STUDIES ON THE MECHANICAL AND TRANSPORT PROPERTIES OF MODIFIED PEANUT SHELL POWDER FILLED STYRENE BUTADIENE RUBBER COMPOSITES

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CERTIFICATE

Certified that the research work embodied in the thesis entitled **"STUDIES ON THE MECHANICAL AND TRANSPORT PROPERTIES OF MODIFIED PEANUT SHELL POWDER FILLED STYRENE BUTADIENE RUBBER COMPOSITES"** has been carried out by **Shaniba.V (Vakketh)** under my supervision at the Department of Chemistry, University of Calicut, Kerala and further, the results embodied in this thesis, in full or in part have not been submitted previously elsewhere for the award of any other degree or diploma.

Calicut University **Dr. E. Purushothaman**

DECLARATION

I hereby declare that the research work embodied in the thesis entitled **“STUDIES ON THE MECHANICAL AND TRANSPORT PROPERTIES OF MODIFIED PEANUT SHELL POWDER FILLED STYRENE BUTADIENE RUBBER COMPOSITES”**, is based on the original research work carried out by me under the guidance of Dr. E. Purushothaman, Professor (Retd.), Department of Chemistry, University of Calicut, Kerala and the same has not been submitted elsewhere previously for the award of any other degree or diploma.

Calicut University **Shaniba.V (Vakketh)**

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to

My Parents

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GLOSSARY OF TERMS

APSP - Alkali treated peanut shell powder
ASTM - American society for testing and materials
BPO - Benzoyl peroxide
CBS - N-Cyclohexyl-2-benzothiazyl sulphenamide
CB - Carbon black
CRI - Cure rate index
D - Diffusion coefficient
DC - Degree of crystallinity
DCP - Dicumyl peroxide
DLS - Dynamic light scattering
DP - Degree of polymerization
DSC - Differential scanning calorimetry
DTG - Differential thermogravimetry
DTA - Differential thermal analysis
ENR - Epoxidised natural rubber
EPDM - Ethylene propylene diene monomer
EVA - Poly (ethylene –co-vinyl acetate)
E_D - Activation energy of diffusion
E_P - Activation energy of permeation
FTIR - Fourier transform infrared spectroscopy
FA - Fly ash
ΔG - Gibb's free energy of sorption
ΔH - Enthalpy of sorption

h - Initial thickness of the polymer membrane
IRM - Industry reference material
Ks - Equilibrium absorption constant
LDPE - Law density polyethylene
MA - Maleic anhydride
MPSP - Maleic anhydride treated peanut shell powder
MMA - Methyl methacrylate
M_H - Maximum torque
M_L - Minimum torque
M - Mass of polymer composites
M_∞ - Mass of solvent sorbed at equilibrium
NR - Natural Rubber
NBR - Acrylonitrile butadiene rubber
P - Permeability coefficient
PP - Polypropylene
PCB - Pyrolytic carbon black
PF - Phenol formaldehyde
PLA - Polylactic acid
PSP - Peanut shell powder
PVC - Polyvinyl chloride
Q_t - Moles of solvent sorbed by 100 g of polymer at time t
Q_α - Moles of solvent sorbed by 100 g of polymer at equilibrium

R - Universal gas constant
RTM - Resin transfer molding
RH - Rise husk
S - Sorption coefficient
θ - Slope of the initial linear portion of the sorption curve
ΔS - Entropy of sorption
SEM - Scanning electron microscopy
SBR - Styrene butadiene rubber
SPSP - Silane modified peanut shell powder
TDQ - 2,2,4-Trimethyl-1,2-dihydroquinoline
t_{10} - Rheometric scorch time
t_{90} - Rheometric cure time
T - Absolute temperature
TEM - Transmission electron miccoscopy
TG - Thermogravimetry
Tg - Glass transition temperature
TVS - Triethoxyvinyl silane
UPSP - Unmodified peanut shell powder
XRD - X ray diffraction
λ - Mean free path

PREFACE

Peanut shell is an agricultural waste and their use as reinforcement material in the development of biocomposites is an attractive choice for both ecological and economic point of view.

The present research work involves the fabrication, characterization and application studies of composites of styrene butadiene rubber reinforced with lignocellulosic filler peanut shell powder. The thesis is titled as "Studies on the mechanical and transport properties of modified peanut shell powder filled styrene butadiene rubber composites" is divided into eight chapters. The first chapter starts with an introduction on the polymer composites and surface modification of natural filler. The earlier reports on the natural fibre reinforced composites are discussed in the second chapter. The third chapter deals with the detailed explanation on various materials, methods and characterization used in the present study. The fourth chapter describes the surface modification of filler, peanut shell powder with triethoxy vinyl silane and maleic anhydride and its characterization by UV-visible spectroscopy, FTIR, XRD, TG, SEM and TEM. The development, cure characteristics and mechanical properties like tensile strength, tear strength, modulus, hardness and abrasion resistance of composites of SBR with different filler loading and particle size are discussed in the fifth chapter. The thermal analysis of composites by TG and DSC are also explained in this chapter. The application studies of the composites are described in the sixth and seventh chapters. The sixth chapter deals the transport properties of composites in aromatic solvents and petroleum fuels at different temperatures. The solvents used were benzene, toluene and xylene as aromatic solvents and petrol, diesel and kerosene as petroleum fuels. The oil resistance of the composites using IRM 901, 902 and 903 oils and aging of the composites are also described in the sixth chapter. The biodegradation behavior of the developed composites by soil burial test is explained in the seventh chapter. The water sorption and SEM studies are carried out to support the biodegradation of the composites. Chapter eight summarises the results of the investigations, the major conclusions that are arrived at and list out the possible areas of future research work.

CHAPTER 1
INTRODUCTION

Abstract: This chapter describes general characteristics and classification of composites with special emphasis on natural fiber reinforced rubber composites. The various methods for the pretreatment of natural fibers and its merits and demerits are explained. The different molding techniques for fabrication of composites are also discussed. The scope and objectives of the proposed research work have been highlighted.

1.1 COMPOSITES

Composites are one of the most advanced and adaptable engineering materials known to society. Recent advances in the field of material science and technology gave birth to these fascinating and wonderful materials. Composite is a combined material created by synthetic assemblies of two or more components, a selected filler or reinforcing agent and a compatible matrix binder in order to obtain specific characteristics and unique properties. The components of composites do not dissolve or otherwise merge completely into each other. Nevertheless, they do act in concert. The components as well as the interface between them can usually be physically identified and it is the behavior and properties of the interface that generally control the properties of the composites. The properties of a composite cannot be achieved by any of the components acting alone. The goal in creating a composite is to combine similar or dissimilar materials in order to develop specific properties that are related to desired characteristics. Composites are used to produce a variety of economical, efficient and sophisticated products ranging from toys and tennis rackets to insulation shields and miniature printed circuits for spacecrafts [1]. They play a key role in aerospace industry automobile industry and other engineering applications as they exhibit outstanding strength to weight and modulus to weight ratio.

Composite materials made from plant fibers are receiving a great deal of attention today since they are considered as environment friendly recourse in the production and applications. Fiber reinforced polymeric composite materials are widely used in aerospace and automotive industries, sports products and medical equipments because of their low density, high stiffness and strength. Composites prepared from glass fibers are widespread high-performance materials. Glass fibres are the widely used to reinforce plastics due to their low cost (compared to aramid and carbon) and good mechanical properties. However, these fibres have serious demerits such as nonbiodegradability, high cost compared to natural fibers, high energy consumption etc. Many of these shortcomings have been highly exploited by proponents of natural fibre composites. Among all reinforcing fillers, natural fillers have gained their importance especially for low load bearing applications. Natural fiber reinforced polymer composites are superior over synthetic fiber reinforced composites in certain properties like enhanced biodegradability, combustibility, lightweight, ease of recyclability etc. These advantages place the natural fibers composites among high performance composites having economical and environmental impacts, with good physical properties [2,3].

It is well known that there are environmental and economical advantages to develop natural filler / thermoplastic elastomer composites. Cellulosic filler–reinforced plastic materials have low cost, lightweight are free from health hazards, have enhanced mechanical properties and thus have the potential for structural applications.

Researchers are currently developing and modifying biobased materials that have various applications in different fields. Ecological concerns are the main reason behind this renewed interest in natural and compostable materials. Tailoring new products with sustainable development is a philosophy that is applied to more and more materials now [4].

1.2 CHARACTERISTICS OF COMPOSITES

Composites are made up of individual materials referred to as constituent materials. There are two main classifications of constituent materials: matrix and reinforcement. The matrix material surrounds and supports the reinforcement materials by keeping their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. A synergism produces material properties unavailable from the individual constituent materials, while the wide variety of matrix and strengthening materials allows the designer of the product or structure to choose an optimum combination. In general the reinforcements are much stronger and stiffer than the matrix. Both constituents are required and each must accomplish specific tasks if the composite is to perform as intended.

A material is generally stronger and stiffer in fiber form than in bulk form. The numbers of microscopic flaws that act as fracture initiation sites in bulk materials are reduced when the material is drawn into a thinner section. In fiber form the material will typically contain very few microscopic flaws from which cracks may initiate to produce catastrophic failure. Therefore, the strength of the fiber is greater than that of the bulk material. Individual fibers are hard to control and form into useable components. Without a binder material to separate them, they can become knotted, twisted and hard to separate. The binder (matrix) material must be continuous and surround each fiber so that they are kept distinctly separate from adjacent fibers and the entire material system is easier to handle and work with. The physical and mechanical properties of composites are dependent on the properties, geometry and concentration of the constituents. Increasing the volume content of reinforcements can increase the strength and stiffness of a composite to a point. If the volume content of reinforcements is too high there will not be enough matrix to keep them separate and they can become tangled. Similarly, the geometry of individual reinforcements and their arrangement within the matrix can affect the performance of a composite. There are many factors to be considered when designing with composite materials. The type of reinforcement and matrix, the geometric arrangement and volume fraction of each constituent, the anticipated mechanical loads, the operating environment for the composite, etc. must all be taken into account [5,6].

1.3 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 phases is known as interface. Figure 1.1 shows the schematic representation of the composites.

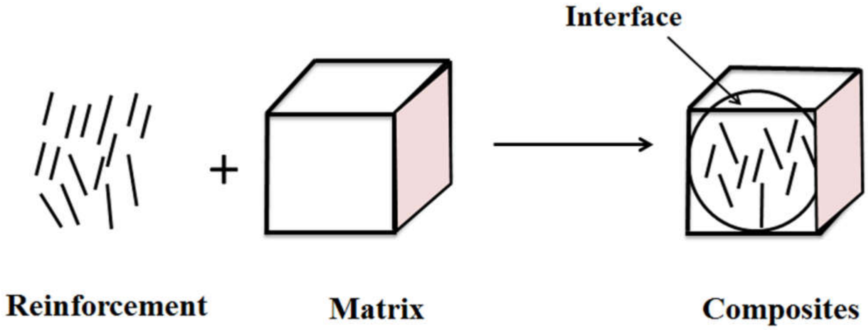


Figure 1.1 Schematic representation of composite

1.3.1 Matrix

The matrix material binds the fiber reinforcement, gives the composite component its shape and determines the quality of its surface. They separate the reinforcement phase in the desired orientation and thereby contribute to the cohesion of the products. They save the reinforcement phase from abrasion and degradation by the influence of surroundings. A matrix can be polymeric, ceramic or metallic. Polymer matrices are the most widely used for composites in commercial and high-performance aerospace applications. Ceramic and metal matrices are typically used in high temperature environments, like engines. Carbon as a matrix is used in very high temperature applications like carbon-carbon brakes and rocket nozzles.

1.3.2 Reinforcement

Reinforcements are second major constituents of composites. Reinforcement is the constituent that primarily carries the structural loads to which the composite is subjected. The reinforcement therefore, to a significant degree, determines the strength and stiffness of the composite. Composite reinforcement may be in the form of fibres, particles or whiskers. Particles have no preferred directions and are mainly a means to improve properties or lower cost of isotropic material. Particles have length to diameter ratios of order unity and dimension that range from that of a fibre diameter to several millimeters. Whiskers have length to diameter ratios of order 1000 and diameter of order 0.1-l pm. Whiskers are pure single crystals manufactured through chemical vapor deposition and thus have preferred directions. Whiskers are more or less randomly arranged in the matrix. Whisker reinforced composites are likely to be considered as macroscopically isotropic. The most common types of fibrous reinforcements used in composite applications are synthetic and natural fibers [7].

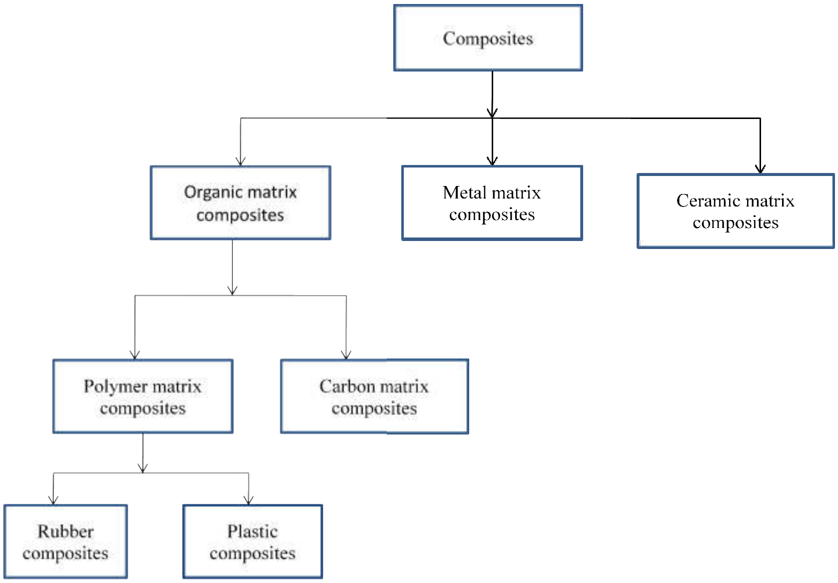
1.4 CLASSIFICATION OF COMPOSITES

Composite materials are commonly classified as the following two distinct levels:

1.4.1 Classification based on matrix

The first level of classification is usually made with respect to the matrix constituent. The major composite classes include Organic Matrix Composites (OMCs), Metal Matrix Composites (MMCs) and Ceramic Matrix Composites (CMCs). The term organic matrix composite is generally assumed to include two classes of composites, namely Polymer Matrix Composites (PMCs) and Carbon Matrix

Composites commonly referred to as carbon-carbon composites. On the basis of matrix phase composites classification of composites are shown as in **scheme 1.1**



Scheme 1.1 Classification of composites based on matrix

1.4.1.1 Metal matrix composites (MMC)

Metal matrix composite (MMC) is composite material with at least two constituent parts, one being a metal necessarily (Aluminium, magnesium, lead, copper, tungsten, nickel etc) the other material may be a different metal or another material, such as a ceramic or organic compound (eg silicon carbide, carbon, boron, alumina, glass etc). When at least three materials are present, it is called a hybrid composite. An MMC is complementary to a cement, which are made by dispersing a reinforcing material into a metal matrix. They have higher temperature resistance than other composite systems and are preferred for service temperatures above 150 °C. They also have good electrical and thermal conductivities. Most of the current applications of them are in automotive and space related areas. Metal matrix composites have many advantages over monolithic metals like high specific modulus, higher specific strength, better properties at elevated temperatures and lower coefficient of thermal expansion. Because of these attributes metal matrix composites are under consideration for wide range of applications *viz* combustion chamber nozzle in rocket, space shuttle, housings, tubing, cables, heat exchangers, structural members etc [8,9].

1.4.1.2 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 [9].

1.4.1.3 Polymer matrix composites (PMC)

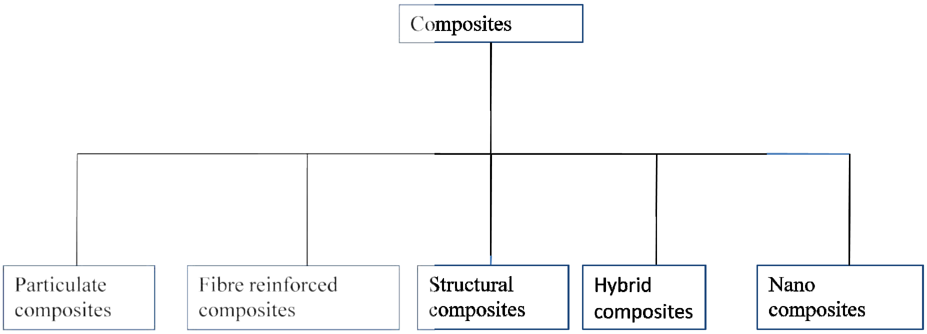
Polymer matrix composite is the material consisting of a polymer matrix combined with a fibrous reinforcing dispersed phase. Polymer matrix composites are very popular due to their low cost and simple fabrication methods. Use of non-reinforced polymers as structure materials is limited by low level of their mechanical properties In addition to relatively low strength; polymer materials possess low impact resistance. The advantages of PMCs are high tensile strength, stiffness, fracture toughness, good abrasion resistance, puncture resistance, corrosion resistance and low cost. The main disadvantages are low thermal resistance and high coefficient of thermal expansion. PMC are again classified into plastic based composites and rubber composites [10–12].

1.4.1.4 Rubber composites

In these composites, elastomers constitute the matrix phase. Elastomers form a special category of polymeric materials characterized by unique combination of useful properties such as elasticity, flexibility, toughness and impermeability. They are commonly known as rubbers and always show a large elongation at break. The matrix may be natural or synthetic rubber or their blends depending on the service requirement of the products. Unlike plastics, a wide variety of flexible products can be made by using elastomers as the matrix phase [13].

1.4.2 Classification based on reinforcement

. Based on the reinforcement composites can be classified as particulate reinforced composites, structural composites, fibre reinforced composites, hybrid composites and nanocomposites. Classification is shown in **scheme 1.2.**



Scheme 1.2 Classification based on reinforcement

1.5 FIBRE REINFORCED COMPOSITES

The components of fiber-reinforced composites are fiber as reinforcement and a polymer as matrix. Polymer like polyethylene [14–16], polypropylene [17–20], PVC [21] etc and rubber like NR [19,22–26], SBR [27–30], EPDM [31] ,NBR [31–33] etc have been reported as matrices [34]. Natural fibers are classified based on their origin, which is from plants, animals or minerals. Cellulose is the main component of plant fibres. The fibres from bast, ie stem or soft scelerenchyma, leaf or hard fibres, seed, fruit, wood and grass fibres are cosidered in the class of plant fibres. The main components of animal fibres are proteins. Hair, silk and wool are examples for animal fibres. Over the last few years, a number of researchers exploit the potential natural fibres as reinforcing materials in the fabrication of composite materials [35]. Advantages of natural fibers over man-made fibers include low density, low cost, low weight, less damage to processing equipment, improved surface finish of moulded parts, relatively good mechanical properties, recyclability and biodegradability [16,36,37]. Natural fiber composites are also claimed to offer environmental advantages such as reduced dependence on non-renewable energy/material sources, lower pollutant emissions, lower green house gas emissions, enhanced energy recovery and biodegradability of components. Since, such superior environmental performance is an important concern, increased future use of natural fiber composites [38].These advantages make natural fibers as potential replacement for glass fibers in composite materials. Mechanical properties of natural fibers, especially flax, hemp, jute and sisal are very good and may compete with glass fiber in specific strength and modulus [39]. Natural fiber-reinforced composites can be applied in the manufacturing industries especially packaging, building construction, plastics, automobile and furniture instead of the harmful and non-renewable materials to cut down on material cost and environmental hazards [34,40,41].

1.5.1 Composition of natural fibres

The nature of cellulose and its crystallinity in natural fibres decides its reinforcing efficiency in the composites A better understanding of the chemical composition and surface adhesive bonding of natural fiber is necessary for developing natural fiber-reinforced composites. Cellulose, hemicellulose, lignin, pectins and waxes are the main components of natural fibres. The composition depends on the growing condition and test methods even for same kind of fibres. It is noted that chemical composition and cell structure of natural fibers are quite complicated. Each fiber is essentially a composite in which rigid cellulose microfibrils are embedded in a soft lignin and hemicellulose matrix as shown in **figure 1.2**. In addition, the microfibrils are helically wound along the fiber axis to form ultimate hollow cells. Uncoiling of these spirally oriented fibrils consumes large amounts of energy and is one of the predominant failure modes. As a result, pretreatment of the fibers would result in chemical and structural changes not only on the fiber surface but also in the distinct cells, which in turn also influences the properties of the fibers and composites [42].

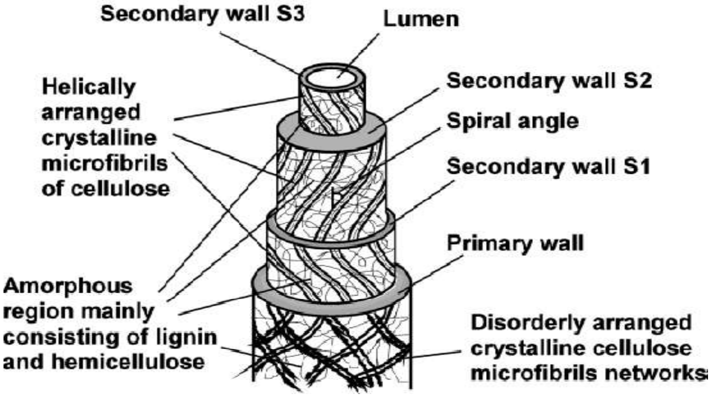


Figure 1.2 Structural constitution of a natural vegetable fiber cell, in which the secondary wall S2 makes up 80% of the total thickness and thus acts as the main load bearing component. Adapted from [42].

Cellulose: The structure of cellulose is represented in the **figure 1.3.** It is a natural polymer and D-anhydroglucose are the repeating unit with three hydroxyl groups, which is joined through 1,4-β-D-glycosidic linkages at first and fourth carbon atoms [43]. The degree of polymerization (DP) is around 10,000 .The hydroxyl group and their ability to form hydrogen bond are the main factors responsible for crystalline packing of cellulose. The physical properties of the cellulose are mainly due to these crystalline packing. Solid cellulose forms a microcrystalline structure with regions of high order crystalline regions and low order amorphous regions. The crystal nature (monoclinic sphenodic) of naturally occurring cellulose is known as cellulose I. Cellulose is easily hydrolyzed by acids ,but it is resistant to strong alkali and oxidizing agents [35,44].

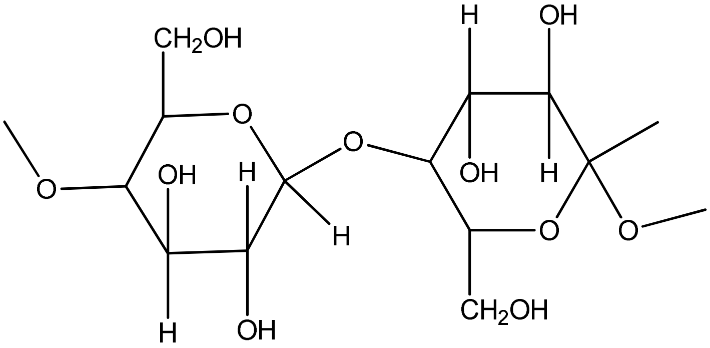


Figure 1.3 Structure of cellulose

Hemicellulose: Hemicellulose is different from cellulose. They consist of a group of polysaccharides with 5- and 6-carbon ring sugar combination. The difference between cellulose and hemicellulose are i) cellulose contains only one sugar unit, but hemicellulose contains many different sugar units. ii) Cellulose is linear polymer, hemicellulose is branched polymer with pendant side groups.iii) Cellulose is ccrystalline in nature, hemicellulose is non crystalline nature. iv) the degree of polymerization of native cellulose is higher than that of hemicellulose. The supportive matrix for cellulose microfibrils are hemicellulose. Hemicellulose is very soluble in alkali and water, hence it is hydrophilic and it is readily hydrolyzed by acids [35,45].

Lignin: Lignin is a complex polymer with both aliphatic and aromatic hydrocarbons. They are insoluble in most of the solvents and it is totally amorphous and hydrophobic in nature. The rigidity to the plants is mainly due to the presence of lignin. It is thought to be a complex with very high molecular weight and three-dimensional copolymer of aliphatic and aromatic constituents. The building unit of lignin is found to contain five hydroxyl and five methoxyl groups. The derivatives of 4-hydroxy-3-methoxy phenylpropane are believed to be their structural units. Eventhough lignin is widely used, in most of the chemical processes there is difficulty to establish a scientific method to isolate lignin in its native state from the fibre. Lignin is considered to be a thermoplastic polymer with glass transition temperature of around 90 °C and melting temperature around 170 °C. It is soluble in hot alkali, but not hydrolyzed by acids. It is easily oxidized and condensable with phenol [46].

Pectin: Pectins are a collective name for heteropolysaccarides. These are responsible for flexibility of plants

Waxes: They are made up of different types of alcohols and make up the last part of fibres.

1.5.2 Advantages and disadvantages of natural fibres reinforced composites.

1.5.2.1 Advantages [15,47–49][50,51]

- world wide availability
- positive environmental impact
- renewable resource with production requiring very little energy
- lesser green house gas emission during combustion
- low cost and low density
- recyclable and biodegradable
- less abrasive and easily processible
- satisfactory mechanical properties
- flexibility during processing
- desirable fiber aspect ratio
- high tensile and flexural modulus

1.5.2.2 Disadvantages.

The major disadvantages of natural fibre reinforced composites with non polar thermoplastic and elastomeric matrix are

- Non uniform dispersion of fibres within the matrix which debilitate the adequacy of the composites, due to inherent polar and hydrophilic nature of fibres.
- Natural fibres undergo degradation at lower temperature, hence restriction of choice of matrix corresponding to processing temperature of vegetable fibre below 200 °C.

- Poor mechanical and dimensional stability of composites results from swelling of fibres through moisture absorption and formation voids at the interface.

- Low microbial resistance and susceptibility to rotting cause serious issue during shipping, storage and composite processing.

- The non uniformity and variation of dimensions of fibres from individual plants in same and different cultivation affect the mechanical properties of their composites [35,45,52–54].

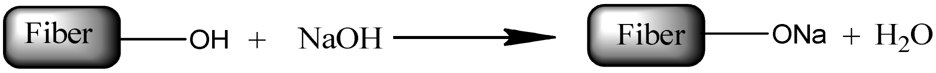
Since the demerits are now more depending on natural fibres, there are several attempts to rectify the disadvantages especially in the form of chemical treatments.

1.6 PRETREATMENT OF NATURAL FIBRES

The low interfacial properties between fiber and polymer matrix often reduce their potential as reinforcing agents due to the hydrophilic nature of natural fibers. Chemical modifications are necessary to optimize the interface of fibers. Chemical modifications of natural fibers aimed at improving the adhesion with a polymer matrix were investigated by a number of researchers [54–58]. Pretreatments of the fiber can clean the fiber surface, chemically modify the surface, reduce the moisture absorption process and increase the surface roughness [54,55]. As the natural fibers bear hydroxyl groups from cellulose and lignin, they are amenable to modification. The formation of hydrogen bond by the hydroxyl groups within the cellulose molecules reducing the activity towards the matrix. It is observed that the chemical modifications may activate these groups or can introduce new moieties that can effectively interlock with the matrix. Mercerization, isocyanate treatment, acrylation, permanganate treatment, acetylation, silane treatment and peroxide treatment with various coupling agents and other pretreatments of natural fibers have achieved various levels of success in improving fiber strength, fiber fitness and fiber-matrix adhesion in natural fiber reinforced composites. Surface tension and polarity of fibres can be altered through surface modification by simple chemical treatments [54]. Brief descriptions of some important fiber chemical modifications are summarized in the following subsections.

1.6.1 Mercerization of natural fibers

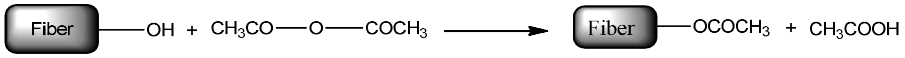
Alkali treatment of natural fibers, are also known as mercerization. It is one of the most widely used chemical treatments of natural fibers, when used to reinforce thermoplastics and thermosets. The most common modification done by alkaline treatment is the disruption of hydrogen bonding in the network structure, thereby increasing surface roughness. This treatment removes a certain amount of lignin, wax and oils covering the external surface of the fiber cell wall, depolymerizes cellulose and exposes the short length crystallites [59]. Addition of aqueous sodium hydroxide to natural fiber promotes the ionization of the hydroxyl group to the alkoxide [57,60]. Therefore, mercerization has a long-lasting effect on the mechanical properties of fibers, mainly on fiber strength and stiffness. The process is represented as **scheme 1.3**



Scheme 1.3 Reaction during alkali treatment of fibers

1.6.2 Acetylation

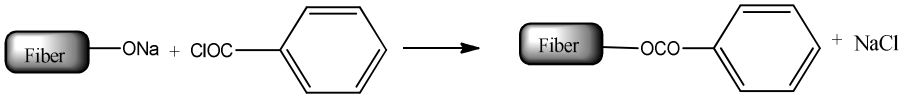
Acetylation is a well known esterification method used to introduce plastisization to cellulosic fibres. It introduces acetyl functional group to an organic compound. The fiber–matrix adhesion is improved by actylation. The method required is pretreatment by an alkali followed by acetylation. The byproduct acetic acid formed in the reaction must be removed from the lignocellulosic material before the use of fiber. The hydroxyl group of cell wall of polymer replaced with acetic anhydride changes the properties of polymer, hence they become hydrophobic [61]. Acetylation is originally applied to wood cellulose to stabilize the cell walls against moisture, improving dimensional stability and environmental degradation. Acetylation treatment was used in surface modification of fiber for use in fiber-reinforced composites [42,61,62]. The reaction of acetic anhydride with fiber is represented in the **scheme 1.4** [61,63]. Acetylation involves reaction of surface hydroxyl group of lignocellulosic fibre with acetic anhydride at elevated temperature. Hydroxyl group of amorphous lignin and hemicellulose also reacts with reagent. But the hydroxyl group of crystalline cellulose are being closely packed with hydrogen bonds have low extent of reaction with the reagent.



Scheme 1.4 Reaction during acetylation of fibers

1.6.3 Benzoylation

Benzoylation is an important transformation reaction in organic synthesis. In benzoylation treatment, benzoyl chloride is most often used in fiber pretreatment and inclusion of benzoyl group in the fiber is responsible for the decreased hydrophilic nature of the treated fiber and improved interaction with the hydrophobic matrix. The reaction of benzoyl chloride with the cellulosic hydroxyl group of fibre is represented as shown in the **scheme 1.5.** It is observed that the progress of fibre matrix adhesion considerably increases the strength of composite, decreasing its water absorption and improving its thermal stability [34].



Scheme 1.5 Reaction during benzoylation of fibers

1.6.4 Peroxide Treatment

Peroxide treatment of cellulose fiber is an important process and has attracted the attention of various researchers due to easy processability and improvement in mechanical properties. In these process free radicals of the form RO· will be formed by the decomposition of organic peroxides. RO· then reacts with the hydrogen group of the cellulose fibers and the matrix. The following **scheme 1.6** represents the example for peroxide initiated free radical reaction between polyethylene matrix and cellulose fibers. Generally in peroxide treatment, fibers are treated with 6% benzoyl peroxide or dicumyl peroxide in acetone solution for about 30 min, after alkali pretreatment [64,65].

$$\mathrm{R{-}O{-}O{-}R} \longrightarrow 2\,\mathrm{RO}^{\cdot}$$

$$\mathrm{RO}^{\cdot} + \mathrm{Matrix{-}H} \longrightarrow \mathrm{ROH} + \mathrm{Matrix}^{\cdot}$$

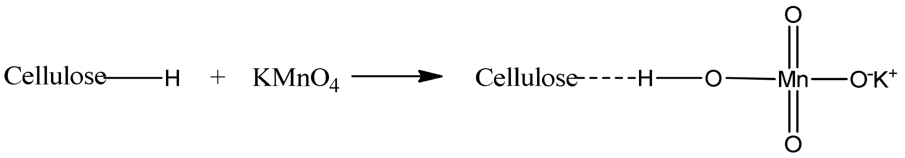
$$\mathrm{RO}^{\cdot} + \mathrm{Cellulose{-}H} \longrightarrow \mathrm{ROH} + \mathrm{Cellulose}^{\cdot}$$

$$\mathrm{Cellulose}^{\cdot} + \mathrm{Matrix}^{\cdot} \longrightarrow \mathrm{Cellulose{-}Matrix}$$

Scheme 1.6 Reaction during peroxide treatment of fibers

1.6.5 Permanganate treatment

In the case of permanganate treatment the major reaction is the production of cellulose radical through MnO^{3-} ion formation. Then, highly reactive Mn^{3+} ions are responsible for initiating graft copolymerization as shown below in **scheme 1.7**. Pretreatments with permanganate are conducted by using different concentration of potassium permanganate solution in acetone with soaking duration from 1 to 3 min after alkaline pretreatment. As a result of permanganate treatment, the hydrophilic tendency of the fibers get was reduced, and thus, the water absorption of fiber-reinforced composite decreased. The hydrophilic tendency of fiber decreased with increase in concentration of $KMnO_4$. But at higher concentrations of $KMnO_4$ that is 1.0%, degradation of cellulosic fiber occurred which resulted in the formation of polar groups between fiber and matrix. To improve the bonding at the fiber-polymer interface, permanganate treatment of natural fibres is one of the best methods [34,54,64–66].



$$\text{Cellulose—H} + KMnO_4 \longrightarrow \text{Cellulose}\cdots H—O—\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Mn}}—O^-K^+$$

Scheme 1.7 Reaction during permanganate treatment of fibers

1.6.6 Graft copolymerization

Graft copolymerization is an effective method of surface chemical modification of natural fibers. In 1943, the first graft copolymer of vinyl and allyl ethers of cellulose copolymerized with maleic acid ester was reported. During the last decades several methods were suggested for the preparation of graft copolymers by conventional chemical techniques. Creation of an active site on the preexisting polymeric backbone is the common feature of most methods for the synthesis of graft copolymers. The active site may be either a free radical or a chemical group which may get involved in an ionic polymerization or in a condensation process. Polymerization of an appropriate monomer onto this activated back-bone polymer leads to the formation of a graft copolymer [54]. For example, the treatment of cellulose fibers with hot polypropylene-maleic anhydride (MAH-PP) copolymers provides covalent bonds across the interface.

Maleated coupling agents are widely used to strengthen composites containing fillers and fiber reinforcements [67–70]. The difference with other chemical treatments is that maleic anhydride is not only used to modify fiber surface but also the polypropylene (PP) matrix to achieve better interfacial bonding and mechanical properties in composites [71]. The PP chain permits maleic anhydride to be cohesive and produce maleic anhydride grafted polypropylene (MAPP). Then the treatment of cellulose fibers with hot MAPP copolymers provides covalent bonds across the interface. The mechanism of reaction of maleic anhydride with PP and fiber can be explained as the activation of the copolymer by heating at 170 °C before fiber treatment and then the esterification of cellulose fiber [72]. After this treatment, the surface energy of cellulose fibers is increased to a level much closer to the surface energy of the matrix. This results in better wettability and higher interfacial adhesion of the fiber.

1.6.7 Silane treatment

In the silane treatment the coupling agents usually improve the degree of crosslinking in the interface region and offer a perfect bonding. Among the various coupling agents, silane coupling agents were found to be effective in modifying the natural fiber-matrix interface. Efficiency of silane treatment was high for the alkaline treated fiber than for the untreated fiber because more reactive site can be generated for silane reaction. Therefore, fibers were pretreated with NaOH for about half an hour before its coupling with silane [54]. In this treatment, Silanes are used as coupling agents to improve the adhesion of fibre to a polymer matrix, stabilizing the composite material. It is also observed that the number of cellulose hydroxyl groups in the fiber–matrix interface is reduced by silane coupling agents. In the presence of moisture, hydrolysable alkoxy group leads to the formation of silanols. The silanol then reacts with the hydroxyl group of the fiber, forming stable covalent bonds to the cell wall that are chemisorbed onto the fiber surface [34,73].Therefore, the covalent bonding between the matrix and fiber form crosslinked network, which restrain the swelling of the fiber by the hydrocarbon chain provided during silane treatment.

Many researchers applied silane treatment in surface modification of glass fiber composites [68,74,75]. It is also claimed that the silane coupling agents were also found to be effective in modifying natural fiber–polymer matrix interface and increasing the interfacial strength. The interaction between the silane coupling agent modified fiber and the matrix was much stronger than that of alkaline treatment, which led to composites with higher tensile strength from silane treated than alkaline-treated fiber [58]. Thermal stability of the composites was also improved after silane treatment.

1.6.8 Plasma treatment

It is well known that the plasma treatment is an effective method to modify the surface of natural polymers without changing their bulk properties. The plasma discharge can be generated by either corona treatment or cold plasma treatment. Both methods are considered as plasma treatment when ionized gas has an equivalent number of positive and negative charged molecules that react with the surface of the present material. The distinguishing feature between the two categories of plasmas is the frequency of the electric discharge. High-frequency cold plasma can be produced by microwave energy, whereas a lower frequency alternating current discharge at atmospheric pressure produces corona plasma [54,76].

1.7 DIFFERENT METHODS FOR FABRICATION OF COMPOSITES

There are various methods for fabricating composite components. Some methods have been borrowed (injection molding, for example), but many were developed to meet specific design or manufacturing challenges. Selection of a method for a particular part, therefore, will depend on the materials, the part design and end-use or application. The fabrication and shaping of composites into finished products, often lead to the formation of the material itself during the fabrication process. The formation of the composite involves the combination of the matrix and fibre such that the matrix impregnates, surrounds, and wets the fibre. The important processing methods involves hand lay-up, bag molding process, filament winding, pultrusion, bulk molding, sheet molding, resin transfer molding, open molding, injection molding and compression molding etc.

1.7.1 Hand lay-up

The oldest, simplest and the most commonly used method for the manufacture of both small and large reinforced products is the hand lay-up technique. A flat surface, a cavity or a positive shaped mould, made from wood, metal, plastics or a combination of these materials may be used for the hand lay-up method. Fibre reinforcements and resin are placed manually against the mould surface. The layers of materials placed against the mould control thickness [77].

1.7.2 Open molding

Open contact molding in one-sided molds is a low-cost, common process for making fiber glass composite products. Typically used for boat hulls, decks, truck cabs and fenders, spas, bath tubs, shower stalls and other relatively large, noncomplex shapes. Open molding involves either hand layup or a semi-automated alternative spray up. In an open-mold spray up application, the mold is first treated with mold release. If a gel coat is used, it is typically sprayed into the mold after the mold release has been applied. The gel coat then is cured and the mold is ready for fabrication to begin. In the spray up process, catalyzed resin (viscosity from 500 to 1,000 cps) and glass fiber are sprayed into the mold using a chopper gun, which chops continuous fiber into short lengths, then blows the short fibers directly into the sprayed resin stream so that both materials are applied simultaneously. In the final steps of the spray up process, workers compact the laminate by hand with rollers. Wood, foam or other core material may then be added, and a second spray up layer imbeds the core between the laminate skins. The part is then cured, cooled and removed from the reusable mold [77].

1.7.3 Resin transfer molding (RTM)

Resin transfer molding sometimes referred to as liquid molding. It is fairly simple process. It begins with a two-part, matched, closed mold that is made of metal or composite material. Dry reinforcement (typically a preform) is placed into the mold and the mold is closed. Resin and catalyst are metered and mixed in dispensing equipment, then pumped into the mold under low to moderate pressure through injection ports, following predesigned paths through the preform. Extremely low-viscosity resin is used in RTM applications for thick parts to permeate preforms quickly and evenly before cure. Both mold and resin can be heated, as necessary, for particular applications. RTM produces parts without an autoclave. However, when cured and demolded, a part destined for a high-temperature application usually undergoes postcure. Most RTM applications use a two-part epoxy formulation. The two parts are mixed just before they are injected. Bismaleimide and polyimide resins also are available in RTM formulations. Light RTM is a variant of RTM that is growing in popularity. In light RTM, low injection pressure, coupled with vacuum, allow the use of less-expensive, light weight two-part molds or a very light weight, flexible upper mold.

The benefits of RTM are impressive. Generally, the dry preforms and resins used in RTM are less expensive than prepreg material and can be stored at room temperature. The process can produce thick, near-net shape parts, eliminating most post-fabrication work. It also yields dimensionally accurate complex parts with good surface detail and delivers a smooth finish on all exposed surfaces. It is possible to place inserts inside the preform before the mold is closed, allowing the RTM process to accommodate core materials and integrate “molded in” fittings and other hardware into the part structure. Moreover, void content on RTM’s parts is low, measuring in the 0 to 2 percent range. Finally, RTM significantly cuts cycle times and can be adapted for use as one stage in an automated, repeatable manufacturing process [77].

1.7.4 Filament winding

It is a continuous fabrication method that can be highly automated and repeatable, with relatively low material costs. A long and cylindrical tool called a mandrel is suspended horizontally between end supports, while the “head” moves back and forth along the length of a rotating mandrel, placing fiber onto the tool in a predetermined configuration. Computer-controlled filament-winding machines are available, equipped with from 2 to 12 axes of motion. Filament winding is a technique used for the manufacturing of surfaces of revolution such as pipes, tubes, cylinders and spheres and is frequently used for the construction of large tanks and pipe work for the chemical industry [78].

1.7.5 Injection molding

Injection molding is the most commonly used manufacturing process for the fabrication of plastic parts. A wide variety of products are manufactured using injection molding, which vary greatly in their size, complexity, and application. The injection molding process requires the use of an injection molding machine, raw plastic material, and a mold. The plastic is melted in the injection molding machine and then injected into the mold, where it cools and solidifies into the final part.

Injection molding is used to produce thin-walled plastic parts for a wide variety of applications, one of the most common being plastic housings. Plastic housing is a thin-walled enclosure, often requiring many ribs and bosses on the interior. These housings are used in a variety of products including house hold appliances, consumer electronics, power tools, and as automotive dash boards. Other common thin-walled products include different types of open containers, such as buckets. Injection molding is also used to produce several everyday items such as tooth brushes or small plastic toys. Many medical devices, including valves and syringes are manufactured using injection molding [79].

Advantages of the injection moulding technique are the most precise control of shape and dimensions, highly automatic process, fast cycle times and the widest choice of materials. The main disadvantages are high capital cost, good only for large number of parts and it requires large mould pressures.

1.7.6 Extrusion

Extrusion is one of the most effective methods of processing of thermoplastic polymers. A thermoplastic polymer (which is usually obtained in pellet or powder form) and the reinforcing fillers are combined and drawn into a heated extrusion barrel by means of a single screw or two co-rotating screws, depending on the type of extruder. The polymer is melted and mixed with the filler to form a composite melt, which is then drawn forwarded through the extruder barrel and further mixed and compressed to improve the melt homogeneity. The extruder melt then exits the barrel through a shaped die, which determines the shape of the extruded composite [80,81].

Unlike melt mixing, extrusion is a continuous process that can accommodate high feed rates and allows the fast and efficient processing of materials. A shaped die can also be used to create a finished product with a desired profile. Extrusion is widely used to fabricate a large variety of products. Simple extrusion is used for tubing, sheets, and complex profiles. Co-extrusion is also used for products made from different hardness, different properties, colours etc. Wire and cable jacketing, hose jacketing, and other similar assemblies are produced by the cross-head extrusion.

1.7.7 Compression molding

It is a commonly used processing technique for producing large, relatively simple composites with good mechanical properties. Compression molding basically involves the hot pressing of filler embedded thermoplastic material. The compression molding operation begins with the placement of a thermoplastic-filler mixture to the bottom half of a preheated mould cavity. The top half of the mould is lowered at a constant rate until the desired processing pressure is reached, thus causing melting of the polymeric matrix and consolidation of the composite. Once the composite has been pressed, it is cooled and removed from the mold. A sketch of a mould used for compression is given in **figure1.4.** The advantages of this technique are lower mould pressures and large parts can be produced. Disadvantages: require more labour, longer cycle than injection molding, each charge is loaded by hand. Compression molding of thermoplastic material is used mainly for the preparation of standard laboratory test specimens from pellets or preformed slabs, with the latter being preferred. The material is first preheated to melting and the melt is molded in a compression mould at 165–190 °C and 200–400 psi pressure. Demolding can be done at low temperatures. In general, compression molding is not used for production of molded parts because it is not economically competitive to the speed and efficiency of injection molding [81,82].

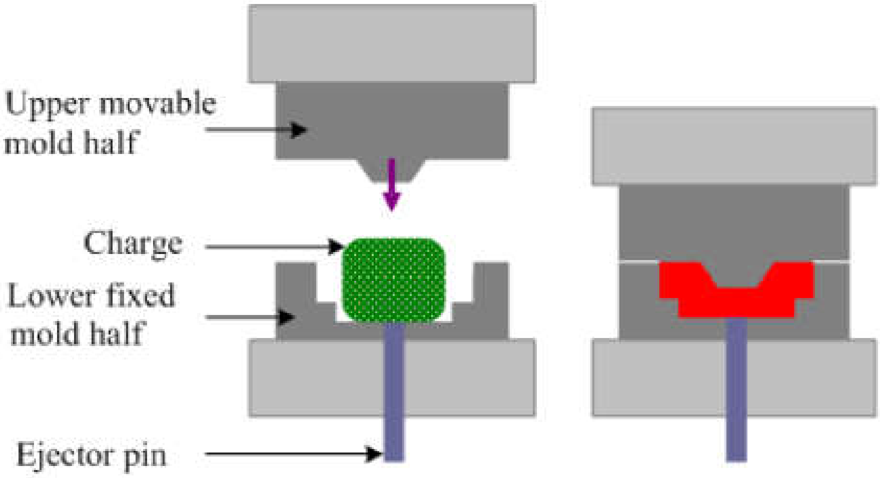


Figure 1.4 Sketch of Compression mould. Adapted from [82].

1.8 EXISTING GAPS IN THE FIELD AND MAJOR OBJECTIVES OF THE PRESENT WORK.

Significant researches are currently being done in the development and characterisation of composites of natural rubber with inorganic filler like carbon black, silica etc and with natural fibres like banana, sisal, rice husk, hemp powder etc. The composites of SBR with inorganic and synthetic fillers were also reported, but with natural fillers there are only very few reports. Styrene butadiene rubber has good mechanical properties. It does not break down easily. Compared to NR, SBR has better processibility, crack resistance, heat, aging and abrasion resistance. Similarly, it has good ozone resistance and greater weatheribility than natural rubber. But its oil resistance is very poor[83][83]. Hence, about 70% of SBR are being used in tyres and allied products. It is also used in conveyer belts, gaskets, hoses, floor tiles, footwear, and adhesive and cable insulator. Tyre manufactures facing serious problem due to the increasing stringent specifications, have found no alternative to SBR for the highly specified components in high performance tyres. In addition, the need to reduce fuel consumption has led to the development of low rolling resistance tyres. These performance improvements cannot be achieved with emulsion polymerization SBR (ESBR). There is a trend towards the increasing use of solution polymerization SBR (SSBR). SBR offers little resistance to oils and chemicals; hence SBR must be specifically compounded to provide resistance to ozone, sunlight and heat.

Bio-composites are the combination of natural fibers (biofibers) such as wood fibers (hard and soft wood) or nonwood fibers (e.g. rice straw, hemp, banana, pine apple, sugarcane, oil palm, jute, sisal and flax) etc with polymer matrices from renewable and non-renewable resources. In recent years, biodegradable composites have attracted more and more interest due to the increasing environmental concern and decreasing fossil resources. This motivates academic and industrial researchers to develop novel materials labelled as “environment friendly”, i.e., materials produced from alternative resources, with lower energy consumption, biodegradable and non-toxic to the environment. Bio-composites are emerging as a realistic alternative to glass reinforced composites since they are derived from renewable resources. Material costs can be markedly reduced with their large scale usage[84,85]. Peanut shell is one of the waste materials in the crop industry and its large scale disposal to land leads to environmental problems. In this context the use of peanut shell as reinforcement filler in the development of biocomposites of SBR is relevant. It is one of the steps towards a remedial measure for waste disposal problems in crop industry and again it leads to the fabrication of ecofriendly products with low cost and better property than pure SBR. Hence the main objectives of the investigation are

- Modification of peanut shell powder (PSP) filler with a view to improving the properties of the filler.
- Characterization of the modified PSP using spectral and analytical techniques like UV, FTIR, XRD and SEM.
- Fabrication of SBR composites using unmodified and modified PSP as filler.
- To study the characteristics of composites of SBR with modified and unmodified PSP with reference to their
- cure characteristics
- mechanical properties
- morphological characteristics
- To study the thermal properties of the composites using TG and DSC
- To study the diffusion and transport properties of composites using the aromatic solvents (benzene, toluene, xylene) and

petroleum fuel (petrol, kerosene and diesel) at different temperatures.

- To study the oil resistance , oil aging and water sorption of the composites.
- To study the biodegradation behavior of the prepared composites under soil burial environment.

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CHAPTER 2

NATURAL FILLER REINFORCED COMPOSITES—A BRIEF REVIEW

Abstract : The work related to the mechanical, transport and biodegradability of the natural filler reinforced composites have been discussed.

2.1 INTRODUCTION

Many researchers reported the fabrication, properties and applications of the composites reinforced with the natural fillers. In the present study an attempt has been made to review the work related to the natural filler reinforced composites from 1989 to 2017.The review reveals that the studies on the composites of SBR reinforced with modified natural seed shell is less addressed and needs more attention.

2.2 REVIEW OF LITERATURE

Arumugam et al [1] fabricated the composites of treated and untreated coconut fibre with NR and their properties were analysed. They observed that the treated fiber imparts better physical properties to the rubber mixes than the untreated fiber. Prasantha Kumar et al [2] developed and characterized the mechanical properties of composites of styrene butadiene rubber (SBR) reinforced with short sisal fiber as a function of fiber length, orientation, loading, and bonding agent. The addition of short sisal fibers to SBR offered good reinforcement and causes improvement in mechanical properties which further gets strengthened by the presence of bonding agent. At 35 phr loading of sisal fiber, composite showed maximum properties, and mechanical anisotropy observed at this loading. Jayamol et al [3] analysed the influence of water environment, fiber loading, temperature and chemical treatment on the sorption characteristics of low-density polyethylene (LDPE) composites rein-forced with short pineapple leaf fiber (PALF). Water uptake was found to increase with fiber loading owing to the increased cellulose content. Sreekala et al [4] studied the influence of fibre surface modifications on the mechanical performance of oil palm fibre reinforced phenol formaldehyde composites. They modified the fibres through chemical modifications such as mercerization, acrylonitrile grafting, acrylation, latex coating, permanganate treatment, acetylation, and peroxide treatment. They observed that mechanical performance of the matrix was greatly enhanced by the chemical treatment of the fibre which led to composites having excellent impact properties. The treatment with silane leads to strong chemical linkage at the hydroxyl groups from cellulose fibre, hemicellulose and lignin with silane. This firmly bound chemical structure could withstand higher mechanical stresses and improves the tensile strength of the fibre. A similar effect was observed in acrylated fibre also. The brittleness of the fibres decreased on treatments. The Young's modulus and elongation at break of individual fibres increased upon modifications. Optimum mechanical performance was observed for silane treated and acrylated fibre.

Richa et al [5] studied the composites of phenol formaldehyde with silane treated and untreated oil palm fibre and they observed that the chemical treatment increased the thermal stability and mechanical properties of the composites. Rong et al [6] analysed the effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites. The chemical treatment such as alkalization, acetylation, cyanoethylation, the use of silane coupling agent and heating was carried out for modification of the fiber and its internal structure. Dipa ray et al [7] studied the effect of alkali treated jute fibres on composite properties. They observed that composites reinforced with alkali treated fibres showed improved mechanical properties. The improvement of mechanical properties was maximum for the composites prepared with 4 h treated fibres at 35% fibre loading. Hundiwale et al [8] compared the elastomer-filler interaction by reinforcing SBR with filler such as calcium carbonate, barium sulphate and fly ash. They observed that the waste product flyash can be used as potential substitute to calcium carbonate. Rajesh et al [9] studied the composites of acrylonitrile butadiene rubber (NBR) reinforced with short nylon fibre and they noticed that addition of nylon fiber to NBR offers good reinforcement and causes improvement in mechanical properties. Sombatsompop et al [10] investigated the effects of untreated precipitated silica (PSi) and fly ash silica (FASi) as fillers on the properties of NR-SBR compounds. Liu et al [11] observed the removal of hemicellulose and lignin on alkali treatment of grass fibers reduced the inter-fibrillar region of the fiber and also reduce the cementing force between fibrils. This led to a more homogenous dispersion of the biofiber in the matrix as well as increase in the aspect ratio of the fiber in the composites, resulting in an improvement in fiber reinforcement efficiency. This eventually led to the enhancement in mechanical properties including tensile and flexural properties as well as impact strength. Wanvimon et al [12] compared the effect of natural filler rise husk (RH) with commercial filler silica and carbon black (CB) on cure characteristics and mechanical properties of natural rubber materials at various loadings, ranging from 0 to 40 phr. The results indicated that RH filler showed lower Mooney viscosity and shorter cure time of the NR materials. The incorporation of RH into natural rubber improved hardness but decreased tensile strength and tear strength. Other properties, such as Young's modulus and abrasion loss showed no significant change. However, RH was characterized by a better resilience property than that of silica and CB. Haghighat et al [13] investigated the influence of cellulose powder on physicomechanical properties of SBR–cellulose composites, including tensile strength, elongation, Young's modulus, tear strength, hardness, abrasion, resilience and compression set before and after aging.

Joseph et al [14] analysed the environmental stability of chemically modified banana fiber reinforced phenol formaldehyde (PF) composites. They observed that the resistance of the banana/PF composites to degradation on outdoor exposure and soil burial improved through chemical modification of banana fiber by alkali, silane and acetylation treatments. Weyenberg et al [15] studied the properties of unidirectional flax fibre reinforced composites by using alkaline fibre treatment. This study proved that alkalization of flax fibres is a simple and effective method to enhance the fibre/matrix bonding with an epoxy resin. Mild, batch wise treatments resulted in significant increase in both longitudinal and transverse composite properties, due to improvement of the fibre/matrix adhesion.

Mwaikambo et al [16] studied the mechanical properties of alkali treated sisal fibres and their potential as reinforcement materials .They observed that the internal structure of sisal fibre can be modified using caustic soda up to a limit in order to improve its performance. The study has shown that the tensile strength and Young's modulus of sisal fibre bundles depends on the physical characteristics of its internal structure such as the cellulose content, crystallinity index and micro-fibril angle. The introduction of a rough surface facilitated mechanical interlocking with the resin-matrices resulting in enhanced interface while improved packing order of the crystalline regions formed by alkalization increases the tensile strength and stiffness of the sisal fibre making it suitable as reinforcement for the manufacture of composites [16]. They also investigated the influence of surface modification of hemp powder through alkali treatment using sodium hydroxide on reinforcing efficiency [17]. Lopattananon et al [18] analysed the effect of fiber surface treatment on the performance of composites of natural rubber with pinapple leaf. Different concentration of sodium hydroxide solutions and benzoyl peroxide were used to modify the surfaces of PALF. It was found that the adhesion and tensile properties increased by chemical treatment of fibres. The treatments with 5% NaOH and 1% benzoyl peroxide (BPO) provided the best improvement in composite strength (28 and 57% respectively) when compared with that of untreated fiber. The PALF-NR composites also exhibited better resistance to aging than its gum vulcanizate, especially when combined with the treated fibers. Idicula et al [19] investigated the influence of chemical modification on thermo physical properties of banana sisal hybrid reinforce composites. They observed that mercerization and polystyrene maleic anhydride (MA) treatments of sisal and banana fiber resulted in an increase of 43% in the thermal conductivity when compared with untreated composites. Mansour et al [20] studied the effect of chemical treatment such as NaOH, maleic anhydride(MA), maleic anhydride-glycidyl methacrylate (GMA) and silane coupling agent on wood flour to improve the dispersion in SBR/polystyrene (PS) composites. They observed that rheological as well as the mechanical parameters under investigation were improved by loading the SBR/PS with different wood flour concentrations with optimum filler loading of 15 phr. An important increment in particle dispersion was obtained by modifying the wood flour with MA and GMA.

Rahman et al [21] studied the impact on the mechanical and degradable properties of photo grafted oil palm fibers through surface modification. They pretreated the fiber surface by alkali, $KMnO_4$ and then grafted by allyl methacrylate to determine the effect of various surface treatment on the physicomechanical properties of grafted fibers. They observed that the alkali treatment increased the surface roughness with better impregnation of the polymer, which increased the tensile properties by about 20%. A minute amount of an additive (urea) and a coupling agent (silane) were added to the optimum formulations. These increased the physical properties of the grafted oil palm fibers because of increased crosslinking. They also observed the degradation under various weather conditions which were lower for treated fibres than untreated fibers. Zafeiropoulos et al [22] studied the effect of surface treatments on the tensile strength of flax fibres. This study focuses on the influence of two pretreatments such as acetylation and stearation upon the tensile strength of flax fibres. The results were discussed in terms of Gaussian statistics and it was found that the treatments did not significantly change the flax fibre tensile strength. In addition, the treatment changed the bulk properties along with the surface properties proved from the SEM analysis of fractured surface of acetylated fiber. The impact of different chemical treatments on the properties of flax fiber-reinforced rotationally molded composites was studied by Wang et al[23]. Benzoylation, peroxide treatment and alkylation were the chemical modifications carried out in this study. They observed an improvement in interfacial adhesion of the composites of polymer matrix with modified fibres. Sreekumar et al [24] analysed the mechanical and water-sorption of ecofriendly banana fiber-reinforced polyester composites fabricated by RTM. Monteiro et al [25] evaluated the structural characteristics and mechanical properties of coir fibre reinforced polyester composites.

Jie et al [26] studied the effect of hemp powder loading on cure characteristics and mechanical properties of filled SBR and Ethylene propylene diene monomer (EPDM) composites using coupling agent bis-(3-ethoxysilylpropyl) tetra sulfide. The results indicated that the addition of hemp powder facilitated the vulcanization process and improved the mechanical properties and storage modulus considerably, but the filler loading above 30 phr resulted in drastic deterioration of properties. They concluded that addition of 30 phr hemp powder was recommended as an economical and ecological benefit to industries for obtaining good properties of rubber composites reinforced by hybrid filler. Yeng Fong et al [27] studied the mechanical and thermal properties of biodegradable green composites of polylactic acid (PLA) reinforced with banana fiber modified by triethoxy vinyl silane (TVS). They observed that the conjugation of modified banana fibre to the PLA chain substantially raised the compatibility and stability of PLA, resulting to elevate mechanical properties and thermal stability of composites. .

Debapriya et al [28] investigated the cure characteristics and mechanical properties of SBR composites with reclaim rubber. Their results indicated that minimum torque and viscosity of the compounds increased with increasing reclaim rubber but cure time exhibited decreasing trend. The modulus, tensile strength and elongation at break also increased on filler loading but it gives better resistance towards swelling. Ismail et al [29] analysed the effect of chitosan loading on the curing characteristics, mechanical and morphological properties of chitosan-filled NR, epoxidised natural rubber (ENR) and SBR compounds. The results indicated that, overall, the scorch time, cure time, tensile strength and elongation at break decreased with chitosan loading, whereas an increment observed in the maximum torque and the tensile modulus (M100 and M300) of all three types of rubber. Haque et al [30] also investigated the influence of fibre surface modification on the mechanical and surface morphological properties of coir reinforced polypropylene composites. The study revealed that better interfacial adhesion as well as minimization of microvoids at the interface occurred upon chemical treatment of fiber, improved the mechanical properties and reduced the water absorption of composites.

El-Sabbagh et al [31] investigated the effects of core-shell kaolin–m et al oxide pigments on the rheological, physicomechanical and dielectric properties of SBR composites. They observed that CaO/kaolin optimum loading in SBR vulcanizates was 40 phr, while that of MgO/kaolin was 2.5 phr. Also, it can be observed that, CaO/kaolin showed the best properties among the prepared pigments, while the mixed oxide MgO/CaO/kaolin showed the least properties but was better than kaolin. The dielectric properties revealed that SBR containing MgO/kaolin and MgO/CaO/ kaolin showed promising dielectric properties with low relative permittivity and electrical insulating properties. Sareena et al [32] developed the composite of natural rubber with untreated and alkali treated coconut shell powder and analysed their cure characteristics and mechanical properties in two particle sizes. They observed that the coconut shell powder is most effective filler in NR at 10 phr loading and better physicomechanical properties shown by composites with modified coconut shell powder. Sareena et al [33] also analysed the cure characteristics and mechanical properties of composites of NR with using unmodified and alkali modified peanut shell powder(PSP). In this study also better properties were shown by composites with alkali modified PSP at 10 phr filler loading.

Onyeagoro et al [34] studied the cure characteristics and mechanical properties of carbonized bamboo fibre filled natural rubber vulcanizates. They observed an increasing trend in specific gravity with increase in filer loading and decrease in particle size. Ismail et al [35] evaluated the curing characteristics and mechanical properties of rattan powder filled natural rubber composites as a function of filler loading and silane coupling agent. They observed that silane coupling agent increased the maximum torque, minimum torque, tensile modulus, tensile strength etc compared with NR composites without silane coupling agent. The reason was attributed to improved bonding of filler with rubber matrix. Mohan et al [36] studied the chemical treatment of sisal fibre using alkali and clay method. The analytical results revealed that the fibre-matrix compatibility, interface strength, adhesion, glass transition temperature and tensile properties of composites were improved through NaOH –clay treatment of fibre. Salmah et al [37] analysed the surface modification of coconut shell powder (CSP) filled PLA biocomposites. They observed that surface modification of CSP using acrylic acid improved the filler-matrix interaction and thus improved the tensile strength, modulus of elasticity and thermal stability of PLA/CSP biocomposites. Kaushik et al [38] studied the effect of mercerization and benzoyl peroxide treatment on morphology, thermal stability and crystallinity of sisal fibers. They concluded that morphology of sisal fiber was changed by chemical treatments. The surface of a sisal fiber became rougher after treatments in comparison with smooth and clear surface of raw sisal fibers. The removal of surface impurities on plant fibers may be an advantage for fiber to matrix adhesion as it may facilitate both mechanical interlocking and the bonding reaction due to the exposure of the hydroxyl groups to chemicals such as resins and dyes. Berki et al [39] compared the properties of SBR containing pyrolytic carbon black (PCB), conventional carbon black (CB) and organo clay. They discussed the effects of the compositions on the filler dispersion, cure behavior, dynamic mechanical thermal parameters (including the Payne effect), tensile mechanical (including the Mullins effect) and fracture mechanical (making use of the J-integralconcept) properties. Though PCB had a higher specific surface weight than CB, the latter proved to be a more active filler with respect to the tensile strength. The opposite tendency was found for the tear strength and fracture mechanical characteristics. This was traced to an enlargement in the crack tip damage zone supported by the dispersion characteristics of the PCB. The performance of PCB was similar to that of CB with respect to some other properties. Organo clay supported the filler networking which positively affected the resistance to crack initiation. Zhao et al [40] analysed the influence of particle type and silane coupling agent on properties of silica and carbon-filled SBR. Minimum torque, maximum torque and tensile strength increased with increase in the filler content.

Chun et al [41] investigated the effect of filler content and chemical modification on the mechanical properties, thermal properties, and morphology of PLA/CSP ecocomposites. They observed that treated composites with maleic anhydride improved the tensile strength, modulus of elasticity, glass transition temperature and thermal stability of PLA/CSP ecocomposites. The improvements in mechanical and thermal properties were attributed to the enhanced interfacial bonding between CSP and PLA matrix.

Singha et al [42] evaluated the damping properties of jute/epoxy polyester composites using chemical treated jute fibre. They noticed that performance of the composites was influenced by the surface properties of the fibres and surface treatment like alkali, permanganate, benzoyl chloride, maleic anhydride and silane. The better intersystem crossing caused for improvement in the mechanical properties of the composites in comparison to composites reinforced with untreated fibres. Dhanalakshmi et al [43] observed that the chemical modification such as mercerization, permanganate treatment, benzoylation, acrylation and acetylation are very important to increase adhesion between the hydrophilic fibers and hydrophobic matrix due to the formation of covalent bond between the fiber and matrix through chemical modification of natural fibers. The chemical bonding facilitated the enhancement of properties of chemically treated natural fiber reinforced polymer composites. Debasish et al [44] studied the effect of grass fiber loading of different mesh sizes and the effect of silane coupling agent on curing characteristics and mechanical properties of NR.

Rosane [45] analysed the thermal properties of composites based on soy protein and corn starch. Films from corn starch were less thermally stable than soy protein films. The films containing both components had lower thermal stabilities when compared to those of the pure biopolymers. El-Nemr [46] analysed the thermal properties of composites of SBR with waste news print fibres, in which TG results indicated that the thermal stability of fibres was enhanced by chemical treatment and irradiation. Yussuf et al [47] compared the thermal stability of PLA with kenaf and PLA with RH composites. It has been found that the addition of natural fibres decreased the thermal stability of matrix and decrement was more prominent in the PLA-RH composites. Julien et al [48] observed that lower oneset degradation temperature in the bagass cellulose whiskers reinforced NR nanocomposites could be due to lower oneset degradation temperature of filler than rubber. The DSC results revealed that no significant effect in Tg of rubber by reinforcing filler. Vishak et al [49] analysed the thermal stability of crab chitin reinforced carboxylated SBR composites, the filler content did not substantially affect the thermal stability of the matrix

George et al [50] studied the influence of crosslink type and crosslink density on the swelling and mechanical behavior of SBR membranes in four aliphatic hydrocarbons. Mathew et al [51] investigated the effect of fibre loading on the swelling behavior of the isora and natural rubber composite in oils like petrol, diesel, lubricating oil etc. The % swelling index and swelling coefficient of the composite were found to decrease with increase in fibre loading. Ranimol et al [52] investigated the effect of penetrant size, filler loading and temperature on the diffusion properties and transport properties of aromatic solvents such as benzene, toluene and *p*-xylene through micron sized fillers reinforced natural rubber, carboxylated styrene butadiene rubber and their 70/30 blend latex membranes. They observed that the filled samples showed reduced swelling of rate and dramatic decrease in diffusion coefficient. The activation energy needed for diffusion of penetrant was found to be higher for filled virgin polymers. They also analysed [53] the solvent resistance properties of nano-structured layered silicates filled NR, carboxylated styrene butadiene rubber (XSBR) and their 70/30 latex blend and these were investigated by equilibrium swelling method using benzene, toluene and *p*-xylene. Priya Dasan et al [54] also analysed the cure characteristics and solvent transport behavior of carbon black filled EVA using benzene, toluene and xylene as penetrant molecules. They concluded that the maximum torque of the composites exhibited a decreasing trend with increasing particle size and an increasing behaviour with the content of filler. The solvent uptake trend of EVA has been observed to be reduced by carbon black incorporation.

Bharath et al [55] investigated the biodegradable property and swelling properties of different volume fraction of randomly distributed areca fibre and maize powder reinforced urea formaldehyde composites. They concluded that the composite were biodegradable, exhibits good moisture resistance and proved to be promising materials for packaging and other engineering and domestic applications. Balachandran et al [56] analysed the properties of nitrile rubber (NBR)-nanoclay composites prepared by a two-step method. viz. preparation of a 3:1 [by weight] masterbatch of NBR and nanoclay followed by compounding on a two roll mill and molding at 150 °C and 20 MPa pressure. The tensile strength, elongation at break, modulus, storage modulus (E′) and loss modulus (E″) increased with the nanofiller content, reached the maximum value at 5 phr and decreased thereafter. The solvent uptake, diffusion, sorption and permeation constants decreased with nanoclay content with the minimum value at 5 phr nanoclay. The mechanism of solvent diffusion through the nanocomposites was found to be Fickian. Ajith Kumar et al [57] investigated the mechanical and barrier properties of the bio composites from ecoflex and ramie fabric. They also analysed sorption characteristics of water, oil and diesel in the textile composites in order to determine its outdoor applications and the influence of macro fibers on the transport phenomena.

Sareena et al [58–60] studied the solvent swelling characteristics of natural rubber composites containing both untreated and alkali-treated CSP in three, aromatic organic solvents (benzene, toluene, and xylene) by conventional weight-gain experiments. They also investigated the transport properties of composites of NR with alkali treated and untreated PSP powder in aromatic solvents and chlorinated solvents (dichloromethylene, cholorform and carbon tetrachloride) at different temperature by conventional weight gain experiments. They discussed the solvent properties in terms PSP content, particle size, nature of solvent, and temperature. They observed that the diffusion coefficient decreases with increase in filler content and on modification, increases with increase in temperature.

Muniandy et al [61] investigated the biodegradation of rattan powder filled NR composites as a function of filler loadings and silane coupling agent by burying the sample in soil for six months, the degradation was evaluated through weight loss and tensile testing. Chun Li et al [62] investigated the effect of methyl methacrylate (MMA) and starch concentration on the mechanical properties, morphology, toluene swelling behavior, water absorption behavior and biodegradability of PMMA-modified starch/SBR biocomposites. Klungsuwan et al [63] studied mechanical properties and biodegradability of cuttlebone/NR composites. They analysed the degradation of the NR vulcanizates in both landfill and liquid bacterial culture assays and revealed that cuttlebone/NR green composite materials could be degradable within 3 months and 8 weeks, respectively. Buenaventurada P et al[64] studied the effect of silane treatment on the mechanical properties, thermal stability, and biodegradability of poly(butylene succinate) composites reinforced by cotton fibe(CF). They observed that the incorporation of CF (with and without silane treatment) in PBS significantly increased the biodegradation rate of the composites. Sareena et al [65] studied the biodegradation behavior of natural rubber reinforced with natural filler by soil burial test. They observed that the tensile strength and hardness were decreased after soil burial testing due to the possible biological attack by microbes onto the samples

The interaction of fly ash (FA) on dichlorocarbene modified SBR (DCSBR) was evalu- ated by Ramesan [66] with reference to their flame and oil resistance. Flame and oil resistance of the composites increased progressively with increasing filler content in DCSBR. The barrier properties of these composites were examined in an atmosphere of petrol, diesel and kerosene. Ramesan et al [67] also analysed the effect of fly ash on thermal stability, flammability, oil resistance and transport properties of chlorinated styrene butadiene rubber composites. Iheoma et al [68] studied the sorption characteristics of cornhub powder (carbonized/uncarbonized) filled NR/NBR using an aromatic solvent. They observed that the percentage swelling index and swelling coefficient of the composites were found to be decreased with increase in filler loadings and this shows an increased hindrance exerted by the fibre. Jiji et al [69] investigated the transport behaviour of some aromatic and aliphatic solvents through carbon nanotube filled styrene butadiene rubber composites as a function of CNT content, nature of solvent and temperature. Peng Yu et al [70] studied the enhanced oil resistance and mechanical properties of NBR /lignin composites modified by epoxy resin. Gejo et al [71] analysed the influence of fiber content and chemical modifications on the transport properties of PP/Jute commingled biocomposites. They observed that the rate of diffusion and apparent weight gain % for the solvents toluene and xylene decreased with increasing jute content and the untreated sample had the highest rate of diffusion. They also compared apparent weight gain % with treated composites.

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CHAPTER 3
MATERIALS AND EXPERIMENTAL METHODS

Abstract: The specifications of the materials used and the experimental methods followed in the present investigation are given in this chapter. The characteristics of the materials and methods for surface modification of filler and characterization techniques such as UV-visible spectroscopy, FTIR, XRD, TG, DSC and SEM have been discussed. The formulations of the composite and sample preparation techniques also have been discussed. The methodologies for the examination of the cure characteristics, mechanical properties, morphological features, transport studies, oil resistance, thermal properties and biodegradation studies of the composites are given.

3.1 MATERIALS

3.1.1 Peanut shell (Arachis hypogaea)

Figure 3.1 Peanut shell

Peanut shell is agricultural waste material in crop industry and purchased from Peanut Industria Firm, Chennai. Peanut shell was dried and powdered in rice flour mills locally. The chemical composition of peanut shell powder (PSP) [1] is as presented in the **table 3.1.**

Table 3.1 Chemical composition of PSP [1]

Composition	weight%
Cellulose	44.8
Hemi cellulose	5.6
Lignin	36.1
Organic matter	4.2
Ash content	3.8
Crude proteins	5.4
Crude fat	0.1

3.1.2 Chemicals used for surface modification of filler

The chemicals used for the pretreatment of peanut shell powder NaOH, ethanol, acetic acid and acetone were of analytical purity purchased from Merck India. Triethoxy vinyl silane and maleic anhydride were purchased from Sigma Aldrich.

3.1.3 Styrene butadiene rubber

Styrene-butadiene rubber (SBR) used was SBR 15O2 with 75% butadiene **(figure 3.2)** content and was purchased from Synthetic and Chemicals Ltd. India. It is a general purpose synthetic rubber and derived from styrene and butadiene. The styrene/butadiene ratio influences the properties of the polymer. The high loading capacity, good flex resistance, crack initiation resistance and abrasion resistance of SBR make it useful in several engineering and industrial applications.

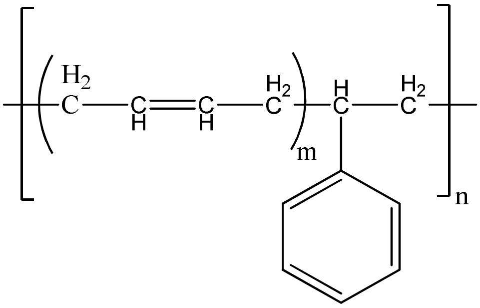

Figure 3.2 Structure of SBR

3.1.4 Chemicals for vulcanization

The vulcanizing agents used for cross linking the matrix were elemental sulphur with specific gravity 1.9. Other compounding ingredients such as zinc oxide, Stearic acid, 2,2,4-trimethyl-1,2-dihydroxyquinoline (TDQ), N,cyclohexyl-2-benzothiazyl sulphenamide (CBS) were of commercial grade and obtained from local suppliers. Zinc oxide and stearic acid act as activators, TDQ as antioxidant and CBS as accelerator during vulcanization.

3.1.5 Solvents

The organic liquids used in this work such as benzene, toluene, xylene were obtained from Merck (India) Ltd. They were of reagent grade (99 % pure) and were distilled twice before use to ensure purity. The fuels petrol, kerosene and diesel used were of commercial grade, obtained from Indian oil corporation. The physical properties of the liquids used are given in **table 3.2**

Table 3.2 Physical properties of the Solvents

Solvent	Molecular Weight(g/mol)	Density (g/cm^3)	Boiling Point(°C)
Benzene	78.11	0.878-0.879	79
Toluene	92.14	0.857-0.864	109-112
Xylene	106.17	0.85-0.87	137-143
Petrol	80-100	0.710-0.737	70-180
Kerosene	150-170	0.810-0.817	140-230
Diesel	170-330	0.820-0.950	240-350

3.2 EXPERIMENTAL METHODS

3.2.1 Sample preparation

3.2.1.1 Surface modification of filler

Peanut shell was powdered well and dried in an air oven at 70 °C, it was sieved through 93 micron size mesh and 53 micron size mesh to obtain unmodified filler in two particle sizes range ie 53-90 µm and <53 µm .Initially the pretreatment of filler was done by 5%

NaOH using mechanical stirrer. The alkali treated PSP (APSP) was subjected to silane modification using triethoxy vinyl silane to form silane modified PSP (SPSP). The alkali treated PSP was also modified by maleic anhydride to form maleic anhydride derivative of PSP (MPSP). The chemically modified PSP was powdered well and sieved through 90 and 53 micron size mesh to form modified PSP in two ranges of particle sizes 53-90 µm and <53 µm respectively.

Alkali treatment: PSP (10g) was added to 5% NaOH solution (10 mL) for 5 h with continuous stirring using a mechanical stirrer and was kept for 24 h. Washed with distilled water until it became neutral which was filtered and dried in air oven at 60 °C for 24 h [1–3].

Silane treatment: The alkali treated fibres were digested with triethoxy vinyl silane (1%, w/w) and dicumyl peroxide (0.5%, w/w) in 90% methanol (250 mL) solution. The pH of the solution was adjusted to 3.5–4 using acetic acid. The solution was stirred continuously for 1 h and kept for 2 h and then washed with distilled water and dried [2,4].

Maleic anhydride treatment: Maleic anhydride (5 % w/w) and acetone was added to a round bottom flask containing pre dried APSP, maintaining fibre to solution ratio of 1:20 by weight. The mixture was refluxed on a heating mantle maintained the temperature at 65 °C for 3 h. Thereafter, the fibres were separated from the solvent and washed with acetone to remove untreated maleic anhydride. Finally the treated fibres were washed thoroughly with water and then dried in an oven at 80 °C for 48 h [5].

3.2.1.2 Fabrication of composites of SBR with modified and unmodified PSP

All components in the composites have same composition except in the amount of filler, which were varied in the range 0-20 parts per hundred rubber (phr), that is 0, 5,10,15 and 20 phr. Mixing formulation of the composites are given in the **table 3.3**.The rubber was masticated and all chemicals used for the mixing was powdered, dried well and weighted accurately. Compounding was carried out on a two roll mixing mill in accordance with ASTM-D15-627. Total mixing time was at a minimum in order to avoid sticking of the rubber compound to the mill rolls. Care was taken to ensure that the mill roll temperature at room temperature to avoid any cross linking during mixing. This has been achieved by cooling with water. The conditions were kept constant for all the composites. The samples were coded as B for composites without filler, U and R for composites with unmodified PSP (UPSP) in the particle size < 53 µm and 53-90 µm respectively, S and T for composites with SPSP in particle size < 53 µm and 53-90 µm respectively, M for composites with MPSP in the particle size < 53 µm. 5, 10, 15 and 20 are given as subscript in sample code depends on the amount of filler used.

Table 3.3 Mixing formulation of the composites

Ingredients	Phr
SBR	100
Zinc oxide	5
Stearic acid	2
Trimethyl dihydroxy quinoline (TDQ)	1
Processing oil	1/20th filler
Filler(PSP)	5,10,15,20
Cyclohexyl benzothiazyl sulphenamide (CBS)	2
Sulfur	2.4

3.2.1.3 Cure characterisitics

Cure characteristics like cure time, scorch time, maximum torque and minimum torque for each compound were determined by using Oscillating Disc Rheometer (ASTM D-5289) operating at 160 °C. The minimum torque, maximum torque scorch time and cure time were determined from the rheographs.

3.2.1.4 Vulcanization of mixed samples

The rubber composites were vulcanized at 160 °C in hydraulic press to the optimum cure time to form moulded sheet with 2 mm thickness using hydraulic press under a pressure of 6.7 MPa. (Mould dimension: 150x150x 2 mm^3). The vulcanized sheets were conditioned for 24 h at room temperature. From the moulded sheets, appropriate samples were cut to make the test specimens for measuring mechanical properties and for sorption experiments.

3.2.2 Mechanical properties

3.2.2.1 Tensile properties

Dumbell shaped samples were used for the measurement of tensile properties of the composites. The thickness of the narrow portion was measured using thickness gauge at three portions and their average values were taken for measurement of tensile properties. The tensile strength, elongation at break, modulus and tear strength were examined on a Universal testing machine at a cross head speed of 500 mm/min and at 25 ± 2 °C.. The tensile properties were examined after conditioning the sample (dumbell shaped sample) at room temperature according ASTM D-412 test method. Instrument software along with equipment calculates the tensile properties.

Tensile strength: Tensile strength is the measurement of the force required to pull something such as rope, wire or structural beam to the point where it breaks. It can be calculated by the equation

$$Tensile\ strength = \frac{Force(load)(N)}{Area\ of\ cross\ section(mm^2)} \qquad (3.1)$$

Elongation at break: Elongation at break, also known as fracture strain, is the ratio between changed length and initial length after breakage of the test specimen. It expresses the capability of a material to resist changes of shape without crack formation.

$$Elongation\ at\ break = \frac{Change\ in\ length\ (elongation)}{Original\ length(Gauge\ length)} \qquad (3.2)$$

3.2.2.2 Tear strength

The tear strength of the samples was determined by using unnicked 90° angle test pieces according to ASTM D-624 (2007) test method. The instrument and the experimental conditions were the same as in the case of tensile testing. The tear strength measures how well a material can withstand the effect of tearing. The tear strength is taken as the force per unit thickness of test piece required to cause a nick cut in the test piece to extend until the test piece is broken or torn. It can be calculated by the equation

$$Tear\ strength = \frac{Ultimated\ load(N)}{Thickness(m)} \qquad (3.3)$$

3.2.2.3 Hardness

Hardness of a material is generally measured by its resistance to local deformation or indentation by a rigid body of a specified dimension under a specified condition. Hardness is a complex property and it is related to mechanical properties such as modulus, strength, elasticity and plasticity. It is a relative concept and it cannot be absolutely defined. Hardness testing is particularly useful in getting an indication of degree of cure in rubber vulcanization. Hardness was measured at room temperature by using a Shore–A hardness tester according to ASTM D 2240-2004.This measures the depth of indentation under load when a hardened steel indenter is forced into specimen by means of calibrated spring. The presented data are average of ten values obtained from different part of same sample.

3.2.2.4 Abrasion resistance

Abrasion is a mechanical property and it is closely related to friction. Abrasion may result in physical damage of surface and built up of high temperature locally at points of abrasion or friction is often accompanied by chemical attack such as oxidation, in some cases which results in embrittlement and wear that is commonly taken as abrasion loss. Abrasion loss is generally the volume abraded in a given time or over a given length of abrasion path and is expressed in the unit mm^3. It was evaluated by pressing a test specimen of specified dimension against a rotating abrasive surface by a constant force. Abrasion resistance was measured using A Zwick Din Abrader as per ASTM D-2228(1994).

3.3 CHARACTERIZATION TECHNIQUES OF THE SAMPLE

3.3.1 FTIR spectroscopy

FTIR spectra were recorded in the range of 4000–400 cm^{-1} with a JASCO FTIR-4100 spectrometer.

3.3.2 UV-Visible spectroscopy

The UV spectra were obtained using Shimadzu UV-2600 UV-VISIBLE Spectrophotometer.

3.3.3 X-ray diffraction analysis

X-ray diffraction studies were performed by using Rigaku miniflex -600 diffractometer with Cu K∞ (λ=1.54 A^0). The samples were scanned at 2θ range of 10 to 80^0, and a step size of 0.02^0 was used for the analysis.

3.3.4 Morphological studies

The morphological observations of the filler and the composites were done by a Field Emission Scanning Electron Microscopy (SEM), model Hitachi, SU 6600 FESEM. The samples were sputtered with gold before examination to prevent charging on the surface and examined under the microscope.

3.3.5 Thermal properties

Thermogravimetry of the samples were carried out by TG instrument TA Q50 under nitrogen atmosphere. The samples were heated from room temperature to 750 °C at a heating rate of 10 °C/min. From the TG curves, the thermal degradation characteristics and temperatures at different weight losses and residual weight in percentages were evaluated.

DSC analysis was carried out by TA instrument DSC Q100 V9.9 Build 303.The sample was heated at a rate of 10 °C/min in nitrogen atmosphere. The sample was inserted into the apparatus and quenched to –100 °C and the DSC scan was taken from -100 °C to 50 °C at a heating rate of 10 °C/min in nitrogen atmosphere.

3.4 SORPTION EXPERIMENTS

Circular samples of diameter 2 cm were punched from the vulcanized sheet using standard die and were dried in vacuum desiccator for 24 h. The initial weight and thickness of the sample were measured before sorption experiments. They were immersed in 20 mL solvents taken in closed sorption bottle and kept at constant temperature in air oven. The samples were periodically removed from the bottles; the adhering solvent removed by using tissue paper and weighed using electronic balance (Shimadzu, Libror AEU-210 Japan) that measured reproducibility within ± 0.0001 g. The samples were then immediately replaced into the diffusion bottle. The experiment was continued until the equilibrium swelling was attained. The weighing was carried out within 40 sec to minimize the possible error due to the removal of samples from the solvents [6,7]. Similar methodology (ASTM D-471) was reported earlier [8–10]. The experiments were repeated using different solvents at different temperatures.The results of sorption experiments are expressed as percentage of solvent sorbed by 0.1kg of composite sample (Qt). The Qt values obtained thereby were plotted as a function of square root of time, to construct the sorption curves [6,8,11,12].

3.4.1 Kinetic parameters

3.4.1.1 Diffusion coefficient

Diffusion coefficient (D) is a kinetic parameter related to the polymer segmental mobility, penetrant nature and to the different crosslinks present in a polymer matrix [10].

3.4.1.2 Sorption coefficient

The sorption coefficient (S) is mathematically defined as the ratio of the mass of the solvent taken up at equilibrium swelling to the mass of the sample [13]. It gives a measure of the extent of sorption [14]. It is a kinetic parameter which depends on the strength of the interactions in the polymer with the penetrant [15].

3.4.1.3 Permeation coefficient

The permeability or permeation coefficient (P) of a penetrant in a polymer membrane depends on the diffusivity as well as solubility or sorption of the penetrant in the polymer membrane [16]. It gives an idea about the amount of solvent permeating through uniform area of the sample per second. The permeability coefficient (P) is mathematically defined as the product of the diffusion and sorption coefficients [14] .

3.4.2 Arrhenius parameters.

3.4.2.1 Activation energy for diffusion (E$_D$ and E$_P$)

Diffusion and permeation are considered to be activated by temperature and hence it is relevant to estimate the activation energy for diffusion (E$_D$) as well as that for permeation (E$_P$) [17]. The values of D and P at different temperatures were used to estimate the activation energy for diffusion. . From the difference between E$_P$ and E$_D$, the heat of sorption, ΔH, was estimated.The values of ΔH give additional information about molecular transport through polymer matrix [17] .

3.4.3 Thermodynamic parameters

The thermodynamic parameters for diffusion ΔH, change in entropy (Δ S) and change in free energy (ΔG) are calculated and interpreted using fundamental principles of thermodynamics.

3.5 OIL RESISTANCE OF COMPOSITES

The experiment was carried out by the same way as that of solvent sorption (ASTM D-471). The preweighed circular samples with definite thickness were immersed in a IRM 901, 902, 903 oil at 30 °C and 100 °C for 72 h. The test specimens were then removed from the oil, dipped in acetone, then wiped with tissue paper to remove the excess oil from the surface, and change in mass after oil immersion was calculated.

Oil resistance is the reciprocal of the degree of swelling in oil and is governed by the competition between the driving force towards ‘‘dissolution of the rubber in the low-molecular-weight oil’’, i.e .swelling, and the elastic force which increases upon oil uptake [18].

3.6 OIL AGING OF COMPOSITES

The dumbbell shape test specimens were immersed in IRM 901 oil at room temperature for 72 h. Thereafter, we removed the specimens were removed from the oil, wiped of the excess oil on the specimen surfaces. The change in tensile strength of the samples after oil immersion is used to determine the oil resistance. In this study, the relative tensile strength (TSrel) is calculated from the ratio of tensile strength after oil immersion to that before oil immersion, was used in order to eliminate the mastication effect probably taking place during mixing process.

$$\mathrm{TS_{rel}} = \frac{\mathrm{TS_{after}}}{\mathrm{TS_{before}}} \qquad (3.4)$$

.where $\mathrm{TS_{before}}$ and $\mathrm{TS_{after}}$ are tensile strength of specimens before and after oil immersions, respectively [19].

3.7 BIODEGRADATION STUDIES OF COMPOSITES

3.7.1 Soil burial test.

SBR composite reinforced with UPSP and SPSP samples of hardness with 6 mm thickness were weighed and buried in garden soil. After three and six months, samples were withdrawn from the soil, washed with water and dried in the oven. Biodegradation behavior was evaluated on the basis of weight loss and hardness.

Dumbell shaped samples with thickness 1.89 mm were cut from the vulcanized sheets, weighed and measured the tensile strength. The preweighed samples were buried in the garden soil for six months. After six months the samples were taken off from the soil, washed and dried in oven. The weight loss and tensile strengths were measured [20,21]. Degradation behavior of soil buried samples was also evaluated from SEM morphology of the sample buried in the soil.

3.8 WATER SORPTION EXPERIMENTS

The extents of biodegradability of the samples were checked by water sorption test. The samples were immersed in distilled water and the percentage weight change was determined until the equilibrium value was reached. After immersion in distilled water, specimens were removed at different times, wiped with tissue paper to remove excess water and weighed with an analytical balance with 0.1 mg resolution. The percentage of weight gain was then calculated [22].

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CHAPTER 4

MODIFICATION OF PEANUT SHELL POWDER (PSP) AND ITS CHARACTERIZATION

Abstract : Peanut shell is one of the major agricultural waste materials and their use as reinforcement material in the fabrication of composites is very attractive. Major disadvantages of the use of PSP are its hydrophilic character. Hence surface modifications are necessary to develop composites with hydrophobic matrix. Surface modifications of PSP was done by coupling agent, triethoxy vinyl silane (TVS) and maleic anhydride (MA) and they were characterized by UV-Visible spectroscopy, FTIR, XRD, TG, SEM and TEM. The detailed analysis of UV and FTIR spectra reveals the exposure of cellulose to the surface and decrease in the concentration of hydrogen bonding. The removal of lignin, hemicellulose etc on modification was supported by the increase in crystallinity observed from XRD. This has been further confirmed by SEM and TG studies.

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4.1 INTRODUCTION

Natural filler reinforced composites developed from organic products show better performance compared to synthetic fillers and they are having the properties such as enhanced biodegradability, combustibility,light weight, non toxic nature decreased environmental pollution, low cost, and recyclability, etc. These added advantages makes the natural fibre composites among the high performance composites [1–5]. Composites of petroleum based matrix reinforced with natural fillers from waste material to develop cost effective products with diverse application is an alternative choice to reduce already depleting petroleum resources. The seed shells of various crops which are usually discarded as wastes, used as natural filler is one attractive and efficient solution for better reuse of the resources. Inspite of its several merits, these natural fillers have inherent drawbacks such as poor wettability, incompatibility with some polymeric matrices, high moisture absorption by the fibres and hence only poor adhesion with polyer matrix. These properties affect the interior strength of the composites. Major reason for the poor compatibility of these seed shells lies with the hydrophobic and non polar nature of matrix whereas the natural fibres and seed shells are hydrophilic and polar in nature. Another important drawback is the high moisture absorption of natural fibers leading to swelling and the presence of voids at the interface, which results in poor mechanical properties and reduces dimensional stability of composites [6–12]. Other restriction to the successful exploitation of natural fibers for durable composite application is the low microbial resistance and susceptibility to degradation. These properties pose serious problems during shipping, storage and composite processing. Surface modification of fibre or seed shell is an attractive alternative to overcome this problem. Many researchers reported that the surface modification through alkali treatment and reaction with coupling agent increase the interfacial bonding with the matrix and this process improves the overall performance of the composites. Certain reagents may activate hydroxyl groups of the fillers or introduce new moieties that can effectively interlock with the matrix. Suggesting a definite theory for the mechanism of bonding by chemicals in composites is a complex problem. Generally, chemical coupling agents perform two functions. The first is the reaction of hydroxyl groups of cellulosic part of the filler and the second is the reaction of the derived group with functional groups of the matrix [12-20].

Joseph et al. studied the environmental durability of chemically modified banana fiber reinforced phenol formaldehyde (PF) composites. They observed that silane, sodium hydroxide and acetylation treatments improved the resistance of the banana/PF composites on outdoor exposure and soil burial [14]. Mohan et al[15] studied the chemical treatment of sisal fibres using alkali and clay. The analytical results revealed that the fibre-matrix compatibility, interface strength, adhesion, glass transition temperature and tensile properties of composites were improved through NaOH--clay treatment of fibre. Richa et al [16] studied the composites of phenol formaldehyde with silane treated and untreated oil palm fibre and they observed that the chemical treatment increased the thermal stability and mechanical properties of the composites. Activation energy and crystallization kinetics of untreated and treated oil palm fibre reinforced phenol formaldehyde composites have also been studied. Rong et al [17] investigated the effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites. Treatments including alkalization, acetylation, cyanoethylation and the use of silane coupling agent were carried out to modify the fiber surface and its internal structure. Sareena et al [18] studied the effect of modification of PSP by sodium hydroxide on the mechanical properties of composites with NR. However, no serious studies were carried out to exploit the potential of surface modification of PSP, which is usually discarded as agricultural waste and the same for composite fabrication using SBR.

Therefore, the present chapter highlights the surface modification of PSP by chemical treatments using two important coupling agent triethoxyvinyl silane (TVS) and maleic anhydride (MA). After chemical modification, they were characterized using differential spectral and analytical techniques as, UV-visible spectroscopy, FTIR, XRD, TG, SEM, TEM and DLS.

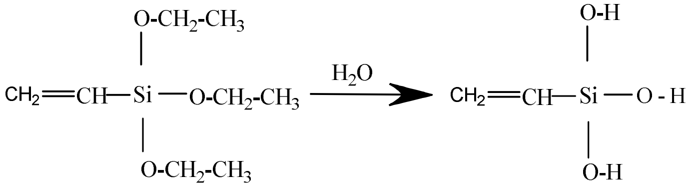
4.2 RESULTS AND DISCUSSION

4.2.1 Chemical treatment of Peanut shell powder

The PSP powder was dried and pretreated with NaOH to get alkali treated PSP (APSP). Then the APSP was treated with triethoxy vinyl silane to develop silane treated PSP (SPSP) and washed and dried to form SPSP in two particle size.

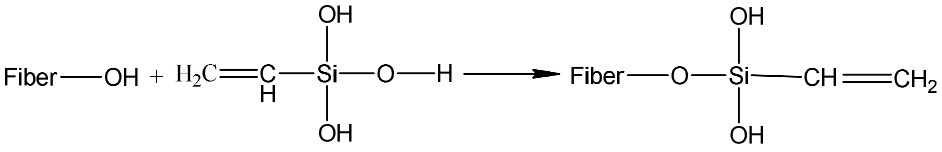
The reaction occurring during alkaline treatment and silane modification can be shown as in **scheme 4.1**[19].

Fibre-OH + NaOH$\longrightarrow$ Fibre-ONa + NaOH (Alkaline pretreatment to activate fibre hydroxyl groups for silane modification)



$$CH_2{=}CH{-}\overset{\displaystyle O\text{-}CH_2\text{-}CH_3}{\underset{\displaystyle O\text{-}CH_2\text{-}CH_3}{Si}}{-}O\text{-}CH_2\text{-}CH_3 \xrightarrow{H_2O} CH_2{=}CH{-}\overset{\displaystyle O\text{-}H}{\underset{\displaystyle O\text{-}H}{Si}}{-}O\text{-}H$$

(Formation of silanol by hydrolysis of silane)

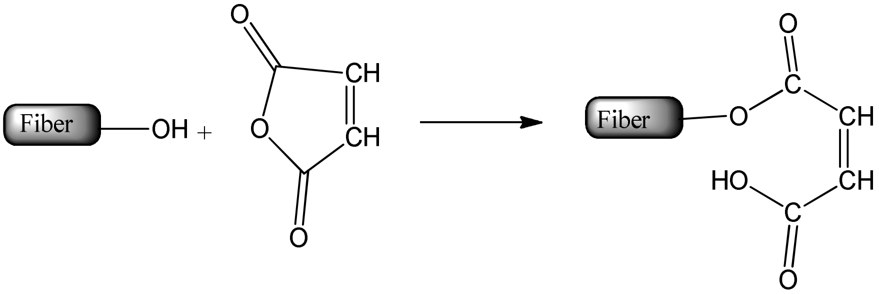


$$\text{Fiber}{-}OH + H_2C{=}\underset{H}{C}{-}\overset{\displaystyle OH}{\underset{\displaystyle OH}{Si}}{-}O{-}H \longrightarrow \text{Fiber}{-}O{-}\overset{\displaystyle OH}{\underset{\displaystyle OH}{Si}}{-}CH{=}CH_2$$

(Reaction of silanol with OH group of natural fibre)

Scheme 4.1 Reaction during silane modification of filler

The APSP was then refluxed with maleic anhydride and acetone to get maleic anhydride PSP (MPSP). The treated fibres were washed thoroughly with water to remove residual chemicals and then dried [20]. The reaction occurring during maleic anhydride treatment can be shown as in **scheme 4.2.**



Scheme 4. 2 Reaction during maleic anhydride treatment of filler

4.2.2 Characterisation of modified PSP

4.2.2.1 UV-Visible Spectroscopy

The UV spectra of PSP before and after treatments are shown in **figure 4.1**. The UV spectrum does not show any intense band. The broad band appeared at 280 nm may be due to the absorption by lignin present in the natural filler. The UV spectra of APSP and SPSP show weak bands at 236 nm can be due to the presence of carbonyl group in the cellulose. The feeble nature of the UV band at 236 nm after modification may be attributed to the functionalization taking place only at the exposed outer surface of the filler. Another weak bands at 227 nm in SPSP and 226 nm in MPSP can be ascribed to the vinyl group [21].

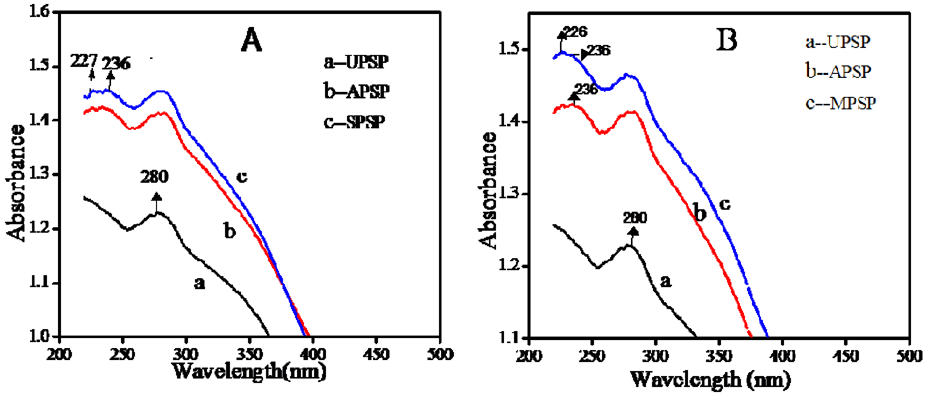


Figure 4.1. UV absorption spectra of (A) UPSP, APSP and SPSP (B) UPSP, APSP and MPSP

4.2.2.2 FTIR spectroscopy

4.2.2.2.1 Characterisation of SPSP

FTIR spectra of UPSP, APSP and SPSP are presented in **figures 4.2 A** and **B**. The stretching frequency at 3393 cm^{-1} is characteristic for –OH group present in the cellulose of fibre. During modification most of the -OH groups are replaced as –ONa group in alkaline treatment and -O-Si-R in silane treatment. The intensity of -OH band is found to be decreases on modification due to decrease in concentration of hydrogen bonding in the fibers between the cellulosic hydroxyl groups [2]. The stretching frequency at 1740 cm^{-1} corresponds to carbonyl group present in the non-cellulose components like lignin in natural lignocellulose filler. The absence of this stretching frequency in **figure 4.2B** reveals that it is partially removed during modification. These observations are analogous to those reported earlier [18,22]. In the FTIR spectrum of SPSP **figure 4.2B** the characteristic stretching frequencies are observed at 1607, 1169 and 1013 cm^{-1}. The frequencies at 1607 and 1013 cm^{-1} are the characteristic absorptions resulting from the C=C of silane coupling agent. The frequency at 1169 cm^{-1} is due to the presence of Si-OEt, which gives evidence for attachment of polysiloxane on the fibre surface and the condensation reaction between the silane coupling agent and the fibre [22]

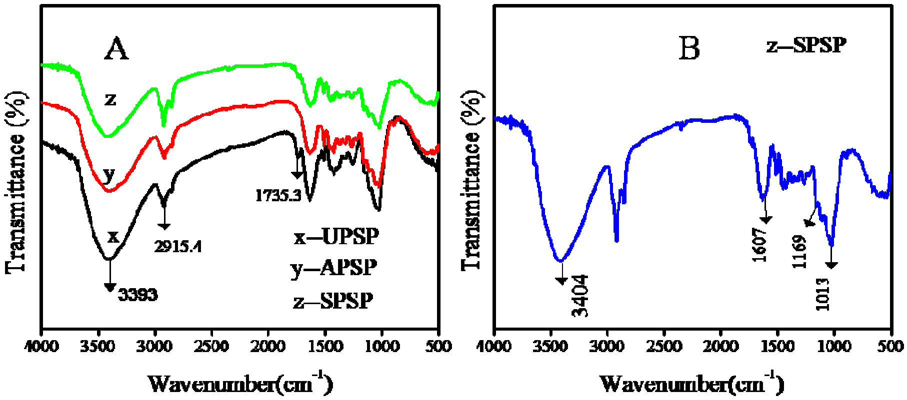


Figure 4.2(A) FTIR spectra of UPSP, APSP and SPSP **(B)** Spectrum of SPSP

4.2.2.2.2 Characterisation of MPSP

FTIR spectra of UPSP, APSP and MPSP are shown in **figure 4.3.** In general three spectra are similar but the frequency at 1735 cm^{-1} disappears after mercerization and reappears after coupling with maleic anhydride. These observations are due to non celluloses including hemicellulose, fats, wax and pectin, which were partially removed after surface modification by alkali. Similar observations has also been made by other researchers [23,24]. The reappearance of small frequency peak at 1725 cm^{-1} in **figure 4.3** after maleation of

APSP by maleic anhydride attributed to the presence of the ester group. The lowering in the intensity of OH stretching frequency in the spectrum **figure 4.3** provided further evidence for successful maleation [20]. Surface morphology (**figure 4.4**) also confirmed the removal of external impurities which appeared to be harder than untreated fibres.

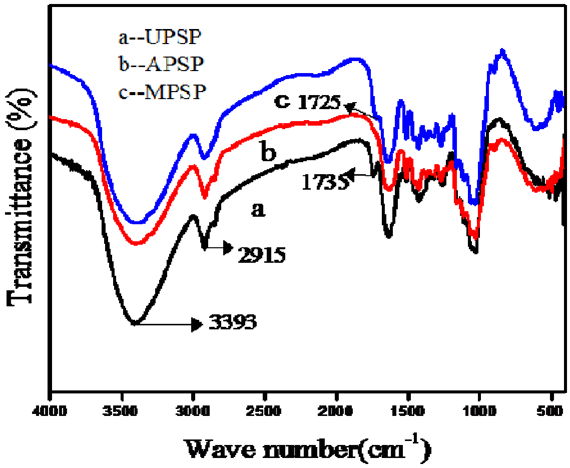


Figure 4.3 FTIR spectra of UPSP, APSP and MPSP

4.2.3 SEM analysis

Figures 4.4 A, B and **C** show the SEM images of PSP before and after chemical treatment with silane and maleic anhydride respectively. These photographs prove that the images of untreated surface are smoother than the treated one. This is due to the partial removal of impurities like hemicellulose, lignin and pectin as a result of mercerization. The rough surface of chemically treated PSP is responsible for both mechanical interlocking and binding reaction, thereby increasing the filler -matrix adhesion [25,26].

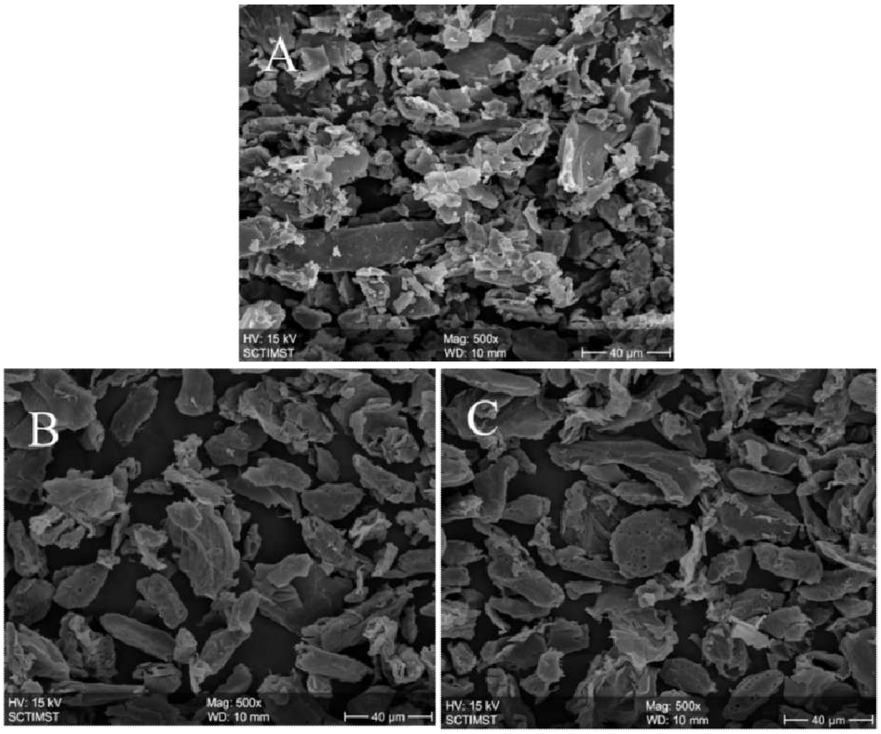


Figure 4.4 SEM images of PSP (a) UPSP (b) SPSP (c) MPSP at 500 magnifications

4.2.4 XRD analysis

Native cellulose, ie cellulose as it occurs in nature, the main component of all samples under study, can be found in the crystalline or amorphous form and can be observed by X- ray diffractogram. X ray patterns of UPSP, APSP, SPSP and MPSP were exhibited in **figure 4.5** Distinct peaks at 2θ =18 and 22° represents the cellulose crystallographic planes 110 and 002 respectively. These can be attributed to crystalline scattered and diffuse peaks associated with disordered regions, ie the highest peak intensity at 2θ =22° represent the crystalline material and peak at 2θ =18° corresponds to amorphous form. The peak at 2θ =22° is sharper for APSP, SPSP and MPSP than

UPSP. The sharper diffraction pattern is an indication of higher crystallinity in the structure of the treated PSP. The percentage of crystallinity can be calculated using the **equation 4.1** and listed in the **table 4.1.** Many researchers [27-29] investigated the effect of surface modification of fibres using chemical treatments from their XRD and observed an increase in the crystallinity index. Similar results were noted in the present study. The X ray diffractogram (**figure 4.5**) shows that the intensity at the I_{002} crystallographic peak is higher for APSP, SPSP and MPSP than UPSP. The increase in the crystallinity can be attributed to the removal of extractives and cementing amorphous components like lignin, hemicellulose and pectin and the calculated crystallinity index values confirm these observations.

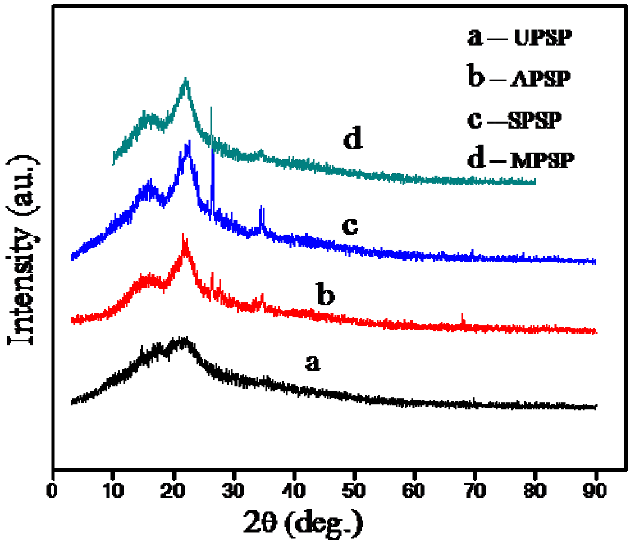


Figure 4.5.XRD spectra of untreated and treated PSP

Degree of crystallinity calculated using the **equation 4.1**

$$DC = \frac{I_{200}-I_{am}}{I_{200}} X\,100 \quad (4.1)$$

are presented in **table 4.1.** This is further supported by SEM and FTIR results. Similar explanations have already been offered by different authors [28,29]

Table 4.1 Percentage crystallinity of different PSPs

Sample	Crystallinity (%)
UPSP	13.9
APSP	42.01
SPSP	43.02
MPSP	40.39

4.2.5 TG and DTG analysis

Figures 4.6A and **B** displays respectively the thermo-gravimetric curves (TG) and the corresponding derivative curves (DTG) of UPSP, SPSP and MPSP. The primary weight loss in the temperature range 90-110 °C is due to the evaporation of surface water. The substantial weight loss of 70% in the temperature range around 200-500 °C is due to the decomposition of major chemical components of natural fibre, hemicelluloses, cellulose and lignin. Kabir [30] and Shibata et al [31] reported that, hemicelluloses are generally supposed to decompose first, followed by cellulose and lignin. UPSP decomposes in the wide range 215-420 °C, the SPSP decomposes in the range 233-362 °C and the MPSP decomposes in the range 248-368 °C The T_{onset} for UPSP is 215 °C, which corresponds to 16% weight loss. But T_{onset} for SPSP is 233 °C and MPSP is 248 °C which corresponds to 10% weight loss. This indicates that the chemical treatments influenced the partial removal of hemicelluloses, lignin, pectin and others. The **figure 4.6B** shows the DTG of unmodified and modified filler. The peak point in dM/dT, DTG_{max} also proved that thermal stability of PSP increased on modification. From **table 4.2** and **figures 4.6A** and **B** it is observed that the thermal stability of PSP increased by surface treatment using silane coupling agent and maleic anhydride which is fully supported by the XRD analysis data.

Table 4.2 TG results of UPSP and SPSP

Sample	T_{onset} (°C)	T_{final} (°C)	T_{50} (°C)
UPSP	215	420	297
SPSP	233	362	342
MPSP	248	368	343

T_{onset}-Onset degradation temperature, T_{final} –Temperature corresponds to maximam weight loss, T_{50}-Temperature corresponds to 50% weight loss.

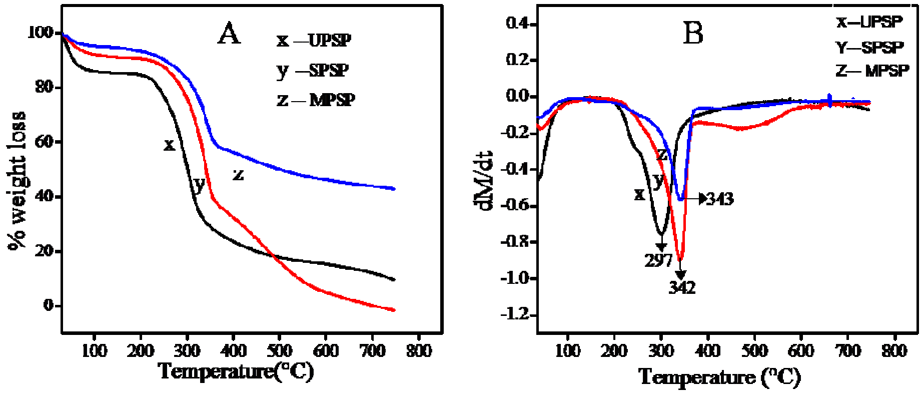


Figure 4.6 (A) TG curves of UPSP, SPSP and MPSP (B) DTG curves of UPSP, SPSP and MPSP

4.2.6 Particle size analysis of the filler

The particle size of filler was measured by Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS). From TEM **(figure 4.7)** only particles agglomerated to form large particle size in micron scale were observed. Similar observations were already by other researchers [32].The PSP was sonicated using water suspended sample and analyzed by the DLS particle size analyzer. **Figure 4.8** also shows the DLS data, which implies that UPSP and SPSP used for composites have particle size above 100 nm with an average particle size of 567 nm [33,34].

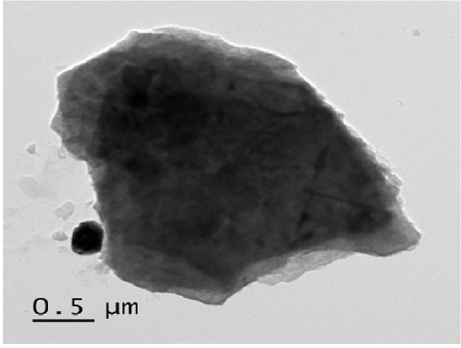


Figure 4.7 TEM image of PSP

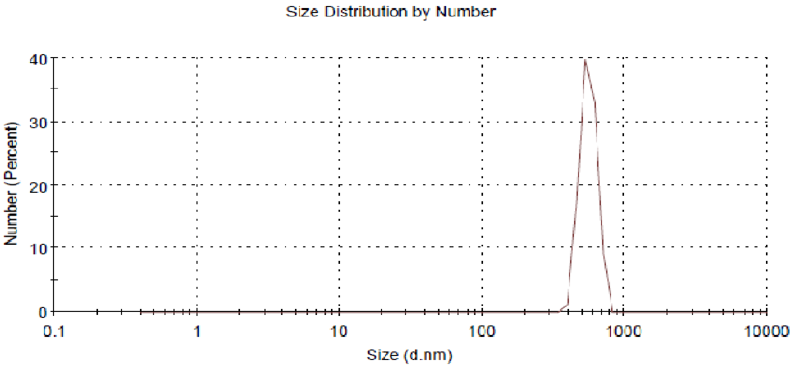


Figure 4.8 DLS data of PSP

4.3 CONCLUSIONS

Chemical treatment has been found to be efficient for improving its hydrophobic character to increase its compatibility with hydrophobic matrix SBR. Chemical treatment of pretreated PSP using alkali removes most of lignin, hemicellulose, wax, fatty substances and other impurities and exposes cellulose to filler surface. Coupling agent such as triethoxy vinyl silane and maleic anhydride were used for surface modification of the filler PSP. This was confirmed by UV-visible spectroscopy and FTIR spectroscopic methods. The chemical treatment of filler increased the crystallinity which was observed by XRD. The change in the morphology of PSP was confirmed by SEM, the surface becomes rough after modification in comparison with smooth and clear surface of untreated PSP. These were also observed through thermogravimetry and differential calorimetry. It was observed that thermal stability of chemically treated PSP was higher than that of untreated PSP. The removal of surface impurities on filler may be an advantage to filler for matrix adhesion as it facilitates both mechanical interlocking and the bonding reactions.

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CHAPTER 5

FABRICATION, MECHANICAL AND THERMAL PROPERTIES OF MODIFIED PEANUT SHELL POWDER FILLED STYRENE BUTADIENE RUBBER COMPOSITES

Abstract: Biocomposites of styrene butadiene rubber (SBR) reinforced with silane treated peanut shell powder (SPSP) and maleic anhydride treated peanut shell powder (MPSP) of different filler loading and particle size were prepared by two roll mixing mill with sulphur as vulcanizing agent. The cure characteristics of composites were studied and they vulcanized at 160 °C. Test samples were prepared by compression moulding and their physicomechanical properties like tensile strength tear strength, modulus, hardness and abrasion resistance of SBR vulcanizates were studied with filler loading 0, 5, 10, 15 and 20 parts per hundred rubber (phr). Composites were characterized by ATR—FTIR and surface morphology by SEM. Composites with 10 phr filler having small particle size exhibited better properties. The interfacial adhesion between filler and matrix has a major role in the properties of composites. Better properties were shown by the composites with SPSP and MPSP. Thermal properties of the composites were carried out by Thermogravimetry (TG) and Differential scanning calorimetry (DSC). Thermal stability of composites reinforced with peanut shell powder are lesser than that of SBR, but thermal stability of composites increases on modification of filler. Glass transition temperature of composites (Tg) slightly increased compared to SBR vulcanizates.

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5.1 INTRODUCTION

Composite materials are one of the most advanced engineering materials, now-a day. Composite materials made from plant fibers are receiving great deal of attention, since they are considered as environmental friendly recourse. Biocomposites are having variety of applications in industries and the development of composites using biological material promotes the ecofriendly products. It is observed that every year large quantities of agricultural wastes are produced worldwide. In the case of peanut, major waste part is its seed shell. Small quantities of seed shells are used as house hold fuel and fertilizer and remaining part is burned in the field itself. As a result, it gives negative effect on the environment due to air pollution. In part, one of the solutions to overcome this problem is to develop biocomposits. Since peanut shell is an important agricultural waste generated in several thousand tones daily, it seems that their use as reinforcement material in the composite fabrication is an attractive choice considering both ecological and economical aspects [1–3].

Biocomposites have several advantages such as light weight, low cost, high specific strength, high modulus, reduced tool wear and safe manufacturing process when compared to synthetic fibre composites. It also offers opportunities for extensive applications such as consumer goods, low cost housing structures, packaging, furniture and automotive fields. Most of the interiors of automobiles like door panels, trunk liners, packages, speaker trays, engine and transmission covers are made of natural fibre composites [2–13]. Incorporating waste materials like seed shells into polymers, not only enhance thermal and mechanical properties, but reduce the cost of materials while forming totally natural green composites. Similar to natural fibres from jute, pineapple, coir, sisal, coconut, oil palm, bamboo, banana stem etc, seed shells were also used as reinforcing filler to develop biocomposites of rubber matrix. It imparts good strength and stiffness to soft and tough rubber matrix [14–18]. Despite its several merits, they have inherent drawbacks such as poor wettability, incompatibility with some polymer matrices, high moisture absorption by the fibres and hence only poor adhesion with rubber matrix. This property affects the interior strength of the composites. The reason for its poor compatibility is mainly due to the hydrophobic and non polar nature of rubber whereas the natural fibres and seed shells are hydrophilic and polar. This drawback can be overcome by methods such as the use of coupling agents like silane, maleic anhydride, polymethylmethacrylate etc or compatibizing agents and fibre surface treatments like alkali treatment, peroxide treatment, permanganic acid treatment, benzoylation and acetylation to improve the wettability of natural fibre by polymers and promote interfacial adhesion [7–10,19–21]. As already explained in chapter 4, silane coupling agents and maleic anhydride are recognized as the efficient coupling agents extensively used in polymer composites. Silane has bifunctional groups which can react with both natural fiber and polymer matrix. This brings to an enhancement in adhesion of natural fiber to polymer matrix and forms a uniform composite structure [1,12]. SBR is the most widely used general purpose elastomer in the world, because of its application in the automotive and tire industry.

The main advantage of SBR matrix is the formation of composites with better abrasion and heat resistance than natural rubber.

Thermal stability of polymers is an important characteristic for many application processes, especially when potential end uses are concerned. Thermal stability is the ability of material to maintain the required properties such as strength, toughness, elasticity *etc* at a given temperature and it is a direct measure of molecular rigidity, because chemical reaction and degradation depends on macromolecular chain excitation and motion gained from the thermal energy during exposure to higher temperature [23]. Thermal analysis can be used with composite materials to determine properties of the matrix material that are important for the analysis of the composite as a whole [24]. Polymers tend to change their microstructure, degree of polymerization, crystallinity and even chemical composition due to heating and increase in temperature and changes do not occur instantaneously, but take its own time. Therefore, by examining the structure and properties of a polymer, information on the thermal history can be obtained. Awareness of the relationship between thermal history, polymer structure and properties are useful for manufacturing process development, quality control and polymer engineering.

TG is a technique where the mass of a polymer is measured as a function of temperature or time while the sample is subjected to a controlled temperature program in a controlled atmosphere. TG determines the weight gain or loss of a condensed phase due to gas release or absorption as a function of temperature. Mass loss may be categorized as volatile components such as absorbed moisture, residual solvents, or low - molecular - mass additives or oligomers that generally evaporate between ambient and 300 °C. The generation of volatile degradation products resulting from chain scission generally requires temperatures between 200 °C and 800 °C. All of these mass loss processes may be characterized by TG to yield information such as composition, extent of cure and thermal stability. The kinetics of these processes may also be determined to predict cure, thermal stability and aging due to thermal and thermo oxidative processes [25].

In differential thermal analysis (DTA), the temperature difference between a reactive sample and a non-reactive reference is determined as a function of time, providing useful information about the temperatures, thermodynamics and kinetics of reactions. DSC has a similar output, but the sample energy change during a transformation is more directly measured. The temperatures of transformations as well as the thermodynamics and kinetics of a process may be determined using DTA and DSC [26]. The DSC technique is also a convenient and useful method to measure the glass transition, melting, and crystallization temperatures of uncured prepregs and cured laminates, and also the degree of cure of the final product, the heat of reaction during prepreg processing, and relative resin reactivity.

Zhichao et al [22] analysed the influence of particle type and silane coupling agent on properties of silica and carbon-filled SBR.

Minimum torque, maximum torque and tensile strength were increased with increase in the filler content. The tensile strength and elongation at break were highest for the bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT) modified silica-filled vulcanizates of SBR. Kumar et al [27] developed and characterized the mechanical properties of composites of SBR reinforced with short sisal fiber as a function of fiber length, orientation, loading, and bonding agent. The addition of short sisal fibers to SBR offers good reinforcement and causes improvement in mechanical properties which further gets strengthened by the presence of bonding agent. Arumugam et al [28] fabricated the composites of treated and untreated coconut fibre with NR and their properties were analysed. They observed that the treated fiber imparts better physical properties to the rubber mixes than the untreated fiber. Jie et al [6] studied the effect of hemp powder loading on cure characteristics and mechanical properties of filled SBR and EPDM composites. The results indicate that the addition of hemp powder facilitated the vulcanization process and improved the meachanical properties and storage modulus considerably, but the filler loading above 30 phr resulted in drastic deterioration of properties.

Soares [29] analysed the thermal properties of composites based on soy protein and corn starch. Films from corn starch were less thermally stable than soy protein films. The films containing both components had lower thermal stabilities when compared to those of the pure biopolymers. Yeng et al [9] studied the thermal stability of polylactic acid (PLA)/banana fibre biodegradable green composites of

PLA reinforced with banana fibres. It was observed that in TG results the decomposition temperatures of the fibre reinforced composites were smaller than those of PLA, but the char residues are larger than those of PLA. However the Tg of composites are slightly slower than those of PLA. Yussuf et al [13] compared the thermal stability of polylactic acid with kenaf and polylactic acid with rise husk composites, it has been found that the addition of natural fibres decreased the thermal stability of matrix and decrement was more prominent in the PLA-RH composites. Vishak et al [30] analysed the thermal stability of crab chitin reinforced carboxylated SBR composites, the filler content does not substantially affect the thermal stability of the matrix. Julien brass et al [31] observed that lower oneset degradation temperature in the bagass cellulose whiskers reinforced NR nanocomposites could be due to lower oneset degradation temperature of filler than rubber. The DSC results revealed that no significant effect in Tg of rubber by reinforcing filler. Nemr [32] analysed the thermal properties of composites of SBR with waste news print fibres in which TG results indicated that the thermal stability of fibres was enhanced by chemical treatment and irradiation.

Since the use of PSP as reinforcement material in the composite has been observed as an attractive choice from both ecological and economical resources. In the present study, PSP was used as reinforcement in SBR matrix to develop bio composites. Triethoxy vinyl silane and maleic anhydride were used as coupling agent to improve the interfacial adhesion between filler and rubber matrix. The composites prepared from SBR and unmodified PSP (UPSP), SPSP and MPSP were compared. The effects of UPSP, SPSP and MPSP contents and particle size on the cure characteristics, mechanical, thermal and morphological behavior of composites were investigated. This chapter also describes the effect of natural filler PSP, its modification by coupling agents such as triethoxy vinyl silane and maleic anhydride and particle size on the thermal properties of these composites using TG and DSC.

5.2 RESULTS AND DISCUSSION

5.2.1 Preparation of SBR composites

Composite fabrication was carried out on a two roll mixing mill in accordance with ASTM-D15-627. **Table 5.1** shows the mixing formulation used for the preparation of composites. All chemicals were powdered and weighted accurately Total mixing time taken was 13 minutes in order to avoid sticking of the rubber compound to the mill rolls. Care was taken to ensure that temperature was not too high to avoid any cross linking during mixing. This has been achieved by cooling with water. These conditions were kept constant for all composites.

Table 5.1 Mixing formulation for preparation of composites

Ingredients	Parts per hundred rubber (Phr)
SBR	100
Zinc oxide	5
Stearic acid	2
Trimethyl dihydroxy quinoline (TDQ)	1
Processing oil	1/20th of filler
Filler(PSP)	5,10,15and 20
Cyclohexyl benzothiazyl sulphenamide (CBS)	2
Sulfur	2.4

The composite sample prepared were designated with codes, the details of which are presented in the **table 5.2**

Table 5.2 Designation of SBR--PSP composites based on filler concentration

Sample code	UPSP	SPSP	MPSP
B_0	0	0	0
U_5	5 (<53 μm)	0	0
U_{10}	10	0	0
U_{15}	15	0	0
U_{20}	20	0	0
S_5	0	5 (<53 μm)	0
S_{10}	0	10	0
S_{15}	0	15	0
S_{20}	0	20	0
R_5	5 (53-90 μm)		0
R_{10}	10		0
R_{15}	15		0
R_{20}	20		0
T_5	0	5 (53-90 μm)	0
T_{10}	0	10	0
T_{15}	0	15	0
T_{20}	0	20	0
M_5	0	0	5 (<53 μm)
M_{10}	0	0	10
M_{15}	0	0	15
M_{20}	0	0	20

B_0 represent the SBR vulcanizates without filler

U represents SBR composites with < 53 μm UPSP; subscript 5,10,15,20 denotes the composition of filler in phr.

S represents SBR composites with < 53 μm SPSP; subscript 5,10,15,20 denotes the composition of filler in phr.

R represents SBR composites with 53-90 μm UPSP; subscript 5,10,15,20 denotes the composition of filler in phr.

T represents SBR composites with 53-90 μm SPSP; subscript 5,10,15,20 denotes the composition of filler in phr.

M represents SBR composites with < 53 μm MPSP; subscript 5,10,15,20 denotes the composition of filler in phr.

5.2.2 Cure characteristics of SBR-UPSP and SBR-SPSP composites

Minimum torque (M_L) is the measure of the stiffness of unvulcanized test specimen. It is the torque shown by the mix at the test temperature before the onset of cure. Maximum torque (M_H) is the measure of the stiffness or shear modulus of the fully vulcanized test specimen at the vulcanization temperature. It is the torque recorded after curing of the mix is completed.

Scorch time (t_{10}) is the time taken for attaining 10 % of the maximum torque. It is a measure of pre-mature vulcanization of a material. It indicates the storage safety of a material. A short scorch time represents a short shelf life of a master batch. Optimum cure times (t_{90}) are time taken for attaining 90 % of the maximum torque. It is the time corresponding to a torque equal to $0.9(MH– ML) +ML$. Cure rate index (CRI) is a measure of the rate of cure.

Table 5.3 represents the effect of filler loading and particle size on the cure characteristics of SBR composites filled by PSP. Cure time and scorch time were found to decrease with increase in filler loading. As filler loading increases the incorporation time of filler into the matrix increases, it develops heat due to friction [14, 16]. Hence cure time decreases with increase in filler loading. The reduction of scorch time with increasing filler loading reveals that the excess PSP would cause potential threats to the scorch safety of rubber composites. The scorch time and cure time of composites with SPSP were found to be higher than composites with UPSP due to uniform dispersion of filler in the SBR matrix. The increase in the hydrophobic character of SPSP on modification increases its compatibility with SBR [33,34]. The maximam torque and minimum torque values increase with increase in filler loading. The incorporation of filler into the rubber matrix decreases the mobility of macromolecular rubber chain and it causes the increase in rigidity of the composites. The more filler is added the more restriction in mobility of rubber chain and as a result the rubber composite become harder and stiffer. The SBR composites with SPSP shows higher torque than composites with UPSP. The modification enhances better rubber-filler interaction leading to additional cross linking in network structure [12]. The increase in crosslink density with filler loading and on silanization is also supported by the cure extent values.

Table 5. 3 Cure characteristics of SBR-UPSP and SBR-SPSP composites

SI No	Sample code	Composition (%)	Cure time (min)	Scorch time (min)	Max. Torque (MH) (dNm)	Min. torque (ML) (dNm)	Cure extent (MH-ML)	CRI
1	B_0	0	11.2	5.08	10.04	0.52	9.52	14.88
2	U_5	5	7.38	3.07	10.29	0.56	9.73	20.62
3	U_{10}	10	6.32	2.29	10.64	0.59	10.05	22.94
4	U_{15}	15	5.44	2.02	10.84	0.65	10.19	25
5	U_{20}	20	5.31	2.01	10.94	0.7	10.24	25.84
6	S_5	5	8.44	3.37	10.6	0.53	10.07	18.25
7	S_{10}	10	8.3	3.28	11.34	0.57	10.77	19.12
8	S_{15}	15	8.22	3.17	11.95	0.67	11.28	19.2
9	S_{20}	20	7.5	2.53	13.03	0.67	12.36	20.12
10	R_5	5	7.2	3.17	9.92	0.54	9.38	22.68
11	R_{10}	10	6.09	2.28	10.36	0.59	9.77	25
12	R_{15}	15	5.39	2.08	10.53	0.65	9.88	26.32
13	R_{20}	20	5.31	2.02	11.03	0.69	10.34	26.53
14	T_5	5	8.27	3.37	10.42	0.52	9.9	18.98
15	T_{10}	10	7.58	3.33	10.88	0.6	10.28	19.92
16	T_{15}	15	7.56	3.18	11.88	0.67	11.21	21.46
17	T_{20}	20	7.52	3.37	12.62	0.76	11.86	21.82

5.2.3 Characterisation of SBR-SPSP composites by ATR –FTIR

Figure 5.1 shows the ATR –FTIR spectra of SBR and its composites with SPSP. The frequency at 2918 and 2845 cm^{-1} are due to stretching vibrations of methyl and methylene group, the frequency at 1530 cm^{-1} may be due to -C=C- stretching vibrations, the frequencies at 1445 and 1393 cm^{-1} can be attributed to -CH_2 and -CH_3 bending vibrations; the frequency at 703 corresponds to styrene units in the rubber. The broad band at 3417cm^{-1} due to –OH stretching vibration of cellulose in the filler, this is not present in the SBR, but the broadness and intensity of this increases on filler loading. The substantial change in the spectrum of composites indicates the incorporation of filler in the composites [35].

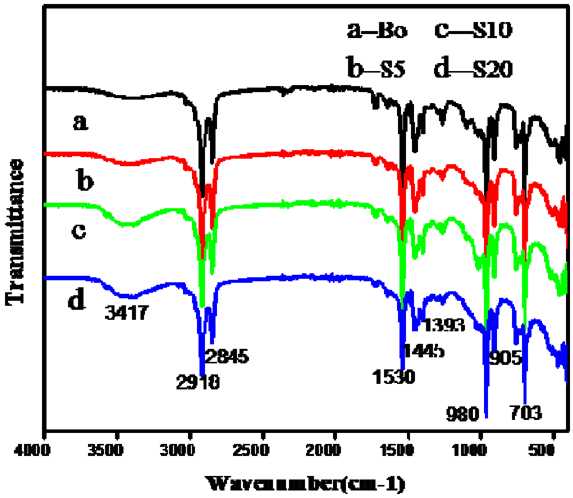

Figure 5.1: FTIR-ATR spectrum of composites of SBR with SPSP

5.2.4 Effect of filler loading on mechanical properties of SBR-UPSP and SBR-SPSP composites

5.2.4.1 Tensile and tear strength

Table 5.4 represents the effect of filler loading on the tensile properties of PSP filled SBR composites. Tensile properties of each sample were measured three times and their average values were recorded. Tensile strength was found to increase on filler loading and the maximum value was shown at 10 phr and then it decreased gradually. The higher value of tensile strength at low filler loading is due to the good interfacial adhesion between filler and matrix by uniform dispersion of filler in rubber matrix. This causes to transfer stress effectively from matrix to filler. Also the interaction between the filler and rubber matrix has a major role in increasing the tensile strength. The higher filler content causes to enhance the microspaces in the filler matrix interfacial region, filler agglomerates due to filler-filler interactions and also incomplete interfacial wetting may lead to decreased stress transfer from matrix to filler. As a result tensile strength decreases with filler loading [36,37].

The hydrophilic nature of PSP causes weak filler matrix interaction in the composite with hydrophobic SBR. The silane treatment decreases the hydrophilic nature of PSP and as a result the interfacial adhesion between filler and matrix increases. Therefore the tensile strength of SBR-SPSP composites is greater than that of SBR-UPSP composites. This shows that the improved interfacial adhesion increases the stress transfer efficiency from matrix to filler. It has also been found that at same phr of filler, tensile strength increased with decreasing particle size. This is due to larger surface area of smaller particles leading to the better transfer of stress from SBR matrix to the PSP phase [17,38].

The tear strength also like tensile strength first increases upto 10 phr filler loading and then decreases with filler loading in SBR composites reinforced with SPSP and UPSP. The maximum value is observed at 10 phr filler loading. The higher filler loading causes the formation of voids in the composites due to its porous nature, which leads to localized stress concentration during deformation. Hence tear strength is reduced at higher filler loading [18].

Table 5.4 Effect of filler loading and particle size on mechanical properties of composites

SI No	Sample code	Composition (%)	Tensile strength (MPa)	Elongation at break (%)	Modulus 100 % (MPa)	Tear strength (MPa)
1	B_0	0	2.28±0.10	326.66±54.2	1.12± 0.01	10.62±1.2
2	U_5	5	2.26±0.06	408.22±55.7	1.23± 0.02	14.19±0.73
3	U_{10}	10	2.46±0.16	454.86±60	1.34± 0.01	14.76±1.00
4	U_{15}	15	2.29±0.07	430.91±70	1.38± 0.03	12.55±0.09
5	U_{20}	20	2.22±0.17	405±54	1.40± 0.01	11.59±0.14
6	S_5	5	2.56±0.11	418.49±83.6	1.21± 0.02	14.96±1.05
7	S_{10}	10	2.93±.012	467.48±45.5	1.39± 0.03	15.11±1.28
8	S_{15}	15	2.57±0.07	442.49±33.8	1.42± 0.01	13.18±0.09
9	S_{20}	20	2.54±0.16	432.86±65.8	1.47± 0.04	11.48±1.3
10	R_5	5	1.99±0.06	250.09±43.2	1.07± 0.001	11.1±0.09
11	R_{10}	10	2.29±0.08	315.14±73.3	1.08±0.003	13.39±0.08
12	R_{15}	15	2.19±0.05	303.9±87.7	1.16±0.03	12.72±0.08
13	R_{20}	20	1.88±0.11	274.97±23.1	1.17±0.03	12.21±0.03
14	T_5	5	2.03±0.02	260.11±50.9	0.97±0.004	12.92±0.06
15	T_{10}	10	2.38±0.03	323.75±38.9	1.04±0.008	14.44±0.09
16	T_{15}	15	2.13±0.07	305.46±88.9	1.16±0.01	14.2±0.07
17	T_{20}	20	1.98±0.08	297.62±65.3	1.09± 0.007	13.95±1.01

5.2.4.2 Modulus

Modulus of composites increases with filler loading. The inclusion of rigid and soft particulate filler introduces restriction on the mobility of the rubber molecule. On increasing filler in composites of rubber the mobility of rubber molecules decreases and consequently the modulus increases. Elastic modulus depends on surface reactivity which determines the polymer filler interactions, aggregates, size, shape and structure of filler particles dispersed in rubber. Hence the modulus increases with decreasing particle size and on surface modification of filler [34,37].

5.2.4.3 Hardness

The variation of hardness is graphically represented in **figure 5.2**. Hardness also increases on increase in filler loading and on decreasing particle size of filler. Chemical modification of filler also increases the hardness of composites. This is due to the fact that the incorporation of more filler into the rubber matrix reduces the plasticity and increases rigidity of composites and also due to enhancement of cross link density. Similar observations have already been noticed [14,16,39].

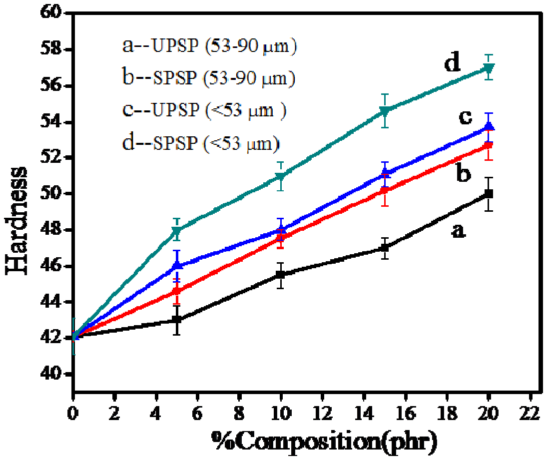

Figure 5.2 Effect of filler loading and particle size on hardness of SBR –UPSP and SBR-SPSP composites

5.2.4.4 Abrasion

Abrasion resistance is the ability of a material to withstand mechanical action such as rubbing, scraping or erosion. It leads to progressive removal of material from its surface. **Figure 5.3** shows the effect of filler loading and particle size on abrasion of the composites. As can be seen from the **figure 5.3** the addition of filler decreases abrasion until a minimum at 10 phr and then increases on filler loading. Hence the abrasion resistance increases upto 10 phr filler loading, and then decreases. The morphology and surface reactivity of reinforcing filler have a major role in the abrasion resistance of composites. The reinforcing filler improves the abrasion resistance due to greater surface area, better filler matrix interfacial adhesion and lower filler-filler interaction. At low concentration of filler the distribution of filler in the matrix is homogenous. Therefore the interaction between filler particle is minimum, interfacial adhesion is maximum. Hence the composite with 10 phr filler loading shows maximum abrasion resistance. The composites with small particle size provide better abrasion resistance than coarse one due large surface area. Analogous explanations have already been offered [37].

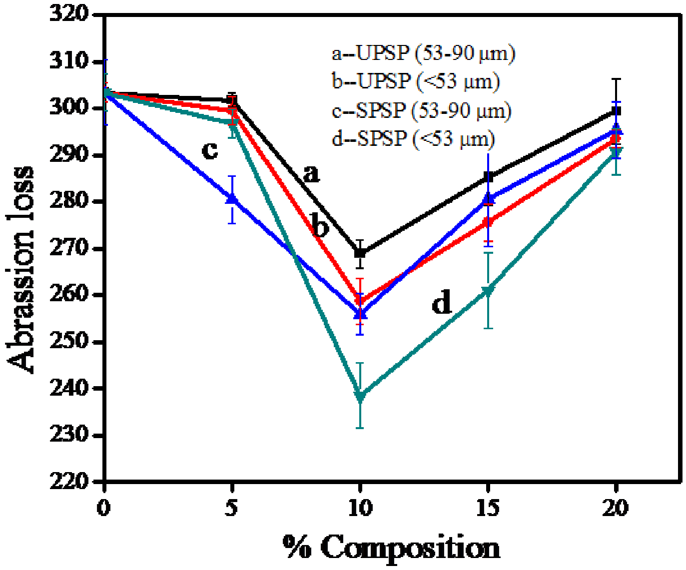

Figure 5.3 Effect of filler loading and particle size on abrasion of SBR – UPSP and SBR-SPSP composites

5.2.5 Surface morphology of composites

Figure 5.4 exhibits the surface morphology of composites of SBR reinforced with SPSP and UPSP of <53 µm particle size. The SEM images show the uniform dispersion of filler throughout the samples. The visual change in the morphology depends upon the amount of filler present in the composites. The surface of SBR composites with 10 phr PSP loading demonstrated smoother plane than of composites with 20 phr loading. Most of the PSP seems to be well dispersed in the rubber matrix as shown in **figure 5.4 B** and **D**.

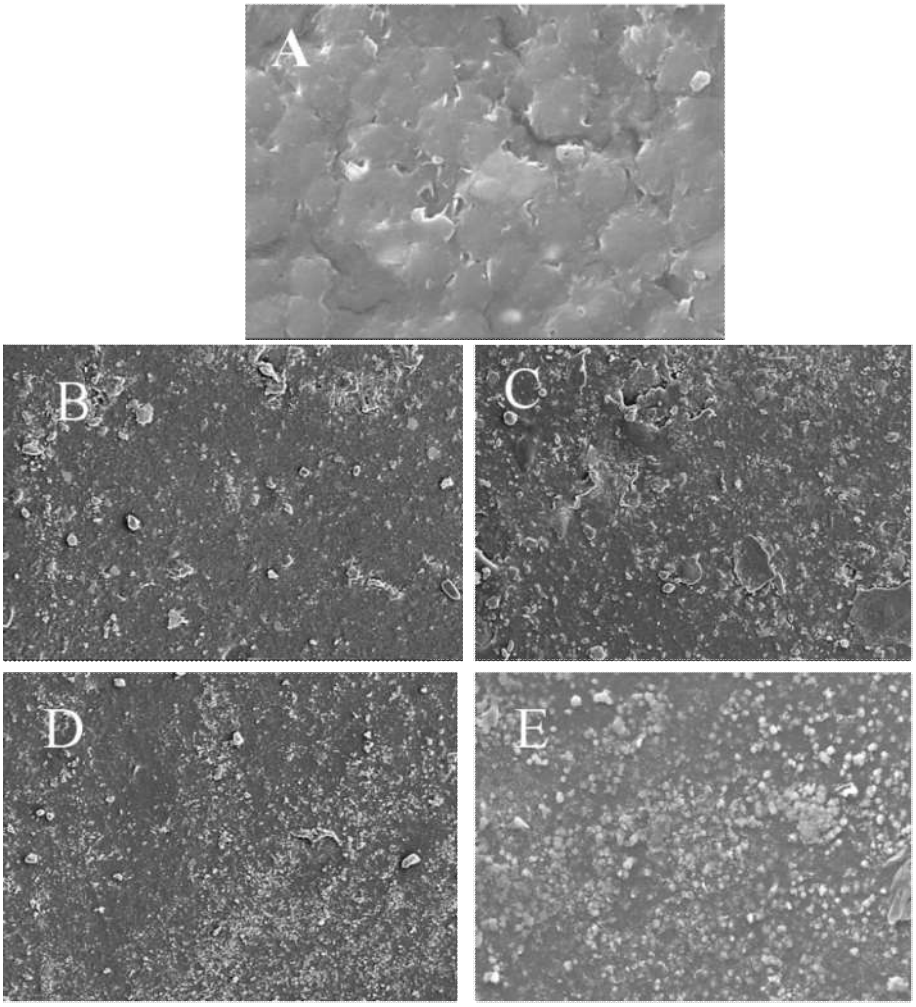

Figure 5.4.SEM images of SBR-PSP composites (A) SBR vulcanizates; (B) SBR/10 phr UPSP (< 53 μm); (C) SBR/20 phr UPSP (< 53 μm); (D) SBR/10 phr SPSP (< 53 μm); (e) SBR/20 phr SPSP (< 53 μm)

Whereas, the agglomeration of PSP on the surface is seen in **figure 5.4 C** and **E** due to increased filler -filler interaction for composites with 20 phr PSP. From this observation it is clear that PSP has good dispersion in the matrix when the loading is low. The morphology also correlates with the mechanical properties, revealing an apparent progress of interfacial adhesion. The better filler matrix adhesion in the composites with silane modified PSP is the probable explanation (**figure.5.4D**). Analogous observations have been found earlier [12][40]. **Figure 5.5** shows the SEM images of SBR vulcanizates filled with modified and unmodified PSP having 53-90 μm particle sizes. Comparing the **figures 5.4 D a**nd **5.5 C**, it is clear that the distribution of filler in the matrix is very poor on increasing the particle size. The filler matrix interactions become weak, which results in low value in tensile strength, tear strength, and modulus as discussed earlier.

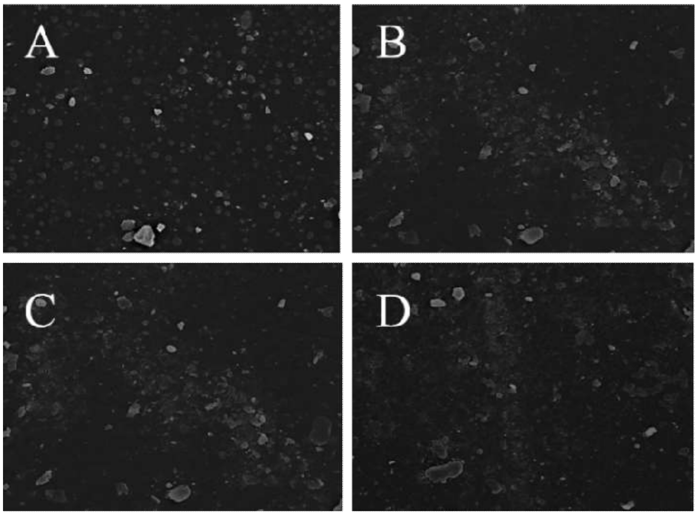

Figure 5.5 SEM images of SBR-PSP (53-90 μm) composites (A) SBR/10 phr UPSP; (B) SBR/20 phr UPSP; (C) SBR/10 phr SPSP; (D) SBR/20 phr SPSP

5.2.6 Cure characteristics and mechanical properties of SBR-MPSP composites

Table 5.5 Cure characteristics of SBR-MPSP composites

Sample code	Cure time (min)	Scorch time (min)	Torque max(M_H) (dNm)	Torque min(M_L) (dNm)	Cure extent M_H-M_L	CRI
B_0	11.20	5.08	10.04	0.52	9.52	14.88
M_5	10.53	4.29	10.54	0.55	9.99	13.35
M_{10}	10.24	3.56	11.24	0.65	10.59	13.02
M_{15}	9.53	2.89	12.12	0.71	11.41	12.34
M_{20}	9.08	2.51	12.74	0.82	11.92	12.04

Curing is heat treatment which changes the physical properties of a substance due to chemical process, resulting in the formation of more durable products. Cure time of the composites of SBR with MPSP decrease with increases in filler loading as shown in the **table 5.5.** The retention of composites more time in mill during mixing and the time of incorporation also increase on increase in filler loading generate more heat due to friction reduces the cure time [26]. The scorch time also decreases with increase in filler loading. The maximam torque and minimum torque increase with filler loading. The addition of filler causes increment in rigidity the composites through reducing the movement of macro molecular chain of the rubber matrix. Similar to composites of SBR with SPSP, the MPSP also introduce additional cross linking in the network structure._Hence a SBR-MPSP composite shows higher torque than corresponding SBR-

UPSP composites. But there is no significant difference on comparing with composites with SPSP.

Table 5. 6 Effect of filler loading on mechanical properties of SBR-MPSP composites.

Sl No	% compos	Code	Tensile Strength (MPa)	Elongation at break (%)	Modulus 100 % (MPa)	Tear Strength (MPa)
1	0	B_0	2.28±0.10	326.66 ±54.2	1.12±0.01	10.62
2	5	U_5	2.26±0.06	408.22 ±55.7	1.23± 0.02	14.19±0.73
3	10	U_{10}	2.46±0.16	454.86±60	1.34± 0.01	14.76±1.00
4	15	U_{15}	2.29±0.07	430.91±70	1.38± 0.03	12.55±0.09
5	20	U_{20}	2.22±0.17	405±54	1.40± 0.01	11.59±0.14
6	5	M_5	2.40±0.07	324.33±15	1.26±0.02	14.49±1.03
7	10	M_{10}	2.68±0.03	289.36±19	1.37±0.04	16.05±0.09
8	15	M_{15}	2.48±0.06	278.40±12	1.40±0.01	15.05±0.06
9	20	M_{20}	2.42±0.05	265.59±13	1.43±0.03	14.25±0.70

Table 5.6 represents the mechanical properties of the composites of SBR with maleic anhydride treated PSP. The tensile strength and tear strength increases with filler loading and then decreases. The formation of ester linkages between the MPSP and rubber matrix leads to strong interfacial bonding. So the composite with MPSP have higher tensile strength and tear strength than that of composite with UPSP. At higher filler loading the agglomeration of

filler loading leads to an insufficient homogeneity, the agglomerated filler particles act as crack initiation sites under loading, and this is always detrimental to properties of the composites, hence the tensile strength and tear strength decreases after 10 phr filler loading [41]. The improved interfacial adhesion was confirmed by the SEM morphology. But the elongation at break decreases with increase in filler loading is attributed to increase in stiffness and brittleness due to adherence of filler to the rubber matrix, which decreases the resistance to stretch on application of strain [11, 26]. On comparing with composites of SPSP the tensile strength of MPSP was found to be lower than that of SPSP, but tear strength was higher than that of SPSP, which are shown in **figure 5.6 (A)** and **5.6 (B)** respectively.

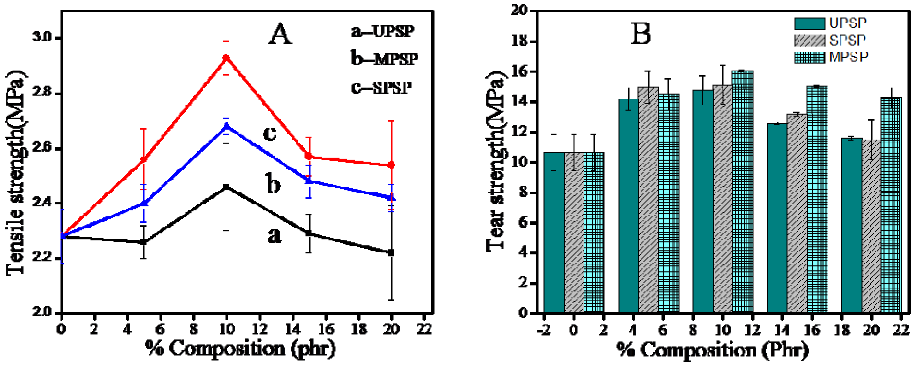

Figure 5.6 Comparison of (A) tensile strength (B) tear strength of composites SBR with MPSP, SPSP and UPSP

Surface reactivity of the composites depends on polymer filler interactions, aggregates, size, shape and structure of filler particles dispersed in rubber matrix. Surface modification improves the homogeneity of filler dispersion, which increases the polymer filler interactions. Therefore the modulus of SBR composites with MPSP was higher than that of UPSP. The modulus increases with increase in filler loading due to reduction in mobility of polymer chain by soft and rigid filler particles. The hardness of the composites of SBR with MPSP was found to be higher than that of composites with SPSP and UPSP **(figure 5.7A**). The filler particles have higher modulus than that of rubber matrix, the inclusion filler reduces the plasticity, increases the rigidity and hence increase in the modulus of the composites.

The surface modification of filler by maleic anhydride also increases the abrasion resistance of the composites upto 10 phr filler loading and then decreases (**figure 5.7B**). This may be due to the increase in interfacial adhesion between filler and matrix as a result of uniform dispersion of filler in the matrix at lower filler loading. The higher filler loading reduces the homogeneity of filler by the increased filler- filler interactions causing agglomeration of filler. The SEM images of the composites at different filler loading support the above findings (**Figures 5.4 and 5.8**).

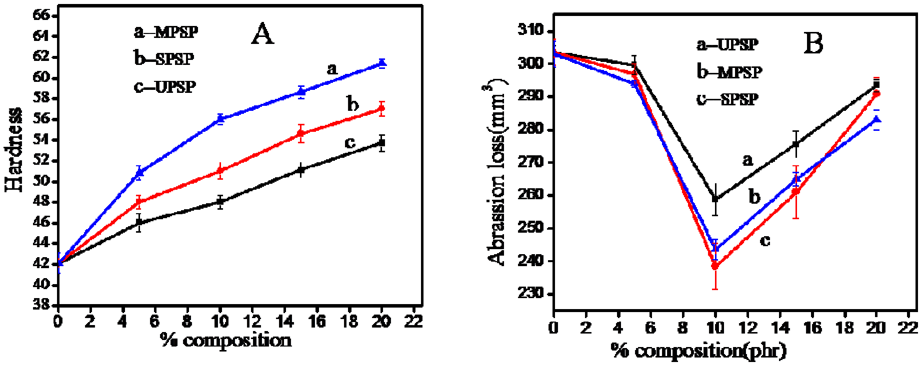

Figure 5. 7 Comparison of (A) hardness and (B) abrasion loss of composites of SBR with UPSP, SPSP and MPSP

5.2.6.1 SEM images

The morphology of the fractured surface of SBR-PSP composites of SBR with untreated and treated PSP at different filler compositions are illustrated in **figure 5.8**.The fractured surface of composites with 10 phr filler content are obviously smoother plane that of composites with 20 phr filler content. Most of the filler was well wrapped in the rubber matrix as shown in **figures 8 A, C** and **E**. In contrast, the higher filler-filler interactions for composite with 20 phr (**figures 8 B,D** and **F**) loading causes the agglomeration of PSP and also it could be seen the existence of more voids resulting from the pulle out of PSP and larger cracks in the vicinity of PSP agglomerates. The above observation supports that the PSP had good dispersion in the rubber matrix when loading was low. When loading was high, the composites showed rough surface with more PSP agglomerates. The pull out of fibre bundles, more broken surface and more agglomerates suggested that the presence of excess PSP would deteriorate reinforcement effect. The composites of SBR with MPSP and SPSP have improved filler matrix adhesion. It was observed from **figures 8 C, D, E** and **F** that the treated PSP has more uniform coat of matrix, reducing the interfacial separation, thereby improving the interfacial attachment. The improved interfacial adhesion was as a result of stress transfer from matrix promoted by modified PSP. The small increment in the mechanical properties of composites of SBR with modified PSP adds testimony to these explanations [6,17].

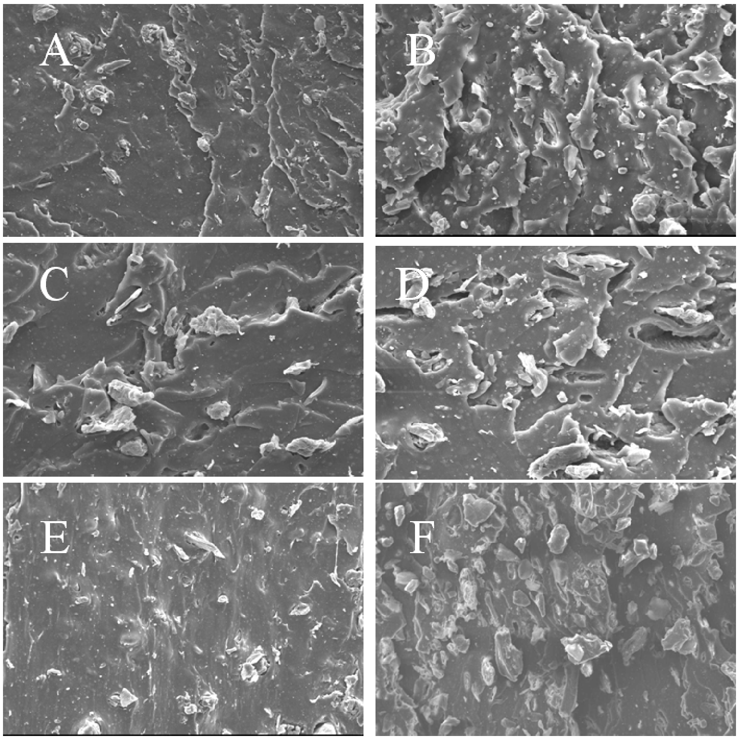

Figure 5. 8 SEM morphology of fractured surface of composites of SBR with (A) 10 phr UPSP (B) 20 phr UPSP (C) 10 phr MPSP (D) 20 phr MPSP (E) 10 phr SPSP (F) 20 phr SPSP

5.2.7 Thermal properties of composites

5.2.7.1Thermogravimetry

The thermal degradation characteristics of SBR composites reinforced with PSP and modified PSP were analyzed by TG. TG was studied as a function of percentage weight loss against temperature. The study of thermal degradation of materials allows identifying the upper use temperature limit for a given material. **Table 5.7** reveals the thermal degradation results of composites obtained from TG curves represented as **figure 5.9 A &B.** T_{onset}, T_{10} and T_{max} are the onset decomposition temperature, decomposition temperature corresponds to 10% weight loss and decomposition temperature corresponds to maximum weight loss respectively.

Table 5.7 Thermal data of SBR composites obtained from TG curves

Sample code	T_{onset} (°C)	T_{10} (°C)	T_{max} (°C)
B_0	298	368.6	476
U_{10}	279	312	471
U_{20}	217	276	457
S_{10}	284	323	468
S_{20}	274	308	462
R_{10}	220	284	460
R_{20}	212	270	457
T_{10}	220	307	457
T_{20}	229	298	451

It was observed that all composites decompose approximately in the temperature range 200-500 °C which is due to the decompositions of the three major constituents of lignocellulosic fillers namely cellulose, hemicelluloses and lignin. The thermal stability of composites was lesser than that of SBR vulcanizates without filler. From **figure 5.9** and **table 5.7** it was observed that the thermal stability of UPSP and SPSP are lesser than that of SBR vulcanizates, because the addition of filler decreases the thermal stability of composites. This is a common trend generally found in composites reinforced with natural filler [13]. Also, thermal stability of composites decreases with increase in filler loading. Thermal stability of composites with SPSP was higher than the corresponding composites with UPSP may be due to i) thermal stability of SPSP is greater than UPSP and ii) the comparatively good interfacial adhesion between filler and matrix [42,43].

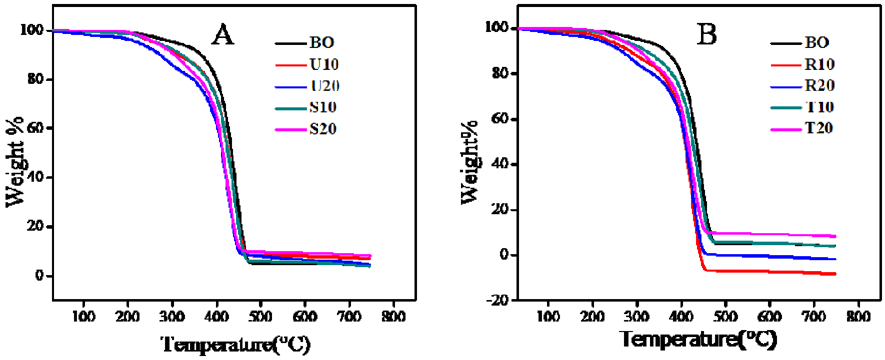

Figure 5.9 TG curves of SBR composites (A) Composites of < 53 μm particle size UPSP and SPSP (B) Composites of 53-90 μm particle size UPSP and SPSP

Table 5.8 Thermal data of SBR composites with MPSP obtained from TG curves

Sample code	Tonset (°C)	T_{50} (°C)	T_{final} (°C)
M_{10}	297	429	471
M_{20}	278	432	463

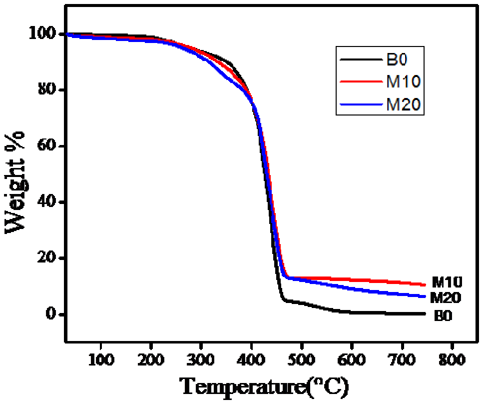

Figure 5.10 TG curves of composites of SBR with <53 μm particle size MPSP

The thermal stability of SBR composites with MPSP was also lesser than that of SBR vulcanizates, anyhow higher than that of composites with UPSP and SPSP. From TG analysis it was observed that the thermal stability of PSP is lesser than SBR, but increased by surface treatment and it is higher for MPSP than SPSP and UPSP. Hence, it can be concluded that the addition of filler MPSP causes a decreases in thermal stability of composites compared to SBR without filler, however this decrease is not significant as that of SBR with SPSP.

5.2.7.2 Differential scanning calorimetry

Theoretically the glass transition temperature indicates the glassy –rubbery transition in the bulk and it is a manifestation of the chain mobility in the polymer. The restriction of molecular mobilization of the rubber matrix in the composites on addition of filler causes slight increase in the Tg of SBR-PSP composites by approximately 2 °C than that of SBR vulcanizates. The filler can obstruct the movements of rubber macromolecular chain through filler matrix interaction [44]. The segmental mobility also depends on the polymer cohesive forces, it was low in nonpolar elastomers and therefore only minor changes in Tg for SBR-PSP composites [44]. **Table 5.9** represents the Tg of composites obtained from the tangent of DSC thermogram of composites of SBR with 10 phr loading UPSP, SPSP and MPSP in different particle sizes (**Figures 5.11 A** and **5.11 B**).

Table 5.9 Tg values of composites of SBR with UPSP, SPSP and MPSP of 10 phr loading

Sample code	Tg (^{0} C)
B_0	-45.4
U_{10}	-43.99
S_{10}	-42.9
R_{10}	-44.4
T_{10}	-43.4
M_{10}	-43.7

The chemical treatment of PSP by coupling agent triethoxy vinyl silane and maleic anhydride increases the filler matrix compatibility, hence the slight increase in Tg values of composites when compared with that of composites with UPSP can be justified. The decrease in particle size also increases the filler matrix adhesion, the Tg of composites with < 53μm size particles (U_{10} and S_{10}) are slightly higher than that of corresponding composites with 53-90 μm size particles (R_{10} and T_{10}). However, there was no noticeable change in the Tg values of composites on increase in filler loading.

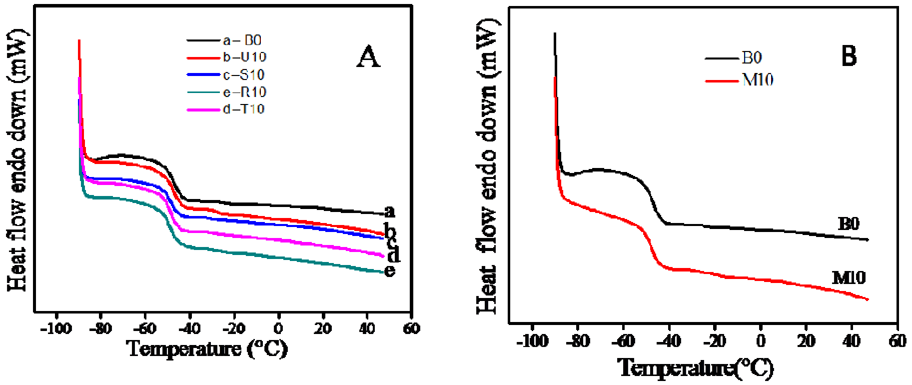

Figure 5.11 DSC thermograms of composites of SBR (A) with UPSP and SPSP of 10phr loading (B) with UPSP and MPSP of 10 phr loading

From **figure 5.11 B** it can be observed that the Tg values of composites of SBR with MPSP (10 phr) is -43.7 °C, slightly higher than that of SBR vulcanizates like composites of SBR with SPSP.

5.3 CONCLUSIONS

From the studies carried out on modified peanut shell powder filled SBR composites it has been concluded that cure time and scorch time decrease with increase in filler loading in SBR composites. Maximum torque and minimum torque increases with increase in filler loading. Torque is higher for composites with chemically treated PSP. Mechanical properties like tensile strength, tear strength, modulus, abrasion resistance and elongation at break first increase with filler loading and then decrease with maximum value at 10 phr filler loading. Hardness of the composites increases with increase in filler loading. This property also increases on modification and decrease in particle size. Better mechanical properties were exhibited by composites of surface modified PSP with smaller particle sizes than with unmodified PSP. Surface morphology of composites observed from SEM images gives additional support to the findings. Composites of modified PSP with smaller particle size at 10 phr loading have been found to exhibit better morphology and mechanical properties as a result of better interfacial adhesion and reinforcing efficiency.

Thermal properties of composites of SBR with unmodified and modified PSP were compared using TG and DSC studies. From TG it was observed that T_{onset} temperature of all composites were slightly lesser than that of SBR matrix. But, the T_{onset} of composites increases upon treatment of filler with triethoxy vinyl silane and maleic anhydride coupling agents, and with a slight decrease in trend on increasing particle size of filler. Higher thermal stability was shown by the composites with silane modified and maleic anhydride composites with 10 phr filler (< 53 μm particle size) loading. From DSC studies it has been observed that the Tg values of composites were slightly higher than that of SBR vulcanizates, this revision may be attributed to the restriction of molecular mobilization of the rubber matrix in the composites on addition of filler particles.

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CHAPTER 6

TRANSPORT PROPERTIES AND OIL RESISTANCE OF MODIFIED PEANUT SHELL POWDER FILLED SBR COMPOSITES

Abstract: In this chapter molecular transport of three aromatic solvents (benzene, toluene and xylene) and petroleum fuel (petrol, kerosene and diesel) through peanut shell powder filled SBR composites were studied at three different temperatures by conventional weight gain experiments. The diffusion process depends on free volume within the matrix, nature of the polymer, nature of filler, temperature, penetrant size and degree of reinforcement. The impact of concentration of filler, the effect of modification by silane treatment on PSP and effect of temperature on the diffusion properties were analysed. The swelling coefficient and diffusion coefficient decrease with increase in filler loading and increase with temperature. The activation energies and thermodynamic parameters were also determined. The relationship between diffusion behavior and morphology was arrived at from SEM studies. The mechanism of transport phenomenon was investigated. The oil resistance of the composites using different oil (IRM 901,902 and 903) were also carried out at different temperatures.

6.1 INTRODUCTION

The basic phenomena such as diffusion, sorption and permeation are relevant because they play vital role in several important areas of engineering and industry. The dimensional stability and integrity of the polymeric materials in presence of liquids are very important in a wide variety of applications such separation process, controlled release of drugs and pesticides, food packaging etc. Hence, the studies of transport properties of organic solvents through polymers are of great technological importance [1]. It is also necessary to study the effect of external forces such as pressure, temperature etc on polymer properties due to its use in the fabrication of structural engineering materials. Most of the products show loss in property due to swelling and relaxation of chain segments on contact with organic solvents [2]. Therefore, the main quality of membrane materials for commercial application is that it should be chemically resistant and retain its mechanical strength and dimensional stability. Hence the diffusion studies have vital role as far as engineering and industrial applications are concerned.

In rubber composites used for the fabrication of materials for transporting gases and liquids, packaging food stuff etc, it is reasonable to carryout diffusion studies to eliminate diffusion and penetration of solvents in products from composites and also to understand the effect of this on the mechanical properties and stabilities. The filler in the composites have profound influence on the transport properties and many reports on the effect of filler on diffusion and sorption properties were reported [3,4]. Aminabhavi and coworkers [4] studied the transport behavior of organic solvents through different polymer membrane and blends. Ranimol et al [1,5] studied the transport of organic solvents through micro and nanocomposites of SBR and their blends. Sareena et al [3,6,7] analyzed the transport of organic solvents through microcomposites of NR. Soney et al studied the transport of organic solvents through cross linked SBR membranes [8]. Lovely et al [9] studied the solvent swelling characteristics of natural rubber composites containing both untreated and alkali treated fibres in aromatic and aliphatic solvents. They also investigated the effect of fibre loading on the swelling behavior of the composite in oils like petrol, diesel and lubricating oil etc. The interaction of fly ash (FA) on dichlorocarbene modified styrene butadiene rubber (DCSBR) was evaluated by Ramesan [10] with reference to their flame and oil resistance. He found that the flame and oil resistance of the composites increased progressively with increasing filler content in DCSBR. The barrier properties of these composites were examined in an atmosphere of petrol, diesel and kerosene. The additives and type of cross linking in the composites are important in the transport studies. The diffusion process depends on free volume within the matrix, nature of the polymer, nature of filler, temperature, penetrant size, natural filler and degree of reinforcement [1,5].

SBR is a general purpose synthetic rubber which has many applications. The high loading capacity, good flame resistance, crack initiation resistance and abrasion resistance of SBR make it useful in several engineering and industrial fields [11]. The reports on sorption and diffusion studies of composites of SBR reinforced with natural fillers are very rare.

The present work explains the molecular transport of organic solvents, petroleum fuel and IRM oils through PSP filled SBR composites. These were studied at different temperatures by conventional weight gain experiments. The impacts of concentration of filler, temperature and penetrant size on the diffusion properties were also investigated. The effect of modification of filler by silane treatment and maleic anhydride on these properties was also investigated.

6.2 RESULTS AND DISCUSSION

The uptake of solvents by modified and unmodified peanut shell powder-filled SBR vulcanizates has been investigated using the conventional weight gain method. The sorption behavior of the rubber vulcanizates, prepared in two different particle sizes of peanut shell powders namely < 53 μm and 53-90 μm were studied at different temperatures. The diffusion of aromatic solvents were studied at 30, 50 and 70 °C petroleum fuel at 30, 45 and 60 °C and IRM oils 901,902 and 903 at 30 and 100 °C. The sorption data obtained for the composites at the temperatures investigated were expressed as the molar percentage uptake (Qt) of the solvents per gram of the rubber vulcanizates. Qt was calculated using the **equation (6.1)** [4,7,8].

$$Qt = \frac{Mt/_{Ms}}{Mp} \times 100 \qquad (6.1)$$

Where Mt is the mass of solvent absorbed, Ms is the molecular mass of solvent and Mp is the mass of polymer.

The Qt of the solvent at particular temperature and particle size was plotted against the square root of time as illustrated in

figures 6.1 to **6.3**. All different curves are similar in nature. It can be seen that for all composites in the initial state the swelling is rapid, then decreases leading to plateau corresponding to equilibrium swelling. Initially the swelling is more due to large concentration gradient and the sample is under intense solvent stress, the swelling decreases on decreasing concentration gradient. At equilibrium swelling the concentration difference is almost nil [11]. The higher initial solvent absorption of polymers has been explained in terms of rapid cavitations, which expose a greater surface area, thus enhancing solvent percolation. On the other hand, at equilibrium, the solvent uptake is counter balanced by solvent extraction from the polymer [12]. Diffusion of solvent through a composite depends on the geometry of the filler (size, shape, size distribution, concentration and orientation), properties of the matrix and interaction between the matrix and filler [13].

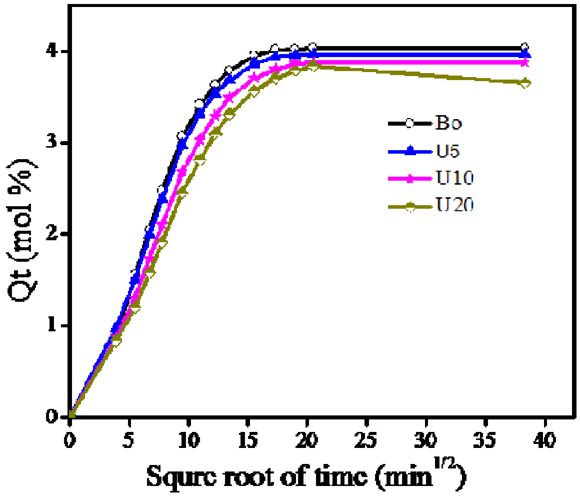

Figure 6.1 Effect of filler loading on mol % uptake of benzene with SBR -UPSP composites at 30 °C

B_0--SBR composite without filler

U--SBR-UPSP composite with particle size < 53 µm, 5, 10 and 20 phr filler

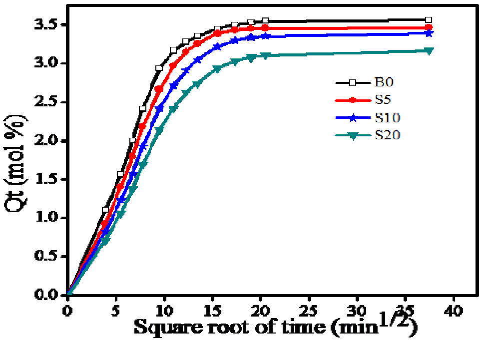

Figure 6.2 Effect of filler loading on mol % uptake of toluene with SBR-SPSP composites at 30 °C

B_0-- SBR composite without filler

S-- SBR- SPSP composite with particle size <53 µm, 5, 10 and 20 phr filler

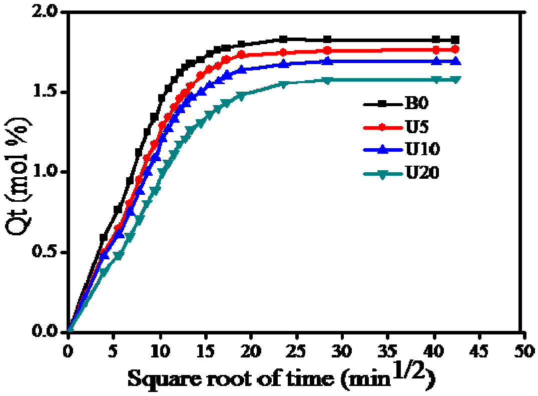

Figure 6.3 Effect of filler loading on mol % uptake of petrol with SBR – UPSP composites at 30 °C

6.2.1 Effect of filler loading

The effect of filler loading on the mol percent uptake by composites of SBR with UPSP, SPSP and MPSP at particular temperature and particle size in benzene and petrol at 30 °C was plotted against square root of time represented in **figures 6.1,2, 3** and **4.** The fillers form physical as well as chemical cross links with polymer chain, which induces certain immobilization in polymer segments, prevents the rearrangement of polymer chain during solvent ingression and reduces the free volume in the composites, thereby causing resistance to the path of penetrants. The decreases in solvent uptake with increase in concentration of filler due to decreased free volume and polymer chain mobility. The nature of filler, degree of adhesion and their compatibility with matrix in the polymer composites influence the diffusion of solvent. The filler takes up the free volume of the polymer matrix and develops a torturous path for the permeating molecules. The degree of tortuosity is tied to the volume fraction of the filler and the shape and orientation of the particles. The tortuosity of path and reduced transport area in the filled system also reduce the solvent uptake [3,13,14]. As the void formation decreases with fibre content, the solvent uptake also decreases. As the filler content increases, the solvent uptake decreases and minimum solvent uptake shown by the composites with 20 phr filler loading. This is due to the increased hindrance of penetrant movement by the filler at higher content [15].

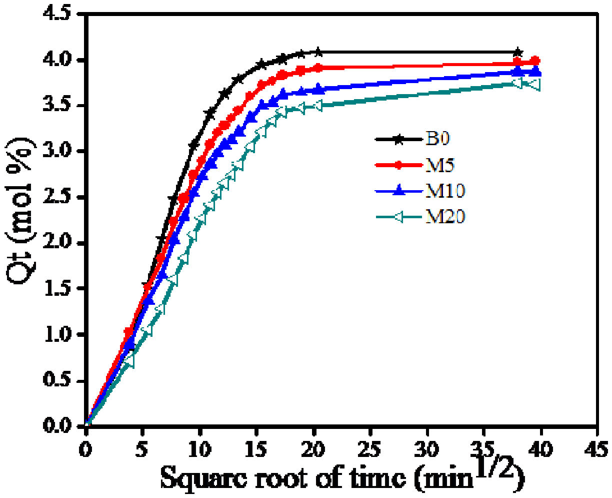

Figure 6.4 Effect of filler loading on mol percent uptake of benzene with composites SBR-MPSP at 30 °C

M-- SBR- MPSP composite with particle size < 53 µm, 5, 10 and 20 phr filler

6.2.2 Effect of penetrant size

Figures 6.5 and **7** represent the systematic trend in the sorption behavior of liquids of different molecular size that is as the size of the solvent molecule increases, the value of Qt (mol%) decreases. Among the solvents benzene, toluene and xylene, benzene shows the higher value of solvent uptake due to activation energy. Similarly among the solvents petrol, diesel and kerosene, petrol shows the high molar percent uptake of solvents **(figure 6.6).** The activation energy of diffusion process increases with increase in molecular size of solvent molecule; hence the bulky group will reduce the migration rate. This also can be explained by free volume theory. According to free volume theory the diffusion rate of molecules strongly depends on the exchange of position of polymer chain with solvent molecules. The ease of exchange decreases with increase in penetrant size, especially in filled system and this leads to decrease in the solvent uptake. It can be seen that the equilibrium solvent uptake also decreases with increase in molecular weight of the penetrant molecules [5,13]. Similar trend was shown by composites with modified fillers also, which is illustrated in **figure 6.7**

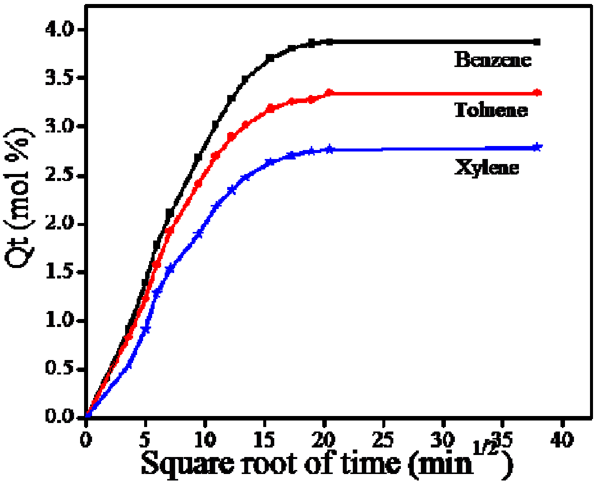

Figure 6.5 Effect of penetrant size on mol % uptake of aromatic solvents with 10 phr SBR–UPSP (< 53 µm) composites at 30 °C

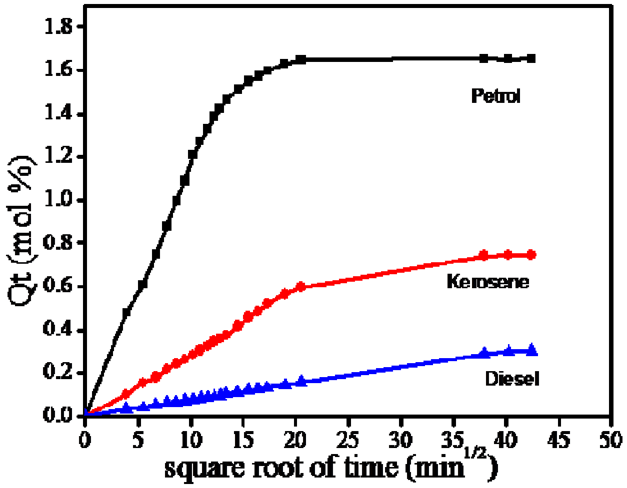

Figure 6.6 Effect of penetrant size on mol % uptake of petroleum fuels with 10 phr SBR–UPSP (< 53 µm) composites at 30 °C

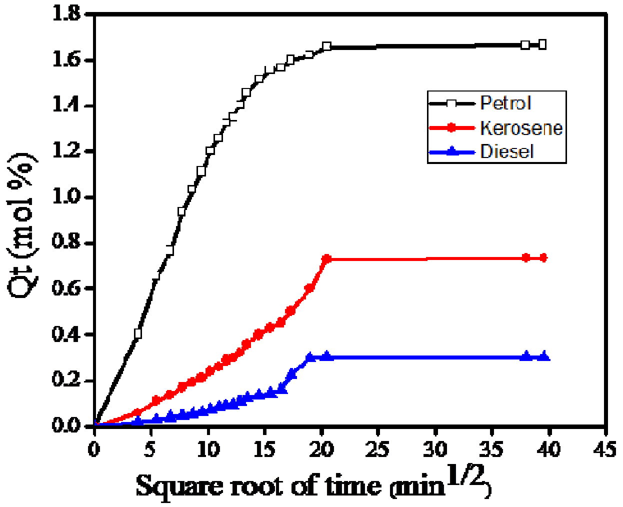

Figure 6.7 Effect of penetrant size on mol % uptake of petroleum fuel with 10 phr SBR-MPSP (< 53 µm) composites at 30 °C

6.2.3 Effect of temperature

The sorption studies were conducted in benzene, toluene and xylene at 30, 50 and 70 ^{0}C to study the effect of temperature on the diffusion of solvents in the composites of SBR with UPSP SPSP and MPSP. **Figures 6.8, 6.9** and **6.10** show that the rate of diffusion and solvent uptake increase with increase in temperature for any particular solvent, because the higher thermal energy at higher temperature facilitates the diffusion of solvent molecules. This causes the reduction of viscosity of solvent molecules and further increase in segmental mobility of the polymer. Activation of diffusion with increase in temperature leading to weakening of filler matrix adhesion and creation of voids in the systems, hence increase in free volume with rise in temperature also increases the rate of diffusion and $Q\infty$. Because the matrix is hydrophobic in nature the variation of temperature largely depends on the adsorption of solvent through filler. Irrespective of the nature of the filler, the initial portions of the sorption curves at all the temperatures were similar. The slope of the linear portion of the curves at different temperature indicates the extent of how diffusion process is activated by raising the temperature. It is found that the slope of the linear portion increases with temperature showing that the transport properties are temperature dependent. This can be attributed to the increase in free volume as a result of the increase in segmental motion of the polymer matrix as well as the gain in kinetic energy by the solvent molecules which resulted from the increased number of collisions at high temperature. Similar trend of increase in rate of sorption of solvent with increase in temperature has been reported earlier [13,16].

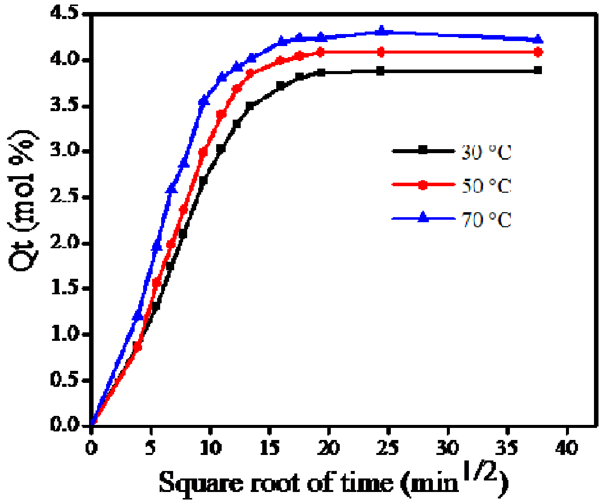

Figure 6.8 Effect of temperature on mol percentage uptake of benzene with 10 phr SBR-UPSP (< 53 µm) composites

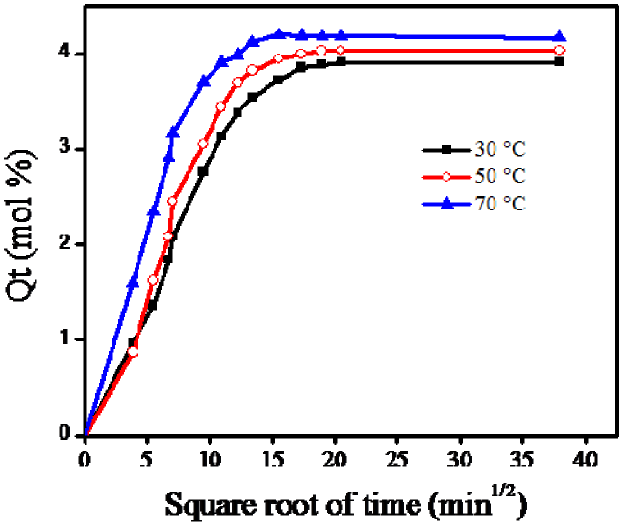

Figure 6.9 Effect of temperature on mol % uptake of benzene with 10 phr SBR-SPSP (< 53 µm) composites

The sorption studies were also conducted in petrol, kerosene and diesel at 30, 45 and 60 °C to study the effect of temperature on the diffusion of solvent and illustrated in **figure 6.10.** These studies also supported the fact that rate of diffusion of solvent uptake increases with increase in temperature.

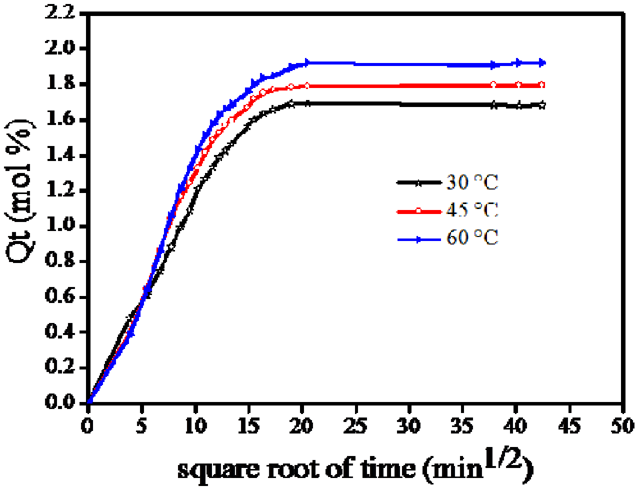

Figure 6.10 Effect of temperature on mol % uptake of petrol with 10 phr SBR-UPSP (< 53 µm) composites

6.2.4 Effect of modification of filler

Figure 6.11 shows that the mol % uptake of solvent for any particular solvent is higher for composite with untreated PSP than with treated PSP. This is clear from the fact that the hydrophilicity of UPSP leading less rubber filler interactions causes easy sorption of solvent than with SPSP and MPSP composites. The modification of filler improved interfacial adhesion between the fibre and the matrix which prevents the diffusion of solvent molecules through the interface. In the presence of a strong interface, there are fewer voids in the interfacial region and this makes it difficult for the solvent molecules to enter the interfacial region. Another factor is that stronger adhesion results in tighter packing within the fibre-matrix network. Hence the distance travelled by the diffusing solvent molecules between two consecutive collisions decreases, resulting in lowering of solvent uptake. The untreated composites have more hydroxyl groups on the surface leading to lower matrix filler interactions creating easy penetration of solvent than the chemically treated composites. The modification of filler by coupling agent increases the compatibility with matrix, improves the surface adhesive characteristics by removing natural waxy materials, hemicelluloses, lignin and other impurities by producing a surface topography and also leads to break down of filler into smaller ones. All these factors provide large surface area result better intersystem crossing between filler and matrix and thus reduces solvent uptake [15,16]. Diffusion is related to the velocity of diffusing molecules by equation

$$D = \frac{1}{3}\lambda C$$

Where C is the mean velocity of molecules and λ = mean free path (distance travelled by molecule between two consecutive collisions). Any factor that reduces the velocity and mean free path of diffusing molecules lowers the sorption of solvent. The velocity is decreased by better interfacial adhesion between filler and matrix because of fewer gaps in interfacial region. The mean free path also decreases by stronger adhesion due to tighter packing within the rubber filler network. The better adhesion in the composites of SPSP and MPSP is also evident from SEM results. At higher filler loading sorption is easier due to filler agglomeration, causes lower solvent uptake.

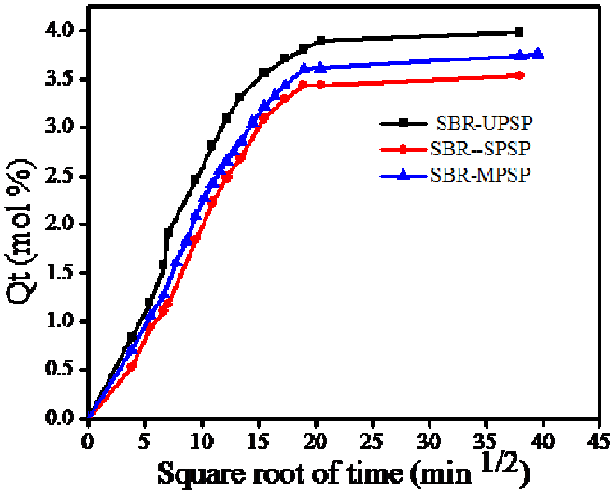

Figure 6.11 Effect of modification of filler on mol % uptake of benzene with 20 phr SBR–PSP (< 53 µm) composites at 30 ^{0}C

The sorption studies using petroleum fuels like petrol, kerosene and diesel at different temperatures also proved that the chemical modification at filler causes the reduction in solvent uptake when comparing to the composites of untreated filler. A typical studies using petrol as solvent is illustrated in **figure 6.12**.

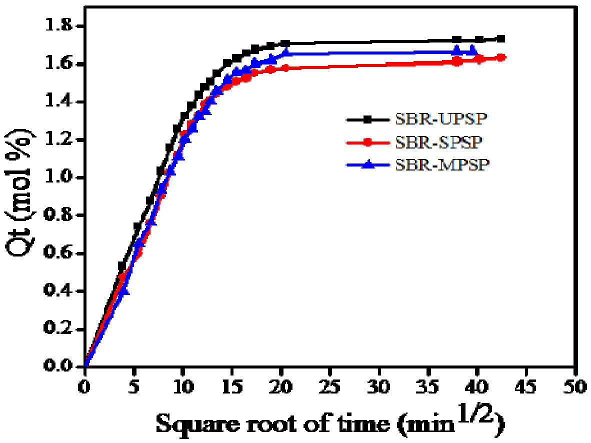

Figure 6.12 Effect of modification of filler on mol % uptake of petrol with 10 phr SBR–PSP (< 53 µm) composites at 30 ^{0}C

6.2.5 Effect of filler particle size

Particle size of the filler has no significant effect, eventhough the Qt of the composites slightly decreases on decreasing the size in a particular solvent at particular temperature, and they are illustrated in the **figures 6.13** and **6.14.**

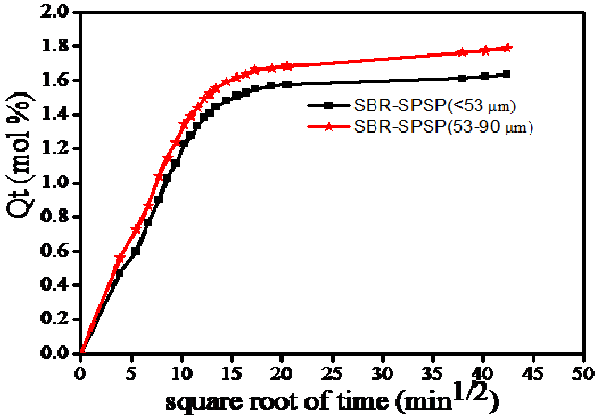

Figure 6.13 Effect of particle size on mol % uptake of benzene with 10 phr SBR–SPSP composite at 30 °C

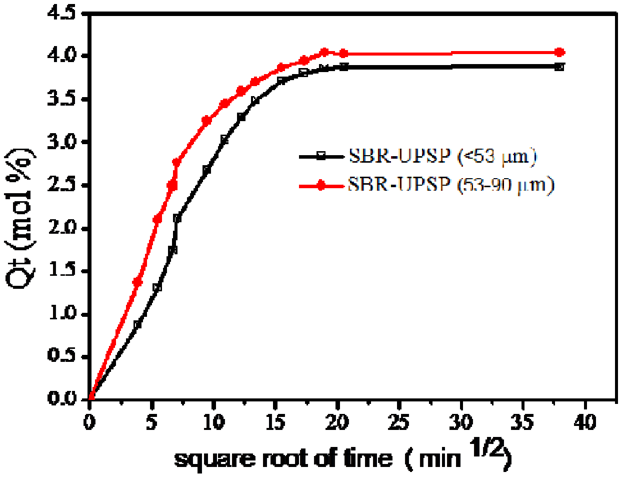

Figure 6.14 Effect of particle size on mol % uptake of petrol with 10 phr SBR–SPSP composites at 30 °C

6.2.6. Kinetic parameters

6.2.6.1 Diffusion coefficient (D)

The diffusion coefficient is a kinetic parameter, it gives an indication of the rate at which a diffusion process takes place and it is related to the polymer segmental mobility, penetrant nature and to the different crosslinks present in the polymer matrix [17]. It is the rate of transfer of the diffusing substance across the unit area of a cross section divided by the space gradient of concentration [13]. Diffusion coefficient can be calculated using the **equation (6.2)** [18].

$$D = \pi\left(\frac{h\theta}{4Q_\infty}\right)^2 \qquad (6.2)$$

Where D is the diffusion coefficient, h is initial thickness of the sample and θ is the slope of the initial portion of the sorption curve and $Q\infty$ is the equilibrium absorption. The slope is calculated from the graph Qt *vs* square root of time [18]. The values of diffusion coefficient, sorption coefficient (S) and permeation coefficient (P) for different SBR-PSP composite systems at different temperatures in aromatic solvent, benzene are represented in **table 6.1** and that for petroleum fuel petrol, kerosene are represented in the **tables 6.3** and **6.4**. It show that the D values increase with increase in temperature in all solvents. The diffusing molecules are facilitated by the higher thermal energies at the increased temperature in all solvents [3,12,18]. From the **tables 6.2** and **6.5,** it reveals that diffusion coefficient values decrease with increase of the penetrant size because of the high activation energy needed with increase in the size of the solvents. The order of the molecular mass of solvents are benzene < toluene < xylene in aromatic solvent and petrol < kerosene < diesel among the petroleum fuels. Hence diffusion coefficient of the particular composite at particular temperature is in the reverse order of molecular mass of the solvents, ie benzene > toluene > xylene and petrol > kerosene > diesel. The decrease in diffusion coefficient of polymer with increase in molecular mass of penetrant molecules were reported [3,17,19,20] earlier. But some authors reported direct proportionality of diffusion coefficient with molecular mass of solvents [7,14]. It is observed that the diffusivity in a given polymer system, whether it is rubbery or glassy, polymer blends, graft or interpenetrating polymer networks as pointed out earlier varies from one polymer system to another. For all solvents the D values decrease from SBR to SBR-PSP composites. SBR with flexible chain will easily adjust with solvent ingression showing highest solvent uptake. Filler acts as obstacle to sorption of solvents, so it is observed that in the two series of solvents studied the D value decreases with increase in filler loading at particular temperature and particle size. As the filler loading increases the diffusion coefficient decreases due to the reduction in free volume with the addition of fillers. From the **tables 6.1** to **6.5** it is clear that the chemical modification of the filler also reduces diffusion coefficient of composites. The chemical treatments tend to remove or replace these cellulosic -OH groups from the natural fibers thereby lowering their hydrophilic nature (thus making it more compatible with the hydrophobic matrix) and hence promote an increase in interfacial adhesion between the SBR matrix and fiber. As a result of this increased interfacial adhesion, the voids and other irregularities present at the interface as well as in the composite decrease resulting in a decrease in the free volume of the whole system and this in turn leads to a decline in the rate of diffusion of solvents [2]. Another reason is that increased interfacial adhesion leads to uniform dispersion of filler in the matrix within the whole composite [13] which is also confirmed from the SEM images given in **figure 6.16.** This leads to a decrease in the distance traveled by the diffusing permeant or solvent molecules, resulting in lower solvent uptake. The tabulated values show that at any particular filler content, solvent, and temperature investigated, the *D* value may slightly increase with filler particle size. The diffusivity depends on the free volume within the polymer and the segmental mobility of polymer chains, the smaller-sized peanut shell powder filled vulcanizates is expected to sorbs less solvent than the larger-sized peanut shell powder filled rubber composites.

6.2.6.2 Sorption coefficient(S)

Sorption is a surface phenomenon and it is an indication of the tendency of the penetrant to dissolve into the polymer. Sorption coefficient is calculated using the **equation 6.3** and represented in the **tables 6.1** to **6.5**.

$$S = \frac{M_\infty}{M} \qquad (6.3)$$

Where M_∞ mass of the solvent taken up at equilibrium swelling and M is the mass of the sample

Similar to diffusion coefficient in all solvents at all temperatures sorption coefficient of SBR-PSP composites are lower than that of SBR vulcanizates. The reason for the decrease in sorption coefficient with increasing filler content is that, the natural filler take up the free volume of the matrix and this in turn creates a very difficult or torturous path for the diffusing penetrant or solvent molecules. On further increase in the filler content the difficulty for the flow of solvent molecules also increases further causing a decrease in the sorption coefficient [2]. Like diffusion coefficient sorption coefficient also decrease on chemical treatment and on reducing the particle size of filler, increase on increasing temperature in all solvents. At all temperatures the sorption coefficient decreases with increase in molecular mass of the solvents. Hence, higher sorption coefficients are shown by the solvent benzene in the studied aromatic solvents and by petrol in the series petroleum fuels.

6.2.6.3 Permeation coefficient (P)

The permeation of a penetrant into a polymer membrane depends on the diffusivity as well as on the sorption. The permeation coefficient (P) gives an idea about the amount of solvent permeated through uniform area of the sample per second. It is given by P = DS, permeation coefficient is the product of diffusion and sorption coefficient [21]. The variation in diffusion coefficient and permeation coefficient for the different UPSP loadings at room temperature in benzene are shown in **figure 6.15**. The diffusion coefficient and permeation coefficient generally decrease as the filler content increases. The lower value for diffusion coefficient indicates the low level of solvent permeation through the polymer. From the tabulated values it is clear that composite without filler shows maximum diffusivity and permeability in all solvents, whereas both are minimum for the composite with 20 phr filler loading. The diffusion coefficient, sorption coefficient and permeation coefficient in a particular solvent at particular temperature and filler loading and maximum for the composites with UPSP and minimum for the composites with SPSP.

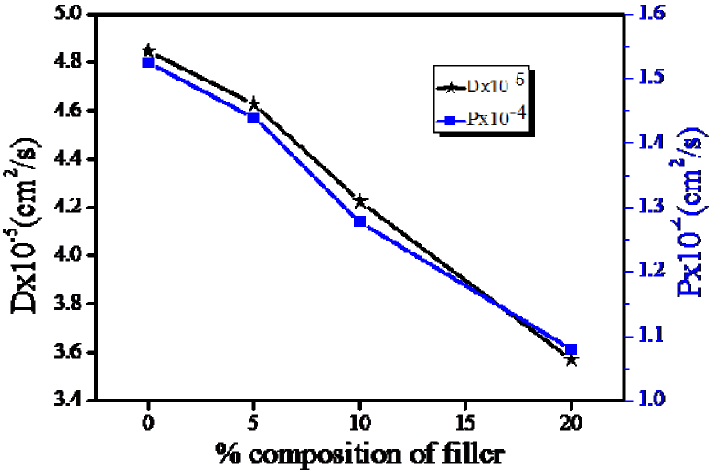

Figure 6.15 Variation in D and P of SBR-UPSP composites with filler loading in benzene at 30 °C

Table 6.1 D, S and P values of SBR-PSP composites at different temperatures in aromatic solvent benzene

Sample code	Diffusion coefficient $Dx10^{-5}$ (cm²/s)			Sorption coefficient S (mol %)			Permeation coefficient $Px10^{-5}$ (cm²/s)		
	30 °C	50 °C	70 °C	30 °C	50 °C	70 °C	30 °C	50 °C	70 °C
B_0	4.8456	5.2815	5.7801	3.1470	3.2918	3.3349	15.249	17.385	19.276
U_5	4.6576	4.8408	5.6485	3.0909	3.2535	3.2946	14.396	15.749	18.610
U_{10}	4.2251	4.3736	5.4562	3.0253	3.1823	3.2279	12.782	13.918	17.613
U_{20}	3.5701	3.9102	5.833	3.0238	3.1733	3.2066	10.795	12.408	16.941
S_5	4.1783	4.7189	5.5481	3.0666	3.1185	3.1739	12.813	14.716	17.609
S_{10}	3.9865	4.0356	4.7917	3.0774	3.1503	3.1612	12.268	12.713	15.148
S_{20}	3.2171	3.7413	4.5564	2.9152	3.0129	3.0339	9.378	11.272	13.824
R_5	4.6761	4.9411	5.6786	3.1263	3.2757	3.3125	15.618	16.185	18.811
R_{10}	4.303	4.6064	5.5395	3.0917	3.2223	3.2672	13.304	14.843	18.099
R_{20}	3.7275	4.2742	5.4402	3.0885	3.2180	3.2112	11.513	13.754	17.470
T_5	4.2708	4.8762	5.5905	3.1084	3.2431	3.2878	13.275	15.813	18.380
T_{10}	4.1266	4.3221	5.2225	3.0899	3.2193	3.2629	12.751	13.914	17.041
T_{20}	3.6128	4.2389	5.1388	3.0552	3.1981	3.2356	11.038	13.550	16.627
M_5	4.3601	4.4964	4.8573	3.0674	3.2339	3.2547	13.370	14.540	15.810
M_{10}	4.2506	4.2458	4.7428	3.0160	3.1562	3.1874	12.820	13.400	15.120
M_{20}	4.1103	3.8494	4.6528	3.0014	3.0805	3.1333	12.340	18.580	14.580

Table 6.2 D, S and P values of SBR-PSP composites at 30 °C temperature in aromatic solvents benzene, toluene and xylene.

Sample code	Diffusion coefficient $Dx10^{-5}$ (cm^2/s)			Sorption coefficient S (mol %)			Permeation coefficient $Px10^{-5}$ (cm^2/s)		
	Benzene	**Toluene**	**Xylene**	**Benzene**	**Toluene**	**Xylene**	**Benzene**	**Toluene**	**Xylene**
B_0	4.8456	4.3916	4.0867	3.1470	3.0227	2.9855	15.249	13.27	12.201
U_5	4.6576	4.1716	3.9328	3.0909	2.9829	2.9701	14.396	12.44	11.680
U_{10}	4.2251	3.8089	3.8872	3.0253	2.9655	2.9531	12.782	11.33	11.479
U_{20}	3.5701	3.1506	3.0022	3.0238	2.9376	2.8894	10.795	9.26	8.670
S_5	4.1783	3.9724	3.5963	3.0666	2.9773	2.9612	12.813	11.83	10.649
S_{10}	3.9865	3.6459	2.8862	3.0774	2.9699	2.9384	12.268	10.83	8.480
S_{20}	3.2171	2.8310	2.4186	2.9152	2.9176	2.7856	9.378	8.26	6.737
R_5	4.6761	4.2576	3.9629	3.1263	2.9946	2.9736	15.618	12.75	11.784
R_{10}	4.303	4.1381	3.9230	3.0917	2.9885	2.9670	13.304	12.37	11.639
R_{20}	3.7275	3.6595	3.2144	3.0885	2.9679	2.9498	11.513	10.86	9.481
T_5	4.2708	4.0438	3.7214	3.1084	2.9848	2.9674	13.275	12.07	11.043
T_{10}	4.1266	3.9676	3.1819	3.0899	2.9869	2.9481	12.751	11.85	9.379
T_{20}	3.6128	3.4762	2.6846	3.0552	2.9545	2.8791	11.038	10.27	7.729
M_5	4.3600	4.0865	3.892	3.0674	2.9755	2.9037	13.37	12.1598	11.3015
M_{10}	4.2506	3.7247	3.6542	3.0160	2.9201	2.8877	12.82	10.8766	10.5523
M_{20}	4.1102	3.1337	2.9585	3.0014	2.9155	2.8467	12.34	9.13673	8.4220

Table 6.3 D, S and P values of SBR-PSP composites at different temperatures in petrol

Sample code	Diffusion coefficient $Dx10^{-5}$ (cm^2/s)			Sorption coefficient S (mol %)			Permeation coefficient $Px10^{-5}$ (cm^2/s)		
	30 °C	**45 °C**	**60 °C**	**30 °C**	**45 °C**	**60 °C**	**30 °C**	**45°C**	**60 °C**
B_0	3.3411	4.3487	4.4532	1.8454	1.8934	2.0302	6.1656	8.2340	9.0411
U_5	2.7926	3.8327	4.2098	1.7026	1.8470	1.96693	4.7546	7.0791	8.2803
U_{10}	2.6224	3.7201	3.7889	1.6984	1.7704	1.9449	4.454	6.5861	7.3689
U_{20}	2.5193	3.3040	3.4885	1.5803	1.7146	1.9256	3.9813	5.6651	6.7173
S_5	2.7337	3.2191	3.6233	1.6669	1.8026	1.9533	4.5568	5.9884	7.0775
S_{10}	2.5769	3.1183	3.4558	1.6333	1.7769	1.9286	4.2088	5.5412	6.6649
S_{20}	2.4514	3.0151	3.2099	1.4490	1.6382	1.8182	3.5522	4.9395	5.8363
R_5	3.1026	4.0867	3.9873	1.8133	1.9902	2.0092	5.6259	8.1334	8.0115
R_{10}	3.0789	3.8084	3.8844	1.7822	1.9383	1.9866	5.4889	7.3819	7.7168
R_{20}	2.8636	3.5802	3.7876	1.7172	1.9144	1.9606	4.9175	6.8543	7.4261
T_5	2.9306	3.4502	3.7362	1.8052	1.9087	1.9893	5.2903	6.5855	7.4326
T_{10}	2.7687	3.3450	3.5830	1.7884	1.8955	1.9619	4.9517	6.3417	7.0294
T_{20}	2.549	3.2643	3.3734	1.6908	1.8698	1.9493	4.3098	6.1038	6.5757
M_5	2.7702	3.1651	3.4189	1.6878	1.8267	1.9491	4.6753	5.782	9.0410
M_{10}	2.556	2.9915	3.3008	1.6660	1.7660	1.9284	4.2584	5.283	6.6640
M_{20}	2.4402	2.7773	2.8487	1.6415	1.6982	2.2795	4.0057	4.717	6.3655

Table 6.4 D, S and P values of SBR-PSP composites at different temperatures in kerosene

Sample code	Diffusion coefficient Dx10^{-5} (cm^2/s)			Sorption coefficient S (mol%)			Permeation coefficient Px10^{-5} (cm^2/s)		
	30 °C	45 °C	60 °C	30 °C	45 °C	60 °C	30 °C	45°C	60 °C
B_0	1.346	1.5793	2.2695	1.4097	1.4504	1.4838	1.898	2.291	3.367
U_5	1.078	1.3523	1.9965	1.2956	1.3759	1.3862	1.397	1.861	2.768
U_{10}	1.006	1.3305	1.9705	1.2702	1.3369	1.3237	1.278	1.779	2.608
U_{20}	0.9008	1.2983	1.7049	1.1951	1.2631	1.305	1.077	1.639	2.225
S_5	1.064	1.3253	1.9063	1.2761	1.3578	1.3777	1.357	1.799	2.626
S_{10}	1.044	1.2980	1.5645	1.2459	1.2632	1.2698	1.300	1.639	1.987
S_{20}	0.8765	1.2656	1.4699	1.1097	1.1530	1.1827	0.973	1.459	1.739
R_5	1.1579	1.3621	2.0733	1.3542	1.4204	1.4047	1.567	1.935	2.912
R_{10}	1.1304	1.3113	2.0165	1.2962	1.3544	1.3511	1.465	1.776	2.725
R_{20}	0.9503	1.2827	1.7989	1.2599	1.3067	1.3145	1.197	1.676	2.365
T_5	1.1279	1.3572	1.9801	1.3064	1.4046	1.3932	1.473	1.906	2.759
T_{10}	1.0711	1.3048	1.7370	1.2920	1.3987	1.3034	1.383	1.825	2.264
T_{20}	0.9267	1.2741	1.6776	1.2155	1.3875	1.2472	1.126	1.767	2.092
M_5	0.9971	1.3004	3.4189	1.2801	1.3380	1.3669	1.276	1.740	1.862
M_{10}	0.9417	1.2179	3.3008	1.2511	1.3197	1.3273	1.176	1.607	1.268
M_{20}	0.8865	1.1221	2.8487	1.1847	1.2350	1.2913	1.050	1.385	1.015

Table 6.5 D, S and P values of SBR-PSP composites at 30 °C temperature in petrol, kerosene and diesel

Sample code	Diffusion coefficient Dx10^{-5}(cm^2/s)			Sorption coefficient S (mol %)			Permeation coefficient Px10^{-5} (cm^2/s)		
	Petrol	Kerosene	Diesel	Petrol	Kerosene	Diesel	Petrol	Kerosene	Diesel
B_0	3.341	1.346	0.4140	1.8454	1.4097	1.1487	6.165	1.898	0.4756
U_5	2.793	1.078	0.3765	1.7026	1.2956	1.0539	4.754	1.397	0.3968
U_{10}	2.622	1.006	0.3617	1.6984	1.2702	1.0038	4.454	1.278	0.3631
U_{20}	2.519	0.9008	0.3383	1.5803	1.1951	0.9150	3.981	1.077	0.3093
S_5	2.734	1.064	0.3529	1.6669	1.2761	1.0415	4.556	1.357	0.3676
S_{10}	2.576	1.044	0.3415	1.6333	1.2459	0.9847	4.208	1.300	0.3363
S_{20}	2.451	0.8762	0.3373	1.4490	1.1097	0.8497	3.552	0.9725	0.2836
R_5	3.102	1.157	0.3886	1.8133	1.3542	1.0807	5.623	1.566	0.4201
R_{10}	3.079	1.130	0.3728	1.7822	1.2962	1.0707	5.488	1.465	0.3992
R_{20}	2.863	0.9503	0.3655	1.7172	1.2599	0.9327	4.917	1.197	0.3409
T_5	2.930	1.128	0.3736	1.8052	1.3064	1.0577	5.290	1.473	0.3953
T_{10}	2.768	1.071	0.3654	1.7884	1.2920	1.0490	4.952	1.383	0.3833
T_{20}	2.549	0.927	0.3483	1.6908	1.2155	0.8943	4.309	1.126	0.3116
M_5	2.770	0.9971	0.3154	1.6878	1.2801	1.0367	4.675	1.276	0.3270
M_{10}	2.556	0.9417	0.3052	1.6660	1.2511	0.9957	4.258	1.1769	0.3039
M_{20}	2.440	0.8865	0.2607	1.6415	1.1847	0.9033	4.005	1.0503	0.2355

6.2.6.4 Activation energy for diffusion (E_D) and permeation (Ep)

The temperature dependence of transport coefficients (P, D, and S) can be used for calculating the energy of activation for the process of diffusion and permeation, from the Arrhenius relationship

$$X = X_o e^{-E/RT} \qquad (6.4)$$

where, X is P, D, or S and X_0 represents P_0, D_0, or S_0, which are constants; E_X is the activation energy, R, the universal gas constant and T, the absolute temperature. From the slopes of the Arrhenius plots of log D and log P *vs* $1/T$, E_P, and E_D can be calculated by linear regression analysis.

Table 6.6 Values of activation energy E_D and E_P of aromatic solvent benzene

Sample code	Benzene		
	E_D (KJ/mol)	E_P (KJ/mol)	ΔH (KJ/mol)
B_0	3.8032	5.0692	1.2659
U_5	4.1109	5.5046	1.3937
U_{10}	5.4347	6.8502	1.4155
U_{20}	8.3646	9.6481	1.2835
S_5	6.1006	6.8428	0.7422
S_{10}	7.9106	8.0700	0.1595
S_{20}	7.4897	8.3624	0.8727
R_5	4.1541	5.4186	1.2645
R_{10}	5.3987	6.6021	1.2034
R_{20}	8.1116	8.9715	0.8598
T_5	5.8083	7.0316	1.2230
T_{10}	8.7167	9.3370	0.6203
T_{20}	7.588	8.9810	1.3930

The correlation coefficients are very close to 0.99. The activation energy of permeation E_P is greater than that of the activation energy of diffusion E_D [20]. The estimated Arrhenius quantities E_D and E_P of the composites in aromatic solvent benzene and petroleum fuel petrol and kerosene are shown in **tables 6.6** and **6.7** respectively. Heats of sorption and activation energies for the sorption processes provide additional information about the transport process [4].

Table 6.7 Values of activation energy E_D and E_P of petroleum fuels petrol and kerosene

Sample code	Petrol			Kerosene		
	E_D (KJ/mol)	**E_P (KJ/mol)**	**ΔH (KJ/mol)**	**E_D (KJ/mol)**	**E_P (KJ/mol)**	**ΔH (KJ/mol)**
B_0	8.677	11.325	2. 648	4.5037	15.9375	1.4338
U_5	11.568	15.610	4.041	17.1434	19.0572	1.9137
U_{10}	18.676	20.893	2.2170	20.0519	22.4668	2.4148
U_{20}	14.485	18.841	4.3561	17.869	20.3438	2.4744
S_5	10.410	14.691	4.2808	16.2439	18.4063	2.1621
S_{10}	10.187	14.691	4.5039	16.2612	20.0043	3.7430
S_{20}	11.055	17.610	6.5550	14.546	16.334	1.7870
R_5	14.716	19.688	4.972	16.1908	17.2391	1.0482
R_{10}	11.342	15.827	4.485	16.0508	17.230	1.1790
R_{20}	11.931	17.738	5.8071	17.8154	19.0130	1.1976
T_5	8.7179	11.698	2.9803	15.6434	17.4769	1.8335
T_{10}	10.105	13.212	3.1073	16.7978	18.6539	1.8561
T_{20}	13.213	16.5890	3.3760	17.0021	20.0698	3.0676

From the **tables 6.6** and **6.7** it is clear that activation energy for diffusion for filled composites is higher than that of unfilled composites. In general, the activation energy is higher for the PSP filled composites compared to the neat SBR in all solvents studied, indicating that the PSP fillers retard the diffusion process. The diffusion of a penetrant molecule through a rubbery matrix can be visualized as a series of jumps through a mass of tangled polymer chains and cavities. The cavities are constantly disappearing and reforming due to thermal fluctuations [22] . The overall diffusion process results from the movement of penetrant molecule from cavity to cavity under the influence of concentration gradient. Each jump requires the disruption of rubber–rubber and rubber to penetrant interactions in order that the surrounding chains can rearrange themselves to allow the passage of the diffusing molecules. The extent of this rearrangement and the amount of energy required depends on the segmental mobility of the rubber. The presence of PSP filler results in decrease in the free movement of the rubber, which accounts for the increase in the activation energy [7]. An increase in the values of diffusion was observed with the increasing size of the penetrants. This suggests that the larger molecules require more energy to create what are known as ``Eyring holes'' within the polymer matrix [8]. E_D is the activation energy required to create an opening between polymer chains large enough to allow the penetrant molecule to pass. Thus, E_D is a function of the inter and intra chain forces that must overcome in order to create the space for a unit diffusional jump of the penetrant. The E_D value will be higher for larger penetrant molecule, the stronger the polymer cohesive energy and the more rigid the chains [4].

The heat of sorption ΔH, is calculated using the following **equation 6.5**

$$\Delta \mathrm{H} = E_D - E_P \quad (6.5)$$

The values of ΔH give additional information about molecular transport through polymer matrix. The ΔH values for aromatic solvent and petroleum fuels are also illustrated in **tables 6.6** and **6.7** respectively. All values are found to be positive suggesting that Henry's type sorption predominates. The formation of newer site involves an endothermic contribution to this process. The endothermicity of the reaction supports the fact that rate of diffusion and maximum solvent uptake increase with increase in temperature [8].

6.2.7 Thermodynamic parameters

6.2.7 .1 Enthalpy of sorption (ΔH) and entropy of sorption (ΔS)

Swelling is the one of the results of sorption of penetrant molecules into the cavities of the polymer matrix. One can consider the process of swelling as the result of two thermodynamic phenomena. They are the increase of entropy of polymer–solvent matrix by the introduction of small molecules as diluents and a decrease of entropy of polymer by isotropic dilation. The entropy of polymer–solvent matrix is actually the entropy of mixing between polymer and solvent molecules. This mixing acts as the driving force for swelling. Thermodynamic sorption constants (Ks) obtained from the equilibrium sorption values can be used for calculating enthalpy of sorption (ΔH) and entropy of sorption(ΔS) using the Van't Hoff **equation 6.6** [2,19].

$$\log K_s = \frac{\Delta H}{2.303R} - \frac{\Delta S}{2.303RT} \qquad (6.6)$$

where ,Ks is the equilibrium sorption constant, which is given by,

$$K_s = \frac{\text{No. of moles of solvent sorbed at equilibrium}}{\text{Mass of polymer}}$$

From the slope and intercept of the curve, van't Hoff plot of log *K vs* 1 /T the values of ΔH and ΔS have been estimated by linear regression analysis. The values of ΔH and ΔS for aromatic solvents and petroleum fuels are tabulated in **tables 6.8** and **6.9** respectively. It can be seen that ΔH values calculated are approximately similar to that obtained from Arrhenius relation and found to be positive suggesting that Henry's type sorption predominates [8,15,23,24]. The ΔS values are negative in all the systems which indicate that the penetrant molecules sorbed are retained as liquid structures within the polymer. The calculated ΔS values for the solvents in all SBR-PSP composites were all negative and did not show any relationship to the filler content, particle size and nature. But the values of ΔS decrease with increase in molecular mass of solvent due to inverse relation of diffusion with penetrant size.

6.2.7 .2 Gibb's free energy of sorption (*ΔG*)

From the values of ΔH and ΔS the free energy ΔG has been calculated as

$$\Delta G = \Delta H - T\Delta S \qquad (6.\ 8)$$

The free energy values are found to be positive and of small magnitude. These results suggest the less spontaneity or non spontaneity of the sorption process [20]. The values show, that there is a slight increase of ΔG as increase in the penetrant size of the solvent molecule. This also supports the fact that the permeation of solvent molecule through composites decreases with increase in penetrant size or molecular mass.

Table 6.8 Values of thermodynamic parameters for solvent benzene

Sample code	ΔH (KJ/mol)	--ΔS (J/mol)	ΔG (KJ/mol)
B_0	1.265	22.4800	8.077
U_5	1.393	22.199	8.120
U_{10}	1.4154	22.309	8.175
U_{20}	1.283	22.746	8.175
S_5	0.7422	24.464	8.154
S_{10}	0.1595	26.192	8.095
S_{20}	0.8727	24.420	8.272
R_5	1.264	22.535	8.093
R_{10}	1.203	22.839	8.124
R_{20}	0.8598	23.960	8.119
T_5	1.223	22.727	8.109
T_{10}	0.620	24.585	8.069
T_{20}	1.253	22.766	8.151

Table 6.9 Values of thermodynamic parameters for petroleum fuels

Sample code	Petrol			Diesel		
	ΔH (KJ/mol)	--ΔS (J/mol)	ΔG (KJ/mol)	ΔH (KJ/mol)	-ΔS (J/mol)	ΔG (KJ/mol)
B_0	2.648	24.523	10.078	1.433	35.114	12.073
U_5	4.041	20.516	10.257	1.913	34.171	12.267
U_{10}	2.217	26.572	10.268	2.414	34.052	12.731
U_{20}	4.356	20.112	10.450	2.474	33.034	12.483
S_5	4.182	20.241	10.315	2.162	33.484	12.308
S_{10}	4.503	19.350	10.367	3.735	36.893	14.913
S_{20}	6.555	13.576	10.668	1.787	35.928	12.674
R_5	4.972	16.935	10.103	1.048	36.650	12.153
R_{10}	4.485	18.687	10.147	1.179	36.598	12.268
R_{20}	5.807	14.632	10.240	1.197	36.794	12.346
T_5	2.980	23.546	10.114	1.833	34.330	12.235
T_{10}	3.107	23.204	10.1384	1.856	35.534	12.622
T_{20}	3.376	21.404	9.8619	3.067	35.213	13.737

6.2.8 Transport mechanism

The mechanism of diffusion of aromatic solvents into SBR composites was analysed using the following empirical relation

$$\mathrm{Log}\frac{Qt}{Q\infty} = \log k + n\log t \qquad (6.\ 9)$$

Where Qt and Q∞ are the mol % uptake of solvent at time t and equilibrium respectively, k is a constant that depends on the structural characteristics of the rubber and gives information between the rubber and solvents. According to the 'n' value three basic modes of transport are distinguished. If n=0.5 the diffusion mechanism is Fickian, in that case the rate of diffusion of permeant molecule is lesser than the polymer segmental mobility. If n=1 the mechanism is non-Fickian, this may be considered in systems in which permeant diffusion rate are faster than the polymer relaxation process. If n lies between 0.5 and 1 the diffusion mechanism is non –Fickian and anomalous, in that case the permeant mobility and polymer segment relaxation rate are similar [3,6]. If the 'n' values below 0.5 the diffusion mechanism is named as less Fickian, in this case the solvent penetration is much below the polymer chain relaxation [13]. The values of 'n' and 'k' for SBR vulcanizates were obtained by regression analysis of log $\frac{Qt}{Q\infty}$ vs log t and the results are given in **table 6.10** for solvent benzene at different temperatures 30, 50 and 70 °C and in **table 6.11** for aromatic solvents at 30 °C. It can be seen that the values 'n' obtained for SBR vulcanizates in aromatic solvents benzene, toluene and xylene are close to less Fickian transport mechanism [13]. But in petroleum fuel the value of 'n' shown in the **tables 6.12** and **13** reveal that the diffusion mechanism is found to be close to Fickian. The values of 'n' did not show any relationship to the composition of filler incorporated into the composites. But the values of 'k' obtained for the composites found to be increased with increase in temperature for all solvents and are presented in in the **tables 6.10, 6.12** and **6.13**. It gives an idea about the nature of interaction between polymer and solvent. The value of 'k' indicates that the presence of filler reduces the interaction of solvent and temperature increase the interaction with the solvents. The similarity in the values of 'k' obtained in the various solvents for the SBR vulcanizates may be an indication of the similarity of interaction of the rubber vulcanizates and solvents [18].

Table 6.10 n and k values of SBR-PSP composites in benzene at different temperature

Sample code	**n**			**k**		
	30 °C	**50 °C**	**70 °C**	**30 °C**	**50 °C**	**70 °C**
B_0	0.3360	0.3033	0.3152	0.4228	0.4630	0.4738
U_5	0.3186	0.3149	0.2228	0.4403	0.4474	0.5676
U_{10}	0.3516	0.3469	0.2596	0.4010	0.4104	0.5160
U_{20}	0.3712	0.3664	0.2685	0.3760	0.3897	0.5042
S_5	0.3252	0.3326	0.1613	0.4314	0.4275	0.6636
S_{10}	0.3352	0.3325	0.1927	0.4185	0.4270	0.6150
S_{20}	0.3385	0.3422	0.2284	0.4085	0.4148	0.5583
R_5	0.3819	0.3692	0.2129	0.3596	0.3709	0.5670
R_{10}	0.2372	0.2052	0.1240	0.5019	0.545	0.6758
R_{20}	0.4127	0.3860	0.2919	0.3294	0.3540	0.4611
T_5	0.3702	0.3481	0.2524	0.3743	0.3961	0.5204
T_{10}	0.4128	0.3736	0.2566	0.3263	0.3671	0.5154
T_{20}	0.4244	0.3961	0.2125	0.3173	0.3386	0.5644
M_5	0.4675	0.3942	0.4179	0.3261	0.3833	0.3316
M_{10}	0.4936	0.4634	0.4507	0.3008	0.3304	0.3433
M_{20}	0.5591	0.4868	0.5355	0.2473	0.3045	0.2783

Table 6.11 n and k values of SBR-PSP composites in benzene, toluene and xylene at 30 **°C**

Sample code	**n**			**k**		
	Benzene	**Toluene**	**Xylene**	**Benzene**	**Toluene**	**Xylene**
B_0	0.3360	0.2882	0.3523	0.4228	0.4777	0.4029
U_5	0.3186	0.3009	0.3563	0.4403	0.4603	0.3983
U_{10}	0.3516	0.3295	0.3715	0.4010	0.4262	0.3810
U_{20}	0.3712	0.3942	0.4366	0.3760	0.3484	0.3115
S_5	0.3252	0.3113	0.3759	0.4314	0.4497	0.3772
S_{10}	0.3352	0.3373	0.4094	0.4185	0.4176	0.3399
S_{20}	0.3385	0.3550	0.4242	0.4085	0.3937	0.3233
R_5	0.3819	0.3873	0.4116	0.3596	0.3529	0.3305
R_{10}	0.2372	0.3590	0.40184	0.5019	0.3734	0.3362
R_{20}	0.4127	0.4200	0.4407	0.3294	0.3218	0.3040
T_5	0.3702	0.3969	0.4165	0.3743	0.3475	0.3285
T_{10}	0.4128	0.4446	0.4568	0.3263	0.2983	0.2861
T_{20}	0.4244	0.4758	0.4510	0.3173	0.2522	0.2970
M_5	0.4675	0.4612	0.5239	0.3261	0.3312	0.2532
M_{10}	0.4936	0.4181	0.5133	0.3008	0.3626	0.2891
M_{20}	0.5591	0.5411	0.5937	0.2473	0.2635	0.2238

Table 6.12 n and k values of SBR-PSP composites in petrol at different temperatures

Sample code	**n**			**k**		
	30 °C	**45 °C**	**60 °C**	**30 °C**	**45 °C**	**60 °C**
B_0	0.4286	0.4940	0.5114	0.3970	0.3464	0.3311
U_5	0.4633	0.5205	0.5672	0.3594	0.3252	0.2859
U_{10}	0.4678	0.5373	0.5748	0.3524	0.3102	0.2800
U_{20}	0.5083	0.5609	0.6187	0.3054	0.2848	0.2477
S_5	0.4361	0.5004	0.5456	0.3787	0.3335	0.2934
S_{10}	0.4677	0.5234	0.5655	0.3518	0.3216	0.2885
S_{20}	0.4628	0.4991	0.5353	0.3542	0.3340	0.3103
R_5	0.5015	0.5391	0.5992	0.3207	0.3019	0.2644
R_{10}	0.5016	0.5301	0.5987	0.3429	0.3177	0.2576
R_{20}	0.5082	0.5258	0.5762	0.3908	0.3152	0.2739
T_5	0.4906	0.5575	0.6032	0.2679	0.2866	0.2569
T_{10}	0.5198	0.5886	0.6806	0.2925	0.2647	0.2042
T_{20}	0.5433	0.5639	0.7062	0.2692	0.2856	0.2916
M_5	0.4875	0.3599	0.2832	0.2284	0.2390	0.3091
M_{10}	0.2754	0.4056	0.2994	0.3335	0.2005	0.2867
M_{20}	0.5845	0.4315	0.2976	0.2808	0.2894	0.3055

Table 6.13 n and k values of SBR-PSP composites in kerosene at different temperatures

Sample code	**n**			**k**		
	30 °C	**45 °C**	**60 °C**	**30 °C**	**45 °C**	**60 °C**
B_0	0.5303	0.5191	0.4609	0.2418	0.2575	0.3387
U_5	0.5148	0.4994	0.4282	0.2376	0.2626	0.3637
U_{10}	0.5292	0.5083	0.4706	0.2258	0.2521	0.3195
U_{20}	0.5171	0.5119	0.4205	0.2270	0.2423	0.3580
S_5	0.5943	0.5454	0.4553	0.1949	0.2331	0.3401
S_{10}	0.5296	0.5319	0.4427	0.2273	0.2379	0.3485
S_{20}	0.5163	0.5171	0.4422	0.2327	0.2413	0.3385
R_5	0.5626	0.4811	0.4635	0.2025	0.2607	0.3167
R_{10}	0.6364	0.4998	0.4327	0.1860	0.2648	0.3508
R_{20}	0.5063	0.4751	0.3993	0.2309	0.2605	0.3806
T_5	0.6152	0.5045	0.4643	0.1798	0.2514	0.3226
T_{10}	0.5750	0.4827	0.4866	0.1870	0.2485	0.2769
T_{20}	0.4948	0.3829	0.4115	0.2299	0.3290	0.3445
M_5	0.7031	0.5158	0.5769	0.1307	0.1836	0.1446
M_{10}	0.6130	0.5295	0.6042	0.1513	0.1543	0.1229
M_{20}	0.6352	0.5146	0.5761	0.1258	0.1861	0.1345

Table 6.14 n and k values of SBR-PSP composites in petroleum fuels at 30 **°C**

Sample code	**n**		**k**	
	Petrol	**Kerosene**	**Petrol**	**Kerosene**
B_0	0.4286	0.5303	0.3970	0.2418
U_5	0.4633	0.5148	0.3594	0.2376
U_{10}	0.4678	0.5292	0.3524	0.2258
U_{20}	0.5083	0.5171	0.3054	0.2270
S_5	0.4361	0.5943	0.3787	0.1949
S_{10}	0.4677	0.5296	0.3518	0.2273
S_{20}	0.4628	0.5163	0.3542	0.2327
R_5	0.5015	0.5626	0.3207	0.2025
R_{10}	0.5016	0.6364	0.3429	0.1860
R_{20}	0.5082	0.5063	0.3908	0.2309
T_5	0.4906	0.6152	0.2679	0.1798
T_{10}	0.5198	0.5750	0.2925	0.1870
T_{20}	0.5433	0.4948	0.2692	0.2299
M_5	0.4875	0.7031	0.2284	0.1307
M_{10}	0.2754	0.6130	0.3335	0.1513
M_{20}	0.5845	0.6352	0.2808	0.1258

6.2.9. SEM morphology

The morphology of fractured surface of SBR vulcanizates with 10 and 20 phr of UPSP, SPSP and MPSP are shown in **figure 6.16**. On comparing the **figure 6.16 A** with others it is observed that the hindrances for the passage of solvent is less and solvent uptake is high.

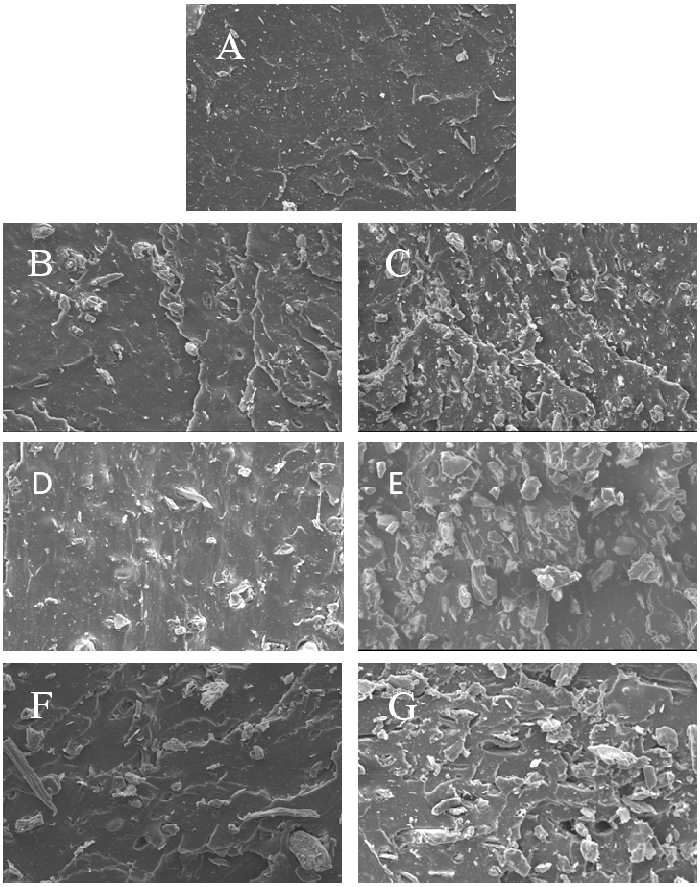

Figure 6.16 SEM images of SBR-PSP (<53 μm) composites: (A) SBR vulcanizates, (B) SBR-UPSP (10 phr), (C) SBR-UPSP (20 phr), (D) SBR-SPSP (10 phr), (E) SBR-SPSP (20 phr), (F) SBR-MPSP (10 phr), (G) SBR-MPSP (20 phr)

At 20 phr filler loading (**figure 6.16 C, E** and **G**) solvent uptake is less due to aggregation of filler, which causes the obstruction to the passage of solvent molecules throughout the membrane and reduces the mol% uptake of solvents than composites with lower filer loading. But at 10 phr filler loading (**figure 6.16 B, D** and **F**) the absorbed solvent molecule is trapped in polymer membrane leads to higher solvent uptake than composites with 20 phr filler loading. Hence the SEM micrographs give additional evidence for lower values of diffusion coefficient and sorption coefficient at higher filler loading.

6.2.10 Oil resistance of composites

The oil resistance of a rubber is one of the key characteristics in the final selection of the rubber to be used, especially in automotive, industrial and seal applications. Oil resistance is the reciprocal of the degree of swelling in oil and is governed by the competition between the driving force towards ‘‘dissolution of the rubber in the low-molecular-weight oil’’, i.e.swelling, and the elastic force which increases upon oil uptake[25].Rubbers such as EPDM, isoprene rubber (IR), NR and butyl rubber (BR) have a high oil swell, due to their hydrocarbon structure, which is very similar to the structure of the oil itself.

Oil resistance of the sample is usually measured by the method ASTM D 3182 using IRM 901, 902 and 903 oil. This test method covers the required procedures to evaluate the comparative ability of rubber and rubber-like compositions to withstand the effect of liquids. Significant and uses of these experiments are certain rubber articles, for example, seals, gaskets, hoses, diaphragms, and sleeves, may be exposed to oils, greases, fuels and other fluids during service. The exposure may be continuous or intermittent and may occur over wide temperature ranges. Properties of rubber articles deteriorate during exposure to these liquids, affecting the performance of the rubber part, which can result in partial failure. This test method attempts to simulate service conditions through controlled accelerated testing, but may not give any direct correlation with actual part performance, since service conditions vary too widely. It yields comparative data on which to base judgment as to expected service quality. This test method is suitable for specification compliance testing, quality control, referee purposes and research and development work.

The percentage of the oil swelling was calculated using the **equation 6.10**

$$\%\ \text{swelling} = \frac{W_2 - W_1}{W_1} \times 100 \qquad (6.10)$$

Where w_1 and w_2 are the weights of the samples before and after immersed in oil respectively.

Oil resistance is the reciprocal of degree of swelling. The percentage mass swelling of the composites of SBR with UPSP, SPSP and MPSP at room temperature and 100 °C are represented in the **figures 6.17** to **6.21**. From the **figures 6.17, 6.18** and **6.19** it is cleared that oil resistance of the composites increased with increase in concentration of filler due increase in crosslink density of composites on filler incorporation. As is well known, oil resistance property is supposed to be primary concern of the composites. The vulcanized composite does not dissolve in the oil but only swells due to the effect of crosslinking. The oil-resistance results are consistent with the results of the cross linking density. The **figures 6.17** to **6.19** exhibited that percentage swelling of composites of SBR with modified and unmodified PSP are higher in IRM 901 oil and lower in IRM 903 because of less polarity of IRM 901 oil. The order of polarity of oil are IRM 903 > IRM 902 > IRM 901. SBR and its composites with PSP are less polar, hence their oil swellings are inversely proportional to its polarity [26]. The oil resistances of the composites are higher in IRM 903 oil.

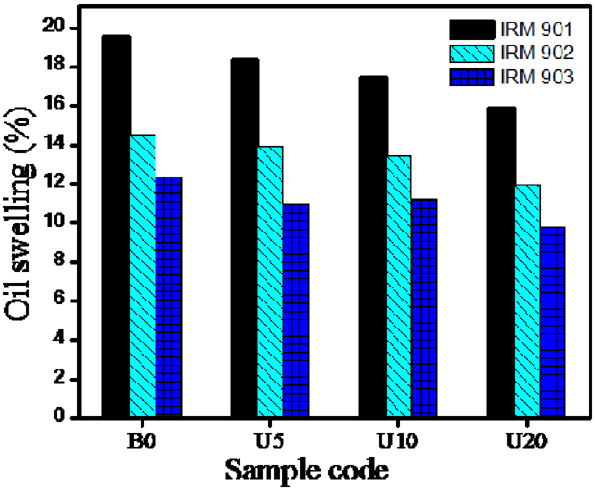

Figure 6.17 Change in oil resistance of SBR-UPSP composites with filler content at 30 °C

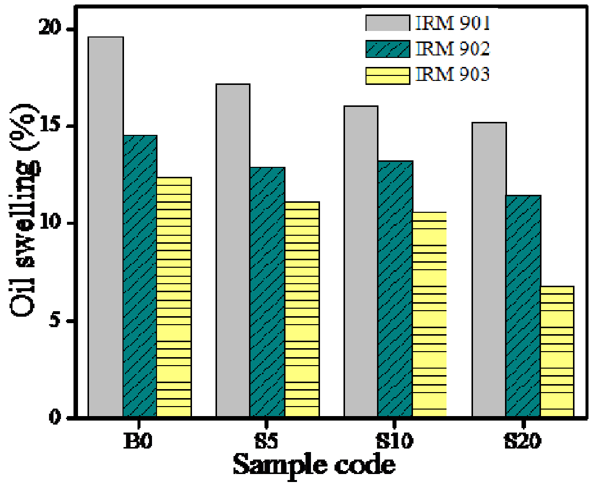

Figure 6.18 Change in oil resistance of SBR-SPSP composites with filler content at 30 °C

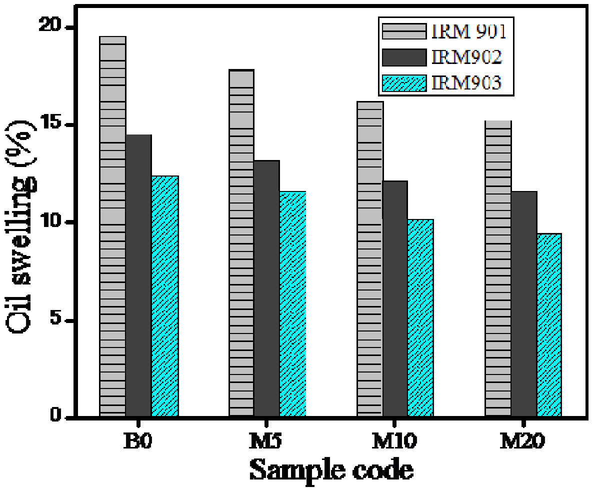

Figure 6.19 Change in oil resistance of SBR-MPSP composites with filler content at 30 °C

On the other hand, the formation of networks also makes the penetrant inevitably travel along a tortuous path and decreases the relative permeability in the composites, which improve the oil resistance property [27]. From the **figures 6.20** and **6.21** it has been revealed that the degree of swelling of composites at 100 °C is higher than that at room temperature, hence the oil resistance decreases with increase in temperature in modified and unmodified PSP filled composites.

Figure 6.22 illustrated the influence of modification of filler on the oil resistance of the composites; it shows that the percentage swelling of the composites in oil decreased on modification of filler, which means the oil resistance of the composites become greater. But there is no significant difference between the composites of SBR with SPSP and MPSP, eventhough the oil resistance is highest for composites with SPSP.

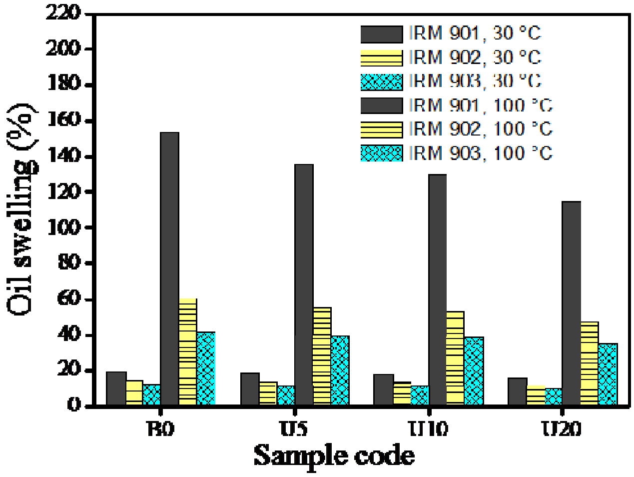

Figure 6.20 Change in oil resistance of SBR-UPSP composites with filler content at 30 and 100 °C

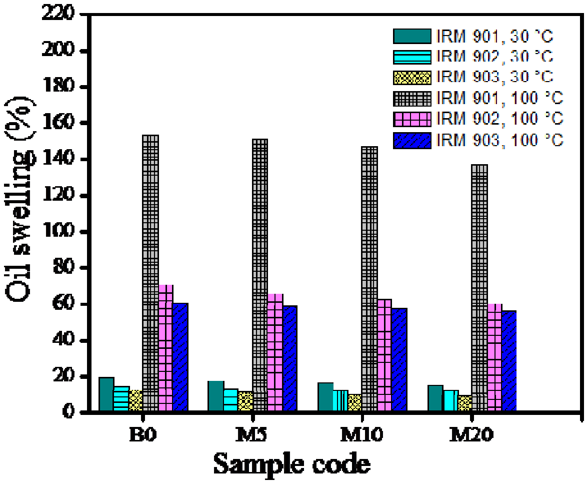

Figure 6.21 Change in oil resistance of SBR-MPSP composites with filler content at 30 °C and 100 °C

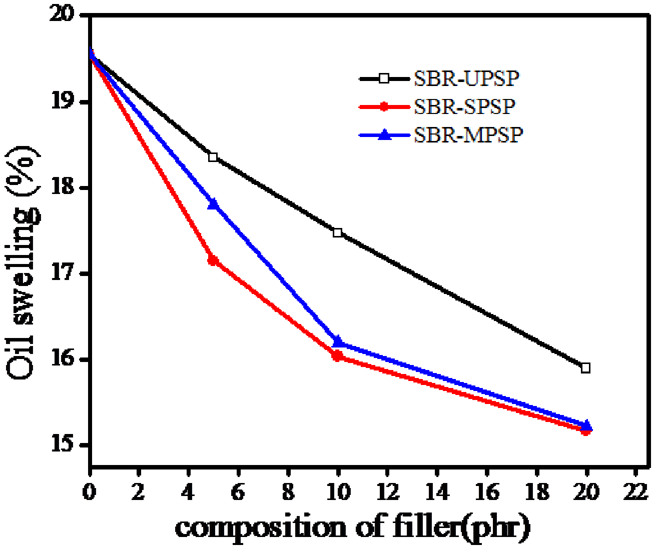

Figure 6.22 Change in oil resistance of composites on modification of filler at 30 °C

The results of oil resistance based on the changes in tensile strength after oil immersion at room temperature for about 72 h are presented in **figure 6.23**. It is obvious from **figure 6.23** that the tensile properties of the composites are decreased after oil immersion and the magnitude of decrease in tensile strength is less with increase in concentration of filler and on surface modification of filler [28].

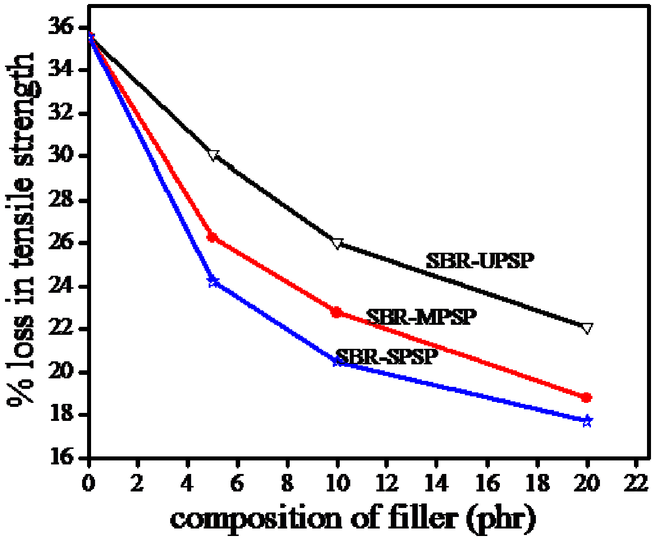

Figure 6.23 Change in tensile strength of composites of SBR with UPSP, MPSP and SPSP after aging in the IRM 901 oil at 30 °C for 72 h

As mentioned in the previous work [29,30] the relative tensile strength (i.e. the ratio of tensile strength after oil immersion to that before oil immersion) is successfully used as an indicator for determining oil resistance. The higher the relative tensile strength, the higher the oil resistance [31]. **Figure 6.24** demonstrates the relative tensile strength of composites of SBR with UPSP, MPSP and SPSP which increases on increases on filler loading and also on modification of filler. Hence oil resistance increases with increase in filler loading and on modification of filler in the composites of SBR reinforced with PSP.

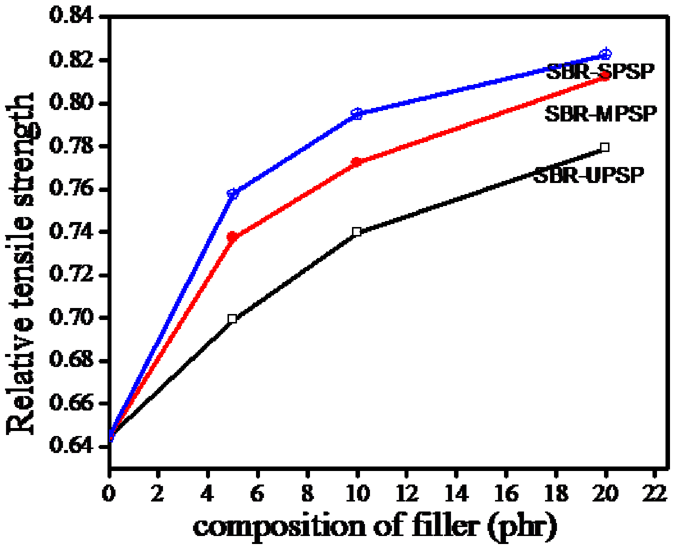

Figure 6.24 Relative tensile strength of composites of SBR with UPSP, MPSP and SPSP after aging in the oil at 30 °C for 72 h

6.3 CONCLUSIONS

The sorption and diffusion studies of aromatic solvents (benzene, toluene and xylene) and petroleum fuel (petrol, kerosene and diesel) at three different temperatures were carried out using unmodified and modified peanut shell powder filled SBR composites. The influence of molecular mass of solvent, effect of filler loading, effect of modification of filler and effect of temperature were analysed. The mol % uptake, diffusion coefficient and sorption coefficient decrease with increase in penetrant size and filler loading. The composites with SPSP and MPSP show more resistance to solvent swelling than with corresponding unmodified composites. But the temperature was found to activate the diffusion process, hence the mol% uptake and diffusion coefficient are higher at higher temperatures. Activation energy for diffusion of composites increases with filler loading and penetrant size. Heats of sorption in all systems were found to be positive suggesting that the Henry's type sorption predominates and support the endothermicity of sorption process. The analysis of transport mechanism shows that the mode of transport of aromatic solvents through PSP filled SBR composites was in less Fickian mode and with petroleum fuel was close to Fickian mode. The data obtained from this study gives an idea about the response of the composites in solvents, which is necessary for the application of this fabricate materials for transportation of solvents. Oil resistance of the samples was measured by ASTM D 3182 method using IRM 901, 902 and 903 oil. Oil resistance is the reciprocal of the degree of swelling of the composites, it increased with increase in concentration of filler due to increase in crosslink density of composites on filler incorporation. Oil resistance also increases on modification of filler and decreases with temperature. The oil resistance of rubber is one of the key characteristics in the final selection of the rubber to be used, especially in automotive, industrial and seal applications.

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CHAPTER 7

BIODEGRADABILITY STUDIES OF COMPOSITES OF SBR REINFORCED WITH MODIFIED PEANUT SHELL POWDER

Abstract: The development of biocomposites and their applications are important in material science due to environmental and sustainability concerns. The extent of degradation depends on the nature of reinforcing filler, particle size and their modification. In this chapter, it is tried to focus on the biodegradation of composites of SBR reinforced with PSP by soil burial test. The composites of SBR with UPSP, SPSP and MPSP of 10 phr and 20 phr filler loading in two particle sizes were buried in garden soil for six months. The microbial degradation was assessed through the measurement of weight loss, tensile strength and hardness at definite period. The study shows that degradation increases with increase in filler loading and particle size. The chemical treatment of filler has been found to resist the degradation. The water sorption studies of the composites support the observations in soil burial test. The morphological characteristics by the SEM also confirmed biodegradation process by the microorganism present in the soil.

7.1 INTRODUCTION

The biocomposites developed from natural filler is gaining importance in the composite technology because they degrade in soil or by composting process effectively and do not evolve any toxic or unhealthy components in the soil. The use of nature based resources as reinforcement in the composites reduces the unsustainable consumption of petroleum products. The natural fillers are more ecofriendly and their use is highly significant in environmental conservation and community awareness as they reduce the waste disposal problems and its management issues. Major advantages of lignocellulosic fillers from natural resources over synthetic fibres such as glass and rubber are renewable, cheaper, low density, high toughness, acceptable specific strength properties and biodegradability [1–6]. Owing to these characteristics, the scientific world has much interest in natural filler reinforced composites. However main drawback lies in their incompatibility with hydrophobic polymer matrix due to its hydrophilic character by high content of hydroxyl and polar groups in cellulosic molecular chains. As a result composites have weak interfacial adhesion and poor properties. These issues are solved by various methods like chemical treatment, coronary treatment, grafting and the use of various coupling agents [7–14].

Cellulose and lignin are the main components present in most of the natural fillers. Biodegradation of composites occurs through different ways such as enzymatic degradation, chemical decomposition associated with living organism like bacteria or fungi or by microorganisms present in the soil [11–19]. Muniandy et al [6] investigated the biodegradation of rattan powder filled natural rubber composites as a function of filler loadings and silane coupling agent by burying the sample in soil for six months, the degradation was evaluated through weight loss and tensile testing. Sareena et al [5] studied the biodegradation behavior of natural rubber reinforced with natural filler by soil burial test. They observed that the tensile strength and hardness were decreased after soil burial testing due to the possible biological attack by microbes onto the samples. Mei-Chun Li etal [13] investigated the effect of methyl methacrylate (MMA) and starch concentration on the mechanical properties, morphology, toluene swelling behavior, water absorption behavior and biodegradability of PMMA-modified starch/SBR biocomposites. Pontawitklungsuwan et al [9] studied mechanical properties and biodegradability of cuttle bone/NR composites. They analysed the degradation of NR vulcanizates in both landfill and liquid bacterial culture assays and revealed that cuttle bone/NR green composite materials could be degradable within three months. Buenaventurada et al [20] studied the effect of silane treatment on the mechanical properties, thermal stability and biodegradability of poly (butylene succinate) composites reinforced with cotton fiber. They observed that the incorporation of CF (with and without silane treatment) in PBS significantly increased the biodegradation rate of the composites. Many researchers also reported the biodegradability of composites of natural rubber reinforced with natural filler [3,5,6,18,19]. But the biodegradability studies of natural filler reinforced SBR composites have not yet reported.

This chapter highlights on the biodegradability of peanut shell powder reinforced SBR composites by soil burial test. We have also analysed the effect of surface modification of PSP using coupling agent triethoxy vinyl silane and maleic anhydride on biodegradability of the composite were also carried out. The present chapter also discusses the water sorption studies of the composites to support the soil burial test.

7.2 RESULTS AND DISCUSSION

7.2.1 Biodegradation studies by soil burial test

The micro composites of SBR reinforced with UPSP and SPSP with two particle sizes below 53 µm and 53-90 µm were formulated. Two selected samples with filler loading (10 phr and 20 phr) of tensile and hardness specimen from vulcanized samples of each series were buried in soil for 180 days. The weight loss and hardness were measured at two time period after 90 and 180 days. The tensile strength was also measured after 180 days. Surface morphology of composites was also compared by SEM studies before and after soil burial. **Figures 7.1** and **7.2** represent the weight loss of specimen of the selected samples with 10 phr PSP and 20 phr PSP respectively. From this it can be seen that filler loading and modification of filler has marked role in the biodegradability of the composites. Weight loss increases with increase in filler loading in each series, which means that the biodegradability of the composites increases with increase in filler loading. The weight loss of composite with modified PSP is less when compared with the composites of unmodified PSP of same filler composition. The modified filler has more resistance to biodegradation since its hydrophilicity decreases and interfacial adhesion increases on modification. The biodegradation also increases with increase in particle size of the filler [6,7,13]**. Figure 7.2A** gives a comparative study of the percentage weight loss of SBR-PSP composites after 180 days of soil burial.

The biodegradation behaviour by microorganisms present in the soil has been found to reduce the mechanical properties of composites. The comparison of mechanical properties of composites before and after soil burial supports the biodegradability of composites. From **figure 7.2 B** it has been observed that the tensile strength of the composites also decreases when it is buried in the soil for a specific period. The loss in tensile strength has been found to increase on filler loading and decreases on modification. The increase in particle size of the filler also has been found to enhance the biodegradation of the composites. The silane modification of the filler improves the intersystem crosslinking in the composites as it resists the degradation in soil by moisture and microorganism. Hence the loss in tensile strength on biodegradation is less for composites with SPSP than with UPSP. The loss in tensile strength is maximam for the composite with UPSP with high particle sizes [6] . Needless to say those other environmental factors such as nature of soil, acidity, alkalinity *etc* also contribute in biodegradation phenomena.

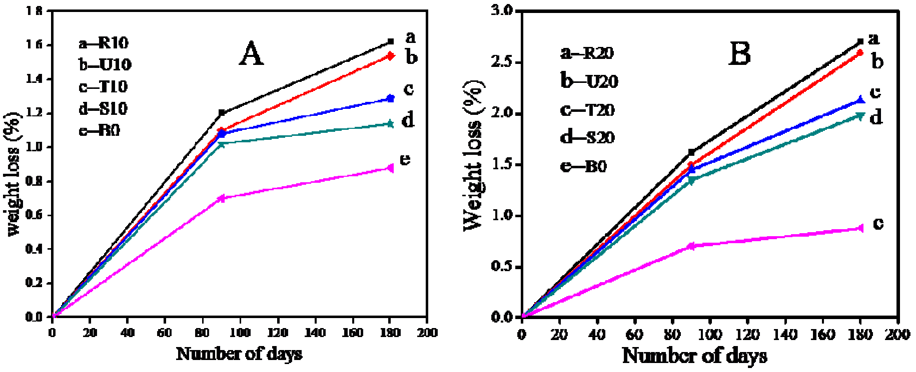

Figure 7.1 (A) Weight loss of SBR-PSP composites (10 phr) **(B)** Weight loss of SBR-PSP composites (20 phr) after 180 days of soil burial

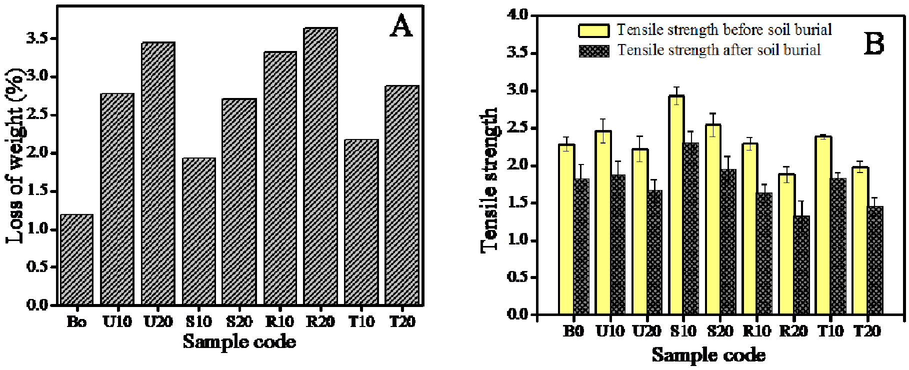

Figure 7.2 (A) Percentage weight loss of tensile specimen of SBR-PSP composites after 180 days of soil burial **(B)** Comparison of tensile strength of SBR-PSP composites after 180 days of soil burial

The hardness of the composites also decreases after soil burial for 180 days. The percentage loss was found to be proportional to particle size and filler loading. The order of percentage loss of hardness is SBR-UPSP$_{53\text{-}90\ \mu m}$ > SBR-UPSP$_{<53\ \mu m}$ > SBR-SPSP$_{53\text{-}90\ \mu m}$ > SBR-SPSP$_{<53\ \mu m}$, which is clear from **figure 7.3.** From these results one can conclude that the chemical treatment and smaller size of filler raises the interfacial adhesion between filler and matrix [6,14] and therefore increase the resistance to degradation and decrease the percentage loss in mechanical properties.

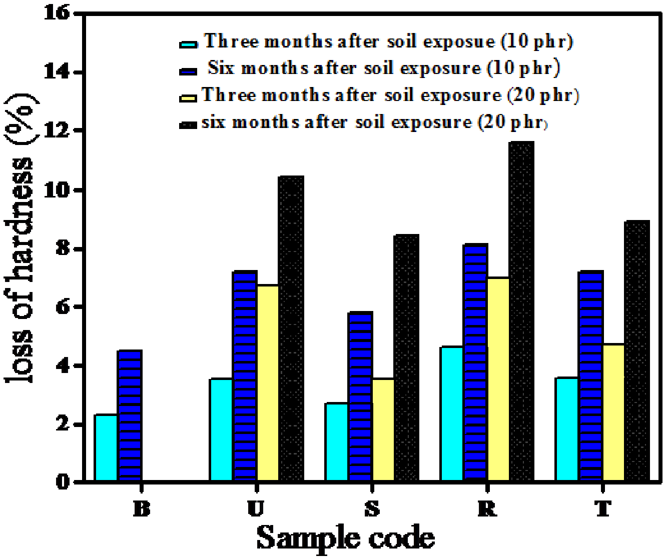

Figure 7.3 Percentage loss of hardness of SBR-PSP composites after 180 days of soil burial

B:SBR vulcanizate without filler, U:SBRvulcanizate with UPSP$_{(<53\ \mu m)}$, S: SBR vulcanizate with SPSP$_{(<53\ \mu m)}$, R; SBR vulcanizate with UPSP$_{(53-90\ \mu m)}$, T: SBR vulcanizate with SPSP$_{(53-90\ \mu m)}$.

The micro composites of SBR reinforced with MPSP with particle sizes below 53 µm were also formulated. Two selected samples with filler loading (10 phr and 20 phr filler) of tensile specimen from vulcanized samples of each series were buried in soil for 180 days. The weight loss and tensile strength were measured after 180 days. The **figure 7.4** illustrates the dependence % of weight loss and tensile strength to filler composition and modifications of filler in the composites. The weight loss and loss in the tensile strength are found to increase on filler loading and decrease on modification. The order of biodegradation of the composites are found to be SBR-UPSP > SBR-MPSP > SBR-SPSP.

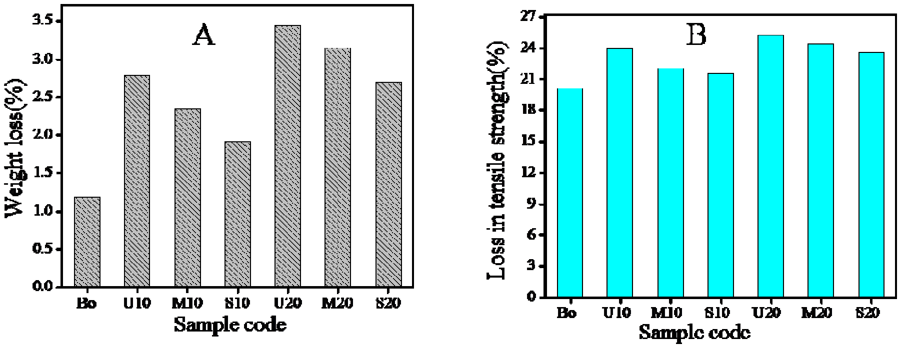

Figure 7.4 (A) Percentage weight loss of SBR-PSP composites after 180 days of soil burial (B) Percentage loss of tensile strength of SBR-PSP composites after 180 days of soil burial

7.2.2 Water sorption analysis of composites

The effect of moisture on composites is investigated as a simulating phenomenon of rain and moisture to which composites are generally exposed [21]. The hydroxyl group is the main chemical entity for the attraction of water molecules in the natural fibers. Another is the physical nature of the natural fibers such as amorphous and crystalline regions, which play important role in diffusion of water in the fibers with latter showing less water intake because of its relatively close packing of molecules [4]. Here water absorptions of the composites of SBR with UPSP,SPSP and MPSP were measured. The samples were immersed in distilled water for 90 days and the percentage weight change was determined at regular interval using the **equation 7.1**

$$\text{Weight gain}(\ \%) = \frac{W_e - W_0}{W_0} \times 100 \qquad (7.1)$$

Where Wg weight gain (%), We =equilibrium weight after water treatment and Wo oven dry weight before water treatment.

As the immersion time increased, the water absorption for untreated and treated PSP composite materials increased. Treated composite materials displayed lower water intake compared to untreated composites. An increase in water absorption for cellulose fillers can be expected due to its hydrophilic nature due to their hydroxyl groups, chemical treatment replaces these hydroxyl groups with hydrophobic groups and also form protective layer thus preventing any further intake of water. Filler size also plays a role in intake of water. The smaller filler size results in strong adhesion between fiber-matrix which reduces any possible voids or gaps that might form capillary for water absorption in composite materials [4,22]. These are illustrated in **figures 7.5 (A), (B) and (C).**

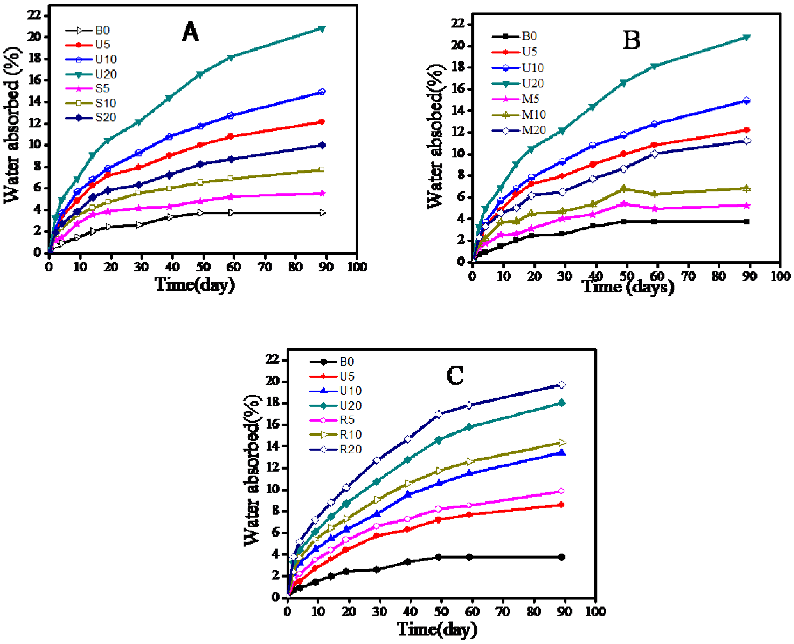

Figure 7.5 (A) Effect of filler loading and silane treatment of filler on the percentage of water sorption (B) Effect of filler loading and maleic anhydride treatment of filler on the percentage of water sorption (C) Effect of particle size of filler on the percentage of water sorption

The equilibrium of water absorption for composites of SBR with UPSP, SPSP and MPSP with different filler loading is given in **figure 7.6**. It was clearly seen that, the water absorption of both composites increased as the filler loading increases. Similar results were reported by other researchers [23,24] that the percentage of water absorption increased with higher filler content. This was due to the highly hydrophilic nature of lignocellulosic filler [1,25]. The free hydroxyl groups come in contact with water through hydrogen bonding, resulting in water uptake and weight gain in composites.

Furthermore, higher filler loading resulted in more pores within composites, thus increasing water accumulation at the interface between the filler and matrix [26]. From these observations it can be concluded that water sorption tendency of composites enhances its biodegradation. Hence the biodegradation of composites are higher at higher filler loading and chemical treatment of filler resists its degradation.

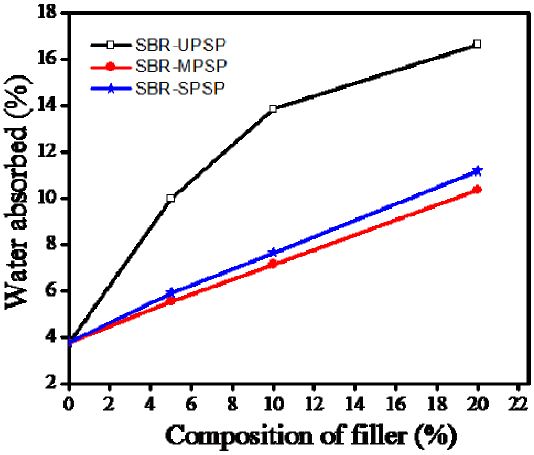

Figure 7.6 Equilibrium water uptake of SBR-UPSP, SBR-SPSP and SBR-MPSP composites at different filler loading

7.2.3 Surface morphology

A close scrutiny of SEM images of the composites after burial in the soil for six months reflects the biodegradability and the extent of biodegradability. **Figures 7.7A** and **7.7B** respectively represents the SEM images of composites SBR without filler before and after soil burial. **Figures 7.8** and **7.9** represent the SEM images of the composites with 10 and 20 phr untreated PSP before and after buried in the soil. **Figures 7.10** and **7.11** are the SEM images of SBR Composites with 10 and 20 phr silane treated PSP before and after burial in the soil for six months. SEM analysis gives additional confirmation to biodegradability. Scanning electron micrographs showed clear evidences for degradation with pits, surface roughening, grooves, cavities and disintegration. From **figures 7.7** to **7.11** the surface of the sample after buried in the soil seems to be is rough. The pits, cavities cracks etc on the surface images increase on filler loading. But comparison of **figures 7.8 B, 7.9B** and **7.10B, 7.11B** shows that the composite with SPSP undergo less degradation than the UPSP. This is mainly due to decrease in hydrophilicity of filler and good intersystem crosslinking between filler and the matrix, which proves that the nature of the filler has important role in the biodegradability of composites [10,14].

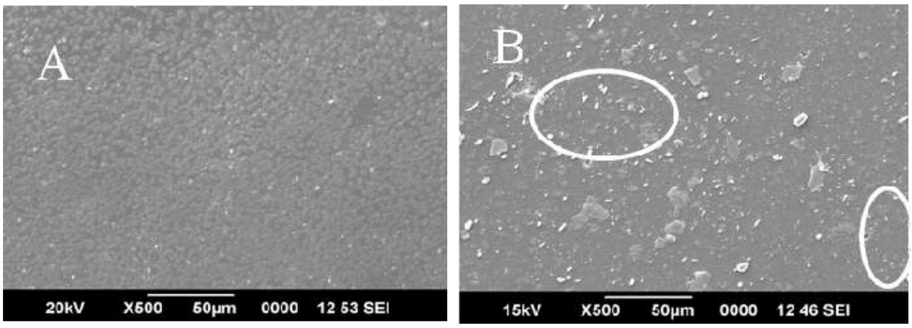

Figure 7.7.SEM of SBR vulcanizate without filler (A) before soil burial (B) after soil burial for 180 days

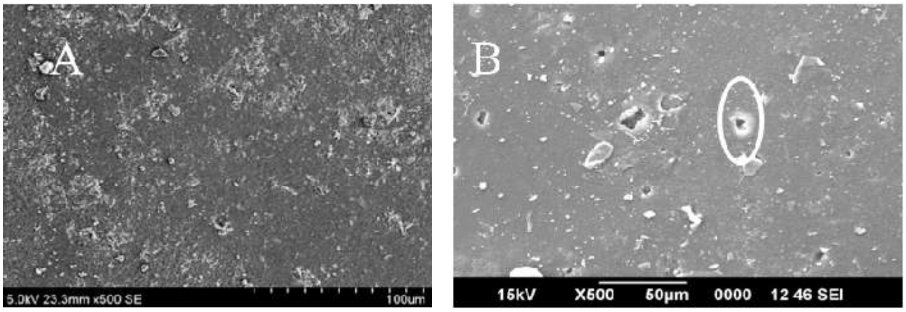

Figure 7.8 SEM of SBR-UPSP (10 phr) composites (A) before soil burial (B) after soil burial for 180 days

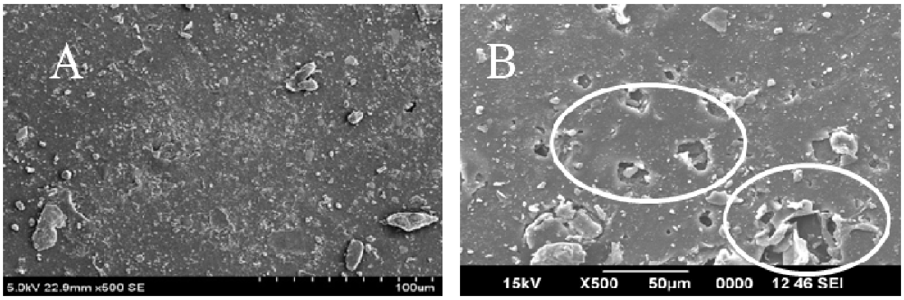

Figure 7.9. SEM of SBR-UPSP (20 phr) composites (A) before soil burial (B) after soil burial for 180 days

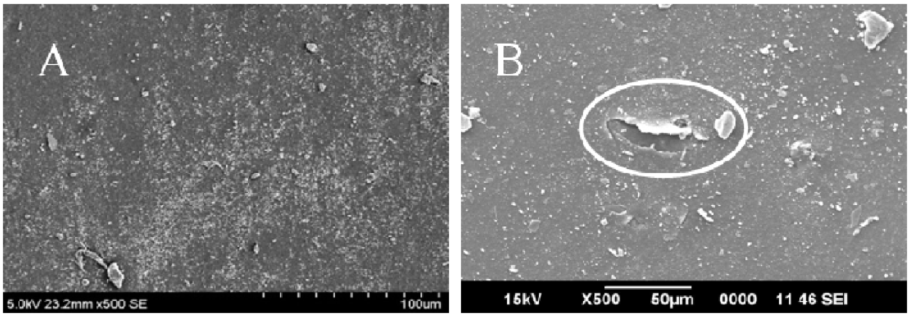

Figure 7. 10 SEM of SBR-SPSP (10 phr) composites (A) before soil burial (B) after soil burial for 180 days

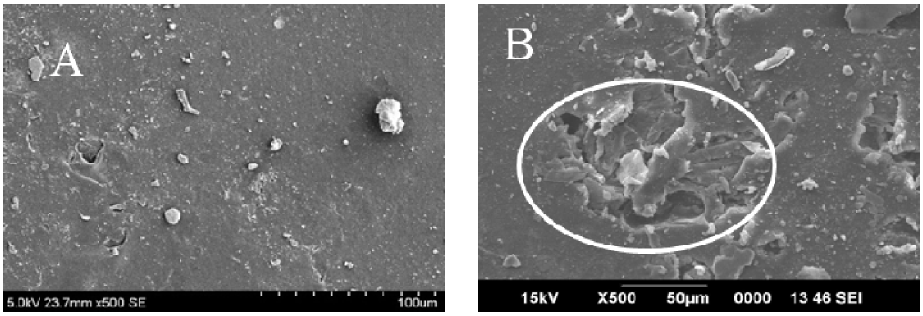

Figure 7. 11 SEM of SBR-SPSP (20 phr) composites (a) before soil burial (b) after soil burial for 180 days

Figures 7.12 and 7.13 represent the SEM images of composites of SBR-MPSP with filler composition of 10 and 20 phr of before and after buried in the soil for 180 days. Similar to the SBR-SPSP, biodegradation of SBR-MPSP composites increases on filler loading and resisted by modification of filler. These were supported by groves, cracks and piths developed on the surface images of composites after soil burial. On comparing with SBR-SPSP, the formation of cracks and roughness were more in SBR-MPSP composites supported that biodegradability was better in those composites. These results are also in favour with the observations in water sorption studies.

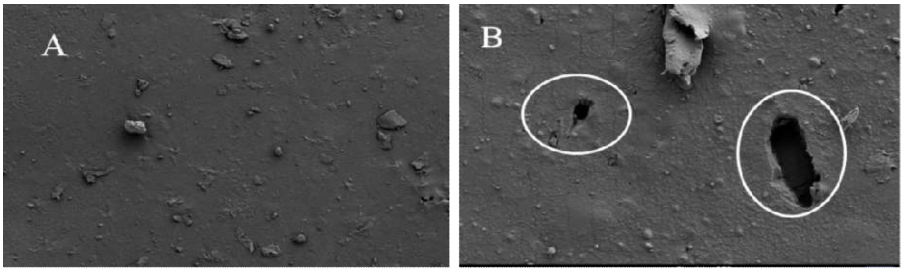

Figure 7. 12 SEM of SBR-MPSP (10 phr) composites (A) before soil burial (B) after soil burial for 180 days

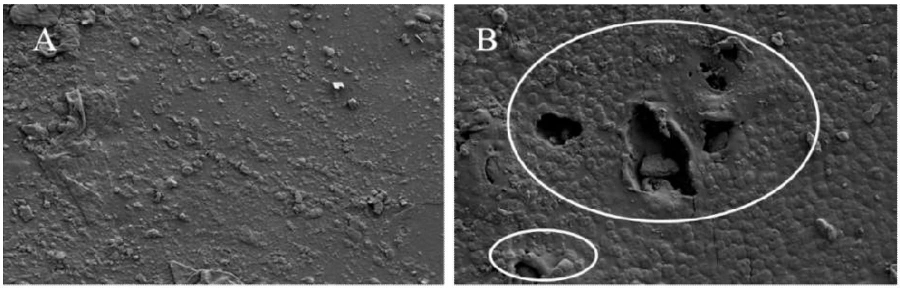

Figure 7. 13 SEM of SBR-MPSP (20 phr) composites (A) before soil burial (B) after soil burial for 180day

7.3 CONCLUSIONS

The selected samples were buried for 180 days in the garden soil to study the biodegradability of SBR-PSP composites. The weight loss and mechanical properties such as hardness and tensile strength were measured at definite intervals. The biodegradability of composites increases with increase in filler loading and particle size. The results reveal that the biodegradability prominently depends on the filler than matrix. Therefore, the weight loss, loss of tensile strength and hardness were found to show increase in trend with filler loading and particle size. But chemically modified fillers are reluctant towards deterioration of properties. So the retention of hardness and tensile strength have been found to be more in silane modified PSP filled composites due to better interfacial adhesion between filler and matrix. The above findings were supported by the water sorption studies of samples. The water sorption increases on increase in filler loading and decrease on modification of filler. The above results were further confirmed from SEM studies of sample buried in the soil. The surface of all samples become rough, the microvoids, the holes and cracks are more on the composites with 20 phr than with10 phr filler. Similarly, the voids and cracks are lesser in composites with silane modified PSP than with untreated PSP. Above all, composites with PSP filler have been found to be biodegradable than SBR vulcanizates.

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CHAPTER 8

CONCLUSIONS AND FUTURE OUTLOOK

Abstract: The major findings on the present investigation have been summarized in this Chapter. The scope for future studies based on the results of the studies carried out on composites of SBR reinforced with chemically modified peanut shell powder has also been discussed.

8.1 CONCLUSIONS

Sustainable development in the manufacture and industrial sector needs technologies having more importance on nature and its resources. The scientific community is also searching alternative technologies for pollution free and economically feasible products especially in the areas of composites. Composite materials made from plant based fibers are receiving wider attention and great deal of applications mainly because, today they are considered as environment friendly materials in the production and large scale application. Fiber reinforced polymeric composite materials are widely used in aerospace and automotive industries, sports products and medical equipment because of their low density, high stiffness and exceptional strength. Composites from glass fibers and inorganic fillers have serious demerits such as nonbiodegradability, high cost compared to natural fibers, high energy consumption etc. Many of these shortcomings of the synthetic fibres have been highly rectified by proponents of natural fibre composites. Among all reinforcing fillers, natural fillers have gained their significance especially for low load bearing applications. Natural fiber reinforced polymer composites are superior over synthetic fiber reinforced composites in certain properties like enhanced biodegradability, combustibility, lightweight, ease of recyclability etc. These advantages place the natural fibers composites among high performance composites having better economical and environmental impacts, with good physical properties. It is well known that there are ecological and economical advantages to develop natural filler/thermoplastic elastomer composites. Cellulosic filler–reinforced plastic materials have low cost, lightweight, are free from health hazards, have enhanced mechanical properties, and thus have the greater potential for structural applications.

Inspite of the several advantages over the synthetic fibres, these natural fillers have inherent drawbacks such as poor wettability, incompatibility with some polymeric matrices, high moisture absorption by the fibres and thus only poor adhesion with rubber matrix. These properties affect the interior strength of the composites. It is observed that surface modification of fibre or seed shell is an attractive alternative to overcome the above problems.

The present work, mainly focuses on the fabrication of composites of styrene butadiene rubber (SBR) with unmodified and modified peanut shell powder (PSP). SBR is the most widely used general purpose elastomer in the world, because of its application in the automotive and tire industry. The main advantage of SBR matrix is the formation of composites with better abrasion and heat resistance than natural rubber.

Coupling agent such as triethoxy vinyl silane and maleic anhydride were used for surface modification of the filler PSP. Chemical treatment has been found to be efficient for improving its hydrophobic character to increase its compatibility with hydrophobic matrix SBR. Chemical treatments of pretreated PSP using alkali removes most of lignin, hemicellulose, wax, fatty substances and other impurities and expose cellulose to surface of filler. This was confirmed by UV-visible spectroscopy and FTIR spectroscopic methods. The chemical treatment of filler increased the crystallinity which was observed by XRD. The change in the morphology of PSP was confirmed by SEM, the surface becomes rough after modification in comparison with smooth and clear surface of untreated PSP. These are also observed through thermogravimetry analysis (TG). It was observed that thermal stability of chemically treated PSP was higher than that of untreated PSP. The removal of surface impurities on filler may be an advantage for filler to matrix adhesion as it facilitates both mechanical interlocking and the bonding reactions.

The composites of SBR with modified and unmodified PSP were developed in this study by two roll mixing mill. From the analysis carried out on modified and unmodified PSP filled SBR composites it has been concluded that cure time and scorch time decrease with increase in filler loading in SBR composites. Maximum torque and minimum torque increase with increase in filler loading. Torque is higher for composites with chemically treated PSP. Mechanical properties like tensile strength, tear strength, modulus, abrasion resistance and elongation at break first increase with filler loading and then decrease having a maximum value at 10 phr filler loading. Hardness of the composites increases with increase in filler loading. This property also increases on modification and decrease in particle size. Better mechanical properties were exhibited by composite of surface modified PSP with smaller particle size than with unmodified PSP. Surface morphology of composites observed from SEM images gives additional support to the above findings.

Composites of modified PSP with smaller particle size at 10 phr loading have been found to exhibits better morphology, and mechanical properties.

Thermal properties of composites of SBR with unmodified and modified PSP were analysed from TG and DSC. From TG analysis it was observed that T_{onset} temperatures of all composites are slightly lesser than that of SBR matrix. But the T_{onset} of composites increases on treatment of filler with triethoxy vinyl silane and maleic anhydride coupling agents and slightly decreases on increasing particle size of the filler. Higher thermal stability was shown by the composites with silane modified and maleic anhydride composites with 10 phr filler (< 53 µm particle size) loading. From DSC, it was observed that the glass transition temperature (Tg) of composites slightly increased than that of SBR vulcanizates on filler loading due to restriction of molecular mobilization of the rubber matrix in the composites on addition of filler.

The sorption and diffusion studies of aromatic solvents (benzene, toluene and xylene) and petroleum fuel (petrol, kerosene and diesel) at three different temperatures were carried out through unmodified and modified peanut shell powder filled SBR composites. The influence of molecular mass of solvent, effect of filler loading, effect of modification of filler and effect of temperature were analysed. The mol % uptake, diffusion coefficient and sorption coefficient decrease with increase in penetrant size and filler loading also were observed. The study reveals that the composite with SPSP and MPSP shows more resistance to solvent swelling than with corresponding untreated composites. It also observed that the temperature was found to activate the diffusion process, hence the mol percentage uptake and diffusion coefficient are higher at higher temperatures. The study highlights that activation energy for diffusion of composites increases with filler loading and penetrant size. Heat of sorption in all systems were found to be positive suggesting that he Henry's type sorption predominates, support the endothermicity of sorption process. The analysis of transport mechanism shows that the mode of transport of benzene, toluene and xylene through PSP filled SBR composites was in less Fickian mode and through petrol, kerosene and diesel was close to Fickian mode. The data obtained from this study gives an insight about the response of the composites in solvents and it is necessary for the application of these to make materials for transportation of solvents. Oil resistance of the samples was measured by method ASTM D 3182 using IRM 901,902 and 903 oil. Oil resistance is the reciprocal of the degree of swelling of the composites; it increased with increase in concentration of filler due to increase in crosslink density of composites on filler incorporation. Oil resistance also increases on modification of filler and decreases with temperature. The oil resistance of a rubber is one of the key characteristics in the final selection of the rubber to be used, especially in automotive, industrial and seal applications.

The selected samples were buried for six months in the garden soil to study the biodegradability of SBR-PSP composites. The weight loss and mechanical properties such as hardness and tensile strength were measured at definite intervals. The results show that the biodegradability prominently depends on the filler than matrix. The biodegradability of composites increases with increase in filler loading and particle size. Therefore, the weight loss, loss of tensile strength and hardness were observed an increasing trend with filler loading and particle size. But chemically modified fillers were reluctant towards deterioration properties of composites. So the retention of hardness and tensile strength have been found to be more in chemically modified PSP filled composites due to better interfacial adhesion between filler and matrix. The above findings were supported by the water sorption studies of samples for 90 days. The water sorption increases on increase in filler loading and decrease on modification of filler. The above results were further confirmed from SEM studies of sample buried in the soil for six months. The surface of all samples become rough, the microvoids, holes and cracks are more on the composites with 20 phr than with10 phr filler. Similarly the voids and cracks are lesser in composites with silane modified PSP than with untreated PSP. The analysis reveals that the composites with PSP filler are biodegradable than the composites of SBR without filler.

8.2 FUTURE SCOPE OF THE WORK

The present study on the composites of SBR reinforced with untreated and chemically treated PSP opens up some new areas for further investigation.

- The present study proved that the surface modification of natural filler PSP improved the mechanical properties, thermal properties, resistance towards solvent swelling and oil resistance of the composites of SBR. Hence further studies through modification of filler by other chemical methods such as acetylation, benzoylation, peroxide treatment *etc* and by physical methods can be envisaged.

- Here the particle sizes are in microscale, particles in the nano scale can be used to fabricate nano composites and compared their properties with micro composites.
- Composites can be developed by extracting microcelluose and nanocellulose from PSP and compared their mechanical, thermal properties *etc.*
- The aging behavior of the composites was examined only by measuring tensile strength after exposing the sample in IRM 901 oil at room temperature for 72 h. The effect of thermal, water and weather aging on observed property can be done by comparing their mechanical properties like tensile strength, tear strength, elongation at break and modulus.
- The performance of the SBR-PSP composites in aromatic hydrocarbons, petroleum fuels such as petrol, diesel and kerosene and industrial oils IRM 901,902 and 903 has been examined in this work. The behavior of these composites in alcohols, aliphatic hydrocarbons, aldehyde and acids can be analysed in future.

- The biodegradability of the composites has been investigated only through soil burial test using garden soil. The biodegradability of the composites can also be analysed by using composite soil and aeorobic and anaerobic digestion.

- TG of the samples has been carried out only at one heating rate, the kinetics of thermal degradation have not been discussed. TG may be carried out at various heating rates and the kinetics of the resulting decompositions may be studied.

- Efforts can be made to fabricate oil seals, gasket, cable insulation etc in collaboration with various industries, so that the studies carried out can be used for product manufacturing.

APPENDIX

I. Refereed Journal

1. **Shaniba V**., Sreejith M.P., Aparna K. Balan., Jinitha T.V., Purushothaman E. Mechanical and thermal behavior of styrene butadiene rubber composites reinforced with silane-treated peanut shell powder. ***Polymer Bulletin,*** 2017; 74 (10), 3977-3994.

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II. Conference Proceedings

1. **Shaniba V**., Aparna K. Balan., Sreejith M.P, Jinitha T.V, Subair N., Purushothaman E. Effect of filler loading and silane modification on the biodegradability of SBR composites reinforced with peanut shell powder. ***AIP Conference Proceedings***, 2017; 1849 (1), 020049

2. Aparna K. Balan., Sreejith M.P., **Shaniba V**., Jinitha T.V., Subair N., Purushothaman E. Transport behavior of aromatic hydrocarbons through coconut shell powder filled thermoplastic polyurethane/natural rubber blend-composites.***AIP Conference Proceeding***s, 2017; 1849 (1), 020046.

3. Sreejith M.P., Aparna K. Balan, **Shaniba V.,** Jinitha T.V., Subair N., Purushothaman E. Biodegradation behavior of styrene butadiene rubber (SBR) reinforced with modified coconut shell powder. ***AIP Conference Proceedings***, 2017; 1849 (1), 020047.

III. Presentations

1. **V. Shaniba**, Aparna K. Balan, M. P. Sreejith, T. V. Jinitha, N. Subair, and E. Purushothaman. Effect of filler loading and silane modification on the biodegradability of SBR composites reinforced with peanut shell powder. ***Optics '17-A Conference on Light.*** NIT Calicut, 9-11th January, 2017.

2. **Shaniba.V,** Sreejith. M.P,Aparna .K.Balan, Jinitha. T.V, Subair N, Purushothaman.E. Transport of aromatic solvents through styrene butadiene rubber composites reinforced with modified peanut shell powder. **International conference on advanced materials Scicon16, A**mrita Vishwa Vidyapeetham, Amritanagar, Ettimadai, Coimbatore, Tamil Nadu,19-21 December 2016.

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ORIGINAL PAPER

Mechanical and thermal behavior of styrene butadiene rubber composites reinforced with silane-treated peanut shell powder

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Abstract Biocomposites of styrene butadiene rubber (SBR) reinforced with silane-treated peanut shell powder (SPSP) of different filler loadings and particle sizes were prepared by two roll mixing mills with sulfur as a vulcanizing agent. The cure characteristics of composites were studied, and they vulcanized at 160 °C. Test samples were prepared by compression moulding, and their physicomechanical properties, such as tensile strength tear strength, modulus, hardness, and abrasion resistance of SBR vulcanizates, were studied with filler loading 0, 5, 10, 15, and 20 parts per hundred rubber (phr). Composites with 10 phr filler having small particle size exhibited better properties. The interfacial adhesion between filler and matrix has a major role in the properties of composites. Surface modification of PSP was done by silane coupling agent to improve the interfacial adhesion and it characterised by FTIR, XRD, TGA, UV, and SEM. Better properties are shown by the composites with SPSP. Thermal stability of the composites was also determined using thermogravimetric analysis.

Keywords Modified peanut shell powder · Surface treatment · Silane coupling agent · Mechanical properties · Biocomposites of SBR

Introduction

Biocomposites are having variety of applications in the industries, and the development of composites using waste biological material promotes the ecofriendly products. It is observed that every year large quantities of agricultural wastes are produced worldwide. In the case of Peanut, major waste is its seed shell. Small quantities of seed shell are used as house hold fuel and fertilizer, and major

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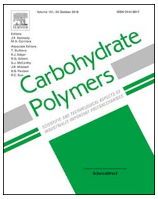

Isolation and characterisation of cellulose nanocrystals from sago seed shells

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ABSTRACT

Sago (*Cycas circinalis*) seed shells are agricultural waste materials discarded after taking the pith. In the present study Cellulose nanocrystals (CNCs) are isolated from the sago seed shells by acid hydrolysis. The hydrolysis was performed with 64% (w/w) sulphuric acid. The resulting CNCs were characterized by FTIR, XRD, SEM, TEM, AFM, DLS, Zeta (ζ) potential and TGA. FTIR spectrum of CNCs shows similar frequencies as that of α-cellulose, but with reduced intensity. XRD diffraction pattern shows co-existence of cellulose I and cellulose II with crystallinity index of 72% for cellulose II, 69% for cellulose I and crystallite size dimension of 9.4 nm for cellulose I. SEM analysis clearly reveals the considerable size reduction during acid hydrolysis. TEM analysis shows that the isolated CNCs contain networked structures and almost spherical shaped particles having 10–15 nm in size. Morphological examination through AFM also shows that isolated CNCs are in nano dimensions, having the size ~50 nm. DLS analysis gives an average size of 50 nm and zeta (ζ) potential measured has a value of −37.8 mV. DLS and AFM analyses support each other. TGA reveals lower thermal stability for CNCs.

1. Introduction

Growing global environmental concerns and new environmental regulations have forced the search for new materials that are environmentally benign. Cellulose being the most abundant biopolymer has attracted considerable interest due to its biodegradability, renewability, sustainability, biocompatibility, amenable for modification and is being exponentially considered as a green alternative to fossil-fuel based polymers (Tingaut, Zimmermann, & Sèbe, 2012). Cellulose consists of polydispersed linear polymer of poly β-(1, 4)-D-glucose with a syndiotactic configuration. The complex structure of biomass-derived cellulose is such that the structure can be analysed on different levels, such as structural, morphological, supramolecular consisting of macrofibrils, fibres, pores, microfibrils, crystalline, amorphous regions and finally the molecular level, consisting of glucan chains and hydrogen bonds (Osong, Norgren, & Engstrand, 2016). The critical constituent responsible for natural fibre strength and stiffness are cellulose microfibrils. These microfibrils have a width ranging from 5 to 30 nm are highly crystalline materials formed by the aggregation of long thread like bundles of molecules stabilized laterally by hydrogen bonds between hydroxyl groups and oxygen of adjacent molecules (Deepa et al., 2011)

The nanometer-sized single fibre of cellulose is commonly referred to as CNCs, whiskers, nanowhiskers, microfibrillated cellulose (MFC), microfibril aggregates or nanofibers. CNCs and nanofibrillated celluloses (NFCs) constituted the two main families of nanocellulose, which are different in morphology. CNCs are extracted from fibres after the complete dissolution of non-crystalline fractions, while the nanofibrillated cellulose results from the application of high shearing forces of disintegration leading to a high degree of fibrillation, which yields highly interconnected fibrils (Kalia, Boufi, Celli, & Kango, 2014). The aspect ratio distinguishes NFC and MFC from CNCs. CNCs have a very low aspect ratio (10–100) while NFC and MFC have a high aspect ratio of > 1000. The microfibrils are formed during the biosynthesis of cellulose and are several micrometers in length. Each microfibril can be considered as a flexible hair strand with cellulose crystals linked along the microfibril axis by disordered amorphous domains (Samir, Alloin, & Dufresne, 2005). Moreover, the amorphous regions of CNCs are digested during processing, thus giving the material a stiff-rod (rice like) structure. NFC and MFC retain both the crystalline and amorphous regions, and have the shape and structure of spaghetti (Osong et al., 2016). The ordered regions are cellulose chain packages that are stabilized by a strong and complex network of hydrogen bonds that resemble nanocrystalline rods (Habibi, Lucia, & Rojas, 2010).

Various top down methods have been adopted for the preparation of cellulose nano objects. These include steam explosion treatment (Deepa et al., 2011), high pressure homogenization (Li, Wei et al., 2012), ultrasonic technique (Li, Yue, & Liu, 2012), acid/alkaline-hydrolysis

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Coconut shell powder reinforced thermoplastic polyurethane/natural rubber blend-composites: effect of silane coupling agents on the mechanical and thermal properties of the composites

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ABSTRACT

The objective of this work is to modify coconut shell powder (CSP) using various silane coupling agents and to study the effect of modification on the interfacial adhesion and mechanical properties of the fillers in the binary blend of thermoplastic polyurethane and natural rubber. Mechanical properties such as tensile strength, tear strength, hardness and abrasion resistance were evaluated. Results revealed that, compared to triethoxyvinylsilane modified CSP composites, glycidyloxypropyltrimethoxysilane treated CSP showed higher tensile strength and better interfacial adhesion with the matrix. The efficiency of the silane treatment is further characterized by the FT-IR analysis of fillers and the morphological study of both the CSP and the composites. FT-IR studies demonstrated that the silyl parts of both silane coupling agents efficiently grafted to the CSP. SEM images of treated CSPs provide ample evidence for the increased mechanical properties of the composites. The increased thermal stability of is evident from the thermo gravimetric analysis.

Introduction

Lignocellulosic fibers have proven their efficiency as good reinforcing agents in polymeric materials with several specific properties such as, low cost, abundant nature, light weight, non-toxic, high specific strength and modulus, desirable fiber aspect ratio, surface containing large number of reactive functional groups, non-abrasive nature during processing, safe for handling, relatively good mechanical properties, complete burning without residue on combustion, etc., [1–3]. Biodegradability of this raw material is the most important in addition to the above. They are mostly obtained from agricultural by-products and the use of such waste products would reduce the dependence on conventional reinforcing materials like glass fibers, aramid fibers etc. The reinforcing efficiency of the natural fiber is related to the nature of

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Development of Green Composites of Poly (Vinyl Alcohol) Reinforced with Microcrystalline Cellulose Derived from Sago Seed Shells

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Reinforcing poly(vinyl alcohol) (PVA) with biopolymers like microcrystalline cellulose (MCC) provides interesting route for the preparation of green composites. In this study, PVA and MCC from sago seed shell in different weight% were prepared by intense sonication followed by solution casting into glass plate. Composites were prepared by adding 1, 2 and 3 weight% of MCC, which were characterized using FTIR, ATR-FTIR, XRD, TGA, DSC, SEM, AFM, UV-Vis, and mechanical testing. Particle size distribution of used MCC was analyzed by DLS. ATR-FTIR spectra reveal the incorporation of MCC into the polymer matrix through hydrogen bonding. XRD pattern shows the decrease in relative intensity compared to PVA film and broadening of peaks at different MCC concentrations. DSC analysis reveals the variations in the glass transition temperature. In addition to lowering in melting temperature, changes in shape and area are attributed to the different degrees of crystallinity due to the existence of polymer-polymer interactions between PVA and MCC. The results obtained from ATR-FTIR, XRD and DSC substantiate each other. TGA results reveal the increased thermal stability compared to the PVA film. The SEM analysis shows the uniform distribution for lower loading, which is further supported by AFM. UV-Visible spectra reveal the good transparency of prepared films. Mechanical testing was also performed, in which 1 weight% gained tensile strength. The TGA and mechanical testing results showed that MCC as reinforcement in PVA film can improve thermal and mechanical strength. DLS measurements show that the particle size of MCC is >100 nm. POLYM. COMPOS., 00:000–000, 2017. © 2017 Society of Plastics Engineers

INTRODUCTION

The growing interest in ecofriendly materials for wide application has motivated the use of biopolymers, where synthetic polymers or mineral fillers are traditionally used [1]. Bio-composites gained much momentum during the past years due to environmental consciousness. Researchers have explored the usefulness of natural fibers as reinforcement in composites. Renewability, biodegradability and sustainability make natural fibers from bast, leaf or hard fibers, seed, fruit, wood, cereal straw, and other grass fibers being used in composites [2]. Not only natural fibers, biopolymers like cellulose, starch etc., that are extracted from biomass resources are also being used in the development of bio-composites. Attention is now focused on the development of green composites, which are green in all respects, in which the reinforcement and matrix are biodegradable. Green composites may be used effectively in many applications such as mass-produced consumer products with short lifecycles or products intended for one-time or short-term use before disposal. Two important matrices mainly used for the preparation of green composites are polyvinyl alcohol and polylactic acid. Starch/poly(vinyl alcohol) (PVA) blends are widely used in packaging and agricultural applications [3]. Polyvinyl alcohol is highly recognized as a biodegradable polymer, readily consumed by microorganisms and enzymes when exposed to natural environment [4, 5]. Due to biodegradability, water-solubility, gas barrier properties, biocompatibility, good thermal stability, availability, flexibility, transparency, toughness and cost make PVA used in packaging, medical, and energy-absorption applications. Moreover PVA is still studied in combination with biopolymers like starch, chitosan, and cellulose [6]. Bio-composite materials with natural fibers and biopolymers such as starch, polylactide, and these materials find their way in commodity and non-structural applications such as casings of electronic products, and interior parts of automobiles [7].

Commercial PVA is available in highly hydrolyzed grades (degree of hydrolysis above 98.5%) and partially hydrolyzed ones (degree of hydrolysis from 80.0 to 98.5%). The degree of hydrolysis or the content of acetate groups in PVA affects its chemical properties, solubility, and crystallizability [8]. It is difficult to assign specific physical properties to solid polyvinyl alcohol as this

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Effect of Silane modification on the Mechanical Properties of Coconut Shell Powder Reinforced Styrene Butadiene Rubber Composites

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ABSTRACT

Natural fiber reinforced polymer composites provide the customers with more alternatives in the material market due to their unique advantages. Natural fibers are rich in cellulose and they are cheap, easily renewable source of fibers with the potential for polymer reinforcement. This article focuses on the use of coconut shell powder (CSP) as reinforcing filler in Styrene Butadiene Rubber (SBR) matrix. Silane modified and unmodified CSP-SBR composites were prepared by an open mill mixing technique. The processing characteristics and the curing behavior of the composites were determined by Monsanto Rheometer. The mechanical properties like tensile strength, Young's modulus and hardness were also measured. Filler reinforcement ability of modified CSP is more when compared with unmodified CSP; there for, silane modified CSP-SBR composites shows better physicomechanical properties.

KEY WORDS: SBR, silane modified coconut shell powder, Tensile strength.

1. INTRODUCTION

Synthetic rubbers in its vulcanized form are used to produce various rubber products such as soles, hoses, belt, mats, tyres, seals etc. Carbon black and silica are the main fillers added in the vulcanization of the rubber. Even though they impart strength and better properties, but they are relatively expensive. In recent years there is increasing interest in the development and use of natural fillers as the reinforcing material in polymer composites. Many researchers have reported the processing advantages and improvement in the mechanical properties of natural fiber reinforced rubber composites (O'Connor, 1977; Coran, 1974; Boustany and Arnoldshort, 1976). The development of cellulosic materials as a rubber reinforcing filler has drawn increasing interest because of its low cost/high volume applications. It has several advantages compared with inorganic fillers, lower density, greater deformability, less abrasiveness to equipments, moreover, lignocellulose based fillers are derived from renewable resources.

The most serious concern with natural cellulosic material is its hydrophilic nature due to the presence of strongly polarized hydroxyl groups, and hence they are inherently incompatible with hydrophobic materials. This may lead to poor interfacial adhesion between the polar filler and the nonpolar matrix. This incompatibility may cause problems in the composite processing and material properties. The formation of hydrogen bond between hydrophilic centers lead to agglomeration of filler particles and unevenly distribute throughout the nonpolar polymer matrix during compounding and processing (Raj, 1989; Kazayawoko, 1999). When two materials are incompatible, introduction of a third material that has properties intermediate between those of the other two by forming a weak bonding layers can make them relatively compatible.

In order to improve interfacial bonding, modification of the filler surface is essential (John, 2005; Hristov, 2004; Tserki, 2005). The treatments to improve the fiber matrix adhesion in composites include chemical modification of filler (using anhydrides, isocyanates, acetylation, benzoylation, alkalization etc) grafting of polymers in to lignocellulosic and use of compatibilizers and coupling agents (Abdul Khalil and Ismail, 2001). A coupling agent is a chemical that functions at the interface to create a chemical bridge between the reinforcement and matrix. Silane coupling agents have been used in the rubber industry for the last three decades to improve the performance of fillers in rubber compounds. They are recognized as efficient coupling agents extensively used in composites and adhesive formulations (Rider and Arnott, 2000). A silane coupling agent contains functional group that can react with the rubber and the filler. In this way, the rubber filler adhesion is increased and consequently the reinforcing effect of the filler is enhanced.

In this work coconut shell powder (CSP) is used as an alternative filler for SBR. The coconut shell powder shows similarity with hard wood powder in chemical composition and exhibits some excellent properties compared to mineral filler (eg; silica, kaolin, mica, talc etc.) such as low cost, renewable, high specific strength-to-weight ratio, low density and environment friendly (Yanjun Xie, 2010; John and Anandjiwala, 2009; Fornko and Gozalez, 2005; Park, 2008). The aim of this work is to investigate the feasibility of using unmodified coconut shell powder (UCSP) and silane modified coconut shell powder (SCSP) as a reinforcing filler in SBR matrix and evaluation of their cure characteristics and mechanical properties.