Development and Characterisation of Nylon Fibre Reinforced NBR Composites

Thesis submitted to

UNIVERSITY OF CALICUT

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

DOCTOR OF PHILOSOPHY

in

CHEMISTRY
under the

FACULTY OF SCIENCE

by

RAJESH C.

forwarded

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT

AUGUST 2007

Certificate

This is to certify that the thesis entitled '**Development and characterisation of nylon fibre reinforced NBR composites**' is an authentic record of the research work carried out by Mr. Rajesh C. under our joint supervision and guidance in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy in Chemistry under the Faculty of Science, University of Calicut, Kerala. The work presented in this thesis has not been presented/ reported earlier for any degree or diploma of any University/ Institute. It is also certified that Mr. Rajesh C. has fulfilled the course requirements and passed the qualifying examination for the Ph. D. degree of the University of Calicut.

Dr E. Purushothaman
Professor
Department of Chemistry
University of Calicut

Unnikrishnan
Dr G. Unnikrishnan
Asst. Professor
Polymer Science and Technology Laboratory
National Institute of Technology Calicut

Declaration

I hereby declare that the thesis entitled '**Development and characterisation of nylon fibre reinforced NBR composites**' is an authentic record of the research work carried out by me under the joint supervision and guidance of Dr E. Purushothaman, Professor, Department of Chemistry, University of Calicut, Kerala and Dr G. Unnikrishnan, Assistant Professor, Polymer Science and Technology Laboratory, National Institute of Technology Calicut, Kerala and that no part of this work has been presented/ reported earlier for any degree or diploma of any University/ Institute.

Rajesh C.

University of Calicut
06-08-2007

Acknowledgements

I express my heartfelt thanks and indebtedness to my supervising teachers **Dr E. Purushothaman**, Professor, Department of Chemistry, University of Calicut, Kerala and **Dr G. Unnikrishnan**, Assistant Professor, Polymer Science and Technology Laboratory, National Institute of Technology Calicut, Kerala for their invaluable help, sincere guidance and constructive criticism, which paved the way for the successful completion of this research work. I am really grateful to them for their fruitful instructions, timely advices and constant encouragement without which this work would not have been completed.

I am extremely thankful to **Prof. (Dr) K. Krishnankutty**, Head, Department of Chemistry, University of Calicut, Kerala for providing me with the facilities to carry out the research programme. I am also thankful to the former Heads **Prof. (Dr) M. P. Kannan** and **Prof. (Dr) K. K. Aravindakshan** for the guidance during my Ph.D programme.

I express my sincere thanks to **Prof. (Dr) G.R.C. Reddy**, Director, National Institute of Technology, Calicut (NITC), Kerala. I am also thankful to the former Directors **Prof. (Dr) M. P. Chandrasekharan** and **Prof. (Dr) S. S. Gokhale** for their help during the course of this investigation.

I am grateful to **Prof (Dr) Sabu Thomas**, School of Chemical Sciences, M.G. University, Kottayam, Kerala for his constructive suggestions and help during my research work. I am thankful to **Dr Lisa Sreejith** and **Dr Soney Varghese**, Department of Science and Humanities (DSH), NITC for the help rendered to me.

My sincere thanks go to **Ms. M. Louly**, Deputy Director, **Mr. R. Arjunan Pillai**, JSO and other staff of CFSC Manjeri, Kerala for providing me with their facilities and help. I am thankful to **Dr K.T. Thomas**, Deputy Director (Rubber Technology), Rubber Research Institute of India, Kottayam, Kerala and **Mr. K. R. Dayas**, Director, Centre for Materials for Electronics Technology (C-MET), Thrissur, Kerala for providing me with the facilities for composite testing.

I would like to acknowledge with thanks all the benefits I have gained from the discussions with **Dr A. Seema**, Scientist, C-MET, Thrissur, Kerala, **Dr Rosamma Alex** and **Dr Siby Varghese** (Rubber Technologists) and Mr. **John Britto**, (Radiological Safety Officer, RVNRL unit of Rubber Technology Division) of Rubber Research Institute of India, Kottayam, Kerala.

I remember with gratitude the help provided by the librarian and the staff of CHMK Library, University of Calicut. I am also thankful to the librarians of NITC, MG University, Kottayam and RRII, Kottayam, Kerala. The help rendered by all the teaching and non-teaching staff of Department of Chemistry, University of Calicut and DSH, NITC is also thankfully acknowledged.

It is a pleasure to pen down the nice time and support I had in working with my co-researchers **Dr A. Sujith, Dr A. P. Haseena, Dr C. K. Radhakrishnan, Dr K. Priya Dasan, Mr. K. Habeeb Rahiman**, **Ms. Prajithakumari, Mr. B. Ganesh**, **Ms. Shyla George**, **Mr. P. A. Sreekumar**, **Mr. K. C. Manoj**,

Mr. T. Hanas, **Mr. P. Aneesh**, **Mr. Sooraj Varma, Ms. M. Padmini** and **Mr. C. Ranjith**. I would like to remember with gratitude the warm support received from all my considerate teachers and loving friends.

I bow my head before the memories of my father who passed away during the course of my research work. I am deeply indebted to all my family members especially to my mother and wife for their unwavering moral support to complete this work.

University of Calicut
06-08-2007

Rajesh C.

Glossary of Terms

α - Swelling coefficient

β - Lattice constant

∂ - Conductivity

χ - Interaction parameter

θ - Angle between fibre orientation and direction of applied stress

ω - Angular frequency

ν - Frequency

Ω - Volume resistivity

σ_c - Stress developed in composite

σ_f - Stress developed in fibres

σ_{fb} - Ultimate fibre strength

σ_m - Stress in matrix

ε_c - Strain in composite

ε_f - Strain in fibres

ε_m - Strain in matrix

δ_r - Solubility parameter of rubber

δ_s - Solubility parameter of solvent

ρ_s - Density of solvent

ϕ_f - Volume fraction of fibre

ϕ_m - Volume fraction of matrix

τ_y - Matrix yield stress in shear

ASTM - American society for testing and materials

a_θ - Ratio of swelling occurred in composites before and after swelling in widthwise direction

a_L - Ratio of swelling occurred in composites before and after swelling in lengthwise direction

a_T - Ratio of swelling occurred in composite before and after swelling in breadthwise direction

a_{SF} - Shift factor

BR - Polybutadiene rubber

C - Capacitance

CR - Chloroprene rubber

D - Weight of specimen after desorption

DCP - Dicumyl peroxide

DMA - Dynamic mechanical analysis

DMF - N, N-dimethyl formamide

DMSO - Dimethyl sulphoxide

DSC - Differential scanning calorimetry

DTG - Differential thermogravimetry

d_f - Diameter of fibre

E' - Dielectric constant

E'' - Dielectric loss factor

E_0 - Permittivity of air

E_a - Energy of activation for glass transition

E_D - Energy of activation for thermal degradation

EPM - Ethylene propylene co-polymer

EPDM - Ethylene propylene diene rubber

F - Applied load

G' - Storage modulus

G'' - Loss modulus

G'_c - Storage modulus of composite

G'_m - Storage modulus of matrix

l_c - Critical fibre length

$\overline{L}_n$ - Number-average fibre length

$\overline{L}_w$ - Weight-average fibre length

$\overline{L}_w / \overline{L}_n$ - Polydispersity index

MBTS - Mercapto benzothiazyl disulphide

M_{CL} - Molecular mass of polymer between crosslinks

M_c - Tensile modulus of composite

M_f - Tensile modulus of fibre

M_H - Maximum torque

M_L - Minimum torque

M_m - Tensile modulus of matrix

M_s - Molecular weight of solvent

n - Cross-link density

NBR - Nitrile rubber

N_i - Number of fibres having length L_i

NR - Natural rubber

phr - Parts per hundred rubber

Q_t - Mole percentage uptake

r - Refractive index of material

$\overline{r_i^2} / \overline{r_o^2}$ - Front factor

SEM - Scanning electron microscopy

SBR - Styrene butadiene rubber

t - Thickness of specimen

T - Absolute temperature

t_{90} - Optimum cure time

tan δ - Dissipation or damping factor

$\tan \delta_c$	-	Dissipation or damping factor of composite
$\tan \delta_f$	-	Dissipation or damping factor of fibre
$\tan \delta_m$	-	Dissipation or damping factor of matrix
T_c	-	Tensile strength of composite
T_f	-	Tensile strength of fibre
T_g	-	Glass transition temperature
TG	-	Thermogravimetry
T_m	-	Tensile strength of matrix
TMTD	-	Tetramethyl thiuram disulphide
V_0	-	Volume fraction of rubber in dry specimen (before swelling)
$V_0 - V_r$	-	Change in volume fraction of rubber before and after swelling
V_c	-	Volume of composite
V_f	-	Volume fraction of fibre
V_m	-	Volume fraction of matrix
V_r	-	Volume fraction of rubber after desorption of composites
V_{r0}	-	Volume fraction of rubber in unfilled vulcanisate
V_s	-	Molar volume of solvent
V_T	-	Ratio of change in volume fraction of rubber before and after swelling to volume fraction of rubber before swelling
W_1	-	Initial weight of sample
W_2	-	Final or swollen weight of sample
x	-	Parameter determining stress transfer between fibre and matrix
X	-	Percentage loss of weight of different composite systems at different temperatures
X_0	-	Pre-exponential factor in Arrhenius relationship

Contents

Page

Preface

Chapter 1

Chapter 3

Chapter 4

Chapter 5

Chapter 6

Chapter 7

Chapter 8

Chapter 9

Chapter 10

Preface

Polymer composites are materials, with light weight, high strength to weight ratio and stiffness, which have come a long way in replacing the conventional monolithic materials. Short fibre reinforced rubber composites combine the stiffness of the fibres with the elasticity of the rubber. They are high performance engineering materials with a wide range of applications. Recently, increased attention has been focused on short fibre rubber composites to expand the scale of properties and applications of established products and to find novel applications to meet the demands from market and industry.

Acrylonitrile butadiene rubber (NBR) is an elastomer extensively used for many industrial applications particularly in the automobile sector. By selecting this elastomer with the appropriate acrylonitrile content in balance with other properties, the rubber compounder can use it in a spectrum of areas requiring oil, fuel, and chemical resistance. Nylon 6 fibre is a semi-crystalline polyamide having high tensile strength and modulus. The goal of the present research programme is to develop and characterise nylon 6 fibre reinforced NBR composites.

The contents of this thesis are presented in ten chapters. The basic concepts of the development of fibre reinforced rubber composite materials, their properties and performance along with a review of the related earlier studies are presented in Chapter 1 of the thesis. The details of the materials used for the preparation of the composites and the experimental procedures adopted for their characterisation are discussed in Chapter 2.

The processing characteristics and mechanical properties of nylon 6/NBR composites are presented in Chapter 3. The modification of the interface of the composite systems by using two different bonding agents and the subsequent improvement in mechanical properties have been discussed in Chapter 4. The results of the investigation of the interfacial adhesion in nylon 6/NBR composites, through restricted equilibrium swelling technique, are presented in Chapter 5. This chapter also describes the results of anisotropic swelling studies carried out to analyse the extent of fibre orientation and fibre–matrix interaction. Chapter 6 presents the results of the evaluation of dielectric properties of the composites. The details of the thermal characterisation of the composites, by thermogravimetry (TG) and differential scanning calorimetry (DSC), are given in Chapter 7. The dynamic mechanical characterisation of nylon 6/NBR composite systems has been presented in Chapter 8. An account of the examination of the ageing characteristics of the composites, after exposing them to various degrading agents such as heat, gamma (γ) radiation and ozone, is given in Chapter 9. The important conclusions based on the present investigation and the future scope of the studies on nylon 6/ NBR composites are presented in Chapter 10.

Chapter 1

Introduction

Abstract

This chapter gives a general account of the different types of composite materials with special focus on fibre reinforced rubber composites. The advantages of short fibre reinforcement and the properties and performance of composites with rubber matrices have been discussed. A review of the earlier studies in this field and the current status have been included. The scope and objectives of the present work have also been highlighted.

1.1 COMPOSITES

The last few decades have witnessed a tremendous growth in the rate of production and novel applications of polymers. For many uses, they are modified or custom engineered to improve specific properties. Reinforcements play a major role in this regard which resulted in the development of highly useful materials known as composites.

Basically, composites are heterogeneous structural materials which are made up of a matrix containing reinforcing agents and are often better suited for specific applications than any of the original components. Nowadays, composites have a premier role among engineering materials with the advantages such as light weight, corrosion resistance, high fatigue strength and faster assembly. Historical examples of composites are abundant in literature. The bricks fashioned by the ancient Egyptians from mud and straw, and laminated metals used in forging sword are the examples of composite materials used by ancient civilisations[1]. The first man made composite appeared around 500 BC in the Middle East, where pitch was used as a binder for reeds in boat building. In the modern world, composites are extensively used in aircraft structures, electronic packaging to medical equipment and space vehicle to home building[2, 3]. More and more researchers are now concentrating their attention onto these materials due to the wide range of applications offered by them.

1.2 COMPONENTS OF COMPOSITE MATERIALS

The matrix and the reinforcement constitute the two chief component phases of composites. Matrix is the continuous phase into which the reinforcement or the discontinuous phase is incorporated. The region between these two components is known as interface. Figure 1.1 shows a schematic representation of a composite system.

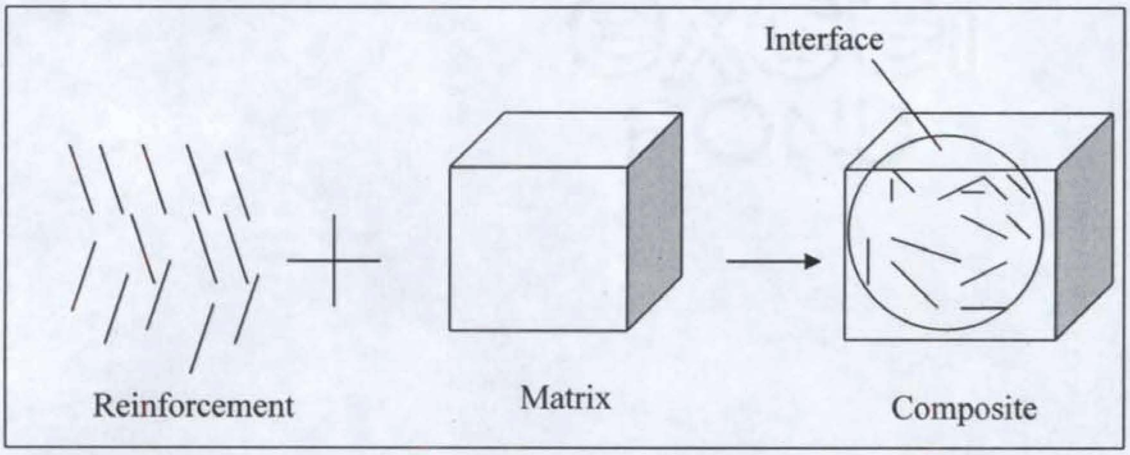
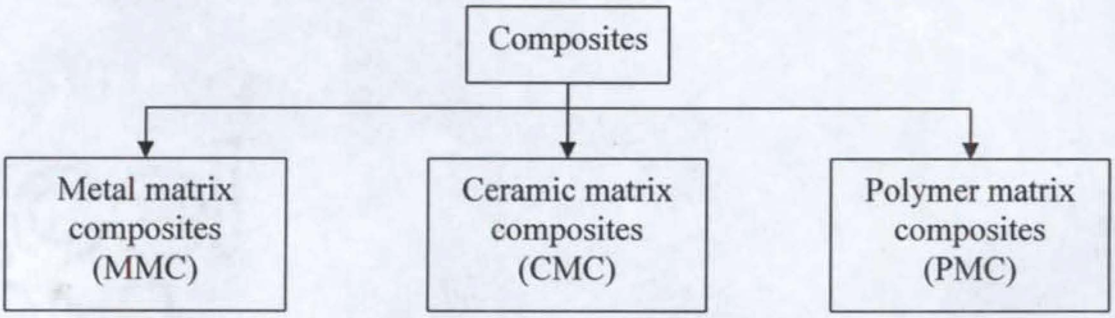


Figure 1.1 Schematic representation of composite

1.2.1 Matrix phase

The matrix is generally continuous, binding the reinforcements together, and acts as a medium by which an externally applied stress is transmitted to the reinforcement. Only a very small proportion of an applied load is sustained by the matrix phase. They maintain the reinforcement phase separately in the desired orientation and thereby contribute to the cohesion of the product. They protect the reinforcing phase from abrasion and degradation by the influence of different environmental conditions. Composites are generally classified into three on the basis of the matrix phase, as shown in Scheme 1.1.



Scheme 1.1 Classification of composites based on matrix phase

1.2.1.1 Metal matrix composites (MMC)

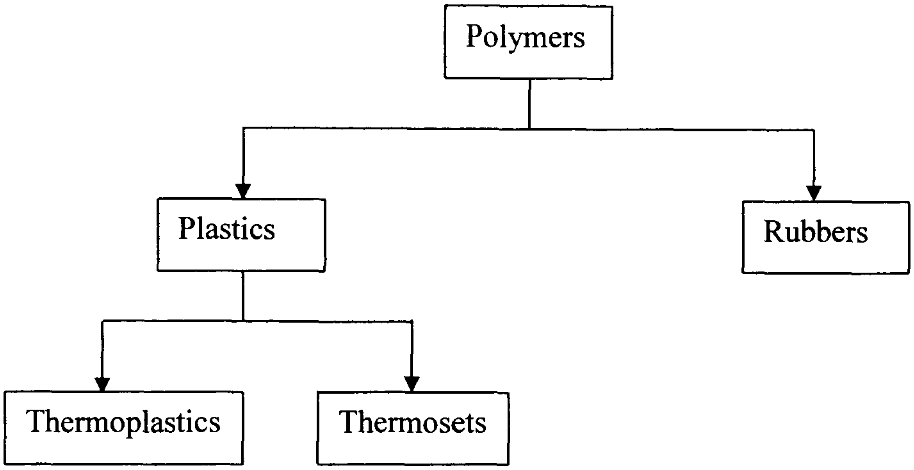
Aluminium, magnesium, lead, copper, tungsten and nickel have been extensively used for making composites. The reinforcement phases in metal matrix composite systems are either metallic or non-oxide ceramic (silicon carbide, carbon and boron) or oxide ceramic (alumina and glass). MMCs have higher temperature resistance than other composite systems and are preferred for service temperatures above 150 °C. They have good electrical and thermal conductivities. Most of the current applications of MMCs are in automotive and space related areas.

1.2.1.2 Ceramic matrix composites (CMC)

Ceramics are strongly bonded materials with ionic and covalent character, which results in high strength and hardness. The development of composite materials based on ceramics has received considerable interest in the recent past, especially with ceramic fibres, since they can be operated at very high temperatures of about 1800 °C. Of late, CMCs such as glass, glass-ceramic and oxide ceramic matrices have gained importance. Some of the most promising applications for CMCs are in the areas of cutting tools and in heat engines where the components require resistance to aggressive environment.

1.2.1.3 Polymer matrix composites (PMC)

Many of the composite materials developed today contain polymers as the matrix phase. Scheme 1.2 represents the classification of polymer matrices. Table 1.1 lists the properties of some of the important polymeric matrices.



Scheme 1.2 Classification of polymer matrices

Table 1.1 Properties of some matrix materials

Polymer	Specific gravity	Young's modulus (GPa)	Tensile strength (GPa)	Extension to break (%)	Specific Young's modulus (GPa)	Specific tensile strength (GPa)
Thermoset						
Epoxy	1.20	4.5	0.08	3	3.75	0.07
Polyester	1.35	3.5	0.06	2	2.59	0.04
Thermoplastic						
Polypropylene	0.90	1.2	0.03*	> 300	1.33	0.03
Polycarbonate	1.10	2.3	0.06*	75	2.09	0.05
Elastomers						
Natural rubber	0.97	0.0013	0.017-0.025*	400-800	-	-
Styrene-butadiene rubber	0.98	0.0016	0.014-0.030	450-500	-	-
Nitrile rubber	1.10	0.0015	0.016	400-600	0.009	0.02

* Yield strength (Source: Reference 4)

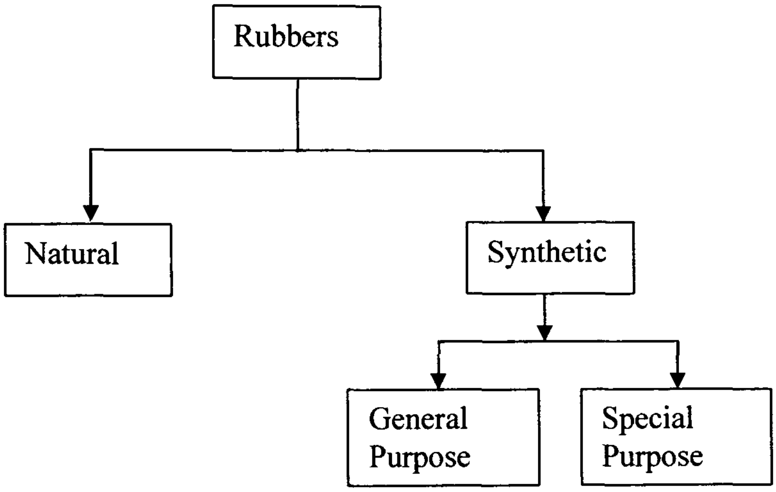
(i) Plastics based composites

Plastics are polymeric materials, having giant organic molecules, which can be transformed into desired shapes through extrusion, moulding, casting or spinning.

The starting materials are resins in the form of pellets, powders or solutions from which the finished plastics are formed. Basically, plastics are divided into two according to their structure and thermal behaviour. These are *thermoplastics* and *thermosetting resins*[5]. The key difference between thermoplastic and more traditional thermoset based composites lies in the behaviour of the matrix during processing. The thermoplastic matrix need not undergo a cure process to achieve its final mechanical properties; all that required is melting, shaping and subsequent solidification. In thermosetting polymers, the liquid resins are converted into hard brittle solids by chemical crosslinking which leads to the formation of a tightly bound three-dimensional network of chains. When thermoplastics form the matrix, the composite products can be manufactured by high speed processes. The range of thermoplastics used for composite fabrication includes polyethylene, polypropylene, polyethylene terephthalate, polyamides, polyvinyl chloride, polyimides, polycarbonate etc [6-8]. Among thermosetting matrices polyester resins, epoxy resins, vinyl ester resins, phenolics, silicones and urethanes are important[9-11].

(ii) Rubber composites

Rubber is a versatile and adaptable material that has been successfully used for many years. Rubbers exhibit many unique characteristics which make them ideal for the selection as matrices in novel composite materials[12]. They stretch rapidly and considerably under tension, reaching high elongations (500-1000%) with low damping. They show high tensile strength and modulus when fully stretched. Rubbers usually exhibit the phenomena of resilience and low permanent set[13]. The resilience of rubbers is related to the molecular flexibility, amorphous structure and very low intermolecular interactions. Unlike plastics, a wide variety of flexible products can be made by using elastomers as the matrix phase [14]. Scheme 1.3 represents the classification of rubbers.



Scheme 1.3 Classification of rubbers

(a) Natural rubber (NR)

Natural rubber is a high molecular weight polymer of isoprene in which most of the isoprene units are in the *cis*-1,4 configuration. The major source of NR is the latex from the bark of *Hevea brasiliensis*. The latex is an aqueous dispersion of rubber, containing 25-40% rubber hydrocarbon. NR has high strength, low hysteresis, tear resistance, abrasion and flex cracking. However, it is readily attacked by solvents, gasoline etc.

(b) Synthetic rubbers

Polymeric materials prepared artificially which exhibit many interesting properties including elasticity and flexibility are termed as synthetic rubbers. The demand for these materials is increasing in the manufacturing sector day by day.

General purpose synthetic rubbers: Among the general purpose rubbers styrene butadiene rubber (SBR), polybutadiene rubber (BR), ethylene propylene rubbers (EPM/EPDM), polyisoprene rubbers (IR) and isobutylene isoprene rubber or butyl rubber (IIR) are the most commonly used.

- *Styrene butadiene rubber (SBR)*: It is a copolymer of butadiene and styrene. It is similar in many ways to NR and is the first widely used synthetic one. It tops all the elastomers in volume of use mainly because of the low cost and use in auto tyres. In general, it has poor oil and chemical resistance. A wide range of property grades are produced by varying the relating amounts of styrene and butadiene. Although they have excellent impact and abrasion resistance, they are somewhat below NR in tensile strength, resilience, hysteresis and some other mechanical properties.

- *Polybutadiene rubber (BR)*: Polybutadiene is a homopolymer of *cis*-1,4-butadiene. Both solution and emulsion polymerisation methods are used for commercial production. BR has very good mechanical properties especially at low temperatures. It retains its rubberiness for a wide range of temperature. BR has high air permeability, low heat build up, high resilience, better flex resistance etc. This rubber is compatible in all proportions with NR and SBR.

- *Ethylene propylene rubber (EPM/EPDM)*: They are available in two types; EPM (ethylene propylene co-polymer) and EPDM (ethylene propylene diene monomer). The raw materials required for the industrial production are ethylene, propylene and catalysts. These rubbers have remarkable resistance to ozone and UV radiation. They have good weather resistance, excellent electrical properties and can be rapidly cured by peroxide.

- *Poly isoprene rubber (IR)*: This is a synthetic rubber similar to NR in processing and properties. Its notable characteristics are low hysteresis, low heat build up, low moisture absorption and high tear resistance. It has excellent flow characteristics and can easily be injection moulded.

- *Butyl Rubber (IIR)*: It is a copolymer of isobutylene and isoprene and is one of the lowest priced synthetic rubbers. IIR has excellent resistance to abrasion, tear and flex. It is noted for low gas and air permeability.

Special purpose synthetic rubbers: They are used in specific applications which require resistance to solvents, fire and heat[15]. These include poly chloroprene rubbers, fluorocarbon rubbers, and nitrile rubbers.

- *Polychloroprene rubber or Neoprene (CR):* Neoprene is the first commercial synthetic rubber. Its resistance to oils, chemicals, sunlight and ozone is outstanding. It has low permeability of gases compared to NR.
- *Fluorocarbon rubbers:* These fluorine containing rubbers have the highest resistance to oxidation, chemicals, oils, solvents and heat among elastomers. They are highest in price also. They can be used continuously at temperatures over 260 °C. They do not support combustion. However, their mechanical and electrical properties are only moderate.
- *Acrylonitrile butadiene rubber or Nitrile rubber (NBR)*: Nitrile rubbers known originally as Buna N are copolymers of acrylonitrile and butadiene. They are mainly known for their outstanding resistance to oils and fuels at both normal and elevated temperatures. Their properties can be altered by varying the ratio of the monomers. In general, as the acrylonitrile content increases oil resistance, tensile strength and processability improve while resilience, compression set and hysteresis characteristics deteriorate.

(c) Rubber vulcanisation

The process by which a network of crosslinks is introduced for an elastomer is called vulcanisation (curing). The profound effect of vulcanisation is that it transforms an elastomer, from a weak thermoplastic mass without useful mechanical properties, into a strong, elastic, tough rubber. Vulcanisation decreases the flow of an elastomer, increases the tensile strength and modulus but preserves its extensibility. The process was discovered by Goodyear in his experiment where rubber was heated with a small quantity of sulphur. The curing of rubber with sulphur alone is quite slow and no longer commercially practiced. It can be speeded up many folds by the addition of small amount of organic or inorganic compounds known as *accelerators*. Many accelerators require the presence of still other chemicals known as *activators* before their full effects are realised. These activators are usually metallic oxides such as zinc oxide. They function best in the presence of rubber soluble soaps, which may be formed during the curing reaction from the activator and a fatty acid. The most efficient combination of chemicals for sulphur vulcanisation includes sulphur, an organic accelerator, a metallic oxide and a fatty acid. The exact mechanism of curing reactions is still under debate. Both free radical and ionic intermediates have been postulated. Apart from sulphur, many non-sulphur vulcanising systems can be used. Dicumyl peroxide (DCP) is one among them.

(d) Compounding

The raw rubber coming to the factory in bales or boxes has practically no value, but it can be compounded (mixed) with numerous chemicals and materials such as vulcanising agents, accelerators, fillers, antioxidants and lubricants. Compounding of raw rubber involves milling down the crumbs into pliable sheets and then incorporating the compounding ingredients. The process is usually done either on a two roll mixing mill or in a Banburry internal mixer. In mill mixing, the operator first puts the rubber on the rolls where it is torn and kneaded. When the rubber has become sufficiently soft the compounding ingredients, all carefully weighed in advance, are added. The mill continues to operate until complete dispersion of the ingredients is accomplished and a uniform roll is secured. When this point is reached, the rubber is usually cut off the mixing rolls into slabs which are dusted with talc to prevent their sticking together. The nature of the uncured compound determines largely how it will have to be shaped to fit the mould cavity for proper flow. The plasticity of the uncured compound also frequently dictates the type of machinery that can be utilised in its preparation for the mould.

(e) Processing techniques

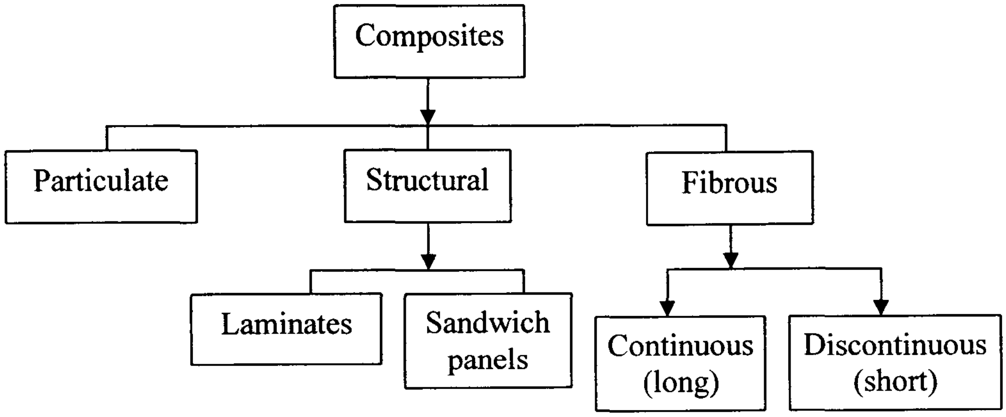
Elastomeric materials are used in many forms such as rods, tubes, sheets and also as moulded and fabricated articles. Therefore, there are variety of ways in which the compounded materials can be processed and converted into finished products. These include calendering and tubing.

- *Calendering*: The calendering process is employed to produce continuous films and sheets. The main part of a calendering machine is a set of highly polished metal rollers rotating in opposite directions with provision for precise adjustment of the gap between them. The gap between the rollers determines the thickness of the sheet calendered out. Compounded elastomeric material is fed between the rollers which are maintained at an elevated temperature and the sheet emerging from the rollers is cooled by passing through cold rollers. The sheets are finally wound up in rolls.

- *Tubing or extruding*: Tubing is the most economical and widely used method for the preparation of rubber goods. The compound is first warmed up on a mill, and then fed directly to the tubing machine (often called an extruder) which extrudes the rubber to a shape and size determined by the die mounted on the front of the pressure barrel. Extruded soft rubber is used in the manufacture of inner tubes, tyre treads, rubber hoses, channel rubbers, gaskets, and thousands of other products.

1.2.2 Reinforcing agents

The reinforcement phase is generally the load carrying agent of the composites. To a significant degree, the reinforcement determines the strength and stiffness of the composite systems. A reinforcing filler in rubber can be defined as the material that is capable of increasing the modulus, tensile strength, tear strength, abrasion resistance etc and improving the heat dissipation properties. The reinforcement phase resists the breaking and bending under an applied load and also protects the matrix from sudden failure. The classification of composites on the basis of nature of the reinforcement phase can be summarized as shown in Scheme 1.4.



Scheme 1.4 Classification of composites on the basis of reinforcement phase

1.2.2.1 Particulate composites

Particulate composites consist of particles dispersed in a matrix. In the composites, the particle dimensions are approximately the same in all directions (equi-axed). Particles have no preferred directions and are mainly used to improve the properties or to lower the cost of the products. Certain particulate fillers like clay, silica etc. are non-reinforcing whereas carbon black and some others are reinforcing in nature. Many theories have been put forward regarding the mechanism of reinforcement in rubbers. Some have postulated that chemical interactions occur between filler and elastomer during mixing and/or vulcanisation. Studies on the mechanism of carbon black reinforcement in rubber vulcanisate have been conducted[16]. Polymer-filler interactions are to be optimised in order to achieve certain properties of rubber compounds[17-19]. Depending upon the reinforcement mechanism, particle reinforced composites are further classified into two: *large particle* and *dispersion strengthened* composites. For most of the large particle composites the particle phase is harder and stiffer than the matrix. The reinforcing particles tend to restrain the movement of the matrix phase in the vicinity of each particle. The degree of reinforcement or improvement in mechanical properties depends on the strong bonding at the matrix/particle interface. These large particle reinforcements are used with all the three major types of matrices, *viz.* metals, ceramics and polymers. Dispersion strengthened composites are composed of metals and metal alloys strengthened and hardened by the uniform dispersion of several volume per cent of fine particles of very hard and inert materials. The strengthening mechanism involves interactions between the particles and dislocations within the matrix.

1.2.2.2 Structural composites

Structural composites are composed of both homogeneous and heterogeneous materials, the properties of which depend not only on the properties of the constituent materials but also on the geometrical design of the various structural elements. Two important structural composites are: (a) Laminar composites, and (b) Sandwich composites. Laminar composite is composed of two-dimensional sheets or panels those have a preferred high strength direction. The different layers are stacked and subsequently cemented together such that the orientation of the high strength direction varies with each successive layer. Laminates may also be constructed by using fabric materials such as cotton, paper or woven glass fibres embedded in a plastic matrix. Sandwich panels consist of two strong outer sheets or faces separated by a layer of less dense material or core which has lower stiffness and lower strength. The faces bear most of the in-plane loading. The core separates the faces and resists deformation perpendicular to the face plane and provides a certain degree of shear rigidity along the planes which are perpendicular to the faces.

1.2.2.3 Fibre reinforced composites (FRC)

Technologically, the most important composites are those in which the dispersed phase is in the form of a fibre. Design goals of fibre reinforced composites often include high strength and /or stiffness on a weight basis. FRCs with exceptionally high specific strengths and moduli have been produced utilising low density fibres and matrix materials. Figure 1.2 shows a schematic model of a fibrous composite[6]. Fibres are dispersed throughout the matrix to increase rigidity and strength further and especially to add impact strength, which often lack in rigid matrices [20]. Fibre is the major load bearing component in the composite [21]. Wide ranges of crystalline (rayon, Kevlar, PET) and amorphous (glass, boron, silica, asbestos) materials are used as fibres [22] for composite development. While glass and steel fibres are obvious candidates, experts have found that many organic fibres offer a superior balance of modulus, strength, impact resistance, vibration resistance, thermal properties, electrical properties and light weight, making them materials of choice in many high-performance composites.

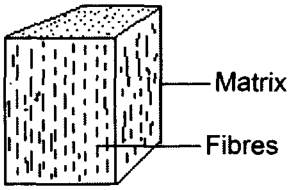


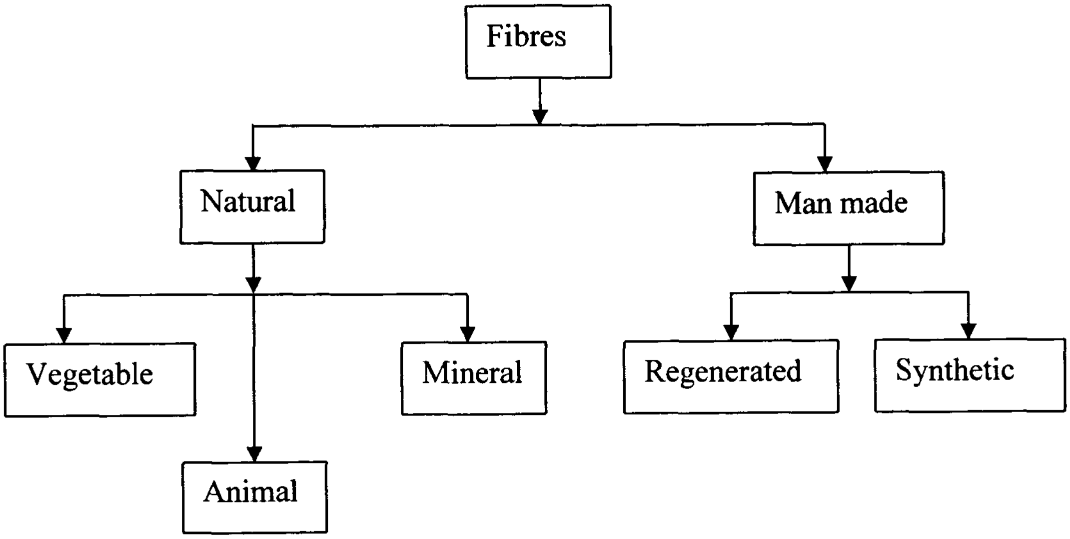
Figure 1.2 Schematic representation of a fibre reinforced composite

Based on fibre length, FRCs are grouped into two: (1) long (continuous) fibre reinforced composites and (2) short (discontinuous) fibre reinforced composites. Fibres of length less than 50 mm are usually considered as short fibres whereas those of length greater than this are long fibres. Long fibre composites possess unidirectional orientation of fibres which give them enhanced properties. For continuous fibre reinforcement, the strain in the matrix and the strain in the fibre under load are initially the same. At low stresses, both fibres and matrix deform elastically but with increasing stress the matrix may deform plastically while the fibre still will be elastic. In the case of discontinuous fibrous composites, the length of the fibre is neither too high to allow individual fibres to entangle with each other nor too low for the fibres to lose their fibrous nature. The reinforcement is uniform in the case of composites containing well dispersed short fibres. Most practical composites those are being developed for engineering applications contain discontinuous fibres.

Short fibre reinforced polymer composites offer many attractive features which include ease of fabrication and better economy at both the incorporation and fabrication stages. Production of complex shaped articles is possible with short fibres which is practically impossible with long fibres.

1.3 FIBRES

Generally fibres are fine hair like substances having length at least hundred times its diameter[5]. Commercially available fibres have diameters in the range 0.004-0.2 mm and they come in different forms as staples, monofilaments, tows or yarn. Fibres are classified according to their origin and chemical structure[4]. They are broadly classified into two types: man-made and natural. These are further classified as shown in Scheme 1.5.



Scheme 1.5 Classification of fibres

1.3.1 Natural fibres

Fibre which come from natural sources such as animals, plants and minerals those do not require reformation are classified as natural fibres. They are one of the major renewable resource materials throughout the world especially in the tropics. There have been attempts to use natural fibre reinforced polymer composites from 1868 for making seats in aircrafts and later in 1940-46, for bearings and fuselage in aircrafts and ships [23]. The natural fibre reinforced composites possess high electrical and impact resistance, good thermal, acoustic and insulating properties in addition to specific strength [24]. Natural fibres are further classified, according to their origin, as vegetable, animal or mineral fibres.

1.3.1.1 Vegetable fibres

Vegetable, or cellulose based fibres include cotton, jute, sisal etc. Chemically, all vegetable fibres consist mainly of cellulose, although they also contain varying amounts of substances like hemicellulose, lignin, pectins and waxes. These fibres can resist alkalies and most of the organic acids. Vegetable fibres are further classified into three types depending on the part of the plant from which they are extracted. They are:

(i) bast or stem fibres (e.g. jute, banana)

(ii) leaf fibres (e.g. sisal, pineapple)

(iii) fruit fibres (e.g. coir, cotton, oil palm)

1.3.1.2 Animal fibres

Fibres obtained from living organisms are known as animal fibres. Chemically these are complex proteins. They are resistant to most organic acids. Major classes of animal fibres are silk, hair, fur and wool. The protein fibroin is the principal component of silk fibre [5]. These fibres are extruded as continuous filaments from the abdomens of various insects and spiders. The natural silk used in commercial textiles is produced from the cocoons of the silkworm. The protein keratin is the principal component of hair fibre and fur fibre [4]. The fibres from animals such as mink and beavers are sometimes blended with other hairs to spin luxury yarns but are most often found as fur felts. Wool is the animal fibre obtained mainly from the fleece of domestic sheep. Wool of other kinds (camel, goat etc.) which is used in comparatively small amounts is clipped or combed from animals during the shedding period. Wool is warm, elastic and strong. Generally, wool is categorised based on fineness, length and crimp of staple, and according to the age of the animal.

1.3.1.3 Mineral fibres

These are fibres composed of naturally occurring minerals. Important mineral fibres are originated from glass, ceramic and asbestos. Glass fibre is an inorganic mineral fibre made from silica sand[6]. There are two types of glass fibres: continuous and staple. The continuous glass fibre is made by drawing molten glass into threads and is used in textile materials. These fibres can be fabricated into mats or bulk-moulding and sheet-moulding compounds with the use of resins or organic binders. Ceramic fibres such as aluminium oxide (Al_2O_3), silicon carbide (SiC) and boron carbide have been developed for heat-resistant composite materials[6]. The components of helicopters, military and civil aircrafts, missiles and spacecrafts including satellites and space shuttles are made from these high-strength, lightweight composites. The most common type of asbestos fibre is chrysotile which represents more than 95% of the total world production. Chemically it is a hydrated magnesium silicate. It has excellent weathering characteristics and is resistant to most of the chemicals except acids and strong bases. In plastics, it improves creep resistance and heat deflection temperature, and imparts flexural strength and modulus.

1.3.1.4 Disadvantages of natural fibres

The lignocellulosic natural fibres are hydrophilic and absorb moisture[25, 26]. The swelling behaviour of natural fibres is generally affected by their morphology as well as physical and chemical properties[27, 28]. Natural fibres are complex mixtures of organic substances and different thermal treatments can therefore lead to a variety of physical and chemical changes[29, 30]. The lignocellulosic natural fibres are degraded biologically because organisms recognize the carbohydrate polymers, mainly hemicellulose in the cell wall and have very specific enzyme systems capable of hydrolyzing these polymers in to digestible units [31-33]. Natural fibres tend to be yellow upon exposure to sunlight and moisture and extended exposure results in the loss of strength.

1.3.2 Man-made fibres

Man-made fibres are classified as regenerated and synthetic depending on the method by which they are prepared.

1.3.2.1 Regenerated fibres

The fibres which are regenerated either from organic or inorganic systems belong to this category. Polymers from natural sources have been dissolved and regenerated after passing through a spinneret to form fibres. Rayon represents an important class of regenerated fibres. Rayons are regenerated cellulose in which different substituents have replaced not more than 15% of hydrogen of the hydroxyl group.

1.3.2.2 Synthetic fibres

Fibres in which the basic chemical units have been formed by chemical synthesis followed by fibre formation are called synthetic fibres. Synthetic fibres may be inorganic or organic.

(i) Inorganic synthetic fibres

Fibres of carbon, boron, alumina, silicon etc. belong to this category. Carbon and graphite fibres are high-strength materials which are used as reinforcing agents in composites [24]. Chemically, carbon fibres are produced from rayon or acrylic fibre by thermal heating. Carbonisation occurs at temperatures of 1000 to 2500 °C in an inert atmosphere. Carbon fibres are converted to graphite at temperatures above 2500 °C. They can also be made from pitch, a residual petroleum product. The products those use carbon fibres include heat-shielding materials, aircraft fuselage and wings, spacecraft structures and sports equipment.

(ii) Organic synthetic fibres

The fibres which are derived from organic polymers are termed as organic synthetic fibres[4]. Good examples are furnished by cellulose acetate, nylon (polyamide), acrylic (polyacrylonitrile), aramid (aromatic polyamide) olefins (polyethylene and polypropylene) etc. Most of them are thermoplastic, i.e., they are softened by heat. During processing, a molten polymer or polymer solution is extruded through tiny holes in a spinneret into an environment that causes the filaments to solidify. The properties of these fibres depend on the base polymer, the spinning process and the post-spinning treatment of the fibre, which can include drawing, annealing, applying a finish and coating. Fibre properties such as weight, abrasion resistance, heat resistance, chemical resistance, moisture resistance, strength, stiffness, elasticity and ease of dyeing and colouring can be optimised by such treatments.

- *Cellulose acetate*: Cellulose acetate or acetate rayon fibre is one of the earliest synthetic fibres and is based on cotton or tree pulp cellulose. These cellulosic fibres have passed their peak as cheap petro-based fibres and have displaced regenerated pulp fibres.

- *Olefin fibre:* It is a synthetic fibre made from alkenes. It is used in the manufacture of various textiles. It can be defined as a manufactured fibre in which the fibre-forming substance is any long-chain synthetic polymer composed of at least 85% by weight of ethylene, propylene, or other olefin units. The fibres are waxy, colourless and often round in cross section. The fibres are also resistant to moisture and chemicals.

- *Acrylic fibre*: These are synthetic fibres made from a polymer with a weight average molecular weight of ~100,000. The polymer contains at least 85% acrylonitrile monomer. Typical co-monomers are vinyl acetate or methyl acrylate. The polymer is formed by free radical polymerisation. Acrylic is lightweight, soft and warm, with a wool-like feel. It dyes very well and has excellent colourfastness. It is resilient, retains its shape, and resists shrinkage and wrinkles. It is quite varied in form and sometimes has an appearance similar to wool or cotton.

- *Polyester fibre*: It is a category of polymers, or, more specifically condensation polymers, which contain the ester functional group in their main chain. Polyester fibres are often spun together with fibres of cotton, producing a cloth with some of the better properties of each. Polyester is combustible but due to its thermoplastic nature, it tends to shrink away from the flame source and often self-extinguishes.

- *Nylons:* These are thermoplastic materials, first used commercially in a nylon-bristled toothbrush followed more famously by women's "nylons" stockings. These are made of repeating units linked by peptide bonds and are frequently referred to as *polyamides*. Nylons were the first commercially successful polymers and the first synthetic fibres to be made entirely from coal, water and air. These are formed into monomers of intermediate molecular weight, which are then reacted to form long polymer chains. Type 6/6 nylon is the most common commercial grade of nylon, and nylon 6 is the most common commercial grade of cast nylon. Most nylons are condensation copolymers formed by reacting equal parts of a diamine and a dicarboxylic acid, so that peptide bonds form at both ends of each monomer in a process analogous to polypeptide biopolymers.

- *Aramid fibre:* Aromatic polyamides are generally called aramids. Two important aramid fibres are Kevlar and Nomex. These synthetic fibres are strong and heat-resistant. They are used in aerospace and military applications, for bullet-proof body armour fabric and as asbestos substitute. They have low flammability and good resistance to abrasion and organic solvents.

A comparison of properties of various natural and synthetic fibres is given in Table 1.2.

Table 1.2 Mechanical properties of some synthetic and natural fibres

Fibre	Density ($\times 10^3$ kg/m^3)	Elongation (%)	Tensile strength (MPa)	Young's modulus (GPa)
Aramid	1.40	3.3-3.7	3000-3450	63-67
Carbon	1.40	1.4-1.8	4000	230-240
Kevlar 49	1.45	2.0	2800	124
Nylon 6,6	1.14	18.0	1000	---
Cotton	1.50	7.0-8.0	287-597	5.5-12.6
Jute	1.30	1.5-1.8	393-773	26.5
Flax	1.50	2.7-3.2	345-1035	27.6
Hemp	-	1.6	690	-
Ramie	-	3.6-3.8	400-938	61.1-128
Sisal	1.50	2.0-2.5	511-635	9.4-22
Coir	1.20	30.0	175	4.0-6.0
E-glass	2.50	2.5	2000-3500	70.0
S-glass	2.50	2.8	4570	86.0
SiC	3.08	0.8	3440	400
Al_2O_3	3.95	0.4	1900	379

(Source: Reference 4)

1.4 SHORT FIBRE REINFORCED RUBBER COMPOSITES

Short fibre reinforced rubber composites have been developed to fill the property gap in between the long fibre reinforced rubber composites and particulate filler reinforced rubber composites, i.e., mainly to achieve the high performance of fibres coupled with the easy processability and elasticity of rubbers. The use of short fibres in rubbers is not new; tyre retreaders have been using chopped cotton and rayon fibres in camel back for quite some time. Composites in which short fibres are oriented uni-axially in an elastomer have a combination of good strength and stiffness from the fibres and elasticity from the matrix. Short fibre reinforced elastomer composites have paramount importance in replacing other types of composites in applications requiring a combination of strength and lightness.

In more recent years, a range of synthetic and natural fibres such as rayon, nylon, polyester, Kevlar, glass, cellulose, asbestos etc. have been used with various rubbers such as natural rubber, SBR, NBR, polyurethane (PU) and neoprene (CR) for making useful composite materials. Short fibre reinforced rubber composites can be conveniently classified into two major categories.

(i) Synthetic fibre reinforced rubber composites

Among synthetics, glass fibres are extensively used as reinforcing agents for polymer composites and their suitability for rubber reinforcement has been thoroughly studied. Lueers [34] reviewed the effect of glass fibre reinforcement on various rubber matrices. The main disadvantage faced during processing of this type of composites was fibre breakage. Czarnekei and White [35] reported the mechanism of glass fibre breakage and severity of breakage with time of mixing. Derringer [36] examined the advantages of short glass fibre reinforced rubber composites, which included high modulus, high resilience and low creep. Comparing the properties of vulcanisates reinforced with various types of short fibres, Monceau [37] reported that glass fibres possessed a markedly lower reinforcing capability compared to cellulose fibres but could undergo higher elongations. Dunnom *et al.*[38] indicated that pre-impregnated glass fibres gave better reinforcement to rubbers. Brokenbrow *et al.*[39] studied the reinforcing effect of asbestos fibres in rubbers. Bament[40] examined the use of asbestos fibre bonded with polychloroprene to improve the dimensional stability of a roofing sheet of unvulcanised chloro-sulphonated polyethylene. Due to the hazards in using them and their poor properties, they find little potential as reinforcing elements. Aramid fibres have been found to reinforce rubbers [41]. O'Connor [42] confirmed the high strength of aramid fibre composites and attributed it mainly to the high strength of the fibrous component. The breakage resistance was reported to be better than that of glass fibres. Carbon fibres also have drawn good attention. Pramanik *et al.*[43] studied the mechanical and electrical properties of short carbon fibre reinforced NBR composites. Sieron [44] observed that these fibres improved the tensile properties of fluoro-elastomers. Ecersley [45] discussed the use of carbon fibres in making abrasion resistant composites. Grimbladt *et al.*[46] reported the effect of carbon fibres on increasing the strength, ageing resistance and resistance to compression set of fluorine containing rubbers. Lewitt [47] examined the effect of carbon fibres on the properties of rubber vulcanisates. However, the use of carbon fibre is limited due to high cost. The technology for developing polytetrafluoro-ethylene fibrils in a rubber stock during compounding was reported by Leonard [48].

(ii) Natural fibre reinforced rubber composites

Short cellulose fibres have been found to provide good reinforcement to rubber vulcanisates. Two advantages reported are their resistance to breakage during mixing and their rough surface, which can give rise to good bonding. Goodloe *et al.*[49] used finely divided wood cellulose for reinforcement in rubbers. This is the earliest reported research work in the field of cellulose fibre reinforcement. Hamed and Coran[50] pointed out that wood cellulose fibres are highly reinforcing materials for rubbers. Anthoine *et al.*[51] reviewed the reinforcement of elastomers with discontinuous cellulose fibres. Boustany and Coran [52] reported the advantages of treated and untreated cellulose fibres. Cellulose fibres have been found to provide good green strength and low die swell. The properties of different types of cellulose fibres and their mechanism of reinforcement have been analysed by Goettler and Shen [53].

1.5 ADVANTAGES OF SHORT FIBRE REINFORCED RUBBER COMPOSITES

In general, short fibre reinforced rubber composites have the following advantages[54-57].

(i) Processing advantages

- Short fibres can be incorporated easily into the rubber compound along with other additives.
- They are amenable to standard rubber processing operations such as extrusion, calendering, compression moulding, injection moulding and transfer moulding.
- They provide high green strength and high dimensional stability during fabrication.

(ii) Design flexibility

- Fibres can be placed in any direction depending on the requirement.
- Complex shaped articles can be fabricated using short fibres, which is quite impractical to accomplish with long fibres.

(iii) Mechanical properties

- Exceptional specific strength and specific stiffness
- Reduced shrinkage in moulded products

- Controlled damping properties
- Improved solvent swell resistance
- Increased abrasion resistance
- Improved cut and tear resistance
- Improved creep resistance
- Anisotropy in properties

(iv) Economy

- Short fibres are less expensive than continuous fibres.
- The processes such as dipping, wrapping, laying and placing of the fibres associated with long fibre reinforced composites can be avoided with the use of short fibres.

Although short fibres have several advantages, they possess some disadvantages such as:

- Difficulties in achieving uniform dispersion
- Fibre breakage during processing
- Difficulties in handling and bonding
- Difficulties in processing such as filament winding, autoclave and vacuum bag techniques which are generally used for continuous fibre reinforced composites.

1.6 THEORY OF REINFORCEMENT WITH SHORT FIBRES

The stiffening effect of a dispersed phase of higher modulus is not easily tractable and its exact treatment is complex. However, if it is assumed that stiffness averaging can be performed among the components of the composites under constant-deformation conditions, the analysis can be considerably simplified. The most common assumption is that either the stress state or the strain is everywhere uniform in the deformed composite material. Stiffness is usually considered in terms of linear elastic Young's modulus (G). Even though elastomers do not exhibit substantial linear elastic regions of deformation, the analysis of elastomer- based composites can proceed on this basis, because in the reinforced state linear elasticity is more closely followed.

In the case of reinforcement short fibres, as long as a substantial orientation is obtained in the direction of applied stress, the assumption of constant strain is valid. Fibres of low extensibility relative to the elastomeric matrix are controlling the overall deformation state, so that matrix experiences the same low extension except for regions of stress concentration in the vicinity of fibre ends. Thus linear elasticity is generally applicable, but actually the matrix exists in a rather complex state of non-uniform tension and shear.

An understanding of stress development in individual fibres and the partition of applied load (stress) between the matrix and the reinforcement is the basic to the calculation of stiffness or strength in short fibre-reinforced elastomers. The tensile stress (σ) generated in a fibre-reinforced elastomer, in general, is distributed between the fibre and matrix phases, such that:

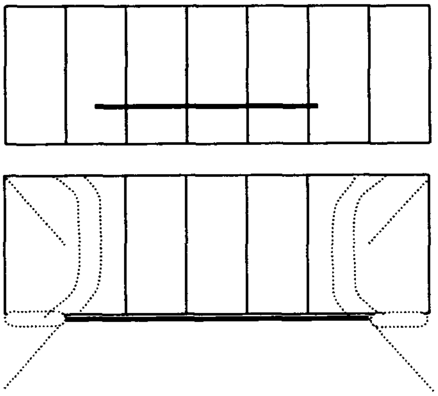
$$\sigma_c = \sigma_f + \sigma_m \qquad \text{..........(1.1)}$$

where c refers to the fibre-rubber composite, f and m refer to the fibre and matrix phases respectively. If each phase is assumed to be linearly elastic, this relationship can be further written as:

$$\sigma_c = G_f\varepsilon_f\phi_f + G_m\varepsilon_m\phi_m \qquad \text{...... (1.2)}$$

where G is the Young's modulus, ε is the tensile elongation and ϕ is the volume fraction of each phase.

In the case of short fibre reinforced rubber composites, the fibre end effects are significant in the deformation behaviour. Figure 1.3 (a) represent a single fibre embedded in a matrix of lower modulus in the undeformed state. When the composite is loaded axially, the longitudinal strain in the matrix will be higher than that in the fibre due to lower modulus of the former. When the force is applied, the imaginary vertical lines running through the fibre-matrix interface in a continuous manner in the unstressed state will be distorted as shown in Figure 1.3 (b). This distortion is due to the greater deformation of the matrix at the region of fibre ends than that along the fibre. This difference in longitudinal strains creates a shear stress distribution around the fibres in the direction of the fibre axis and therefore the fibre is stressed in tension. The applied load is transferred from matrix to the fibres across the interface because of this shear stress distribution.



(a) Short fibre composite (Undeformed)

(b) Short fibre composite (Deformed)

Figure 1.3 Effect of stretching force on the strain around a short fibre in an elastomeric matrix

When a mechanical force is applied to the polymeric matrix, it spreads smoothly through the matrix until it reaches the matrix-fibre interface. If the interface is well bonded, the stress is transferred across it into the fibre and then spreads throughout the fibre. This process occurs at all the fibre-matrix interfaces in the composite. Thus it is obvious that the load will be transferred to the fibre only if the interface is strong and a perfect bond exists between the two constituents. Hence a strong interface is compulsory for the better performance of composite systems.

1.7 FACTORS AFFECTING THE PROPERTIES OF SHORT FIBRE REINFORCED RUBBER COMPOSITES

Several factors have been identified which determine the properties of short fibre reinforced rubber composites. These include mixing, dispersion of fibres, fibre breakage and critical fibre length[58]. By controlling these factors properly, reasonably better rubber products can be fabricated using short fibres which possess good dimensional stability.

1.7.1 Mixing of rubber compounds

The conventional mixers such as Banbury and open mixing mill can be utilized for mixing short fibres with elastomers as described by Boustany and Coran[52]. The mixing procedure may be distributive or dispersive which is adopted depending on the type of the fibre used. The distributive mixing increases the randomness of distribution of the minor constituent within the major base material without further size reduction, while dispersive mixing serves to reduce the agglomerate size. Thus, brittle fibres such as glass or carbon, which break severely during mixing, require more distributive mixing, but for organic fibres such as nylon, silk and natural cellulosic fibres like jute and sisal, dispersive mixing is called for since these fibres tend to agglomerate during mixing procedure. Goettler and Lambright[59] developed a technique for controlling fibre orientation during extrusion by the use of an expanding mandrel die. Calendering can also achieve the same level of fibre orientation in the machine direction[60].

1.7.2 Dispersion of short fibres

Good dispersion of short fibres in rubber compounds is an essential requisite for high performance composites. The major factors associated with good dispersion of fibres are: (1) level of fibre-fibre interaction and (2) fibre length. The naturally occurring cellulosic fibres tend to agglomerate during mixing due to hydrogen bonding. A pre-treatment of fibres is at times necessary to reduce fibre-fibre interactions. Such treatments include the making of pre-dispersions and formation of a soft film on the surface. Natural cellulose fibres treated with compositions containing latex were found to be dispersing well in the rubber matrix[38]. The homogeneous pre-dispersion of chopped polyester, glass and rayon fibres in neoprene latex and their dispersion in neoprene rubber was studied by Leo and Johansson[61].

The fibre length has some effect for facilitating better dispersion. Derringer[62] used commercially available fibres such as nylon, rayon and polyester cut into smaller fibre lengths for better dispersion. The better dispersion of fibres could be achieved by adding fibres first in the masticating or mixing machine. Boustany and Arnold[63] noticed that composites produced by the dispersion of selected short cellulose fibres in elastomeric matrices were useful engineering materials. These fibres were pre-treated to provide dispersion in conventional mixing equipment while minimising fibre damage, and to give bonding for better reinforcing.

1.7.3 Fibre breakage

Several researchers examined the importance of fibre length and its influence on the properties of composites [64-67]. In a composite material, fibre length is a critical parameter and it should not be too long so that they entangle with each other causing problems of dispersions. However, a very small length of fibre does not offer sufficient stress transfer from matrix to fibre. Due to the high shear force caused during mixing fibres usually undergo breakage. Fibre breakage also results from fibre–polymer interactions, fibre–fibre interactions, and fibre contact with the surfaces of the processing equipment[68]. Due to the increased fibre–fibre interactions and fibre–equipment wall contact, fibre length decreases with increasing fibre content and also with the processing time[68, 69]. This reduction in fibre length then reduces the reinforcing efficiency of the fibre. The severity of fibre breakage depends mainly on the type of the fibre and its initial aspect ratio (length/diameter); for example, the fibres such as glass and carbon are brittle and they possess a low bending strength than the ductile fibres like cellulose, which are more flexible and resistant to bending. Depending on the resistance to bending there exists a certain aspect ratio for each type of fibre below which no further breakage can occur. The aspect ratio of glass fibres is very low compared to the cellulose fibres. If the mix viscosity is high more shear will be generated during mixing, exceeding the critical bending stress of the fibre, which eventually results in severe breakage.

O'Connor[42] reported the fibre breakage during mixing. The lower reinforcing ability of glass fibre has been attributed to the severe reduction in their length compared to cellulose fibres during mixing. The mechanism of fibre damage using glass, aramid and cellulose fibres in polystyrene melts has been reported by Czarnekei and White [35]. Studies on the effects of mastication time and mixing on fibre damage indicated that the extent of breakage depended on the mastication time. Murthy *et al.*[70] suggested that the breakage of fibres was due to a buckling effect. De and co-workers [57, 71, 72] studied the breakage of jute and silk fibres in NR, carboxylated nitrile rubber (XNBR) and NBR and found that the breakage of silk fibres was less than that of jute fibres. Rezadoust and Esfandeh [73] examined the fibre breakage and length distribution during the compounding of glass-NBR-phenolic composites.

1.7.4 Critical fibre length

In a perfectly oriented uni-directional fibre reinforced polymer composite containing fibres of uniform radius, the rate of increase of fibre stress is proportional to the interfacial shear stress. The ends of fibres in short fibre composites play a major role in the stress transfer mechanism.

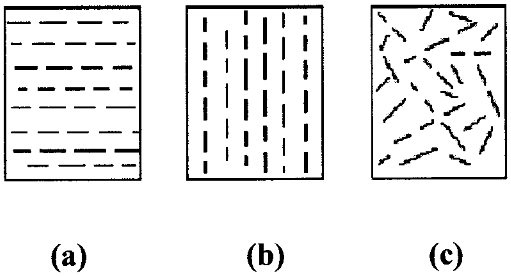
Fibre length, over which the stress transfer allows the fibre to be stressed to its maximum stress or at which efficient fibre reinforcement can be achieved, is termed as the critical fibre length of the composite. Broutman and Agarwal [64] did a theoretical analysis on the mechanism of stress transfer between fibres of uniform radius and length. They determined the critical fibre length (l_c) from the equation:

$$l_c / d_f = \sigma_{fb} / 2\tau_y \qquad \text{......(1.3)}$$

where, d_f is the diameter of fibre, σ_{fb}, the ultimate fibre strength and τ_y is the matrix yield stress in shear. Based on the structure-stress properties of short fibre/rubber composites and Cox shear lag, a new model of critical fibre aspect ratio has been proposed by Zhang *et al*[74]. Their results showed that the new model could better suit the characters of short fibre/rubber composites and it reflected totally the relations between the structure of short fibre composites and the critical aspect ratio.

1.7.5 Fibre orientation

The orientation of fibres relative to one another considerably influences the performance of composites as structural materials. Fibre orientations as well as fibre concentration have significant influence on the physico-mechanical properties of fibre reinforced polymer composites. With respect to orientation, three limits are explained; longitudinal orientation (along machine direction), transverse orientation (across machine direction) and random orientation, as shown in Figure 1.4



(a) (b) (c)

Figure 1.4 Schematic representation of different orientations of short fibres (a) longitudinal (b) transverse (c) random

(a) Longitudinal orientation of fibres

The longitudinally oriented fibrous composites are inherently anisotropic. Since effective stress transfer from the matrix to the fibres occurs in the direction of fibre alignment, maximum strength is shown by them [Figure 1.4 (a)].

(b) Transverse orientation of fibres

In the transversely aligned fibrous composites, the fibre reinforcement is virtually non-existent [Figure 1.4 (b)]. The fracture of the sample occurs at very low tensile stresses, which may be equal to or less than the strength of the matrix[75]. Thus the transverse compressive strength is limited by the strength of the matrix and so is less than the longitudinal compressive strength[76].

(c) Random orientation of fibres

The strength of randomly oriented fibrous composites lies between the limits of longitudinally and transversely aligned systems [Figure 1.4 (c)]. These types of composites can be constructed by randomly orienting fibres in a plane or by using multilayered laminates containing different orientations of fibres. These are essentially isotropic in plane, i.e., they have desirable properties in all directions in a plane. In random orientation also, the modulus increases with fibre concentration[76]. Applications involving totally multidirectional applied stresses normally use discontinuous fibres, which are randomly oriented in the matrix material. The reinforcement efficiency is only one fifth of that of an aligned composite in the longitudinal direction; however the mechanical characteristics are isotropic.

1.7.5.1 Effect of flow behaviour on fibre orientation

During mixing and subsequent processing operations of short fibre reinforced elastomer composites, the fibres orient preferentially in one direction and the ultimate properties of the material depend mainly on the angle between the orientation and the direction of the applied stress. Fibres orient in a direction depending on the nature of the flow, viz. convergent, divergent, shear or elongational. If the flow is convergent type, the fibres align themselves in the direction of flow and away from the direction of flow if the flow is divergent. During shear flow, the fibre orientation can be from random to uni-directional depending on the shear rate and if the flow is of elongational type the fibre orientation takes place mainly in the direction of flow and the rate of fibre rotation is controlled by the magnitude and direction of velocity gradient (i.e., +ve or -ve) which will be generated by normal forces occurring in the flow resulting from the changes in the cross-sectional area of the channel. In a convergent flow, the flow gets accelerated because of a reduction in the cross-sectional area of the channel; the velocity gradient thus becomes positive and the fibres tend to align in the direction of flow making a small angle with the flow axis. Fibre orientation during mixing was discussed by Moghe [77]. The effects of mill parameters such as number of passes, nip gap and mill-roll speed ratios have been studied and it has been found that the nip gap has a significant effect on fibre orientation. The maximum fibre orientation takes place in the first pass itself. However, the fibre orientation is controlled by the manner in which the mix sheet is folded and sufficient care is generally ensured to obtain maximum orientation along the machine direction.

1.7.5.2 Fibre orientation distribution

It is very difficult to achieve 100% orientation of fibres in one direction in composites. A maximum of 60-80% will orient within ±10 degrees to the normal alignment direction[78]. McNally [79] reviewed the factors controlling the distribution of fibres in different orientations and their effects on the properties of composites. The mechanical performance of composites is greatly influenced by the fibre alignment. A theoretical prediction, based on swelling of the composites in solvents, can be considered for the evaluation of fibre distribution. Swelling is a uniform restrictive force imposed on fibre reinforced composites[80]. The modulus of a composite can be related to the angle between the fibre orientation and the direction of applied stress by the equation[81]:

$$1 / G_0 = (\mathrm{Sin}^2\theta / G_T) + (\mathrm{Cos}^2\theta / G_L) \qquad \text{....} (1.4)$$

where G_L and G_T are the moduli of the composite in longitudinal and transverse orientations respectively and θ is the angle between the fibre orientation and the direction of applied stress. Halpin-Tsai's equation predicts the modulus of a uni-directional oriented composite[82]. Moghe[83] took two extremes as uni-directional and random orientations in his theory. He also stated that the modulus of a perfectly oriented composite described in Halpin-Tsai's theory is six times that of a randomly oriented composite. The construction of balanced angle ply composites by overlapping method with short fibre compounds is another way of obtaining isotropic composites[84].

1.7.6 Fibre-matrix adhesion

The behaviour of a composite material is explained on the basis of the combined behaviour of the reinforcing element, polymeric matrix and the fibre-matrix interface. The reinforcing element should not be weakened by surface or internal flaws and the applied load should be effectively transferred from the matrix to the fibre through the interface. The components of a composite system are chosen on the basis of their mechanical and physical characteristics in isolation. The process of fabrication of a composite involves interfacial interactions those can cause modifications in the interface structure.

When the fibre-matrix interface of a short fibre composite is sufficiently strong, the load will be effectively transferred to fibres to obtain a high performance composite. A reasonably good level of adhesion is required for the better performance of short fibre reinforced composites. At elevated temperatures, the interface deteriorates and the values of physical properties decrease.

1.7.6.1 Bonding at the interface

The fibre-matrix adhesion is evaluated at the interface of the composites. Interface is a bounding surface where a discontinuity of some kind occurs as sharp or gradual. It is the boundary region between two phases in contact. Interface is an essentially bi-dimensional region through which material parameters such as concentration of an element, crystal structure, atomic registry, elastic modulus, density and coefficient of thermal expansion change from one side to other. The composition, structure or properties of the interface may vary across the region and may also differ from the composition, structure or properties of either of the two contacting phases[85]. In short fibre-rubber composites, the large difference between the elastic properties of the fibre and the matrix is communicated through the interface. This interfacial region exhibits a complex interplay of physical and chemical factors those exert a considerable influence and control the properties of fibre reinforced composites. The interfacial interaction depends on the fibre aspect ratio, strength of interaction, anisotropy, orientation, aggregation etc[86].

The interface in certain systems has enough natural affinity due to polar hydrogen-bonding, electronic attraction or primary covalent bonding. The methods generally adopted to increase the interfacial adhesion are the utilisation of coupling agents, surface modification of fibres by chemical or physical methods, coating of fibres with appropriate resins, graft copolymerisation and by the use of bonding agents.

There are two types of interfacial bonding in fibre reinforced composites. They are: (a) mechanical interfacial bonding and (b) chemical interfacial bonding.

(a) Mechanical interfacial bonding

It is a simple mechanical anchoring between two surfaces, which can lead to a considerable degree of adhesion. Moreover, any contraction of the polymeric matrix onto the fibre would result in a gripping of the fibre by the matrix.

(b) Chemical interfacial bonding

Two types of bonding are formed at the fibre- matrix interface, by chemical treatments. They are: (1) dissolution and wettability bonding and (2) reaction bonding. In dissolution and wettability bonding, the interaction between the components (fibre and matrix) occurs on an electronic scale. In reaction bonding, a transport of atoms occurs from fibre, matrix or both to the interface. These polar surfaces can form bonding owing to the diffusion of matrix molecules to the molecular network of the fibre, thus forming twisted molecular bonds at the interface.

1.7.6.2 Interface modification

The interface in fibre reinforced rubber composites can be modified by different ways to obtain optimum fibre-matrix properties. The wettability of polymers on the fibre surface depends on the viscosity of the polymer and the surface tension of both materials. For better wetting of the polymer on the fibre, the surface tension of the polymer must be as low as possible. It should be at least lower than the surface tension of the fibre.

There are different methods of modification to change the surface energy of polymers and the fibres. The surface of hydrophobic matrices can be modified by the introduction of polar groups by treating them with oxidative chemicals like chromic acid/acetic acid or chromic acid/sulphuric acid[87,88]. Cold plasma chemistry opens up a new way for the surface modifications of materials for composites and other applications [89-93]. Introduction of highly polar functional groups like carbonyl group at the surface of polymers is done by corona discharge treatment. Various mechanisms have been proposed for the improvement of adhesive properties by corona discharge treatment; some attributed to electric charge formation and some others to hydrogen bonding[94, 95]. UV radiation on polymer matrix has also been employed to introduce functional groups[96].

Several physical and chemical methods have been used for the surface modification of fibres also. The physical methods include corona discharge and cold plasma treatment similar to those used for the matrices[97]. Mitchenko *et al.*[98] reported the use of low temperature plasma to improve the adhesion properties of polyester fibre. Different types of chemical modifications have been reported for fibres, some of which are based on the action of coupling agents. Asbestos fibres are hard to adhere with a rubber matrix but a treatment of the fibres with silane coupling agents and with isocyanate, as 2% solution in dichloromethane have been found to improve the adhesion[22]. Glass fibres have drawn considerable attention recently and their treatment also is mainly carried out with silane coupling agents[99]. Other coupling agents like isocyanates and titanates have been employed by different researchers[100, 101]. Dipping of reinforcing fibres with the polymer dispersions having low viscosity compatiable with the polymer matrix enhances the strength of the composite[102].

Graft polymerisation is a method of attaching polymer to the fibre by free radical initiation when exposed to a high energy radiation[103]. Various oxidative or non-oxidative chemical treatments are available for natural and synthetic fibres in order to improve the bonding at the interface[104, 105]. Several researchers investigated the use of treated short natural fibres as reinforcing elements for polymer composites[106-112].

Interface modification can be effected by the use of dry bonding systems also. Dunnom [113] observed a marked difference in the adhesion level of short fibre reinforced elastomers by adding silica to a composite containing resorcinol and hexa. Silica reduces the resin formation to a low molecular weight species and these low molecular weight species can diffuse easily through the matrix thereby developing adhesion[114]. Thomas and co-workers [115-117]successfully tried resorcinol and hexa bonding system without silica for various short natural fibre reinforced rubber composites.

1.8 CHARACTERISATION OF SHORT FIBRE REINFORCED RUBBER COMPOSITES

There are different methods commonly accepted for the characterisation of fibre reinforced composites.

(i) Mechanical properties

The mechanical properties of short fibre reinforced composites are intermediate between those containing cords and particulates. The factors affecting the mechanical properties of short fibre composites are related to the aspect ratio, volume fraction, fibre orientation, state of dispersion and degree of adhesion of fibres to the matrix. The important mechanical properties of fibre reinforced composites include tensile strength, modulus, tear strength, elongation at break, creep and fatigue properties.

(ii) Surface morphology

Polymer morphology covers the study of the arrangement of macromolecules and the overall physical structure of the molecular aggregates. Scanning electron microscopy (SEM) is one of the important techniques used for morphological analysis. It is used to study the fracture and failure mechanisms of composites under tear, tension and abrasion.

(iii) Solvent resistance

The resistance to penetration of solvents can be studied by sorption experiments. These studies are useful especially in the characterisation of composites made from oil resistant rubbers like NBR.

(iv) Dielectric properties

The evaluation of the performance of many polymer composites as dielectric materials has grown as an active area of research over years. Dielectric measurements for the dielectric constant and the dielectric loss reveal significant information about the chemical and physical states of polymers.

(v) Thermal analysis

Thermal analysis is another important tool in the characterisation of polymer composites. During the fabrication of new composite products from polymers, a knowledge of the thermal stability of their components is essential[118]. Thermal properties are conveniently studied by employing techniques as thermogravimetry (TG), and differential scanning calorimetry (DSC). TG can help in understanding the degradation mechanism while DSC helps us to obtain quantitative information about melting and phase transitions.

(vi) Dynamic mechanical analysis

Dynamic Mechanical analysis has widely been employed for investigating the visco-elastic behaviour, stiffness (modulus), damping (energy dissipation) characteristics, phase transitions and the interfacial adhesion of polymer composites as they are deformed under periodic stresses[119, 120]. It is particularly useful because of its non-destructive nature unlike other static mechanical testing methods. It can yield an insight into various aspects of material structure.

(vii) Ageing resistance

During long period of service, polymer composites gradually lose many of their properties due to the degrading effects of heat, light, ozone or high energy radiation.

Thus ageing resistance in different environment is usually studied for the better utilisation of composite materials for a wide variety of applications.

1.9 APPLICATIONS OF SHORT FIBRE REINFORCED RUBBER COMPOSITES

Composite materials possess a unique combination of processing advantages, design flexibility, mechanical properties and economy. Hence they are extensively used in many applications. Campbell [121] reviewed the various applications of short fibre reinforced elastomers. Major areas where rubber composites find application are discussed below.

(a) Belts

Short fibres can be used under the continuous tension members to provide crosswise stiffening in drive belts. In V-belts, short fibre rubber composites must be transversely oriented so that the fibres can offer good resistance to compressive forces with better flexibility in axial direction. V-Belts are designed by considering the fact that the compressive force acts in the transverse direction and the fatigue in the axial direction. Here the anisotropy of those fibre-rubber composites which exhibit high modulus in transverse direction and low modulus coupled with high flexibility in the axial direction has been found to be very useful. Rogers[122] and Yantinskaya *et al.*[123] studied the use of short cellulose fibre along with polyester fibre as reinforcement for V-belt compounds. Cellulose fibre composites have higher anisotropy, increased flex life and are more easily dispersible than other fibres. The formulations and thermal degradation of various fibres used for belting products based on ethylene propylene diene (EPDM) rubber have been investigated by Shinda and Hazelton[124].

(b) Hoses

Short fibres can be utilized as the sole reinforcement for a moderate performance hose[125] (utility, automotive heater, radiator, fuel line etc.) or as an auxiliary reinforcement with cord constructions. They can provide stiffening to soft inner tubes for the application of metal braids and can extend hose life by bridging the stresses across weakened filaments. In hoses, short fibres are used as replacement in knit or spiral wound cords. The main advantages are easy processing, economy and high production rates. The braiding operations can be excluded by using short fibre reinforcement without affecting physical properties adversely. Goettler *et al.* [126] examined extensively the production and performance of short fibre reinforced hoses. They analysed the use of short fibre reinforcement in the production of heater hoses, radiator hoses and fuel hoses. The resultant composites provided necessary burst strength. Extrusion shaping in a programmed sequence to produce hoses with bends has also been attempted by them.

(c) Tyres

Short fibres have the potential for reinforcing low performance tyres[127]. In automotive and truck tyres they find application in reducing cord shadowing in the innerliner, in stiffening of the bead filler, in better abrasion resistance for chafer strip and in improved cut resistance to treads, especially for trucks and OTR vehicles[128]. Short fibres can be used in all parts of tyre construction due to their high green strength. They find application in the construction of tyre tread due to their high chipping and chunking resistance. Inoue *et al.*[129] reported the improvement in modulus and cut/crack resistance of urethane rubber composites when chopped organic fibres *viz.* nylon, polyester, polyacrylonitrile were added to them.

Boustany and Coran[130] highlighted other tyre applications of short fibre reinforced rubbers. The extrusion of a bead filler stock containing short glass fibres to increase stiffness has been reported by Dzyura *et al*[131]. Their group also reported the advantages of using rubber-fibre composites in extending the service life of tractor tyres[132]. Goettler *et al.*[133] studied the extrusion of treated cellulose fibre reinforced rubber profiles with controlled fibre orientation and their use as tyre components. Nesiolovskaya *et al.*[134] analysed the use of modified fibrous fillers in tyre tread compounds.

(d) Sheeting

Short fibres provide higher green strength and cut, tear and puncture resistance. Some applications for such reinforced sheeting are in roofing membranes. Georgieva and Vinogradova[135] studied the application of cotton and other cellulose fibre reinforced thermoplastic polyisoprene as sheeting in shoe fabrication.

(e) Diaphragms

Short fibres increase the stiffness and reduce the extensibility of products in this category. Many directional properties can also be attained.

(f) Gaskets

Short fibres provide strength against blowout and reduce swell. If oriented in the plane, they allow thickness swell to improve sealing.

(g) Energy management

Short fibres can reinforce and stiffen rubber in fenders and other impact applications, in accordance with simple design equations.

(e) Other applications

The use of cellulose fibre reinforced EPDM composites for automotive applications has been reviewed[136]. The shrinkage during vulcanisation in cup seals manufactured from cotton fibre reinforced NBR has been reported by Orlov *et al*[137]. Ratliff[138] investigated the advantages of short cellulose fibres over nylon in providing dimensional stability to air cylinder packing cups.

Apart from these, many novel products based on short fibre reinforced rubber composites are being developed. In all these applications a good dispersion of fibres within the rubber matrix is of prime consideration to obtain maximum performance. Fibres pre-treated for improved mixing (as well as for better bonding to the rubber phase) are generally preferred. In the design engineering of fibre reinforced composites these considerations are perhaps of more importance than the mechanical properties of the short fibres themselves.

1.10. EARLIER STUDIES ON SHORT FIBRE REINFORCED RUBBER COMPOSITES

Several researchers have extensively studied many short fibre-rubber composite systems due to their processing and fabrication advantages and better economy[139]. The efficiency of the composites can be increased by controlling the factors such as aspect ratio and degree of dispersion of fibres[140]. An aspect ratio of 100-200 is generally required for reinforcement in short fibre elastomeric composites [141].

The pioneering efforts on the development and characterisation of short fibre-rubber composites have been made by O'Connor[42], Hamed and Coran[50] among others, who described the effects of fibre reinforcement on the properties of rubber stocks. Short glass fibres and synthetic fibres such as nylon, rayon, aramid, carbon and polyester have been used by many researchers for reinforcing rubbers because of their high modulus, high strength and low creep [142-152]. The reinforcing effect of polyester and carbon fibres on EPDM, urethane and neoprene rubber has been studied by Noguchi *et al*[143]. Jana and De[144] studied the processing characteristics of short carbon fibre filled polychloroprene compounds. They prepared the composites by mill mixing and by making cement in a solvent before being vulcanised by a thermo-vulcanisation technique, i.e., by heating at an elevated temperature (160 °C) in the absence of any vulcanising agent. The effects of various processing parameters such as nip gap, friction ratio and roll temperature, on the tensile properties of short kevlar/aramid fibre-polyurethane composites have been investigated by Kutty and Golok[145]. Sreeja and Kutty[146] studied the cure characteristics and mechanical properties of short polyamide fibre reinforced NR. They found that the rheometric torque and the cure rate increased with increasing fibre concentration. Tensile strength, tear strength, abrasion resistance and heat build up also increased with the addition of fibres, whereas elongation at break decreased. Wada and Uchiyama [147] analysed the effect of fibre diameter on the abrasive wear of short fibre reinforced rubber composites. Rezadoust and Esfandeh[148] reported that in preparing short fibre composites, processing conditions were of great importance as they affected the final fibre length. The effects of short polyester fibre concentration, orientation and aspect ratio and adhesives on the mechanical properties of composites have been studied by Zhanxun *et al*[151]. Cure characteristics and mechanical properties of short nylon fibre reinforced neoprene composites have been investigated by Seema and Kutty[152]. The effect of glass fibre on the oil-resistant performance of CR and NBR based mixed rubbers in engine oil and petrol was studied by Guan *et al* [153]. Mechanical properties of fibre reinforced styrene–butadiene rubbers using surface-modified ultra-high molecular-weight polyethylene (UHMWPE) fibres under electron beam irradiation have been studied by Kondo *et al*[154]. Ibarra and Palma[155] compared the cure characteristics and elastic properties of short oxidized carbon fibres and untreated fibres in epoxidised NR matrix and observed that the treated fibres enhanced the rate of vulcanisation and provided better properties.

Manchado and Arroyo[156] investigated the effects of aramid, glass and cellulose short fibres on the processing behaviour, crosslink density and mechanical properties of NR, SBR, and EPDM rubber. Ibarra and Chamorro [157] examined the mechanical properties of carbon and polyester fibre in chloroprene and nitrile rubber matrices. The general mechanical properties of cellulose fibre in NR, CR and SBR have been analysed by Subic *et al.*[158]. Thomas and co workers [115-117, 159-161] extensively studied the mechanical properties of various natural fibre reinforced rubber composites. Martins *et al.*[162] and Job *et al.*[163] analysed the properties of vegetable fibre-reinforced NR composites. Studies on sisal fibre and its composites have been reviewed by Li *et al*[164]. Ismail and co-workers[165-167] studied the physico-mechanical properties of oil palm wood flour (OPWF) filled NR composites. The utilisation of coir pitch as a low cost filler in micro-cellular soles based on NR and high styrene resin was investigated by Srilathakutty *et al.*[168] and Abad *et al*[169]. Arumugam *et al.*[170] reported that coconut fibres could act as reinforcing fillers in NR matrix when loaded above 10 phr. Bhatacharya *et al.* [171] investigated the effect of short pineapple leaf fibre in NR matrix.

Short silk fibres as reinforcement for rubber have been the subject of a number of studies of Setua and co-workers[172-175]. Fibres have been found to be more effective than carbon black in increasing the tear resistance of various types of rubbers. The selection of fibre matrix bonding systems and their effects on the failure properties have also been investigated. The effect of bonding levels on the visco-elastic properties of composites has been investigated by Murthy *et al.*[176]. Ismail *et al.*[177, 178] used oil palm fibre as reinforcing agent for rubber and studied the effects of various bonding systems on the mechanical properties of composites. The effect of compatibilisers on the mechanical properties of wood fibre reinforced thermoplastic NR has been examined by Sameni *et al*[179]. Ibrahim *et al.*[180]studied the effect of graft copolymerisation of methyl methacrylate onto oil palm empty fruit bunch fibre on the mechanical properties of the resultant composites. Gustav *et al.*[181] examined the effects of plasma treatment on the mechanical properties of rubber/cellulose fibre composites. The bonding of polyaramid fibres to rubber in their composites has been investigated by Hepburn and Aziz[182]. Joseph *et al.*[183] highlighted the physical and mechanical properties of green composites from NR and oil palm fibre. Tensile and impact properties of thermoplastic NR hybrid composites with short glass fibre and empty fruit bunch fibre were analysed by Anuar *et al*[184]. NR composites based on cellulose fibres (raw or chemically modified) as reinforcing elements were prepared and characterised, in terms of mechanical performances, by Abdelmouleh *et al*[185].

Murthy[186] carried out studies on the failure surfaces of short glass fibre rubber composites by scanning electron microscopy. Low fracture toughness has been found to be one of the major drawbacks of short-fibre composites caused by a weak fibre-matrix interface. A strong interface is required for effective load transfer from the matrix to the fibre. Rajeev *et al.*[187] used atomic force microscopy (AFM) to investigate the morphology and interfacial properties of un-aged and aged EPDM-melamine fibre composites. Interfacial adhesion between the fibre and the matrix was weak in the absence of a dry bonding system consisting of hexamethylene tetramine, resorcinol and hydrated silica (HRH). AFM images revealed the formation of an interface between the fibre and the matrix with the addition of the bonding agents. Ismail and Ghoneim[188] observed that the addition of HRH adhesion system to SBR-polyester fibre vulcanisates improved the physico-mechanical properties, electrical properties and ageing resistance. Ibarra and Jorda[189] studied the effect of diazide as an adhesive agent in short polyamide fibre reinforced elastomeric composites. The effect of urethane resin based bonding agents on the mechanical properties of short polyester fibre reinforced polyurethane composite was studied by Suhara *et al*[190]. Kavita *et al.*[191] examined the effect of fibre surface treatment on Kevlar fibre reinforced NBR composites. Zhou *et al.* [192] reported the results of coupling agents. Zinc oxide whisker with a tetrapod shape was treated with a coupling agent using an orthogonal design and was mixed into the substrate of NR to obtain the composites. The results of the experimental tests showed that the tensile strength and wear resistance of the composites progressively increased with an increased amount of the whisker. Grafted chopped fibres were introduced in polychloroprene rubber mixes by Bary *et al.*[193] in order to improve the interfacial adhesion between fibres and matrix. It has been found that the improvement in the mechanical properties of rubber composites depended markedly on the fibre concentration in the rubber mixture. The effect of the HRH adhesion system on the physico-mechanical properties of EPDM mixes was studied by Wazzan[194].

Cristine *et al.*[195] studied the dielectric properties of flame resistant EPDM composites. The kinetic parameters for the vulcanisation process and the swelling mechanism of IIR/CF composites have been reported in their studies. Das *et al.*[196] studied the variation of electrical resistivity of carbon black and short carbon fibre (SCF) filled rubber composites. They found that the incorporation of SCF imparted higher conductivity to the composite than the powderous carbon black at the same level of loading. The mechanical and dielectric properties of polyester fibre reinforced SBR composites loaded with high abrasion carbon black have been investigated by Bishai *et al*[197]. Maya *et al.*[198] studied the dielectric characteristics of sisal–oil palm hybrid biofibre reinforced NR biocomposites. Conductivity of NBR, EPDM, silicone rubber, butyl rubber and NR containing different loading of carbon fibre has been investigated by Sau *et al*[199]. Short carbon fibres were used as conductive fillers in different composites of NBR, silicon rubber, butyl rubber, EPDM and NR[48, 200].

Yonan *et al.* [201] examined the thermal stability of NR-polyester short fibre composites. The thermal and ablative properties of the vulcanisates based on EPDM, maleated EPDM and NBR reinforced with melamine fibre has been reported by Rajeev *et al*[202].The thermal stability of untreated and treated isora fibre reinforced NR composites has been studied by Lovely *et al.*[203] who found that the different chemical treatments improved the resistance against thermal degradation.

Geethamma *et al.*[204] investigated the dynamic mechanical behaviour of NR and its composites reinforced with short coir fibres. Per and Bengt[205] reported the stress/strain and dynamic mechanical properties of NR/allyl acrylate and allyl methacrylate grafted cellulose fibre composites. Ashida and Noguchi [206] investigated the dynamic mechanical properties of short fibre reinforced chloroprene composites. The effects heat, gamma radiation and ozone on the mechanical properties of short sisal fibre reinforced NR composites have been assessed by Varghese *et al*[207].

New approaches to the use of short fibre rubber composites in engineering applications were analysed by Stone and Campbell[208]. Xie and Chai[209] made a study on the manufacture and performance of fibre-reinforced cork and rubber sheet gasket materials. The results showed that fibres could improve the tensile strength, oil resistance, heat resistance and creep relaxation resistance of the sheet. Microstructure and strength of injection moulded natural fibre composites were analysed by Nyström *et al*[210]. A parametric study showed that length to diameter ratio strongly affected the composite strength. The performance of rubberwood fibre–thermoplastic natural rubber composites has been evaluated by Sameni *et al*[211]. The potential of glass fibres as reinforcement for tyre tread elastomers was studied by Rios *et al*[212].

1.11 SCOPE OF THE PRESENT INVESTIGATION AND OBJECTIVES

One of the important discoveries in the field of rubber technology was the reinforcement of rubbers by particulate fillers such as carbon black and silica. However, the reinforcement by particulate fillers alone was not sufficient in certain rubber products. The search for an alternative reinforcing agent resulted in the use of continuous fibres to meet certain specific requirements of rubber products such as tyres, hoses, conveyor belts and V-belts. But the use of continuous fibres has faced several problems which included extra processing operations like dipping, coating, wrapping, braiding and ply making. The quest for a suitable replacement for continuous fibre resulted in the emergence of short fibres as reinforcing agents in rubbers to produce versatile composite materials.

NBR is a synthetic elastomer widely used in many industrial applications especially in automotive products. The properties of NBR depend on its acrylonitrile content. It has good resistance to fuel and oil even at elevated temperatures. On the industrial side NBR finds uses in roll covers, hydraulic hoses, conveyor belting, graphic arts, oil field packers and seals for all kinds of plumbing appliances. In the automotive area NBR is used in fuel and oil handling hoses, seals and grommets. With a temperature range of – 40 °C to +125 °C, NBR materials can withstand all but the most severe automotive operating conditions. Nylon 6 fibre is a semicrystalline polyamide. It has high melting point (220 °C), tensile strength and modulus. The aim of the present work is to develop and characterise short nylon 6 fibre reinforced NBR composites.

The important objectives of the present investigation are:

- To develop composites by reinforcing NBR with short nylon 6 fibres,
- To analyse the cure characteristics and mechanical properties of the composites with special reference to the effects of fibre length, loading and crosslinking systems,
- To modify the rubber-fibre interface by the incorporation of two bonding agents, viz; hexamethylene tetramine-resorcinol and phthalic anhydride,
- To investigate the extent of interfacial adhesion by restricted equilibrium swelling technique,

- To study the dielectric properties of the newly developed composites,
- To find out the use temperature, degradation behaviour, thermal stability and the phase transitions of the new composite system,
- To follow the visco-elastic behaviour, fibre/matrix interactions and damping characteristics of the composites, by dynamic mechanical analysis,
- To examine the ageing characteristics of the composites under varying conditions of temperature, high energy radiation and ozone.

References

1. Baer E. and Moet A., *High Performance Polymers: Structure, Properties, Composites, Fibres,* Hanser Publishers, New York (1991).
2. Autar Kaw K., *Mechanics of Composite Materials,* CRS Press, New York (1997).
3. Manson J.A. and Sperling L.H., *Polymer Blends and Composites*, Plenum Press (1976).
4. Cook J. G., *Handbook of Textile Fibre and Natural Fibres,* Fourth Edn., Morrow Publishing, England (1968).
5. Richardson T., *Composites: A Design Guide*, Industrial Press Inc., New York (1987).
6. Mallick P. K., *Fibre Reinforced Composites: Materials, Manufacturing and Design,* Marcel Dekker Inc., New York (1988).
7. Wolfgang G. G., Razaina T., Rajesh K. J. and Ron K., *J. Appl. Polym. Sci.,* **73** (1999) 1329.
8. Jana S .C. and Prieto A., *J. Appl. Polym Sci.*, **86** (2002) 2168.

9. Hill C .A. S. and Abdul Khalil H. P .S., *J. Appl. Polym Sci.*, **77** (2000) 1322.

10. Zarate C. N., Arangrn M.I. and Reboredo M.M., *J. Appl. Polym Sci.*, **77** (2000) 1832.

11. Varma I. K. and Gupta V. B., *Thermosetting Resin Properties in Comprehensive Composite Materials,* Talreja R., Kelly A. and Zwetzen C. (Eds.), Elsevier Science Ltd, Oxford, UK, Vol. **2** (2000).

12. Fried J. R., *Polymer Science and Technology,* Prentice Hall, PTR, New Jersey (1995).

13. Billmeyer F.W Jr. , *Text Book of Polymer Science*, Wiley Interscience, New York (1984).

14. Morton M., *Rubber Technology,* Van Nostrand Reinhold, New York (1987).

15. Blow C.M. and Hepburn C., *Rubber Technology and Manufacture*, Second Edn., Butterworths, London (1982).

16. Kawabata S., Yamashita Y., Ooyama H. and Yoshida S., *Rubber Chem. Technol.*, **68** (1995) 311.

17. Medelia A.I., *Rubber Chem. Technol.*, **60** (1987) 45.

18. Kraus G., *Reinforcement of Elastomers,* Wiley, New York (1965).

19. Eirich F. R., *Science and Technology of Rubber*, Academic Press, New York (1978).

20. Rubin I. L., *Plastic Materials and Technology,* Wiley Inter Science, New York (1990).

21. Milewski J. V. and Katz H. S., *Handbook of Reinforcements for Plastics,* Van Nostrand Reinhold, New York (1987).

22. Gachter R. and Muller H., *Plastics Additives Handbook*, Hanser Publishers, New York (1990).

23. Astrom B. T., *Manufacturing of Polymer Composites,* Chapman and Hall, London (1997).

24. Bunsell A. R., *Fibre Reinforcement, Handbook of Composite Reinforcements,* Lee S. M., (Ed.), VCH Publishers, New York (1993).

25. Rowel R.M., Gutzmer D. I., Sachs I.B. and Kinney R. E., *Wood Sci.*, **9** (1976) 51.

26. Hill C.A.S. and Abdul Khalid H.P.S., *J. Appl. Polym. Sci.*, **78** (2000)1685.

27. Rowel R.M. and Banks W.B., Gen. Tech. Report No. FPL-GTR-50, USDA Forest Service, Forest Products Laboratory, Madison, WI (1985) 24.

28. Feiughelman M. and Nordan P .J., *J. Appl. Polym. Sci.*, **6** (1962).

29. Tinh N., Eugene Z. and Edward M.B., *J. Macromol Sci. Rev. Macromol. Chem.*, **C 20** (1981)1.

30. Tinh N., Eugene Z. and Edward M.B., *J. Macromol Sci. Rev. Macromol. Chem.* **C 21**(1981)1.

31. Rowel R.M., *Emerging Technologies for Materials and Chemicals,* Rowel R. M., Schultz T. P.and Narayan R. (Eds.) (1992) 476.

32. Rowel R.M., Esenther G.R., Youngquist J.A., Nicholas D., Nilson T., Imamura Y., Kerner Gang W., Trong L. and Deon G., *Proc. IUFRO Wood Protection Subject Group*, Canadian Forestry Service, Honey Harbor, Ontario, Canada (1988) 238.

33. Rowel R.M., Ed., *The Chemistry of Solid Wood*, Adv.Chem. Ser. 207, Americal Chemical Society, Washington D C (1986).

34. Lueers W., *Gummi Asbest. Kust.,* **27** (3) (1974) 166.

35. Czarnekei L. and White J. L., *J. Appl. Polym. Sci.,* **25** (1980) 1217.

36. Derringer D. C., *J. Elastoplast.,* **3** (1971) 230.

37. Monceau F., *Rev. Gen. Caoutch. Plast.,* **95** (1979) 542.

38. Dunnom D. D., Wagner M. P. and Derringer G. C., Chemical Divsn., PPG Industries Inc., US Patent No. 3746669 (1973).

39. Brokenbrow B. E., Simes D. and Stokoe A. L., *Rubber J.,* **151** (1969) 61.

40. Bament J., *Eur. Rub. J.,* **158** (1976) 24.

41. Bergomi L., Ger. Offen Patent No. 2115444 (1971).

42. O'Connor J. E., *Rubber Chem. Technol.,* **50** (1977) 945.

43. Pramanik P. K., Khastgir D. and Saha T. N., *Compos.*, **23** (3) (1992) 183.

44. Sieron J. K., *Rubber World,* **148** (1963) 50.

45. Ecersley T., *Developments in Rubber and Rubber Composites,* Evans C., (Ed.), Applied Science Pub., New York, Vol. **2** (1982).

46. Grimbladt M. P., Lundstrem A. M., Levit R. M. and Veselinova N. M., *Kauch. Rezina*, **33** (1974) 15.

47. Lewitt R. M., *Kauch. Rezina,* **8** (1981) 27.

48. Leonard J. D., Chicago Rawhide Mfg. Co., US Patent No. 3552755, (1971).

49. Goodloe P. M., Reiling T. L. and Mc Murtrie D. H., *Rubber Age,* **61** (1947) 697.

50. Hamed P. and Coran A. Y., *Additives for Plastics,* Seymour R. B., (Ed.), Academic Press, New York (1972).

51. Anthoine G., Arnol R. L., Boustany K. and Campbell J. M., *Eur. Rub. J.,* **157** (1975) 28.
52. Boustany K. and Coran A. Y., US Patent No. 33679364 (1972).
53. Goettler L. A. and Shen K. S., *Rubber Chem. Technol.,* **56** (1983) 619.
54. Abrate S., *Rubber Chem. Technol.,* **59** (1986) 384.
55. Gupta V. B., *Ind. J. Fibre Text. Res.,* **26** (2001) 327.
56. Ivioghe S. R., *Rubber Chem. Technol.,* **47** (1974) 1074.
57. Chakraborty S.K., Setua D.K. and De S.K., *Rubber Chem. Technol.*, **55** (1982) 1286.
58. Goettler L. A., US Patent No. 4248743 (1981).
59. Goettler L. A. and Lambright A. J., US Patent No. 4056591 (1977).
60. Goettler L. A. and Lambright A. J., US Patent No. 4057160 (1977).
61. Leo T. J. and Johansson A. M., US Patent No. 4263184 (1981).
62. Derringer D. C., *Rubber World,* **45** (1971) 165.
63. Boustany K. and Arnold R. L., *J. Elasto. Plast.*, **8** (2) (1976) 160.
64. Broutman L. J. and Agarwal B. D., *Analysis and Performance of Fibre Composites,* John Wiley and Sons, New York (1980).
65. Monette L., Anderson M. P. and Grest G. S., *Polym. Compos.,* **14** (2) (1993) 101.
66. Termonia Y., *J. Mater. Sci. Lett.,* **12** (1993) 732.
67. Rosen B. W., *Fibre Composite Materials,* Am. Soc. Metals, Metal Park, Ohio (1965).

68. Shiao M.L., Nair S.V., Garrett P.D. and Pollard R.E., *J. Mater. Sci.*, **29** (1994) 1739.
69. Fu S.Y., Hu X. and Yue C.Y., *Mater. Sci. Res. Int.*, **5** (1999) 74.
70. Murthy V. M., Bhowmick A. K. and De S. K., *J. Mater. Sci.,* **17** (1982) 709.
71. Setua D. K. and De S. K., *Rubber Chem. Technol.,* **56** (1983) 808.
72. Setua D. K. and De S. K., *J. Mater. Sci.,* **19** (1984) 983.
73. Rezadoust A.M. and Esfandeh M., *Polym-Plast. Technol. Engg.*, **44** (2005) 63.
74. Zhang L., Jin R., Geng H., Chen S., Liu L. and Wu S., *Acta Materiae Compositae Sinica,* **15** (3) (1998) 86.
75. Callister Jr W. D., *Materials Science and Engineering,* John Wiley and Sons Inc., New York (1985).
76. Neilson L. E. and Landel R. F, *Mechanical Properties of Polymers and Composites,* Marcel Decker, New York (1994).
77. Moghe S. R., *Rubber Chem. Technol.,* **49** (1976) 1160.
78. Coran A .Y., Hamed P. and Goettler L. A., *Rubber Chem. Technol.*, **47** (1974) 396.
79. McNally D. N., *Polym-Plast. Technol. Engg.,* **8** (1976) 101.
80. Coran A. Y., Boustany K. and Hamed P., *Rubber Chem. Technol.,* **47** (1974) 396.
81. Coran A. Y., Hamed P. and Goettler L. A., *Rubber Chem. Technol.,* **49** (1976) 1176.

82. Halpin J. C. and Tsai S. W., *Environmental Factors in Composite Materials Design,* AFML-TR, USA (1969) 67.

83. Moghe S. R., *Rubber Chem. Technol.,* **47** (1974) 5.

84. Coran A. Y. and Patel R., *Proc. Rubber Divsn.,* ACS, Chicago (1982).

85. Chandra N. and Ghonem H., *Compos. Part A,* **32** (2001) 575.

86. Sreekala M. S., Thomas S. and Neelakandan N. R., *J. Polym. Engg.,* **16** (4) (1997) 265.

87. Nakao K. and Nishiuchi M., *J. Adhes. Sci. Jpn.,* **2** (1966) 239.

88. Briggs D., Brewis D. M. and Konieczo M. B., *J. Mater. Sci.,* **11** (1976) 270.

89. Boening H.V., *Plasma Science and Technology,* Cornel University Press, New York (1982)

90. Rowell J., Manolache S., Mattoso L. H. C., Sarfaty M., Young R. A. and Denes F. S., *Proc. Second International Symposium on Natural Polymers and Composites,* Mattoso L. H. C., Frollini E. and Leao A., (Eds.), UNESP, Sao Polo, Brazil (1998) 45.

91. Hua Z. Q., Sitaru R., Denes F. S. and Young R., *Plasm. Polym.,* **2** (3) (1997) 199.

92. Martin A. R., Manolache S., Matasso L. H. C., Rowel R. M. and Denes F. S., *Proc. Third International Symposium on Natural Polymers and Composites (ISNAPOL),* Brazil (2000) 431.

93. Martin A. R., Manolache S., Denes F. S. and Mattaso L. H. C., *J. Appl. Polym. Sci.,* **85** (2002) 2145.

94. Owens D .K., *J. Appl. Polym. Sci.,* **19** (1975) 265.

95. Kim C.Y., Evans J. and Goring D.A., *J. Appl. Polym. Sci.*, **15** (1971) 1365.

96. Kimurand H. and Nakayama H., *Color Mater. Jpn.*, **54** (1981) 1149.

97. Wakida T. and Tokino, *Ind. J. Fibre and Textile Res.*, **21** (1996) 69.

98. Mitchenko Y. I., Krylova U.V., Lelikova T. E. and Chegolya A. S., *Fibre Chemistry*, **15**(4) (1984) 259.

99. Moe Moe Thwe. and Kin Liao., *Plast. Rubber Compos.,* **31** (10) (2002) 422.

100. Mittal K. L., *Silanes and Other Coupling Agents,* VSPBV, Netherlands (1992).

101. Pluddemann E. P., *Silane Coupling Agents,* Plenum Press, New York (1982).

102. Khazanchi A.C., Saxena M. and Rao T. C., *Text. Comp. Build. Constr.*, **20** (1990) 69.

103. Ugbolue S .C. O., *Text. Inst. J.*, **20** (1990) 1.

104. Chawla K. K., *Composite Materials; Science and Engineering,* Springer, New York (1987).

105. Richardson M. O. W., *Polymer Engineering Composites,* Applied Science Publishers, London (1977).

106. Barkakaty B. C., *J. Appl. Polym. Sci.,* **20** (1976) 2921.

107. Zuev Y. S., Karpovich T. I. and Bukhina M. F., *Kauch. Rezina,* **6** (1978) 28.

108. Usmani A. M., Salyer I. O., Ball G. L. and Schwendeman J. L., *J. Elasto. Plast.,* **13** (1981) 46.

109. Murthy V. M. and De S. K., *J. Appl. Polym. Sci.,* **29** (1984) 1355.

110. Arumugam N., Talmareselvy K. and Venkata Rao K., *J. Appl. Polym. Sci.,* **37** (1989) 2645.

111. Chand N., Varma S. and Khazanchi A. C., *J. Mater. Sci. Lett.,* **8** (1989) 1307.

112. Haseena A.P., Namitha, Priya Dasan K., Unnikrishnan G. and Thomas S., *Composite Interfaces,* **11** (7) (2004) 489.

113. Dunnom D. D., *Hi-Sil Bulletin No. 40,* Chemical Divsn., PPG Industries Inc., Pittsburgh (1969).

114. Creasy J. R., Russel D. B. and Wagner M. P., *Rubber Chem. Technol.,* **41** (1968) 1300.

115. Varghese S., Kuriakose B., Thomas S. and Koshy A. T., *J. Adhes. Sci. Technol.,* **8** (3) (1994) 235.

116. Prasantha Kumar R., Geetha Kumari Amma M. C. and Thomas S., *J. Appl. Polym. Sci.,* **58** (1995) 597.

117. Jacob M., Thomas S. and Varughese K. T., *Compos. Sci. Technol.,* **64** (7) (2004) 955.

118. Mc Neill I.C., *Comprehensive Polymeric Science*, Vol.**6**, Allen, G (Ed), Pergamon Press, New York (1989).

119. Kevin P. M., *Dynamic Mechanical Analysis-A Practical Introduction,* CRC Press, New York (1999).

120. Murayama T., *Dynamic Mechanical Analysis of Polymeric Materials,* Elsevier, New York (1999).

121. Campbell J. M., *Prog. Rubber Technol.,* **41** (1978) 43.

122. Rogers J. W., *Rubber World,* **27** (1981) 183.

123. Yantiskaya S. M., Goldberg B. B., Dubinker E. M. and Pozdnyakava C. V. *Kauch. Rezina,* **32** (1973) 28.

124. Shinda Y. and Hazelton D. R., *Rubber. Chem. Technol.,* **51** (1978) 253.

125. Goettler L. A., Lambright A. J., Leib R. I. and Dimauro P. J., *Rubber Chem. Technol.,* **54** (1981) 277.

126. Goettler L. A., Leib R. I., Di Muro P. J. and Kear K. F., *Presentation to the Detroit Rubber Group,* USA (1979).

127. Beatty J. R. and Hamed P., *Elastomer.,* **27** (1978) 110.

128. Walker L.A. and Harber J B., *Kauts. Gummi Kunst.,* **38** (1985) 494.

129. Inoue S., Nishi T., Shibata S., Matsunaga T. and Kaneko Y., US Patent No. 3968 (1976).

130. Boustany K. and Coran A. Y., To Monsanto Co., US Patent No. 3802 (1974) 478.

131. Dzyura E. A., Mamon V. L., Krivonos A. M. and Putakin K. S., *Intl. Polym. Sci. Technol.,* **4** (4) (1977) 101.

132. Dzyura E. A., Kuzmin A. V., Klimenko L. G. and Belkovskii V. N., *Kauch. Rezina,* **12** (1982) 27.

133. Goettler L. A., Sezena J. A. and DiMauro P. J., *Rubber World,* **134** (1) (1982) 33.

134. Nesiolovskaya T. N., Solovev E. M., Zakharov N. D., Emellyanov D. P., Sergeeva N. L. and Galybin G. M., *Polym. Sci. Technol.*, **10** (3) (1983) 73.

135. Georgieva V. S. and Vinogradova G. G., *Kauch. Obvun. Promst.*, **22** (4) (1980) 45.

136. Skogman R. T. and Scheie C. E., *Tappi,* **52** (1969) 1549.

137. Orlov Z. D., Semenok E. I., Lomakina T. V. and Tokmantseva L. F., *Kauch. Rezina,* **11** (1981) 38.

138. Ratliff O. D., *Proc. Rubber Divsn.*, ACS, Minneapolis (1976).

139. Holyster G. S. and Thomas C., *Fibre Reinforced Material,* The Metallurgical Society, Warrendale, USA (1985).

140. Ashby M. F. and Brechet Y. J. M., *Acta. Mater.*, **51** (2003) 5801.

141. Ibarra R. L., Chamorro A. C. and Taberneoro M. C., *Polym. Compos.*, **9** (3) (1988) 198.

142. Foldi A. P., *Rubber Chem. Technol.*, **49** (1976) 379.

143. Noguchi T., Ashida M. and Satishi M., *Nipp. Gomu Kyak.*, **57** (1984) 829.

144. Jana P. B. and De S. K., *Plast. Rubber Compos. Proces. Appl.*, **17** (1) (1992) 43.

145. Kutty S. K. N. and Golok N. B., *Plast. Rubber Compos. Proces. Appl.*, **19** (2) (1993) 105.

146. Sreeja T. D. and Kutty S. K. N., *J. Elasto. Plast.*, **33** (3) (2001) 225.

147. Wada N. and Uchiyama Y., *Intl. Polym. Sci. Technol.*, **21** (10) (1994).

148. Rezadoust A. M. and Esfandeh M., *Polym. Polym. Compos.,* **9** (6) (2001) 403.

149. Vajrasthira C., Amomsakchai T. and Bualek Limcharoen S., *J. Appl. Polym. Sci.,* **87** (2003) 1059.

150. Tascioglu C., Goodell B. and Anido R. L., *Compos. Sci. Technol.,* **63** (2003) 979.

151. Zhanxun C., Fe S., Kexin W. and Xu S., *Hecheng Xiang jiao Gongye,* **14**(5) (1991) 323.

152. Seema A. and Kutty S. K .N., *Polym-Plast. Technol. Engg.,* **44** (2005) 1139.

153. Guan C., Li J. and Ren Y., *Corros. Sci. and Prot. Technol,* **17**(4) (2005) 252.

154. Kondo Y., Miyazaki K., Yamaguchi Y., Sasaki T., Irie. S. and Sakurai K., *Eur. Polym. J,* **42** (5) (2006) 1008.

155. Ibarra L. and Palma E., *Kauts. Gummi Kunst.,* **52** (5) (1999) 329.

156. Manchado M .A .L. and Arroyo M., *Polym. Compos.,* **23** (2002) 666.

157. Ibarra L. and Chamorro C., *J. Appl. Polym. Sci.,* **37** (1989) 1197.

158. Subic H., Musjak J., Lesar J., Peerdish N., Skofic I. and Vizocisek I., *Plast. Gumma. Suppl.,* **1** (1985) 21.

159. George J., Joseph K., Bhagawan S. S. and Thomas S., *Mater. Lett.,* **18** (1993) 163.

160. Varghese S., Kuriakose B. and Thomas S., *Plast. Rub. Compos. Appl.,* **20** (1993) 930.

161. Prasantha Kumar R., Manikandan Nair K. C., Thomas S., Schit S. C., Ramamurthy K., *Compos. Sci. Technol.,* **60** (9) (2000) 1737.

162. Martins A. F., Suarez J. C. M., Visconte L. L. Y. and Nunes R. C. R., *J. Mater. Sci.,* **38** (2003) 2415.

163. Job A. E., Oliveira F. A., Alves N., Giacometti J. A. and Mattoso L. H. C., *Synth. Metals.,* **135** (2003) 99.

164. Li Y., Mai Y. W. and Ye L., *Compos. Sci. Technol.,* **60** (2000) 2037.

165. Ismail H. and Nurdin H., *Iran. Polym. J.,* **7** (1) (1998) 53.

166. Ismail H. and Jaffri R. M., *Polym. Test.,* **18** (5) (1999) 381.

167. Ismail H., Jaffri R. M. and Rozman H. D., *Polym. Intl.,* **49** (6) (2000) 618.

168. Srilathakutty R., Joseph R. and George K. E., *Plast. Rub. Compos.,* **29** (2000) 96.

169. Abad M., Noguera P., Puchades R., Maquieira A. and Noguera V., *Bioreso. Technol.,* **82** (2002) 241.

170. Arumugam N., Tamereselvey K. and Venketa Rao K., *J. Appl. Polym. Sci.,* **37** (1989) 2645.

171. Bhattacharya T.B., Biswas A.K. and Chatterjee J., *Plast. Rubber Proc. Appl.,* **6** (1986) 119.

172. Setua D.K., *Kauts. Gummi Kunst.,* **37** (1984a) 962.

173. Setua D. K. and De S.K., *Rubber Chem. Technol.,* **56** (1983) 808.

174. Setua D. K. and De S .K., J *Mater. Sci.,* **19** (1984) 983.

175. Setua D .K. and Dutta B. J., *J. Appl. Polym Sci.,* **29** (1984) 3097.

176. Murthy V. M., De S. K., Bhagawan S. S., Sivaramakrishnan R. and Athithan S., *J. Appl. Polym. Sci.,* **28** (1983) 3485.

177. Ismail. H., Rosnah N. and Rozman H. D., *Eur. Polym. J.*, **13**(8) (1997) 1231.

178. Ismail H., Rosnah N. and Rozman H.D., *Polymer*, **38** (16) (1997) 4059.

179. Sameni J. K., Ahmad S. H. and Zakaria S., *Plast. Rubber Compos.*, **31** (4) (2002) 162.

180. Ibrahim N. A., Yunus W. M. Z. W., Abullaiwi F. A., Rahman M. Z., Bin Ahmad M. and Dahlan K. Z. M., *J. Appl. Polym. Sci.,* **89** (2003) 2233.

181. Gustav Ahlblad., Kron Anna. and Stenberg Bengt, *Polym. Intl.*, **33** (1) (1994) 103.

182. Hepburn C. and Aziz Y. B., *Int. J. Adhesion and Adhesives.*, **5**(3) (1985)153.

183. Joseph S., Joseph K. and Thomas S., *Int. J. Polym. Mater.* **55** (11) (2006) 925.

184. Anuar H., Ahmad S.H., Rasid R. and Nik Daud., *Polym-Plast. Technol. Engg.,* **45** (9) (2006)1059.

185. Abdelmouleh M., Boufi S., Belgacem M.N. and Dufresne A., *Comp. Sci. Technol.*, **67** (2007) 1627.

186. Murthy V. M., *Intl. J. Polym Mater.,* **10** (1983) 149.

187. Rajeev R. S., De S. K., Bhowmick A. K., Kao G. J. P. and Bandyopadhyay S., *J. Mater. Sci.,* **36** (11) (2001) 2621.

188. Ismail M. N. and Ghoneim A. M., *Polym. Plast. Technol. Engg.,* **38** (1) (1999) 71.

189. Ibarra L. and Jorda C., *J. Appl. Polym. Sci.,* **48** (1993) 375.

190. Suhara F., Kutty S .K. N. and Nando G.B., *Polym-Plast. Technol. Engg.*, **37**(2) (1998) 241.

191. Kavita A., Setua D. K. and Mathur G. N., *Def. Sci. J.*, **52** (3) (2002) 337.

192. Zhou Z., Liu S. and Gu L., *J. Appl. Polym. Sci.,* **80** (9) (2001) 1520.

193. Bary Abdel E. M., Helaly F. M. and El Nesre E. M, *Polym. Adv. Technol.,* **8** (10) (1997) 587.

194. Wazzan A. A., *Int. J. Polym. Mater.*, **53** (2004) 59.

195. Cristine C., Leila Lea Yuan Visconte, Marcio Antonio Sens and Regina Celia Reis Nunes, *Polym. Degrad. Stab.*, **70** (2) (2000) 259.

196. Das N. C., Chaki T. K. and Khastgir D., *Polym. Intl.,* **51** (2) (2002) 156.

197. Bishai A.M., Ghoneim A.M., Ward A. A. M. and Younan A.F., *Int. J. Polym. Mater.,* **51** (2002) 793.

198. Maya J., Varughese K.T. and Thomas S., *J. Mater. Sci.*, **41** (2006) 5538.

199. Sau K .P., Chaki T . K. and Khastgir D., *Polymer,* **39** (25) (1998) 6461.

200. Kanamori K., *Int. Polym Sci. Technol.*, **13**(2) (1986).

201. Yonan A.F., Ismail M. N. and Khalaf A .I., *Polym. Degrad. Stab.*, **48** (1995) 103.

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

203. Lovely M., Joseph K. and Rani Joseph., *Prog. Rubber Plast. Recycl. Technol.*, **20** (4) (2004) 337.

204. Geethamma V. G., Kalaprasad G., Gabriël Groeninckx and Thomas S., *Compos. Part A*, **36** (11) (2005) 1499.

205. Per Flink and Bengt Stenberg, *Brit. Polym. J.*, **22** (2) (1990) 147.

206. Ashida M. and Noguchi, *J. Appl. Polym. Sci.*, **30** (1985) 1011.

207. Varghese S., Kuriakose B. and Thomas S., *Polym. Degrad. Stab.*, **44** (1) (1994) 55.

208. Stone C.R. and Campbell J. M., *Proc. Conference on Materials Engineering*, London, **133** (1984).

209. Xie Sujiang and Chai, *Acta Mater.*, **15** (4) (1998) 6.

210. Nyström B., Joffe R. and Långström R., *J. Reinf. Plast. Compos.*, **26** (2007) 579

211. Sameni J K., Ahamed S.H. and Zakaria S., *Polym-Plast. Technol. Engg.*, **42** (2003) 139.

212. Rios S., Chicure R. and Castillo L.F.D., *Mater. Des.*, **22** (2001) 369.

Chapter 2

Materials and Methodology

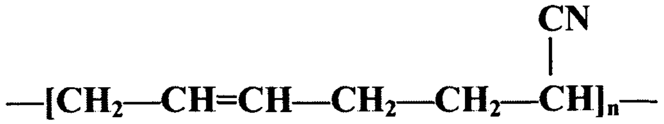
Abstract

The materials and experimental methods used for the development and characterisation of short nylon 6 fibre reinforced NBR composites are presented in this chapter. The characteristics of the base materials and the fabrication procedure for the composites are described. The methods for the examination of fibre breakage, cure characteristics, mechanical properties, interfacial adhesion, dielectric properties, thermal features, dynamic mechanical behaviour and ageing under different environmental conditions have also been discussed.

2.1 MATERIALS

2.1.1 Acrylonitrile butadiene rubber (NBR)

NBR is a copolymer of acrylonitrile and butadiene. It is generally prepared by free radical emulsion polymerisation using redox initiators such as hydrogen peroxide or ferrous sulphate. It is a special purpose rubber, having good resistance to a wide variety of non-polar oils, fats and solvents. Therefore it is extensively used for making oil resistant appliances such as oil seals and automobile parts[1]. The properties of NBR depend on its acrylonitrile content. The NBR used in the present work was supplied by Gujarat Apar Polymers Ltd, Mumbai, India. The structure of NBR is given in Scheme 2.1 and its basic characteristics are listed in Table 2.1.



$$-[CH_2-CH=CH-CH_2-CH_2-\overset{\overset{CN}{|}}{CH}]_n-$$

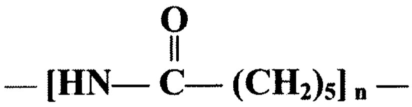
Scheme 2.1 Structure of NBR

Table 2.1 Basic characteristics of NBR

Property	Value
Bound acrylonitrile (%)	35.0
Volatile matter (%)	0.13
Anti oxidant (%)	1.40
Organic acid (%)	0.25
Soap (%)	0.004
Mooney viscosity ($ML_{1+4:\ 100^{o}C}$)	40.0
Intrinsic viscosity (dl.g)	1.53

2.1.2 Nylon 6 fibre

Nylon 6 is generally prepared by the ring opening polymerisation of caprolactam. It is used as a plastic as well as a fibre. It has good tensilte strength, abrasion resistance and toughness[1]. Nylon 6 for the present work was obtained from Sri Ram Fibres Ltd. Chennai, India in yarn form. The structure of nylon 6 is presented in Scheme 2.2 and its characteristics are listed in Table 2.2



$$-[HN-\overset{\overset{O}{\|}}{C}-(CH_2)_5]_n-$$

Scheme 2.1 Structure of Nylon 6

Table 2.2 Physical properties of nylon fibre

Physical Property	**Value**
Density (g cm^{-3})	1.14
Diameter (μm)	25.00
UTS* (GPa)	0.90
Modulus (GPa)	4.90
Melting Point (°C)	220.00
Glass transition temperature (°C)	47.00

* Ultimate tensile strength

2.1.3 Rubber chemicals

Sulphur (specific gravity 1.9) and dicumyl peroxide (DCP; 40% active) were used as crosslinking agents. The other rubber chemicals used were accelerators, tetramethyl thiuram disulphide (TMTD) and mercapto benzothiazyl disulphide (MBTS) and the activator combination of zinc oxide and stearic acid. All these reagents, of commercial grade, were obtained from Indian Rare Earths, Aluva, Ernakulam, Kerala, India.

2.1.4 Special chemicals

The bonding agent components, resorcinol and hexamethylene tetramine used were of pure grade supplied by S. D. Fine Chemicals, Mumbai, India. The resorcinol was ground well and added in the powdered form in order to disperse it homogeneously in the masticated NBR matrix[2]. Phthalic anhydride, another bonding agent used, was of laboratory grade and was obtained from New India Chemical Enterprises, Cochin, Kerala, India.

2.1.5 Solvents

The polar solvents dimethyl formamide, dimethyl sulphoxide and acetonitrile used were of laboratory reagent grade supplied by E. Merck (India) Ltd., Mumbai, India. They were distilled twice before use to ensure purity.

2.2 PREPARATION OF COMPOSITES

The composites were prepared by incorporating nylon 6 fibres of different length and loading into NBR matrix according to a base formulation. All the mixes were prepared by using a laboratory two roll mixing mill (150 × 300 mm) manufactured by Kelachandra Machines, Chingavanam, Kerala. The compounding was done as per ASTM D15-627 (1994). The nip gap, mill roll speed ratio and the number of passes were kept the same for all the mixes. Initially, NBR was masticated on the mill for 2 minutes followed by the addition of the ingredients. The additive stearic acid was ground well before addition and added in the powdered form. Fibres were added at the end of the compounding process, and the samples were milled for sufficient time to confirm the uniform fibre distribution. The rolling direction was kept constant because of its importance for fibre orientation. After the complete mixing, the stock was sheeted out and finally passed through the mill at a tight nip gap to ensure maximum fibre orientation in the grain direction [3]. All ingredients were added in the master-batch form.

The formulations of sulphur cured mixes are given in Table 2.3. The gum sample without any fibres has been denoted as A. Mixes B, C and D represent the systems containing fibres of length 2 mm, 6 mm and 10 mm at a constant loading of 6 phr.

Table 2.3 Formulations of sulphur cured mixes (phr[a])

	A	B	C	D	E	F	G
NBR	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
MBTS[b]	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TMTD[c]	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Hexa[d]	---	---	---	---	---	---	1.92
Resorcinol	---	---	---	---	---	---	3.84
Nylon 6 fibre (phr)	---	6	6	6	15	24	24
Fibre length (mm)	----	2	6	10	6	6	6

[a] Parts per hundred rubber
[b] Mercapto benzo thiazyl disulphide
[c] Tetramethyl thiuram disulphide
[d] Hexamethylene tetramine

E and F denote mixes containing 15 phr and 24 phr fibres of length 6 mm. G represents the composite with 24 phr fibres of length 6 mm containing hexa-resorcinol bonding agent.

In DCP cured composites, the gum sample has been denoted as H. Mixes containing 6, 12, 15, 18, 24 and 30 phr fibres of length 6 mm have been represented as I, J, K, L, M and N respectively. O and P represent mixes containing fibres of length 2 and 10 mm at a constant loading of 6 phr. Q and R represent hexa-resorcinol and phthalic anhydride bonded composites respectively, both containing 24 phr fibres of length 6mm. The formulations of DCP cured mixes are given in Table 2.4.

Table 2.4 Formulations of mixes (phr)

	H	**I**	**J**	**K**	**L**	**M**	**N**	**O**	**P**	**Q**	**R**
NBR	100	100	100	100	100	100	100	100	100	100	100
DCP	5	5	5	5	5	5	5	5	5	5	5
Hexa	---	---	---	---	---	---	---	---	---	1.92	---
Resorcinol	---	---	---	---	---	---	---	---	---	3.84	---
Phthalic anhydride	---	---	---	---	---	---	---	---	---	---	3
Nylon 6 Fibre	---	6	12	15	18	24	30	6	6	24	24
Fibre length (mm)	---	6	6	6	6	6	6	2	10	6	6

2.3 FIBRE BREAKAGE ANALYSIS

The extent of fibre breakage during mixing was estimated by immersing 1 g of the unvulcanised mix, containing nylon 6 fibres, in acetonitrile in order to dissolve the rubber components and to separate the fibres intact. The fibres were washed with acetonitrile to ensure complete removal of rubber from the surfaces. The washed fibres were then collected and examined under a travelling microscope. The fibre breakage pattern has been indicated by the fibre length distribution curve. The distribution of fibre lengths has been represented in terms of moments of distribution[4, 5].

The number and weight-average fibre length are defined by the equations;

$$\overline{L_n} = \Sigma N_i L_i / \Sigma N_i \qquad \text{......(2.1)}$$

$$\overline{L_w} = \Sigma N_i L_i^2 / \Sigma N_i L_i \qquad \text{......(2.2)}$$

Where $\overline{L_n}$ is the number-average fibre length, $\overline{L_w}$ is the weight-average fibre length, and N_i is the number of fibres having length L_i.

The value of $\overline{L_w} / \overline{L_n}$, known as the polydispersity index, is a measure of the breadth of the fibre length distribution. The values of $\overline{L_n}$ $\overline{L_w}$ and $\overline{L_w} / \overline{L_n}$ were calculated from the data for 100 numbers of chopped nylon 6 fibres extracted from the mix.

2.4 CURE TIME EVALUATION

The cure characteristics of the mixes were followed by using a Monsanto Rheometer R-100 at a rotational frequency of 100 cycles/ min as per ASTM standard D-5289 (2001). The optimum cure time corresponds to the time to achieve 90% of the cure (t_{90}) which was calculated by using the equation:

$$t_{90} = 0.9 (M_H - M_L) + M_L \qquad \text{............ (2.3)}$$

where M_H and M_L are the maximum and minimum torques respectively expressed in dNm.

2.5 VULCANISATION OF MIXES

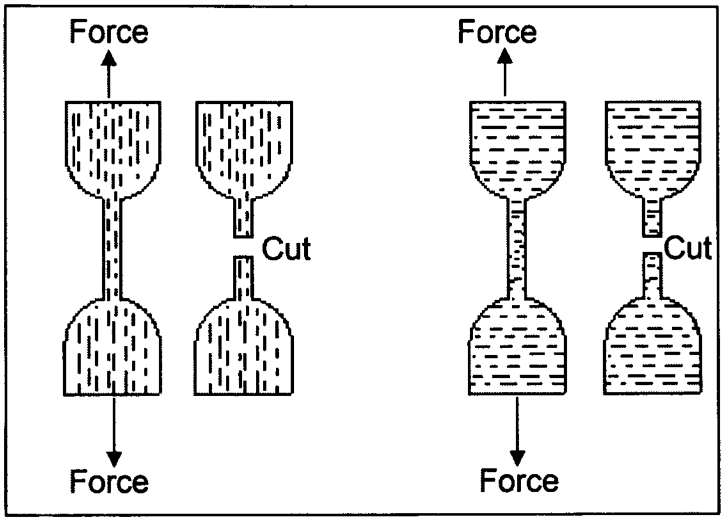
Vulcanisation of the mixes was done at 153 °C using a hydraulic press having electrically heated platens (150 mm × 150 mm × 2mm) at a pressure of 689.4 kPa (100 psi) to their respective cure times as obtained from the rheographs. The sheets were cooled quickly in water at the end of the curing process and stored in a cold and dark place for 24 hours. In order to prepare the samples with fibres oriented longitudinally, the compounded sheets were moulded along the grain direction. Similarly, for samples with fibres oriented transversely, the sheets were moulded across the grain direction.

2.6 MEASUREMENT OF MECHANICAL PROPERTIES

2.6.1 Tensile properties

Tensile measurements of the composites were carried out using dumb bell shaped samples cut along (longitudinally oriented fibre) and across (transverse orientation) the grain direction. Figure 2.1 shows the longitudinal and transverse fibre orientations in tensile samples. The thickness of the narrow portion was measured by a thickness gauge. Stress-strain measurements were carried out using a Universal Testing Machine (ZWICK-1474) at a crosshead speed of 50 cm min^{-1} using dumb bell shaped samples. Modulus, tensile strength, and elongation at break were determined according to ASTM test method D 412 (2002). The tensile strength was calculated by using the equation:

$$\text{Tensile strength} = \frac{\text{Ultimate load or load at break}\left(\text{N}\right)}{\text{Cross sectional area}\left(\text{m}^2\right)} \qquad \text{......} (2.4)$$



(a) **(b)**

Figure 2.1 Longitudinal and transverse orientations in tensile samples (a) longitudinal (b) transverse

2.6.2 Tear strength

Tear strength was determined by cutting the samples along (longitudinal) and across (transverse) the grain direction, as per ASTM D-624 (2002). The thickness of the narrow portion was measured by a thickness gauge. The tests were carried out using a Universal Testing Machine (ZWICK-1474). Tear strength was calculated by using the equation:

$$\text{Tear strength} = \frac{\text{Ultimate load (N)}}{\text{Thickness (m)}} \qquad \text{......}(2.5)$$

2.6.3 Hardness

Hardness was measured at room temperature by using a Shore–A hardness tester (Durometer-Mitutoyo Shore-A meter) as per ASTM D-2240 (1999). The samples having a thickness of 6 mm were used. The instrument used a calibrated spring to provide the indenting force. The load imposed by the spring varied with indentation.

2.7 SCANNING ELECTRON MICROSCOPY (SEM)

The surface morphology of the composite systems was examined by scanning electron microscopy (SEM), as per the principles reported by Johari and Samudra [6] and De and Dhindaw[7]. The surface of the composite systems and the fracture front of the samples were sputter-coated with gold and the photographs were taken using a scanning electron microscope (Cambridge Instrument S-360).

2.8 RESTRICTED EQUILIBRIUM SWELLING (RES) EXPERIMENTS

For swelling studies, circular specimens were punched out from the vulcanised composite sheets by using a sharp steel die having a diameter of 1.9 cm. The weighed dry specimens were immersed in polar aprotic solvents such as N, N-dimethyl formamide (DMF), dimethyl sulphoxide (DMSO) and acetonitrile contained in diffusion test bottles, kept in an air oven at constant temperature. After a particular time, they were removed from the solvent and wiped by using tissue papers. The weights of these specimens after swelling in the solvents were determined by using a highly sensitive electronic balance (Shimadzu Libror–210, Japan) at regular intervals until no further increase in solvent uptake was detected; i.e.; weighing was done until equilibrium sorption was reached. The thickness and diameter of the samples before and after swelling were determined by using a gauge micrometer and vernier calipers respectively. Similar methodology has been followed by several other researchers[8,9].

2.8.1 Swelling data analysis

(a) Swelling coefficient

Swelling coefficient is an index showing the extent to which the samples swell. The gum and fibre filled vulcanisates were swollen in a suitable solvent at room temperature and the swelling coefficient was evaluated by the equation[8, 9]:

$$\text{Swelling coefficient } (\alpha) = \frac{W_2 - W_1}{W_1} \times \frac{1}{\rho_s} \qquad \text{...... (2.6)}$$

where W_1 is the initial weight of the sample , W_2, the final or swollen weight of the sample and ρ_s, the density of the solvent used.

(b) Calculation of Q_t (mol %)

The uptake of liquid during swelling has been expressed as moles of liquid sorbed by 100g of the polymer composite. This method has been found to be more convenient for the comparison of sorption data[8,10]. The mole percentage uptake, Q_t, for the composite samples has been determined as[9]:

$$Q_t = \frac{W_2 - W_1/M_s}{W_1} \times 100 \qquad \text{...... (2.7)}$$

where M_s is the molecular weight of the solvent. The sorption data was evaluated by plotting the mole percentage uptake (Q_t) of the solvent versus the square root of the time of immersion in different solvents.

(c) Correlation with adhesion

The extent of adhesion between short fibres and rubber at different fibre loadings and in presence of bonding agents has been evaluated from the relation[11]:

$$V_T = \frac{(V_0 - V_r)}{V_0} \qquad \text{...... (2.8)}$$

where V_T is the ratio of change in volume fraction of rubber before and after swelling (V_0 - V_r) to the volume fraction of the rubber before swelling (V_0). The quantity V_r has been used to evaluate the extent of crosslinking. It was determined as[11]:

$$V_r = \frac{(D - V_f W_1)\rho_r^{-1}}{(D - V_f W_1)\rho_r^{-1} + A_0 \rho_s^{-1}} \qquad \text{......(2.9)}$$

where D is the weight after drying out, V_f, the volume fraction of fibre, ρ_r, the density of the polymer, and A_0, the weight of the imbibed solvent.

(d) Flory- Rehner equation

The interaction of organic solvents with rubbery polymers can be well explained by absorption and diffusion phenomena[12]. The molecular mass between the crosslinks can be calculated by using the following Flory–Rehner equation[13]:

$$M_{CL} = -\frac{\left[\rho_r V_s V_r^{1/3}\right]}{\left[\ln(1 - V_r) + V_r + \chi V_r^2\right]} \qquad \text{.....(2.10)}$$

where M_{CL} is molecular mass of polymer between crosslinks, V_s, the molar volume of the solvent and χ, the interaction parameter given by the Hildebrand equation[12]:

$$\chi = \left[\beta + V_s(\delta_s - \delta_p)^2 / RT\right] \qquad \text{....(2.11)}$$

where β is the lattice constant, R, the universal gas constant, T, the absolute temperature and δ_s and δ_p are the solubility parameter of solvent and polymer respectively.

2.8.2 Swelling anisotropy

The swelling process of a composite is significantly controlled by the direction of orientation of the fibres. To analyse the swelling geometry of the composite samples (anisotropic swelling), sorption studies were conducted by using rectangular strips (25 × 10 × 2 mms) cut at various angles (θ) with respect to the orientation of fibres, from the tensile sheets. These samples were swollen in N, N-dimethyl formamide at room temperature for 72 hours.

2.9 MEASUREMENT OF DIELECTRIC PROPERTIES

Disc shaped samples having a thickness of 2 mm and a diameter of 10 mm were used to evaluate the dielectric properties. The test samples were coated with conductive silver paint on either sides and copper wires were fixed on both sides of the samples as electrodes. The capacitance, resistance and dissipation factor were measured directly by using a HP 4 192 A Impedance Analyser (Hewlett-Packard, Japan). The measurements were done at varying frequencies ranging from 10 KHz to 13 MHz as per ASTM standard D-150 (2004).

2.9.1 Analysis of dielectric properties

(a) Dielectric constant

The dielectric constant of an insulating material is defined as the ratio of the charge stored in the material placed between two metallic plates to the charge stored when it is replaced by air (or vacuum). The dielectric constant, E′, was determined from capacitance using the equation:

$$E' = Ct/E_0A \qquad \ldots(2.12)$$

where C is the capacitance, t, the thickness, E_0, the permittivity of air (8.85×10^{-12} Fm^{-1}) and A, the area of cross section of the samples.

(b) Dielectric loss factor

The electrical loss or the amount of energy dissipated by an insulating material when the voltage is applied to the circuit can be represented by means of dissipation factor. Most of the elastomers have lower dissipation factor at room temperature. The loss factor (E″), dielectric constant (E′) and dissipation factor (tan δ) are related by the equation:

$$\tan\delta = E''/E' \qquad \text{....(2.13)}$$

(c) Conductivity

When the conductivity, ∂, due to the free charge is negligibly small (good dielectric), the effective conductivity is due to electric polarization[14] and is represented as:

$$\partial = \omega E_0 E'' = \omega E_0 \tan\delta\, E' \qquad \text{....(2.14)}$$

where ω represents the angular frequency i.e.; ω = 2 πν, where ν is the frequency.

(d) Volume resistivity

The resistance of an insulating material depends on its volume resistivity (Ω), which has been calculated by using the equation:

$$\Omega = 1/\partial \qquad \text{....(2.15)}$$

2.10 THERMOGRAVIMETRY (TG)

The thermal behaviour of nylon 6 fibre and nylon/NBR composites was analysed by using a thermogravimetric analyser TGA Q50 V2.34 Build 127 system. A small amount (1-4 mg) of the sample was taken for the analysis and the samples were heated from 30 to 800 °C at a heating rate of 10 °C/minute. The instrument recorded the thermogravimetric (TG) and differential thermogravimetric (DTG) profiles of each sample.

2.11 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The heat flow and glass transition temperature (T_g) of composite systems were measured by using a DSC Q 100 V 3.5 Build 175 system. The samples were first cooled to -80 °C using liquid nitrogen and the scan was made from -80 to100 °C at a heating rate of 10 °C/minute. For the determination of T_g, two tangents were drawn from the base lines of the DSC curve and the perpendicular bisector gave the T_g of the samples.

2.12 DYNAMIC MECHANICAL ANALYSIS (DMA)

Vulcanised rectangular sheets of specimens having length 50 mm, width 10 mm and thickness 2 mm were used for DMA. The dynamic storage modulus (G'), loss modulus (G''), mechanical damping ($\tan \delta$) and the glass transition temperature (T_g) were measured by using a dynamic mechanical thermal analyser (NETZSCH DMA 242). The temperature range through which the properties were determined was -110 to 104 °C, with a dynamic force of ±3 N, at a heating rate of 2 °C/min. Three point bending or flexural modes were used as forced vibration at varying frequencies such as 0.1, 1, 10 and 50 Hz with a strain amplitude of 120 μm.

2.13 AGEING CHARACTERISTICS

2.13.1 Effect of temperature

The effect of thermal ageing was studied by keeping the dumb bell shaped tensile samples (having thickness 2 ± 0.2 mm) in an oven at 100 °C for 7 and 14 days. Tensile properties before and after thermal ageing were examined according to ASTM D-412 (2002) test method at a cross head speed of 50 cm min^{-1}, by using dumb bell shaped samples. The results have been expressed in terms of the percentage retention of modulus and tensile strength after ageing.

2.13.2 Effect of gamma (γ) radiation

The effect of high energy radiation on the composites was studied by irradiating the dumb bell shaped tensile samples (having thickness 2 ± 0.2 mm) with γ- rays from a ^{60}Co source. The samples were irradiated for different radiation doses such as 5, 10 and 15 Mrad at a dose rate of 0.228 Mrad/h. Tensile properties before and after γ-ray irradiation were studied according to ASTM D-412 (2002) test method. The results have been expressed in terms of the percentage retention of modulus and tensile strength after ageing.

2.13.3 Ozone resistance

Ozone resistance of the composite systems was examined according to ASTM D-11349 (2001). Samples were exposed to ozonised air in an ozone test chamber (MAST Model 700-1, USA) for 40 h. The chamber provided an atmosphere with controlled concentration of ozone and temperature. The concentration of ozone was maintained at 50 pphm and the temperature inside the chamber at 38 °C. The initiation of cracks by the ozone attack on the samples was analysed by optical photography.

References

1. Billmeyer F. W Jr., *Text Book of Polymer Science*, Third Edn., Wiley Interscience (1994).
2. Rajeev R. S., De S. K., Bhowmick A. K., Kao G. J. P. and Bandyopadhyay S., *J. Mater. Sci.*, **36** (11) (2001) 2621.
3. O'Connor J. E., *Rubber Technol.*, **50** (1977) 945.

4. Mora Wetz H., *Macromolecules in Solution,* Second Edn., Inter Science, New York (1975).
5. Czarnekei L. and White J. L., *J. Appl, Polym. Sci.,* **25** (1980) 1217.
6. Johari O. and Samudra A. V., *Characterisation of Solid Surfaces,* Kane P. F. and Larrabe G. B., (Eds.), Plenum Press, New York (1974).
7. De S. K. and Dhindaw B. K., *J. Scan. Electron Micros.,* **3** (1982) 973.
8. Toti U. S., Kariduraganavar M. Y., Soppimath S. and Aminabhavi T. M., *J. Appl. Polym. Sci.,* **83** (2002) 259.
9. Geethamma V. G. and Thomas S., *J. Adhes. Sci. Technol.,* **18** (8) (2004) 951.
10. Khinnavar S. and Aminabhavi T. M., *J. Appl. Polym. Sci.,* **42** (1991) 2321.
11. Prasantha Kumar R. and Thomas S., *J. Adhes. Sci. Technol.,* **6** (2001) 633.
12. Flory P. J., *Principles of Polymer Chemistry,* Cornell University, Ithaca, New York (1953).
13. Flory P. J. and Rehner J., *J. Chem. Phys.,* **11** (1943) 521.
14. Honey John., Biju Kumar S., Mathew K. T. and Rani Joseph, *Plast. Rub. Compos. Macro. Mole. Engg.,* **32** (7) (2003) 306.

Chapter 3

Processing Characteristics and Mechanical Properties of Nylon 6/NBR Composites

Abstract

The cure characteristics and mechanical properties of short nylon 6 fibre reinforced NBR composites have been analysed with special reference to the effects of fibre length, loading, orientation and rubber crosslinking systems. Addition of nylon fibres to NBR has been found to offer good reinforcement and to improve the mechanical properties. It has been observed that the maximum rheometric torque of NBR matrix increases in the presence of fibres. A fibre length of 6 mm has been observed to be optimum for the best balance of properties. Tensile properties increase with fibre loading up to 24 phr. Composites vulcanised by dicumyl peroxide (DCP) system have better mechanical properties than those by sulphur system. The experimental results have been compared with the theoretical values by using parallel and Hirsch models.

Contents of this chapter have been published in:
Journal of Applied Polymer Science, **92** *(2004) 1023*

3.1 INTRODUCTION

Short fibres are used as reinforcements in rubber matrices due to the considerable processing advantages and improvement in most of the mechanical properties. Several researchers have studied the processing characteristics and the mechanical properties of short fibre reinforced rubber composites. The effect of the concentration of carbon fibre (CF) on the physico-chemical properties of CF reinforced butyl rubber composites was studied by Deghaidy[1]. It has been pointed out that the addition of carbon fibres accelerated the vulcanisation process by acting as a catalyst and improved the physico-chemical properties of butyl rubber.

The mechanical properties of short jute fibre reinforced SBR have been studied by Murthy and De [2], who found that jute fibres offered a good reinforcement to SBR compared to glass fibres. Armugam *et al.*[3] examined the mechanical properties of coir fibre reinforced NR. They reported that the tensile strength and tear strength decreased with increase in filler loading and the presence of a bonding agent enhanced the adhesion between the fibres and rubber.

Tensile and tear properties of short fibre reinforced chloroprene rubber (CR) have been studied by Ryu and Lee[4]. Use of sisal and coir fibres as reinforcing fillers for NR has been investigated by Varghese *et al.*[5] and Geethamma *et al.*[6] Prasantha Kumar *et al.*[7] studied the use of sisal as reinforcing fillers in SBR matrix. Nunes and Affonso[8] examined the interaction of NBR with cellulose fibres. Setua and co-workers[9-14] tried short silk fibres as reinforcement for rubbers. Murthy[15] studied the reinforcing effect of fibre glass on the physico-mechanical properties of NR. Ibarra and Chamorro [16, 17] investigated the mechanical properties of carbon, polyester, glass, polyamide, and cellulose fibre reinforced EPDM, NR, CR, NBR and SBR. Coran *et al.*[18] reported the effect of various fibres such as glass, nylon, rayon, and cellulose on both natural and synthetic rubber matrices.

The present chapter deals with the curing characteristics and mechanical properties of short nylon 6 fibre reinforced NBR composites with special attention to the effects of fibre length, fibre loading, fibre orientation and rubber crosslinking systems. The fibre breakage during the processing of the composite systems has been analysed. The surface morphology and the fracture topography have also been examined by scanning electron microscopy (SEM).

3.2 RESULTS AND DISCUSSION

3.2.1 Fibre breakage

Fibres usually undergo breakage due to the high shear force caused during mixing. The severity of fibre breakage depends mainly on the type of fibre, the initial aspect ratio and the magnitude of the stresses and strains experienced by the fibres during processing. The breakage pattern of fibres is indicated by the fibre length distribution curve. Figure 3.1 shows the fibre length distribution curves of short nylon 6, which was cut to 6 mm, before and after mixing. The majority of the fibres are of length between 5.1 and 5.3 mm, after mixing. The distribution of fibre lengths can be represented in terms of moments of distribution[19, 20]. It can be seen from Table 3.1 that the ratio of weight and number average fibre length ($\overline{Lw} / \overline{Ln}$) remains almost the same before and after mixing indicating that no considerable fibre breakage occurred during mixing.

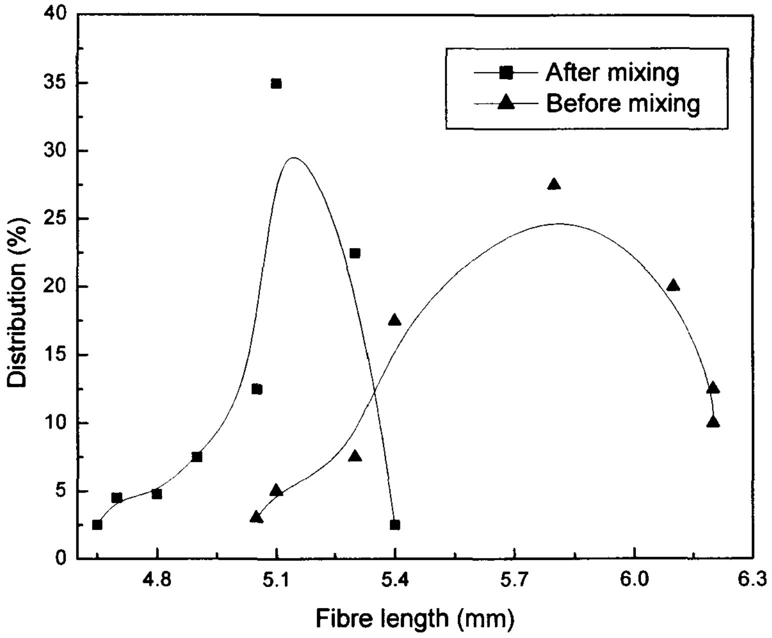


Figure 3.1 Fibre length distribution curve

Table 3.1 Fibre length distribution index

	Fibre length (mm)	$\overline{Ln}$ (mm)	$\overline{Lw}$ (mm)	$\overline{Lw}/\overline{Ln}$
Before mixing	2	1.94	1.87	0.963
	6	5.92	5.97	1.008
	10	9.78	9.62	0.983
After mixing	2	1.50	1.41	0.940
	6	4.60	5.07	1.102
	10	8.31	8.11	0.975

3.2.2 Processing characteristics

The cure characteristics and thus the processibility of the compounds have been studied from the rheographs. The maximum torque in the rheograph is a measure of crosslink density and the stiffness of the NBR matrix. In general, for all mixes, the torque initially decreases and then increases and finally levels off. The initial decrease in torque to a minimum value is due to the softening of the rubber matrix while the increase in torque is due to the crosslinking of the rubber. The leveling off is an indication of the completion of curing. It is found that, generally the presence of fibres increases the maximum torque.

3.2.2.1 Effect of fibre length

The rheographs of the mixes H, O, I and P, containing 6 phr nylon fibres of length 0 (gum), 2, 6 and 10 mms respectively cured by DCP, are given in Figure 3.2. It can be seen that the maximum rheometric torque increases with increase in fibre length up to 6 mm and then decreases. The increase in torque is due to the increased restriction to deformation caused by the fibre reinforcement. The decrease in torque after 6 mm clearly indicates that the effective reinforcement thereafter decreases due to fibre entanglement and 6 mm is the optimum length for short nylon reinforcement into NBR matrix. It is reported that the increase in torque is directly proportional to crosslink density [21]. Table 3.2 (a) shows the effect of fibre length on the cure characteristics of composites cured by DCP. It can be seen that at constant

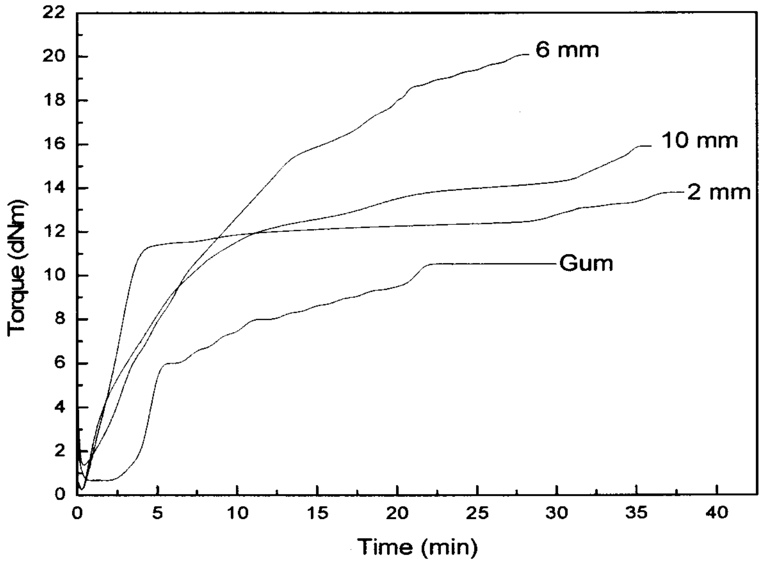


Figure 3.2 Rheographs of mixes containing fibres of different length

fibre loading of 6 phr as the fibre length increases the cure time (t_{90}) increases. This is due to the fact that for the same loading as the fibre length decreases the number of fibre ends increases. The increased ends generate more heat due to friction [8] and thus decreases the cure time. It has been observed that the scorch time also increases with fibre length. Table 3.2 (b) shows the effect of fibre length on the cure characteristics of composites cured by sulphur (Mixes A, B, C and D). The variation in cure characteristics with fibre length of the composites cured by sulphur shows the same trend as that of the samples cured by DCP.

Table 3.2 (a) Effect of fibre length on the cure characteristics of DCP cured mixes

Fibre length (mm)	Max Torque (dNm)	Min. Torque (dNm)	dT (dNm)	t_{90} (min)	Scorch time (min)
0 (gum)	10.65	0.33	10.32	19.98	0.69
2	13.79	2.11	11.68	27.28	1.01
6	19.60	1.20	18.40	29.75	1.03
10	15.90	2.88	13.02	30.90	1.35

Table 3.2 (b) Effect of fibre length on the cure characteristics of sulphur cured mixes

Fibre length (mm)	Max Torque (dNm)	Min. Torque (dNm)	dT (dNm)	t_{90} (min)	Scorch time (min)
0 (gum)	11.79	0.50	11.29	4.60	3.18
2	12.31	0.64	11.67	4.88	3.43
6	15.20	0.48	14.72	7.22	3.50
10	13.45	0.42	13.03	9.32	4.12

3.2.2.2 Effect of fibre loading

Figure 3.3 shows typical rheographs of mixes H, I, J, L and M cured by DCP containing 0 (gum), 6, 12, 18 and 24 phr nylon 6 fibres respectively of length 6 mm. The presence of fibres causes an increase in viscosity and torque of the mixes. This clearly suggests an increased stiffness of nylon/NBR systems with increase in fibre loading. Table 3.3 shows the effect of fibre loading on the cure characteristics of composites. It can be seen that increase in fibre loading from 6 phr to 24 phr has no considerable effect on the cure time. The scorch time has been found to be increased with fibre loading.

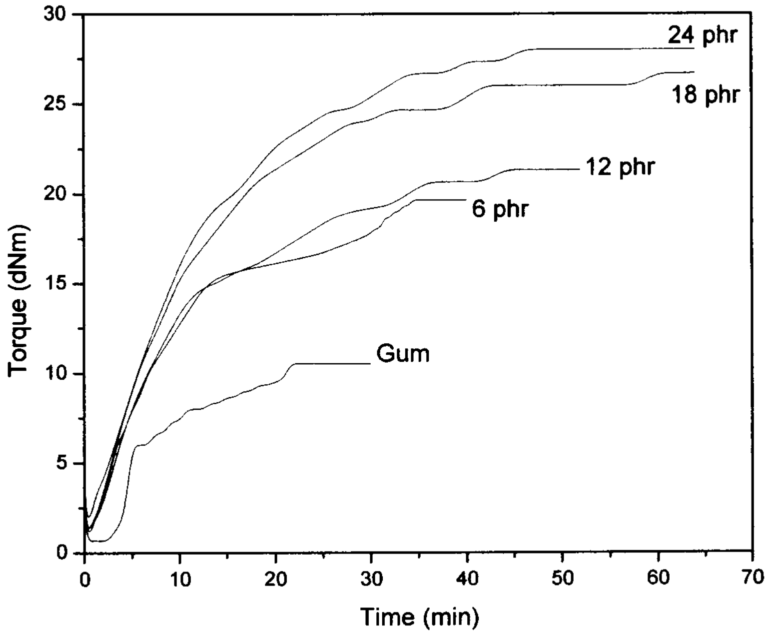


Figure 3.3 Rheographs of mixes at different fibre loading

Table 3.3 Effect of fibre loading on the cure characteristics of mixes

Fibre loading (phr)	Max Torque (dNm)	Min. Torque (dNm)	dT (dNm)	t_{90} (min)	Scorch time (min)
0 (gum)	10.65	0.33	10.32	19.98	0.69
6	19.60	1.20	18.40	29.75	1.03
12	21.33	0.83	20.50	30.42	1.04
18	25.96	1.15	24.81	30.00	1.06
24	27.88	1.37	26.51	30.06	1.08

3.2.2.3 Effect of curing systems

Figure 3.4 shows the rheographs of the mixes E and K representing samples containing 15 phr of nylon 6 fibres of length 6 mm cured by sulphur and DCP system respectively. It is seen that the maximum torque is higher in the DCP system than the sulphur system at a fibre loading of 15 phr. The cure time of DCP mix is higher and scorch time lower than the sulphur system as shown in Table 3.4.

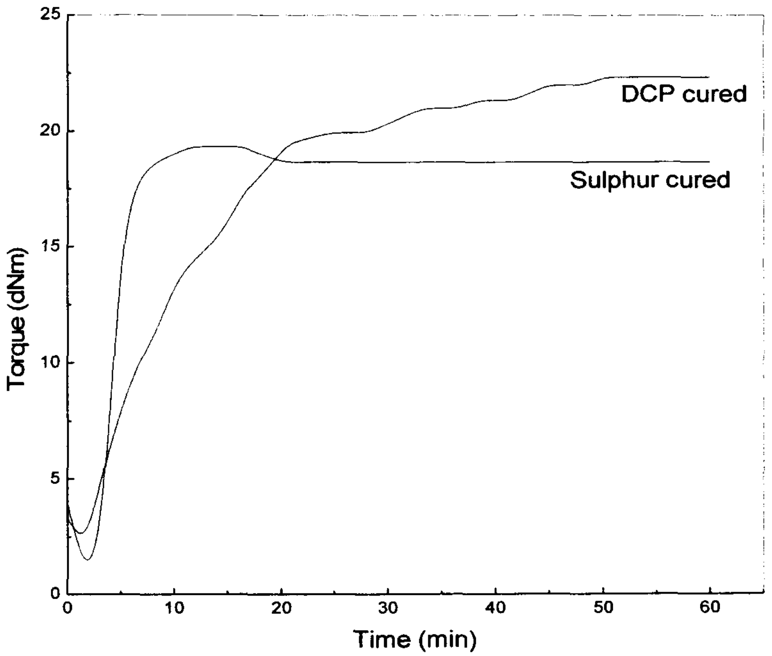


Figure 3.4 Rheographs of mixes cured by sulphur and DCP

Table 3.4 Effect of crosslinking system on the cure characteristics of mixes

Curing system	Max. Torque (dNm)	Min. Torque (dNm)	dT (dNm)	t_{90} (min)	Scorch time (min)
Sulphur	18.63	0.87	17.76	6.15	2.92
DCP	22.09	1.04	21.05	29.72	1.17

The difference in the torque values and cure time can be explained on the basis of the different types of crosslinks introduced between the macromolecular chains of

NBR during vulcanisation. The reinforcement of fillers varies with the flexibility of the macromolecular networks due to the different crosslinks present. DCP forms rigid C-C linkages whereas sulphur introduces flexible mono, di and polysulphidic linkages as shown in Figures 5 (a), and (b). In DCP cured system, there is more restriction to chain deformation due to the rigid C-C linkages, whereas in sulphur system the restriction to deformation is lesser because of the flexible nature of the polysulfidic linkages. This indicates that nylon/NBR systems cured by DCP are stiffer than that by sulphur.

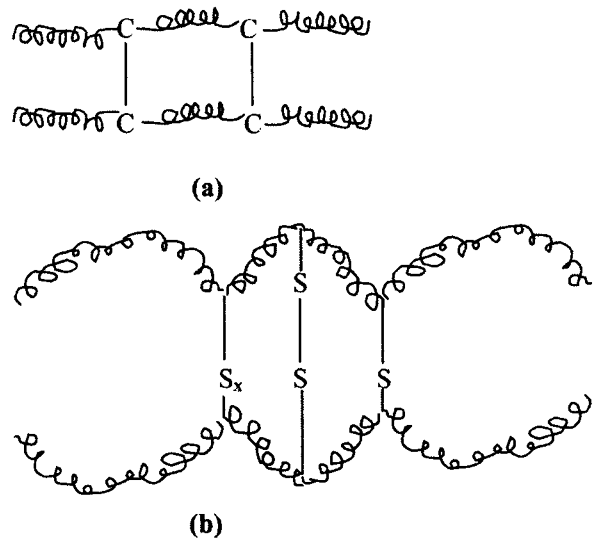


Figure 3.5 (a) C-C linkages in DCP cured system
(b) Poly sulphidic linkages in sulphur cured system

3.2.3 Mechanical properties

3.2.3.1 Effect of fibre length

The properties of short fibre reinforced elastomer composites depend heavily on the degree to which an applied load is transmitted to the fibres. Fibre length influences the extent of load transmittance. At a critical fibre length, the load transmittance from the matrix to the fibre is maximum. If the critical fibre length is higher than the length of the fibre, the stressed fibre will debond from the matrix and the composite will fail at a low load. If the critical fibre length is lesser than the length of the fibres, the stressed composites will lead to the breaking of the fibres.

The stress-strain curves of mixes H, O, I and P, representing gum and samples containing 6 phr nylon 6 fibres of length 2 mm, 6 mm and 10 mm respectively, are shown in Figure 3.6. The deformation of the composites can be understood from the stress-strain curve. Addition of fibres increases the modulus of the composite.

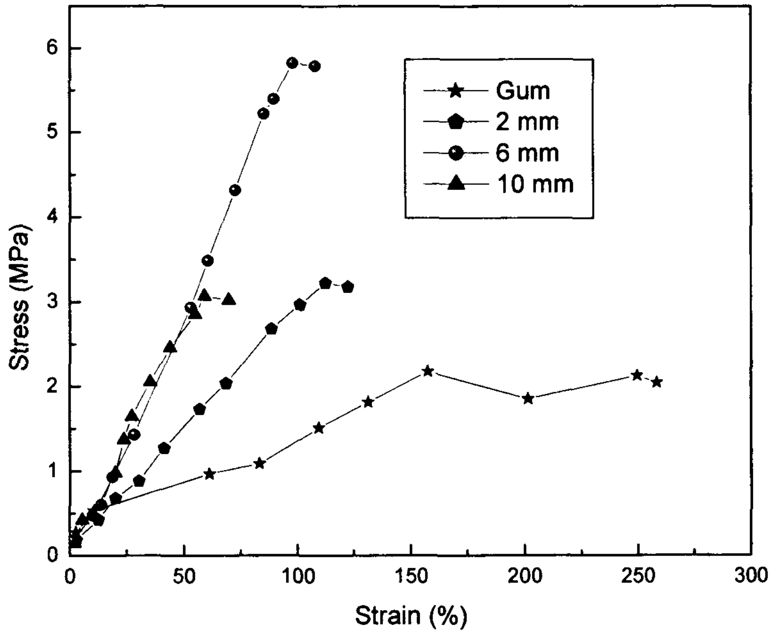


Figure 3.6 Stress-strain curves of composites at different fibre length

Table 3.5 shows the effect of fibre length on the mechanical properties of the composites. The composite with nylon fibres of length 6 mm shows the maximum tensile strength (Mix I). Increase in fibre length beyond 6 mm reduces the strength of the composite system probably due to fibre entanglement. The moduli at 10 and 20% elongation also show a maximum value for the composite containing nylon fibres of length 6 mm. Composite with fibres of length 6mm shows the maximum tear strength and hardness. The elongation at break however, has been found to be reduced regularly with increase in fibre length because the increase in fibre length can decreases the possibility for rearrangement and deformation of the macromolecular chains under an applied load.

Table 3.5 Effect of fibre length on the mechanical properties of composites

Mechanical property		Fibre length (mm)			
		0 (gum)	**2**	**6**	**10**
Tensile strength (MPa)	**L**	2.22	3.22	5.82	3.07
	T	2.08	2.40	2.50	2.40
Tear strength (kN/m)	**L**	7.38	17.27	37.25	30.00
	T	7.14	16.40	24.50	22.50
Modulus (MPa) 10% elongation	**L**	2.68	3.09	4.77	4.75
	T	2.90	2.89	3.52	3.40
20% elongation	**L**	2.35	3.25	5.00	4.89
	T	2.62	2.80	3.02	2.91
Elongation at break (%)	**L**	256.30	122.60	97.60	93.30
	T	260.30	128.40	124.00	96.40
Hardness-Shore A		56	68	75	71

L: Longitudinal orientation T: Transverse orientation

3.2.3.2 Effect of fibre loading

The stress-strain behaviour of short nylon fibre- NBR composites containing fibres of length 6 mm at different loadings, cured by DCP is shown in Figure 3.7. It can be seen that the addition of fibres results in an increase in modulus and reduction in elongation at break. Table 3.6 shows the effect of fibre loading on the mechanical properties of the composites cured by DCP. The tensile strength has been found to be increased with increase in fibre concentration upto 24 phr. As the fibre concentration increases the stress is more evenly distributed and the strength of the composite increases. Moduli at 10 and 20% elongation also show a continuous increase up to a fibre loading of 24 phr. The tear strength of the composites shows the same gradation as that of tensile strength and thus the composite with 24 phr fibre loading shows the highest tear strength. It can be seen from Table 3.6 that there is a decline in tensile strength, modulus and tear strength of the composites above a fibre loading of 24 phr. This can be attributed to the agglomeration of fibres within the matrix above 24 phr. This agglomeration blocks the effective stress distribution in the composites leading to deterioration in properties above 24 phr.

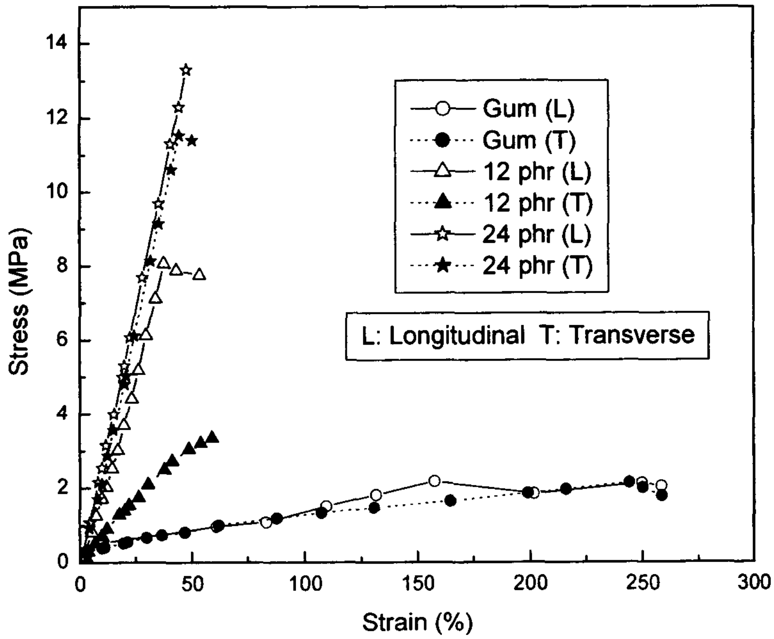


Figure 3.7 Stress-strain curves of composites at different fibre loading

Table 3.6 Effect of fibre loading on the mechanical properties of composites

Mechanical property		Fibre loading (phr)					
		0(gum)	**6**	**12**	**18**	**24**	**30**
Tensile Strength (MPa)	**L**	2.22	5.82	8.05	11.86	13.29	11.96
	T	2.08	2.50	3.34	7.61	11.03	7.76
Tear Strength (kN/m)	**L**	7.38	37.25	41.40	56.47	80.20	72.80
	T	7.14	24.50	32.61	53.95	75.90	49.50
Modulus (MPa) 10% elongation	**L**	2.68	4.77	17.11	23.30	25.36	24.98
	T	2.90	3.52	7.13	16.98	20.90	16.23
20% elongation	**L**	2.35	5.00	18.46	24.90	26.51	25.64
	T	2.62	3.02	6.97	16.98	24.00	17.11
Elongation at break (%)	**L**	256.30	97.60	54.00	53.30	47.67	44.30
	T	260.30	124.00	59.30	56.00	51.60	47.67
Hardness-Shore A		56	75	80	81	84	88

L : Longitudinal orientation **T** : Transverse orientation

From Table 3.6, it is also clear that hardness of the composites increases with increases in fibre loading. Elongation at break of the mixes decreases with fibre loading; the initial decrease being more dominant. With increase in fibre loading the stiffness and brittleness of the composites increased regularly with an associated decrease in elongation at break.

3.2.3.3 Effect of curing systems

Figure 3.8 shows the stress-strain curves of the composites containing 24 phr fibre cured by dicumyl peroxide and sulphur (Mixes M and F). It can be seen that composite with DCP system shows a more brittle type behavior than that with the sulphur system at higher strain values. At lower strain values, however, the effect of vulcanising systems cannot be differentiated. This can be attributed to the coiled nature of the long macromolecular chains of NBR (Figure 3.5). When a stress is applied decoiling happens irrespective of the vulcanising system. After a threshold strain, the different crosslinking systems exert resistance to deformation to different extents.

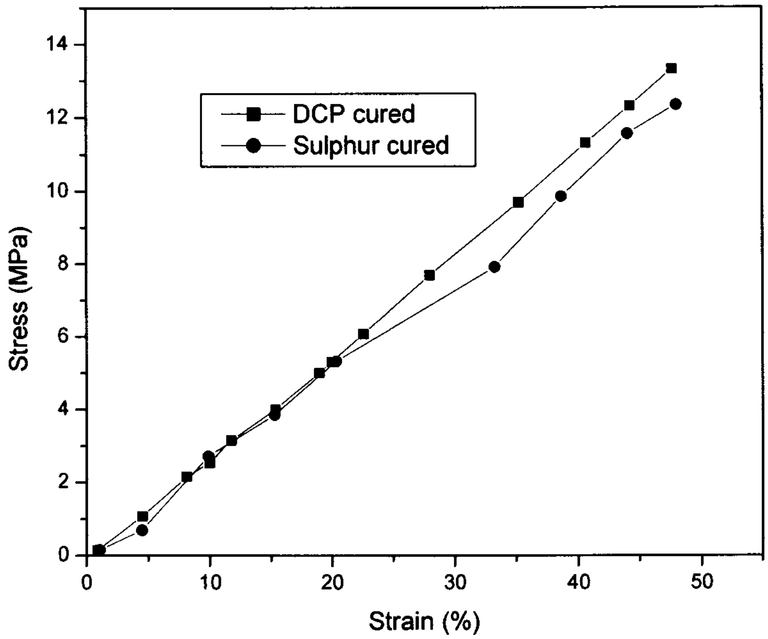


Figure 3.8 Stress-strain curves of composites cured by sulphur and DCP

Table 3.7 shows the effect of crosslink systems on the mechanical properties of the composites. Comparison has been made with composites containing 24 phr fibres of length 6 mm cured by DCP and sulphur (Mixes M and F). It can be seen that there are differences in the tensile strength, tear strength and modulus of the composites. The composite cured by DCP system has been found to have comparatively higher tensile strength, tear strength and modulus. The composites also show differences in the elongation at break when cured by different crosslinking systems. The composite with DCP as the crosslinking agent has been found to have lower elongation at break than that with the sulphur crosslinking system. Hardness is also higher for composites cured by DCP system. This differences in mechanical properties can be explained in terms of the difference in the crosslinks introduced by sulphur and DCP during vulcanisation (Figure 3.5). The different crosslinking systems exert restriction to deformation to different extents.

Table 3.7 Effect of curing systems on the mechanical properties of composites

Mechanical property		Curing system	
		Sulphur	**DCP**
Tensile Strength (MPa)	**L**	12.32	13.29
	T	11.32	11.43
Tear Strength (kN/m)	**L**	49.87	80.20
	T	38.90	75.90
Modulus (MPa) **10% elongation**	**L**	24.80	25.36
	T	19.30	20.90
20% elongation	**L**	25.90	26.51
	T	23.20	24.00
Elongation at break (%)	**L**	48.00	47.67
	T	52.70	51.60
Hardness-Shore A		82	84

3.2.3.4 Effect of fibre orientation

Fibre orientation influences the composite properties[22]. For example, a balanced fibre orientation gives a hose its optimum design strength[23]. For a fixed mill opening, maximum possible fibre orientation will be achieved during the first pass. However, a poorly dispersed fibrous composite requires more than one pass. The properties of milled short fibre elastomer composites depend only on mill opening and not on mill-roll speed, roll-speed ratio or number of passes[24]. The complete orientation of fibres in a given direction is practically impossible. However, depending on the fibre type, fibre loading and rubber matrix it is possible to orientate the majority of fibres. During the milling of rubber composites, the fibres tend to orientate along the flow direction, causing the mechanical properties to vary in different directions[25]. The optimum properties of the composites can be obtained by controlling the flow direction. A large shear flow during milling forces the fibres to orient along the mill direction.

When the fibres are aligned longitudinally, the maximum stress transfer occurs between the fibres and the matrix. The maximum strength and reinforcement are achieved along the direction of fibre alignment. Thus mechanical properties such as tensile strength, tear strength and modulus are found to be higher in the longitudinal than in the transverse direction (Tables 3.3, 3.4 and 3.5 and Figure 3.7) for nylon 6/NBR composites.

Scanning electron microscopy (SEM) can be used to examine the fracture topography of composites. The presence of fibres in the mix changes the fracture modes. The fracture of fibre-reinforced composites occurs in two modes[26] (i) breakage of fibres leading to fracture and (ii) pull out of several fibres from the composite. Figure 3.9 (a) shows how fibres are longitudinally oriented in nylon 6/NBR composites. In longitudinally oriented fibrous composites the fibres are oriented perpendicular to the fracture point and the pull out of fibres takes place during tensile testing. The broken ends of the fibres protruding in the fracture surface can be seen in the photomicrograph given in Figure 3.9 (b).

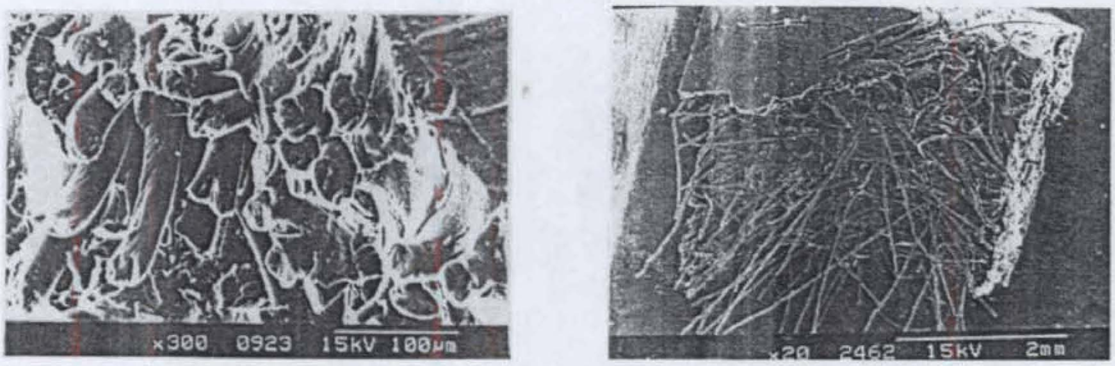


Figure 3.9 (a) SEM photograph showing longitudinal orientation of fibres in the composite (Mix K)

(b) SEM photograph showing fibres protruding from the tensile fracture surface (Mix K)

3.2.4 Theoretical modeling

Several theories have been proposed to evaluate the experimental values obtained for mechanical properties by using different parameters such as fibre length, fibre orientation, fibre dispersion, fibre geometry, fibre loading, interfacial adhesion between fibres and matrix and the properties of constituent components of the composites[27, 28]. These theories take into account the nature of the matrix and reinforcements[29-31]. The reinforcing effect of fibres can be calculated by using the parallel and Hirsch models[32, 33]. According to the parallel model, the tensile strength is given by the following equation:

$$T_c = T_m V_m + T_f V_f \qquad \text{.........(3.1)}$$

where T_c, T_m and T_f are the tensile strength of the composite, matrix and fibre respectively. V_m and V_f are the volume fractions of the matrix and fibre respectively. For the parallel model, isostrain conditions have been assumed for both the matrix and the fibres[31].

According to Hirsch's model, the tensile strength is calculated using the following equation:

$$T_c = x\left(T_m V_m + T_f V_f\right) + \left(1 - x\right)\frac{T_m T_f}{T_m V_f + T_f V_m} \qquad \text{...... (3.2)}$$

where 'x' varies between 0 and 1.

Figure 3.10 compares the theoretical and experimental tensile strength of longitudinally oriented composites. The experimental values of the tensile strength of the present composite systems show a good agreement with the Hirsch's model. The experimental values of tensile strength however, show large deviation from the parallel model. Usually parallel model describes the strength of continuous fibre-reinforced polymeric composites. The assumption of either uniform stress or uniform strain used in Parallel model is clearly an over-simplification of the real case. The stress-transfer mechanism for continuous fibre-reinforced composites is different from that of short fibre composites. In the case of short-fibre composites, stress transfer depends largely on the fibre orientation, the stress concentration at the fibre ends, critical fibre length, etc.

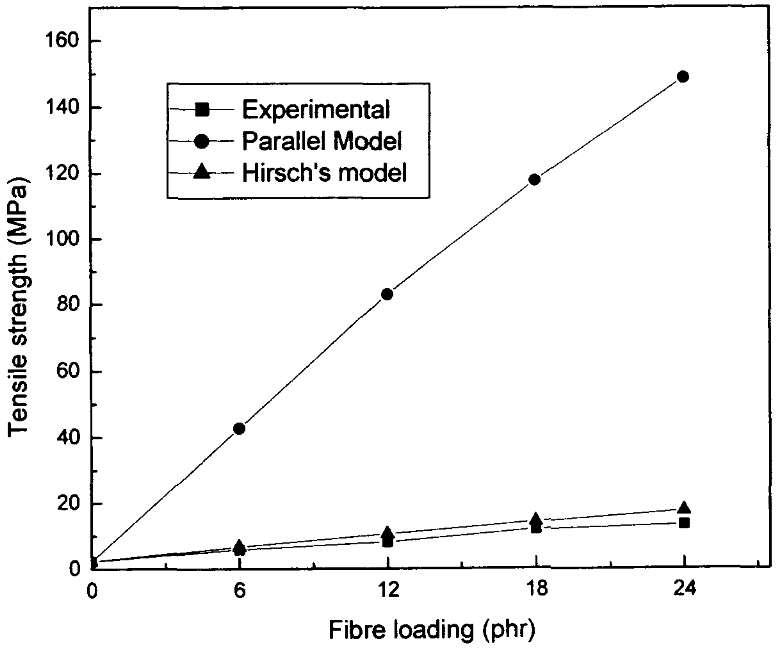


Figure 3.10 Comparison of experimental tensile strength of composites with theoretical models

The experimental values of tensile strength show good agreement with Hirsch model when the value of 'x' is 0.1 for longitudinally oriented composites. The controlling factors for the value of 'x' have been found to be mainly the fibre orientation, fibre length and stress amplification effect at the fibre ends.

3.3 CONCLUSIONS

The processing characteristics and mechanical properties of short nylon fibre reinforced NBR composites have been analysed in terms of fibre length, loading, orientation and rubber crosslink systems. The initial analysis showed that there was no significant breakage, during processing. Addition of nylon fibre to NBR offered good reinforcement and improved the mechanical properties. A fibre length of 6 mm has been found to be optimum for the best balance of properties. Tensile properties have been found to be increased with fibre loading up to 24 phr. Composites vulcanised by DCP system showed better mechanical properties than those by the sulphur system. The experimental results were compared with the theoretical values by using parallel and Hirsch models.

References

1. Deghaidy F. S., *Egyp. J. Solids*, **23** (1) (2000) 167.
2. Murthy V. M. and De S. K., *J. Appl. Polym. Sci.*, **29** (1984) 1355.
3. Armugam N., Tamara Selvy K., Venkata Rao K. and Rajalingham P., *J. Appl. Polym. Sci.*, **37** (1989) 2645.
4. Ryu S.R. and Lee D. J., *Ksme Int. J.*, **15** (2001) 35.
5. Varghese S., Kuriakose B., Thomas S. and Koshi T. A., *Ind. J Nat. Rubber. Res.*, **4** (1) (1991) 55.
6. Geethamma V. G., Joseph R. and Thomas S., *J. Appl. Polym. Sci.*, **55** (1995) 583.

7. Prasantha Kumar R., Geethakumari Amma M. L. and Thomas S., *J Appl. Polym Sci*, **58** (1995) 597

8. Nunes R. C. R. and Affonso J. E. S., *Kauts. Gummi Kunst.*, **52** (1999) 787.

9. Setua D.K., *Kauts. Gummi Kunst.*, **37** (1984) 962.

10. Setua D.K. and De S.K., *Rubber Chem . Technol.*, **56** (1983) 808.

11. Setua D.K. and De S.K., *J. Mater. Sci.*, **19** (1984) 983.

12. Setua D.K. and De S. K., *J. Mater. Sci*, **20** (1985) 2653.

13. Setua D.K. and Dutta B.J., *J. Appl. Polym Sci*, **29** (1989) 3097.

14. Setua D. K., *Polym.Commun.*, **25** (1984b) 345.

15. Murthy V. M., *Int. J. Polym. Mater.*, **10** (1983) 149.

16. Ibarra L. and Chamorro C., *J. Appl. Polym. Sci.*, **37** (1989) 1197.

17. Ibarra L., *J. Appl. Polym.Sci.*, **49** (1993) 1295.

18. Coran K., Boustany K. and Hamed P., *Rubber Chem. Technol.*, **47** (1974) 396.

19. Morawetz H., *Macromolecules in solution*, Second Edn., Interscience, New York (1975).

20. Czarnekei L. and White J. L., *J.Appl. Polym. Sci.*, **25** (1980) 1217.

21. Ibarra L. and Jorda C., *J Appl. Polym.Sci.*, **48** (1993) 375.

22. Ashton J. E., Halpin J. C. and Petit P. H., *Primer on Composite Materials,* Technomic Publication Co., West Fort, CT, USA (1969).

23. Goettler., Patent No. 46068 W 28 DT, Monsanto, Germany (1975).

24. Moghe S. R., *Rubber Chem. Technol.*, **49** (1976) 1160.

25. Coran A. Y., Boustany K. and Hamed P., *J. Appl. Polym. Sci.,* **15** (1971) 2471.

26. Murthy V .M., Bhowmik A. K ., and De S. K., *J.Mater. Sci.*, **17** (1982) 709.
27. Brostow W. and Corneliussen R. D., *Failure of Plastics,* Hanser, New York (1986) 443.
28. Hull D., *An Introduction to Composite Materials,* Cambridge University Press, London (1981).
29. Robinson I. M. and Robinson J. M., *J. Compos. Technol. Res.,* **29** (1995) 4663.
30. Kelly A. and Tyson R., *J. Mech. Phys. Solids,* **13** (1965) 329.
31. Chawla K. K., *Composites in Materials Science and Engineering,* Springer, New York (1987) 177.
32. Broutman L. and Krock R., *Modern Composition of Materials,* Mir Publishers, Moscow (1970).
33. Hirsch T. J., *J. Am. Con. Inst.,* **59** (1962) 427.

Chapter 4

Interface Modification of Nylon 6/NBR Composites through Bonding Agents

Abstract

The interface modification of short nylon 6 fibre reinforced NBR composites has been carried out by the incorporation of two different bonding agents, viz., hexamethylene tetramine-resorcinol and phthalic anhydride. The cure characteristics and mechanical properties of the bonded composites have been analysed. The addition of bonding agents increases the maximum torque while reducing the optimum cure time and scorch time of the composites. The bonding agent added composites exhibit superior mechanical properties than the corresponding unbonded systems. The improved adhesion between fibres and rubber in bonding agent added composites has been confirmed by scanning electron microscopy.

4.1 INTRODUCTION

The properties of fibre reinforced composite materials depend on the combined behaviour of the reinforcing fibres, polymeric matrix and the fibre-matrix interface. Existence of good interfacial bonding between fibres and matrix is an essential requirement to achieve good physical properties. In composites, the matrix molecules may be anchored to the fibre surface by chemical reactions or adsorption which determines the extent of interfacial adhesion. Interaction at the interface can be improved either by using a bonding agent or by different surface treatments for the fibre. These additives can modify the interface by interacting either chemically or physically with both the fibres and the matrix[1].

Several researchers have reported the use of different bonding agents to modify the interfacial strength of fibre-rubber composites. A tricomponent dry bonding system based on hydrated silica-resorcinol-hexamethylene tetramine (HRH) has been used successfully in many short fibre elastomer composites[2-12]. Hewitt[13] has demonstrated the importance of zinc oxide and stearic acid in the HRH system to promote fibre-matrix adhesion. Dunnon[14] proposed the rough guidelines for the manipulation of the compounding and processing factors in the course of designing an optimum adhesion compound. Darwish and Lawandy[15] reported the use of HRH as an adhesion promoter for nylon cord to NBR. They also studied the effect of replacement of resorcinol with *o*-aminophenol, *m*-aminophenol, *p*-aminophenol and *m*-phenylene diamine. Pokluda and Osoha[16] used different types of cresols to replace resorcinol in HRH bonding system. Varghese *et al*[17] showed that silica was not needed as a component in the dry bonding system when sisal fibre was used as reinforcement. The effects of urethane resins based on polymeric 4, 4'-diphenylmethane diisocyanate (MDI) and different diols on the mechanical properties of short polyester fibre reinforced polyurethane composite were studied by Suhara *et al*[18, 19]. The urethane based bonding system affected the processability of the composites adversely. However, the tensile strength, modulus, and the abrasion resistance of the composites were improved by the urethane bonding system. Sreeja and Kutty[20] investigated the effect of a bonding agent, based on urethane, on the cure characteristics and mechanical properties of NR/whole tyre reclaim–short nylon fibre composites. Haseena *et al.*[21] reported the use of a two component bonding system consisting of hexamethylene tetramine and resorcinol in short sisal/coir hybrid fibre reinforced NR composites.

The interface modification of short nylon 6 fibre reinforced NBR composites by using two different bonding systems, namely hexamethylene tetramine- resorcinol and phthalic anhydride is the subject matter of this chapter. The efficiency of these bonding agents has been evaluated in terms of cure characteristics and mechanical properties.

4.2 RESULTS AND DISCUSSION

4.2.1 Curing behaviour

The addition bonding agents has a considerable effect on the cure characteristics of short nylon 6 fibre reinforced NBR composites. Figure 4.1 represents the typical rheographs of mixes containing hexa-resorcinol and phthalic anhydride bonding agents (Mixes Q and R) and that of the mix without bonding agent (Mix M), cured by DCP containing 24 phr nylon fibres of length 6 mm.

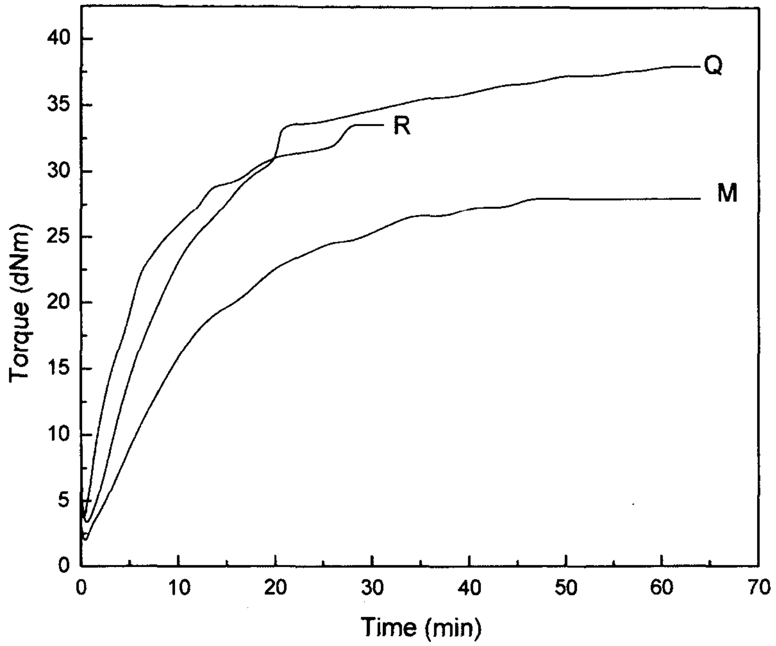


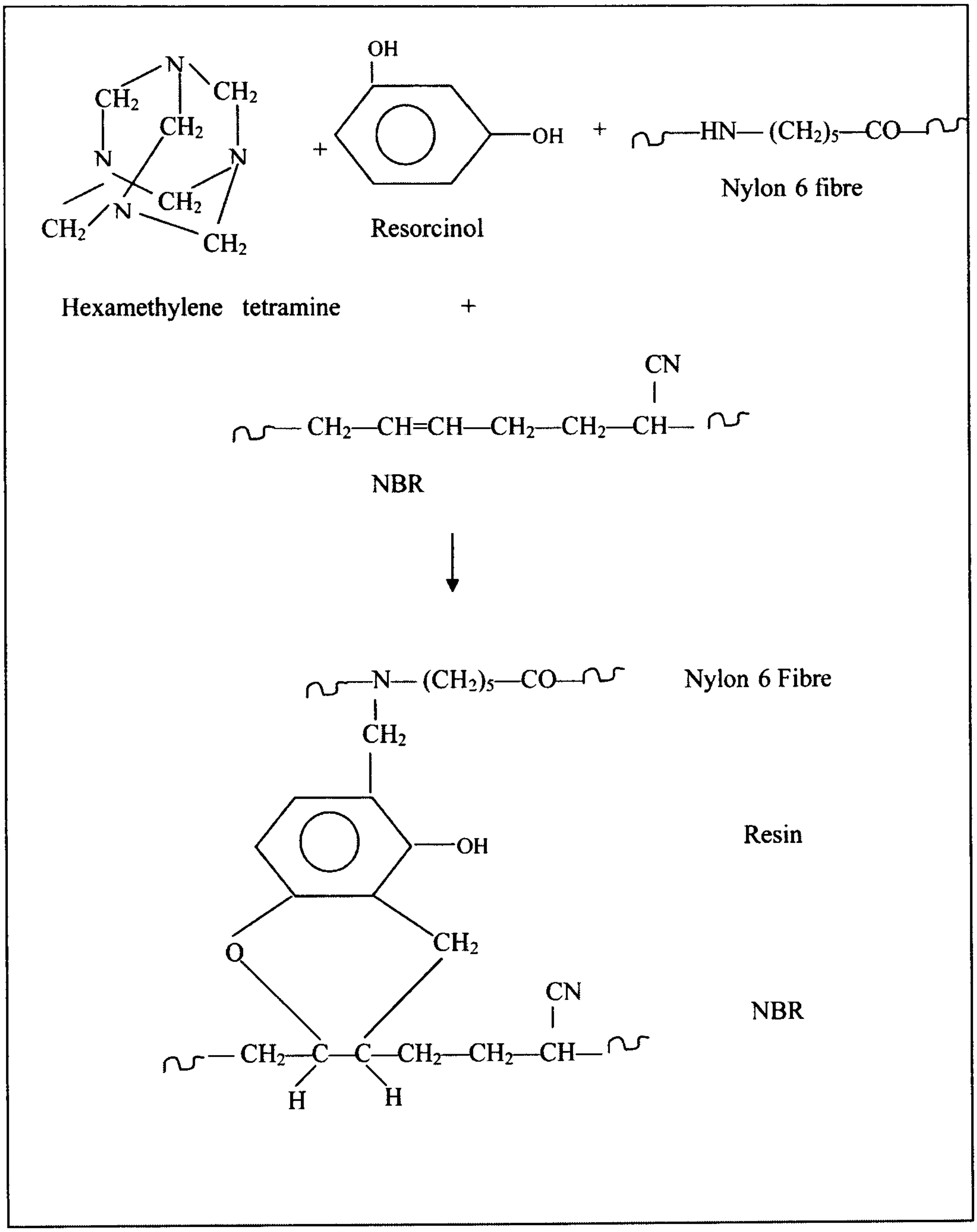
Figure 4.1 Rheographs of mixes M, Q and R

Table 4.1 shows the cure characteristics of sulphur and DCP vulcanised composites containing different bonding agents along with the corresponding unbonded ones. It can be seen that in both sulphur and DCP cured samples the torque values of the mixes containing bonding agents are higher than those of mix without bonding agent. The difference between the maximum and minimum torque value (M_H-M_L) indicates a higher crosslinking density for the bonding agent added composites. In the case of resorcinol-hexa bonding agent added mixes, the higher crosslink density can be attributed to the increased adhesion between the fibre and matrix through the formation of an *in-situ* resin. During the curing of the composite, polymerisation of resorcinol and hexamethylene tetramine is initiated and, as the vulcanisation of rubber proceeds, the resin is formed by the condensation reaction between these two components. Meanwhile, the low molecular weight polymer species of the resin are able to diffuse into the interfacial region between the rubber and the fibre. Thus, a boundary layer is formed at the rubber surface which is rich in resin formation and it forms chemical bonds with the rubber and the fibre. Scheme 4.1 represents a hypothetical mechanism showing the interface bonding in hexa-resorcinol bonded composites.

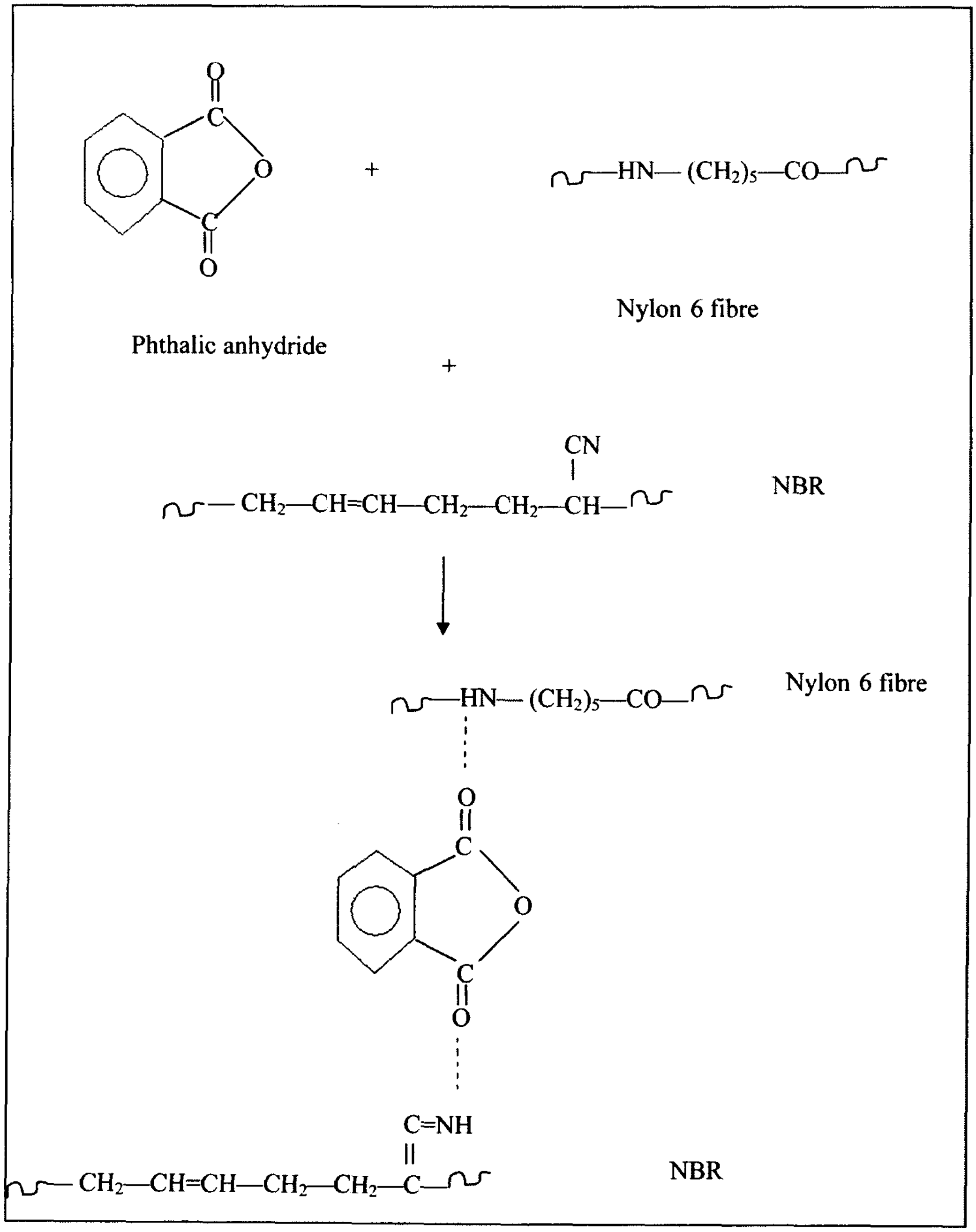
Table 4.1 Cure characteristics of various mixes

Mix	Max Torque (dNm)	Min. Torque (dNm)	dT (dNm)	t_{90} (min)	Scorch time (min)
F	19.45	0.86	18.59	3.95	0.25
G	20.82	1.22	19.60	2.30	0.20
M	27.88	1.37	26.51	30.06	1.06
Q	37.08	2.71	34.37	20.75	0.59
R	33.49	6.25	27.24	17.00	0.70

In the case of phthalic anhydride added mix the increased crosslinking density can be due to the improved adhesion between fibres and matrix through intermolecular hydrogen bonding (Scheme 4.2). It is also found that the addition of bonding agent reduces the optimum cure time and scorch time (Table 4.1). The decrease in scorch time, however, indicates a reduction in scorch safety of the compound containing bonding agents.



Scheme 4.1 Mechanism of interfacial adhesion in hexa-resorcinol bonded composites



Scheme 4.2 Mechanism of interfacial adhesion in phthalic anhydride bonded composites

4.2.2 Mechanical Properties

Figure 4.2 shows the stress-strain curves of the unbonded and bonded composite systems cured by DCP. The effects of different bonding agents on the mechanical properties of the longitudinally oriented composites can be understood from

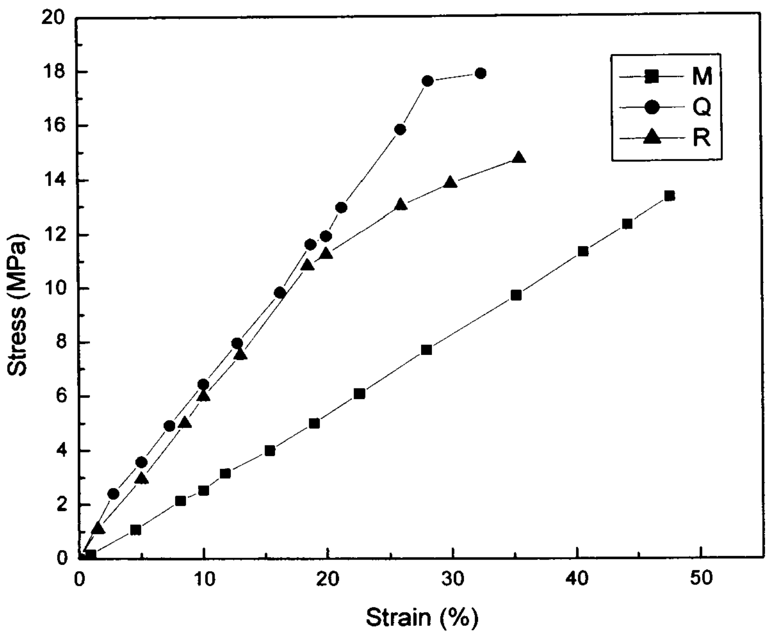


Figure 4.2 Stress-strain curves of bonded and unbonded composites

Table 4.2. It can be seen that composites containing bonding agents show superior mechanical properties than those without bonding agents. Tensile strength, tear strength, modulus and hardness of the composites have been found to be increased by the incorporation of bonding agents, whereas the elongation at break to be reduced. The improvement in tensile strength and modulus is comparatively higher for the hexa-resorcinol bonded composites than the phthalic anhydride bonded systems. This can be attributed to the difference in the extent of interfacial interaction between the fibres and rubber resulted *via* the incorporation of bonding agents. It is also obvious from Table 4.2 that the effect of hexa-resorcinol boding agent is more pronounced in DCP cured composites than in the sulphur cured one (Mixes Q and G respectively). This can be attributed to the difference in the type of crosslinks introduced by DCP and sulphur during vulcanisation which has been explained earlier (Chapter 3, Section 3.2.2.3).

Table 4.2 Mechanical Properties of bonded and unbonded composites

	F	G	M	Q	R
Tensile Strength (MPa)	12.32	13.72	13.29	16.46	14.64
Tear Strength (kN/m)	49.87	60.65	80.20	85.30	81.59
Modulus (MPa) **10% elongation**	24.80	31.65	25.36	63.12	59.70
20% elongation	25.90	31.31	26.51	59.55	56.15
Elongation at break (%)	48.00	46.25	47.67	40.07	41.17
Hardness-Shore A	82	85	84	87	85

The extent of interfacial adhesion has been better understood by examining the tensile fracture surface of the composite by scanning electron microscopy (SEM). Typically, Figure 3 (a) shows the tensile failure surface of unbonded composite (Mix M). The breakage and pull out of fibres indicate poor wetting between fibres and matrix. Figure 3 (b) shows the SEM of tensile failure surface of bonding agent added composite (Mix Q). It is seen that, for Mix Q, the rubber particles remain adhered to the fibre surface, and also there is no considerable fibre breakage due to the bonding between the fibres and the matrix.

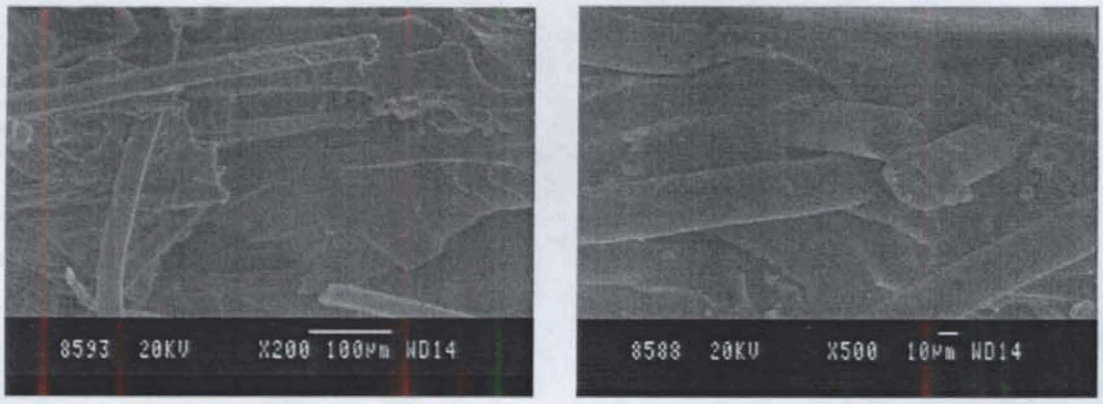


Figure 4.3 (a) Scanning electron micrograph of the tensile failure surface of mix M

(b) Scanning electron micrograph of the tensile failure surface of mix Q

4.3. CONCLUSIONS

Hexamethylene tetramine- resorcinol and phthalic anhydride were used as bonding agents to modify the interfacial interaction in nylon 6 fibre reinforced NBR composites. The cure characteristics and mechanical properties of the bonded composites have been analysed. The addition of bonding agents increased the maximum torque and reduced the optimum cure time and scorch time. The addition of bonding agents enhanced the tensile strength and modulus. SEM studies revealed improved adhesion between the fibre and rubber in the composites. The effects of these bonding agents on the properties of the composites have been included in the subsequent chapters.

References

1. Gaylord G., *Copolymers, Polyblends and Composites*, N. Platzer, (Ed.), Academic, New York (1975) 76.
2. Akthar S. and De P.P., *J. Appl. Polym. Sci.*, **32** (1986) 5123.
3. Coran A .Y., Boustany K. and Hamed P., *Rubber Chem. Technol.*, **47** (1974).
4. O'Conner J.E., *Rubber Chem. Technol.*, **50** (1977) 945.
5. Roy R., Bhowmick A. K. and De S.K., *J. Appl. Polym. Sci.*, **49** (1993) 263.
6. Derringer D. C., *Rubber World*, **45** (1971) 165.
7. Chakraborty S. and De S .K., *J. Appl. Polym. Sci.*, **55** (1982) 1286.
8. Geethamma V. G., Mathew K. T., Lakshminarayanan R. and Thomas S., *Polymer*, **39** (1998) 6.
9. Murthy V .M. and De S. K., *Rubber Chem. Technol.*, **55** (1982) 287.

10. Setua D.K. and Dutta B., *J.. Appl. Polym. Sci.*, **29** (1984) 3097.

11. Creasy J.R. and Wagner M.P., *Rubber Age*, **100** (10) (1968) 72.

12. Morita E., *Rubber Chem. Technol.*, **53** (1980) 795.

13. Hewitt N.L., *Rubber Age*, **104** (1972) 59.

14. Dunnon D. D., *Hi-Sol Bulletin No. 40*, Chemical Divn., PPG Industries Inc., Pittsburgh (1969).

15. Darwish N .A. and Lawandy S. N., *Polym-Plast. Technol. Engg.*, **39** (5) (2000) 793.

16. Pokluda I. and Osoha J., *Proc. International Rubber Conference (IRC), 1986*, Goteborg, Sweden, **2**(1986) 546.

17. Varghese S., Kuriakose B. and Thomas S., *J. Adhesion Sci. Technol.*, **8** (1994) 235.

18. Suhara F., Kutty S. K. N. and Nando G. B., *Polym-Plast, Technol. Engg.*, **37**(2) (1998) 241.

19. Suhara F., Kutty S .K. N. and Nando G. B., *Plast. Rubber Comp. Proc. Appln.*, **24** (1995) 37.

20. Sreeja T. D. and Kutty S .K. N., *Polym-Plast. Technol. Engg.*, **41**(1) (2002) 77.

21. Haseena A. P., Namitha, Priya Dasan K., Unnikrishnan G. and Thomas S., *Composite Interfaces,* **11** (7) (2004) 489.

Chapter 5

Investigation of Interfacial Adhesion in Nylon 6/NBR Composites by Restricted Equilibrium Swelling Technique

Abstract

The interfacial adhesion in short nylon 6 fibre reinforced NBR composites has been evaluated by a restricted solvent swelling technique. The solvents used are N, N- dimethyl formamide (DMF), dimethyl sulphoxide (DMSO) and acetonitrile. As the fibre content increases the solvent uptake decreases which has been attributed to the increased resistance to solvent penetration due to better fibre-rubber interaction. The ratio of change in volume fraction of rubber before and after swelling to the volume fraction of rubber before swelling (V_0–V_r / V_0) *is lower for a bonding agent added composite, compared to the unbonded one. Anisotropic swelling studies have been carried out to analyse the extent of fibre alignment and fibre–matrix interaction. In strongly bonded composites the swelling mainly takes place in the thickness direction. The rubber-fibre interaction has been examined by the Lorenz-Parks and Kraus equations.*

Contents of this chapter have been communicated to:
Composite Interfaces

5.1 INTRODUCTION

The performance of short fibre reinforced rubber composites depends on the degree of adhesion of the fibres to the rubber matrix. A good extent of adhesion between the matrix and fibres is required to achieve a satisfactory level of improvement in properties of the composites[1-3]. However, extremely high adhesion will some times adversely affect the composites by generating more heat at the interface and there by weakening it [4]. Restricted swelling of the composites in a suitable liquid can be utilised as an effective measure to follow the degree of adhesion in composite systems. The adhesion level can also be qualitatively assessed by examining the tensile fracture surfaces of the composites by scanning electron microscopy (SEM).

Coran *et al*[5] studied the solvent swelling nature of unidirectional rubber-fibre composites. Whitby *et al.*[6] reported that vulcanised rubber possessed a structure, which could not be broken down completely by any solvent; the material had swollen, but did not disintegrate. Vinod *et al.*[7] tried the equilibrium swelling as a means to measure the adhesion between NR and aluminum powder. The results showed that the bonding agent reduced the swelling due to increased adhesion which was more pronounced in a conventional vulcanising system. El Sabbagh *et al.*[8] examined the swelling behaviour of kenaf fibre reinforced NR composites. Hwang *et al.*[9] investigated the diffusion and sorption behaviour of glycidyl methacrylate in SBR as a function of its waste tyre powder content, sulphur content and temperature by using a gravimetric sorption method. Thomas and co-workers [10-13] studied the interfacial adhesion between different types of natural fibres and elastomers by restricted equilibrium technique. Unnikrishnan and co-workers[14, 15] also examined the transport characteristics of different filler reinforced rubbery systems.

The present chapter deals with the evaluation of the interfacial adhesion in short nylon 6 fibre reinforced NBR composites by a restricted equilibrium swelling method with special reference to the effects of fibre loading and the presence of bonding agents. The effect of fibre orientation on the swelling properties has further been confirmed by anisotropic swelling studies. The dimensional tolerance to swelling and crosslink density of the present composite systems has also been analysed through this study. The rubber–fibre interactions have been examined by using Lorenz-Park and Kraus equations.

5.2 RESULTS AND DISCUSSION

5.2.1 Transport of polar aprotic solvents through composites

The phenomenon of transport through rubbery polymers is controlled by the polymer structure, its crosslink density, the mode of crosslinking, the presence of fillers, their interaction with the polymer matrix, temperature etc [16-18]. The swelling can be anisotropic if the matrix of a fibrous composite is a crosslinked polymer [19].

5.2.1.1 Effect of fibre loading, curing system and bonding agents on swelling coefficient

Table 5.1 shows the swelling coefficient values of the composites. It can be seen that, in DCP cured samples (Mixes H, I, J, L and M), as the loading of the fibre increases, the swelling coefficient value decreases in all the solvents. This is attributed to the reduction in free volume available for solvent transport.

Table 5.1 Swelling coefficient values of various mixes

Mix	DMF	DMSO	Acetonitrile
H	2.638	0.902	1.009
I	1.856	0.749	0.824
J	1.436	0.340	0.600
L	1.319	0.330	0.570
M	1.232	0.170	0.525
Q	1.166	0.165	0.351
R	1.228	0.166	0.372
F	1.455	0.268	0.632
G	0.747	0.222	0.552

The swelling coefficient values of mixes cured by DCP are lower than those cured by sulphur. It can be seen from Table 5.1 that the mix M containing 24 phr nylon 6 fibres cured by DCP has lower swelling coefficient value than the corresponding mix F cured by sulphur. This can be explained in terms of the nature and distribution of crosslinks between rubber chains. The mono, di and polysulphidic linkages in sulphur system impart high chain flexibility to the polymer network and this helps in accommodating more solvent between the polymer chains.However, the rigid C-C linkages present in DCP system offer more resistance to swelling. The swelling coefficient values for bonding agent added composites (Mixes Q, R and G) are found to be lower than those for the unbonded ones. This can be attributed to the improved interfacial adhesion in presence of bonding agents.

5.2.1.2 Effect of fibre loading and bonding agent on Q_t (mol %)

Figures 5.1 (a), (b) and (c) indicate the sorption curves of the composites at room temperature, (27 °C) in DMF, DMSO and acetonitrile respectively. It can be seen that the sorption curves show the same trend, but the quantity of solvent sorbed by the composite is different for different solvents. The gum compound (Mix H) takes

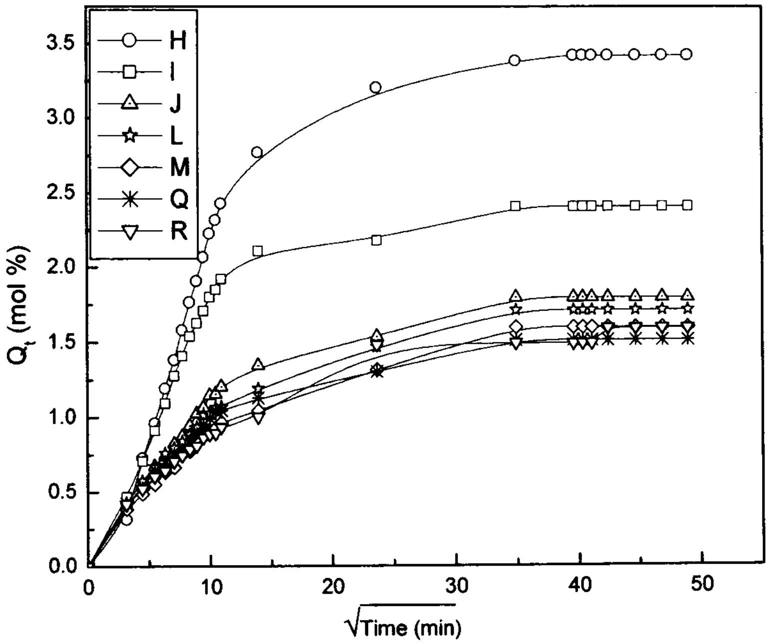


Figure 5.1 (a) Transport of DMF through nylon 6/NBR composites at 27 °C

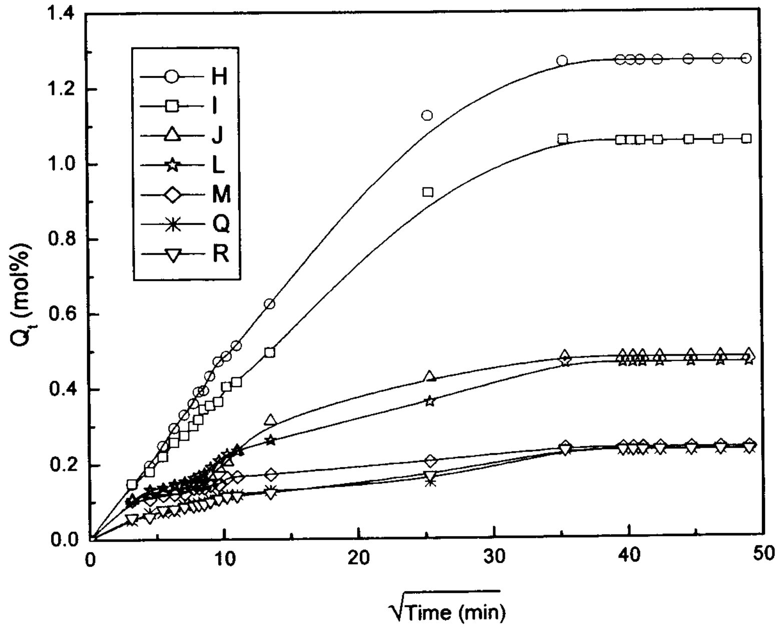


Figure 5.1 (b) Transport of DMSO through nylon 6/NBR composites at 27 °C

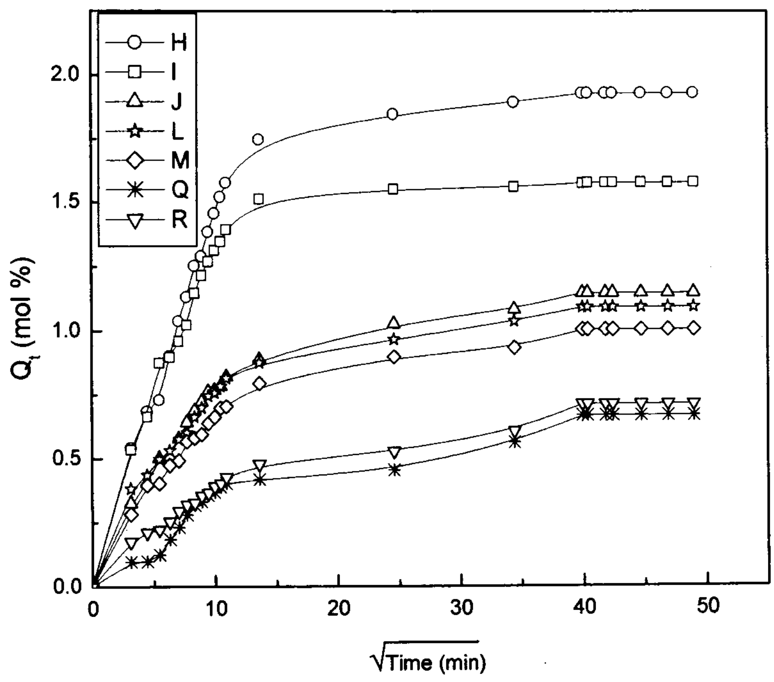


Figure 5.1 (c) Transport of acetonitrile through nylon 6/NBR composites at 27 °C

up more amount of solvent throughout the time of immersion, due to the lesser restriction for the penetrant to enter into the vulcanisates. The restriction to solvent transport increases with the increase in the concentration of fibres in NBR matrix.

It is also noted that the swelling of unbonded composites is higher than that of bonded ones. In unbonded fibre-rubber composites, the solvent can penetrate in to the polymer along the thickness direction and also through the weak interfaces, parallel and perpendicular to the fibre direction. The interfaces allow the easy entrance of the penetrant and act as solvent pockets at equilibrium.

Figure 5.2 shows the Q_∞ (mol %) values of different mixes in various solvents. The uptake of penetrants by the mixes at equilibrium is restricted by the increase in the fibre loading. Due to the increased hindrance exerted by the increase in concentration of short fibres, the uptake of the solvents decreases gradually. The Q_∞ values of bonding agent added composites are found to be lower than that of the unbonded ones due to the higher restriction to swelling attributed to the better interfacial adhesion generated by the bonding agent.

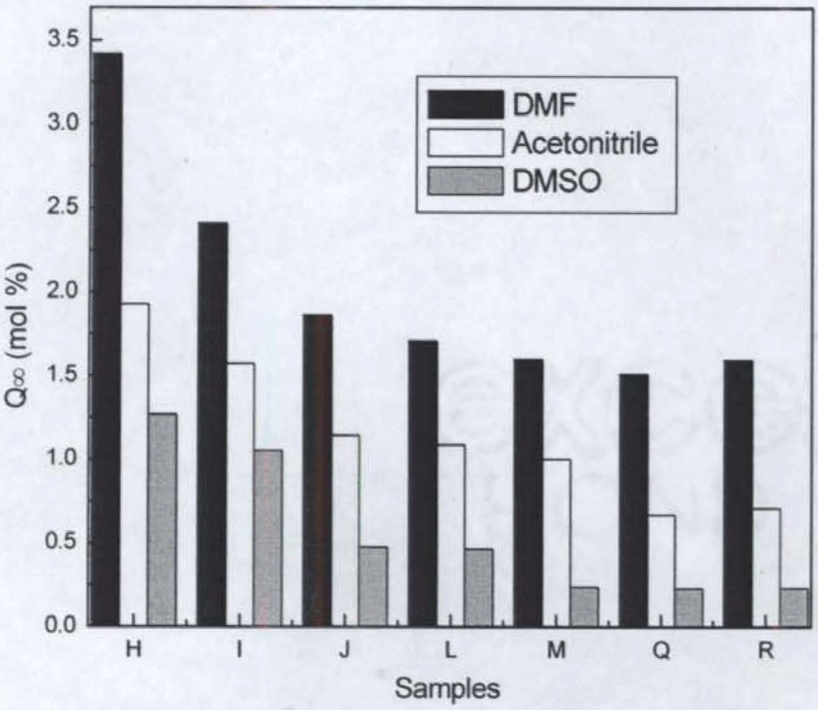


Figure 5.2 Effect of fibre loading and bonding agent on Q_∞ (mol%)

5.2.2 Correlation with adhesion

Table 5.2 shows the V_0, V_r and V_T values for the mixes having different fibre loadings and with bonding agents in N,N- dimethyl formamide. It is observed that as fibre loading increases, the solvent uptake of samples decreases and hence the V_r of NBR in the specimens I, J, L, M, Q and R swollen in N,N-dimethyl formamide is higher than that for gum (Mix H) in the swollen state. Therefore, as fibre loading increases (Mixes H to M) the volume fraction of rubber before swelling (V_0) decreased whereas V_r, the volume fraction rubber after swelling is increased. This is because the amount of penetrant taken by the specimen at equilibrium swelling decreases due to the increased hindrance exerted by the fibres at higher loading. Thus the V_T or the ratio V_0-V_r / V_0 value decreases with increase in fibre loading. Composites containing the bonding agent (Mixes Q and R) have considerably lower V_0-V_r / V_0 values than those with out the bonding agent. A highly bonded system would exhibit higher resistance to swelling, compared to an unbonded one. Thus, V_r would have a relatively higher value and V_T would have a relatively lower value.

Table 5.2 Volume fraction of rubber

Sample	Volume fraction of rubber in the dry sample (V_o)	Volume fraction of rubber in swollen sample (V_r)	V_T
H	0.941	0.275	0.708
I	0.898	0.324	0.640
J	0.859	0.397	0.538
L	0.815	0.398	0.512
M	0.776	0.404	0.479
Q	0.749	0.469	0.373
R	0.755	0.406	0.462

5.2.3 Crosslink density

The extent of crosslinking of the matrix has been established from the values of the volume fraction of rubber in the swollen composites (V_r) given in Table 5.2. A higher value of V_r for Mixes Q and R indicates a better adhesion between fibres and matrix in presence of the bonding agent and therefore it has a higher degree of crosslinking. A comparison of crosslink density values, in terms of apparent crosslinking, has also been made from the reciprocal swelling value at equilibrium, $1/Q_\infty$ [20,21]. Table 5.3 shows the effects of fibre loading and bonding agents on the apparent crosslinking values, in N, N-dimethyl formamide. It can be seen that as fibre loading increases the apparent crosslinking increases. The higher values of apparent crosslinking are due to the better reinforcing effect of the fibres; particularly in presence of bonding agents. This effect can further be explained by using the basic Flory–Rehner concept, given as Equation 2.10. The calculated values of molecular mass between crosslinks (M_{CL}) are given in Table 5.3. The M_{CL} values regularly decrease as fibre loading increases (Mixes H to M). M_{CL} is inversely related to crosslink density (n) as:

$$M_{CL} = \frac{1}{2n} \qquad \text{......(5.1)}$$

It follows that an increase in fibre content causes an increase in crosslink density. Therefore, as loading increases the amount of solvent absorbed by the samples decreases which leads to an increase in V_r values. M_{CL} values of mixes Q and R which contain bonding agent are lower than that of the corresponding unbonded one (M) and hence the former has the highest crosslink density; attributed to the increased interaction between the fibres and the matrix.

Table 5.3 Effect off fibre loading and bonding agent on crosslink density

Sample	Apparent crosslinking ($1/Q_\infty$)	M_{CL} (Kg/mol)
H	0.292	41.38
I	0.415	11.80
J	0.536	12.16
L	0.584	12.28
M	0.625	11.18
Q	0.661	6.02
R	0.711	7.55

5.2.4 Swelling anisotropy

Anisotropic swelling studies provide information on the strength of the interface, degree of dispersion of fibres, their alignment in the elastomer matrix and apparent crosslinking of fibre reinforced rubber composites[22]. During swelling, due to the interaction between the macromolecular chains of the elastomers and solvents, the composites are deformed to a state where the elasticity of the elastomer and the tension of the fibres reach equilibrium.

Figure 5.3 represents a unidirectional composite specimen before swelling (solid line) and after swelling (dotted line). The length of the line l_0 taken at an angle θ with the fibre direction grows during swelling to a length l_s; a_L is taken in the direction of fibre orientation OY (lengthwise), a_T is taken in the OX direction (breadthwise), while a_θ value is taken in the OZ direction (widthwise).

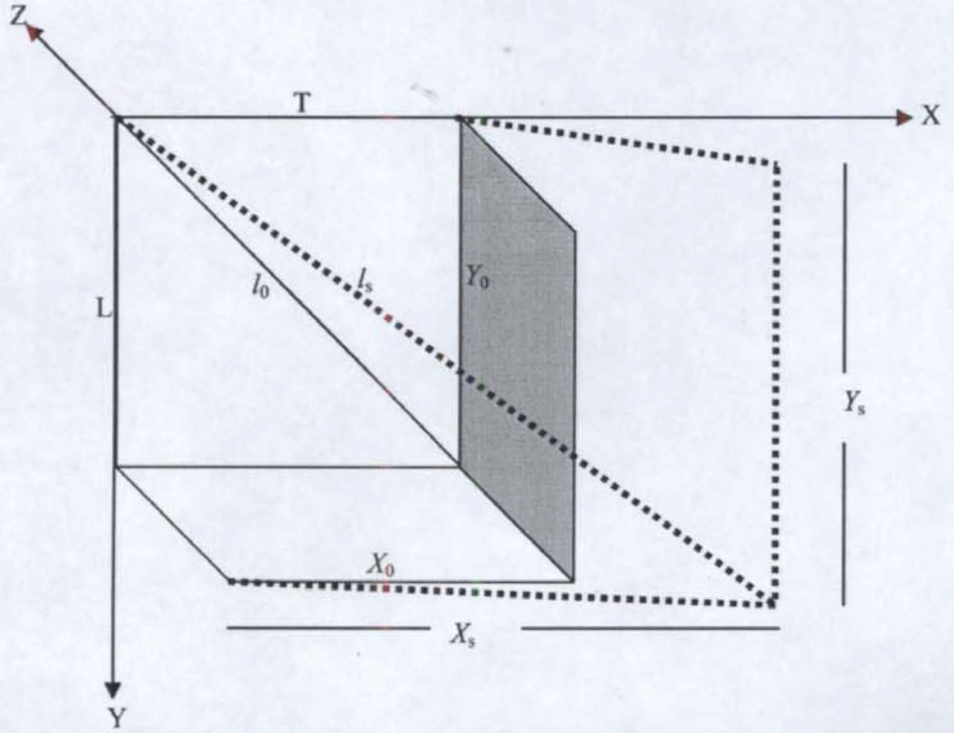


Figure 5.3 Geometry of swelling of unidirectional composites

If $X_s / X_0 = a_T$, $Y_s / Y_0 = a_L$ and $l_s / l_0 = a_\theta$, the swelling ratio a_θ in any direction forming an angle θ with fibre orientation is given by the expression[23]:

$$a^2_\theta = (a^2_T - a^2_L)\sin^2\theta + a^2_L \qquad \text{......(5.2)}$$

where a_L and a_T are the dimensional swelling variations with an angle θ between measurement direction and fibre orientation.

Table 5.4 shows the linear swelling deformation for various fibre orientations in different mixes. The values of a^2_θ calculated using equation (5.2) increases linearly as the angle of orientation increases from 0 to 90°. This indicates the preferential fibre orientation in the grain direction. The plots of a^2_θ against $\sin^2\theta$ for these mixes have been found to be straight lines, as shown in Figure 5.4, having slope $a^2_T - a^2_L$ and intercept a^2_L. Noughi *et al.*[24] reported that the steeper the line, the higher the degree of fibre alignment. The extent of fibre alignment can be understood from the slope. It can be seen that composite containing R-H bonding agent and 24 phr fibres (Mix Q) has the highest slope, indicating a better interfacial bonding between fibre and matrix in mix Q.

Table 5.4 Linear swelling induced deformation

Orientation θ (degrees)	a^2_θ					
	H	I	J	L	M	Q
0	1.480	1.247	1.068	1.103	1.068	1.068
30	1.756	1.253	1.210	1.138	1.094	1.085
45	1.778	1.325	1.247	1.229	1.102	1.094
60	1.960	1.401	1.310	1.386	1.112	1.183
90	2.068	1.562	1.440	1.605	1.156	1.690

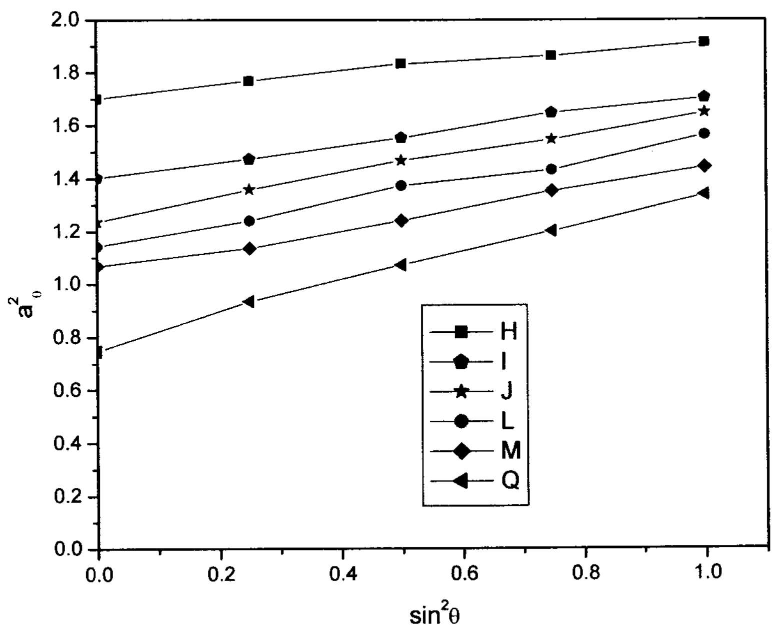


Figure 5.4 Linear swelling induced deformation of various mixes

5.2.5 Variation in dimensions due to swelling

5.2.5.1 Thickness

Rubber composite samples will swell to a greater extent in the direction perpendicular to the fibre orientation. This is because the oriented fibres will prevent the penetration of the liquid in the direction perpendicular to the flat surfaces of the specimen. Hence the penetrant can diffuse into the polymer only in the direction parallel to the fibre orientation. Thus, swelling can be considered to be constrained in one direction and, as a result, the thickness of the specimen increases considerably.

Figure 5.5 shows the change in thickness of various mixes after swelling. The gum sample shows the lowest extent of swelling in the thickness direction due to the sharp alignment of the macromolecular chains in a particular direction during the milling and moulding operations. The anisotropic swelling becomes pronounced when the fibres were added. As the number of fibres in unit volume increases the penetrant molecules find it more difficult to diffuse in to the polymer and therefore the entire swelling takes place only in the thickness direction. When the bonding is poor, the matrix swells both in the diameter and thickness directions. As a result, at lower loading of fibres and also in the absence of bonding agent, swelling in the thickness direction will be less. However, as the fibre loading increases, the swelling takes place predominantly in the thickness direction, which makes a higher contribution for the increase in thickness. Though the increase in thickness during swelling is shown by both bonded and unbonded composites, the effect is more pronounced in the case of composites containing the bonding agent (Mixes Q and R). Due to the higher interfacial adhesion, the bonded composite swells only in the thickness direction.

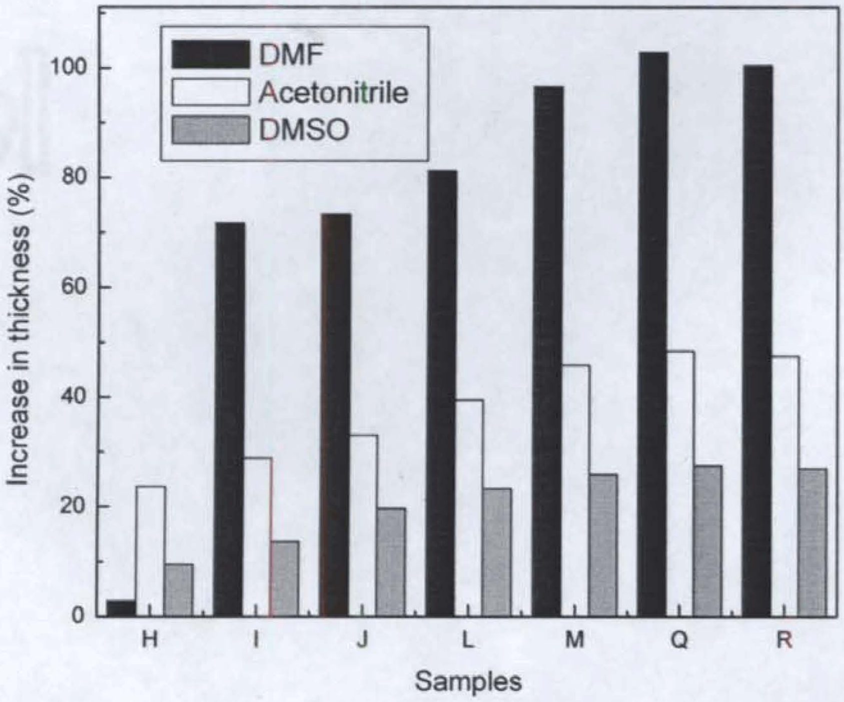


Figure 5.5 Effect of solvent swelling on the thickness of nylon/NBR composites

5.2.5.2 Diameter

The increase in diameter of the composite specimen at equilibrium swelling against fibre loading is shown in Figure 5.6. It can be seen that the there is no marked change in diameter with increase in fibre loading. At higher fibre loading and in presence of bonding agent swelling is restricted and takes place mostly in the thickness direction. Hence the increase in diameter is less predominant.

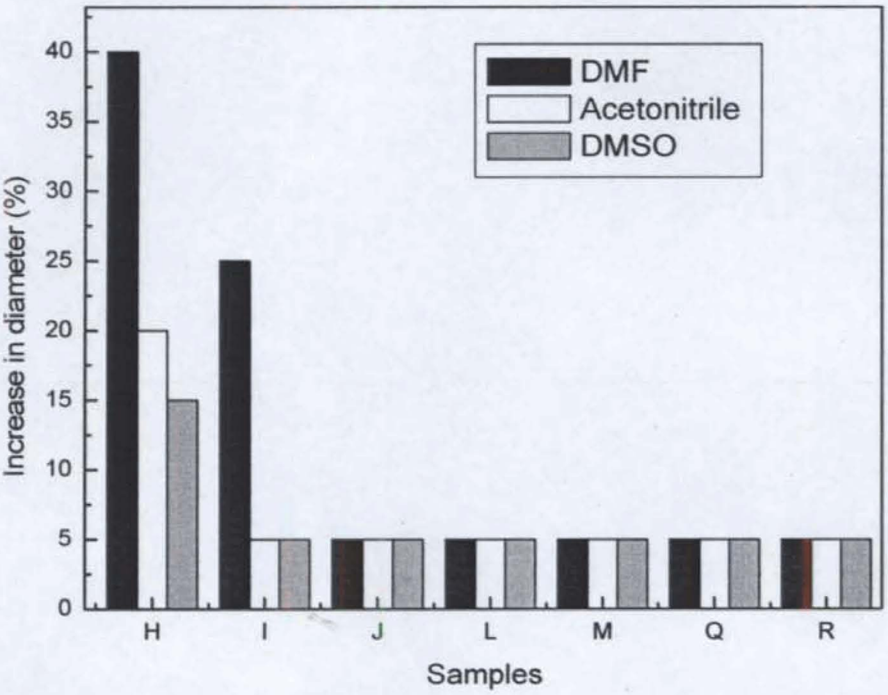


Figure 5.6 Effect of solvent swelling on the diameter of nylon/NBR composites

5.2.6 SEM studies on the composites

The extent of interfacial adhesion and restriction to swelling have been better understood by examining the tensile fracture surfaces of the composites by scanning electron micrographs (SEM). Figure 3 (a), in Chapter 3, shows the tensile failure surface of the unbonded composite (Mix M). The breakage and pull out of fibres indicate the poor wetting between fibres and matrix. Figure 3 (b) shows the SEM of tensile failure surface of bonding agent added composite (Mix Q). It is seen that, for Mix Q, the rubber particles remain adhered to the fibre surface, and also there is no considerable fibre breakage due to the better bonding between the fibres and the matrix. This offers a higher restriction to swelling.

5.2.7 Rubber-fibre interactions

Several researchers have studied the interaction between rubber matrices and fibres. Chakraborty *et al.*[25] investigated the rubber-filler interaction in silica and jute fibre filled carboxylated nitrile rubber (XNBR) composites. The polymer–filler interaction in silica filled epoxidized natural rubber (ENR) has been studied by Alex *et al*[26]. The interaction between the rubber and filler in carbon black filled NR and SBR vulcanisates has been analysed by Bhowmick and Neogi[27]. The following equations have been applied to study rubber-fibre interactions.

5.2.7.1 Kraus equation

Kraus[28, 29] studied the degree of cure in particulate filler-reinforced vulcanisates by swelling method. The degree of restriction exerted by reinforcing filler has been given by the equation:

$$V_{ro} / V_r = 1 - m\,[V_f / (1 - V_f)] \qquad \text{......(5.3)}$$

where V_{r0} is the volume fraction of rubber in the unfilled vulcanisate, V_r, the volume fraction of rubber in the filled vulcanisate after swelling as per Equation (2.9), V_f, the volume fraction of filler and m, the polymer-fibre interaction parameter.

Table 5.5 gives the V_{r0}/V_r values of various mixes. It is observed that as the fibre loading increases, the solvent uptake of samples decreases and hence the volume fraction of rubber in the swollen gel, V_r, is always higher than that for the pure gum (Mix H) in the swollen state, V_{ro}. Therefore, the ratio V_{ro}/V_r decreases with increase in filler loading. The ratio represents the degree of restriction to swelling of

Table 5.5 Validation of rubber- fibre interaction

Sample	V_r	V_{ro}	V_{ro}/V_r	Q_f/Q_g
H	0.275	0.275	1.000	1.00
I	0.324	0.275	0.848	0.70
J	0.397	0.275	0.693	0.52
L	0.398	0.275	0.691	0.50
M	0.401	0.275	0.686	0.47
Q	0.469	0.275	0.586	0.44
R	0.406	0.275	0.677	0.46

the rubber matrix, due to the presence of filler. The V_{ro} / V_r values of bonding agent added mixes (Q and R) are lesser than the corresponding unbonded one indicating the enhanced fibre–rubber adhesion due to the presence of the bonding agent. Since Equation 5.3 represents a straight line, a plot of V_{ro} / V_r versus V_f / (1-V_f) should give a straight line, whose slope 'm' will be a direct measure of the reinforcement of fibres (Figure 5.7). As V_{ro} / V_r decreases with increase in fibre loading the plot has a negative slope indicating the reinforcement effect of fibres as given by Kraus theory.

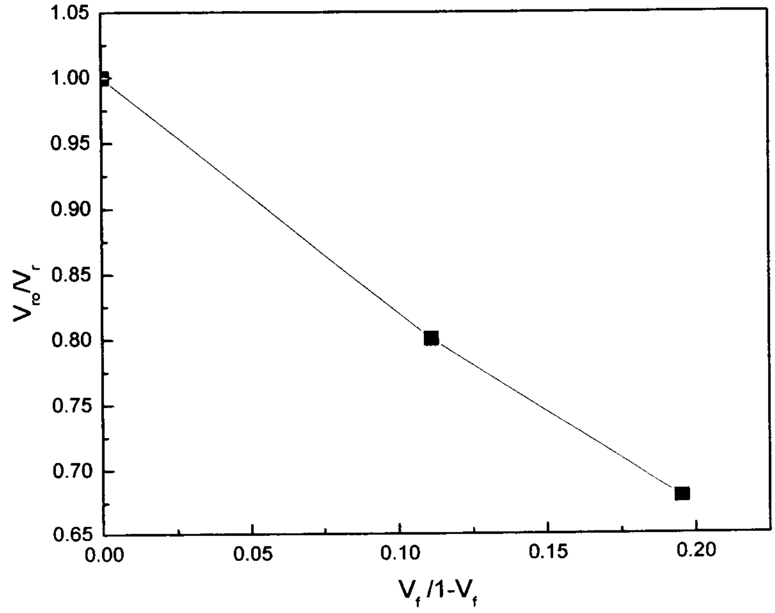


Figure.5.7 Kraus plot showing the variation of V_{ro} / V_r with V_f / (1-V_f)

5.2.7.2 Lorenz and Parks equation

The restriction to swelling exerted by the fillers has been investigated by Lorenz and Parks[30] according to the following relation:

$$Q_f/Q_g = ae^{-z} + b \qquad \text{......(5.4)}$$

where Q_g and Q_f are the weights of the swelling agent imbibed per unit weight of rubber in the gum and in filler added compounds respectively. z is the weight of filler per unit weight of the rubber; a and b are constants. The dependence has been explained in terms of the restricted swelling of rubber matrices in the neighborhood of filler particles.

Table 5.5 also shows Q_f/Q_g values for various fibre loadings in NBR matrix. It can be seen that as fibre loading increases from Mix H to Mix M, Q_f/Q_g values decrease due to increased fibre–rubber interaction. Higher the Q_f/Q_g value, the lower will be the extent of interaction between the fibres and the matrix. The Q_f/Q_g value of bonding agent added mixes (Q and R) are lower than that of the

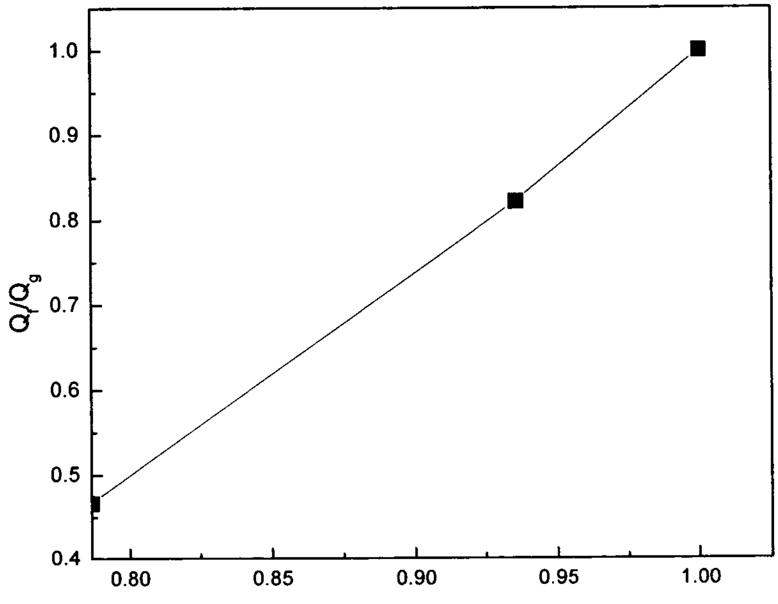


Figure 5.8 Lorenz-Parks plot (Variation of Q_f/Q_g with e^{-wf})

corresponding unbonded ones due to the higher interaction between the fibres and rubber. A plot of Q_f / Q_g versus e^{-wf} gave a straight line (Figure 5.8) with a positive slope which complements the observation that the extent of reinforcement increases with fibre loading.

5.3 CONCLUSIONS

The restricted equilibrium swelling behaviour of short nylon 6 fibre reinforced NBR composites was investigated with special reference to the effects of fibre loading, curing systems, bonding agents and fibre orientation. The equilibrium sorption value and swelling coefficients have been found to be decreased with increase in fibre loading. The swelling coefficient values of mixes cured by DCP were found to be lower than those cured by sulphur. The bonding agent added mixes showed higher restriction to swelling due to the stronger interfacial adhesion and the resultant higher crosslink density. It has been confirmed that for the rubber composite containing bonding agent, the quantity V_T i.e.; the ratio of change in volume fraction of rubber before and after swelling to the volume fraction of rubber before swelling $(V_0 – V_r / V_0)$, was lower than that for the composites with no bonding agent. The factor V_T has been found to decrease with increase in fibre loading. The anisotropic swelling studies revealed that the bonding agent added composite showed maximum fibre alignment; attributed to the stronger interfacial adhesion. In strongly bonded composites, the swelling has been observed to take place mainly in the thickness direction. SEM studies also confirm good interfacial adhesion in bonding agent added composites. The rubber-fibre interaction was also studied by using Lorenz-Parks and Kraus equations.

References

1. Ibarra L., Chamorro C. and Tabernero R. M .C., *Polym. Compos.,* **9** (3) (1988) 198.
2. Darwish N. A., Lawandy S. N., El-Shazly and Abou kandil A. I., *Polym-Plast. Technol. Engg,* **39** (5) (2000) 793.
3. Sreeja T.D. and Kutty S. K. N., *Polym- Plast Technol. Engg,* **41**(1) (2002) 77.
4. John Milewski V. and Harry Katz S., *Handbook of Fillers for Plastics,* Van Nostrand Reinhold, New York (1987).
5. Coran A.Y., Boustany K. and Hamed P., *J. Appl.Polym. Sci.,* **15** (1971) 2171.
6. Whitby J., Evans S. and Pasternack B., *Trans. Faraday Soc.,* **38** (1942) 269.
7. Vinod V.S., Varghese S. and Kuriakose B., *J. Mater. Sci.,* **35** (22) (2000) 5699.
8. El Sabbagh S. H., El Hariri D. M., and Abd El Ghaffar M. A., *Polym. Polym. Compos.,* **9** (8) (2001) 549.
9. Hwang K. K., Ryu S.H. and Hong S.U., *J. Appl. Polym. Sci.,* **86** (2002) 2701.
10. Varghese S., Kuriakose B., Joseph K. and Thomas S., *Rubber Chem. Technol.,* **68** (1995) 37.
11. George S.C., Ninan K. N. and Thomas S., *Polymer,* **37** (1996) 5839.
12. Prasantha Kumar R. and Thomas S., *J. Adhes. Sci. Technol.,* **6** (2001) 633.
13. Jacob M., Thomas S. and Varughese K. T., *Compos. Sci. Technol.,* **64** (2004) 955.

14. Priya Dasan K., Haseena A. P., Unnikrishnan G., Rosamma Alex and Purushothaman E., *Polym. Polym. Compos.*, **12** (7) (2004) 599.
15. Sujith A. and Unnikrishnan G., *J. Mater. Sci.*, **40** (2005).
16. N Rennar. and Opperman W., *Colloid Polym. Sci.*, **270** (1992) 527.
17. Andreopoulos A.G., Polyzois G.L. and Evangelatou M., *J. Appl. Polym. Sci.*, **50** (1993) 729.
18. Guo C.J., De Kee D. and Harrison B., *J. Appl, Polym. Sci.*, **56** (1995) 817.
19. Das B., *J. Appl. Polym. Sci.* **17** (1973)1019.
20. Chakraborty S.K., Setua D.K and De S.K., *Rubber Chem. Technol.*, **56** (1983) 808.
21. Prasantha Kumar R., Geetha Kumari Amma M.L. and Thomas S., *J. Appl. Polym. Sci.*, **58** (1995) 597.
22. Mears P., *Polymers, Structure and Bulk Properties,* Van Nostrand, London (1965).
23. Ibarra L. and Chamorro C., *J. Appl. Polym. Sci.*, **43** (1991) 1805.
24. Noughi T., Ashida M. and Mashimo S., *Nipp. Gomu Kyok.*, **57** (1984) 171.
25. Chakraborty S.K., Setua S.K. and De S. K., *Rubber Chem. Technol.*, **55** (1982) 1286.
26. Alex R., Mathew N. M., De P. P. and De S.K ., *Kaust. Gummi Kunst.*, **42** (1989) 674.
27. Bhowmick A.K. and Neogi C., *J. Appl. Polym. Sci.*, **41** (1990) 917.
28. Kraus G., *J.Appl.Polym.Sci.*, **7** (1963) 861.
29. Kraus G., *Rubber Chem. Technol.*, **37** (1964) 6.
30. Lorenz O. and Parks C. R., *J. Polym .Sci.*, **50** (1961) 299.

Chapter 6

Dielectric Properties of Nylon 6/NBR Composites

Abstract

The dielectric properties such as dielectric constant, volume resistivity and dielectric loss factor of nylon 6 fibre reinforced NBR composites have been studied as a function of frequency at different fibre loadings. The effects of curing systems and bonding agents on the dielectric properties have also been studied. The dielectric constant decreases with increase in frequency; attributed to the decreased orientation polarization at higher frequencies. The dielectric constant values have been found to be lower for fibre filled systems than the gum. The DCP cured composite samples exhibit higher dielectric constant than the corresponding sulphur cured systems. The addition of bonding agents reduces the dielectric constant of the composites. The volume resistivity of the composites increases with the addition of fibres and with the incorporation of the bonding agents. The added fibres and the different bonding agents decrease the dielectric dissipation factor of the matrix.

6.1 INTRODUCTION

Polymers are, in general, good electrical insulators with volume resistivities up to 10^{20} ohm m. They are commonly used in the electronics industry as housings or assemblies. Electrical conductivity is an important factor in many rubber and plastic compounds which are used for antistatic applications, wire and cable sheathing, and shielding against electromagnetic interference[1-3]. For some applications polymers are made conductive by adding conductive materials like metals, carbon black, fibres and so forth. Incorporation of a conducting polymer into a host polymer substrate to develop a blend, composite or an interpenetrating network has been widely used as an approach to combine electrical conductivity with the desirable physical properties of a polymer[4-7]. The process of conduction through a polymeric system depends upon its composition, chemical structure, physical texture, morphology and the conditions of measurement[8].

Dielectric properties such as the dielectric constant and the dielectric loss reveal significant information about the chemical and physical states of polymers. These properties are significantly affected by the presence of another polymer or a dopant in the polymer[9-13]. Miyauchi and Togashi[14] explained the electrical properties and the conduction mechanism of polymer-filler particles using polymer grafted carbon black. Burton *et al.*[15] made the electrical and electromechanical measurements of carbon black filled NR. Modification of dielectric and mechanical properties of rubber - ferrite composites containing manganese zinc ferrite has been studied by Mohammed *et al*[16]. Todorova *et al.*[17] investigated the electrical properties of elastomer composites filled with titanium diboride. The electrical and mechanical properties of conductive rubber composites derived from different blends of EPDM and NBR containing acetylene black were analysed by Sau *et al*[18]. The electrical resistivity of SBR-carbon black composites has been examined by Mohanraj *et al*[19]. Bishai *et al.*[20] investigated the electrical conductivity of SBR-polyester short fibre reinforced with different types of carbon black. George *et al.*[21] followed the electrical properties of pineapple fibre reinforced polyethylene composites.

In many cases the analysis of dielectric properties provides a measure of the amorphous fraction of the material which is sensitive to orientation effects, mobility and to the number and interaction of participating dipoles. Dutta *et al.*[22] reported the studies on the mechanical and electrical anisotropy of pineapple fibres. They found a sharp increase in dielectric constant and a fall of loss factor along the fibre direction compared to the transverse direction. Prasantha Kumar and Thomas[23] studied the dielectric properties of short sisal fibre reinforced SBR composites. They pointed out that the chemically treated fibrous composite systems exhibited lower dielectric constant values compared to the untreated ones. The modeling of the dielectric properties of wood-polymer composites, by considering them as multi-component layered systems, was done by Hoffman *et al*[24].

NBR has only moderate insulating properties and higher values of permittivity (17–14 Fm^{-1}). The considerably high dielectric loss values (1.33–2.00) cause NBR to lose its insulating properties. The present chapter deals with the investigation of the dielectric properties of nylon 6 fibre reinforced NBR composites.

6.2 RESULTS AND DISCUSSION

6.2.1 Dielectric Constant

Dielectric polarization is the polarized condition of a dielectric resulting from an applied AC or DC field and it can be expressed as the total induced dipole moment per unit volume of the dielectric. The total polarizability of the dielectric is the sum of the contributions due to the several types of displacement of charges produced in the material by an applied field. Generally, the dielectric constant of a composite material arises due to the polarization of the molecules.The dielectric constant increases with increase in polarizability. The dielectric constant (E′) of a composite has contributions from interfacial, orientation, atomic and electronic polarizations. The interfacial polarization occurs in a composite due to the differences in the conductivities or the polarizations of the matrix and fillers [25]. The orientation polarization is produced, when polymers containing polar groups are placed in an electric field [26].

The effect of fibre loading on the dielectric constant (E′) values of nylon 6 fibre reinforced NBR composites as a function of logarithm of frequency is shown in Figure 6.1. It is evident from the figure that the dielectric constant decreases with increase in fibre loading at a given frequency. The highest E′ values are exhibited by the gum sample (0 phr). This is due to orientation polarization owing to the presence of permanent dipoles in the NBR matrix (-C≡N group). As nylon 6 fibre is added some of the dipoles are cancelled by the dipoles present in nylon (⟩C=O) and thus the dielectric polarization decreases. Therefore the dielectric constant value decreases with increase in fibre loading. It is also found that for a given fibre loading, the E′ shows higher values at lower frequencies. This can be accounted by the fact that the orientation polarization decreases with increase in frequency. The complete orientation of the molecules is possible only at lower frequencies and the orientation polarization requires more time to reach the equilibrium static field value compared to electronic and atomic polarizations. Therefore as frequency increases the E′ reduces due to the lag in orientation polarization.

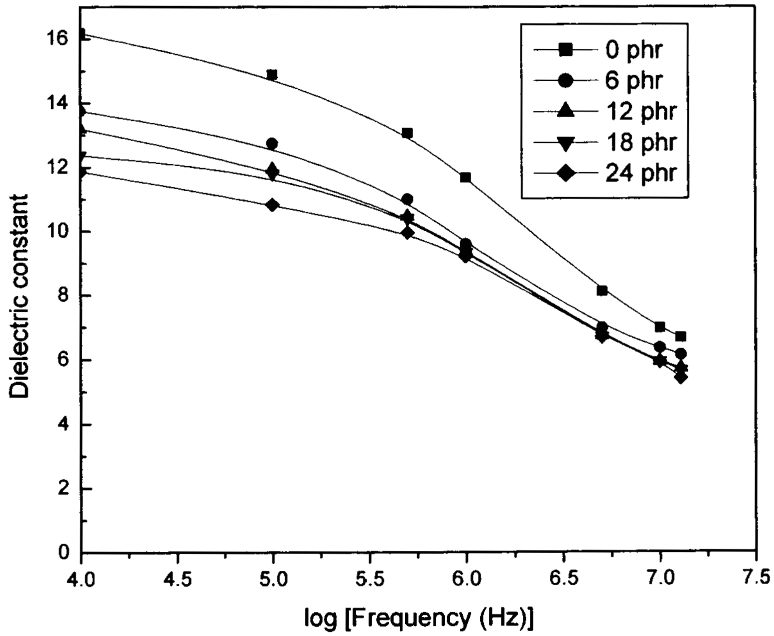


Figure 6.1 **Effect of fibre loading on dielectric constant as a function of frequency**

Figure 6.2 shows the effect of different curing systems on the dielectric constants of nylon 6 fibre reinforced NBR composites as a function of frequency. Comparison has been made with samples containing 24 phr loading of fibre cured by sulphur and DCP (Samples F and M). It can be seen that the values of dielectric constant are higher for DCP cured sample than for sulphur cured sample at all frequencies. This can be attributed to the presence of polar -OH groups in the former. These

-OH groups are produced during the vulcanisation process initiated by dicumyl peroxide, where the peroxide free radical (R-O·) abstract a hydrogen from the polymer chain to form R-OH.

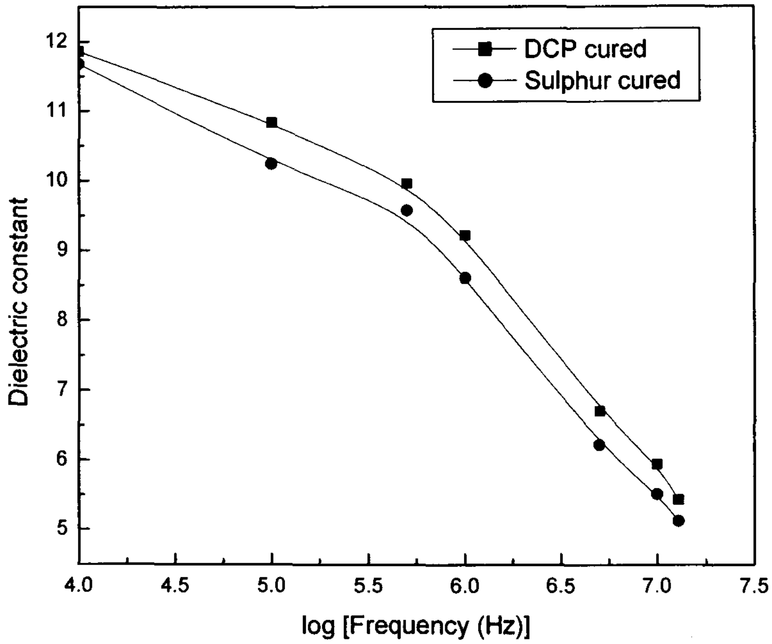


Figure 6.2 **Effect of curing systems on dielectric constant as a function of Frequency**

Figure 6.3 shows the effect of different bonding agents on the dielectric constants of the composites as a function of frequency. It can be seen that the dielectric constant values are lower for bonding agent added composites at all frequencies. The dielectric constant value of phthalic anhydride bonded system is slightly lower than that of hexa-resorcinol bonded composite. The good interfacial adhesion in presence of bonding agent removes the voids between the fibres and matrix thereby eliminating the pockets for moisture absorption. Thus, the modified interface reduces the dielectric constant values. In the case of phthalic anhydride bonded systems, in addition to this, the interfacial adhesion between nylon fibres and NBR through the formation of hydrogen bonding involving the bonding agent, also reduces the polarization and hence the dielectric constant value is lower than that of hexa-resorcinol bonded systems. The mechanism of interfacial adhesion in phthalic anhydride bonded composites has been explained earlier in Chapter 4 (Scheme 4.2).

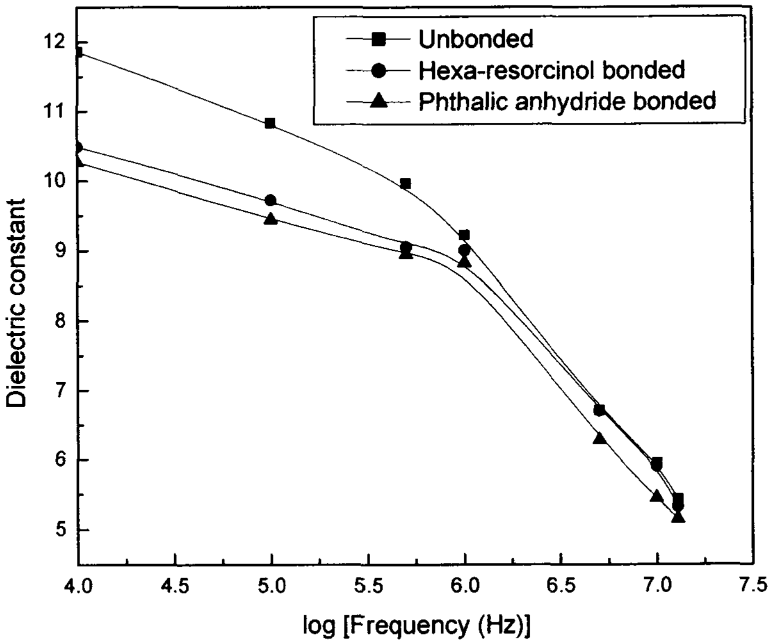


Figure 6.3 **Effect of bonding agent on the dielectric constant as a function of frequency**

Figure 6.4 shows the effect of hexa-resorcinol bonding agent on the dielectric constant of sulphur and DCP cured composites as a function of frequency. It can be seen that in the presence of bonding agent sulphur cured sample has higher dielectric constant values than DCP cured sample. This can be attributed to the difference in total polarizability in the two systems. In the former, permanent dipoles due to –OH groups in resorcinol are present, whereas in the latter these –OH groups may be involved in hydrogen bonding with the R-OH produced by the abstraction of hydrogen from polymer chain by peroxide free radical.

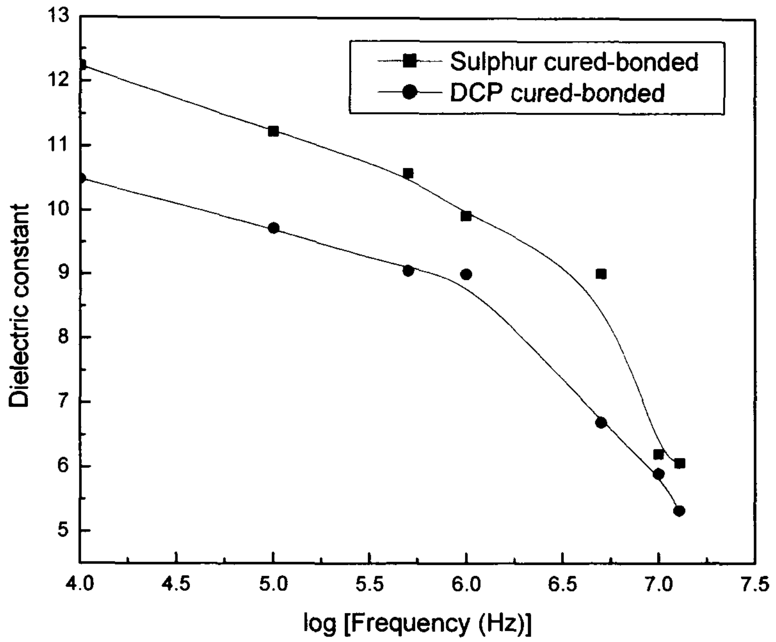


Figure 6.4 **Effect of hexa-resorcinol bonding agent on the dielectric constant of sulphur and DCP cured composites**

6.2.2 Volume resistivity

The study of the volume resistivity of an insulating material is important because the most desirable property of an insulator is its ability to resist the leakage of electric current. Figure 6.5 shows the plot of volume resistivity as a function of frequency at different loadings of fibres. The volume resistivity has been found to be decreased with frequency and increased with fibre concentrations. The increase in volume resistivity with fibre loading can be attributed to the decreased dielectric polarization upon the incorporation of nylon 6 fibre into the polar NBR matrix. Figure 6.6 shows the dependence of electrical conductivity (∂), which is the reciprocal of resistivity, on fibre loading at varying frequencies (10 and 13 MHz). It has been found that, as fibre concentration increases the conductivity decreases.

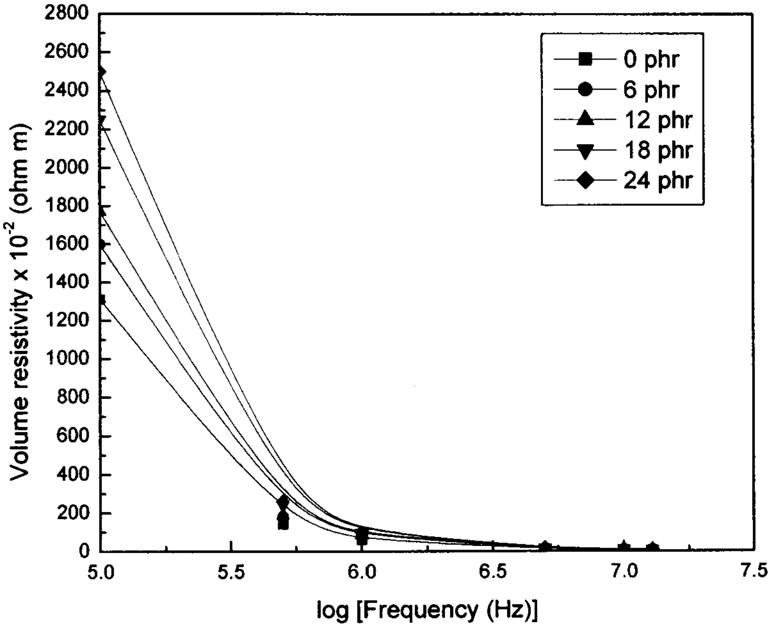


Figure 6.5 Effect of fibre loading on the volume resistivity as a function of frequency

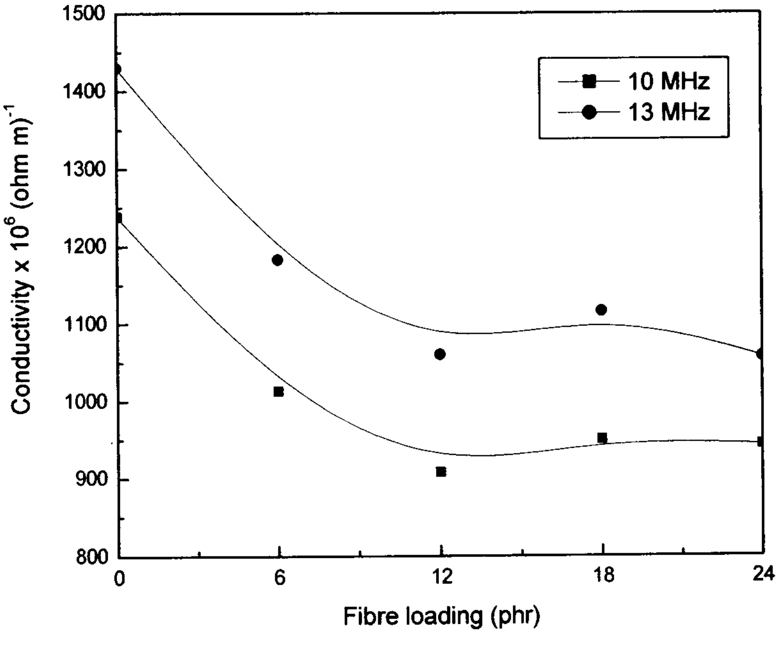


Figure 6.6 Variation of conductivity with fibre loading at different frequencies

However, the conductivity has been found to be increased with frequency. The variation of volume resistivity as a function of frequency in sulphur and DCP cured composites is shown in Figure 6.7. It can be seen that the volume resistivity of DCP cured sample is lower than that cured by sulphur. This is due to the higher polarizability in the former.

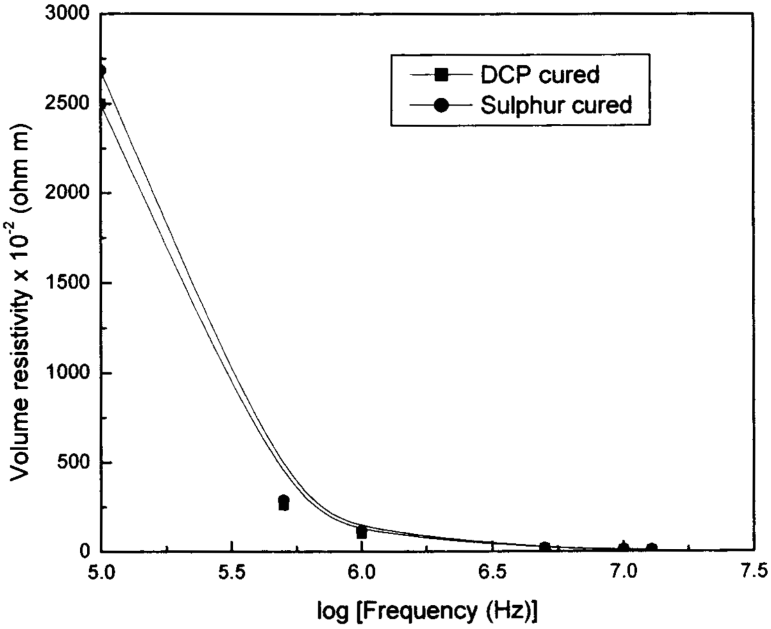


Figure 6.7 **Effect of curing system on the volume resistivity as a function of frequency**

The variation of volume resistivity, for bonding agent added composites, is given as a function of frequency in Figure 6.8. The dielectric constant depends on the resistivity by the equation[27]:

$$\log R\,(298\,K) = 23 - 2\,E'\,(298\ K) \qquad \text{......(6.1)}$$

The equation shows that the electrical resistance of composites decreases exponentially with increasing dielectric constants. The incorporation of bonding agent enhances the interfacial adhesion between the fibres and the matrix, which in turn reduces the voids at the interface thereby enhancing the volume resistivity. It can also be seen from Figure 6.8 that the volume resistivities of composites containing both hexa-resorcinol and phthalic anhydride bonding agents are higher than that of the unbonded one at the same fibre loading.

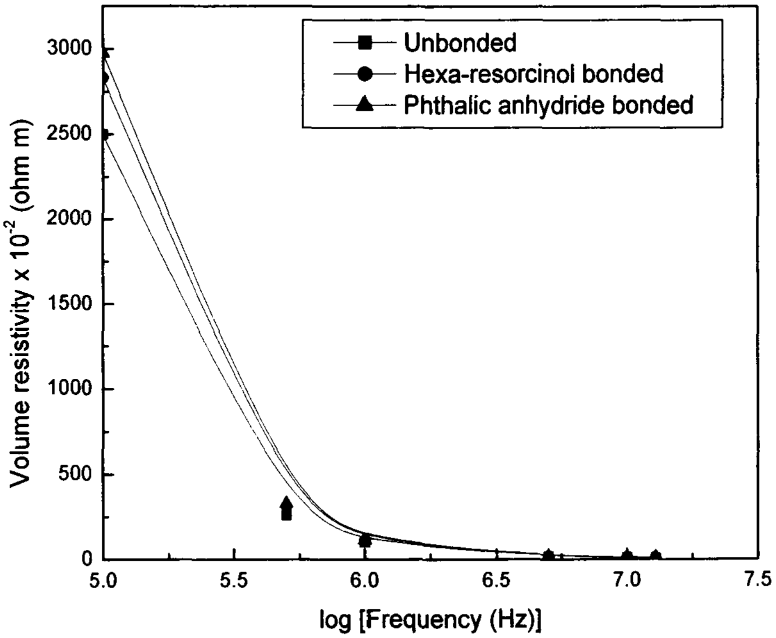


Figure 6.8 Effect of bonding agent on volume resistivity as a function of frequency

Figure 6.9 shows the effect of hexa-resorcinol bonding agent on the volume resistivities of sulphur and DCP cured composites as a function of frequency. It can be seen that the volume resistivity of hexa-resorcinol bonded composite cured by DCP is higher than that cured by sulphur. The difference in behaviour is attributed to the difference in the total polarizability of the two systems.

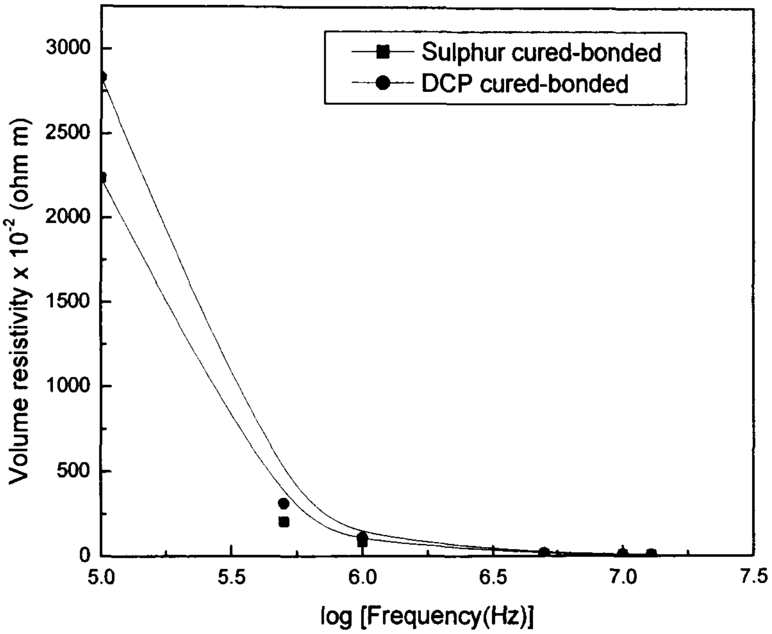


Figure 6.9 **Effect of hexa-resorcinol bonding agent on the volume resistivities of sulphur and DCP cured composites**

6.2.3 Dissipation factor

Dissipation factor or loss tangent is the ratio of the electrical power dissipated in a material to the total power circulating in the circuit. It is the tangent of the loss angle, directly analogous to the tan δ function relevant to the dynamic mechanical testing, describing the relationship between storage (G′) and loss (G″) moduli (tan δ = G″/G′). The visco-elastic nature of NBR matrix creates similarities in the material responses to both mechanical and electrical stimuli. Under the dynamic excitation, the independent and measured variables move out of phase (stress and strain in mechanical tests, voltage and current in electrical tests). Most of the polymers exhibit more than one region of dielectric loss. The measurement of dissipation factor (tan δ) of an insulating material is thus important since the loss tangent is a measure of the electrical energy which is converted to heat in an insulator. This heat raises the insulator temperature and accelerates its deterioration.

The effect of dissipation factor (tan δ) as a function of the logarithm of frequency at different fibre loading is given in Figure 6.10. The dissipation factor has been found to be increased with frequency and decreased with fibre concentration. A strong relaxation is observed, with a peak at a frequency of 5 MHz, which is due to the α-transition. The positions of peaks are identical for both filled and unfilled systems. The addition of fibres decreases the relaxation magnitude at each frequency. The two prime factors contributing to the loss factor (E″) are the dipole polarization and ionic conductance[26]. Most of the polymers exhibit more than one region of dielectric loss. The numerical value of dissipation factor is determined by both polarity and carrier mobility[26]. The polarity determines the nature of relaxation and the relaxation time determines the value of tan δ at specific frequency for that relaxation.

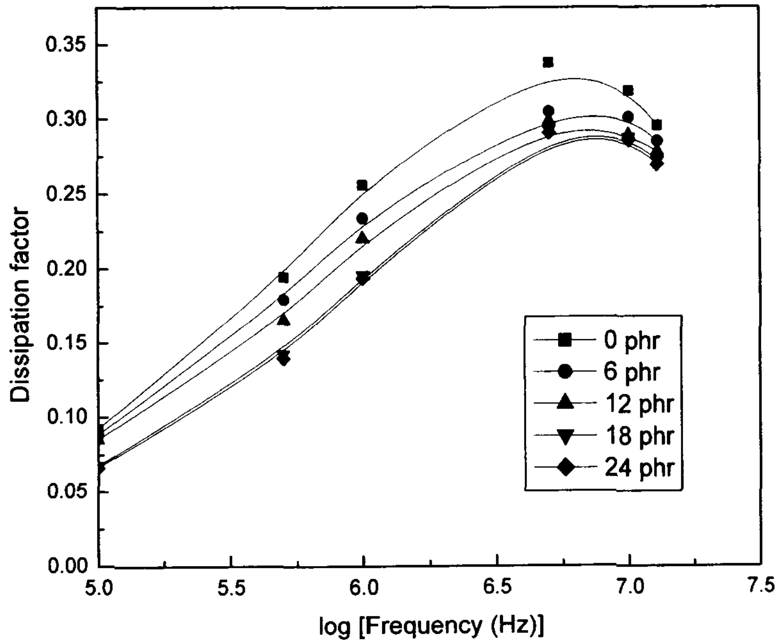


Figure 6.10 Effect of fibre loading on dissipation factor as a function of frequency

It can be seen from Figure 6.10 that, at any given frequency, the intensity of dielectric loss peak decreases regularly as a function of fibre loading i.e.; higher for gum (0 phr) and decreases with fibre loading. The increment in dissipation factor with frequency for the gum sample is associated with its amorphous phase relaxation. Since NBR contains polar groups it may also be due to dipolar relaxation. The decrease in tan δ value with the incorporation of nylon fibres into NBR matrix can be attributed to the increase in relaxation time. This can be due to the dipole–dipole interaction between the nylon 6 fibres and NBR, both of which containing polar groups.

Figure 6.11 shows the effect of different curing systems on the dissipation factor, as a function of the logarithm of frequency. It can be seen from the figure that the dissipation factor values of DCP cured sample is higher than that of sulphur cured sample.

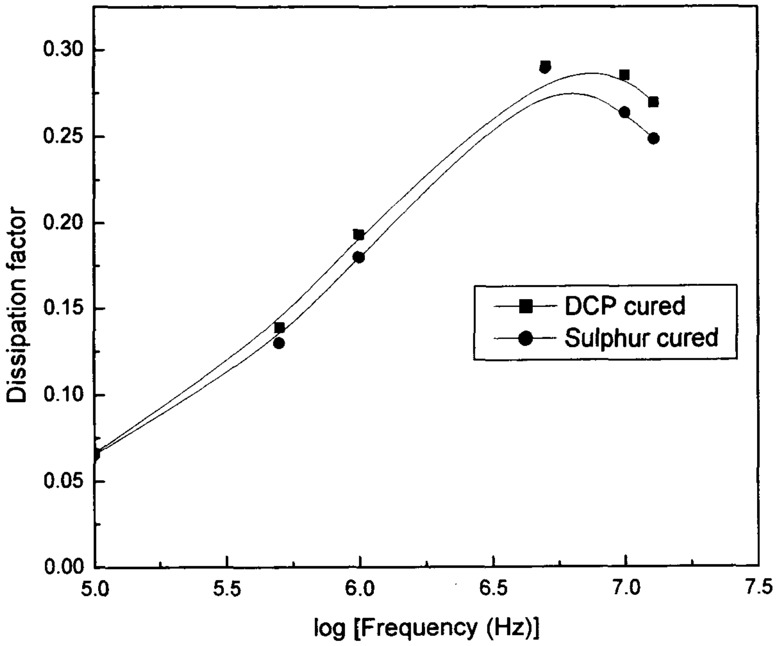


Figure 6.11 **Effect of curing system on dissipation factor as a function of Frequency**

The effect of bonding agents on the dissipation factor (tan δ) as a function of the logarithm of frequency is given in Figure 6.12. The dissipation factor of both hexa-resorcinol and phthalic anhydride bonded composites are lower than that of the unbonded one.

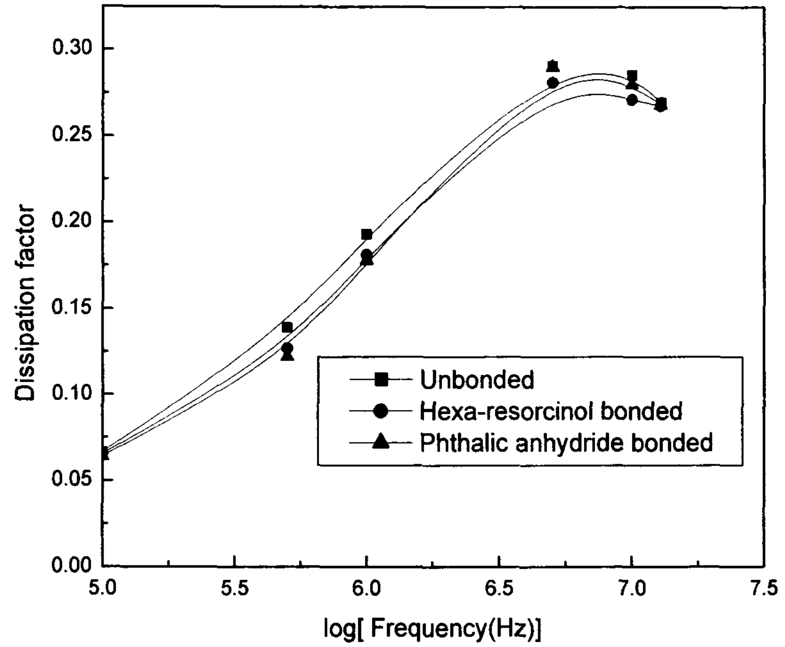


Figure 6.12 Effect of bonding agent on dissipation factor as a function of Frequency

Figure 6.13 shows the effect hexa-resorcinol bonding agent on the dissipation factor of sulphur and DCP cured composites as a function of frequency. It can be seen that the dissipation factor of hexa-resorcinol bonded composite cured by sulphur is higher than that cured by DCP. The difference in the dissipation factor values of bonded composites can be attributed to the difference in the relaxation magnitudes.

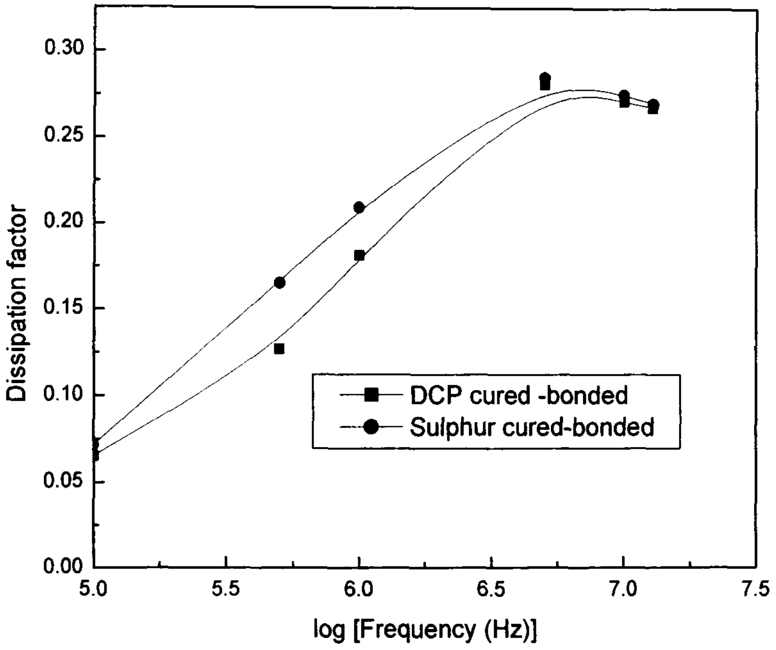


Figure 6.13 **Effect of hexa-resorcinol bonding agent on the dissipation factor of sulphur and DCP cured composites**

6.3 CONCLUSIONS

The dielectric properties such as dielectric constant, volume resistivity and dielectric loss factor of short nylon 6 fibre reinforced NBR composites have been studied as a function of frequency at different fibre loadings. The effect of curing systems and bonding agents on the dielectric properties has also been studied. The dielectric constant values have been found to be lower for fibre filled systems than gum. Composite sample cured by DCP exhibited higher dielectric constant value than that cured by sulphur which can be attributed to the presence of polar -OH groups in the former. The addition of the bonding agent reduced the dielectric constant of the composites. It has been found that in the presence of hexa-resorcinol bonding agent the sulphur cured sample has higher dielectric constant values than DCP cured sample which has been attributed to the difference in the total polarizability of the two systems. The volume resistivity of the composites was found to be increased with the addition of fibres and with the incorporation of bonding agents. The conductivity of the composites decreased with increase in fibre loading. The added fibres and different bonding agents decreased the dielectric dissipation factor of the matrix. A dielectric relaxation has been observed at a frequency of 5 MHz.

References

1. Brydson J. A., *Plastic Materials,* Fifth Edn., Butterworths, London (1990).
2. Crossman R. A., *Polym. Eng. Sci.,* **25** (1985) 507.
3. Ponomarenkoman A. T., Schevchenko V. G. and Enikolopyan N. S., *Advances in Polymer Science,* Springer, Berlin (1990).
4. Andreatta A., Heeger A .J. and Smith P., *Polym Commun.,* **31** (1990) 275.
5. IM S. S. and Byun S.W., *J. Appl. Poly. Sci.,* **51** (1994)1221.
6. Acosta J. L., Ojeda M .C. and del Rio C., *Polymer Bulletin,* **57** (2006).
7. Miah M .J., Ahmed F., Hossain A. and Khan A .H., *Polym-Plast. Technol. Engg.* , **44** (2005)1443.
8. Birley A. W., Hayworth B. and Batchelor J., *Physics of Plastics Processing, Properties and Materials Engineering,* Hanser Publishers, New York (1992).
9. Saito H. and Stuhn B., *Polymer (U. K.).,* **35** (1994) 475.
10. Ramu Ch, Naidu Y. R. V. and Sharma A. K., *Ferroelectrics.,* **159** (1994) 275.

11. Mosaad M. M., *J. Mater. Sci. Lett.*, **9** (1990) 32.
12. Turch R., *Phys. Stat. Sol. (a)*, **121** (1990)119.
13. Tsujita.Y., Murafuje Y., Yano K. and Takizawa A. J., *Macromol Sci. Phys. B.*, **23** (1984) 311.
14. Miyauchi S. and Togashi E., *J. Appl. Polym. Sci.*, **30** (1985) 2743.
15. Burton L. C., Wang K. and Zhang T., *Rub. Chem. Technol.*, **62** (1989) 838.
16. Mohammed E. M., Malini K. A., Philip Kurian. and Anantharaman M. R., *Mate. Res. Bull.*, **37** (4) (2002) 735.
17. Todorova Z., Dishovsky N., Dimitrov R. and El Tantawy F., *J. Elasto. Plast.*, **39** (1) (2007) 69.
18. Sau K. P., Chaki T.K. and Khastgir D., *J Mater. Sci.*, **32** (21) (1997).
19. Mohanraj G. T., Chaki T. K., Chakraborty A. and Khastgir D., *J. Appl. Polym. Sci.*, **92** (4) (2004) 2179.
20. Bishai A.M, Ghoneim A.M., Ward A. M. and Younan A.F., *Polym-Plast Technol. & Engg.*, **22** (4) (2003) 701.
21. George J., Bhagawan S.S. and Thomas S., *J. Polym. Engg.*, **17** (5) (1997) 383.
22. Dutta A. K., Samantary B. K. and Bhattchderjee S., *J. Mater. Sci. Lett.*, **3** (1984) 667.
23. Prasantha Kumar R. and Thomas S., *Sci. Engg. Compos. Mater.*, **8** (6) (1999) 311.
24. Hoffman G., Poliszako S. and Hilczer T., *J. Appl. Polym. Sci.*, **3** (1990) 153.

25. Ku C. C. and Liepins R., *Electrical Properties of Polymers and Chemical Principles,* Hanser Publishers, New York (1987).
26. Mathes K.N., *Encyclopedia of Polymer Science and Engineering,* Vol. **5**, J.I. Kroschwitz, (Ed.) John Wiley and Sons, New York (1986) 507.
27. George J., Janardhan R., Anand R., Bhagwan S. S. and Thomas S., *Polymer,* **37** (1989) 3057.

Chapter 7

Thermal Characterisation of Nylon 6/NBR Composites

Abstract

The thermal behaviour of nylon 6 /NBR composites has been studied by thermo gravimetry (TG) and differential scanning calorimetry (DSC). The degradation temperatures of fibre filled composite systems have been observed to be higher than that of NBR. The percentage weight loss at different temperatures during thermal scanning has been found to be decreased with fibre loading. Composite samples cured by DCP exhibit a higher decomposition temperature compared to the sulphur cured samples indicating that the vulcanisation routes can significantly affect the thermal features of fibre filled polymer systems. The addition of bonding agents enhances the thermal stability of the composites. The DSC studies indicate that the fibre filled systems possess higher glass transition temperatures (T_g) *than the gum. The bonding agent added composite shows higher* T_g *compared to the other composite systems, which has been attributed to the higher interaction between the fibres and the matrix in the former.*

Contents of this chapter have been communicated to:
Polymers and Polymer Composites

7.1 INTRODUCTION

Thermal analysis is an important tool in the characterisation of polymeric materials. During the fabrication of new products from polymer composites, a knowledge of the thermal stability of their components is essential[1]. The threshold temperature for break down determines the upper limit of temperature in fabrication. Optimisation of the processing temperature and time with an understanding of the matrix, the reinforcing element and the interface can lead to a best balance of composite properties.

Thermogravimetry (TG) can help in understanding the degradation mechanism and thus to assist any effort to enhance the thermal stability of a polymeric material[2].This analysis needs only a small quantity of the sample. It is possible to quantify the amount of moisture and volatiles present in the composites which have a deteriorating effect on the properties[3, 4]. Thermogravimetric data provides the different stages of thermal breakdown, weight of the material in each stage, threshold decomposition temperature etc. Both TG and differential thermogravimetry (DTG) curves provide information about the nature and conditions of degradation of materials.

Differential scanning calorimetry (DSC) helps us to obtain quantitative information about the melting and phase transitions by measuring the heat flow rate associated with a thermal event as a function of time and temperature. This technique can explore the heterogeneous nature of polymeric composites and can provide information about the glass transition temperature (T_g). Miscible systems will show a single and sharp transition peak intermediate between those of the components. Separate peaks are generally obtained for heterogeneous systems[5].

The thermal stability of individual polymers can be enhanced to a greater extent by blending it with other polymers or by reinforcing with fibres. The synergism so obtained is usually attributed to the interfacial adhesion of the components. Various researchers have previously studied the thermal behaviour of rubber blends and composites in detail [6, 7]. Corre^a *et al.*[8] examined the influence of short fibres on the thermal resistance of the matrix, its T_g and kinetic parameters of the degradation reaction of thermoplastic polyurethane. They also found that the thermal resistance of aramid fibre-reinforced composites was greater than that of carbon fibre-reinforced composites. The degradation characteristics of Kevlar fibre-reinforced thermoplastics were reported by Kutty *et al*[9]. TG has been used by Faud *et al.*[10] to determine the filler content of wood-based composites. Suhara *et al.*[11] reported the thermal degradation of short polyester fibre-polyurethane elastomer composites. They observed that incorporation of short fibres enhanced the thermal stability of the elastomer. George *et al.*[12] characterised the thermal behaviour of pineapple fibre reinforced polyethylene composites. Ahmed *et al.*[13] reported the thermal studies on sulphur, peroxide, and radiation cured NBR and SBR gum vulcanisates and also with fillers such as carbon black and silica. It was found that the radiation cured NBR and SBR vulcanisates possessed better thermal stability. Seema and Kutty [14] investigated the thermal degradation of short nylon 6 fibre reinforced SBR composites.

The present chapter deals with the thermal analysis of short nylon fibre reinforced NBR composites by thermogravimetry and differential scanning calorimetry. The effects of fibre loading, vulcanising systems and the bonding agents on the thermal features of the composites have been examined.

7.2 RESULTS AND DISCUSSION

7.2.1 Thermal analysis of nylon 6

Figure 7.1 represents the TG and DTG curves of nylon 6 fibre. The onset temperature (T_{onset}) and the temperature of maximum decomposition (T_{max}) are 408 °C and 454 °C respectively. The major decomposition step of nylon, which occurs in the range 330 °C - 480 °C, is due to volatilisation[15]. In this stage, probably a crosslinked structure is also formed. Because of the formation of a thermally more stable structure the rate of degradation slows down after 480 °C. On further heating, the crosslinked structure decomposes and yields 1.1% thermally stable char at 800 °C. The DTG curve of nylon 6 fibre shows a degradation peak at 454 °C corresponding to the major decomposition step.

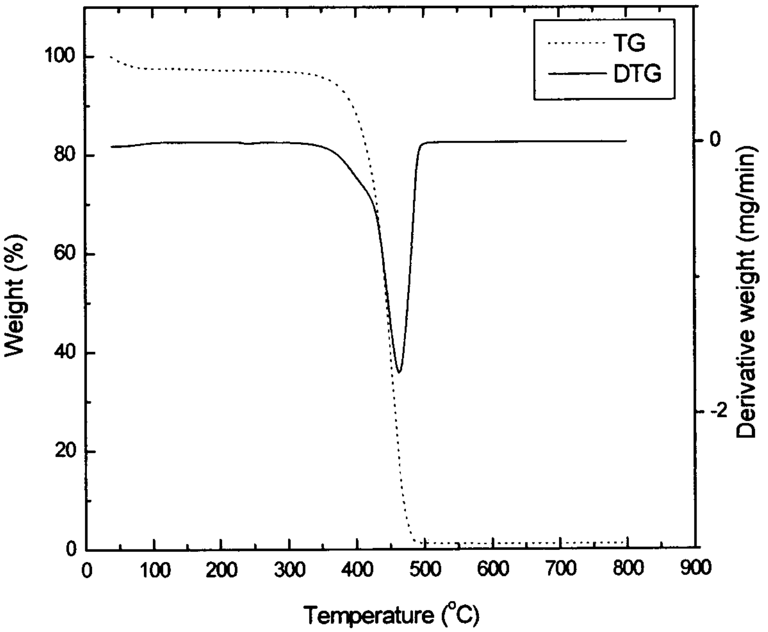


Figure 7.1 TG and DTG curves of nylon 6 fibre

7.2.2 Thermal analysis of composites

Figures 7.2 and 7.3 show the thermal degradation behaviour (TG and DTG curves) of gum (NBR) and fibre filled composite system consisting of 24 phr fibres cured by DCP (Mix M). In the case of NBR gum sample, a two stage degradation is observed (Figure 7.2). This is due to the presence of both acrylonitrile and butadiene units in nitrile rubber[16]. The first step of degradation is from 365 °C to 425 °C and the second step is from 426 °C to 530 °C. Mass losses during the first and second stages of degradation are 70% and 13.7 % respectively. Only 6 % of the sample remains at 800 °C.

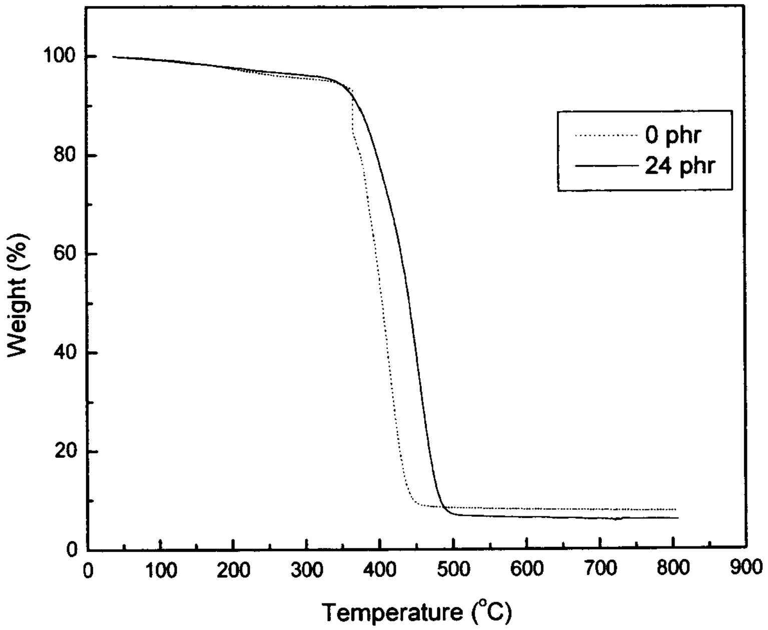


Figure 7.2 TG curves of DCP cured gum and fibre filled sample

The DTG curve (Figure 7.3) of NBR shows two peaks; one at 425.8 °C and the other at 452.5 °C. The first peak is mainly due to the degradation of butadiene segments and the second one corresponds to the degradation of acrylonitrile units.

From the TG curve of fibre filled composite (Figure 7.2) it is clear that the onset of thermal degradation is shifted to a higher temperature (370 °C). The major decomposition occurs in the range of 370- 460 °C and at 800 °C the weight loss observed is about 90 % compared to 94 % in the case of gum sample. The DTG curve of fibre filled composite (Figure 7.3) shows only one major decomposition peak. It can be seen that there is only one major decomposition step which occurs at 456.5 °C. The temperature of maximum degradation is higher than that of the gum sample. Thus it is evident from the thermo-gravimetric scan that the thermal stability of fibre reinforced NBR system is higher than that of the gum sample. This is reflected in the weight losses of NBR (gum) and nylon-NBR composite systems at different temperatures (Table 7.1). It can be seen from the table that the weight losses are lower in the case of composite systems compared to the gum sample.

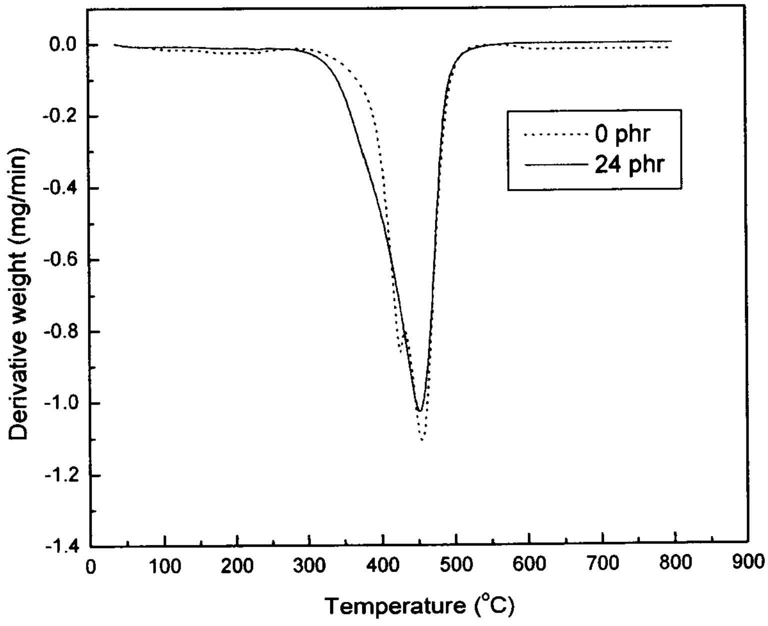


Figure 7.3 DTG curves of DCP cured gum and fibre filled sample

Table 7.1 Thermal degradation of various mixes at different temperatures

Sample	Percentage weight loss at various degradation temperature					
	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
H	4.46	43.73	91.54	93.30	93.90	94.05
J	4.40	19.91	91.35	92.32	92.64	93.02
L	3.88	19.29	89.77	90.60	90.80	90.95
M	3.78	18.95	87.77	88.58	89.59	90.10
Q	3.60	18.40	87.10	88.21	88.30	89.50
R	3.57	18.60	86.90	88.04	87.68	88.40
A	4.76	44.73	92.38	94.50	95.20	95.70
F	3.86	19.20	88.90	89.80	90.20	91.40

7.2.2.1 Effect of fibre loading

Figures 7.4 shows the TG curves and Figures 7.5 represents the DTG curves of composite samples consisting of 0, 12, 18 and 24 phr fibres respectively (Mixes H, J, L and M). On comparing the thermograms, it is clear that the increment in the loading of short nylon fibres has a retarding effect on the extent of degradation of fibre reinforced NBR composites. From Table 7.1, it is obvious that, at each temperature, the percentage of weight loss decreases with increase in fibre loading. As fibre loading increases, the degradation temperature also increases as indicated in Figure 7.5. Thus the resistance to degradation increases with fibre loading due to the enhanced interaction between the fibres and rubber at higher loading.

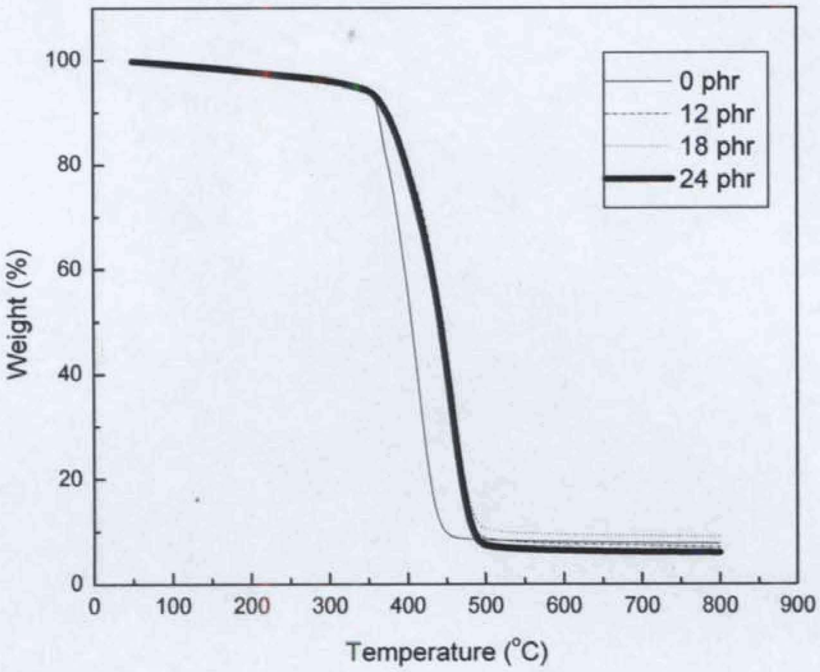


Figure 7.4 **TG curves of short nylon 6 fibre reinforced NBR composites at different fibre loadings**

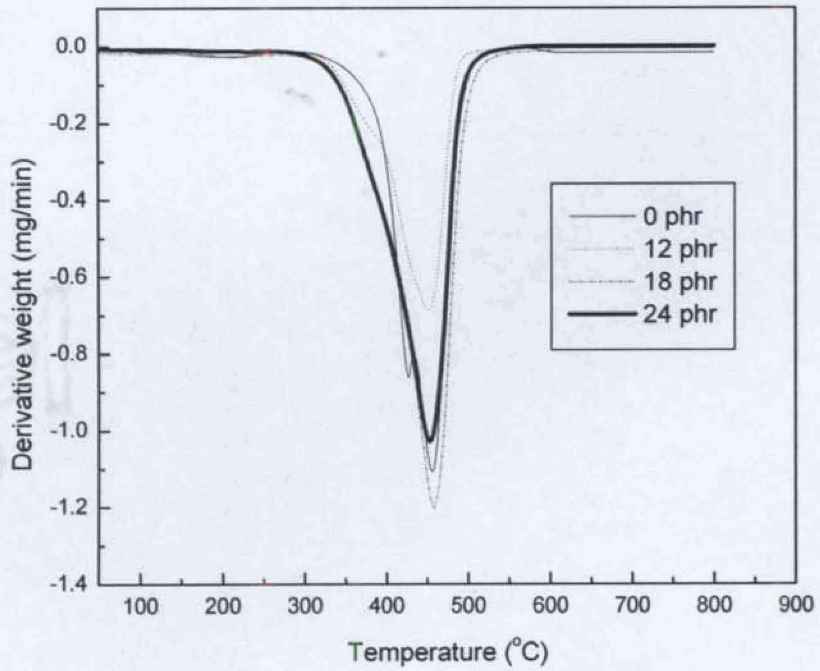


Figure 7.5 **DTG curves of short nylon 6 fibre reinforced NBR composites at different fibre loadings**

The degradation temperatures evaluated from the thermograms of nylon 6-NBR composites at different fibre loading are tabulated in Table 7.2. From the table it is clear that the onset temperature (T_{onset}), temperature at which 50% weight loss takes place (T_{50}) and the temperature of maximum degradation (T_{max}) increase as the fibre loading increases (Mixes H to M). The increase in decomposition temperature confirms the increased interaction between the fibres and the matrix, which enhances the overall thermal stability of the composites.

Table 7.2 Degradation temperatures of different mixes

Mix	T_{onset} (°C)	T_{50} (°C)	T_{max} (°C)
H	366.0	404.3	452.5
J	368.2	443.6	453.2
L	369.5	444.0	456.0
M	370.1	446.8	456.3
Q	371.0	447.2	458.2
R	370.8	447.0	457.0
A	365.2	403.1	451.3
F	367.6	446.1	455.5

Figure 7.6 shows the plot of onset temperature, temperature at which 50% weight loss takes place, and the temperature of maximum degradation against fibre loading. From the figure it is clear that the degradation temperatures increase with fibre loading.

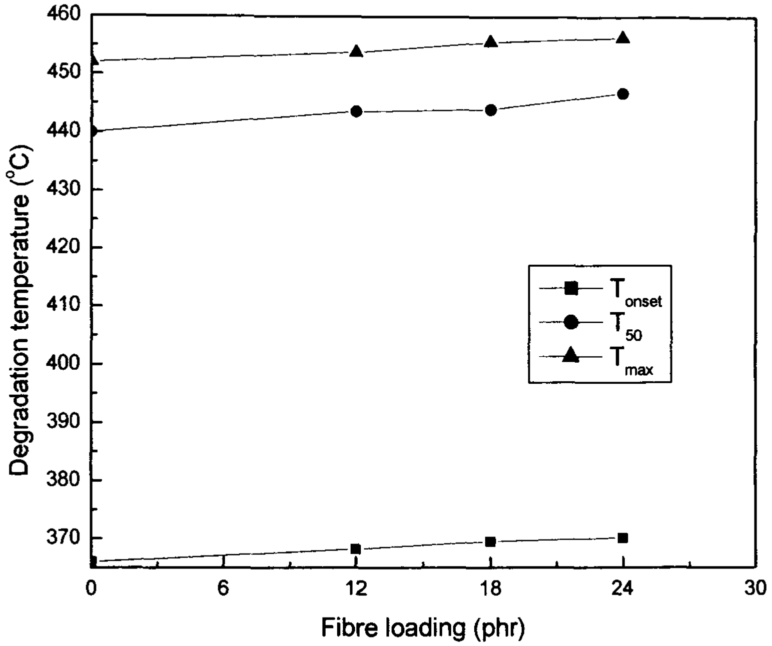


Figure 7.6 Variation of different degradation temperatures with fibre loading

7.2.2.2 Effect of curing systems

The thermal degradation behaviour of nylon 6 fibre–NBR composites cured by different vulcanising systems is found to be different. This can be seen from the TG (Figure 7.7) and DTG (Figure 7.8) curves of samples containing 24 phr fibre cured by sulphur and DCP (Mixes F and M). The onset temperature and temperature of maximum decomposition are highest for DCP cured samples indicating their higher thermal stability (Table 7.2). This can be explained on the basis of the difference in the type of crosslinks produced by sulphur and DCP. The C-C linkages in peroxide cured system are less flexible with higher bond energy (85 kcal mol^{-1}) compared to the polysulphidic linkages in sulphur cured system. From Table 7.1 it can be seen that the mass loss observed at a particular temperature is lesser for DCP cured system.

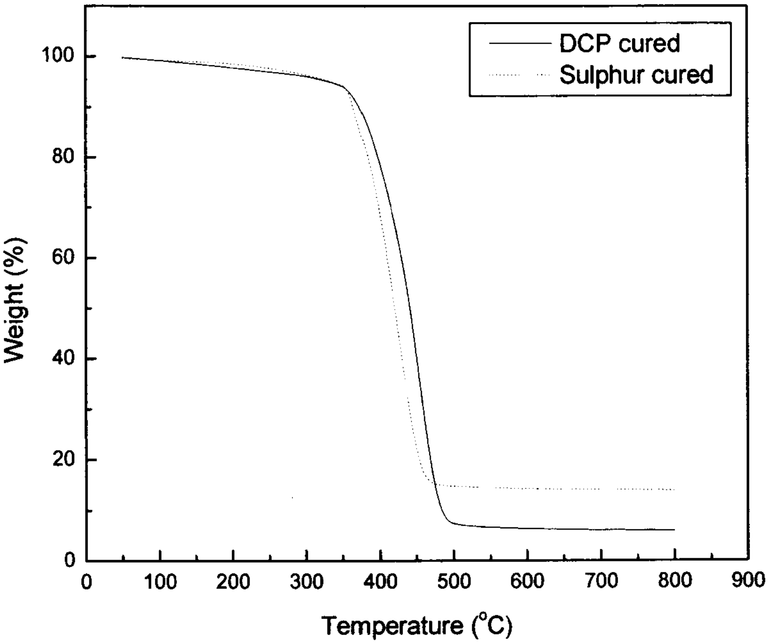


Figure 7.7 TG curves of mixes cured by sulphur and DCP systems

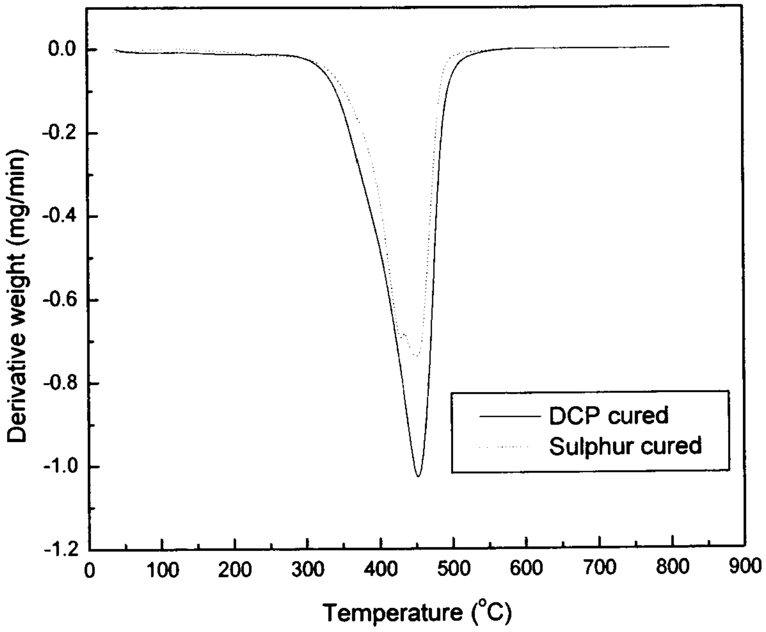


Figure 7.8 DTG curves of mixes cured by sulphur and DCP systems

7.2.2.3 Effect of bonding agents

The incorporation of bonding agents, namely hexa-resorcinol and phthalic anhydride plays a significant role on the thermal degradation of nylon fibre reinforced NBR composites. This is evident from the TG (Figure 7.9) and DTG (Figure 7.10) curves of unbonded and bonding agent added composite systems. The extent of degradation is comparatively lesser in both hexa-resorcinol and phthalic anhydride bonding agent added systems (Mixes Q and R) than that of the unbonded one (Mix M). This is also evident from the weight losses at different temperatures given in Table 7.1. It has been found that the onset temperature, temperature at which 50% weight loss takes place, and the temperature of maximum degradation of bonding agent added composites are higher than that of the corresponding unbonded one (Table 7.2). The effect of bonding agents on the increased thermal resistance of the composites can be attributed to the strengthening of the interface.

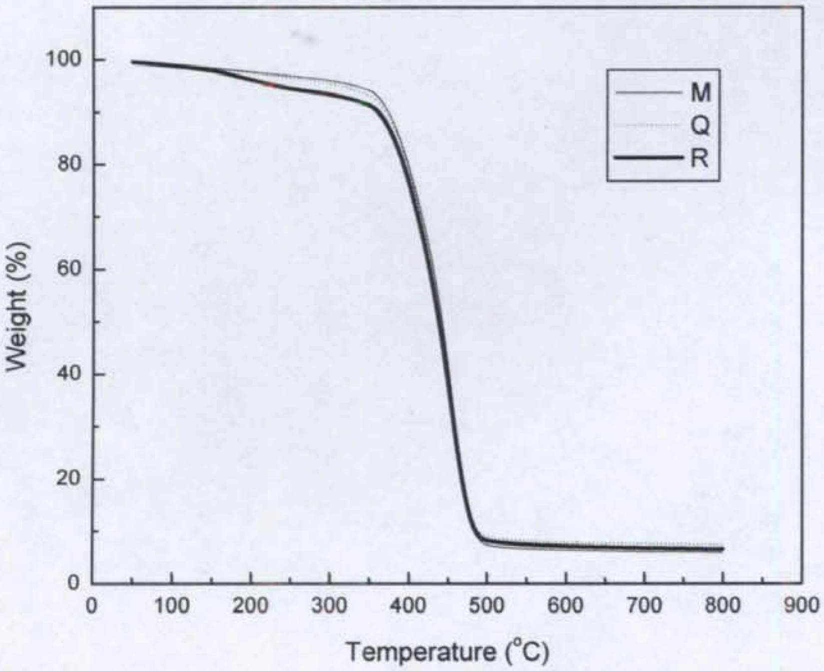


Figure 7.9 TG curves of unbonded and bonding agent added composites

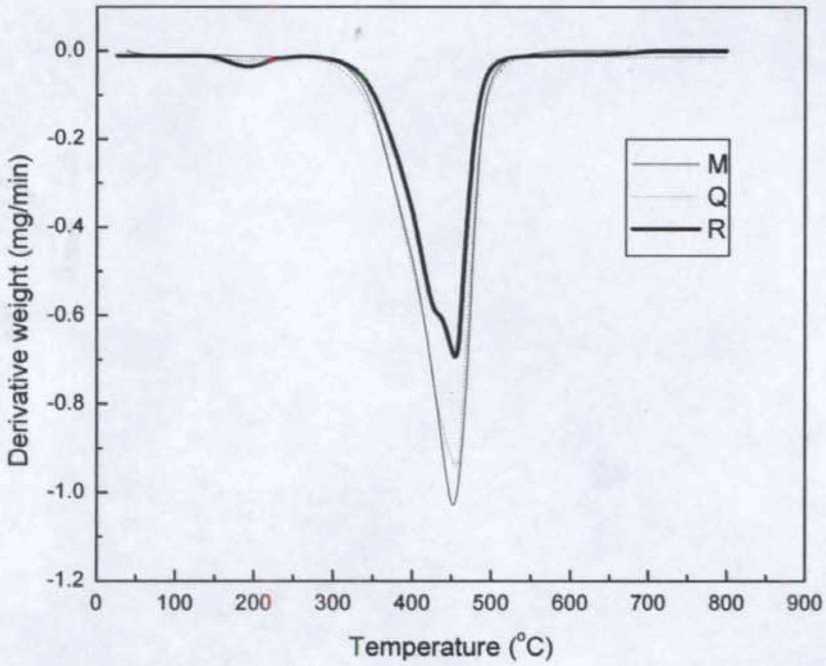


Figure 7.10 DTG curves of unbonded and bonding agent added composites

7.2.3 Energy of activation for thermal degradation

The activation energy for the process of thermal degradation has been calculated using the basic Arrhenius relationship;

$$\log X = \log X_0 - E_D / 2.303\, RT \qquad \ldots (7.1)$$

where X is the percentage loss of weight of composite at temperature T. X_0 is the pre-exponential factor and E_D represents the activation energy for the thermal degradation, obtained from the slope of the typical Arrhenius plots of log X versus 1/T. The calculated values of E_D at different fibre loadings are given in Table 7.3. From the table it can be seen that the E_D is least for the gum sample. This indicates that the degradation occurs easily in the absence of fibres without consuming much energy. However, as the fibre loading increases the process of degradation takes place only at higher temperatures, consuming more energy. These observations parallel with the higher thermal stability of the composite systems at higher fibre loading.

Table 7.3 Activation energy at different fibre loadings

Fibre loading (phr)	Energy of activation (kJ/mol)
0	24.76
12	25.46
18	26.07
24	26.94

7.2.4 Differential scanning calorimetric studies

Figure 7.11 shows the DSC curves of gum (NBR) and nylon 6 fibre reinforced NBR composite containing 24 phr fibres (Mix M) cured by DCP. Unlike the gum

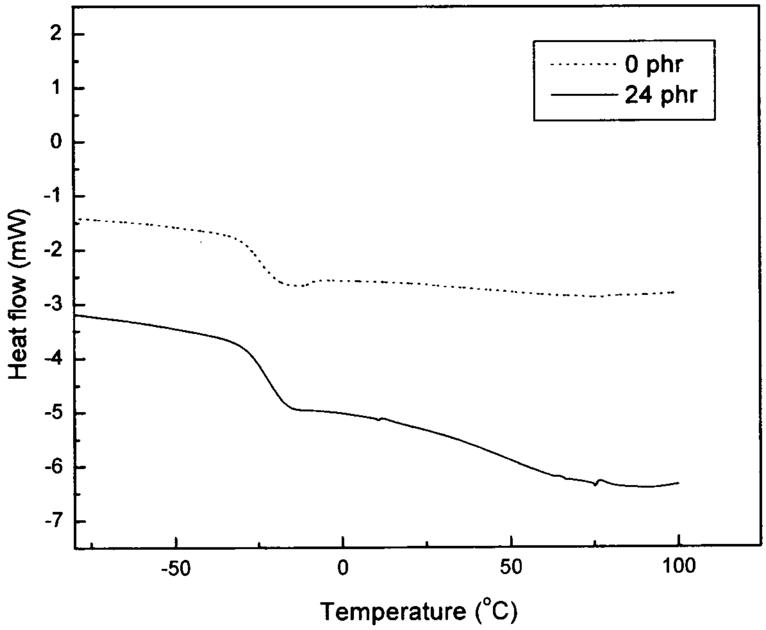


Figure 7.11 DSC curves of gum and composite sample containing 24 phr fibre

sample, the composite system shows two endothermic peaks, indicating two different transitions and also the heterogeneity of the system. The T_g value of gum compound is found to be -24.8 °C and is very close to that of uncrosslinked NBR (-26 °C). The T_g value increases with fibre loading (Table 7.4). The T_g value of the sample containing 24 phr fibres is found to be -22.3 °C. The increment in T_g is due to the stiffness and rigidity provided by the fibres. The change in T_g of the composites upon the incorporation of fibres has been reported by several authors[17,18].

Table 7.4 T_g of matrix of various mixes

Mix	T_g of matrix (°C)
H	-24.8
J	-23.3
L	-23.0
M	-22.3
Q	-21.8
R	-22.0

Figure 7.13 shows the DSC curves of hexa-resorcinol and phthalic anhydride bonded composite samples (Mixes Q and R). It is observed that the T_g value corresponding to the matrix increases on the addition of the bonding agent. The bonding agent added composite systems show higher T_g values compared to the others (Table 7.4). The higher interaction between the fibres and matrix, in the presence of bonding agent, provides higher stiffness to the resultant composite system and as a result the T_g value increases.

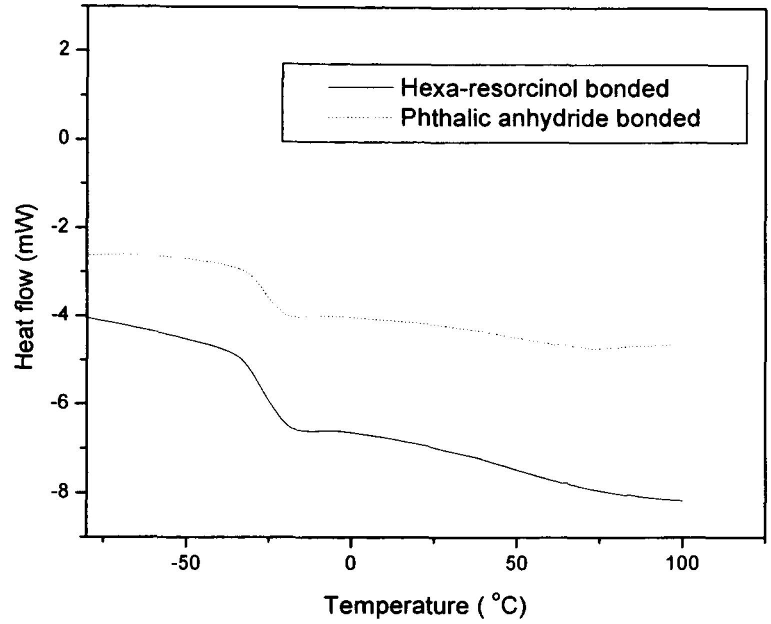


Figure 7.13 DSC curves of unbonded and bonded composite samples

7.3. CONCLUSIONS

The thermal behaviour of nylon 6 fibre, and nylon/NBR composites has been studied by TG and DSC with special reference to the effects of fibre loading, curing systems and the incorporation of bonding agents. The degradation temperatures of fibre filled composite systems were observed to be higher than those of the gum. As the fibre loading increased, the decomposition temperature has been shifted to higher temperature range. The percentage weight loss at different temperatures decreased with fibre loading. The decomposition temperature of DCP cured sample was higher than that of sulphur cured one. The extent of degradation was comparatively lower for bonding agent added fibrous composite systems compared to the unbonded one. The activation energy for thermal degradation of the composites increased with fibre loading. The DSC studies of composites indicated that the fibre filled systems possessed higher T_g values than the pure gum due to the higher rigidity and stiffness of the matrix provided by the fibres. The bonding agent added fibrous composite systems showed higher T_g values compared to the others due to improved fibre-matrix interaction. These results have been found to be complementary to those obtained from the evaluation of the mechanical properties of nylon 6/NBR system.

References

1. Mc Neill I.C, *Comprehensive Polymeric Science*, Vol.**6**, Allen, G (Ed), Pergamon Press, New York (1989).
2. Kenyon A. S., *Techniques and Methods of Polymer Evaluation,* First Edn., Slade Jr. P. E. and Jenkins L. T., (Eds.), Marcel Dekker, New York (1966).
3. Laired J. L. and Liolios G., *Amer. Lab.*, H-16782 (1990)
4. Ninan K. N., *Proc. Adv. Polym. Technol. Symp.*, CUSAT, Kochi, India (1996).
5. Brown M.E., *Introduction to Thermal Analysis: Techniques and Applications*, Chapman and Hall, New York (1988).
6. Chaki T. K., Bhattacharya A. K. and Gupta B. R., *Kauts. Gummi Kunst.,* **43** (5) (1990) 408.
7. Fu S. Y. and Mai Y. W., *J. Appl. Polym. Sci.*, **88** (2003) 1497.
8. Corre^a., R A., Nunes R.C. and Lourenco V L.,. *Polym. Degrad. Stab.,* **52** (1996) 245.
9. Kutty S.K.N., Chaki T.K. and Nando G.B., *Polym. Degrad. Stab.*, **38** (1996) 187.
10. Faud M. Y. A., Zaini M. J., Jamludin M. and Ridzuan R., *Polym. Test.,* **13** (1994) 15.

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

12. George J., Bhagawan S. S. and Thomas S., *J. Therm. Anal.*, **47** (1996) 1121.

13. Ahmed S., Basfar A. A. and Abdel Aziz M.M., *Polym.Degrad.* Stab., **67** (2000) 319.

14. Seema A. and Kutty S .K .N., *Int. J. Polym. Mater.*, **55** (2006) 25.

15. Levchik S.V., Edward D.W. and Menachem L., *Polym Int*, **48** (1999) 532.

16. Amrace I.A., Katbab A.A. and Aghafarajollah S.H., *Rubber Chem. Technol.*, **69** (1995) 180.

17. Rebenfeld L. and Desio G. P., *J. Appl. Polym. Sci.*, **42** (1991) 801.

18. Hon D. N. S. and Chao Y. W., *J. Appl. Polym. Sci.*, **50** (1993) 7.

Chapter 8

Dynamic Mechanical Analysis of Nylon 6/NBR Composites

Abstract

The dynamic mechanical properties of short nylon 6 fibre reinforced NBR composites such as storage modulus (G'), loss modulus (G") and the damping behaviour (tan δ) have been analysed with reference to the effects of fibre loading, curing systems and bonding agents over a range of temperature (-100 to 100 °C) and at varying frequencies (0.1, 1, 10 and 50 Hz). The storage modulus has been found to be increased with increment in fibre loading. The loss modulus and damping characteristics decrease with fibre loading. The glass transition temperature has been found to be shifted to higher temperature upon increment in fibre loading. DCP cured composites show higher storage modulus and lower damping than the corresponding sulphur cured one. The addition of hexa-resorcinol and phthalic anhydride as bonding agents enhances the dynamic mechanical properties of the present composites. The Cole-Cole plots further indicate the heterogeneous nature of the composite system. The experimental results have been evaluated by comparing with Einstein, Guth and Nielsen models.

8.1 INTRODUCTION

Rubbers show both elastic and damping behaviour because of their visco-elastic nature. When they are deformed by a sinusoidal stress within the linear visco-elastic region, the resulting strain will also be sinusoidal but will be out of phase with the applied stress. Dynamic losses are usually associated with hysteresis and specific mechanisms of molecular or structural motion in polymeric materials. The damping in the system or the energy loss per cycle can be measured from the tangent of the phase angle or loss tangent (tan δ) which is defined as $\tan\delta = G'' / G'$ where G' is the storage modulus due to stored elastic energy in the materials and G'' is the loss modulus due to viscous dissipation. One method that has been used to investigate the storage modulus, loss modulus and loss tangent is dynamical mechanical thermal analysis (DMTA). This technique has widely been employed for investigating the visco-elastic behaviour, stiffness (modulus), damping (energy dissipation) characteristics, phase transitions and the interfacial adhesion of polymer composites as they are deformed under periodic stresses[1, 2]. It is particularly useful because of its non-destructive nature unlike other static mechanical testing methods.

Dynamic mechanical properties of polymeric materials are of considerable practical significance when determined over a range of temperatures and frequencies. They can yield an insight into various aspects of material structure, by providing a convenient measure of T_g. These properties are also of direct relevance to a range of unique polymer applications, concerned with the isolation of vibrations or dissipation of vibrational energy in engineering components. For fibre reinforced polymer composites, the dynamic mechanical properties depend on the type of fibre, fibre length, fibre orientation, fibre loading, fibre dispersion and fibre-matrix adhesion. Some of the major objectives of the works carried out on the dynamic mechanical properties of fibrous composite materials have been the study of chemical or physical modifications of the matrix induced by the introduction of surface treatment of fibres and the related analysis as a function of the properties of each phase. The importance of dynamic mechanical testing as a powerful tool for characterising the interfacial adhesion is well known[3-9].

Several researchers have studied the dynamic mechanical thermal properties of rubber composites[10-17]. Ashida and Noguchi[10] investigated the dynamic mechanical properties of short fibre reinforced chloroprene composites. The effects of carbon black and china clay on the visco-elastic properties of thermoplastic 1, 2-polybutadiene rubber have been investigated by Bhagwan *et al*[11]. Visco-elastic properties, role of adhesion and the effect of particulate fillers on short jute fibre reinforced NR composites have been investigated by Murthy and De [12-14]. Sombatsompop[15] examined the visco-elastic properties of NR vulcanisates filled with polyurethane foam particles and carbon black in terms of storage modulus, loss tangent and T_g. It was highlighted that a shift of T_g to higher temperature with a decrease in loss tangent peak indicated the higher interaction between the fillers and the rubber phase. The dynamic visco-elasticity of isoprene rubber reinforced with short cellulose fibres have been analysed by Yano *et al*[16]. Finegan and Gibson[17] predicted the importance of different fibre-matrix combinations on the enhancement of damping in polymer composites. Pothan *et al.*[18] carried out the dynamical mechanical analysis of banana fibre reinforced polyester composites. Saha *et al.*[19] made comparative studies on the damping of unmodified and chemically modified jute polyester composite samples. The visco-elastic properties of wood fibre reinforced polyurethane composites were analysed by Rials *et al*[20]. The addition of fibre was found to increase the storage modulus indicating an extensively bonded network. Ibarra and Chamorro[21] pointed out that the loss modulus values increased with the loading of short polyethylene fibres into NR, SBR, CR and NBR matrices.

The present chapter examines the dynamic mechanical properties of nylon 6 fibre reinforced NBR composites at varying frequencies and temperatures. The properties of the composites have been analysed with special reference to the effects of fibre loading, curing systems and bonding agents.

8.2 RESULTS AND DISCUSSION

8.2.1 Effect of fibre loading

Figure 8.1 shows the variation of storage modulus (G') with temperature of nylon 6/NBR composites, as a function of fibre loading, at a frequency of 10 Hz. The gum compound, without fibres, has the lowest stiffness and hence the lowest storage modulus at a given temperature. When fibres are incorporated in to the rubber matrix, they can participate in effective stress transfer and as a result the stiffness of the composites increases leading to higher storage modulus. This can be attributed to the combination of the hydrodynamic effects of the fibres embedded in a visco-elastic medium and to the mechanical restraint introduced by the filler at their higher concentrations, which reduce the mobility and the deformability of the matrix [22]. It has been observed that the storage modulus increases with increasing fibre loading at all temperatures. As the fibre loading is increased the stress is more

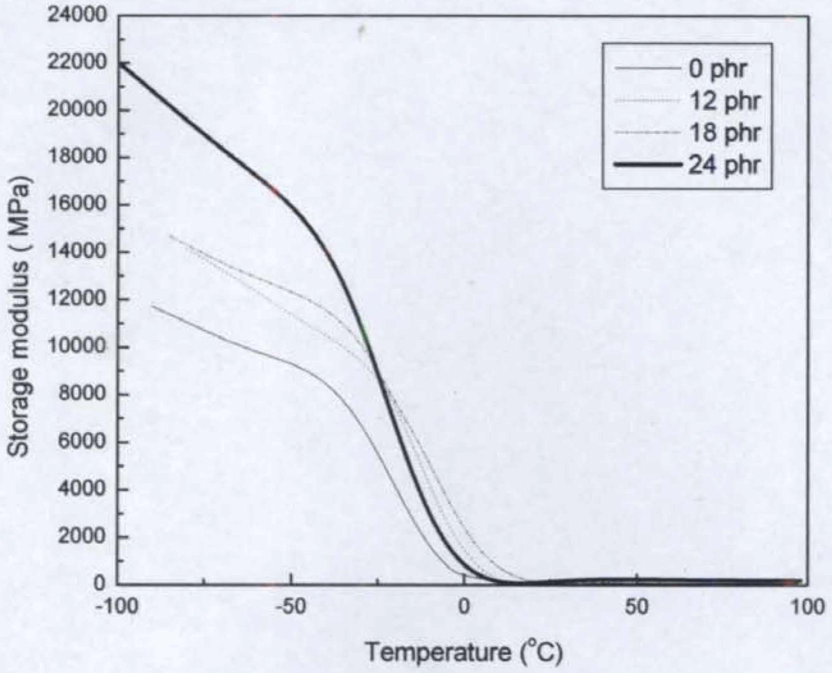


Figure 8.1 Effect of fibre loading on storage modulus as a function of temperature at a frequency of 10 Hz

evenly distributed and the storage modulus of the composite increases. The increment in G′ is prominent in the glassy state, below T_g, while it is not so significant in the rubbery plateau region. This is demonstrated in Figure 8.2, which shows the variation of storage modulus with fibre loading in the glassy and rubbery regions. It can be seen that in the glassy region the modulus values gradually increase while in the rubbery region the change is relatively very less. In the glassy region, the components are in a frozen state i.e.; highly immobile. In such a state, there exists a close and tight packing in the composite structure resulting in higher modulus. It is important to mention that the modulus in the glassy state is determined primarily by the strength of the intermolecular forces and the way the polymer chains are packed. As temperature increases the components become more mobile and lose their close packing arrangement. As a result, in the rubbery region, there is no significant change in the modulus.

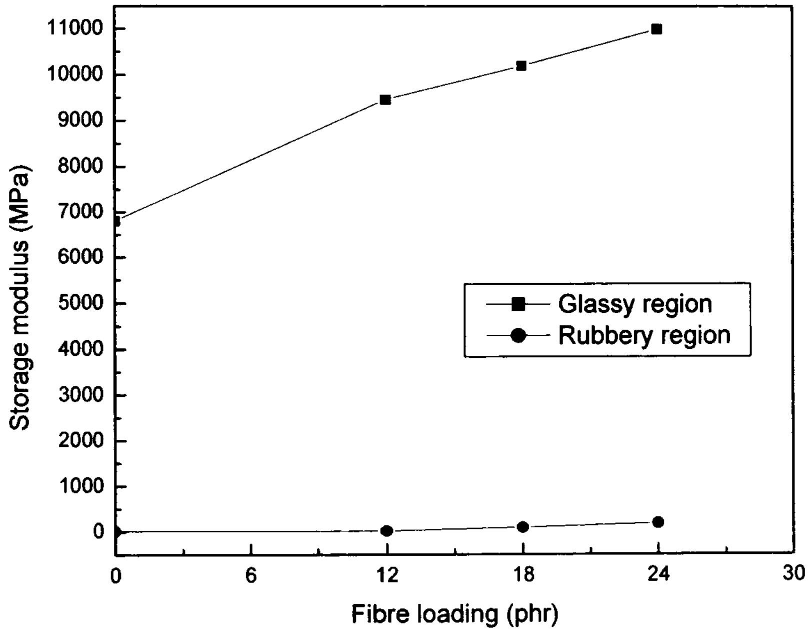


Figure 8.2 **Variation of storage modulus with fibre loading in glassy and rubbery regions**

The effectiveness of fillers on the moduli of composites can be represented by a coeffiecient C which is given as [23]

$$C = \frac{G'_g / G'_r \text{comp}}{G'_g / G'_r \text{resin}} \qquad \text{......(8.1)}$$

Where G'_g and G'_r are the storage modulus values in the glassy and rubbery region respectively. The lower the value of the constant C, the better is the effectiveness of the filler. The values obtained for different systems at a frequency of 10 Hz are given in Table 8.2. It can be seen that the value of C decreases with fibre loading upto 24 phr which shows the increased reinforcing effect of fibres with increment

Table 8.1 Values of the coefficient C

Fibre loading (phr)	Value of C
0	1.0
12	0.97
18	0.22
24	0.12

in loading. From Figure 8.1 it can be seen that the storage modulus of all systems decreases with increase in temperature. At higher temperatures, the close packing of fibres would be disturbed due to the relaxation of macromolecular chains and the weakening of the physical bonds between the fibres and polymer phases, resulting in the deterioration of the composite structures and thus lowering the storage modulus[24].

Figure 8.3 shows the variation of loss modulus (G″) with temperature as a function of fibre loading at a frequency of 10 Hz. Loss modulus is a measure of the energy dissipated or lost as heat per cycle of sinusoidal deformation. It is in fact the viscose response of the material. Loss factors are more sensitive to molecular motions. It can be seen from Figure 8.3 that the loss modulus values generally increase with increase in fibre concentration at temperatures well below the glass transition. In the region of transition the loss modulus peak values are lesser for fibre filled samples than for the gum. Figure 8.4 shows a schematic representation of the fibre, matrix and the immobilized polymer layer. A specific interaction between the filler and the polymer layer would create a layer of immobilized polymer between the filler and matrix. The matrix surrounding the fibres can be taken as an inter-layer which is in a different state compared to the rest of the matrix where the molecular motions are relatively hindered[25]. A shell of immobilized polymer surrounds the fibres[26] and, the higher the volume fraction of the matrix, the more the restraint at the interface.

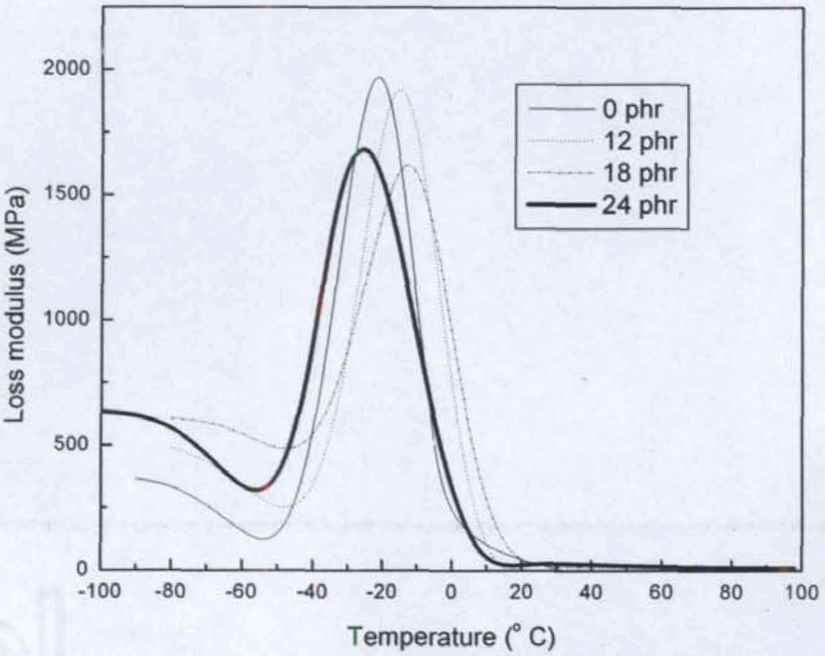


Figure 8.3 **Effect of fibre loading on loss modulus as a function of temperature at a frequency of 10 Hz**

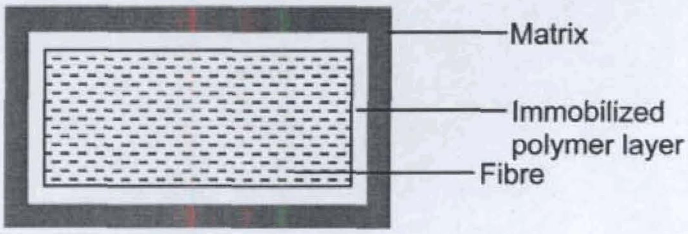


Figure 8.4 **Schematic representation of the fibre, matrix and immobilized polymer layer.**

The effect of fibre loading on the damping characteristics (tan δ) as a function of temperature at a frequency of 10 Hz is illustrated in Figure 8.5. The tan δ is a damping term that can be related to the impact resistance of the material. Since the damping peak occurs in the region of glass transition where the material changes from a rigid to a more elastic state it is associated with the movement of small groups and chains of molecules within the polymer structure, all of which are initially frozen in. In a composite system, damping is affected through the incorporation of fibres. This is mainly due to shear stress concentrations at the fibre ends in association with the additional visco-elastic energy dissipation in the matrix material. It can be seen from Figure 8.5 that tan δ value is highest for the gum sample and it decreases with increase in fibre loading. The lowering of tan δ values is due to the improvement in the interfacial bonding in composites with increment in fibre loading. When the fibre concentration is lower, the packing of fibres will not be efficient in the composites. This leads to matrix rich regions and thus to an easier failure of the bonding at the interfacial region. At higher fibre loading, when

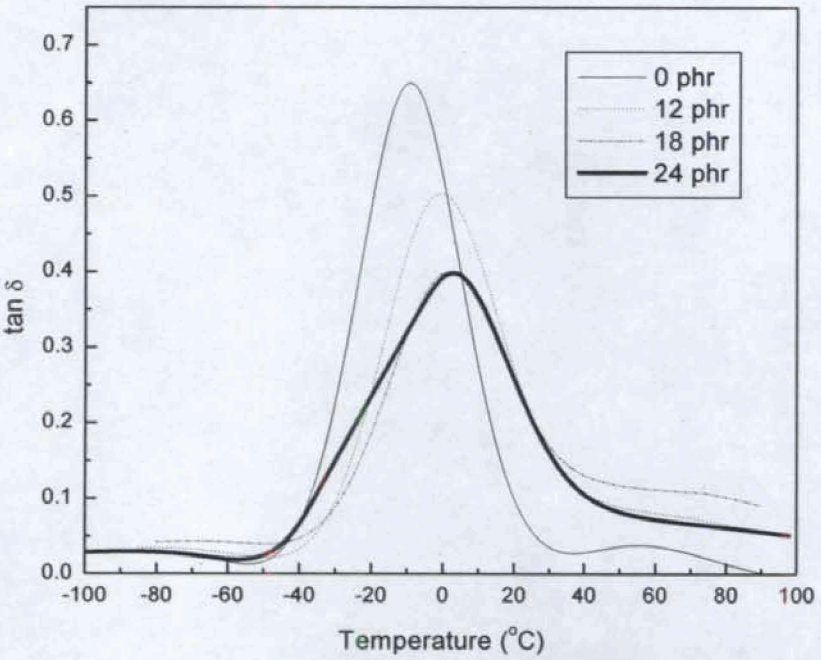


Figure 8.5 Effect of fibre loading on damping characteristics (tan δ) as a function of temperature at a frequency of 10 Hz

there is relatively high close packing of fibres, crack propagation will be prevented by the neighboring fibres.

Incorporation of fibres reduces the tan δ peak height by restricting the movement of polymer molecules. The temperature at which maximum damping occurs (tan δ_{max}) represents the glass transition temperature (T_g) of the system. As the fibre loading increases, the tan δ_{max} decreases and the T_g values show a positive shift (Table 8.2). The shifting of T_g to higher temperatures can be associated with the decreased mobility of the chains by the addition of fibres. Elevation in T_g is taken as a measure of interfacial interaction. Composites with poor interface bonding tend to dissipate more energy than those with good interfacial bonding[27]. At higher fibre content, an applied strain has to be controlled mainly by the fibres themselves. As a result the interface strains only to a lesser degree, since it is assumed to be the more dissipative component of a composite[28, 29]. The higher restrictions on the amorphous phase result in a higher or broader glass transition behaviour. The broadening of the tan δ peaks is indicative of the increased volume at the interface. Table 8.2 shows the relative peak height and peak width at half height from the damping curves of the samples. It can be seen that peak height decreases and peak width increases with

Table 8.2 Effect of fibre loading on the damping characteristics of composites at a frequency of 10 Hz

Fibre loading (phr)	tanδ (max)	T_g (°C)	Peak height (cm)	Peak width (cm)	Energy of activation for glass transition (Ea), (kJ/mol)
0	0.67	-9.0	5.22	4.1	174.06
12	0.50	-0.5	3.40	5.1	212.75
18	0.41	1.4	3.04	5.8	223.38
24	0.40	1.9	3.03	9.6	239.34

fibre loading. Increase in concentration of fibre increases the interfacial interaction[30].

8.2.2 Effect of curing systems

Figure 8.6 shows the variation of storage modulus of composite samples cured by DCP and sulphur, as a function of temperature. It can be seen that, at optimum fibre loading, the storage modulus of DCP cured sample is higher than that of sulphur cured one in the glassy region whereas the difference is not so significant in the rubbery plateau. The difference in this behaviour can be attributed to the difference in crosss-links introduced by sulphur and DCP. These results are in well agreement with the observations from the static mechanical tests of the present composite system discussed in Chapter 3.

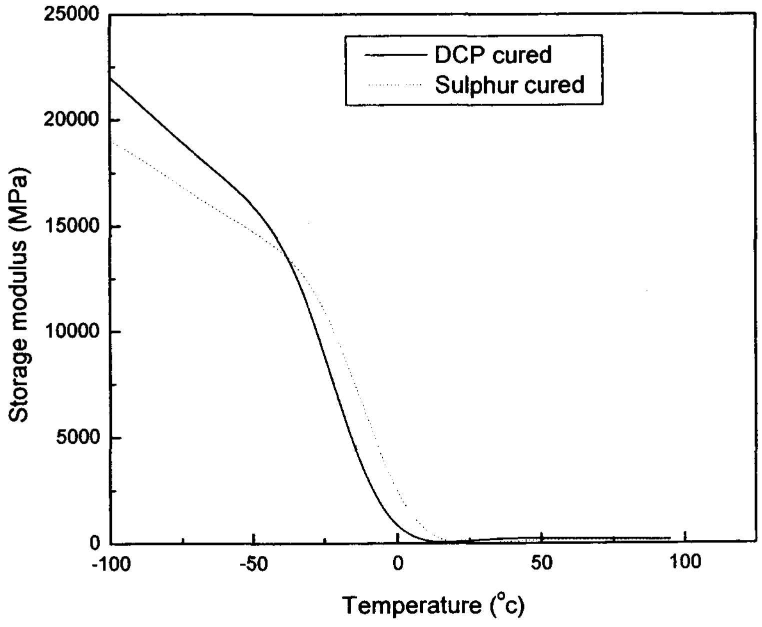


Figure 8.6 **Variation of storage modulus of DCP and sulphur cured samples with temperature at a frequency of 10 Hz**

Figure 8.7 shows the variation of tan δ with temperature of DCP and sulphur cured samples. It can be seen that DCP cured sample shows the lower tan δ_{max} compared to corresponding sulphur cured one.

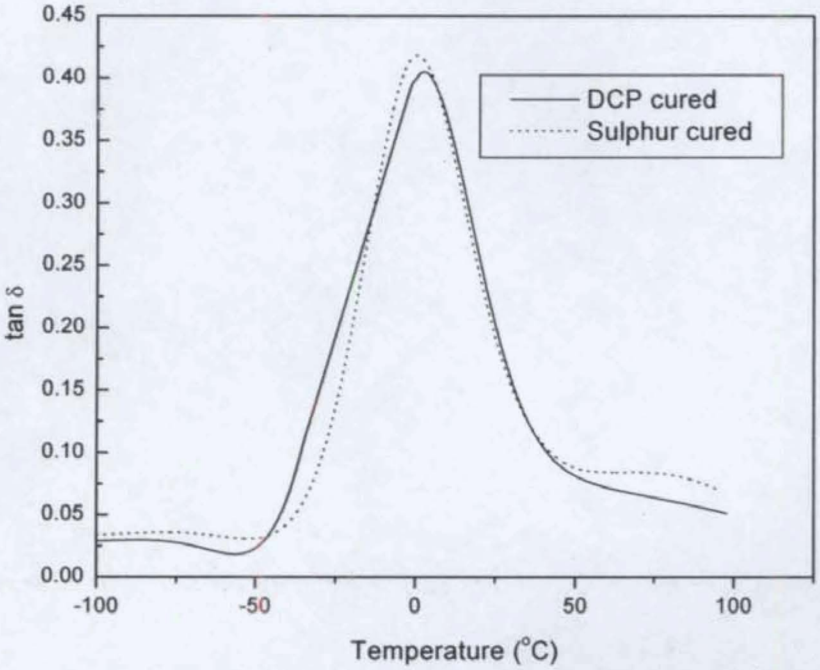


Figure 8.7 **Variation of tan δ of DCP and sulphur cured samples with temperature at a frequency of 10 Hz**

8.2.3 Effect of bonding agents

Figure 8.8 shows the effect of two bonding agents viz; hexa-resorcinol and phthalic anhydride on the storage modulus (G′), as a function of temperature, at a frequency of 10 Hz. It is evident that the G′ values of composites containing bonding agents are higher than that of the unbonded one at 24 phr fibre loading. This is due to the better interfacial adhesion in bonding agent added composites. The variation of tan δ with temperature for the unbonded and bonding agent added composites at a frequency of 10 Hz is given in Figure 8.9. It is obvious that the presence of bonding agent reduces the tan δ values. The tan δ_{max} of the bonding agent added composite is lower than that of the unboned one. Also the T_g values are shifted to higher temperatures due to greater interfacial interaction. The broadening of tan δ peak is also indicative of the improved interfacial adhesion in bonding agent added composites.

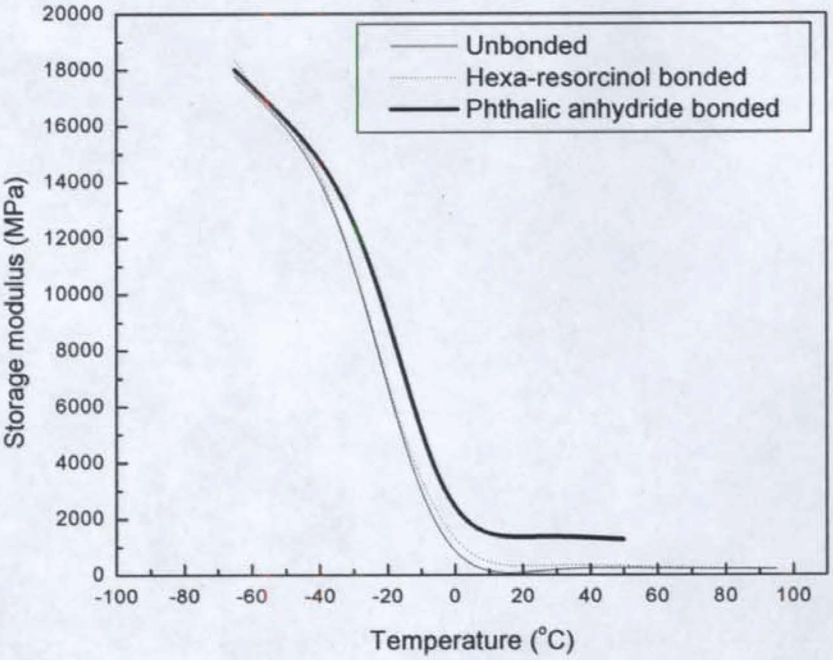


Figure 8.8 **Variation of storage modulus with temperature of unbonded and bonded composites at a frequency of 10 Hz**

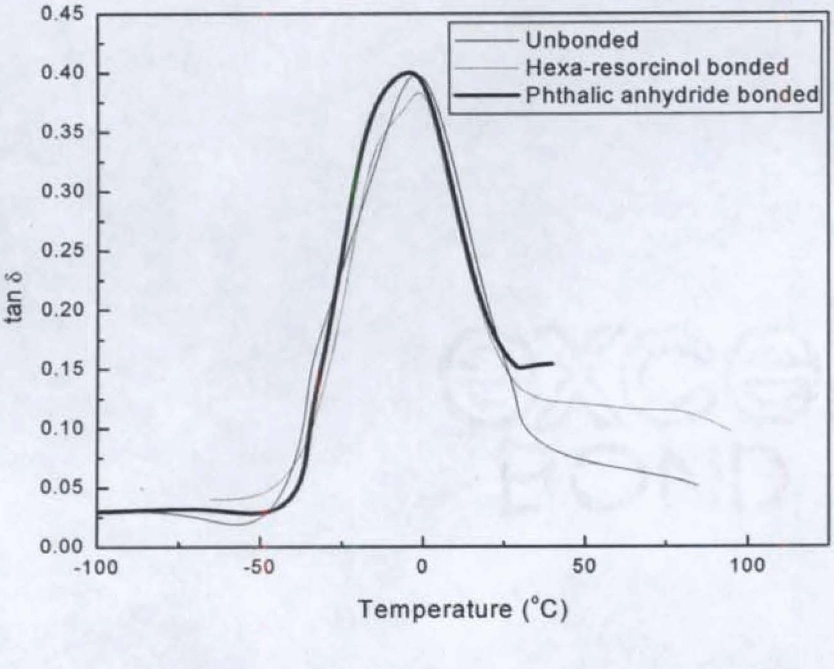


Figure 8.9 **Variation of tan δ with temperature of unbonded and bonded composites at a frequency of 10 Hz**

8.2.4 Effect of frequency

8.2.4.1 Influence on visco-elastic properties

Figure 8.10 shows the variation of storage modulus (G′) of composite sample containing 24 phr fibres (Mix M) as a function of temperature. It can be seen that the storage modulus increases with increase in frequency from 0.1 to 50 Hz, whereas it decreases with increasing temperature. The visco-elastic properties of a material are dependent on temperature, time and frequency. If a material is subjected to a constant stress, its elastic modulus will decrease over a period of time. This is due to the fact that the material undergoes molecular rearrangement in an attempt to minimise the localised stresses. Therefore, the modulus measurement performed over a short time (high frequency) results in higher values whereas measurements taken over a long time (low frequency) result in lower values[2]. Moreover, the time-temperature equivalence of visco-elastic materials proves that the dynamic mechanical behaviour tested at lower frequency is equivalent to that of

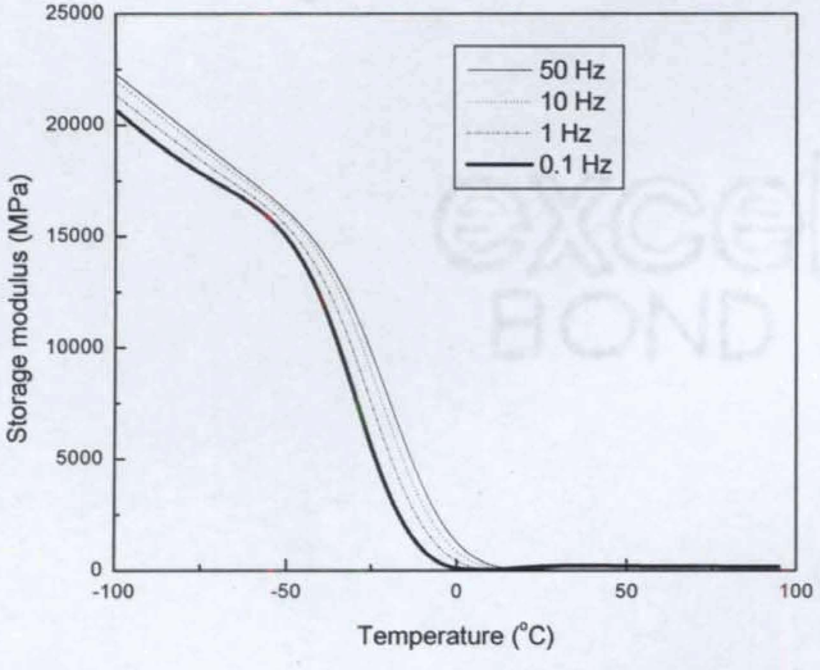


Figure 8.10 Effect of frequency on storage modulus (G′) of composite containing 24 phr fibres (Mix M) as a function of temperature

higher temperature[31]. The lesser mobility of polymeric chain at higher frequencies results in better binding between the fibres and matrix, which thereby increases the stiffness of the composite.

Figure 8.11 shows the effect of frequency on loss tangent (tan δ) of composite sample containing 24 phr fibres (Mix M) as a function of temperature. At lower temperature regions, the tan δ values are found to be decreased with an increase in frequency. However, the reverse occurs in the higher temperature regions. Below T_g, the deformation by the fillers are non-virtual, the components are in a frozen state i.e.; highly immobile and hence the damping is mainly dependent on the segmental mobility of the matrix. In such a case, an increment in frequency can induce the segmental mobility or molecular motions of the matrix resulting in lower damping properties. However, in higher temperature regions (above T_g) as the frequency increases, the molecules will not get time to undergo rearrangement and

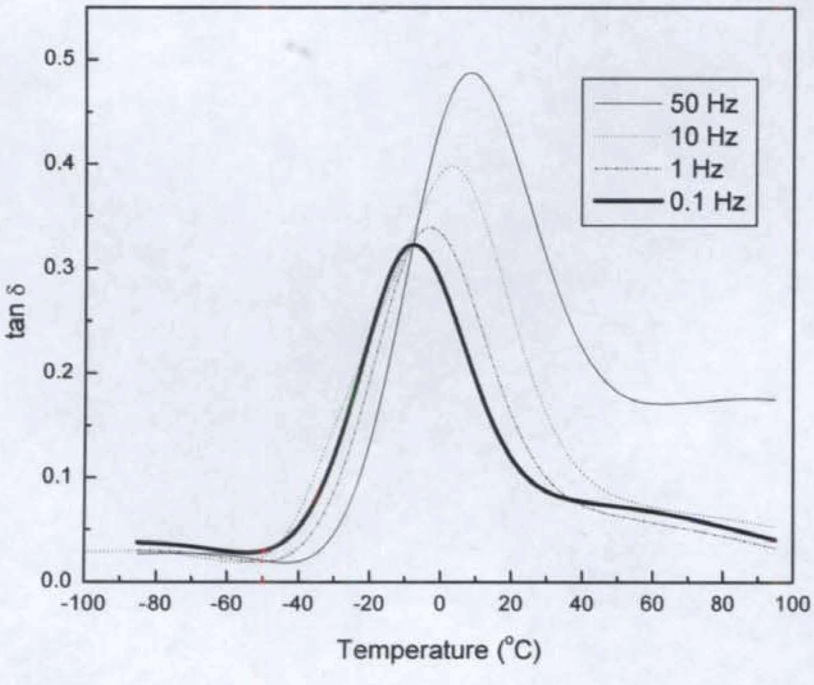


Figure 8.11 Effect of frequency on tan δ of composite containing 24 phr fibres (Mix M) as a function of temperature

as a result the material behaviour will be more like a liquid with enhanced damping properties. Due to the same reason it has been observed that the temperature corresponding to tan δ_{max} or T_g is shifted to the high temperature region at higher frequencies.

8.2.4.2 Master curve

Dynamic modulus is a function of temperature as well as of frequency or time. The visco-elastic property measured at one given temperature can be superimposed upon the data collected at different temperatures by shifting the curves according to the time-temperature superposition principle[32, 33]. Figure 8.12 shows the plot of the storage modulus (G′) of the composite sample with 24 phr fibre loading (Mix M) as a function of logarithm of frequency at different temperatures ranging from 40 to 80 °C. The curves obtained by plotting the experimental moduli at different temperatures against log ν have been superposed by horizontal shifts along a

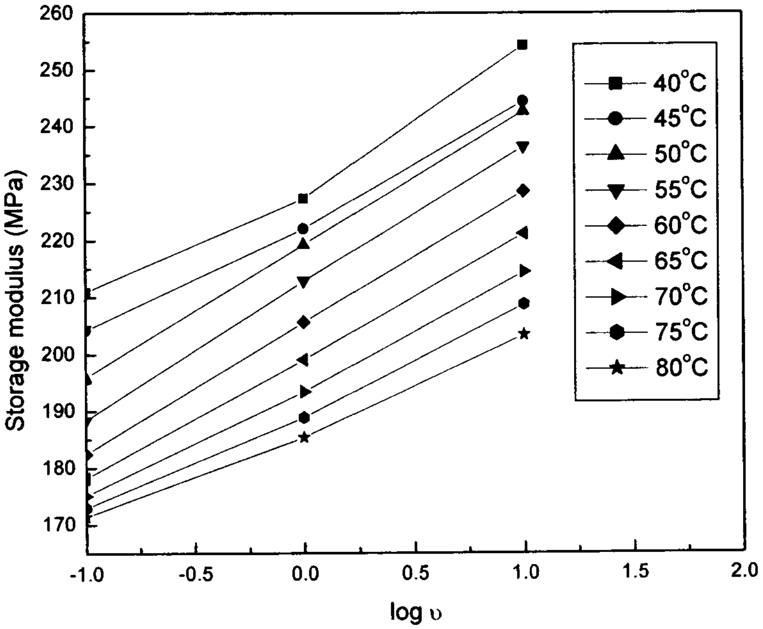


Figure 8.12 Plot of the storage modulus (G′) of composite sample with 24 phr fibre loading (Mix M) as a function of logarithm of frequency at different temperatures

logarithmic frequency scale to give a single curve (master curve) covering a very large range of time or frequency. The amount of horizontal shift or distance between the curves of log G′ versus log ν is given by the shift factor, 'a_{SF}'. The shift factor characterises the rate of relaxation mechanism at some temperature T in comparison with a reference temperature T_R. In the present case 80 °C is taken as the reference temperature for constructing log a_{SF} *vs* temperature graph which is shown in Figure 8.13. The method of relating the horizontal shifts along the

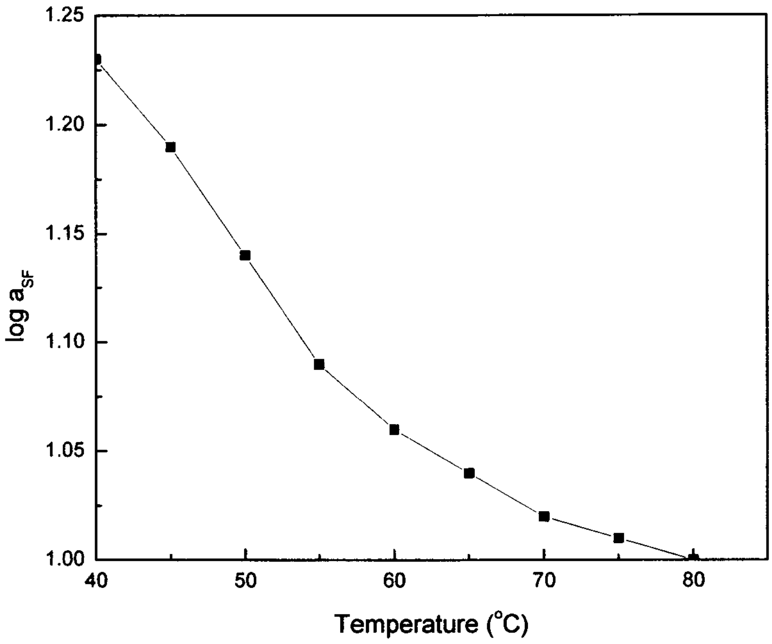


Figure 8.13 Variation of shift factor (log a_{SF}) with temperature

Logarithamic time scale to temperature changes as developed by Williams, Landel and Ferry is known as W-L-F method[32,34]. The master curve can be used where the variations of the storage modulus at different frequencies and temperatures are not experimentally accessible.

8.2.5 Energy of activation for glass transition

The apparent activation energy (E_a), for the glass transition of different composite systems, was calculated using the modified form of Arrhenius relationship[2, 35]:

$$\log \nu = \log \nu_0 - (E_a / 2.303\ R\ T_{max}) \qquad \text{......(8.2)}$$

where ν is the measuring frequency, ν_0 is the frequency when temperature T approaches infinity, R the gas constant, T_{max}, the temperature corresponding to the maximum of tan δ curve and E_a, the energy of activation for glass transition, obtained from the slope of the typical Arrhenius plot of log ν against 1/T. Table 8.2 gives the values of energy of activation (E_a) for the glass transition, for nylon 6 fibre reinforced NBR composites as a function of fibre loading. As fibre loading increases, the process of transition becomes more difficult to occur and takes place at higher temperatures by consuming larger quantity of energy which is indicated by a shift in T_g to higher temperatures. At lower levels of loading, the fibre/matrix interaction will be less and hence the activation energy is also low. The systems with higher activation energy have lower chain mobility and a better interfacial adhesion. Thus the calculations of activation energy can be used as a criterion for measuring the interfacial adhesion between the fibres and the matrix.

8.2.6 Cole-Cole plots

Structural changes taking place in crosslinked polymers after fibre addition to the matrix can be studied using Cole-Cole method. The dissipation or loss factor measured during dielectric measurements is directly analogous to the tan δ function relevant to the dynamic mechanical testing. The visco-elastic nature of NBR matrix creates similarities in its response to both mechanical and electrical stimuli. Cole-Cole is a particular treatment of dielectric relaxation data, obtained by plotting the dielectric loss (E″) against dielectric constant E′, each point corresponding to one frequency.

The dynamic mechanical properties examined as a function of temperature and frequencies are represented on the Cole-Cole complex plane. Figure 8.14 shows the Cole-Cole plots of various composite systems, where the loss modulus data (log G") are plotted as a function of the storage modulus (log G') at a frequency of 10 Hz.

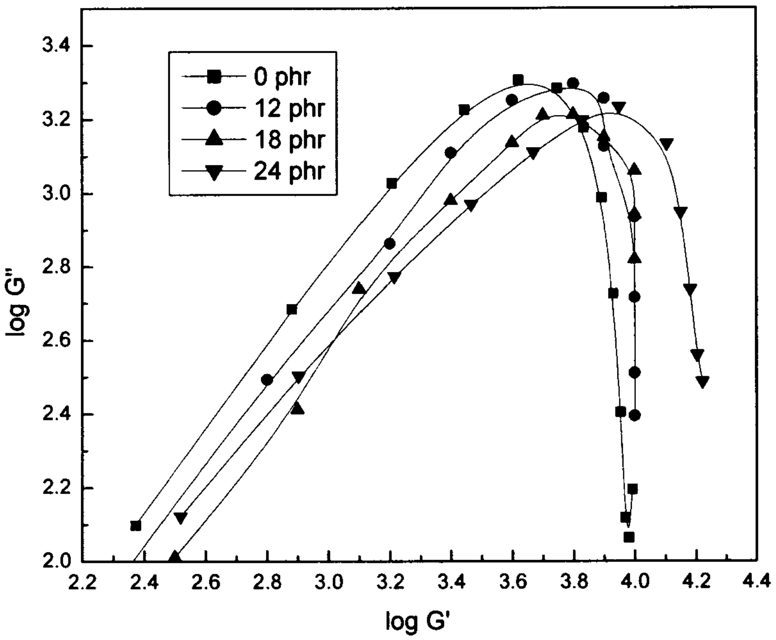


Figure 8.14 Cole-Cole plots of composites with different fibre loadings at a frequency of 10 Hz

The nature of Cole-Cole plot is reported to be indicative of the nature of the system. The homogeneous polymeric systems are reported to show a semicircle diagram[2] whilst the two-phase systems show modified semicircles[30, 36] .On analysing the Cole-Cole plots of the present composite systems it is seen that the curves show the shape of imperfect semicircles. The shape of the curves thus points towards the good fibre-rubber adhesion.

8.2.7 Crosslink density

The crosslink density of macromolecular networks can be evaluated from storage modulus measurements. It represents the number of active network chains per unit volume and is some times called the network density. Crosslink density can be calculated from the theory of rubber elasticity. The modulus G′ of a crosslinked rubber is given by the equation[37],

$$G' = nRT\left(\overline{r_i^2}/\overline{r_0^2}\right)\left(2\varphi^2 + 1/\varphi\right) \qquad ......(8.3)$$

where n represents the crosslink density, T is the absolute temperature and φ represents the fractional change in shape in three directions, i.e.; $\varphi = (L / L_0)_i$, where i = x, y or z . The quantity $\left(\overline{r_i^2}/\overline{r_0^2}\right)$ known as the front factor. It is the ratio of the mean square end-to-end distance between the crosslink sites binding the polymer chain in the sample to the same quantity in a randomly coiled chain (mean square end-to-end distance of the equivalent free chain). In fact, the simpler derivations of the equation of state for rubber elasticity do not treat this quantity, implicitly assuming it to be unity[38]. Equation 8.3 represents the engineering modulus, which utilises the actual cross section (three dimensional fractional changes in shape, φ). However, in relaxed state the value of φ = 1 and by assuming $\left(\overline{r_i^2}/\overline{r_0^2}\right) \cong 1$, the modulus becomes[37]:

$$G' = 3\ nRT \qquad ......(8.4)$$

The crosslink density of the composites can thus be calculated from the above equation. For the present systems, G′ is measured in the rubbery plateau region above T_g. The variation of crosslink density with fibre loading at ambient temperature is shown in Figure 8.15. It can be seen that as fibre loading increases the crosslink density values increase, supporting the observed increment in storage moduli. It is apparent from the figure that the composite containing bonding agent shows the highest crosslink density.

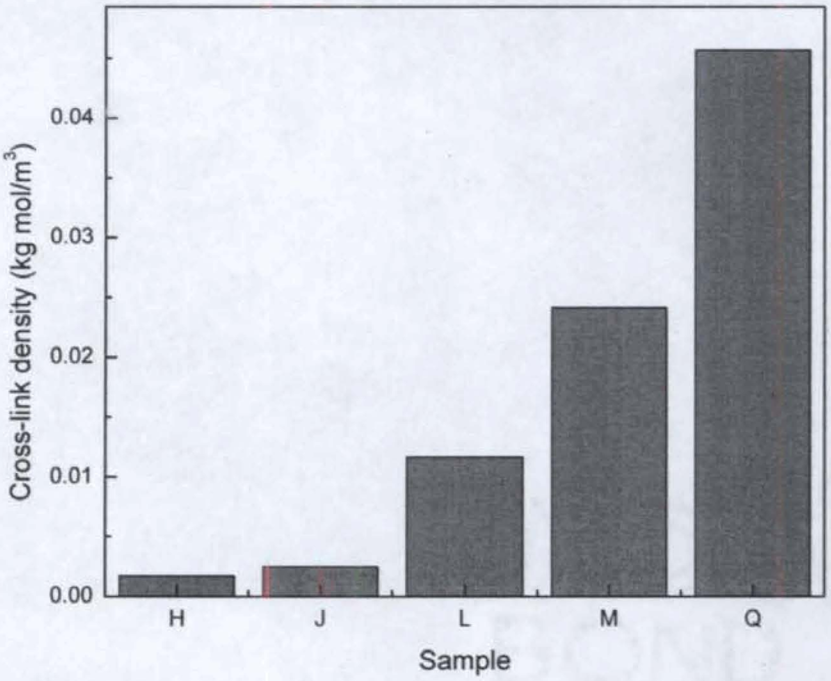


Figure 8.15 Crosslink densities of different samples

8.2.8 Theoretical modeling

8.2.8.1 Storage modulus

The simplest equation for calculating the reinforcement in polymer matrix, theoretically, is given by Einstein[39],

$$G'_c = G'_m (1 + V_f) \qquad ......(8.5)$$

where G′ is the storage modulus, the subscripts 'c' and 'm' represent the composite and matrix respectively and V_f is the volume fraction of fibre. The Einstein's equation has been modified by Guth[40] as,

$$G'_c = G'_m [1 + 2.5 V_f + 14.1 V_f^2] \qquad ......(8.6)$$

The experimental and theoretical storage moduli (G′) as a function of fibre loading at a temperature of -50 °C and at a frequency of 10 Hz are given in Figure 8.16. The experimental values of the storage modulus of the composite system show a reasonably good agreement with Einstein's and Guth's models. The experimental G′ values show a good agreement with Guth's model especially at 24 phr fibre loading (Mix M). This clearly indicates that at 24 phr fibre loading, the fibre population is just right for maximum orientation so that the fibres can actively participate in stress transfer and the composites show optimum properties.

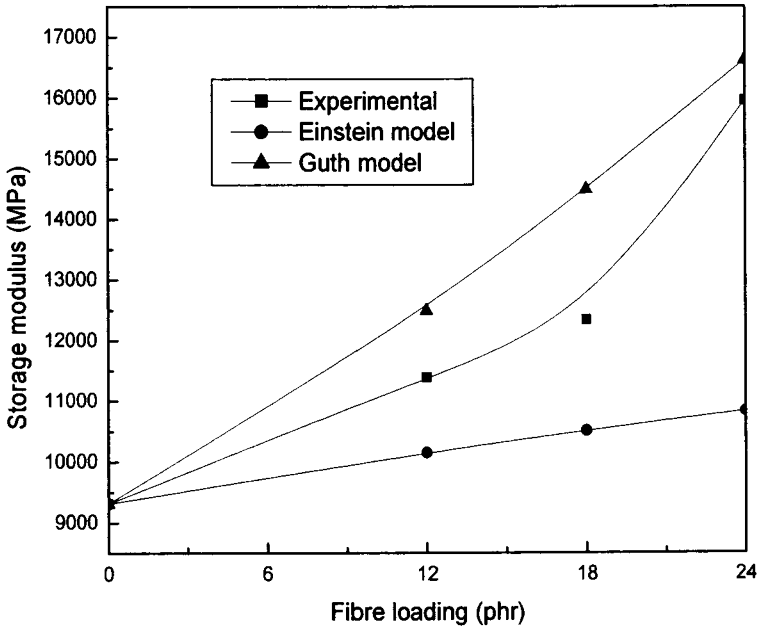


Figure 8.16 Comparison of experimental and theoretical storage modulus (G′) of composites as a function of fibre loading

8.2.8.2 Damping behaviour

Composite damping features result from the inherent damping of the constituents. This can be represented as[41]:

$$\tan \delta_c = V_f \tan \delta_f + [1 - V_f] \tan \delta_m \qquad \text{..........(8.7)}$$

where tan δ_c, tan δ_f, and tan δ_m represent the damping values of the composite, the fibre and the matrix respectively. According to Nielsen[3], the damping of a composite (tan δ_c), is given by the proportional contribution of the matrix based on its relative content. The rigid fillers and fibres usually decrease the damping to an extent and hence the first two terms can be neglected and the Equation (8.7) thus becomes,

$$\tan \delta_c = \tan \delta_m \, [1 - V_f] \qquad \text{......(8.8)}$$

Figure 8.17 represents the experimental and theoretical plots of tan δ against fibre loading at a frequency of 10 Hz and at their respective glass transition temperatures. It can be seen that the experimental and theoretical values show the same trend. In both the experimental and the theoretical plots, the tan δ values of composites at varying fibre loading are found to be lower than that of the gum (0 phr).

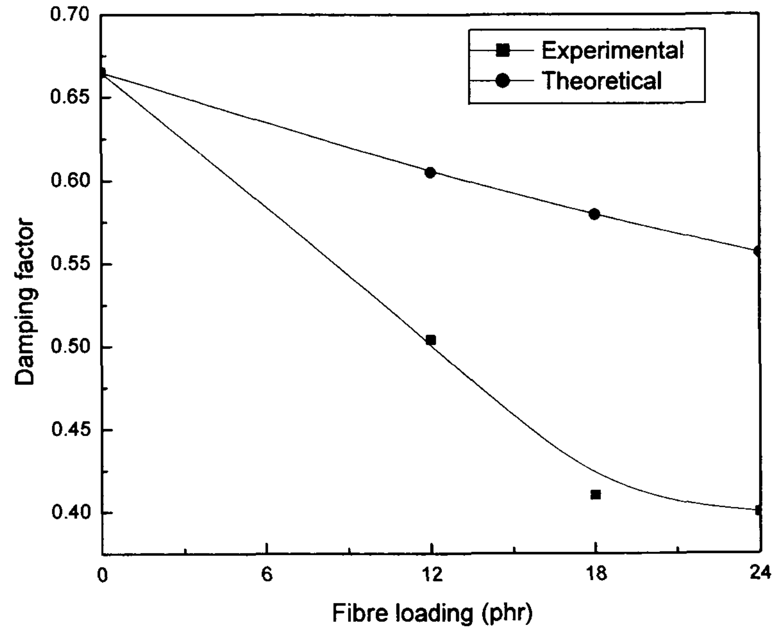


Figure 8.17 Comparison of experimental and theoretical tan δ_{max} of composites as a function of fibre loading

8.3 CONCLUSIONS

The dynamic mechanical properties such as storage modulus (G′), loss modulus (G″), and damping behaviour (tan δ) of nylon 6 fibre reinforced NBR composites have been studied as a function of fibre loading, crosslinking systems and the bonding agents, at varying temperatures (-100 to 100 °C) and frequencies (0.1, 1, 10 and 50 Hz). The storage modulus was found to be increased with increment in fibre loading whereas it decreased with temperature. The loss modulus and damping characteristics were observed to be decreased with fibre loading. The change in dynamic mechanical properties was more prominent in the glassy state, below T_g. The glass transition temperature was found to be shifted to higher temperature upon increment in fibre loading. The DCP cured composites showed higher storage modulus and lesser damping than the corresponding sulphur cured one. It has been found that the addition of hexa-resorcinol and phthalic anhydride as bonding agents enhanced the dynamic mechanical properties of the present composite system. It caused an increase in storage modulus and decrease in damping.

The study of the effect of frequency on the stiffness of the composites showed that as frequency increased the storage modulus increased. The damping behaviour decreased initially with an increase in frequency. However, after passing through the transition region an increment was observed. T_g was shifted to higher temperatures with increase in frequency. The time-temperature superposition principle and master curve were also used to predict the visco-elastic behaviour of the material outside the used frequency range. The energy of activation for glass transition of the composites was found to be increased with increase in fibre loading indicating improved interfacial adhesion. The Cole-Cole plots of the present composite systems showed the shape of imperfect semicircles pointing towards the relatively good fibre-rubber adhesion. The crosslink density, calculated from storage modulus, was found to be highest for bonding agent added composite supporting the existence of strong interfacial adhesion in such system. The experimental values of the storage modulus of the composite system showed a reasonably good agreement with Einstein's and Guth's models.

References

1. Kevin P.M., *Dynamic Mechanical Analysis-A Practical Introduction*, CRC Press, New York (1999).
2. Murayama T., *Dynamic Mechanical Analysis of Polymeric Materials*, Elsevier, New York (1999).
3. Nielsen L. E., *Mechanical Properties of Polymers and Composites*, Dekker, New York (1974).
4. Naskar A. K., Bhowmick A. K. and De S. K., *J. Appl. Polym. Sci.,* **84** (2002) 622.
5. Foley M. E., Obaid A. A., Huang X., Tanoglu M., Bogetto T. A., McKnight S. H. and Gillespie Jr. J. W., *Compos. Part A.,* **33** (2002) 1345.
6. Khatibi A. A. and Mai Y. W., *Compos. Part A.,* **33** (2002) 1585.
7. Kumnuantip C. and Sombatsompop N., *Mater. Let.,* **57** (2003) 3167.
8. Manchado L. M. A., Biagiotti J., Arroyo M. and Kenny J. M., *Polym. Engg. Sci.,* **43** (2003) 1018.
9. Hashmi S. A. R., Kitano T. and Chand N., *Polym. Compos.,* **24** (2003) 149.
10. Ashida M. and Noguchi, J. *Appl. Polym. Sci.,* **29** (1984) 661.

11. Bhagwan S. S., Tripathy D. K. and De S. K., *J. Appl. Polym. Sci.*, **34** (1987) 1581.
12. Murthy V. M. and De S. K., *Rubber Chem. Technol.,* **55** (1982) 287.
13. Murthy V. M. and De S. K., *J. Appl. Polym. Sci.,* **27** (1982) 4611.
14. Murthy V. M. and De S. K., *J. Appl. Polym. Sci.,* **28** (1983) 3485.
15. Sombatsompop., *Polym- Plast. Technol. Engg.,* **37** (1998) 1.
16. Yano S., Hirose S. and Hatakeyama., *J. Appl. Polym. Sci.*, **40** (1990)657.
17. Finegan I. C. and Gibson R. F., *Compos. Strs.,* **44** (1999) 89.
18. Pothan L. A., Oommen Z. and Thomas S., *Comp. Sci. Technol.,* **63** (2003) 283.
19. Saha A. K., Das S., Bhatta D. and Mitra B.C., *J. Appl Polym. Sci.,* **71** (1999) 1505.
20. Rials T. G., Wolcott M. P. and Nassar J. M., *J. Appl. Polym. Sci.,* **80** (2001) 546.
21. Ibarra L. and Chamorro C., *J. Appl. Polym. Sci.,* **44** (1991) 805.
22. Marcovich N. E., Reboredo M. M. and Arangurenn M. I., *J. Appl. Polym. Sci.,* **70** (1998) 2121.
23. Tan J. K., Kitano T. and Hatakeyama T., *J. Mater. Sci.*, **25** (1990) 3380.
24. Murayama T., *Dynamic Mechanical Analysis of Polymeric Materials,* Second Edn., Elsevier, Amsterdam, New York (1978).
25. Maurer F.H. J., *Controlled Interphases in Composite materials*, Elsevier (1990) 491.
26. Thoamson J. L., *Polym. Compos.,* **11** (2) (1990) 105.
27. Chua P. S., *Polym. Compos.*, **8** (1987) 308.

28. Guo W. and Ashida M., *J. Appl. Polym. Sci.,* **56** (1993) 1435.
29. Ibarra L., Macias M. and Palma E., *J. Appl. Polym. Sci.,* **57** (1995) 831.
30. Landel R.F., *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York (1994).
31. Wismie C., Maria G. and Monge P., *Eur. Polym. J.,* **21** (1985) 479.
32. William M. L., Landel R. F. and Ferry J. D., *J. Am. Chem. Soc.,* **77** (1954) 3701.
33. Ferry J. D., *Visco-elastic Properties of Polymers,* Third Edn., Wiley, New York (1980).
34. Aklonis J. J. and McKnight W. J., *Introduction to Polymer Visco-elasticity,* John Wiley, New York (1983).
35. Folkes M. J., *Short Fibre Reinforced Thermoplastics,* Wiley, New York (1982).
36. Ibarra L., *J. Appl. Polym Sci.*, **49** (1993), 1595.
37. Sperling L. H., *Introduction to Physical Polymer Science,* Third Edn., John Wiley and Sons Inc., New York (2001).
38. Treloar L. R. G., *The Physics of Rubber Elasticity,* Third Edn., Clarendon Press, Oxford (1975).
39. Einstein A., *Investigation on Theory of Brownian Motion,* Dover, New York (1956).
40. Guth E., *J. Appl. Phys.,* **16** (1951) 21.
41. Richardson M. O. W., *Polymer Engineering Composites,* Applied Science Publishers, London (1977).

Chapter 10

Conclusions and Future Outlook

Abstract

The major findings of the investigation based on short nylon 6 fibre reinforced NBR composites have been summarised in this chapter. The results of the examinations of the cure characteristics, mechanical properties, interfacial adhesion, dielectric properties, thermal features, dynamic mechanical behaviour and ageing characteristics of the composites have been consolidated. The scope of future studies based on the results of the present work has also been discussed.

10.1 CONCLUSIONS

Short fibre reinforced rubber composites have by now received wide acceptance as useful engineering materials, offering advantages such as low weight, high stiffness to weight ratio, excellent durability, design flexibility, corrosion resistance, high fatigue strength and faster assembly. The properties and performance of short fibre composites depend mainly on; (a) type of fibre and matrix, (b) fibre content, (c) aspect ratio of the fibre, (d) degree of dispersion of the fibre and (e) adhesion of the fibres to the matrix.

Acrylonitrile butadiene rubber (NBR) is a special purpose synthetic rubber used in a wide variety of application areas requiring oil, fuel, and chemical resistance. Nylon 6 is a synthetic fibre having high tensile strength and modulus. In the present work, a systematic attempt has been made to develop and characterise a composite material in which the NBR matrix is reinforced with nylon 6 fibre.

The nylon 6 fibre/NBR composites were prepared on a two roll open mixing mill by using dicumyl peroxide and accelerated sulphur vulcanisation systems. The fibre breakage analysis showed that the fibres used for reinforcement were not undergoing considerable breakage during processing. This clearly indicated the viability of developing composite systems based on these fibres. The analysis of cure charactestics showed that the addition of fibres increased the rheometric torque, due to the higher stiffness of the matrix provided by the fibres. It was seen that the maximum torque was higher in composite systems cured by DCP than those by sulphur which indicated the higher stiffness of the former.

The mechanical properties of the composites were analysed as a function of fibre length, loading, orientation and rubber crosslinking systems. Addition of nylon fibres to NBR offered good reinforcement and improved the mechanical properties. A fibre length of 6 mm has been found to be optimum for the best balance of properties. Tensile properties have been observed to be increased with fibre loading up to 24 phr. The composite systems showed anisotropic properties and those containing longitudinally oriented fibres exhibited better mechanical properties. Composites vulcanised by DCP system showed higher mechanical properties than those by sulphur system. The experimental results were compared with the theoretical values by using parallel and Hirsch models.

Two different bonding agents, *viz.* hexamethylene tetramine- resorcinol and phthalic anhydride, were used to modify the interfacial interaction in nylon 6 fibre reinforced NBR composites. The cure characteristics and mechanical properties of the bonded composites have been analysed. It has been found that the addition of bonding agents increased the maximum torque and reduced the optimum cure time and scorch time. The addition of bonding agents enhanced the tensile strength and modulus. SEM studies supported the observation of better interfacial adhesion between the fibres and matrix, in presence of the bonding agents.

The extent of interfacial adhesion between short nylon fibres and the NBR matrix in the present composite system has been evaluated by restricted equilibrium swelling technique (RES). The gum compound which did not contain any fibres took maximum amount of solvent at equilibrium, due to the lesser restriction for the penetrants to enter into the vulcanisates. The increment in the concentration of fibres and the addition of bonding agents offered a higher restriction to swelling. The swelling in the composites was significantly controlled by the direction of fibre orientation. Swelling mainly took place in a direction perpendicular to the direction of fibre orientation. As a result, in highly bonded composite systems, swelling was highly constrained in one direction i.e., the thickness direction. The rubber-fibre interactions were evaluated by using Lorenz-Parks and Kraus equations. The anisotropic swelling measurements revealed that the system consisting of bonding agent and 24 phr fibres exhibited good fibre-rubber interaction and better fibre alignment.

The dielectric properties such as dielectric constant, volume resistivity and dielectric loss factor of nylon 6 fibre reinforced NBR composites have been studied as a function of fibre loading and frequency. The effects of different crosslinking systems and bonding agents also have been studied. The dielectric constant values have been found to be lower for fibre filled systems than the gum. Composite samples cured by DCP exhibited higher dielectric constant value than those cured by sulphur which has been explained in terms of the presence of polar -OH groups in the former. It has been found that the addition of the bonding agents reduced the dielectric constant of the composites. In the presence of hexa-resorcinol bonding agent, the sulphur cured sample showed higher dielectric constant values than the DCP cured sample; attributed to the difference in total polarizability in the two systems. The volume resistivities of the composites were found to be increased with the addition of fibres and with the incorporation of bonding agents. It has been found that the conductivity of composites decreased with increase in fibre loading. The dielectric dissipation factor of the matrix was decreased by the addition of fibres and the incorporation of bonding agents.

The use temperature and the heterogeneity of nylon 6 fibre/NBR composites have been evaluated by thermal analysis. The thermal behaviour of nylon fibre, and the composites has been studied by TG and DSC with special reference to the effects of fibre loading, curing systems and the bonding agents. The degradation temperatures of fibre filled composite systems were observed to be higher than those of gum. It has been found that as the fibre loading increased, the decomposition temperature was shifted to higher temperature range. The percentage weight losses at different temperatures also were decreased with fibre loading. The decomposition temperatures of DCP cured samples were higher than that of the sulphur cured ones. The bonding agent added fibrous composite system showed lower thermal degradation features compared to the unbonded one. The activation energy for thermal degradation of composites increased with fibre loading. The T_g values of fibre filled systems, as measured by DSC, were found to be higher than that of pure gum due to the higher rigidity and stiffness of the matrix provided by the fibres. The bonding agent added fibrous composite systems showed higher T_g values compared to the others due to the enhanced fibre-matrix interaction.

The visco-elastic properties such as storage modulus (G′), loss modulus (G″), and damping behaviour (tan δ) of nylon 6 fibre reinforced NBR composites have been studied as a function of fibre loading, crosslinking systems, and the bonding agents at varying temperatures (-100 to 100 °C) and frequencies (0.1, 1, 10 and 50 Hz). The storage modulus was found to be increased with increment in fibre loading whereas it decreased with temperature. This has been attributed to the increase in stiffness of the composites. The loss modulus and damping characteristics were decreased with fibre loading. The change in dynamic mechanical properties was more prominent in the glassy state, below T_g. The glass transition temperature was found to be shifted to higher temperature upon increment in fibre loading. The DCP cured composites showed higher storage modulus and less damping than the corresponding sulphur cured one. The addition of hexa-resorcinol bonding agent enhanced the visco-elastic properties of the present composite system. The storage modulus has been found to be increased with frequency. The loss modulus and damping behaviour decreased initially with increase in frequency and after passing through the transition region an increment was observed. The increment in frequency shifted the T_g to higher temperatures.

The time-temperature superposition principle and master curve were also used to predict the visco-elastic behaviour of the material outside the used frequency range. The Cole-Cole plots of the present composite systems showed the shape of imperfect semicircles pointing towards a relatively good fibre-rubber adhesion. The crosslink density, as calculated from storage modulus, was found to be highest for bonding agent added composite supporting the existence of strong interfacial adhesion in such system. The experimental results of storage modulus and tan δ values were evaluated theoretically by using Einstein, Guth and Nielsen models.

The ageing characteristics of nylon 6 fibre reinforced NBR composites were analysed by exposing them to degrading agents such as heat, gamma (γ) radiation and ozone. Thermal and gamma ageing resistance have been studied by measuring the percentage retention of tensile modulus. The composites consisting of higher concentration of fibres showed better percentage retention of modulus after exposure to thermal and gamma radiation. In the case of DCP cured sample, the percentage retention of tensile strength decreased as the ageing period increased from 7 to 14 days. However, a reverse trend was observed in the case of sulphur cured samples. An increment in the dosage of γ-radiation from 5 to 10 Mrad increased the percentage retention of modulus of sulphur cured composites; however a higher dose of 15 Mrad lowered it due to polymer chain degradation. In the case of DCP cured samples a continuous a decrease in the percentage retention of modulus was observed with increase in radiation dose from 5 to 15 Mrad. The ozone resistance of NBR increased with fibre loading. The bonding agent added fibrous composite systems exhibited better thermal, γ-radiation and ozone resistance than the unbonded one.

10.2 FUTURE SCOPE

The present study on nylon 6 reinforced NBR composites offers many interesting extensions to it.

(i) Non-destructive testing of composites

For getting a better understanding of the interface, fracture mechanism, failure characteristics and crystallinity, non-destructive tests such as acoustic emission analysis, X-ray diffraction and atomic force microscopy (AFM) could be employed for the present system.

(ii) Modification with particulate fillers

The properties of short nylon 6 fibre reinforced NBR composites can further be improved by the incorporation of particulate fillers. Fillers such as carbon black, silica and other white fillers could be tried along with the fibres for giving more effective reinforcement for the development of suitable products. The electrical properties of the composite system could be modified by the incorporation of different types of carbon black fillers.

(iii) Modification of interface

In the present study interface modification has been done by using two different bonding agents, *viz.* hexamethylene tetramine–resorcinol and phthalic anhydride. The use of other suitable bonding agents could be tried.

(iv) Commercial exploitation

The use of nylon 6 fibre reinforced NBR composites for the manufacture of various rubber goods is worth attempting. The production of cost effective V-belts, hoses, gaskets, oil seals and automotive products could be worked out with these composites. This has to be done in collaboration with the industry.

◆

Chapter 9

Ageing Characteristics of Nylon 6/NBR Composites

Abstract

The ageing characteristics of nylon 6 fibre reinforced NBR composites have been analysed by exposing them to degrading agents such as temperature, gamma (γ) radiation and ozone. The effects of fibre loading, curing systems and bonding agents on the percentage retention of tensile properties of the composite samples after being exposed to these degrading agents have been studied. The addition of fibres improves the ageing resistance of NBR. The percentage retention of modulus of DCP cured composites decreases with increment in thermal ageing period from 7 to 14 days, whereas a reverse trend is observed for sulphur cured samples. In the case of sulphur cured samples, increase in the dosage of γ-radiation from 5 to 10 Mrad increases the percentage retention of modulus whereas a further higher dose of 15 Mrad lowers it. However, a continuous decrease in percentage retention is observed in DCP cured samples. The surface morphology of the composite systems exposed to ozone has been analysed by using optical photographs. Composite system containing hexa-resorcinol as the bonding agent shows better resistance to heat, γ-radiation and ozone than the unbonded one.

9.1 INTRODUCTION

Most of the polymer products gradually lose their properties during long period of service due to the macromolecular chain degradation. This is mainly caused by the action of degrading agents such as heat, oxygen, ozone and high energy radiation on them. The effects of these degrading agents depend mainly on the chemical structure of the polymer chain. The thermo-oxidative degradation of particulate and fibre reinforced polymer composites has been extensively studied. Paiva Ju'nior *et al.*[1] studied the accelerated ageing of hybrid ramie-cotton resin matrix composites in boiling water. Sun *et al.*[2] analysed the thermal oxidative oven ageing of carbon black filled ethylene propylene rubber (EPR) at 125 °C. The analysis of weight and density indicated that the substantial resistivity decreased mainly due to the mass loss of the polymer matrix and the sample shrinkage during the thermo-oxidative ageing process. Schwartza *et al.*[3] performed an extensive work to analyse how and why electrical properties of carbon black filled rubber compounds changed during thermal aging. Morrell *et al.*[4] conducted studies to investigate the life of O-rings based on NBR. The results indicated the good ageing resistance of the O-rings. Celina *et al.*[5] studied the thermal degradation of a commercial, stabilised, filled and unfilled chloroprene rubber at temperatures up to 140 °C.

The effect of radiations on polymeric materials has been reported by several research groups[6-8]. The crosslinking of ethylene-vinyl acetate rubber by high energy radiation has been reported by Sweet[9]. Koshy *et al.*[10] studied the effects of blend ratio and cure systems on the degradation of blends of NR and ethylene-vinyl acetate rubber. The effect of gamma-radiation on both the electrical and thermal properties of SBR loaded with different concentration ratios of copper and iron fine powders has been analysed by Gwaily *et al*[11]. The effects of short-carbon fibres on the anisotropic swelling, mechanical and electrical properties of radiation vulcanised SBR composites have been investigated by Aziz *et al*[12]. The degradation and protection of polymers in presence of ozone has been examined by Ungar[13]. The resistance towards flame, heat, gamma radiation and ozone, of aluminium powder filled NR composites, was studied by Vinod *et al*[14].

The present chapter deals with the ageing characteristics of nylon 6/NBR composites under the influence of heat, gamma radiation and ozone. The effects of temperature and γ-radiation have been analysed by measuring the percentage retention of the tensile modulus of the composites after exposing them to these degrading agents. The ozone resistance of the composite system has been examined from the initiation of cracks in the matrix.

9.2 RESULTS AND DISCUSSION

9.2.1 Thermal ageing

During thermal ageing, main chain scission, crosslink formation and crosslink breakage can take place. It is also possible that the existing crosslinks may break and a more stable type of crosslink can be formed. In composites, bonded resin formation also takes place during ageing. The relative ratios and magnitudes of such reactions will govern the percentage change in properties and the performance of the composites.

9.2.1.1 Effect of fibre loading

Figure 9.1 shows the effect of fibre loading on the percentage retention of tensile strength of nylon 6 fibre reinforced NBR composites, cured by DCP, after ageing for 7 and 14 days at 100 °C. The addition of fibres offer better thermal resistance to NBR and the retention in tensile modulus increases continuously with fibre loading. The first degradation step of the vulcanisates is controlled by the fibres, whereas the fibre as well as the matrix contributes to the second degradation step. An increment in fibre loading decreases the rate of degradation. Therefore, as the fibre loading increases from 6 to 24 phr the percentage retention of tensile strength of composites has been found to be increased. However, as the ageing period is increased from 7 to 14 days, the composites show a lower retention of tensile strength. This indicates that the polymer degradation or chain scission starts due to the prolonged increment in ageing time. The modulus at 10% elongation shows the same trend on ageing as that of tensile strength. As it can be seen from Figure 9.2, the percentage retention of modulus of composites increases with increase in fibre loading. The composites show a lower retention of modulus as the ageing period is increased from 7 to 14 days.

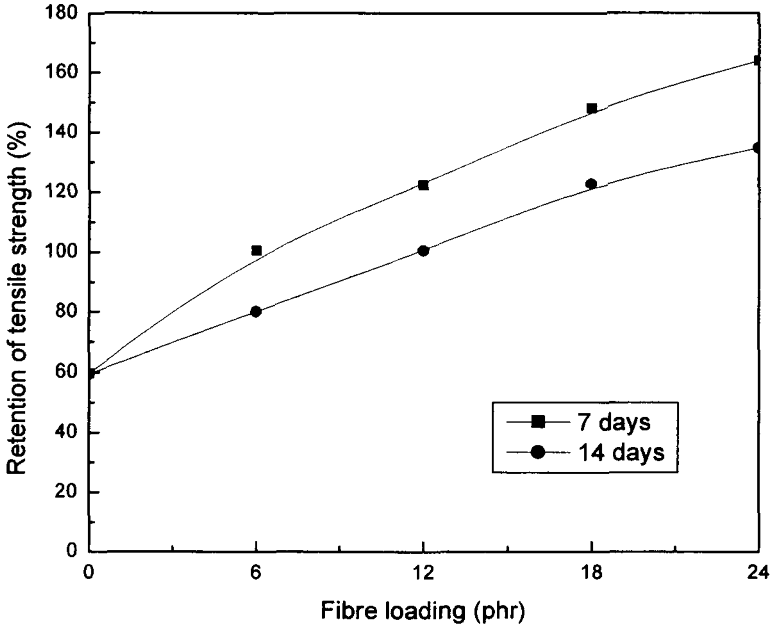


Figure 9.1 **Effect of fibre loading on percentage retention of tensile strength of composites after thermal ageing**

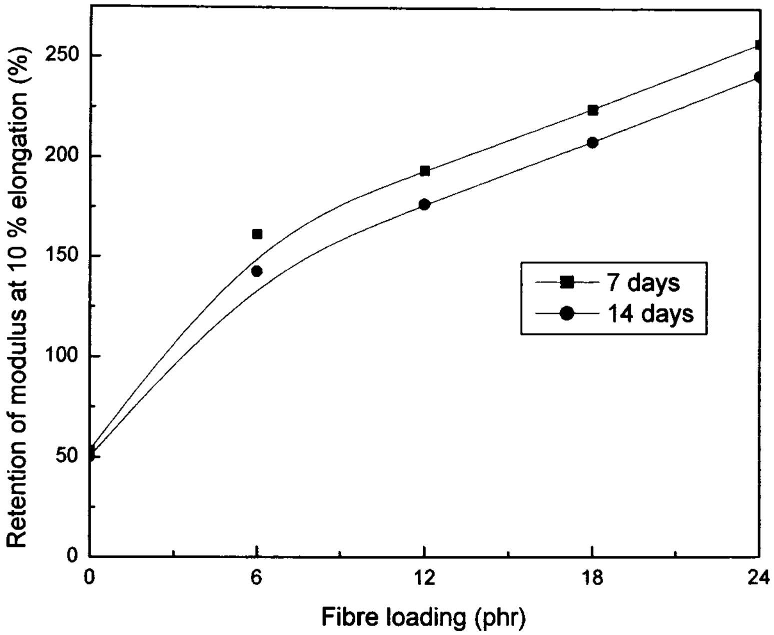


Figure 9.2 **Effect of fibre loading on the percentage retention of modulus at 10% elongation of composites after thermal ageing.**

9.2.1.2 Effect of curing systems

Figure 9.3 shows the effects of different curing systems on the percentage retention of tensile strength of composites after being subjected to thermal ageing for 7 and 14 days. Comparison has been made with samples containing 24 phr fibres cured by sulphur and DCP systems (Samples F and M). It has been found that, in the case of DCP cured sample, the percentage retention of tensile strength decreases as the ageing period increases from 7 to 14 days. This can be due to the polymer degradation or chain scission upon prolonged ageing. However in sulphur cured samples the percentage retention of tensile strength increases with increment in ageing time from 7 to 14 days. This indicates that bonded resin formation predominates over polymer chain degradation. The percentage retention of modulus at 10% elongation of composites cured by sulphur and DCP systems after being subjected to thermal ageing for 7 and 14 days is shown in Figure 9.4. The variation shows the same trend as that of tensile strength. The difference in the behaviour of composites cured by DCP and sulphur on thermal ageing can be attributed to the different crosslinks introduced between the macromolecular chains of NBR during vulcanisation.

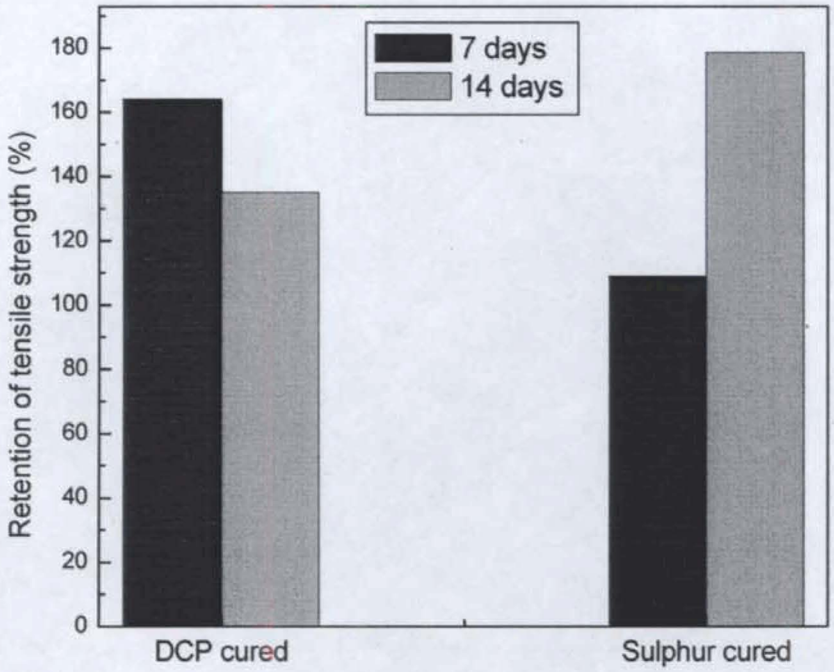


Figure 9.3 **Effect of curing systems on the percentage retention of tensile strength of composites after thermal ageing**

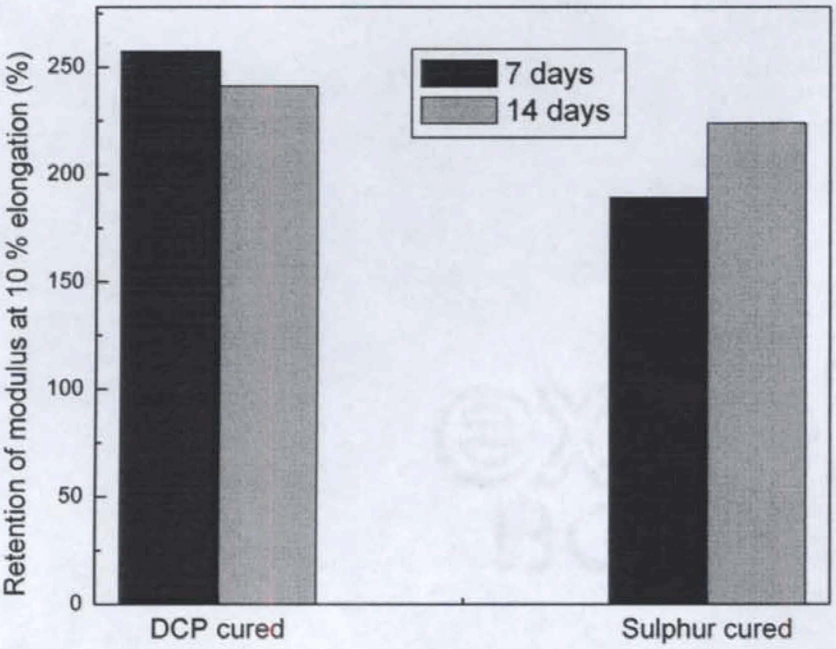


Figure 9.4 **Effect of curing systems on the percentage retention of modulus at 10% elongation of composites after thermal ageing**

9.2.1.3 Effect of bonding agents

Figure 9.5 shows the effect bonding agent on the percentage retention of modulus at 10% elongation of composites after being subjected to thermal ageing for 7 and 14 days. Comparison has been made with samples containing 24 phr fibre cured by sulphur with and without hexa-resorcnol bonding agent (Samples F and G). The percentage retention of tensile strength for hexa-resorcinol bonding agent added composite is found to be higher than that of the unbonded one. As the ageing period was increased from 7 to 14 days, the bonding agent added composites show better percentage retention of tensile strength. This indicates the predominance of resin formation over chain degradation in these composites.

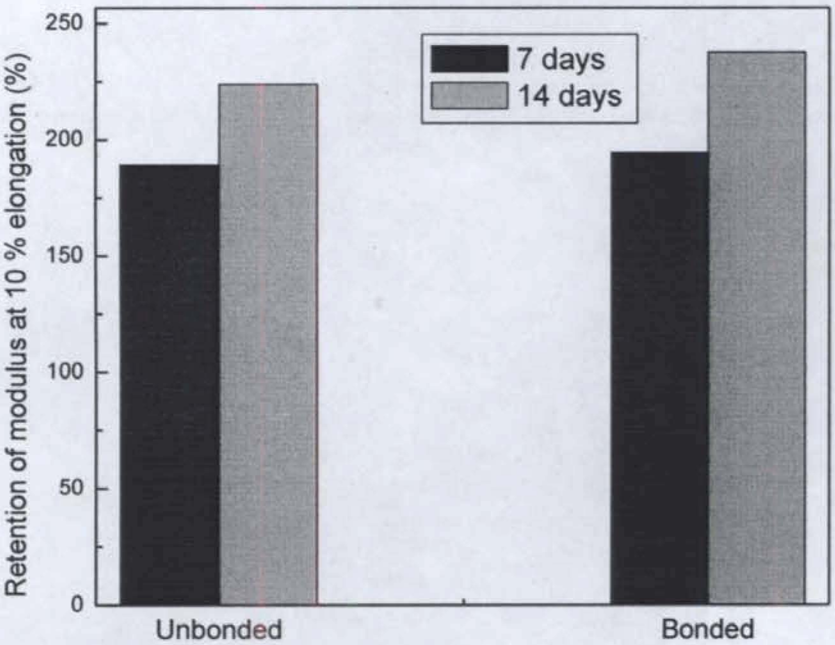


Figure 9.5 **Effect of bonding agent on the percentage retention of modulus at 10% elongation of composites after thermal ageing**

Figure 9.6 compares the effect of bonding agents (hexa-resorcinol and phthalic anhydride) on the percentage retention of modulus at 10% elongation of nylon 6 fibre reinforced NBR composites (Mixes Q and R cured by DCP). It can be seen that the percentage retention of modulus for composite containing phthalic anhydride as bonding agent is lower than that containing hexa-resorcinol bonding agent. The difference in this behaviour can be attributed to the different bonding mechanisms offered by hexa-resorcinol and phthalic anhydride which influence the relative proportions of chain degradation and resin formation. However, as the ageing period increases from 7 to 14 days percentage retention of tensile strength decreases in both hexa-resorcinol and phthalic anhydride bonded composites.

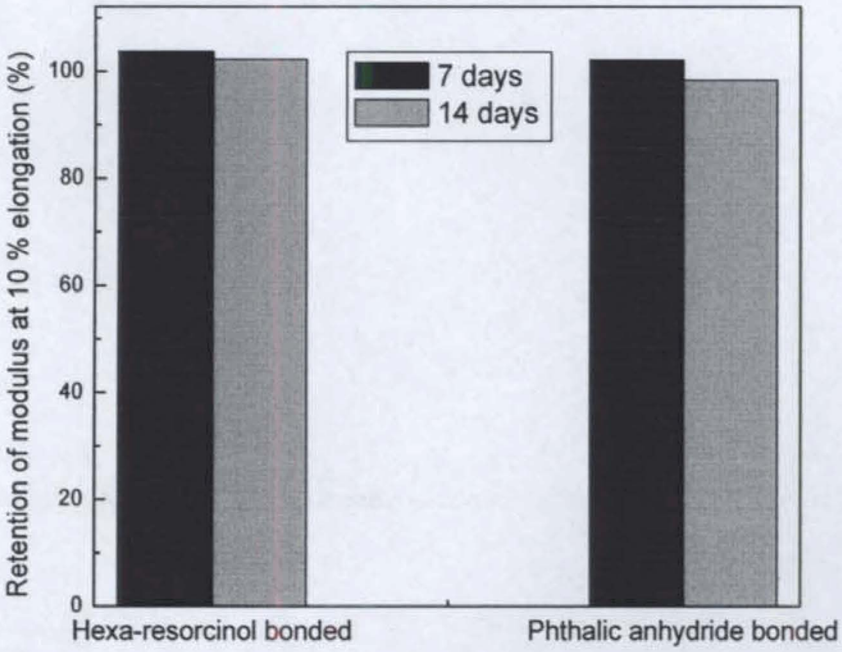


Figure 9.6 **Effect of different bonding agents on the percentage retention of modulus at 10 % elongation of composites after thermal ageing**

9.2.2 Gamma (γ) radiation ageing

9.2.2.1 Effect of fibre loading

Figure 9.7 shows the plots of percentage retention of tensile strength of composites against fibre loading at three different radiation doses (5 Mrad, 10 Mrad and 15 Mrad). The percentage retention of tensile strength has been found to be increased with fibre loading. As fibre loading increases, more reactive sites are created at the interface leading to the formation of covalent bonds between the matrix and fibres. It has been found that when the radiation dose is increased from 5 Mrad to 15 Mrad the percentage retention of tensile strength decreases. This is due to the increased degradation of polymer chain with increment in radiation dose. The percentage retention of modulus at 10% elongation also shows the same pattern of variation as that of tensile strength (Figure 9.8).

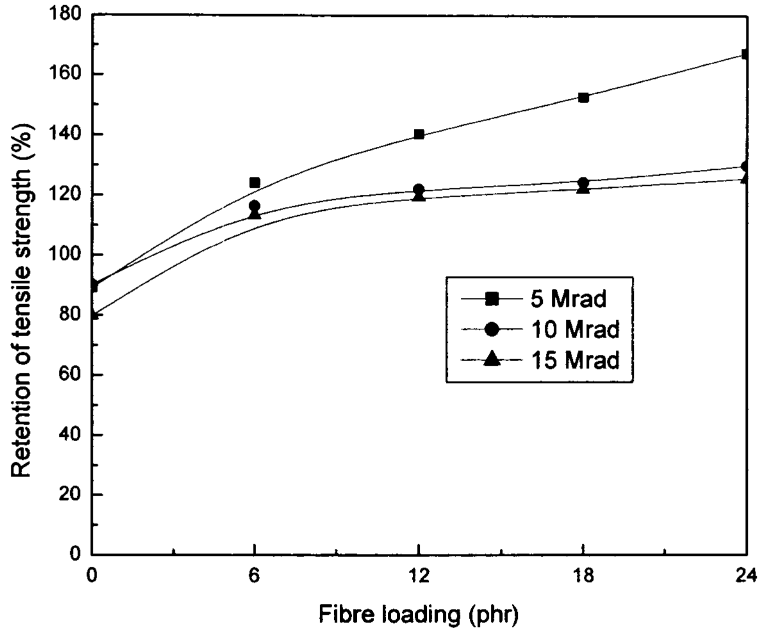


Figure 9.7 **Effect of fibre loading on percentage retention of tensile strength of composites after γ-radiation ageing**

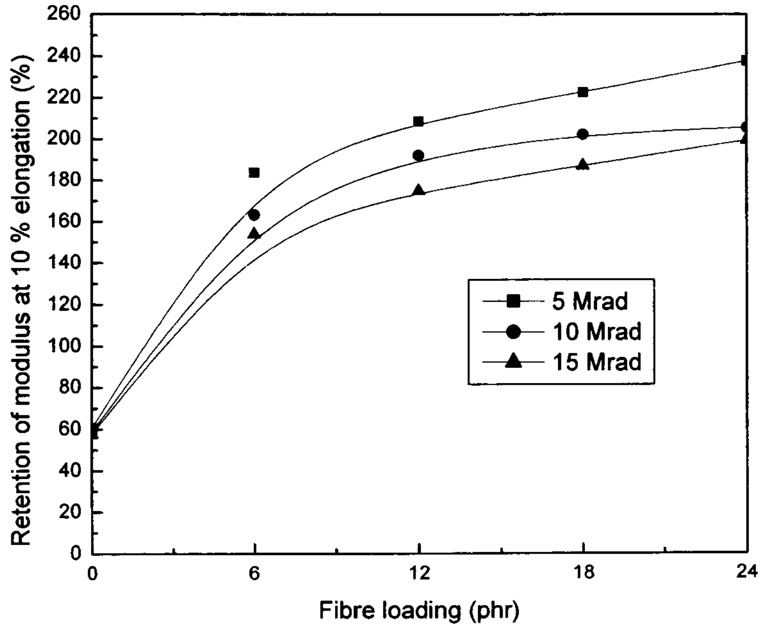


Figure 9.8 **Effect of fibre loading on percentage retention of modulus at 10 % elongation of composites after γ-radiation ageing**

9.2.2.2 Effect of curing systems

Figure 9.9 shows the effects of different curing systems on the percentage retention of modulus at 10% elongation of composites after being subjected to γ-radiation ageing for different doses. Comparison has been made with samples containing 24 phr fibres cured by sulphur and DCP systems (Samples F and M). In the case of DCP cured sample the percentage retention of tensile strength is decreased continuously as the γ-radiation dose increased from 5 Mrad to 15 Mrad.

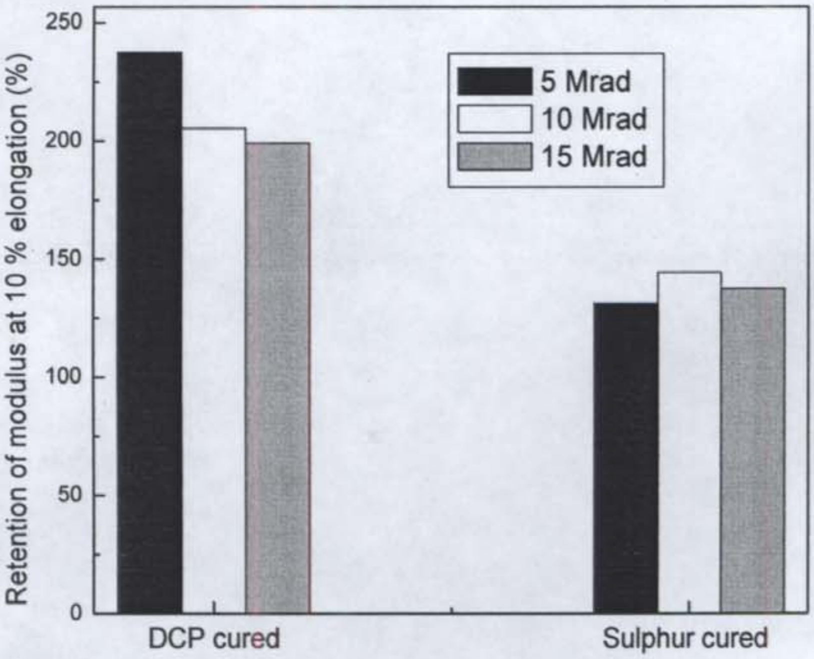


Figure 9.9 **Effect of curing systems on percentage retention of modulus at 10 % elongation of composites after γ-radiation ageing**

This indicates the increased chain degradation upon increment in γ-radiation dose. In the case of sulphur cured sample the percentage retention increases as the radiation dose is increased from 5 Mrad to 10 Mrad. This can be attributed to the formation of covalent bonds between the matrix and fibres at the interface. However, as the radiation dose is further increased from 10 Mrad to 15 Mrad the percentage retention of modulus decreases. This indicates that polymer chain degradation is the main reaction taking place at higher radiation doses. It thus follows that a radiation dose of 10 Mrad is ideal for establishing some kind of permanent bonds between fibres and rubber in the case of sulphur cured composites.

9.2.2.3 Effect of bonding agents

Figure 9.10 shows the effect bonding agent on the percentage retention of modulus at 10% elongation of composites after being subjected to γ-radiation ageing. Comparison has been made with samples containing 24 phr fibres cured by sulphur with and without hexa-resorcnol bonding agent (Samples F and G). The percentage retention of modulus for hexa-resorcinol bonding agent added composites is higher

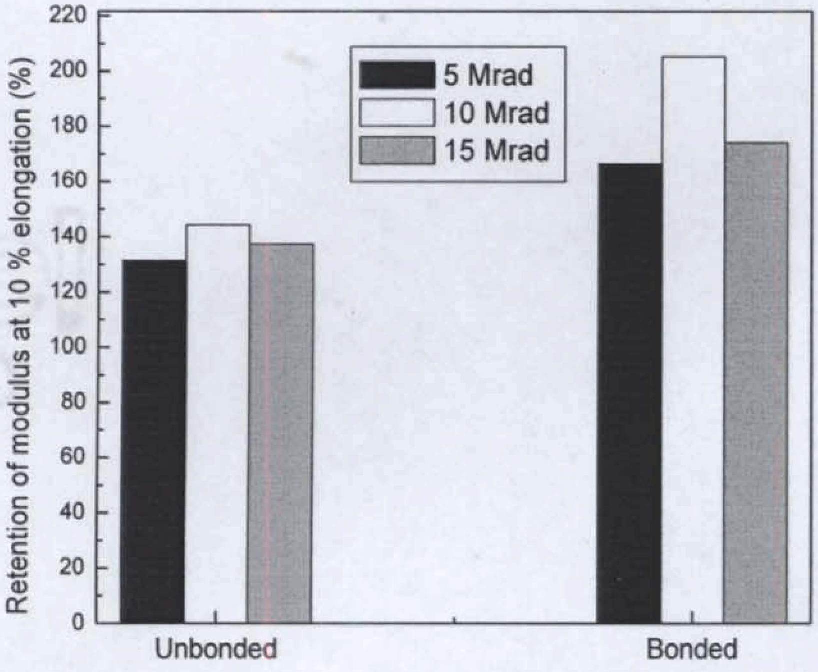


Figure 9.10 Effect of bonding agent on the percentage retention of modulus at 10 % elongation of composites after γ-radiation ageing

than that of the unbonded ones. As the radiation dose is increased from 5 Mrad to 10 Mrad the percentage retention of modulus increases and with further increase in radiation dose to 15 Mrad the percentage retention decreases. This trend is observed in both bonded and unbonded composites.

Figure 9.11 shows the effect of different bonding agents on the percentage retention of modulus at 10% elongation of nylon 6 fibre reinforced NBR composites. Comparison has been made with composites containing 24 phr fibres vulcanised DCP system (Samples Q and R). It can be seen that the percentage retention of modulus for composite containing phthalic anhydride as bonding agent is lower than that containing hexa-resorcinol bonding agent. The carbonyl group (〉C=O) present in phthalic anhydride makes them more susceptible to high energy or ionizing radiations. The presence of carbonyl group initiates the free radical mechanism thereby causing damage to the fibres. Therefore the first step degradation of fibres easily takes place in the phthalic anhydride bonded composites.

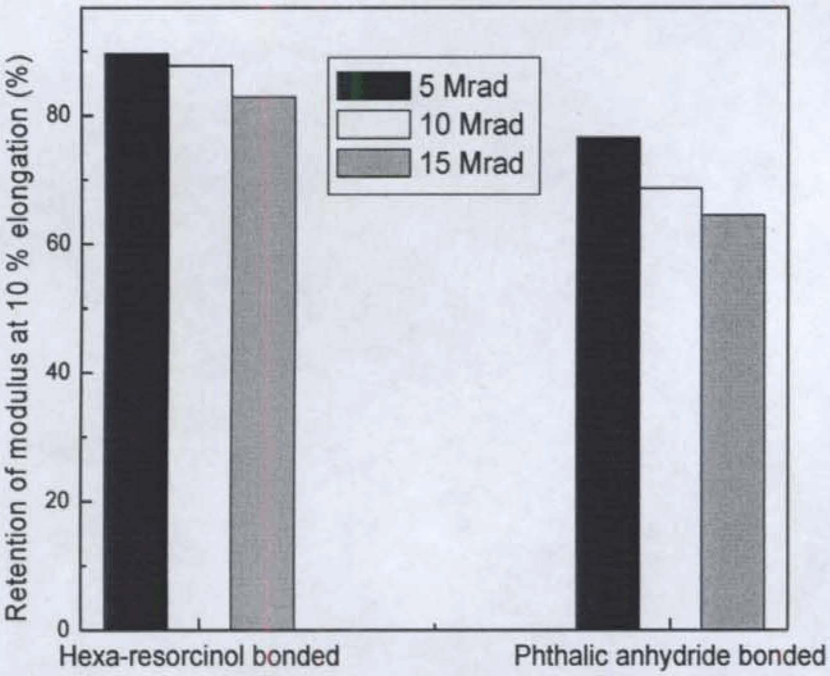


Figure 9.11 Effect of different bonding agents on the percentage retention of modulus at 10 % elongation of composites after γ-radiation ageing

9.2.3 OZONE AGEING

Unsaturated elastomers, especially those containing activated double bonds in the main chain, are severely attacked by ozone, resulting in deep cracks in a direction perpendicular to the applied stress. Protection against ozone attack can be achieved by blending with any saturated elastomers or by mixing with antiozonants. In the case of composites, the fibres are incorporated in the elastomers to prevent crack initiation and propagation in two ways; firstly, by a fibre orientation perpendicular to the direction of crack propagation and secondly by good bonding between the fibres and rubber[15]. Figure 9.12 shows the optical photographs of short nylon 6 fibre reinforced NBR composites, at varying fibre loading, after exposure to ozone (Samples H, I , L and M) . The gum, which contains no fibres, is being attacked easily by ozone as evident from the crack initiated on the surface. The intensity of cracks decreases with increase in fibre loading. Due to the uniform distribution of stresses among the fibres, they are highly resistant to crack propagation.

Figure 9.12 also shows the optical photograph of bonding agent added fibrous composite system (sample Q) after exposure to ozone. The bonded composite system prevents the ozone attack much better than the unbonded one, due to the better interfacial adhesion between the fibres and rubber. If the bonding between the fibres and rubber is sufficiently strong, the resulting composites can easily prevent the crack propagation by ozone attack.

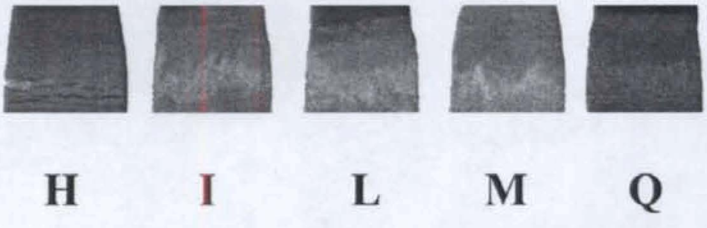


Figure 9.12 Optical photographs of typical composite samples after exposure to ozone

9.3 CONCLUSIONS

The ageing characteristics of short nylon 6 fibre reinforced NBR composites were analysed by exposing them to degrading agents such as temperature, gamma (γ) radiation and ozone. The addition of fibres enhanced the ageing resistance of NBR. In the case of DCP cured sample, the percentage retention of tensile strength decreased as the thermal ageing period increased from 7 to 14 days. However, a reverse trend was observed in the case of sulphur cured samples. An increment in the dosage of γ-radiation from 5 to 10 Mrad increased the percentage retention of modulus whereas a higher dose of 15 Mrad lowered it in sulphur cured composite samples. However, in case of DCP cured samples there was a continuous decrease in percentage retention of modulus with increment in γ-radiation dosage from 5 Mrad to 15 Mrad. The ozone resistance of the composites increased with fibre loading. The bonding agent added fibrous composite systems showed better thermal, γ-radiation and ozone resistance than the unbonded ones. The ageing resistance of hexa-resorcinol bonded composite was comparatively higher than that of phthalic anhydride bonded one.

References

1. Paiva Ju′ nior C.Z., de Carvalho L.H ., Fonseca V.M., Monteiro S.N. and D' Almeida J.R. M., *Polym-Plast. Technol. Engg.*, **43** (2004) 1365.
2. Sun Y., Luo S., Watkins K. and Wong C.P., *Polym. Degrad. stab.*, **86** (2004) 209.
3. Schwartza G. A., Cerveny S., Marzocca A. J., Gerspacher M. and Nikiel L., *Polymer,* **44** (2003) 7229.
4. Morrell P.R., Patel M. and Skinner A. R., *Polym. Test.*, **22** (2003) 651.

5. Celina M., Wise J., Ottesen D K., Gillen K T. and Clough R L., *Polym. Degrad. Stab.,* **68** (2000) 171.
6. Bohm G.G.A. and Treekrem J .O., *Rubber Chem. Technol.*, **55** (1982) 575.
7. Charlesby A., *Plast. Rubb. Proc. Appl.,* **2** (1982) 289.
8. Makhlis F.A., *Radiation Physics and Chemistry of Polymers,* John Wiley, New York (1972) 288.
9. Sweet G .C., *Developments in Rubber Technology,* First Edn., Whelan A. and Lea K .S., (Eds.), Applied Science Publishers, London (1979) 90.
10. Koshy A.T., Kuriakose B. and Thomas S., *Polym. Degrad. Stab.*, **36** (1992) 137.
11. Gwaily S. E., Nasar G .M. and Badawy M .M., *Egypt. J. Solids*, **24** (2) (2001) 193.
12. Aziz A.M.M., Youssef H.A., El Miligy A A., Yoshii F. and Makuuchi K., *Polym. Polym. Compos.*, **4** (4) (1996) 259.
13. Ungar G., *J. Mater. Sci.*, **16** (1981) 2635.
14. Vinod V .S. Varghese S. and Kuriakose B., *Polym. Degrad. Stab.,* **75** (3) (2002) 405.
15. Varghese S., Kuriakose B., Thomas S. and Koshy A .T., *Ind. J. Nat. Rubber Res.*, **4** (1) (1991) 1731.