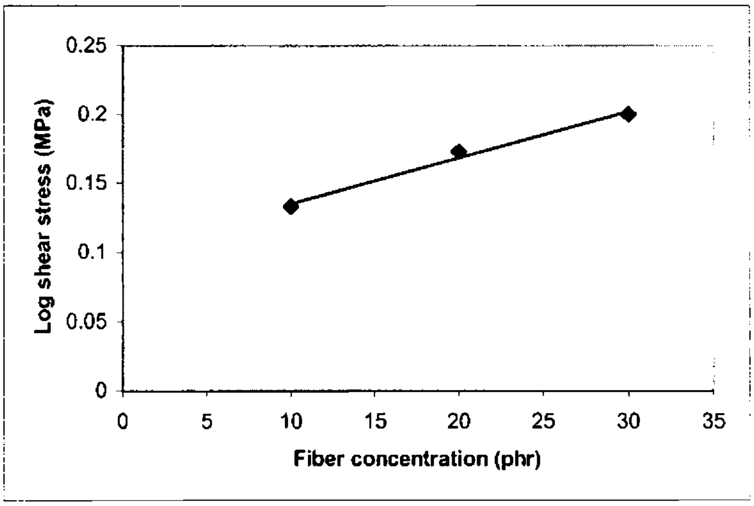

Figure 4.B.2.7b. Variation of shear stress at the point of inflection with fiber loading at 90°C

4.B.2.2. Effect of Fiber Content

Viscosity increases with increase in fiber concentration at all shear rates (Figures 4.B.2.1. -4.B.2.3.). The presence of fiber restricts the molecular mobility under shear, resulting in higher viscosity. The increase in viscosity on introduction of fiber is temperature dependent and is more at higher temperatures. Rise in viscosity with fiber concentration decreases at higher shear rates. This means the effect of fiber on shear viscosity is prominent at lower shear rates only. This is in agreement with the earlier observations[3-4]. All fiber- containing mixes have more or less equal viscosity at higher shear rates which is higher than that of the gum compound.

4.B.2.3. Effect of Temperature

The variation of shear viscosity with shear rate for mixes A & D at various temperatures and shear rates is shown in the Figures 4.B.2.8. & 4.B.2.9., respectively. The effect of temperature on the viscosity is found to be shear rate dependant. In the case of gum compound, at lower shear rates, the log viscosity drops from 4.94

Pa.s to 4.76 Pa.s as the temperature is changed from 80 to 100 °C while at higher shear rate all the viscosity values tend to merge to a common point. Similar trends are shown by the fiber filled sample. The changed temperature sensitivity of the composite is also reflected in the activation energy values calculated (Table. 4.B.2.2.).

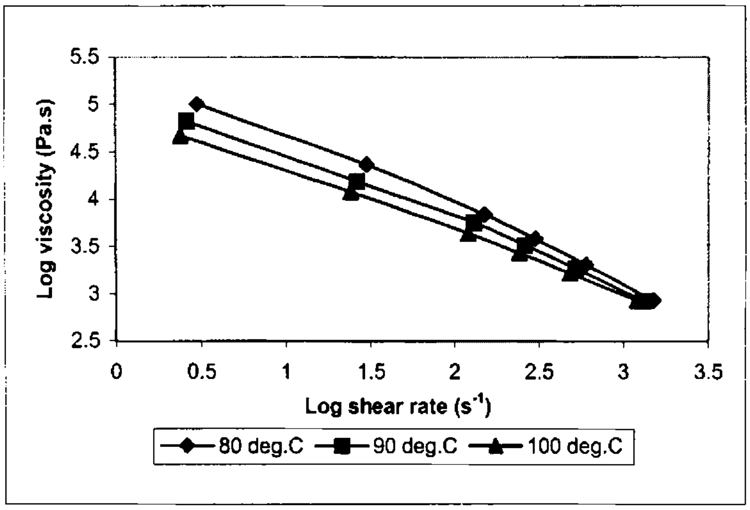

Figure 4.B.2.1.8. Shear viscosity versus shear rate for Mix A

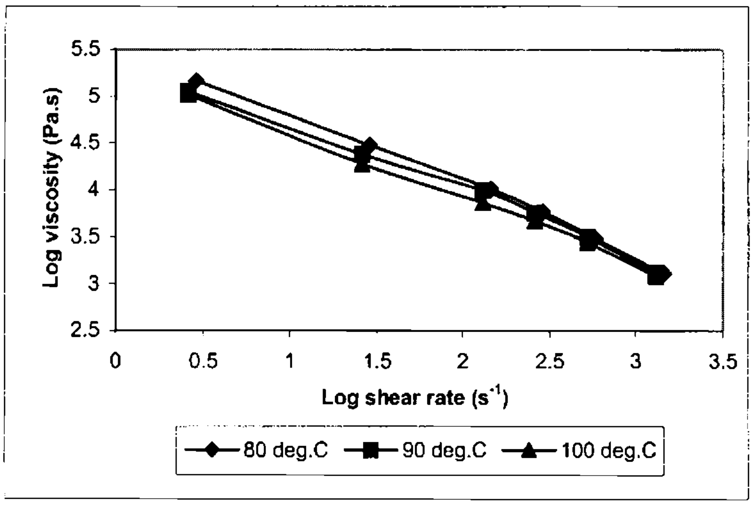

Figure 4.A.2.9. Shear viscosity versus shear rate for Mix D

4.B.2.4. Activation Energies

The activation energies of mixes A to D were given in the Table. 4.B.2.2. The activation energies were calculated from the Arrhenius plots of viscosity and temperatures at different shear rates. The activation energy of flow is reduced by the introduction of 10 phr fiber but further increase of fiber concentration to 30 phr activation energy remains more or less constant. The higher temperature sensitivity of flow of rubber matrix is reduced in the presence of fibers. Similar trends were reported in the case of short Kevlar fiber reinforced thermoplastic polyurethane by Kutty et al.[3]. The activation energy of gum compound decreases as shear rate increases indicating that the temperature sensitivity of the gum is also shear dependent and the sensitivity is lesser at higher shear rates. But in the case of fiber filled mixes activation energy does not vary much with shear rate.

Table. 4.B.2.2. Activation energies of flow of mixes A-D (kcal/mol)

Mixes	Shear rates (s^{-1})			
	1.6	16.6	83.1	166.2
A	10.06	8.81	6.08	4.61
B	5.89	5.64	2.49	--
C	4.80	5.45	5.34	4.94
D	4.20	6.20	4.56	3.03

4.B.2.5. Flow Behaviour Index

Figure 4.B.2.10. shows flow behaviour indices of mixes A to D at different temperatures. It is found that for all the mixes flow behaviour increases as temperature increases indicating that the melt became more Newtonian in nature as the temperature is increased.

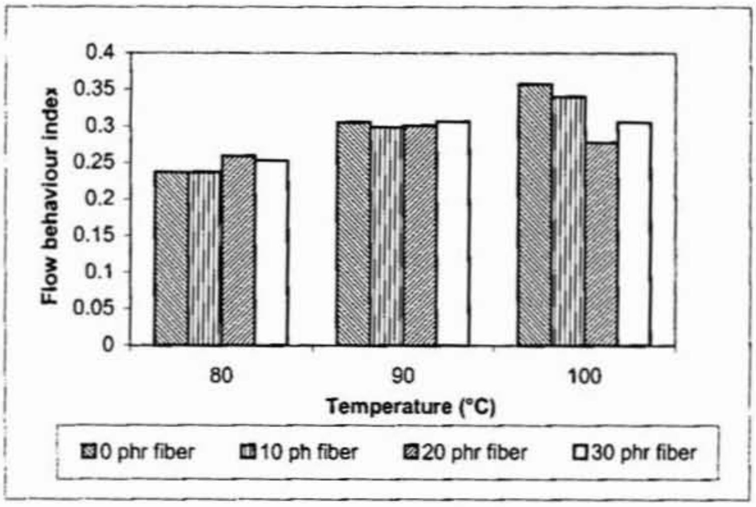

Figure 4.A.2.10. Flow behaviour index versus temperature

Flow behavior index remains almost constant by the addition of fiber at low temperatures indicating that Newtonian behaviour is not much affected by the addition of fibers in the presence of a bonding agent.

4.B.2.6. Die Swell

The die swell ratio, (d_e/d_c) of the gum and fiber filled mixes with bonding agent, at different temperatures and shear rates is given in Table. 4.B.2.3. There is not much variation in die swell of the gum compound with shear rates. Die swell decreases sharply by the addition of fiber. The reduction in the die swell in the presence of short fibers has been reported earlier[3-4]. The reduction in die swell with fiber loading may be due to the irreversible orientation of the fibers in the matrix. In the case of fiber filled mixes the die swell remains almost constant with shear rates and temperatures.

Table. 4.B.2.3. Die swell ratios of mixes A-D at different temperatures

Mix	Temperature (°C)	Shear rate (s^{-1})					
		1.6	16.6	83.1	166.2	332.5	831.2
A	80	1.62	1.35	1.67	1.67	1.76	1.76
	90	1.41	1.54	1.58	1.54	1.67	2.00
	100	--	1.98	1.84	1.98	1.69	2.20
B	80	1.11	1.24	1.47	1.41	1.54	1.54
	90	1.01	1.22	1.49	1.49	1.62	1.75
	100	1.14	1.24	1.43	1.57	1.66	1.52
C	80	1.03	1.03	1.15	1.26	1.15	1.26
	90	0.972	1.11	1.25	1.25	1.25	1.11
	100	0.946	1.04	1.04	1.08	1.22	1.08
D	80	1	1.04	1.19	1.25	1.21	1.25
	90	1.02	1.02	1.28	1.15	1.02	1.24
	100	0.926	0.879	1.16	1.25	1.11	1.11

4.B.2.7. Effect of Bonding Agent

The effect of bonding agent has been quantified in terms of relative viscosity, defined as the ratio of the viscosity of the mixes with bonding agent to the viscosity of the mixes without bonding agent. Table. 4.B.2.4. gives the relative viscosity of mixes at different shear rates and temperatures. Relative viscosity increases with shear rate for fiber- containing mixes at all temperatures. In the case of gum compound the relative viscosity increases as shear rate increases up to 83.1s^{-1} afterwards remains more or less constant with increase in shear rates. In general the relative viscosity increases as fiber concentration increases, the effect being more pronounced at higher temperature. This is due to better fiber matrix adhesion in the presence of bonding agent forming more restrained matrix. At higher temperature the relative viscosity is less than one for gum compound. This may be due to the plasticizing action of the resin in the gum compound.

Table. 4.B.2.4. Relative viscosities at different temperatures for various fiber loadings

Temperature (°C)	Fiber loading (phr)	Shear rate (s^{-1})					
		1.6	16.6	83.1	166.2	332.5	831.2
80	0	0.880	1.046	1.077	1.074	1.017	0.962
	10	0.856	1.083	1.170	1.154	1.159	1.196
	20	0.909	0.916	1.120	1.170	1.196	1.200
	30	0.779	0.981	1.179	1.197	1.259	1.269
90	0	0.749	0.824	0.932	0.932	0.924	0.940
	10	0.781	0.903	1.094	1.119	1.188	1.135
	20	0.679	0.841	0.969	1.058	1.189	1.172
	30	0.757	0.920	1.106	1.090	1.146	1.183
100	0	0.757	0.872	0.983	0.973	1.043	1.178
	10	0.815	0.969	1.105	1.120	1.215	1.148
	20	0.910	0.873	0.891	0.924	0.868	0.983
	30	0.901	0.876	1.048	1.097	1.154	1.232

The relative activation energy (A_r) is greater than one for all the mixes at all shear rates (Figure 4.B.2.11.). This indicates that the temperature sensitivity of the mixes increases in the presence of bonding agent. A_r remains more or less constant with shear rate for gum and lower fiber loading (10 phr). But A_r increases sharply with shear rate at higher fiber loading. At higher fiber loading there is more fiber matrix interface, which is strengthened in the presence of bonding agent.

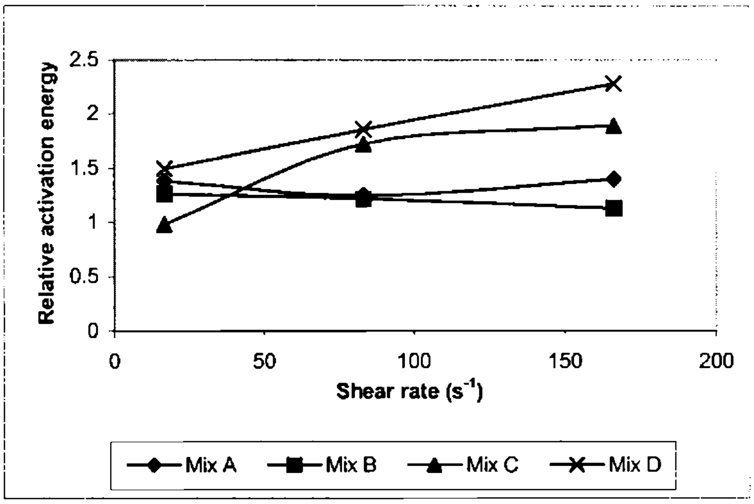

Figure 4.A.2.11. Relative activation energy versus shear rate

The relative die swell (D_r) is greater than one for all the mixes at all shear rates and temperatures (Table. 4.B.2.5.). Higher die swell in the presence of bonding agent is due to more elastic deformation occurring during the flow. D_r remains more or less constant with respect to shear rate and temperature for all the mixes.

Table. 4.B.2.5. Relative die swell ratios at different temperatures

Temperature (°C)	Mix	Shear rate (s^{-1})					
		1.6	16.6	83.1	166.2	332.5	831.2
80	A	1.26	1.11	1.37	1.37	1.08	1.00
	B	1.08	1.20	1.43	1.37	1.31	1.16
	C	1.06	1.06	1.08	1.30	1.18	1.19
	D	1.01	1.06	1.26	1.40	1.35	1.36
90	A	1.13	1.23	1.26	1.19	1.24	1.28
	B	1.07	1.28	1.47	1.37	1.50	1.30
	C	1.05	1.21	1.30	1.30	1.19	1.05
	D	1.11	1.11	1.22	1.10	1.11	1.18

REFERENCES.

1. Suhara F., Kutty S.K.N. and Nando G.B., Polym. Plast.Technol.Eng., **36** (1997) 399.
2. Suhara F., Kutty S.K.N, & Nando G.B. and Bhattacharya A.K Polym. Plast.Technol.Eng., **37** (1998) 57.
3. Kutty S.K.N., De P.P and Nando G.B., Plast. Rub. Compos. Process Appl., **15** (1991) 23.
4. Chan Y., White J.L. and Oyanagi Y., J. Rheol. **22** (1978) 507.

Chapter V

THERMAL DEGRADATION

Section A
Thermal studies of short Nylon –6 –fiber- NBR composite

5.A.1. Effect of bonding agent

Section B
Thermal studies of short Nylon –6 –fiber- SBR composite

5.B.1. Effect of bonding agent

SECTION A

THERMAL STUDIES OF NBR- SHORT NYLON -6 FIBER COMPOSITES

A thorough understanding of the thermal stability of NBR and the composites is important in many applications. The thermal stability of elastomer may be influenced by the presence of the short fibers and bonding agent. Thermal degradation studies of short fiber composites were reported earlier[1-4]. Rajeev et al. studied thermal degradation of short melamine fiber reinforced EPDM, maleated EPDM and nitrile rubber composite with and without bonding agent and found that the presence of melamine fiber in the vulcanizates reduced the rate of decomposition and the effect was pronounced in the presence of the dry bonding system[5]. Various investigations on thermal stability of NBR were also reported[6-7].

In this section thermal property of short Nylon -6 fiber reinforced NBR rubber composites with and without epoxy bonding agent is discussed. Thermogravimetry has been used to study the thermal degradation behaviour of the composite.

The formulation of the mixes is given in the Table 5.A.1. Sample preparation and test method employed are given in the chapter II. Thermogravimetric analyses were carried out using Universal V3 2B TA Instrument with a heating rate of 10°C/min under nitrogen atmosphere.

Table 5.A.1. Formulation of mixes

Ingredients	Mix No.											
	A	B	C	D	A3	B3	C3	D3	A5	B5	C5	D5
NBR	100	100	100	100	100	100	100	100	100	100	100	100
Nylon	0	10	20	30	0	10	20	30	0	10	20	30
Resin*	0	0	0	0	3	3	3	3	5	5	5	5

* Epoxy resin formed by 1:0.5 equivalent combination of epoxy resin and amine type hardener; (Zinc Oxide – 4phr; Stearic acid –2phr; Sulphur – 0.7phr; MBTS – 1phr; TMTD –1.8 phr are common to all mixes)

The derivative TGA curves of mixes A-D and neat fiber are shown in Figure 5.A.1. The temperature of onset of degradation (T_i), the temperature at which the rate of decomposition is maximum (T_{max}), the peak degradation rate and the residue at 600°C are given in the Table 5.A.2. The NBR degrades in single step. The degradation starts at a temperature of 330.5°C and the peak rate of degradation is 9.17 %/min. Neat Nylon fiber also degrades in single step with peak rate of degradation 47.13 %/min and corresponding temperature 455.08°C. Residue remaining at 600°C is 1.255% for fiber. From Figure 5.A.1. it can be seen that the composites also show similar degradation pattern as that of gum compound. As fiber fraction increases the temperature of onset of degradation is shifted to higher temperature up to 20 phr fiber loading (330.5 to 336.1°C), indicating improved thermal stability of the composites (Table 5.A.2.). Similar results have been reported earlier by Kutty et al.[2]. Beyond 20 phr fiber concentration T_i is not improved. T_{max} marginally decreases as fiber concentration increases. The peak rate of degradation decreases with fiber concentration and 30 phr fiber loaded composite has the minimum peak rate of degradation. The percentage weight of residue remaining at 600°C is less for fiber containing mixes compared to the gum compound. The residue remaining at 600°C for the neat fiber is 1.255% and hence when fiber is introduced to the rubber, percentage residue remaining at 600°C decreases.

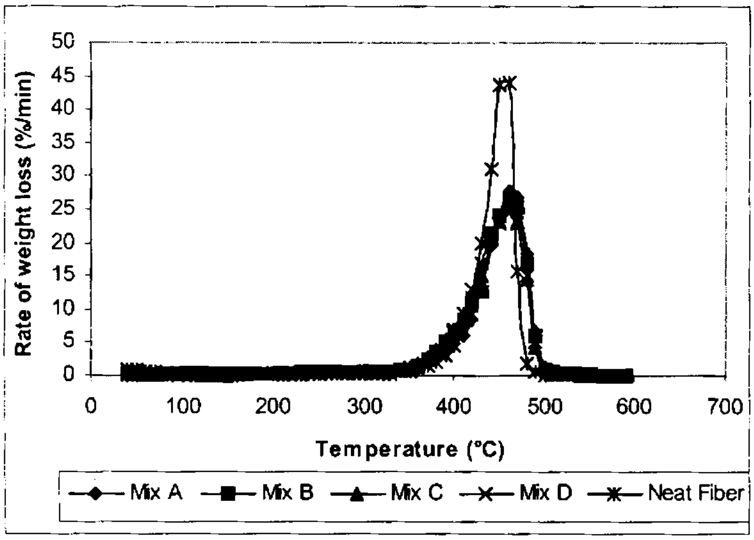

Figure 5.A.1. TGA traces of Mix A, Mix B, Mix C, Mix D

Table 5.A.2. Degradation characteristics of mixes A-D

Mix No.	Temperature of initiation (T_i) (°C)	Peak temperature (T_{max}) (°C)	Peak rate of decomposition (%/min)	Residue (%)
Mix A	330.50	464.4	28.19	9.170
Mix B	333.30	463.4	26.94	7.531
Mix C	336.10	462.44	25.25	9.322
Mix D	333.33	461.93	24.162	7.736
Neat Nylon fiber	362.50	455.08	47.13	1.255

The order of degradation was calculated by Freeman- Carroll method[8] using the equation

$$\Delta \log(dW/dt) = n \cdot \Delta \log W_r - (\Delta E / 2.3R)\, \Delta(1/T) \quad (1)$$

where dW/dt is the rate of reaction, n is the order of reaction, Δ E is the activation energy of the reaction, R is the gas constant, T is the absolute temperature and W_r is proportional to the amount of reactant remaining.

The above equation can be rearranged to

$$\frac{(\Delta \log dW/dt)}{\Delta \log W_r} = n - \frac{(\Delta E/2.3R)\Delta(1/T)}{\Delta \log W_r} \qquad (2)$$

The order of the reaction and activation energies can be obtained from the intercept and gradient of the plot of the left hand side of equation (2) versus $\Delta(1/T)/\ \Delta\ \log W_r$ and such plots are given in Figure.5.A.2. The intercepts show that the degradation of gum and composites follow first order kinetics. Similar results in the case of short Kevlar fiber- reinforced thermoplastic polyurethane composite have been reported by Kutty et al.[2].

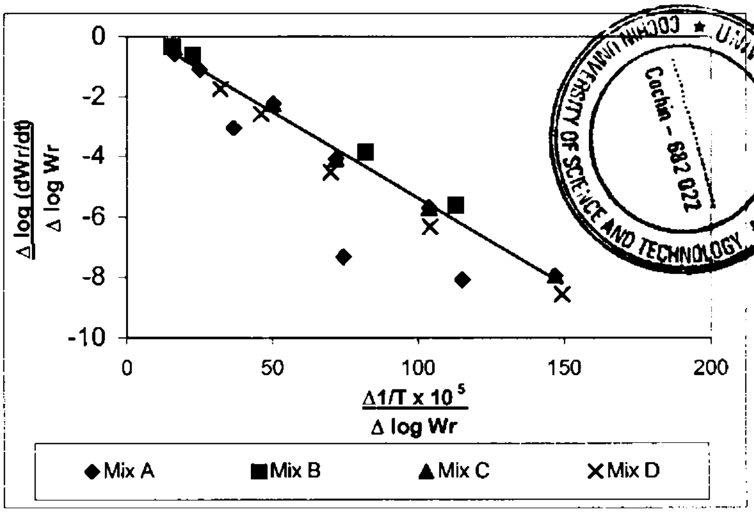

Figure 5.A.2. Freeman - Carroll Plot of Mix A, Mix B, Mix C, Mix D

5.A.1. Effect of Bonding Agent

The degradation of virgin elastomer and composites with epoxy resin as bonding agent was also studied. Figure. 5.A.3. shows the TGA traces for mixes A, A3 & A5. From the figure it is clear that the mixes containing bonding agent also show similar degradation pattern as that of virgin rubber. The T_i is shifted from 330.5 to 336.1°C in the presence of epoxy resin, indicating improved thermal stability of the gum compound in the presence of bonding agent. (Table 5.A.3.). Beyond 3 phr, T_i is not improved. Peak degradation temperature remains constant with resin concentration. The peak rate of degradation decreases marginally with resin concentration. Residue at 600°C remains more or less constant with resin content. The Freeman –Carroll plot for the degradation of mix A, A3 & A5 shows that all the mixes follow first order kinetics (Figure. 5.A.4.).

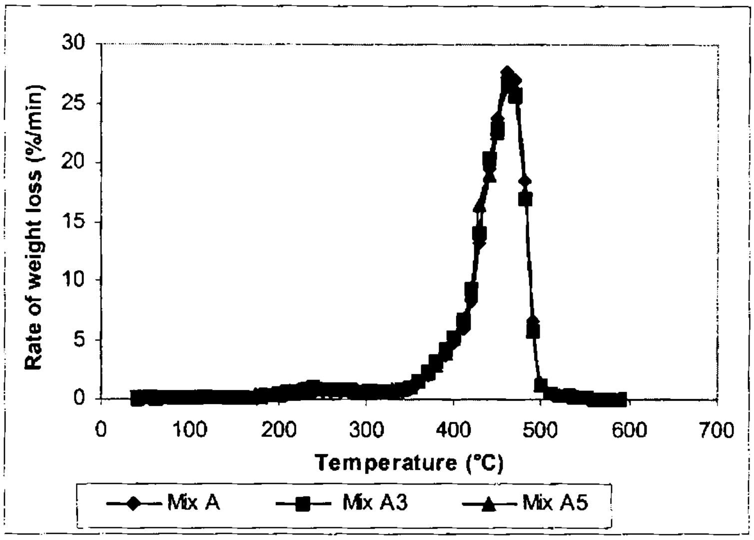

Figure 5.A.3. TGA traces of Mix A, Mix A3, Mix A5

Table 5.A.3. Degradation characteristics of various mixes

Mix No.	Temperature of initiation (T_i) (°C)	Peak temperature (T_{max}) (°C)	Peak rate of decomposition (%/min)	Residue at 600 °C (%)
Mix A	330.50	464.40	28.19	9.170
Mix A3	336.10	463.70	27.22	8.965
Mix A5	336.10	463.67	26.94	9.622
Mix B	333.30	463.43	26.94	7.531
Mix B3	341.67	458.33	26.94	9.436
Mix B5	333.33	463.70	26.38	8.624
Mix C	336.10	462.44	25.25	9.322
Mix C3	336.10	461.47	26.00	9.017
Mix C5	336.10	462.42	25.28	8.816
Mix D	333.33	461.93	24.16	7.736
Mix D3	333.33	458.75	23.75	12.52
Mix D5	330.55	461.29	24.37	8.020

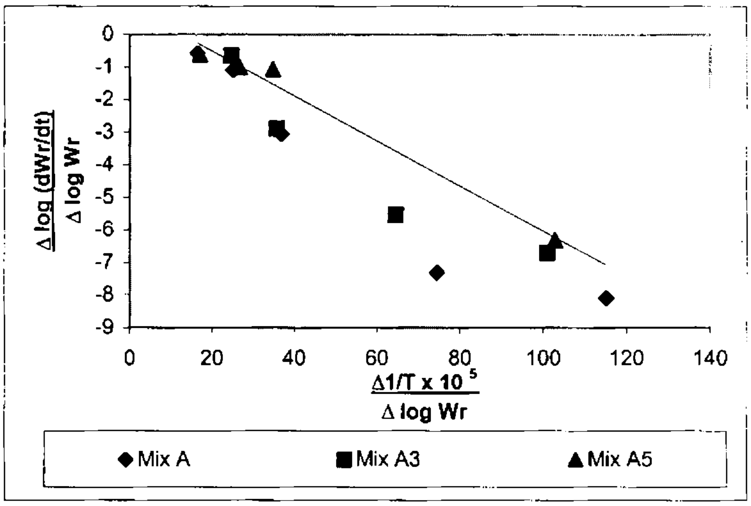

Figure 5.A.4. Freeman - Carroll Plot of Mix A, Mix A3, Mix A5

The TGA traces of composite mixes with bonding agents are shown in Figures 5.A.5.-5.A.7. At low fiber concentration (10 phr) the degradation starts at higher temperature in the presence of epoxy resin, indicating a better thermal stability of the composite (Table 5.A.3.). In the case of higher fiber loaded composites, on introduction of resin, T_i is not much affected however at 5 phr level of resin, there is a decrease in T_i.

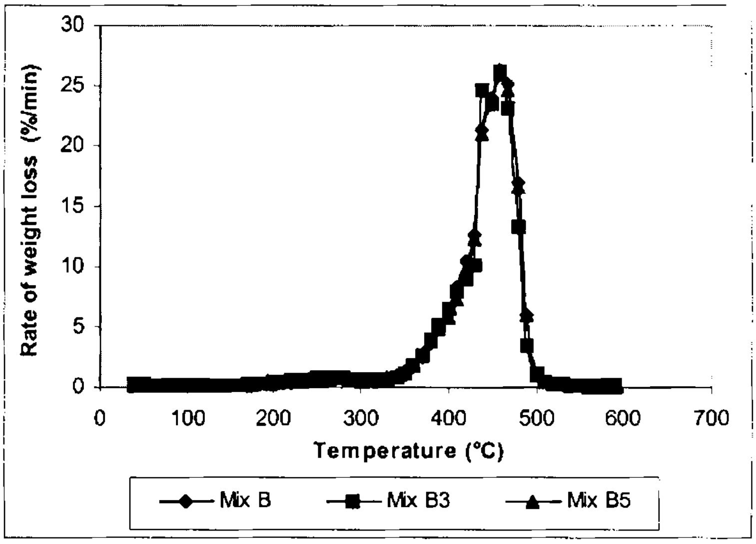

Figure 5.A.5. TGA traces of Mix B, Mix B3, Mix B5

There is no significant change in T_{max} with resin content at all fiber loading. Peak rate of degradation is not much affected by the presence of resin for all composites. Residue at 600°C shows an increase when resin is introduced and further increase in resin concentration residue decreases.

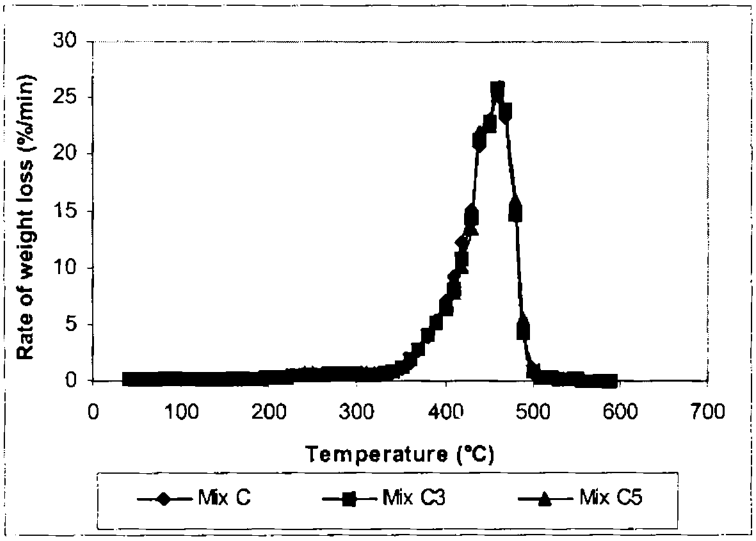

Figure 5.A.6. TGA traces of Mix C, Mix C3, Mix C5

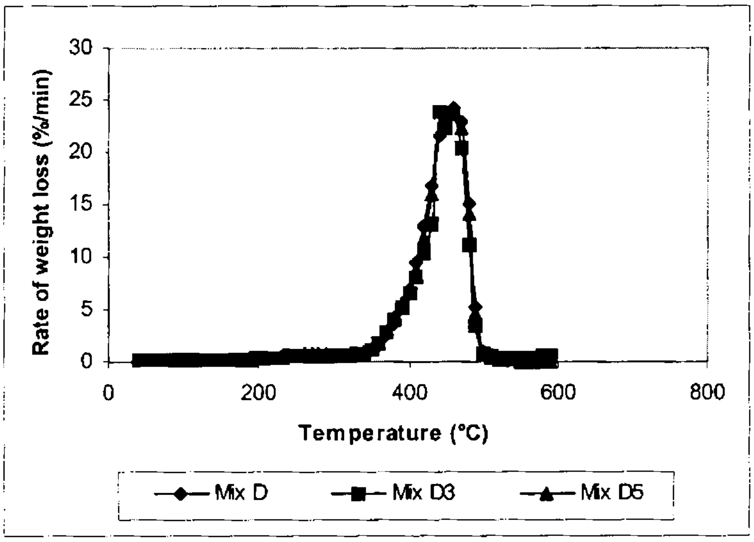

Figure 5.A.7. TGA traces of Mix D, Mix D3, Mix D5

The Freeman -Carroll plots for the degradation of composites with and without bonding agent are shown in the Figures 5.A.8.-5.A.10. The presence of bonding agent does not alter the degradation kinetics and all the mixes follow first order kinetics. Similar results were reported in the case of polyester fiber -poly urethane elastomer with bonding agents based on polypropylene glycol and glycerol with 4,4' diphenyl methane diisocyanate by Suhara et al.[4].

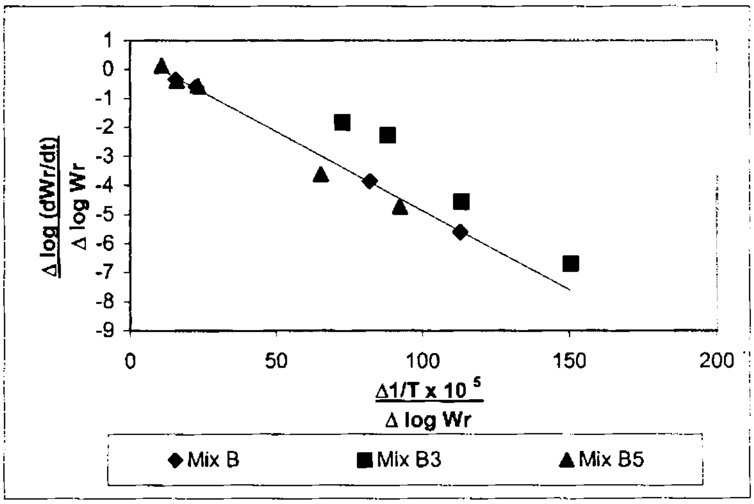

Figure 5.A.8. Freeman - Carroll Plot of Mix B, Mix B3, Mix B5

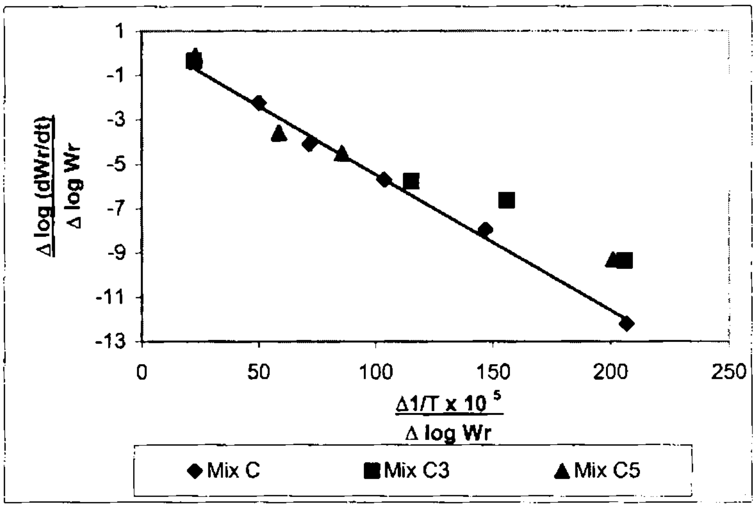

Figure 5.A.9. Freeman - Carroll Plot of Mix C, Mix C3, Mix C5

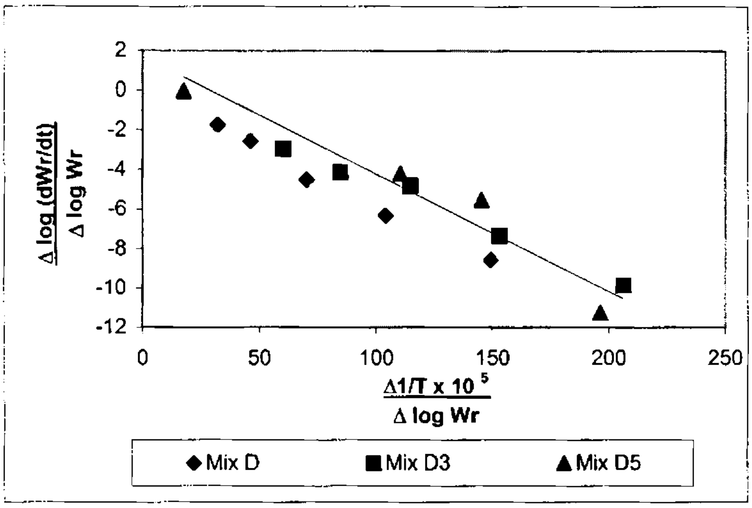

Figure 5.A.10. Freeman - Carroll Plot of Mix D, Mix D3, Mix D5

REFERENCES

1. Correa Ronaldo A., Nunes Regina C.R. and Lourenco Vera L., Polym. Degrad. Stab., **52** (3) (1996) 245.

2. Kutty S.K.N., Chaki T.K. and Nando G.B., Polym. Degrad. Stab., **38** (1992) 187.

3. Younan A.F., Ismail M.N. and Khalaf A.I., Polym. Degrad. Stab., **48** (1) (1995) 103.

4. Suhara F., Kutty S.K.N. and Nando G.B., Polym. Degrad. Stab., **61**(1) (1998) 9.

5. Rajeev R.S., De S.K., Bhowmick A.K. and John, Baby., Polym. Degrad .Stab., **79** (3) (2003) 449.

6. Stephanie R. Shield, Ghebrehiwet N. and Cebron Hendrix., Rubber Chemistry and Technology, **74** (5) (2001) 803.

7. Shanshad Ahmed, Basfar A.A. and Abdel Aziz M.M., Polym. Degrad. Stab., **67**(2) (2000) 319.

8. Freeman E.S and Carroll B., J. Phys Chem., **62** (1958) 394.

SECTION B

THERMAL STUDIES OF SBR - SHORT NYLON -6 FIBER COMPOSITE

Knowledge of thermal degradation characteristics of SBR/Nylon-6 composite at different fiber loading is important in many applications. Sea Cheon et al. studied the kinetics of the degradation of Styrene - Butadiene rubber[1]. Shamshad et al. reported thermal studies on sulphur, peroxide and radiation cured NBR and SBR gum vulcanizates and also with fillers like carbon black and silica[2].

This section describes thermal degradation studies of short Nylon -6 fiber reinforced SBR rubber composites with and without epoxy bonding agent using Thermogravimertic technique.

The formulation of the mixes is given in the Table 5.B.1. Sample preparation and test method employed are given in the chapter II. Thermogravimetric analyses were carried out on Universal V3 2B TA Instrument with a heating rate of 10°C/minute under nitrogen atmosphere

Table 5.B.1. Formulation of mixes

Ingredients	Mix No.											
	A	B	C	D	A3	B3	C3	D3	A5	B5	C5	D5
NBR	100	100	100	100	100	100	100	100	100	100	100	100
Nylon	0	10	20	30	0	10	20	30	0	10	20	30
Resin*	0	0	0	0	3	3	3	3	5	5	5	5

* Epoxy resin formed by 1:0.5 equivalent combination of epoxy resin and amine type hardener; (Zinc Oxide - 5 phr; Stearic acid -1.5 phr; CBS - 0.8 phr, Sulhur - 2 phr; TMTD -0.2 phr are common to all mixes)

The derivative TGA curves of mixes A-D and neat nylon fiber are shown in the Figure 5.B.1. The temperature of initiation of degradation (T_i), the peak rate of degradation and the corresponding temperature are given in the Table 5.B.2. It is clear from the figure that the degradation of SBR occurs in single step. The onset of degradation is at 325°C and peak degradation temperature (T_{max}) at 460.79°C for the gum compound. The neat nylon fiber degrades in single step with peak rate of degradation 47.13 %/min and corresponding temperature is 455.08°C. Residue remaining at 600°C is 1.255% for fiber. The fiber- containing mixes also show the similar pattern as that of gum vulcanizate. As fiber concentration increases the onset of degradation is shifted to higher temperature, and degradation starts at 338.89°C for 30 phr fiber loaded sample. This indicates that thermal stability of SBR is enhanced in the presence of Nylon fibers. Similar results in the case of short Kevlar fiber- reinforced thermoplastic polyurethane composite have been reported by Kutty et al. [3].

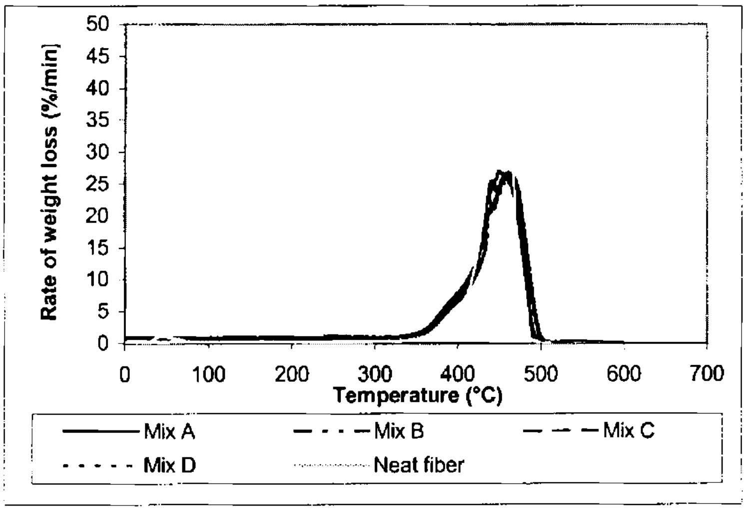

Figure 5.B.1. TGA traces of Mix A, Mix B, Mix C, Mix D

Table 5.B.2. Degradation characteristics of mixes A-D

Mix No	Temperature of Initiation (T_i) (°C)	Peak Temperature (T_{max}) (°C)	Peak rate of degradation (R_{max}) (%/min)	Residue at 600°C (%)
Mix A	325.00	460.79	27.00	5.822
Mix B	336.11	462.77	26.00	4.814
Mix C	356.22	449.84	27.00	4.556
Mix D	337.50	459.71	28.91	4.596
Neat Nylon fiber	362.50	455.08	47.13	1.255

Peak degradation temperature and peak rate of degradation remains more or less constant with fiber concentration. For 20 phr fiber filled sample the peak degradation temperature is 450°C. The percentage of residue remaining at 600°C is decreased when fiber is introduced to the matrix. This is because neat Nylon fiber has less residue at 600°C, hence the presence of fiber in the composite leads to lower residue. But further increase in fiber concentration residue remaining at 600°C decreases only marginally.

Figure 5.B.2. shows the Freeman-Carroll plots of gum and composites. As in the case of NBR composites order of the degradation can be evaluated from the plots of (Δ log dW/dt)/ Δ logW_r against Δ(1/T)/ Δ logW_r.

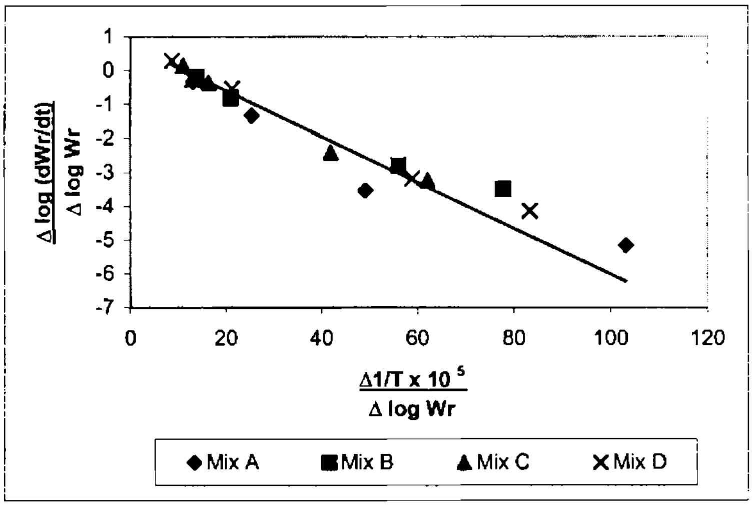

Figure 5.B.2. Freeman - Carroll Plot of Mix A, Mix B, Mix C, Mix D

The order can be obtained from the intercept of the plot. The intercepts show that the degradation of gum and composites follows first order kinetics. Similar results have been reported earlier[3-4].

5.B.1. Effect of Bonding Agent

The thermal degradation of the gum and the composites in the presence of epoxy resin based bonding agent were also studied. Figures 5.B.3. - 5.B.6. show the derivative TGA curves of gum and the composites with bonding agent. It is observed that all the mixes containing bonding agents also show single step degradation pattern. The T_i, T_{max} and peak rate of degradation are given in Table 5.B.3. For the gum compound the onset of degradation remains constant with resin concentration and maximum temperature of degradation is also not varied much in the presence of resin. The peak degradation rate and the residue at 600°C are marginally decreased when the resin is introduced to the SBR.

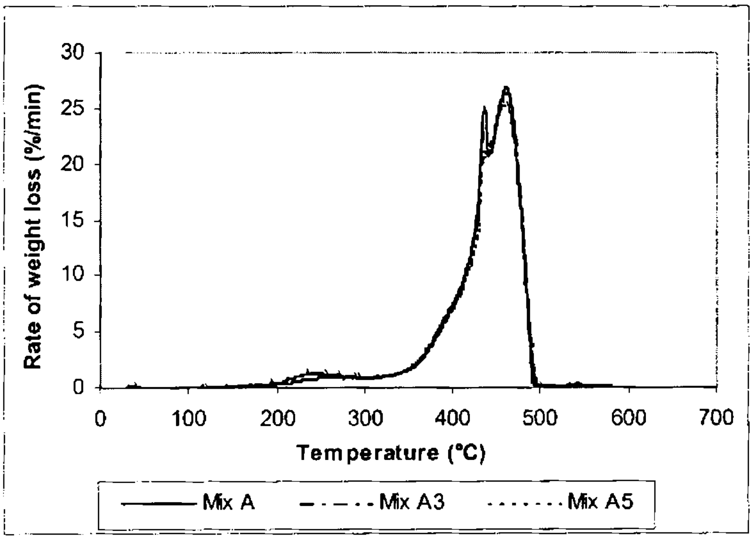

Figure 5.B.3. TGA traces of Mix A, Mix A3, Mix A5

Table 5.B.3. Degradation characteristics of various mixes

Mix No	Temperature of Initiation (T_i) (°C)	Peak Temperature (T_{max}) (°C)	Peak rate of degradation (%/min)	Residue at 600°C (%)
Mix A	325.00	460.79	27.00	5.822
Mix A3	325.00	456.37	25.25	5.043
Mix A5	325.00	460.09	26.50	5.120
Mix B	336.11	462.77	26.00	4.814
Mix B3	334.72	456.52	26.08	4.749
Mix B5	337.50	458.05	25.25	4.924
Mix C	337.50	449.84	27.0	4.556
Mix C3	337.50	450.65	26.00	4.396
Mix C5	336.23	455.96	25.75	5.524
Mix D	338.90	459.71	28.91	4.596
Mix D3	340.3	451.13	28.00	3.008
Mix D5	338.46	453.00	26.99	4.516

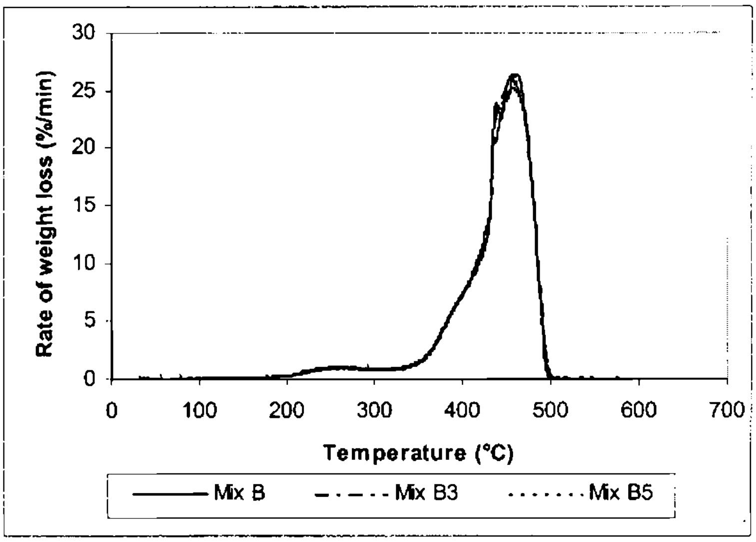

Figure 5.B.4. TGA traces of Mix B, Mix B3, Mix B5

In the case of composites the initiation of degradation (T_i) is shifted to higher temperature in the presence of bonding agent, indicating that the thermal stability is improved in the presence of resin for all the composites. T_{max} is found to be increasing with resin content for 20 phr fiber loaded sample and the peak rate of degradation is found to decrease with resin concentration.

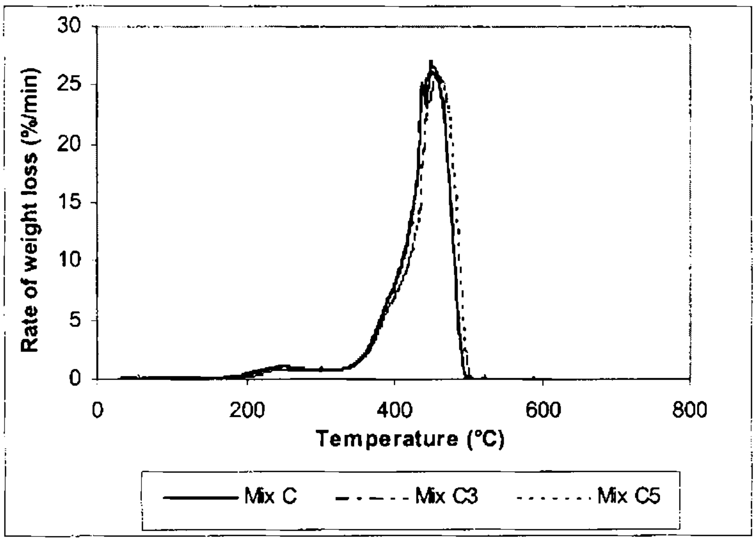

Figure 5.B.5. TGA traces of Mix C, Mix C3, Mix C5

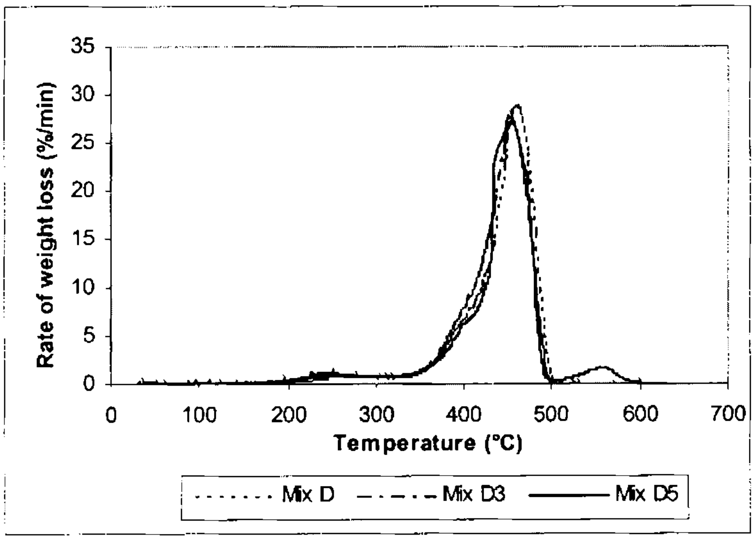

Figure 5.B.6. TGA traces of Mix D, Mix D3, Mix D5

The increase in T_{max} indicates a lower diffusion of the degraded products out of the matrix, as indicated by the lower peak rate of degradation observed in these temperatures. This may be due to the formation of more constrained matrix in the presence of resin. The T_{max} of 10 phr and 30 phr fiber decreases on introduction of resin, but further increase in resin concentration T_{max} increases marginally. Peak rate of degradation is not varied considerably with resin content. The residue remaining at 600°C remains more or less constant with resin concentration for all the composites.

The Freeman –Carroll plots for the degradation of gum and composite mixes with and without bonding agent is shown in the Figures 5.B.7. - 5.B.10. The presence of bonding agent does not alter the degradation kinetics and all the mixes follow first order kinetics. Similar results were reported in the case of polyester fiber –poly urethane elastomer with bonding agents based on polypropylene glycol and glycerol with 4,4' diphenyl methane diisocyanate by Suhara et al.[4].

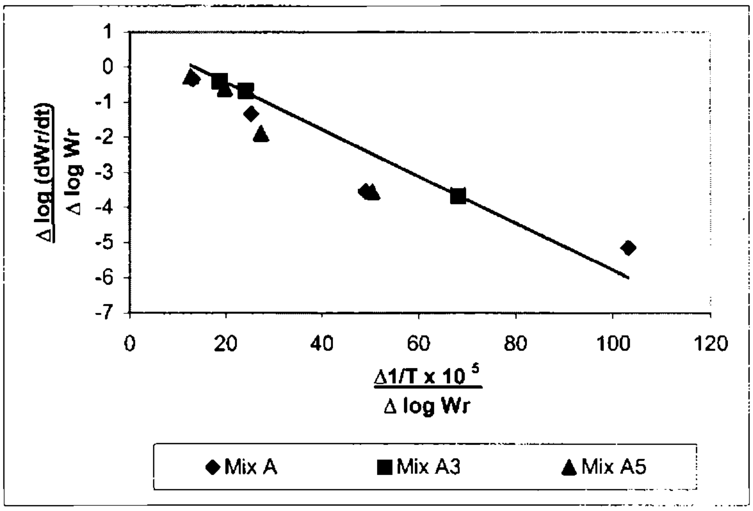

Figure 5.B.7. Freeman - Carroll Plot of Mix A, Mix A3, Mix A5

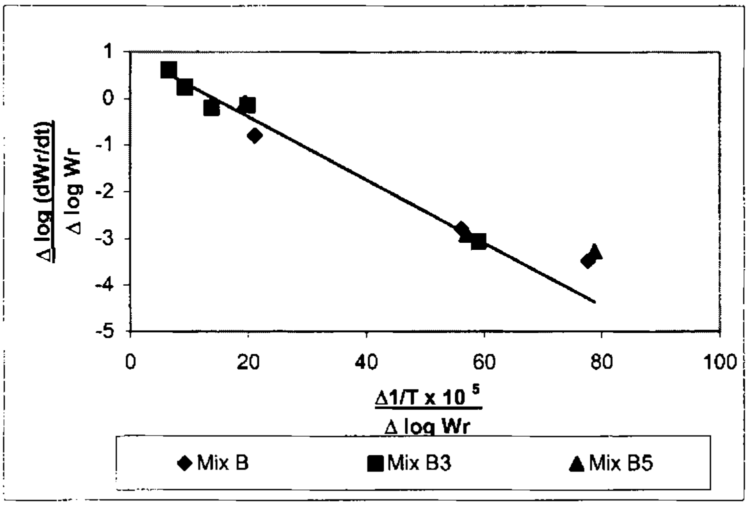

Figure 5.B.8. Freeman - Carroll Plot of Mix B, Mix B3, Mix B5

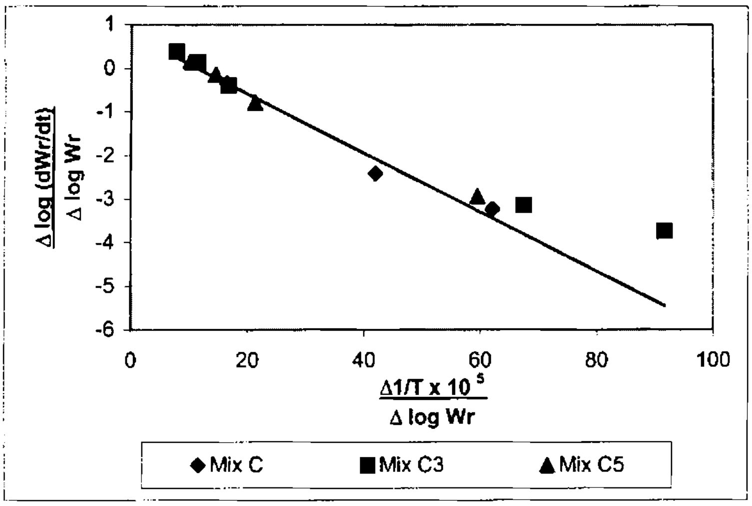

Figure 5.B.9. Freeman - Carroll Plot of Mix C, Mix C3, Mix C5

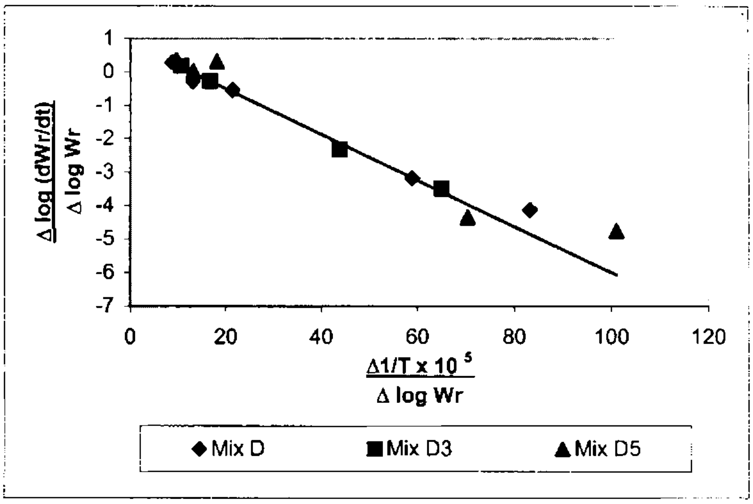

Figure 5.B.10. Freeman - Carroll Plot of Mix D, Mix D3, Mix D5

REFERENCES

1. Sea Cheon Oh, Hae Pyerong Lee, Sung-Chul Yi and Kyong Ok Yoo , J. of Fire Sciences, **17** (1999) 362.
2. Shanshad Ahmed, Basfar A.A. and Abdel Aziz M.M., Polym. Degrad. Stab., **67** (2) (2000) 319.
3. Kutty S.K.N., Chaki T.K. and Nando G.B., Polym. Degrad. Stab., **38** (1992) 187.
4. Suhara F., Kutty S.K.N. and Nando G.B., Polym. Degrad. Stab., **61**(1) (1998) 9.

Chapter VI

CONCLUSIONS

Short Nylon -6 fiber can be used to reinforce NBR, CR and SBR. Epoxy resin can successfully be used as interfacial bonding agent in short Nylon-6 fiber reinforced NBR and CR composites. Epoxy resin is not an effective bonding agent in the case of short Nylon-6 fiber - SBR composite. The major conclusions from the study can be summarized as:

Short Nylon -6 fiber improves most of the mechanical properties of NBR. The processability of NBR is affected in the presence of fiber. Minimum torque increases with fiber content. (Maximum - Minimum) torque improves in the presence of fiber. Scorch time and cure time reduces with fiber loading. The tensile strength, tear resistance, modulus and abrasion resistance improve with fiber loading. Elongation at break and resilience decreases as fiber concentration increases. Heat build up and ageing resistance increase with fiber concentration. Anisotropy in mechanical properties is shown by the composite. Tensile strength, tear resistance and abrasion resistance are higher in the longitudinal orientation of fiber

Epoxy resin is an effective interfacial bonding agent for short Nylon-6 - NBR composite. The mechanical properties of the composite are, in general, improved in the presence of epoxy resin. (Maximum - minimum) torque increases with resin concentration where as scorch time decreases. Minimum torque is not much affected by the presence of resin. Tensile strength and modulus increase while abrasion loss decreases as resin concentration increases. Tear strength and resilience decrease with resin concentration and compression set increases as resin content increases.

Minimum torque and (Maximum – Minimum) torque increases with short Nylon-6 fiber concentration in Neoprene rubber. Scorch safety and cure time are not much affected by the presence of short Nylon fibers. Tensile strength shows a minimum at 10 phr fiber loading and beyond this it increases with fiber loading. Tear strength, modulus and abrasion resistance increase with fiber content. Elongation at break decreases while heat build up increases as fiber concentration increases. Ageing resistance is increased with fiber content. The composite exhibits anisotropy in mechanical properties.

Introduction of resin to the short Nylon fiber – Neoprene composites improves mechanical properties. Minimum torque and cure time increase as the resin is introduced. Scorch time of the composites decrease with the resin content. Tensile strength and abrasion resistance increase as resin concentration increases. These properties are higher in longitudinal direction. Elongation at break and hardness of the composite are not much affected by the presence of resin. For higher fiber concentration modulus increases with resin content. Resilience and heat build up increases with resin concentration in the case of composites.

Short Nylon –6 fiber SBR composite show improvement in tensile strength, tear resistance, modulus and abrasion resistance when compared to virgin SBR. Elongation at break and compression set decrease with fiber concentration. Heat build up increases with fiber concentration. The composite registers less resistance to ageing when compared to gum vulcanizate. Anisotropy in mechanical properties is observed.

Tensile strength of the virgin SBR increases with resin concentration while the tensile strength of the short Nylon fiber – SBR composite decreases with resin concentration. Elongation at break increases with resin concentration. Modulus and tear resistance of the composites decrease as resin concentration increases. Abrasion loss shows considerable reduction with resin content in the case of gum vulcanizate; while a marginal rise in abrasion loss is observed in the case of composites. Ageing resistance is improved in the presence of resin. Epoxy is not an effective bonding agent for short Nylon-6-SBR composite.

Short Nylon fiber reinforced Acrylonitrile butadiene rubber composites exhibit pseudoplastic rheological behaviour, which decreases with temperature. The shear viscosity is increased in the presence of fibers and the effect is pronounced at lower shear rates. Introduction of the fiber reduces Newtonian behaviour. But at higher fiber loading and higher temperatures the flow behaviour index of composite melts approaches to that of gum compound. The fibers get oriented in the direction of flow at higher shear rates. Die swell is reduced in the presence of fibers.

NBR- short Nylon fiber composites with epoxy resin as bonding agent also show pseudoplasticity that decreases with increase in temperature. The shear viscosity increases with fiber concentration, especially at lower shear rates. Composite melts deviate from Newtonian behaviour as fiber concentration increases. Die swell is reduced in the presence of fibers. The melt viscosity is higher in the presence of bonding agent in the case of fiber-filled samples at all shear rates. Die swell is increased in the presence resin for composites at all shear rates.

Pseudoplastic behaviour is exhibited by short Nylon-6 fiber reinforced SBR composites. Pseudoplasicity decreases with temperature. The shear viscosity is increased with fiber loading and the effect is more prominent at lower shear rates. The presence of fibers reduces the temperature sensitivity of the flow at a given shear rate. The fibers get oriented in the direction of flow at higher shear rates. There is a reduction in die swell in the presence of fibers.

Epoxy resin is not altering the pseudoplastic nature of SBR - short Nylon fiber composites. The temperature sensitivity of the gum compound is reduced on introduction of fibers. The temperature sensitivity of the melts is also shear dependent and is lower at higher shear rates. Die swell is reduced in the presence of fibers. Relative viscosity increases with shear rate for composites at all temperatures. Temperature sensitivity of the mixes increases in the presence of bonding agent. Die swell is increased in the presence of resin at all shear rates and temperatures.

The thermal degradation of NBR gum compound and composites follows single step degradation pattern. Nylon -6 fiber increases the thermal stability of NBR, the optimum being 20 phr fiber loading. The presence of epoxy resin bonding agent improves the thermal stability of the virgin rubber and composites containing lower fiber loading. At higher fiber loading the resin is not effectively improving the thermal stability. The degradation of the virgin elastomer and the composites with and without bonding agents follow first order kinetics.

Thermal stability of the SBR is increased in the presence of short Nylon fiber. The thermal degradation of SBR gum compound and composites with and without epoxy bonding agent show single step degradation pattern. Thermal stability of SBR vulcanizate is not affected by the presence of bonding agent. Bonding agent improves the thermal stability of the composites and the effect is more pronounced at lower fiber concentrations. The degradation of the virgin elastomer and the composites with and without bonding agents follows first order kinetics.

List of Publications

1. Rheology of short Nylon-6 fiber reinforced Styrene Butadiene Rubber, Seema A. and Kutty S.K.N. Int. J. Polym. Mater. (Accpeted).
2. Cure characteristics and mechanical properties of short Nylon-6 fiber - Neoprene rubber composite containing epoxy resin as bonding agent, Seema A. and Kutty S.K.N., Polym. Plast. Technol. Eng., (communicated).
3. Studies on short Nylon-6 fiber -Neoprene rubber composite, Seema A. and Kutty S.K.N. Journal of Elastomers and Plastics (communicated).
4. Studies on effect of epoxy based bonding agent on the cure characteristics and mechanical properties of short Nylon fiber reinforced Acrylonitrile –Butadiene rubber composite, Seema A. and Kutty S.K.N., Journal of Applied Polymer Science, (communicated).
5. Rheology of short Nylon fiber reinforced Acrylonitrile butadiene rubber, Seema A. and Kutty S.K.N. Journal of Elastomers and Plastics (communicated).
6. Rheological characteristics of short Nylon fiber reinforced Acrylonitrile Butadiene rubber containing Epoxy resin as bonding agent, Seema A. and Kutty S.K.N., Polym. Plast. Technol. Eng., (communicated).
7. Rheological characteristics of short nylon fiber reinforced styrene butadiene rubber containing epoxy resin as bonding agent, Seema A. and Kutty S.K.N. Int. J. Polym. Mater. (communicated)
8. Thermal degradation of Short Nylon –6-fiber Acrylonitrile butadiene rubber composite, Seema A. and Kutty S.K.N, Polym Degrad Stab (communicated)
9. Thermal degradation of Short Nylon –6-fiber Styrene butadiene rubber composite, Seema A. and Kutty S.K.N, Polym Degrad Stab (communicated)

CONFERENCES

1. Epoxy resin as bonding agent in Nylon-6 / chloroprene composite, Seema A. and Kutty S.K.N., International seminar on Advances in Polymer Technology, Jan 16-17, 2004, Kochi, India

List Of Abbreviations

γ_a	Apparent Shear rate
γ_w	Shear rate at wall
η	Shear viscosity
τ_w	Shear stress at wall
η_b	Viscosity with bonding agent
η_0	Viscosity without bonding agent
η_r	Relative viscosity
A_b	Activation energy with bonding agent
A_0	Activation energy without bonding agent
A_r	Relative Activation Energy
ASTM	American society for testing and Materials
CR	Neoprene rubber
CBS	N-Cyclohexy-2-benzthiazylsulphenamide
D_b	Die swell ratio with bonding agent
D_0	Die swell ratio without bonding agent
d_c	Diameter of capillary
d_e	Diameter of extrudate
D_r	Relative die swell
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

L	Longitudinal
L/D	Length to diameter ratio
LDPE	Low density polyethylene
MBTS	2,2'-benzothiazyl disulfide
MPa	Mega Pascal
μm	Micrometer
n'	Flow behaviour index
N.m	Newton meter
NR	Natural rubber
NBR	Nitrile rubber
PE	Polyethylene
PET	Polyethylene terephthalate
PU	Polyurethane
RFL	Resorcinol formaldehyde latex
SEM	Scanning Electron microscope
SBR	Styrene butadiene rubber
T.	Transverse
TMTD	Tetramethylthiuramdisulfide
TGA	Thermogravimetric analysis
T_i	Temperature of initiation
Tmax – Tmin	Difference between maximum and minimum torque
TPU	Thermoplastic polyurethane
TPNR	Thermoplastic natural rubber
UTM	Universal testing machine
WTR	Whole tyre reclaim
XNBR	Carboxylated nitrile rubber