REINFORCEMENT OF THERMOPLASTIC POLYURETHANE-NATURAL RUBBER BLEND WITH SURFACE MODIFIED COCONUT SHELL POWDER

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by

APARNA K. BALAN

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
KERALA

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
THENJIPALAM, MALAPPURAM
KERALA-673 635

Dr. E.Purushothaman **Tel: +91-9447683351**
Professor (Retd.) **E-mail: epurushot@yahoo.com**

Date: …………….

CERTIFICATE

Certified that the work embodied in the thesis entitled **"REINFORCEMENT OF THERMOPLASTIC POLYURETHANE-NATURAL RUBBER BLEND WITH SURFACE MODIFIED COCONUT SHELL POWDER"** has been carried out by **Aparna K Balan** 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**

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
THENJIPALAM, MALAPPURAM
KERALA-673 635

Dr. E.Purushothaman **Tel: +91-9447683351**
Professor (Retd.) **E-mail: epurushot@yahoo.com**

Date: ....

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The adjudicators of the thesis entitled "**REINFORCEMENT OF THERMOPLASTIC POLYURETHANE-NATURAL RUBBER BLEND WITH SURFACE MODIFIED COCONUT SHELL POWDER**" submitted by **Aparna K Balan**, have not suggested any major changes in the scientific content, results and interpretations. However some typographic errors and minor corrections suggested by the examiners are incorporated in the revised thesis.

Calicut University **Dr. E. Purushothaman**

DECLARATION

I hereby declare that the matter embodied in the thesis entitled **"REINFORCEMENT OF THERMOPLASTIC POLYURETHANE-NATURAL RUBBER BLEND WITH SURFACE MODIFIED COCONUT SHELL POWDER"**, 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 **Aparna K Balan**

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For

Unnikutty...

with love and tears...

GLOSSARY OF TERMS

ASTM	-	American society for testing and materials
CRI	-	Cure rate index
CSP	-	Coconut shell powder
D	-	Diffusion coefficient
DCP	-	Dicumyl peroxide
DSC	-	Differential scanning calorimetry
E_D	-	Activation energy of diffusion
E_P	-	Activation energy of permeation
FT-IR	-	Fourier transform infrared spectroscopy
GPTMS	-	Glycidyloxypropyltrimethoxy silane
ΔG	-	Gibbs free energy of sorption
ΔH_S	-	Enthalpy of sorption
IRM	-	Industrial reference materials
ISNR	-	Indian standard natural rubber
Ks	-	Equilibrium sorption constant
M_H	-	Maximum torque
M_L	-	Minimum torque
NR	-	Natural rubber
P	-	Permeability coefficient
PE	-	Polyethylene
Phr	-	Parts per hundred of rubber
PLA	-	Polylactic acid
PP	-	Polystyrene
PVA	-	Polyvinyl alcohol
PVC	-	Polyvinylchloride

Q_t - Moles of solvent sorbed by 100 g of polymer at time t

Q_∞ - Moles of solvent sorbed by 100 g of polymer at equilibrium

R - Universal gas constant

R% - Swelling ratio

S - Sorption coefficient

SBR - Styrene butadiene rubber

ΔS - Entropy of sorption

SEM - Scanning electron microscopy

TEVS - Triethoxyvinylsilane

ts_2 - Scorch time

t_{90} - Optimum cure time

T - Absolute temperature

T_g - Glass transition temperature

TG - Thermogravimetry

TPU - Thermoplastic polyurethane

V_r - Volume fraction

XRD - X-ray diffraction

v - Crosslink density

χ - Interaction parameter

CONTENTS

PREFACE

The extreme desirable properties offered by polymers such as low cost, biological inertness, mechanical properties, persistence, *etc.*, make them an inevitable material in day-today life of mankind. The imprudent use of non-biodegradable polymeric materials started altering the environment and atmosphere. Development of blends and composites provides new polymeric materials with excellent properties in an economical pathway. The search for sustainable, non-petroleum based, energy saving and environment friendly fillers led to natural fibres. Natural fibre filled polymer composites are fully or partially biodegradable in which the biodegradability of synthetic polymer component is enhanced by the incorporation of biodegradable filler material. The main aim of this investigation is to develop unmodified and modified coconut shell powder (CSP) reinforced TPU/NR (TN) blend-composites and to study their properties such as cure characteristics, mechanical properties, sorption properties, thermal analyses, aging studies and biodegradation studies. The thesis entitled ***"Reinforcement of thermoplastic polyurethane-natural rubber blend with surface modified coconut shell powder"*** is divided into seven chapters.

Chapter 1 gives a general introduction to polymer blends, composites, natural fibres, chemical treatments and related literature review. This chapter also highlights the scope and objectives of the present investigation. **Chapter 2** gives an account of the different materials and experimental methods used in the course of this study.

Chapter 3 contains the evaluation of silane treatments on CSP. The details of the development, cure characteristic studies and crosslink density evaluation of CSP filled TN blend-composites also are described here. **Chapter 4** presents the effect of silane treatment and filler loading on the mechanical and thermal properties of CSP filled TN blend-composites. Density, hardness, tensile strength, elongation at break and abrasion resistance were determined. **Chapter 5** deals with the transport studies of samples using aromatic solvents, petroleum fuels and industrial reference oils. The solvents used were benzene, toluene and xylene for aromatic solvents, petrol, kerosene and diesel for petroleum fuels and IRM 901, 902 and 903 for oils. Kinetic and thermodynamic parameters were determined for aromatic and petroleum fuels and % swelling for oils was determined with special references to the effect of filler loading, filler modifications, penetrant size and temperature. **Chapter 6** describes the aging and biodegradation of different CSP loaded TN blend-composites under various conditions. Aging studies include oil-aging, thermal aging and water-aging. Biodegradation analysis includes soil-burial test and morphological analysis. **Chapter 7** presents major conclusions arrived at touching upon future outlook of the research.

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Chapter 1

Introduction and Review of Literature

Part A

Part B

Abstract: *This chapter gives an account of fundamentals of polymer blends and composites. A brief description of different types of fillers also has been presented. Natural fibres and surface treatments of natural fibres are discussed in detail. A review of earlier work in this area is given. Scope and objectives of the present investigation are highlighted.*

PART A
INTRODUCTION

Our ancient civilizations have been successful in figuring out the applications of polymers. Polymers, with large number of repeated units linked through covalent bonds, possess high molecular weight. It is the most important property of polymers, which accounts for almost all the characteristic physical properties [1]. The term polymer was coined by Berzelius in 1833. The modern era of polymers started with the use of rubbers. The name, rubber, coined by the great scientist Joseph Priestley, explained the first reported use, 'to rub-out' the pencil marks in 1770 [2]. The first artificial material, which led to the development of man-made plastic industry, began with the synthesis of cellulose nitrate by Braconott in 1832. But the credit of discovery of cellulose nitrate is given to Schonbein who produced stable nitrocellulose in 1846 [3-4]. In 1839, Charles Goodyear discovered vulcanized rubber, which was more durable than the unvulcanized rubber. In 1909, Bakeland developed the first synthetic thermosetting plastic phenol-formaldehyde, which named as Bakelite, with greater hardness and higher heat resistivity. It was the first breakthrough in the industrial production of synthetic polymers. Later he developed composites comprised of various fillers such as cotton, powdered bronze, slate dust, wood, asbestos fibre, *etc*. In 1912, Thomas Hancock prepared first polymer blend, by mixing natural rubber with gutta-percha [5]. The development of polymer science took a new turn in 1920, when Hermann Staudinger, the father of macromolecular chemistry, suggested the long chain nature of polymers in his famous article entitled 'Uber polymerization' [6]. Next revolution was the invention of nylon by Carothers in 1938.

Commercially important polymer blends started developing after World War II. The first widely used synthetic polymer blend was the Nitrile rubber-polyvinyl chloride (NBR–PVC) system. NBR was widely used as hood applications in automobiles. It aged badly because of the ozone attack in these applications. Introducing PVC into NBR improved its aging at the expense of stiffening [5]. In 1968, Kato's Osmium tetroxide (OsO_4) staining was invented for the elucidation of two phase morphology of polymer blends [7]. The knowledge of structure-property relationships, availability of different high-end polymerization techniques and enormous number of monomers made us enable to design end-products with almost any qualities. Thus, polymers became an inevitable material in day-today life of mankind. The extreme desirable properties of polymers such as low cost, biological inertness, mechanical properties, persistence, *etc.*, caused the deposition of non-biodegradable polymer products in nature. The imprudent use of polymeric materials started altering our environment and atmosphere. All the water sources were getting contaminated with plastic waste materials. A worldwide concern over this issue has emerged in recent years. The concept of biodegradability emerged when the accumulation of plastics along with other materials, was becoming a serious problem for all countries in the world. These materials occupy significant volume in landfills and dumps. Recently, the presence of huge amounts of plastic fragments on the oceans has been observed, considerable part of them originating from the streets, going through the drains with the rain into the rivers, lakes and oceans [8-9].

Environmental concerns associated with conventional, non-degradable polymers were gained attention in 1980s. Major concern is the solid waste problem associated with the decreasing availability of landfills around the world. Other concerns include the global warming caused by the increased amount of carbon dioxide in the atmosphere, in which one of the main culprits is the use of petrochemical sources for the production of polymers. To find sustainable and renewable sources as an alternative to petrochemical sources became the responsibility of the scientific community. In response to these concerns, commercial development of biodegradable polymers started at 1990s [10]. One of the main constraints to the widespread use of biopolymers has been the high cost. For this reason, the development of biodegradable polymer application has not shown a significant growth as expected. Moreover, most of the biopolymers are affected by the exposure to natural weathering forces, i.e., durability of these materials are poor. Combining the properties such as biodegradability and durability with processability, strength and cost-effectiveness for a synthetic biopolymer is practically not possible. Thus, the concept of modification of synthetic non-degradable polymers with naturally occurring biodegradable materials has been gaining momentum. Modification of synthetic polymers can be done either *via* blending with a naturally occurring biodegradable polymer or with addition of biodegradable filler materials such as natural fibres or polysaccharide materials. According to Bohlman, since 1970s, numerous attempts have been made to enhance the biodegradability of synthetic polymers by incorporating polysaccharide derived materials [11]. The microstructure plays a fundamental role in determining the biodegradation rate of this class of products. The proposed sequence for biodegradation is: (i) the filler material is first consumed by the microorganisms which lead to the weakening and fragmentation of synthetic polymer matrix, (ii) the remaining synthetic polymer fragments, as a result of other environmental mechanisms, which are eventually small enough to be assimilated by the microorganisms [12]. Uses of natural fibres in composite system have been known since the time of Egyptian civilization. They managed to mix clay and wheat straw together to build walls. Nowadays also, natural fibre reinforced polymer composites have gained increasing attention. Not only from the academic world, but also from various industries such as automobile, furniture, building and textile, *etc*.

1.1 Polymer blends

When polymers were developed specifically for a particular application, the researchers encountered certain short comings of polymer, which made it inadequate for those applications. In order to overcome this, blending with one or more polymers was employed and found to be successful. Two or more existing polymers could provide new products with desired properties. According to IUPAC recommendations 2004, macroscopically homogeneous mixtures of two or more different species of polymers are called polymer blends

[13]. Nowadays, polymer blends are being widely used in wide range of applications such as membrane transport, electrical insulators, conducting polymers, *etc.*, [14-20]. Blending of polymers can be achieved by a number of methods such as mechanical blending, solution blending, latex blending, polymer nanosphere blending, *etc.*

1.1.1 Types of polymer blends

Polymer blends can be classified based mainly on their constituents and miscibility.

1.1.1.1 Based on constituents

Based on the individual components used for blending, blends can be of rubber-rubber, plastic-plastic and plastic-rubber. The constituents of a blend are separable by physical means.

Rubber-rubber blends

They are the combination of two or more elastomers. The need of such blending occurs when single elastomers could not provide all the desired properties for a particular use. The rubbers used can be of natural rubber with synthetic rubber or synthetic rubber with synthetic rubber. Several examples are known in the literature. Various rubber-rubber blends are mainly used in automobile industry.

Plastic-plastic blends

Plastic-plastic blends obtained when thermoplastic materials are only used for blending. They are mainly designed for the applications such as sensors, membranes for osmosis, pervaporation, *etc.*

Plastic-rubber blends

These blends are commonly known as thermoplastic elastomers (TPE). They combine the characteristic properties of both elastomers and plastics. They possess the excellent mechanical performance of conventional vulcanized elastomers simultaneously with the processability of thermoplastics. Both thermoplastics such as polycarbonates, thermoplastic polyurethanes, polyethylene, polystyrene, polypropylene, PVA, PVC, PMMA, PET, nylon, *etc.*, and thermosetting plastics such as polyurethanes, bakelite, polyester resins, epoxy resins, silicones, *etc.*, can be used for blending.

1.1.1.2 Based on miscibility

Miscibility is the capability of a mixture to form a single phase over certain ranges of temperature, pressure and composition [13]. Based on the degree of miscibility, they are divided into miscible, partially miscible and immiscible polymer blends. For a two-component system, the necessary criteria for miscibility are i) $\Delta_{mix}G \approx \Delta_{mix}H \leq 0$ and ii) $\left(\frac{\partial^2 \Delta_{mix}G}{\partial \emptyset^2}\right)_{T,P} > 0$, where $\Delta_{mix}G$ is the Gibbs free energy of mixing, $\Delta_{mix}H$ is the enthalpy of mixing and $\emptyset$ the composition, where $\emptyset$ is taken as the volume fraction of one of the components.

Miscible polymer blends

They are the blends homogeneous down to the molecular level having a single phase structure, confirmed by single glass transition temperature (T_g) that lies between the T_gs of constituent homopolymers. For a polymer blend to be miscible, it must satisfy the criteria for miscibility. It is expected to have the properties of average values between the values of properties of its individual components depending on its composition.

Partially miscible polymer blends

In partially miscible blends one of the components is partially soluble in the other components, *i.e.*, they are miscible in a certain range of composition and temperature, and show a macroscopic homogeneity. Eventhough the different phases show distinct T_g, they are shifted from that of constituent homopolymers. Their interfacial adhesion is not as good as that of miscible systems.

Immiscible polymer blends

Immiscibility is the inability to form a single phase in a multi-component system. It's free energy of mixing $\Delta_{mix}G \approx \Delta_{mix}H > 0$. Since it possesses very poor interfacial adhesion, the phases are segregated and show different T_g which are similar to that of corresponding constituent homopolymers.

The purpose of blending two or more homopolymers is to achieve the most favourable properties for a particular composition of blend. **Figure 1.1** shows idealized property combinations by blending two polymers, A and B, which are miscible, immiscible and uncompatibilized, or immiscible and compatibilized.

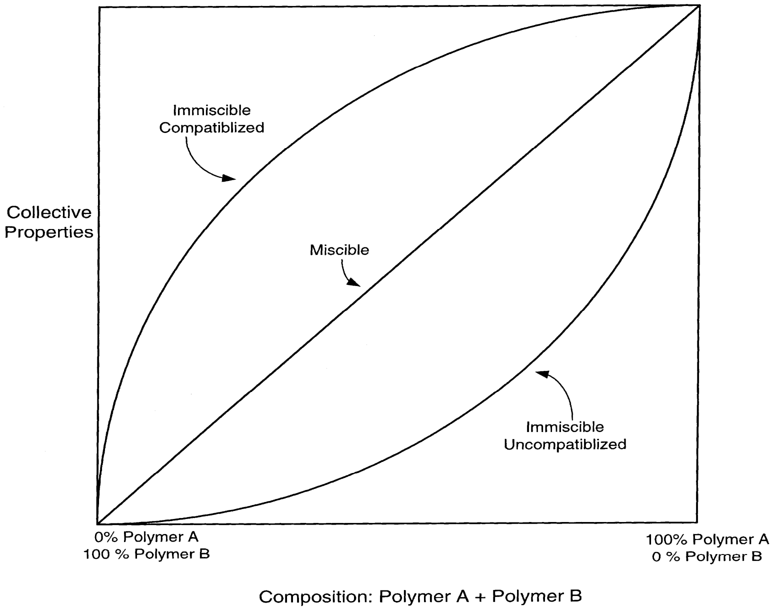


Figure 1.1: Idealized property combination for blend combining polymer A and B [21].

1.1.2 Reinforcement of immiscible polymer blends

When two immiscible polymers are blended without compatibilization, one generally obtains a mixture with physical properties worse than those of individual polymer. Usually such a blend has poor structural integrity and poor heat stability, since there is no mechanism for stabilizing a dispersion of one polymer in a matrix of the other. Hence, results in weak interfacial adhesion between the components. For an immiscible blend, interface is the weakest part which leads to poor mechanical behaviour [22]. On a macroscopic scale the blend may appear heterogeneous and in the extreme case delaminated. In order to get optimum properties for a blend, the particle size of dispersed phase and stabilization of the phase morphology are to be optimized. If the dispersed phase has large particle size, practically there is no interfacial adhesion exists between the phases, and hence no mechanism for morphology stabilization. An established method for the reinforcement of immiscible blends is the addition of compatbilizers and fillers. Both of these materials can control the phase morphology and the size of dispersed phase which leads to the enhancement of interfacial adhesion. The intentionally modified compatibilized blends always show better phase morphology and mechanical properties than that of the immiscible system [21, 23] .

1.1.2.1 Compatibilizers

A compatibilizer is a polymer or copolymer which is added intentionally to an immiscible blend to modify the interface between the two phases in the blend and stabilize the phase morphology. The compatibilizer works in a manner that penetrates deeply into the interface and forms entanglements between the faces and thus enhances the interfacial adhesion. It retards the phase segregation, coalescence and thus reduces the size of dispersed phase and forms fine phase morphology. Different strategies adopted for compatibilization include physical compatibilization and reactive compatibilization [23]. Physical compatibilization involves the addition of a copolymer of two immiscible polymers. At the interface, the segments of copolymer dissolve in respective bulk phases of same identity and acts as an emulsifying agent for the blend to reduce the interfacial tension between the phases. A polymer which is miscible with all the immiscible phases of a blend also can be used as compatibilizer. Reactive compatibilization is the process of *in-situ* generation of copolymer by a chemical reaction during the development of immiscible blends. Here, the copolymer directly forms at the interface where it can serves as a compatibilizer and penetration to the interface is not needed as in the case with physical compatibilization and seems to be more efficient than physical compatibilization.

1.1.2.2 Fillers

Fillers are the solid additives added to the polymeric materials for various technical and/or economic reasons [13]. They provide improved mechanical properties, durability and processability while reducing the cost to a considerable extent by decreasing the expensive rubber partition in the mixture. Most commonly used fillers in polymers are carbon black, silica, clay, aluminium oxide, zinc oxide, calcium carbonate, talc, magnesium silicates, glass fibres, natural fibres, *etc.* Reinforcement provided by fillers depends on various factors such as size, surface chemistry, state of aggregation and quantity of fillers [7]. But the primary factor determining the extent of reinforcement is the particle size of the filler. Fillers with fine particle size provide the maximum reinforcement. While using fillers in immiscible blend system, which always consists of segregated coalescent structures having large sizes, they affect the interface in a positive manner. Fillers reduce the size of segregated phases by creating localized filler networks and filler-polymer networks. They also impart compatibility between the constituent homopolymers to some extent and reinforce the immiscible blend system [24].

1.2 Composites

A macroscopic combination of two or more chemically distinct phases, having a recognisable interface between them can be called as a composite [13]. They have superior properties compared to its constituent materials. Composites possess the properties of an ideal engineering material, such as high strength to weight ratio, stiffness, toughness and lightweight which other conventional engineering materials like metals and wood do not have. Therefore, fibre reinforced composites are found to be the best candidate as engineering materials, leading to their rapid development and successful use in many applications over the last few decades. Nowadays it plays the pivotal role in automobile industry, aerospace, household furniture industry, and in other engineering applications.

Composites basically consist of two materials, continuous phase or matrix and discontinuous phase or the reinforcement. Based on the continuous phase, composites are broadly classified into metal matrix composites (MMC), ceramic matrix composites (CMC) and polymer matrix composites (PMC). Among these, polymer matrix composites got the advantage over the others due to their easy processability, lower service temperature and light weight. Based on the type of reinforcement, composites can be classified into particulate composites, fibrous composites, laminate composites, hybrid composites and nanocomposites. The properties of the composites depend on the properties, concentration, distribution, orientation of the constituent materials, geometry of the filler and the interfacial adhesion between the matrix and filler.

1.2.1 Matrix

Matrix is the continuous phase in which the discontinuous phase embedded. It binds filler particles together and acts as medium for both matrix-filler and filler-filler interactions and transfers stress between the reinforcing fillers. It protects discontinuous phase from dislocations and damage to a certain extent. Matrix provides the structural integrity for the composite material and determines the processability. Metals, ceramics and polymers can act as matrix material. Among these, polymers are considered to be the best choice as matrix for composite materials mainly due to its light weight nature and ease of processing. Based on the type of polymer used, whether a single homopolymer or a combination of two or more polymers, classified as homopolymer composites and polymer blend-composites. A homopolymer composite sometimes, may not provide all the desired properties for a particular application. By suitable selection of two or more polymers and their mixing, we can have tailored-end products with all desired properties.

1.2.2 Dispersed phase of filler

According to IUPAC recommendations 2004, filler or the dispersed phase is the solid extender which may be added to modify the properties of a material, or simply to serve as extender [13]. Based on the shape of the filler, the dispersed phase may be broadly classified as particle reinforced and fibre reinforced composites.

1.2.2.1 Particle reinforced composites

Particle reinforced composites usually consist of fillers in discontinuous form. The basic parameters of the filler responsible for reinforcement are particle size, surface area, specific surface activity/chemical composition and structure. They are generally used in rubber industry and are of three types depending on their origin-black filler, non black filler and natural fillers. Varieties of carbon blacks are proved as efficient reinforcing agents. Carbon blacks are classified into furnace blacks, channel blacks, thermal blacks, lamp black and acetylene black depending on their method of manufacture. The major types of rubber reinforcing carbon blacks are manufactured by the furnace process. Non-black fillers include a variety of fillers such as, silica, clay, metal oxides, silicates, *etc*. Natural fillers include cellulose, starch, and various natural fibres and seed shells ground in the form of fine powder. They are extremely desirable when considering the biocompatibility and environmental aspects. An overview of some of the various fillers that are conventionally used in polymeric systems are given below.

Carbon black

Carbon black is the most extensively used reinforcing agent in tyre industry. The history of carbon black started when Mote and Mathews discovered them in 1904. It enhances abrasion resistance, overall mechanical properties and solvent resistance of various polymers. They are obtained from combustion or thermal degradation of natural gas, crude oils, and aromatic hydrocarbons under controlled oxygen conditions. They are 90-99 % elemental carbon combined with oxygen and hydrogen complexes. They include agglomerates consisting of sphere shaped particles called aggregates. Particle size of carbon black ranges from 10 to 40 nm [25]. They are obtained from various sources and are classified based on their origin. Furnace black includes super abrasion furnace (SAF), intermediate super abrasion furnace (ISAF), high abrasion furnace (HAF), super conducting furnace (SCF), *etc.*, [26].

Silica

Silica with general formula SiO_2 is an excellent reinforcing filler after carbon black, because of their small particle size and high surface area of 125-250 m^2/g. Ground mineral silica, precipitated silica, fumed silica are of three specific types used in rubber industry [27]. Ground silica is used as cheap heat resistant filler which does not improve the cure properties. Precipitated silica, obtained from the reaction of sodium silicate and acids, forms aggregates like carbon black because of the presence of hydrogen bonds among silica particles. Fumed silica has smaller particle size and higher surface area than precipitated silica. Both precipitated silica and fumed silica contain adsorbed water, which can affect the dispersion of filler in the matrix and vulcanization rate. However, they are reinforcing fillers which provide products excellent mechanical strength. Surface modification with silane coupling agents further improves the reinforcing ability of silica [28].

Clay

Clays are the layered silicates of metals like aluminium and magnesium. Individual layers are aggregated together by van der Waals forces to form clay particle. The intrinsic hydrophilicity of clay leads to poor compatibility with hydrophobic polymer matrices. Organically modified clays can be used instead of clay to enhance the interfacial adhesion and to get better mechanical properties. There are five main groups of clay; kaolinite, illite, smectite, palygorskite and vermiculite. Particle size of clay generally ranges from 0.5 to 5 µm.

Metal oxides

Zinc oxide (ZnO) is the first non-black reinforcing filler used in rubber compounds. It could provide high mechanical properties. It also acts as efficient activator for sulphur cure systems. Titanium dioxide (TiO_2) is also used as filler to get white and coloured compounds. It's optical properties and heat resistant properties are excellent.

Silicates

Silicates other than clay compounds come under this category. Sodium aluminium silicates are derived from kaolin, but with smaller size. Hence they are having better reinforcing properties than kaolin with a slower vulcanization rate. Calcium silicate ($CaO.3SiO_2.xH_2O$) is produced by mixing solutions of sodium silicate with calcium chloride. It is commonly used together with accelerators. Aluminium potassium silicate is generally known as mica, which is abundant in nature. It provides excellent electrical insulation, thermal stability, water resistance, chemical resistance, *etc.*, to the polymer. But surface modified mica only gives the reinforcing effect to the polymer. Talc, chemically known as magnesium silicate, provides excellent barrier properties to the composites. Talc when used as a hybrid filler together with carbon black or silica improves the mechanical strength and thermal stability of the material [24].

Calcium carbonate

Calcium carbonate in the form of ground limestone and precipitated $CaCO_3$ are used for rubber compounding. Ground limestone is used mainly for the purpose of reducing cost, but it can give moderate hardness and resilience at high loading. Precipitated $CaCO_3$ also gives low cost products with good appearance.

Carbon nanotubes

Carbon nanotubes (CNTs) are allotrope of carbon with sp^2 hybridization and are cylindrical in shape. CNTs have a diameter in the order of a few nanometers, but they may be millimetres or even centimetres long. CNTs can be synthesized by arc-discharge, laser ablation, high pressure carbon monoxide (HiPCO) and various chemical vapour deposition (CVD) techniques [29-30]. CNTs can be classified as (i) single walled CNTs (SWCNT) and (ii) multi-walled CNTs (MWCNT). Achieving homogeneous dispersion of CNTs in polymer matrix is difficult due to the weak interaction between filler and matrix. To overcome this, pre-treatment and functionalization are carried out in CNTs [31].

Polyhedral oligomeric silsesquioxane

Polyhedral oligomeric silsesquioxane (POSS) is a reinforcing nanofiller. The structure of POSS contains 8 silicon atoms linked together with oxygen atoms and possess an empirical formula $(RSiO_{1.5})_n$, where n=4, R is hydrogen or any aliphatic or aromatic group. These R functionalities in the outer surface make it compatible with any polymers and are able to initiate the grafting of POSS with the polymer chain. The incorporation of POSS to the polymer compounds bring excellent improvement in properties such as mechanical properties, flammability and thermal stability [32].

Bio-based fillers

Bio-fillers are the right candidate that satisfies our primary concerns about the environment. The search for sustainable, non-petroleum based, energy saving, economical and environmental friendly fillers led to various bio-based fillers. Examples are starch, chitin, and natural fibres of plant origin and of animal origin and agricultural wastes and biomass derived from various industries. Coir fibre, sisal, jute, oil-palm, rice husk, kapok fibre, bagassi fibre, chitin and chitosan, protein fibres, *etc.*, are some of the examples for natural fibres. Researchers also can extract nanocellulose from various biomasses which are proven to be very efficient in composites. Biocompatibility, biodegradability and cost-effectiveness are the unique advantages of bio-based fillers over the conventional fillers.

1.2.2.2 Fibrous composites

In fibrous composites, fibres are the load carrying members, while the surrounding matrix keeps them in desired location and orientation. The matrix acts as a load transfer medium, provides shape to the composite structure and protects the fibres from environmental damage. Fibres are of two types, natural fibres and synthetic fibres. Flax, jute, sisal, cotton, coir, *etc.,* are some examples of natural fibres. Carbon, aramid, polyester, nylon, boron, glass fibre, *etc.*, are some synthetic fibres. Fibrous composites are classified also as long fibre or continuous fibre reinforced composites and short or discontinuous fibre reinforced composites, depending upon the fibre-length.

1.2.2.3 Structural composites

Structural composites are considered as a special category of composites. Properties of these composites depend not only on the properties of the constituents but also on geometrical design of various structural elements. Two classes of these composites widely used are: laminar composites and sandwich structures. Laminar composites composed of two-dimensional layers of materials such as metal sheets, cotton, paper, woven glass fibres, *etc.*, embedded in plastic matrix, having a preferred strength direction. These layers are stacked and cemented together according to the requirement. Sandwich structures consist of thin layers of a facing material joined to a light weight filler material. Neither the filler material nor the facing material is strong or rigid, but the composite possesses both properties. Classification of composites is summarized in **figure 1. 2**.

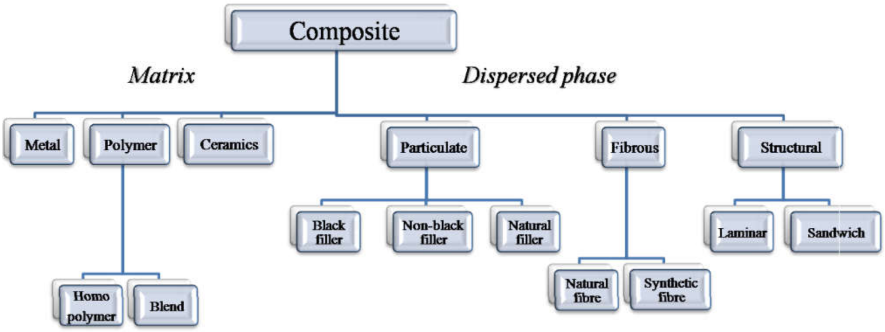


Figure 1.2: Classification of composites

1.3 Natural fibres

Natural fibres are subdivided based on their origin. All plant fibres consist of cellulose and animal fibres consists of proteins. Plant fibres are also called lignocellulosic fibres. Detailed classification of plant fibres is shown in **figure 1.3**. Mechanical properties of some of the natural fibres and that of glass fibre are given in **table 1.1** [33]. Tensile strength of glass fibres and natural fibres are incomparable. But, specific modulus (modulus/ specific gravity) of natural fibres are comparable with that of glass fibre. Weight reduction is also a desired property for the use of natural fibres.

Table 1.1: Mechanical properties of natural fibres and glass fibre.

Fibre	Specific gravity	Tensile strength (MPa)	Modulus (GPa)	Specific modulus
Jute	1.3	393	55	38
Sisal	1.3	510	28	22
Flax	1.5	344	27	50
Pineapple	1.56	170	62	40
Glass fibre-E	2.5	3400	72	28

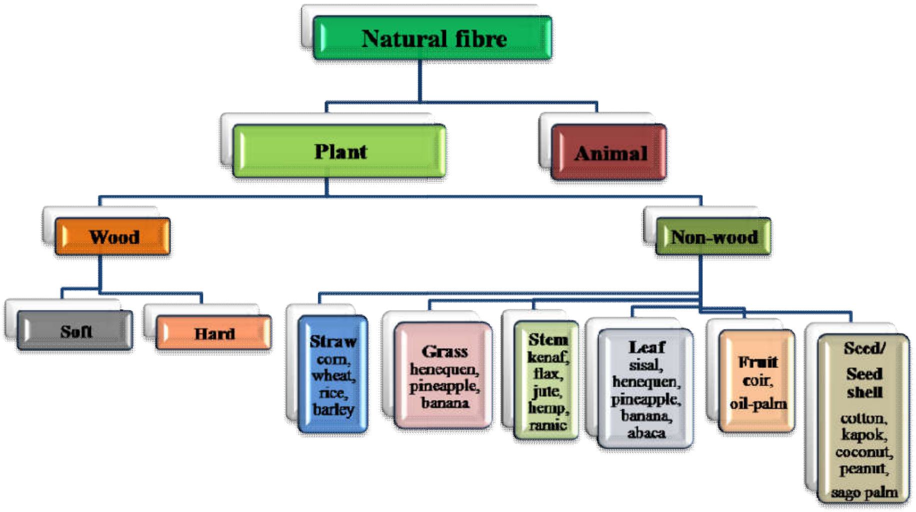


Figure 1.3: Classification of natural fibres.

1.3.1 Microstructure and chemical constitution of natural fibres

Natural fibres consist of cellulose micro fibrils embedded in an amorphous matrix of lignin and hemicelluloses. Lignocellulosic fibres are characterized by their cellular structures composed by cells that contains crystalline (highly ordered) and amorphous (disordered) regions interconnected through lignin and hemicellulose fragments [34]. These regions do not possess well-defined borders and present a transition from an ordered arrangement of the cellulose chains to amorphous. The hydrogen bonds and other linkages provided necessary strength and stiffness to the fibres. A model for the natural fibre is shown in **figure 1. 4**.

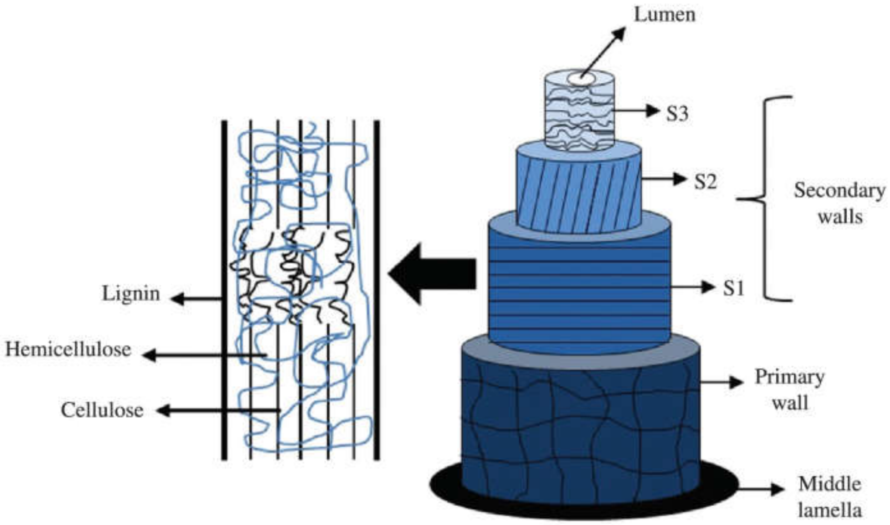
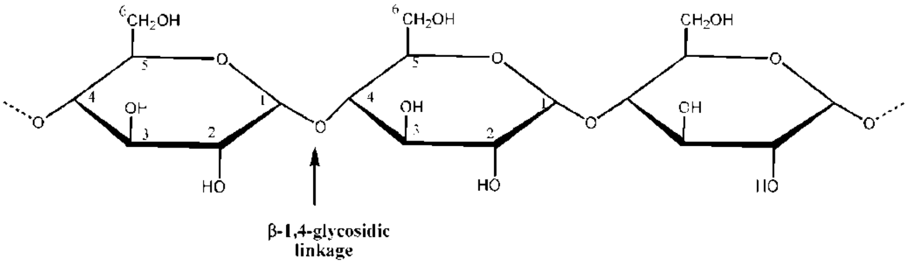


Figure 1.4: Plant fibre structure [35].

The fibre strength can be an important factor in selecting a natural fibre for a specific application. A high aspect ratio (length/width) is very important in cellulose-based fibre composites as it gives an indication of possible strength properties. Fibre dimensions, defects, strength, variability, crystallinity and structure must be taken into consideration [36]. Vegetable fibres have complex structures, made of wide variety of organic compounds such as lignin, hemicellulose, waxes, fatty acids, fats, pectin, *etc*. Cellulose, hemicellulose and lignin are the three main constituents of vegetable fibres. For this reason, they are also referred to as cellulosic or lignocellulosic fibres.

1.3.1.1 Cellulose

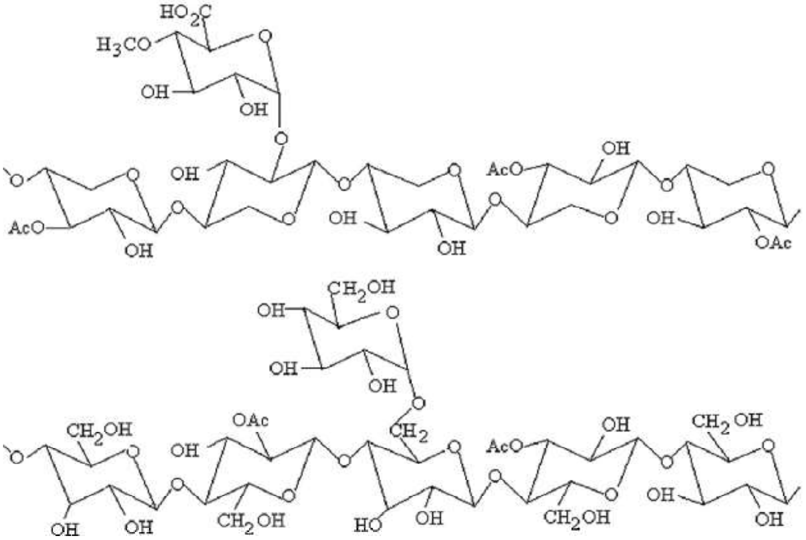
Cellulose is a linear polysaccharide macromolecule composed of β-D-glucose units, which are linked together by β -1, 4-glycosidic linkages, always at the C1 and C4 positions of the cyclic structure, as shows in **scheme 1.1**. The repeating units contain hydroxyl groups which form hydrogen bonds with the macromolecule itself and with neighbouring celluloses. For this reason, cellulose tends to form tightly packed, mostly crystalline, elongated structures called micro fibrils. These have high tensile strength and are the reason why cellulose is considered the main structural component in plants and natural fibres. Due to the great concentration of hydroxyls, cellulose is also hydrophilic in nature, although it is insoluble in water, due to its compact and difficult to access the structure [37].



Scheme 1.1: Cellulose structure.

1.3.1.2 Hemicellulose

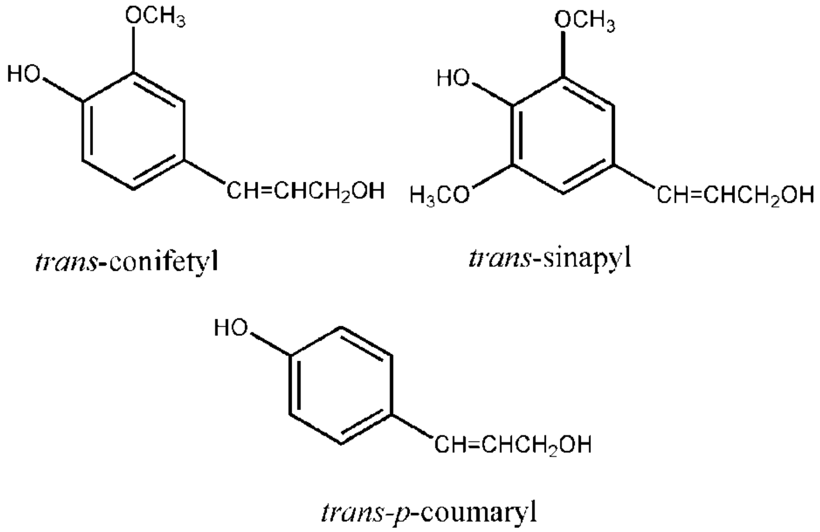
Hemicellulose is also a polysaccharide, *i.e.*, formed by bonded sugar monomers. However, unlike cellulose, hemicellulose is a heteropolymer, meaning its macromolecules can have a variety of different sugar monomers besides glucose (**scheme 1.2**) arranged in different ways as the backbone and side chains. The macromolecule is also ramified, instead of linear, and has lower molecular weight than cellulose. In the plant structure, hemicellulose is bonded to cellulose micro fibrils, lignin and sometimes pectin. It is responsible for the biodegradation, moisture absorption, and thermal degradation of the fibre. Together with lignin, hemicellulose acts as a kind of matrix for the cellulose micro fibrils.



Scheme 1.2: Structures of hemicellulose [37].

1.3.1.3 Lignin

Lignin is a polymeric natural product formed mainly by three phenol precursors: *trans*-coniferyl, *trans*-sinapyl, and *trans-p*-coumaryl (**scheme 1.3**).



Scheme 1.3: Phenols constituting the lignin macromolecules.

These can be combined in many different configurations in a three dimensional complex structure. Lignin is partially covalently bound to hemicellulose and is a fundamental part of the cell wall structure, assuming the role of a coupling agent and matrix material, increasing the stiffness of the cellulose/hemicellulose network [38]. Though, lignin is thermally stable, it easily undergoes UV reduction [33].

1.3.2 Surface treatments

Since natural fibres exhibit strong polarity and hydrophilicity, poor compatibility arises between natural fibres and polymer matrix which often shows significant hydrophobicity. This incompatibility leads to poor interfacial adhesion, inadequate wetting of filler in the matrix, agglomeration of filler particles and finally in lowering material properties [39]. Surface modification of natural fibres is, therefore, inevitable in order to improve the compatibility [40-42]. Hydrophobicity is induced into the hydrophilic natural fibres, either *via* physical or chemical methods.

1.3.2.1 Physical methods

Physical treatments change structural and surface properties of the fibre and thereby influence the mechanical bonding of polymers. Physical treatments do not extensively change the chemical composition of the fibres. Therefore, the interface is generally enhanced *via* an increased mechanical bonding between the fibre and the matrix. It is noteworthy that physical treatments appear as the most eco-friendly ones. Some physical methods that used to change the properties of the natural fibres are plasma treatment, corona treatment, steam explosion treatment, high energy ray radiation processing, autoclave treatment and also mechanical methods [43-46].

Corona treatment

Corona treatment is one of the most interesting techniques for surface oxidation activation. This process changes the surface energy of the cellulose fibres. Corona-treated fibres exhibited significantly higher polar components of free surface energy with increasing treatment energy output. Corona discharge treatment on cellulose fibre and hydrophobic matrix was found to be effective for the improvement of the compatibilization between hydrophilic fibres and a hydrophobic matrix. It was also proved that there is no further improvement achieved when longer time corona treatments are applied, because the exposed surface of the fibre does not improve even after 15 min of treatment. Instead, the degradation of the fibres proceeds further [47].

Plasma treatment

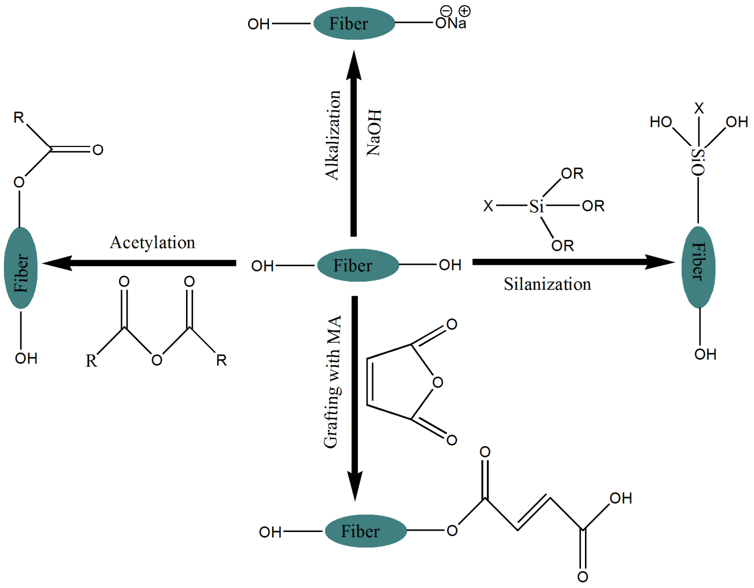
Plasma treatment is similar to corona treatment. The property of plasma is exploited in order to induce changes on the surface of a material. A variety of surface modifications can be achieved depending on the type and nature of the gases used. Reactive free radicals and groups can be produced, the surface energy can be increased or decreased and moreover, surface cross-linking can be introduced. Many researchers found that plasma treatment improves the fibre/matrix adhesion and enhances the mechanical property stiffness [48-49].

Steam explosion

Steam explosion process, a high-pressure steaming involves heating of lignocellulosic materials at high temperatures and pressures followed by mechanical disruption of the pre-treated material by violent discharge (explosion) into a collecting tank. This process has been applied to many lignocellulosic materials to enhance dispersibility and adhesion with the polymer matrix. Steam explosion results in improved properties of lignocellulosic materials, which include reduced stiffness, smoother surface, improved bending properties, and better distribution [37].

1.3.2.1 Chemical methods

Chemical approaches are far more explained in the literature than physical methods. Chemical treatments include a variety of methods such as alkali treatment, acetylation, silane treatment, peroxide treatment, benzoylation, permanganate treatment, isocyanate treatment, acrylation, *etc.*, in addition to the treatment with maleated anhydride grafted coupling agent [50-58]. Among these alkali treatment, acetylation, silane treatment and treatment with maleated anhydride grafted coupling agent are popular. **Scheme 1.4** shows the modification of fibre surface using different chemical methods.



Scheme 1.4: Modification of fibre surface using different chemical methods.

Nowadays enzyme treatment is gaining attraction due to its environmental friendliness [59]. These different types of surface modifications of natural fibres have resulted in improving fibre strength, fibre fitness and fibre-matrix adhesion in natural fibre composites [41, 60-63]. The chemical modification may make the fibre cell walls more dimensionally stable, reduce water sorption, or increase resistance against fungal decay. But there may be an associated problem of reduced dynamic strength such as impact strength due to embrittlement [39].

Alkali treatment

Alkali treatment or mercerization is one of the most popular, oldest, yet cost-effective chemical methods for natural filler to reinforce thermoplastics and thermosets [64-67]. It removes a significant amount of lignin, wax and oils that covers the external surface of the fibre cell wall of natural fibres and exposes the crystalline cellulose within the fibre. The important modification achieved with alkaline treatment is the disruption of the hydrogen bonding in the network structure, thereby increasing the surface roughness [68-69]. Improvement of fibre strength has also been obtained using alkali treatment [70-72]. It's efficiency depends on the type and concentration of the alkaline solution, time of treatment, and the temperature used for modification [73-74]. Moreover mercerization increases the number of possible reactive sites and allows better fibre wetting. Mercerization has an effect on the chemical composition of the natural fibres, degree of polymerization and molecular orientation of the cellulose crystallites due to cementing substances like lignin and hemicellulose which were removed during the mercerization process. As a result, mercerization had a long-lasting effect on the mechanical properties of natural fibres [75-76]. Many studies have reported the improvements in interfacial adhesion, tensile strength, Young's modulus, impact strength, fracture toughness and flexural properties of composites. Thermal stability and moisture resistance of natural fibre composites also can be improved with the chemical treatment of natural fibres [71, 77-80].

Silane treatment

Silane is a multifunctional molecule which is used as a coupling agent to modify fibre surfaces. Silane was found to be the most effective among many coupling agents for the natural fibre surface treatment [37, 67, 81-83]. Silanes for treatment of fibres possess different functional groups at different ends. Hydrophilic groups of the fibre interact at one end and hydrophobic groups in the matrix can interact with the other end and forms a bridge between them. Silane treatment of natural fibres involves different steps in which hydrolysis of alkoxy groups on silane with water takes place initially to form silanol (Si–OH) groups which can then react with hydroxyl groups on the fibre surface [84]. Commonly used silanes for the treatment of fibres are amino, methacryl, glycidoxy and alkyloxy silanes. Silanes have been found to increase the hydrophobicity of natural fibres and strength of natural fibre composites [85] . Detailed description on silane coupling agents is given in **section 1.3.3**.

Acetylation

Acetylation treatment is known as esterification methods for plasticizing natural fibre. Acetyl group (CH_3COO-) reacts with the hydrophilic hydroxyl groups of the fibre and removes the existed moisture. As a result, hydrophilic nature of the fibre is reduced while improves the dimensional stability as well as dispersion of fibre into polymeric matrices. After acetylation, the adsorbed moisture considerably reduced as the fibre become more hydrophobic due to the substitution of hydroxyl groups with acetyl groups [86]. Reduction of about 50 % moisture uptake for acetylated jute fibres and of up to 65 % for acetylated pine fibers has been reported by Bledzki and Gassan [87]. It has also been reported that acetylation of natural fibres deteriorate the mechanical properties by the degradation of cellulose and cracking of fibres [88].

Maleated coupling

The fundamental difference of maleated coupling with other chemical treatments is that maleic anhydride is not only used to modify fibre surface, but also the polymeric matrix to achieve better interfacial bonding between fibre and matrix and improved mechanical properties in composites. The addition of a maleic anhydride (MA) grafted coupling agent provides efficient interaction with the functional surface of the fibre-matrix [71, 89-92]. The maleic units induce the formation of covalent bonds (*via* condensation reactions) and physical interactions (*via* hydrogen bonds) with hydroxyl groups of natural fibre surface, thus acting as a linkage phase and providing a stronger interconnection and a better wettability between components. These interactions allow both the reduction of the hydrophilic nature of fibre and the improvement of fibre-polymer compatibility. It can be used as an additive during processing of composites or can be grafted to the fibre prior to processing. Improvement in tensile and flexural strength and stiffness as well as impact strength of polypropylene (PP) matrix composites are reported by the use of MA grafted coupling agents, mainly due to its ability to wet fibre and enhance its dispersion [88-89, 93-94].

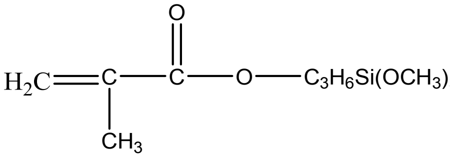
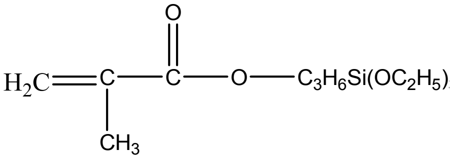
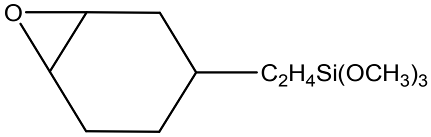
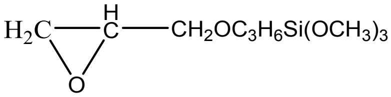
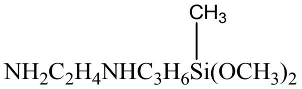
Enzyme treatment

The use of enzyme technology is becoming increasingly substantial for the processing of natural fibres. Currently the use of enzymes in the field of textile and natural fibre modification is also rapidly increasing. A major reason for embracing this technology is the fact that the application of enzymes is environmental friendly. The reactions catalyzed are very specific and have a focused performance [95]. An alternative to chemical and physical methods is represented by the rapidly expanding use of biological agents such as fungi and enzymes [96-97]. Biological modifications offer several advantages over chemical and physical methods. They can selectively remove hydrophilic pectin and the hemicellulosic material with less energy input [98-101]. Improvement of composite properties has been observed with the application of enzyme treatment. The tensile and flexural strength of abaca/PP composites is improved by 45 % and 35 % respectively by the removal of fibre components and increased surface area, which leads to increased interfacial bonding. Impact properties were also found to be increased by 25 % [95].

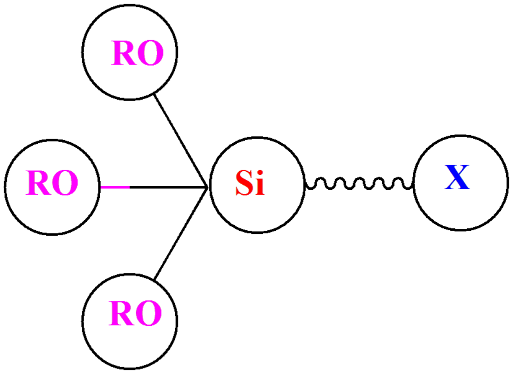
1.3.3 Silane coupling agents

Organosilanes are the main group of coupling agents used in natural fibre-polymer composites. They have been developed to couple virtually any polymer to the filler, which are used in reinforced composites [102-103]. In the past decades, various silane structures were tested for coupling of inorganic reinforcements such as glass fibre and organic polymer matrices [104-105]. The silane structures used to couple the natural fibres and polymer matrices were relatively limited. Most of the established silanes used for natural fibre composites are trialkoxysilanes. The organofunctionality of the silane interacts with the polymer matrices with their interaction modes depending on the functionality or compatibility towards the polymer. A non-reactive alkyl group of the silane may increase the compatibility with non-polar matrix due to their similar polarities. However, the reactive organofunctionality may covalently bonded as well as being physically compatible with the polymer matrices. These organofunctionalities of silanes are typically amino, mercapto, glycidyloxy, vinyl or methacryloxy groups. List of commercially available silane coupling agents, based on their functionality are summarized in the **table 1. 2**.

Table 1.2: List of some silane coupling agents.

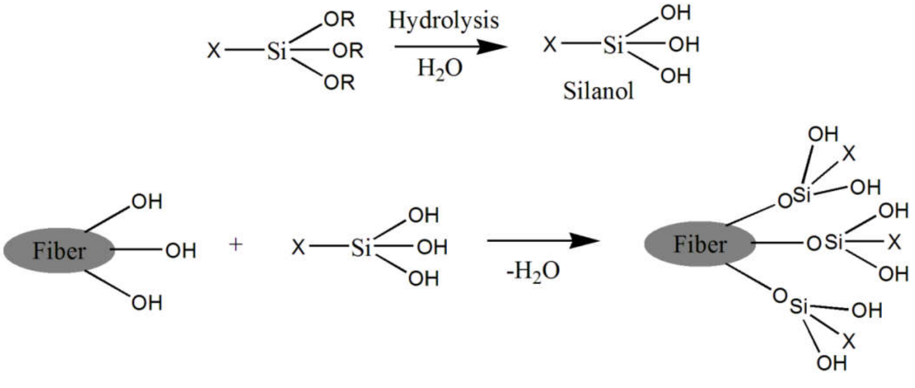
Functional group	Chemical name	Structural formula
Vinyl	vinyltrichlorosilane	$H_2C{=}CHSiCl_3$
	vinyltris(β-methoxysilane)	$H_2C{=}CHSi(OC_2H_4OCH_3)_3$
	vinyltriethoxysilane	$H_2C{=}CHSi(OC_2H_5)_3$
	vinyltrimethoxysilane	$H_2C{=}CHSi(OCH_3)_3$
Methacryloxy	γ-methcryloxypropyl trimethoxysilane	 $H_2C{=}\underset{CH_3}{\underset{\mid}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}C_3H_6Si(OCH_3)$
	γ-methcryloxypropyl triethoxysilane	 $H_2C{=}\underset{CH_3}{\underset{\mid}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}C_3H_6Si(OC_2H_5)$
Epoxy	β-(3,4epoxycyclohexyl ethyltrimethoxysilane)	
	γ–glycidyloxypropyl trimethoxysilane	
Amino	N-β(aminoethyl)-γ-aminopropyltrimethoxy silane	$NH_2C_2H_4NHC_3H_6Si(OCH_3)_3$
	N-β(aminoethyl)-γ-aminopropylmethyl dimethoxy silane	 $NH_2C_2H_4NHC_3H_6\overset{CH_3}{\overset{\mid}{Si}}(OCH_3)_2$
	γ-aminopropyltriethoxy silane	$NH_2C_3H_6Si(OC_2H_5)_3$
	N-phenyl-γ-aminopropyl trimethoxy silane	$C_6H_5HNC_3H_6Si(OCH_3)_3$
Mercapto	γ-mercaptopropyl trimethoxysilane	$SHC_3H_6Si(OCH_3)_3$

Most of the silane coupling agents can be represented generally as shown in the **scheme 1.5**, in which –OR is the reactive group that forms chemical bond with the filler (e.g. methoxy and ethoxy groups) and X is the reactive group that forms chemical bond with the matrix, like vinyl, methcryloxy,epoxy, amino, mercapto etc.



Scheme 1.5: General structure of silane.

Alkoxysilanes undergo hydrolysis, condensation and the bond-formation stages. Silanols, in the presence of moisture, form hydrolysable alkoxy groups. During condensation process, one end of silanol reacts with the cellulose hydroxyl group and other end reacts with the functional group of matrix [106]. This co-reactivity provides molecular continuity across the interface of the composite. It also provides the hydrocarbon chain that restrains the fibre swelling into the matrix [107]. An effective means to covalently bond the silane to a thermoplastic matrix is by free radical grafting [39, 108-109]. The most reported applications are to graft vinyltriethoxy silyl or methacryloxypropyl silyl groups onto a thermoplastic matrix in the presence of peroxide initiators such as benzoyl peroxide (BPO) or dicumyl peroxide (DCP). At an elevated temperature the peroxide first decomposes, generating oxy radicals. The oxy radicals not only have the potential to abstract hydrogen from the backbone of thermoplastic molecules or natural fibres, but can also add to vinyl double bonds of vinylsilane, producing vinyl radicals. The vinyl free electron may either combine with each other (homo-polymerization) or attack other molecules in a similar fashion to propagate the free radical reaction. Accordingly, the radical reaction would ultimately result in a grafting of vinylsilane onto thermoplastics [110]. As a result, fibre matrix adhesion improves and stabilizes the composite properties [63, 111]. The general mechanism of how alkoxysilanes form bonds with the fibre surface which contains hydroxyl groups is depicted in **scheme 1.6**.



Scheme 1.6: Reaction of silane coupling agent with fibre.

Natural fibres exhibit micro-pores on their surface and silane coupling agents act as a surface coating. This penetrates into the pores and develops mechanically interlocked coatings on fibre surface.

Silane treated fibre composites provide better tensile strength properties than the alkali treated fibre composites [42, 112-113]. In addition to these reactions of silanols with hydroxyls of the fibre surface, the formation of polysiloxane structures also can take place.

Silane coupling chemicals offer three main advantages: (i) they are commercially available in a large scale; (ii) at one end, they bear alkoxysilane groups capable of reacting with OH-rich surface, and (iii) at the second end, they have a large number of functional groups which can be tailored as a function of the matrix to be used. The last feature ensures good compatibility between the reinforcing element and the polymer matrix or even covalent bonds between them [114]. Aminosilanes, especially γ-aminopropyltriethoxysilane (APS), are the most extensively reported in the literature as coupling agents between natural fibres and thermoplastics or thermosets [115]. Vinyl- and acryl-silanes are coupling agents that are able to establish covalent bonds with polymeric matrices in the presence of peroxide initiators [39].

PART B
REVIEW OF LITERATURE

1.4 Polymer composites of silane treated natural fibres- A review

Chemical modification of natural fibres is necessary for increased adhesion between the hydrophilic fibres and hydrophobic matrix [116-117]. The most promising approach seems to be the use of silane coupling agents, in which chances of forming covalent bonds between the fibre and matrix are higher. The reaction of silane coupling agents with lignocellulosic fibres was found to be quite different with that of glass surface, in the sense that with cellulose macromolecules, only prehydrolyzed silanes underwent the reaction with cellulose surface [118]. The surface modification of cellulosic fibres was carried out using organofunctional silane coupling agents in an ethanol/water medium by Abdelmouleh *et al.* They found that silane coupling agents adsorbed on cellulose fibre surfaces followed by heat treatment condense with the OH groups of the substrate to give Si–O–Si and Si–O–C couplings respectively. These reactions ensured efficient and irreversible chemical bonding of the silane onto the cellulose surface, which was confirmed by the modification of cellulose [119]. Herrera-Franco *et al.,* used a silane coupling agent to promote adhesion between henequen fibres and a high density polyethylene (HDPE) matrix. The results showed that the adhesion between the natural fibre and the matrix played an important role on the final mechanical properties of the composites [120]. Later they used different silane coupling agents to increase the extent of adhesion between henequen fibres and HDPE. The increase in tensile strength was found to be possible when the henequen fibres were treated first with an alkali solution. It was also showed that the silane treatment produced an increase of 13 % in flexural strength while the flexural modulus remained relatively unaffected [121]. They also found that the tensile strength of HDPE reinforced with continuous henequen fibres was increased, which were treated by the optimum concentration (0.015 wt. %) of silane coupling agent. However, none of the fibre–matrix interface improvements had any significant effect on the value of Young's modulus of continuous henequen fibre reinforced HDPE composites [122]. Singh *et al.*, also observed improved mechanical properties on treatment of a sisal–polyester composites [50].

Colom *et al.*, studied the effect of different chemical modifications on the interfacial characteristics of aspen fibre-reinforced HDPE composites. The interaction between aspen fibres and HDPE was improved by the addition of two coupling agents, namely, maleated polyethylene (epolene C-18) and γ-methacryloxy-propyl trimethoxy silane (silane A-174). The authors observed that silane A-174 was a better coupling agent than epolene [123]. Ismail *et al.*, investigated the effects of a silane coupling agent bis(triethoxysilyl propyl) tetra sulphide (Si69) on curing characteristics and mechanical properties and observed that scorch time and cure time of the composites decreased with the presence of a silane coupling agent. The mechanical properties of composites were found to be improved with the addition of Si69. It can be observed that tensile strength increased from 7 to 12 MPa due to chemical modification [62]. The influence of chemical modification on dynamic mechanical properties of banana fibre-reinforced polyester composites was studied by Pothan *et al*. A number of silane coupling agents were used to modify the banana fibres. The damping peaks were found to be dependent on the nature of chemical treatment. Both storage modulus and damping values were found to be consistent and indicated the effectiveness of silane A174 coupling agent for improving fibre–matrix adhesion. They characterized the modified fibres using X-ray photoelectron spectroscopy (XPS) and observed the presence of an increased concentration of silicon elements on the surface of fibres [124].

Nishino *et al.,* investigated the influence of glycidyloxypropyltrimethoxy silane (GPTMS) on kenaf fibre-reinforced polylactic acid (PLA). It was found that the stress on the composite was effectively transferred to the incorporated kenaf fibre through the matrix, because of the relatively strong interaction between the kenaf fibre and PLA. In addition, the silane-coupling treatment to the kenaf fibre was found to be more effective for the reinforcement [125]. The influence of a number of chemical modifications on oil palm fibre was investigated. The chemical treatments employed were mercerization, latex coating, γ-radiation, acetylation, and peroxide. The aforementioned modifications were found to decrease the mechanical properties of fibres, but increase the water resistance of fibres. The silane-treated fibre exhibited the highest tensile strength among all the treated fibres [126].

Reinforcement capability of silane-treated jute fibre on PP composites was investigated by Sreekala and Thomas. Surface of jute fibres was chemically modified using GPTMS as silane-coupling agent in methanol/water medium. IR spectral characterization confirmed the existence of a condensation reaction between silane molecules and the cellulose polymers present in jute fibres. In addition, an intermolecular condensation occurred between adjacent silanol groups deposited on the fibres. Silane treatment increased the tensile properties of the jute-PP composites, because of an improved adhesion between the silanized jute fibre and the PP matrix [31]. Hashemi *et al.*, investigated PP/bagasse fibre composites prepared by compounding PP with bagasse fibres as reinforcing filler. Surfaces of fibres were modified through the use of silane coupling agents vinyltrimethoxysilane (VTMS) and GPTMS. It was found that modification of surface fibre changed the physical, mechanical, morphological, and rheological properties of composite. It was observed from scanning electron microscopy (SEM) that fibre adhesion to matrix improved and so as dispersion. The tensile strength and tensile modulus increased in modified fibres compared with the unmodified on the same loading, but elongation at break decreased. The effect of coupling agent on properties of filled PP depends on the content of coupling agents and optimum amount was achieved through measurement of water absorption [82].

The effectiveness of coupling agents on the wood-fibres in the PVC-wood fibre composites has been studied by Matuana *et al.*, The results showed that the adhesion between PVC and wood veneer laminates was significantly improved when wood veneers treated with aminopropyltriethoxy-silane (APS). The improvement was attributed to the fact that APS treated wood veneer chemically reacted and formed an ionic bond with the polymer matrix because of the highly electronegative nature of chlorine atoms [127]. The interfacial shear strength between jute fibres and PP, determined by a micro droplet micromechanical test, was improved by treating jute fibres with a 0.5 % APS aqueous solution [128]. A study of the melt rheological behaviour showed that treatment of pineapple fibres with vinyltriethoxysilane (VTES) (4.0 wt.% of fibre) and peroxide DCP (2.0 wt.% of fibre) caused an increase in the melt viscosity of the resulting low density polyethylene (LDPE) composites. This was attributed to the increased fibre–matrix interfacial interaction due to a grafting reaction [129]. Abu Bakar *et al.,* used silane and zirconate coupling agent to treat the oil palm empty fruit bunch fibre to reinforce acrylic-impact modified PVC. They found that the softening effect generated by acrylic impact modifier was compensated by both coupling agents, mainly silane, to improve the stiffness of composites. The presence of silane coupling agent improved the fibre-matrix interface and which was further confirmed by the reduction in water absorption and formation of new functional groups of treated composites [130].

Iorga *et al.,* applied different treatments to hemp fibres (HF) and the efficiency of treated HF as reinforcement in PP was evaluated in comparison with untreated HF. The results showed that tensile strength and Young's modulus of untreated fibres increased by 78 % and 61 % respectively. Further improvement of tensile strength and modulus, of over 100 %, was obtained for PP composites with treated HF. Aminosilane treatment of HF was the most efficient, leading to simultaneous improvement of tensile strength and modulus and also of impact strength of PP composites [131]. Several silane treatments were directly applied on HF and their influence on the surface properties and thermal stability of HF was investigated by Panaitescu *et al.,* Thermogravimetriy (TG) highlighted the favourable effect of silane treatments on the thermal stability of HF. The HF treatments influenced the mechanical properties of PP/HF composites. The tensile modulus of elasticity of PP increased with 67 % in the composite with 40 wt.% HF– MPS and only 30 % when PP was reinforced with the same amount of untreated fibres. Nano-indentation results show good modulus and hardness for the composites with silane modified HF [132].

1.5 Coconut shell powder as potential filler in polymer composites- A review

Coconut (Cocos nucifera) is a member of the palm family. Virtually every part of the coconut palm has some human use. Efficiency of coir as reinforcing filler has been studied extensively [133-134]. Coconut shell is non food part of coconut which is hard lignocellulosic agro waste. Coconut shell is 15–20 % of coconut [135]. The first reported use of coconut shell powder (CSP) as filler was done by Aminabhavi *et al.,* in 1983. They found that CSP and other aggrowaste fibre materials successfully bound with phenol-formaldehyde resin and were efficient to replace the heavy use of asbestos as filler [136]. They continued the research on CSP to develop inexpensive lightweight polymer composites having better properties than ordinary cement concrete [137]. In 1998, the effect of CSP with PVC was studied by Zurale and Bhide. They have shown that, after proper treatment, CSP could be extruded with PVC resin and suggested that they could be used for the preparation of laminates and pipes for low-cost housing projects, drip-irrigation and other applications [138]. Sapuan and Harimi presented the tensile and flexural properties of composites made from coconut shell filler particles and epoxy resin in 2003. They pointed out that the tensile and flexural strengths of the epoxy coconut filler composites were affected by the amount of filler in the composites. The more the filler content, the higher the strength [139]. S K Pradhan *et al.,* experimented with a mixture of ultrahigh molecular weight polyethylene (UHMWPE) powder and CSP. Powder metallurgy was used to compact the blended compositions at 200 °C. The composite material remained tough when the CSP content was 20–30 vol.%, as revealed by notch impact tests and fractography studies. However, the compressive strength of the UHMWPE–CSP composite decreased rapidly beyond 20 vol.% CSP [140].

The effects of CSP as fillers on the mechanical properties and biodegradability of LDPE plastic film was studied by Rathanak *et al.* The integration of CSP has resulted increment in modulus of elasticity, burst strength and biodegradability. They claimed that CSP is a potential agro wastes that can be used as fillers in plastic film to initiate decomposition by bacteria. This is due to its high lignin content which serves as carbon source for bacteria attacks. CSP also decreases the use of the virgin resin thus cost effective [141]. However, most of the mechanical properties decreased due to lack of adhesion between the fibre and polymer matrix. This can be improved by implying effective filler treatments. In 2005, Ramaraj and Poomalai prepared polyvinyl alcohol (PVA) composite films with CSP at different compositions. These composite films show enhanced elastic modulus, degradability, solubility resistance, and moisture vapour transmission rate with the addition of CSP. However, the introduction of CSP varied the tensile strength and affected percentage of elongation, tear and burst strengths, moisture content, density, and swelling capacity considerably [142]. Bledzki *et al.,* inspected the feasibility of utilizing coconut shell as alternative filler for soft wood fibre as reinforcement for PP composites material. Coconut shell showed 80 % better elongation at break and 20 % better charpy impact strength than softwood composites [135].

In 2011, Sarki *et al.,* examined the feasibility of utilizing of grain by-products such as coconut shell as alternative fillers in polymer composites material. CSP filled composites were prepared from epoxy polymer matrix containing up to 30 % coconut shell fillers. The obtained results of the developed composites have shown that the coconut shell waste could be used as alternative biodegradable eco-friendly reinforcement. Further optimization of the conditions are necessary in order to obtain materials with improved mechanical properties [143]. The effects of CSP on the mechanical properties, thermal properties, and morphologies of polylactic acid (PLA) bio-composites were investigated by Chun *et al*. It was found that increasing the CSP content decreased the tensile strengths and elongations at break of the PLA/CSP bio-composites. However, incorporating CSP increased their modulus of elasticity. The tensile strengths and modulus of elasticity of the PLA/CSP biocomposites were enhanced by use of silane coupling agents. In another work, they studied the effect of maleic acid treatment on CSP and found that maleic acid also enhanced interfacial bonding between CSP and PLA matrix [144-145]. Sareena *et al.*, in 2012 used untreated and alkali treated CSP as reinforcing filler in natural rubber and studied mechanical properties, transport properties and biodegradability. Modified CSP composites show better physico-mechanical properties and solvent resistance. Composites containing chemically treated fillers were found to be more resistant to soil erosion [80, 146-147]. Later, Jinitha *et al.*, used permanganate treated CSP in natural rubber and confirmed the efficiency of CSP as filler in natural rubber composites [148]. The morphology and mechanical properties of coconut shell reinforced polyethylene composite have been evaluated to establish the possibility of using it as a new material for engineering applications. CSP reinforced composite was prepared by compacting LDPE matrix with 5-25 % volume fraction coconut shell particles. The effect of the particles on the mechanical properties of the composite prepared was investigated. The result showed that the hardness of the composite increased with increase in coconut shell content, though the tensile strength, modulus of elasticity, impact energy and ductility of the composite decreased with increase in the particle content.

Agunsoye *et al,.* assumed that the non-uniform distribution of coconut shell particle in the microstructure of the composite is the major factor responsible for the decrease in strength [149]. In 2013, Salmah *et al.,* investigated the effect of untreated and treated CSP reinforced unsaturated polyester (USP) composites. The alkali treatment with sodium hydroxide enhanced the mechanical and thermal properties of USP/CSP powder composites. The treated USP/CSP composites indicated higher tensile strength, modulus of elasticity, flexural strength, flexural modulus and thermal stability compared to untreated composites [150]. Nidhi Thaker *et al.*, also conducted the studies on USP/CSP composites and obtained similar trends as that of results of Salmah *et al.,* [151]. Singh *et al.,* reported tensile strength, flexural property and hydrophilic behaviour along with engineering application of epoxy- resin/CSP composites. The experimental investigation on mechanical properties *viz*. density, tensile strength and flexural strength of CSP epoxy composite materials was greatly influenced by CSP. Consequently, the composite prepared with 20-30 % CSP was found to be suitable for the application in the interior part of an aircraft, motor car and automobile [152].

Utilization of CSP as filler in recycled polypropylene (rPP) was first carried out by Chun *et al.,* in 2013. Sodium dedecyl sulfate (SDS) was used as coupling agent in these composites. The effect of filler content and SDS on tensile properties, thermal properties, water absorption and morphology of rPP/CSP composites were investigated. In this study, modified rPP/CSP composites with SDS showed significant increase in tensile properties, thermal stability, crystallinity and low water absorption compared unmodified rPP/CSP composites. They suggested that SDS was an efficient candidate to improve the interfacial properties of CSP [153]. Ohja *et al.,* compared the mechanical and tribological properties of the both wood apple shell and coconut shell particulate epoxy resin composite. The results showed that maximum flexural strength was obtained 78.19 MPa for wood apple shell and 68.25 MPa for coconut shell at 15 % filler content. The wood apple particulate composite showed best erosion and mechanical properties than coconut particulate composite [154]. Sreejith *et al.,* focused on the use of CSP as reinforcing filler in Styrene Butadiene Rubber (SBR) matrix. The results showed that the vulcanizates containing 20 phr filler loading exhibited better properties. VTES treated CSP composites exhibited relatively higher tensile strength and hardness than unmodified CSP composites suggested the improvement in interface by the use of silane coupling agent [155].

1.6 Scope and objectives of the study

In a systematic study carried out by our group, we have already developed and characterised thermoplastic polyurethane/ natural rubber (TN) blends, and found it as a promising thermoplastic elastomer. It has been found that, both the properties of NR and TPU were improved. NR, which is characterised by good elastic properties, good resilience and damping behaviour improved with better resistance to solvents and processability. Tensile strength, toughness and elongation at break of TPU could be improved on blending. Since

TN blend is an immiscible blend; it is necessary to compatibilize the interface between NR and TPU to get better properties. Different strategies can be adopted for the reinforcement of immiscible blends like addition of compatbilizers or fillers. Addition of chitin, a natural filler with animal origin to the TN blend was found to be a success in improving various properties and cost-effective in our pilot study. By incorporating chitin, solvent resistance and thermal stability of blends were improved. More important finding was about the biodegradability of the polymer.

Extensive use of TPU, especially as footwear material and many other household applications, being a synthetic plastic is detrimental to our home-planet earth. Blending with NR obviously decrease the amount of TPU for a particular application. But it is noticeable that blending with NR does not assure the biodegradability for the material, since NR is non-biodegradable. Chitin added TN blend shows better biodegradation behaviour. Thus, we could efficiently prepared biodegradable, thermally stable, blends and composites with superior mechanical properties. It is found prudent to use different cellulosic natural fibres, which is available in plenty to optimize the properties of TN blend. CSP was confirmed as a potential filler for natural rubber composites in another study [80]. The primary concern of this study is to fabricate cost-effective and environment friendly composites using TN blend and to evaluate the potential of coconut shell powder as reinforcing filler in the blend TN. Thus, the following specific objectives were set for this study.

- Modification of CSP using silane coupling agents VTES and GPTMS and monitor these modifications using FT-IR, SEM and TG.
- Development of TN blend and unmodified and silane modified CSP filled TN blend-composites according to ASTM standards.
- Characterization of composites using experimental techniques such as Rheometry, FESEM, TG and DSC.
- Application studies with special reference to the effect of filler particle sizes, filler loading and the effect of silane treatments on filler.
    - Mechanical properties such as tensile properties, tear strength, hardness and abrasion resistance according to ASTM standards.
    - Transport behaviour in aromatic solvents (benzene, toluene and *p*-xylene) and petroleum fuels (petrol, kerosene and diesel).
    - Oil resistance in industrial reference oils (IRM 901, IRM 902 and IRM 903).
    - Aging studies (Oil-aging in IRM 903 oil for 70 h at varying temperatures, thermal aging at 100 °C for 24 h and water aging at room temperature for 30 days).
    - Biodegradability of the composites estimated by soil-burial test for 90 days.

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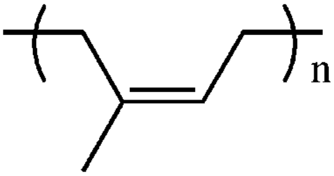
Chapter 2
Materials and Methods

Abstract: *This chapter accounts for the materials and experimental methods used in the present investigation. Brief descriptions on formulations and preparation procedures of the coconut shell powder (CSP) filled TPU/NR (TN) blend-composites were given. The methodologies for the analysis of cure characteristics, mechanical properties, crosslink density, transport properties, thermal properties, aging properties, biodegradation and morphology have also been given.*

2.1 Materials

2.1.1 Natural rubber

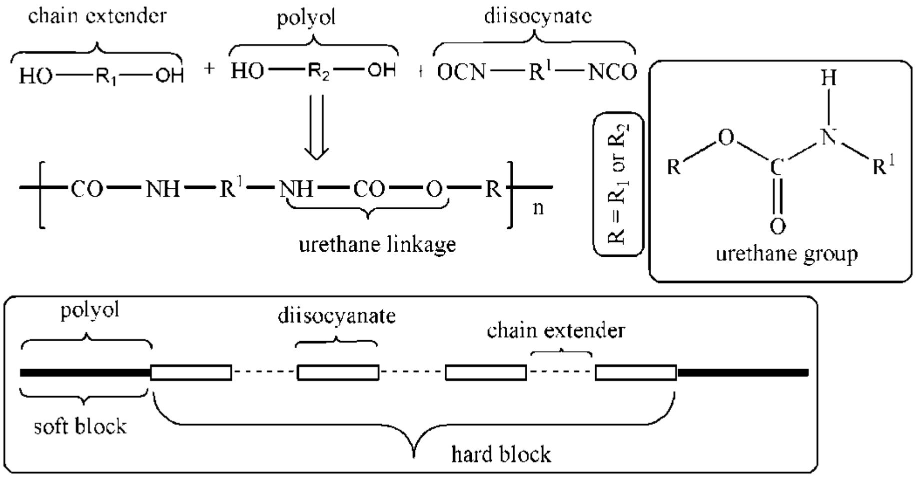
Natural rubber (NR) is chemically known as *cis*-1, 4-polyisoprene. Indian standard natural rubber (ISNR-5), produced from field latex or high quality field coagulum, supplied by Rubber Research Institute of India, Kottayam is used in this study. The structure of NR is as shown in **scheme 2.1.**



Scheme 2.1: Structure of NR.

2.1.2 Thermoplastic polyurethane

Thermoplastic polyurethane (TPU) is a multiphase block copolymer that is created when three basic raw materials are combined together in a specific way. The individual components required to produce a TPU are: (i) polyol or long-chain diol (ii) chain extender or short-chain diol and (iii) diisocyanate. **Scheme 2.2** shows the formation of TPU from it's components. The soft block, built out of a polyol and an isocyanate, is responsible for the flexibility and elastomeric character of TPU. The hard block, constructed from a chain extender and isocyanate, gives TPU its toughness and physical performance properties.



Scheme 2.2: Formation of TPU.

Figure 2.1 shows how physical crosslinks in TPU melts out under heat and repack when the material is cooled.

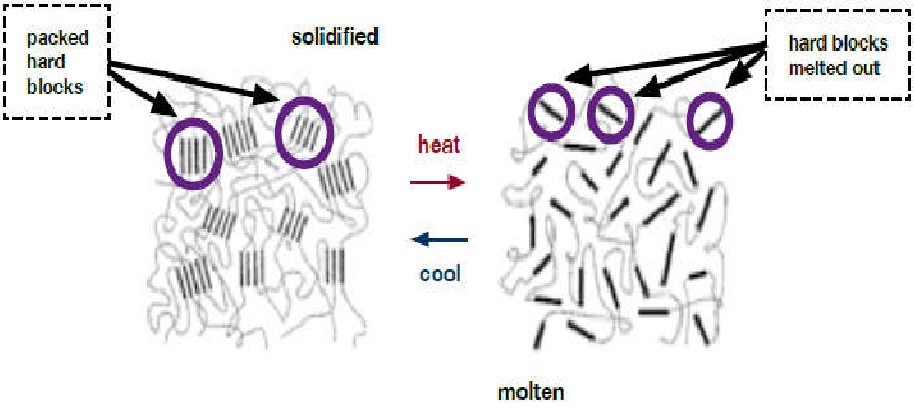
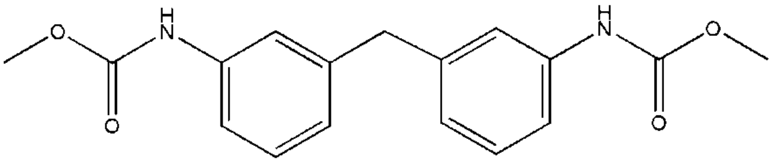


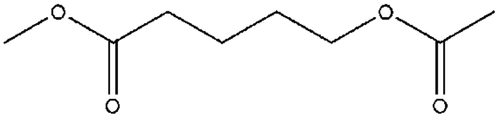
Figure 2.1: The morphology of TPU.

Polyether-thermoplastic polyurethane (Irogran), purchased from Huntsman polyurethane, Germany was used for this study. It contains 10 % isocyanate, which forms the hard segment, 32 %

adipate, which forms the soft segment and 58 % butyl-diol, which is the chain extender. **Scheme 2.3** represents the structure of Irogran.



10% (Hard segment) (Isocyanate)



32% (Soft segment) (Adipate)

58% chain extender (Butyl diol)

Scheme 2.3: Structure of Irogran.

Table 2.1 shows the characteristic physical properties of the polymers used to prepare the blend-matrix.

Table 2.1: Physical properties of NR and TPU.

Polymer	Property		Source
Natural rubber (ISNR-5)	Glass transition temperature (T_g)	-72 °C	RRII, Kottayam
	Density	0.92 Kgm^{-3}	
	Solubility parameter	16.2 $(Jm^{-3})^{1/2}$	
	Number average molecular weight	1×10^6	
Thermoplastic polyurethane (Irogran)	Density	1.09-1.1 Kgm^{-3}	Huntsman polyurethane, Germany
	Melt mass flow rate	1.2-55 g/10 min	
	Flexural modulus	0.407-104 MPa	
	Tensile strength	23.9-56.3 MPa	
	Tensile elongation	190-740 %	

2.1.3 Coconut shell powder

Coconut shell powder (CSP) was obtained from SIP India Exporters (Erode, Tamilnadu, India). Chemical composition of coconut shell is presented in **table 2.2**.

Table 2.2: Chemical composition of Coconut shell [1].

Compositions of CSP	(%)
Cellulose	34
Hemicellulose	21
Lignin	27
Starch	0
Protein	2
Fat	5

2.1.4 Solvents and chemicals

Dicumyl peroxide (DCP) of commercial grade (40 % active) was used as the crosslinking agent. Triethoxyvinylsilane (TEVS) and 3-glycidyloxypropyltrimethoxy silane (GPTMS) were purchased from Sigma Aldrich. Other common chemicals and solvents such as sodium hydroxide, ethanol and acetic acid were obtained from Merck India Ltd. The solvents benzene, toluene and xylene used were of laboratory reagent grade supplied by Merck and used as received. The petroleum solvents petrol, diesel and kerosene were obtained from Indian Oil Corporation. Details of all the solvents used for sorption studies are summarized in **table 2.3.**

Table 2.3: Characteristics of solvents used.

Solvents	Characteristics	
Benzene	Molecular weight ($gmol^{-1}$)	78.11
	Density (gcm^{-3})	0.874
	Boiling point (°C)	80
	Solubility parameter ($(cal\ cm^{-3})^{1/2}$)	9.2
	Molar volume	89.17
Toluene	Molecular weight ($gmol^{-1}$)	92.14
	Density (gcm^{-3})	0.867
	Boiling point (°C)	109
	Solubility parameter ($(cal\ cm^{-3})^{1/2}$)	8.9
	Molar volume	105.90
Xylene	Molecular weight ($gmol^{-1}$)	106.17
	Density (gcm^{-3})	0.860
	Boiling point (°C)	138
	Solubility parameter ($(cal\ cm^{-3})^{1/2}$)	8.8
	Molar volume	123.45
Petrol	Molecular weight ($gmol^{-1}$)	80-100
	Density (gcm^{-3})	0.710-0.737
	Boiling point (°C)	70-150
Kerosene	Molecular weight ($gmol^{-1}$)	150-170
	Density (gcm^{-3})	0.810-0.817
	Boiling point (°C)	140-230
Diesel	Molecular weight ($gmol^{-1}$)	170-330
	Density (gcm^{-3})	0.82-0.95
	Boiling point (°C)	240-350

Industrial reference oils IRM 901, IRM 902 and IRM 903 oils (Calumet Lubricants Company) were of commercial grade and used as received. Various properties of industrial reference oils are shown in **table 2.4**.

Table 2.4: Properties of oils used.

Property	**IRM 901**	**IRM 902**	**IRM 903**	**ASTM method**
Aniline point °C	124±1	93±3	70±1	D 611
Viscosity-Gravity constant	0.790-0.805	0.860-0.870	0.875-0.885	D 2140
Refractive index	1.4848	1.5105	1.5026	D 1747
Aromatics (C_A%)	3	12	14	D 2140

2.2 Methodology

2.2.1 Modification of CSP

CSP was dried at 80 °C for 24 h to remove the moisture. The powder was sieved to get unmodified CSP of particle size of < 60 µm. The sieve permitted the smaller sized particle (< 60 µm) to go through the filtering web. Prior to the silane treatment, alkalization of CSP was carried out to ensure the removal of certain amount of lignin, wax and oils covering the external surface of fibre cell wall [2]. Here CSP was treated with NaOH solution (5 %) for 5 h with continuous stirring using a mechanical stirrer and kept for 24 h. Rinsed and washed with water until the solution became neutral. Filtered and dried in air oven at 70 °C for 24 h. Silane (1 %) and DCP (0.5 %) (w/w with respect to the powder) dissolved in a mixture of ethanol-water (90/10 v/v) were used. The pH of the solution was adjusted to 3.5 using acetic acid and stirred continuously for 10 min. Then the powder was immersed in the solution and kept agitated for 1 h. Finally the powder dried at 70 °C for 24 h [3]. Again the powder was sieved to get modified CSP of particle size of < 60 µm. Here the unmodified CSP was designated as

UCSP, TEVS treated CSP as T-CSP and GPTMS treated CSP as G-CSP. **Figure 2.2** is the flow chart of chemical treatment of CSP.

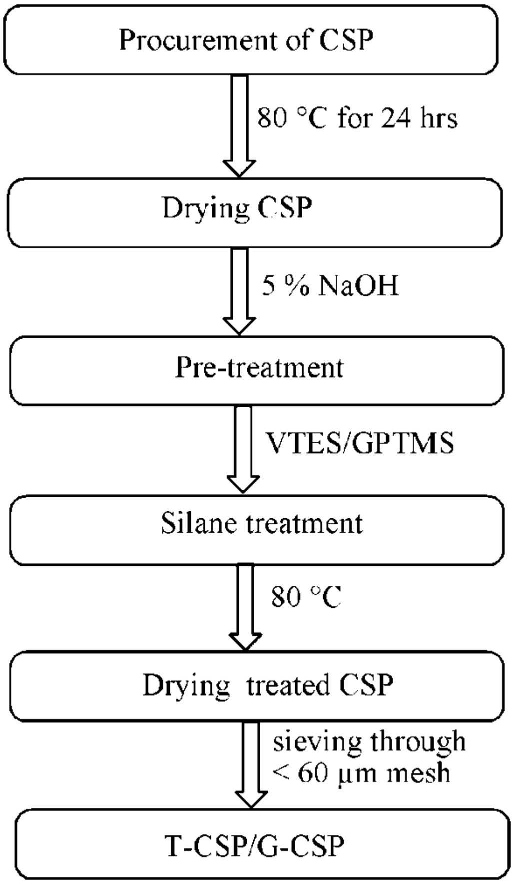


Figure 2.2: Chemical treatment of CSP.

2.2.2 Sample preparation

2.2.2.1 Preparation of blends and composites

Mixing of the composites was done on a two-roll mill (150×300 mm) with a nip gap of 1.3 mm and at a friction ratio 1:1.4 at room temperature. The vulcanizing agent, DCP, 4 parts per hundred (phr) was incorporated as per ASTM D15-627. CSP was added during mixing in the two-roll mill. The temperature was maintained constant by circulating water through the rolls. The composites were coded as TN, U5, U10, U15, U20, T5, T10, T15, T20, G5, G10, G15 and G20 where TN represents thermoplastic polyurethane/natural rubber blend of composition 20:80, U represents unmodified CSP, T represents the TEVS treated CSP and G represents the GPTMS treated CSP. 5, 10, 15 and 20 denotes the amount of CSP (g) in 100 g of blend. Designation of samples and formulation details of CSP filled TPU/NR blend-composites are summarized in **table 2.5**.

Table 2.5: Designation of samples and formulation details of CSP filled TPU/NR blend-composites.

Designation	TPU/NR	DCP (phr)	U-CSP (phr)	T-CSP (phr)	G-CSP (phr)
TN	20/80	4	0	0	0
U5	20/80	4	5	0	0
U10	20/80	4	10	0	0
U15	20/80	4	15	0	0
U20	20/80	4	20	0	0
T5	20/80	4	0	5	0
T10	20/80	4	0	10	0
T15	20/80	4	0	15	0
T20	20/80	4	0	20	0
G5	20/80	4	0	0	5
G10	20/80	4	0	0	10
G15	20/80	4	0	0	15
G20	20/80	4	0	0	20

2.2.2.2 Cure characteristics and vulcanization

Optimum cure time (t_{90}) for each compound was determined using a moving die rheometer (MDRB), operating at 160 °C. After that, the rubber compounds were vulcanized in a hydraulic press to the optimum cure time along the mill grain direction under a pressure of 6.7 MPa (Mold dimension: $150\times150\times2$ mm^3). The sheets were cooled quickly in water at the end of the curing process.

2.3 Characterization and property analysis

2.3.1 Spectroscopic analysis

Chemical modification of the CSP with silanes was monitored using Jasco FT-IR spectrometer. CSP was mixed with analytical grade KBr, ground, pressed to obtain pellets and subjected to FT-IR analysis.

2.3.2 XRD analysis

The X-ray diffraction of the unmodified CSP and treated CSPs was carried out using the Rigaku Miniflex-600 diffractometer with CuK∞ (λ = 1.54 A°). The samples were scanned at the 2θ range of 10°-50° and a step size of 0.02° was used for analysis.

2.3.3 Density of composites

Density of different samples was measured using electronic densimeter MD-200S as per ASTM specifications.

2.3.4 Mechanical properties

All data presented here are average values of at least three independent values with ± S.D.

2.3.4.1 Tensile strength

Testing of rubber vulcanizates was done on Universal testing machine Instron-3365 (Series IX Automated Materials Testing System 1.38, Model-441, Instron Corporation). Tensile properties of the composites were examined with dumb bell shaped samples, according to the ASTM D 412-1998, at a cross head speed of 500 mm/min after conditioning at 27 °C. The specimens were positioned vertically in the grips of the testing machine. The grips were then tightened evenly and firmly to prevent any slippage with gauge length kept at 50 mm. As the tensile test starts, the specimen elongates; the resistance of the specimen increases and is detected by a load cell. This load value (F) is recorded until the rupture of the specimen occurred. Instrument software provided along with the equipment will calculate the tensile properties for instance tensile strength, elongation at break and modulus values.

2.3.4.2 Tear strength

Tear test was conducted as per ASTM D 624-2000, with the 'Die B' crescent-shaped test pieces, which were mounted on the Universal Testing Machine with a speed of 500 mm/min at 27 °C.

2.3.4.3 Hardness

Shore-A-Durometer was used to measure the hardness of the prepared composites according to ASTM D 2240-2004. The samples having a thickness of 6 mm were used. Shore hardness is a measure of the resistance of a material to penetration of a spring loaded needle like indenter. The measured hardness is determined by the penetration depth of the indenter under the load. Shore hardness value may vary in the range from 0 to 100.

2.3.4.4 Abrasion resistance

Abrasion resistance was done on an abrasion tester (DIN 53516) according to ASTM D-2228. The test specimens are of cylindrical shape of (16 + 0.2) mm diameter and at 6 mm thickness, was kept on a rotating sample holder and 10 N load at a constant speed of 0.32 m/s, was applied. The abrasion distance is 40 m. Initially a pre-run was given for the sample and its weight was taken. The weight after the final run was also noted. The loss of mass of the test specimen in mg is determined within 1 mg by weighing and its volume loss calculated on the basis of the density determined according to DIN 53479. The volume loss is referred to a nominal abrasive power S_o of 200 mg for the test emery paper. The difference in weight is the abrasion loss.

2.3.5 Thermal properties

The thermal stability study of fillers and composites was carried out using Thermo gravimetric analyzer (TGA, Shimadzu TGA

50). The samples were heated from room temperature to 600 °C at the heating rate of 10 °C min^{-1} in nitrogen atmosphere with flow rate of 50 mLmin^{-1}. The calorimetric measurements were carried out using a Perkin Elmer DSC7 calorimeter. DSC traces were recorded between -80 °C to 200 °C at heating rate of 10 °C/min under nitrogen atmosphere.

2.3.6 Morphology

The surface morphology of CSP was studied using JEOL Model JSM-6390LV SEM, with magnification of X3500. The SEM images were taken at a voltage of 15 kV. The morphology of tensile fractured surfaces of composites was observed at magnification of 1K and 3K and analyzed using SEM-EVO MA (M/s Carl Zeiss, SMT Ltd, Germany).

2.3.7 Sorption experiments

2.3.7.1 Solvent-resistance

Circular samples of diameter 1.94 cm were punched out from the vulcanized sheets using a sharp steel die and were used in sorption experiments that monitored liquid sorption gravimetrically. Initially the samples were dried in a vacuum desiccator over anhydrous $CaCl_2$ at room temperature for about 24–28 h. The original weight and thickness of the samples were measured before sorption experiments. They were then immersed in penetrants (15–20 mL) in closed diffusion bottles, kept at constant temperature in an air oven. Periodically the samples were removed from the bottles and damp dried between filter papers to remove excess solvent on their surface. They were then weighed immediately using an electronic balance (Shimadzu, Libror AEU-210 Japan) that measured reproducibility within ± 0.0001 g. The samples were immediately placed back into the test bottles. The process was continued until equilibrium swelling was achieved. To avoid the possible error due to the removal of samples from the solvents, the weighing was carried out within 40 sec [4]. The results of solvent sorption experiments were expressed as mol % uptake (Q_t moles %). The solvents used were aromatic solvents *viz.*, benzene, toluene and xylene, petroleum fuels *viz.*, petrol, kerosene and diesel. The experiments were conducted at 30 °C, 45 °C and 60 °C. Various parameters were like mode of transport, kinetic parameters and energy of activation also were determined.

2.3.7.2 Oil-resistance

Oil resistance studies were carried out by immersing the test specimens of circular shape with diameter 1.94 cm in IRM oils 901, 902 and 903. The weight of oil uptake was evaluated by measuring the swollen weight of samples after a specific time. The swollen samples were immersed in acetone wiped with filter paper and transferred to weighed bottle and the final weight of the sample was taken. Oil-resistance was reported in terms of % mass swell.

2.3.8 Aging studies

2.3.8.1 Thermal aging

Test samples of dumbbell shape were aged at 100 °C for 24 h in an air-circulating aging oven according to ASTM D573 [5]. The tensile properties were measured before and after ageing. The percentage retention of properties after ageing was calculated.

2.3.8.2 Oil aging

This test was conducted according to ASTM D471. The tensile test specimens were immersed in IRM 903 oil at room temperature for 70 h. When the specific time was reached, the test specimens were removed from the oil, wiped with tissue paper to remove the excess oil from the surface and tested for tensile properties. The percentage retention of properties after ageing was calculated [6-7].

2.3.9 Biodegradation studies

2.3.9.1 Water sorption experiment

The possibility of biodegradation was monitored using water sorption test. Circular samples of diameter 1.94 cm were used in sorption experiments, with water as solvent. Results were presented as Q_t moles %.

2.3.9.2 Soil burial test

Soil-burial test, which was efficiently used by several researchers to study the biodegradability of polymers and composites, was carried out in garden soil [8-15]. Biodegradation studies under real soil burial conditions were carried out within the campus of the University of Calicut. The soil biodegradation test lasted for 90 days. The sample weighed before and after soil biodegradation test was recorded accordingly. Dumb bell- shaped samples were cut from vulcanized rubber sheets, weighed and buried in soil for 90 days. After 90 days, the samples were withdrawn, washed with distilled water and dried at room temperature. The degradation was assessed and evaluated by measuring the weight loss, tensile strength and hardness before after soil burial. Evaluation of soil buried samples was carried out using SEM.

Weight loss experiment

The specimens for weight loss test were taken out at an interval of 30 days, washed with distilled water, air dried in an oven and then weighed.

Tensile measurements

The tensile measurements after 90 days of soil burial were carried out.

Morphology

Surface morphology of the samples after 90 days was studied to evaluate the extent of biodegradability.

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Chapter 3

Filler modification, development and characterization of coconut shell powder (CSP) filled thermoplastic polyurethane/natural rubber (TN) blend-composites

Abstract: *Modification of coconut shell powder (CSP) was carried out using different silane coupling agents and evaluated using IR, TG and SEM. CSP filled TPU/NR (TN) blend-composites were prepared by master batch technique on a two-roll mixing mill. Cure characteristics, crosslink density and rubber-filler interactions with special reference to filler loading and filler modification were determined for the composites.*

3.1 Introduction

Natural fillers are the right candidate to produce polymer composites for various applications that satisfies our primary concerns about the environment. Lignocellulosic fibres 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 nature, high specific strength and modulus, desirable fibre 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. These are mostly obtained from agricultural by-products and the use of such waste products would reduce the dependence on conventional reinforcing materials like glass fibres, aramid fibres, *etc*. The reinforcing efficiency of the natural fibre is related to the nature of cellulose and its crystallinity [4-5]. Eventhough the tensile strength of some conventional inorganic fillers such as glass fibres and carbon black with that of natural fibres are incomparable, specific modulus (modulus/specific gravity) of natural fibres are comparable with that of glass fibre. Biocompatibility, biodegradability, weight reduction and cost-effectiveness are the unique advantages of bio-based fillers over the conventional fillers. The main disadvantage of using natural lignocellulosic fibres as reinforcing filler for composite material is the poor interaction between them and polymer matrix. This incompatibility leads to poor interfacial adhesion, inadequate wetting of filler in the matrix, agglomeration of filler particles and finally in lowering material properties [6]. Surface modification of natural fibres is, therefore, critical in order to improve the compatibility [7-9]. Hydrophobicity is induced into the hydrophilic natural fibres, either *via* physical or chemical methods. Chemical modification methods include the development of hydrophobic coating on the surface of filler. Different successful methods adopted for the chemical modification are silane treatments, isocyanate treatment, graft copolymerization, alkalization, peroxide treatment, acylation and benzoylation. The improvement in interfacial properties leads to the enhanced surface properties such as wetting, adhesion, *etc.*,[10-11]. Several experiments have demonstrated the efficacy of various silane coupling agents in the modification of natural fibres [8, 12-15].

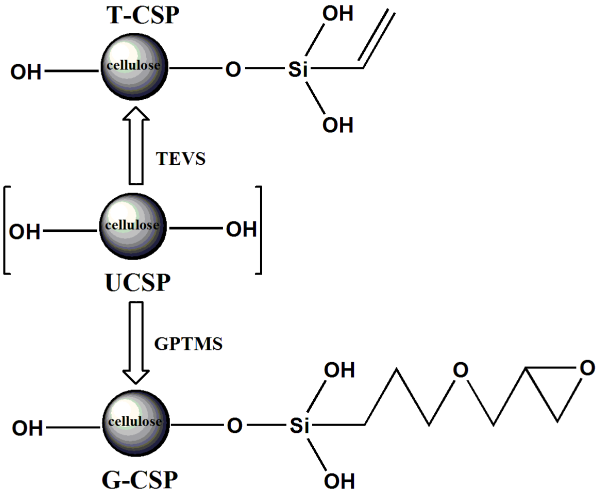
Cocos nucifera (Coconut) is considered as one of the most beneficent crop grown in India. Coconut shell is an economically cheaper agricultural co-product which can be obtained in large quantities from the local market. It often considered to be a hard wood, as the lignocellulosic present in the shells are tougher than wood [16]. Efficiency of coir as reinforcing filler has been studied extensively [17-18]. Requisite studies on CSP as the filler were appeared in literature [19-23]. In this chapter, we describe the chemical treatment applied to CSP and the study of effectiveness of silane treatment in CSP. We also intend to investigate the cure properties of the developed TN blend composites filled with different silane treated CSP. The swelling studies were carried out to observe the crosslink density, rubber-filler interaction and the reinforcing nature of the filler on the blend, which are essential in determining various properties such as mechanical strength and transport properties of the composites.

3.2 Results and discussions

3.2.1 Filler modification and characterizations

3.2.1.1 Modification of CSP with silane coupling agents

Silane treatment involves the hydrolysis, condensation and bond formation stages. Possible reaction of silane coupling agents TEVS and GPTMS with UCSP is shown in **scheme 3.1**. Hydrolysable alkoxy group present in the silanes forms silanols in the presence of moisture, which eventually chemisorbed on to the fibre surface and react with hydroxyl group of the fibre to form stable covalent bonds [24-25]. Alkali pre-treatment of natural fibres before silane modification increases the effectiveness of silane coupling agent [11]. Hydrophilic and smooth filler surface is changed to rough hydrophobic surface having chemical moieties from the coupling agent which can effectively bind the active functional groups of polymers and increase the adhesion between polymer and filler [26].



Scheme 3.1: Schematic representation of the reaction of silane coupling agents with UCSP.

3.2.1.2 Filler characterization

FT-IR

Most of the researchers confirmed the efficacy of the filler modification using silane coupling agents from IR spectral studies [24, 27]. **Figures 3.1 (a** and **b)** demonstrate the efficiency of grafting of silane coupling agents TEVS and GPTMS respectively to the UCSP. **Figure 3.1 (c)** compares T-CSP and G-CSP to UCSP.

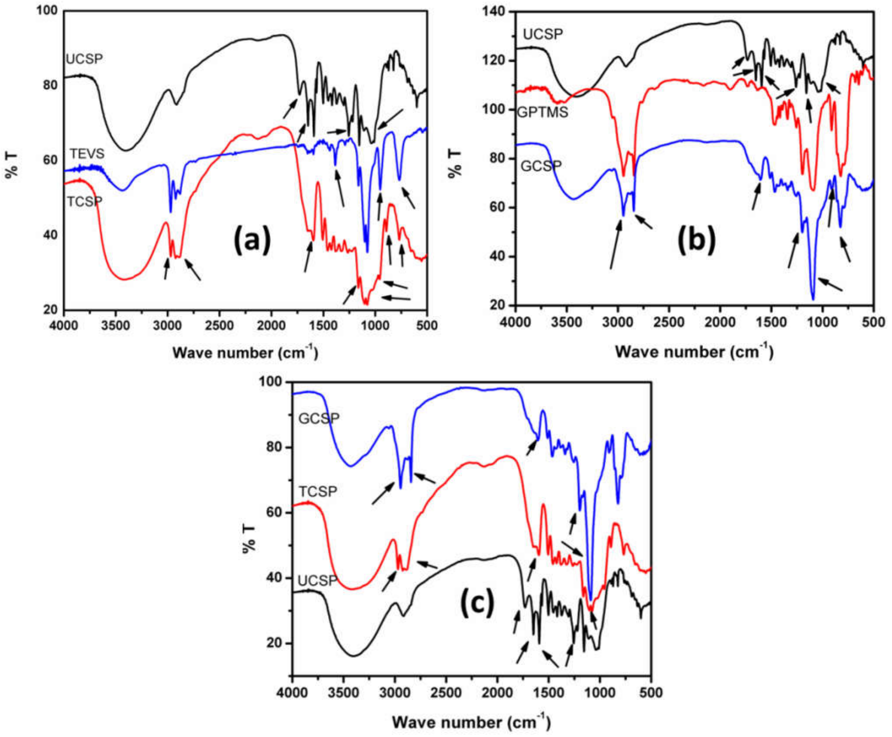


Figure 3.1: (a) IR spectra of UCSP, TEVS, and T-CSP **(b)** IR spectra of UCSP, GPTMS, and G-CSP **(c)** IR spectra of UCSP, T-CSP, and G-CSP.

In the IR spectrum of UCSP the broad band at 3421 cm^{-1} is due to the hydrogen bonded O-H stretching mainly of cellulose. It implies the hydrophilic tendency of UCSP due to the –OH rich components in it [23]. The frequency at 2919 cm^{-1} is related to the –CH asymmetric and symmetric stretching from aliphatic moieties in cellulose and hemicelluloses [28]. Stretching frequency at 1732 cm^{-1} is assigned to the carbonyl of ester groups of hemicelluloses [29]. Intense frequency at 1650 cm^{-1} in UCSP represents the C-O stretching of amide group which is present in the secondary structure of protein [28]. The 1251 cm^{-1} frequency refers to the acetyl stretching and deformation band in cellulose and lignin [30]. C-O deformation frequency in secondary alcohol appears at 1036 cm^{-1} [23]. The frequencies at 1732 cm^{-1} and 1251 cm^{-1} seen in unmodified filler disappears after treatment. This clearly indicates the removal of lignin and hemicellulose [31]. In the IR spectrum of T-CSP the frequencies at 2966 cm^{-1} and 2885 cm^{-1}, and in G-CSP the frequencies at 2941 cm^{-1} and 2843 cm^{-1} appear due to the symmetric methylene stretching from silyl part of modified CSP [32]. These frequencies are absent in the IR spectrum of UCSP. The frequencies observed in T-CSP at 1597 and 1086 cm^{-1} denote the Si-O-C vibrations [33]. These vibrations appear in G-CSP at 1603 and 1093 cm^{-1}. Si-O-Si is represented by the frequencies at 1155 cm^{-1} in T-CSP and 1196 cm^{-1} in G-CSP [27]. The epoxy group of the glycidyoxypropylsilyl part of G-CSP appears at 906 cm^{-1} [34]. Thus, the chemical grafting of silane in the fibre surface is fully established from the FT-IR spectra of the grafts. Important frequencies that appeared in the IR of UCSP, T-CSP and G-CSP are summarized in **table 3.1.**

Table 3.1: IR stretching frequencies of UCSP, T-CSP and G-CSP.

Frequency assignment	**UCSP (cm^{-1})**	**T-CSP (cm^{-1})**	**G-CSP (cm^{-1})**	**Reference**
Hydrogen bonded –OH stretching	3421	3436	3435	[23]
-CH symmetric/asymmetric stretching	2919	-	-	[28]
-CH_2 symmetric stretching	-	2966, 2885	2941, 2843	[32]
C=O stretching of ester group	1732	-	-	[29]
C=O stretching of amide group	1650	-	-	[28]
Si-O-C vibrations	-	1597, 1086	1603, 1093	[33-34]
Si-O-Si	-	1155	1196	[27]
Acetyl stretching and deformation	1251	-	-	[30]
C-O deformation bands in secondary alcohol	1036	-	-	[23]
Epoxy group	-	-	906	[34]

XRD

Crystallinity of cellulose plays a crucial role in the mechanical properties shown by the composites. **Figure 3.2** shows the XRD patterns of unmodified and modified CSPs from which the effect of modifications in the crystallinity of the cellulose present in the CSP can be evaluated. Cellulose is characterized by XRD peaks at 2θ = 15.1, 16.8, 22.8 and 34.6° corresponding to (110), (110), (200) and (004) crystallographic planes respectively [35]. In the plot of UCSP, the only peak is observed at 2θ = 22.8°. The peaks other than 22.8° are not well-defined. After chemical treatments, peaks are observed at 2θ = 15.6, 16.1, 22.8 and 34.4. Degree of crystallinity is calculated using the **equation 3.1** [36].

$$CrI = \frac{(I_{200} - I_{am})}{I_{200}} \times 100 \qquad \textbf{(Eq. 3.1)}$$

Where I_{200} is the intensity of the (200) peak at 2θ = 22.8° and I_{am} is the minimum intensity at the amorphous region of 2θ = 18°. Degree of crystallinity is found to increase from 35.5 % (UCSP) to 45.1 % for T-CSP and 49.6 % for G-CSP. The increase in crystallinity is supposed to be resulted from the efficient removal of non-crystallite materials such as amorphous hemicellulose, lignin, wax, *etc*., of UCSP [37].

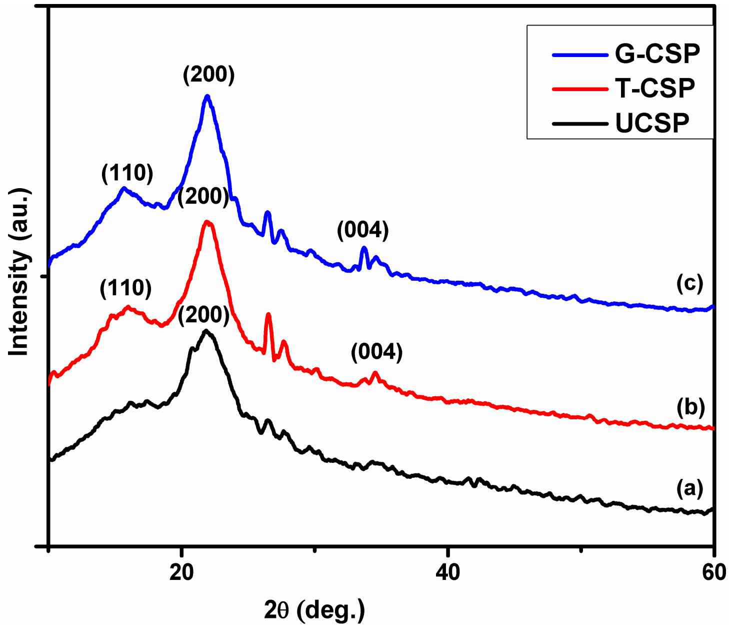


Figure 3.2: XRD of **(a)** UCSP, **(b)** T-CSP and **(c)** G-CSP.

SEM

SEM images of UCSP, T-CSP and G-CSP are shown in **figure 3.3 (a-c)**. As shown in **figure 3.3** (a), UCSP has a glabrous surface due to the presence of lignin, pectin, wax, *etc*. The white flakes within the image of UCSP may be the impurities present in the surface of UCSP. Comparing **figure 3.3** (**b**) and **(c)** with **(a)**, the surface is cleaner and higher amount of cellulose is exposed in the treated fibre. The smooth texture of untreated fibre is lost after chemical treatment, due to the structural changes occurred during treatment. The increase in roughness increases the surface area and provides additional sites for interlocking of the filler with matrix. When these are used as reinforcement, the rougher surface would be expected to promote the mechanical interlocking between fibre and matrix [38]. When compared with T-CSP, G-CSP exhibits more coarse grained and flaky structure than that of the layer like structure of T-CSP. Due to higher roughness than T-CSP, G-CSP is supposed to show higher mechanical properties than that of T-CSP.

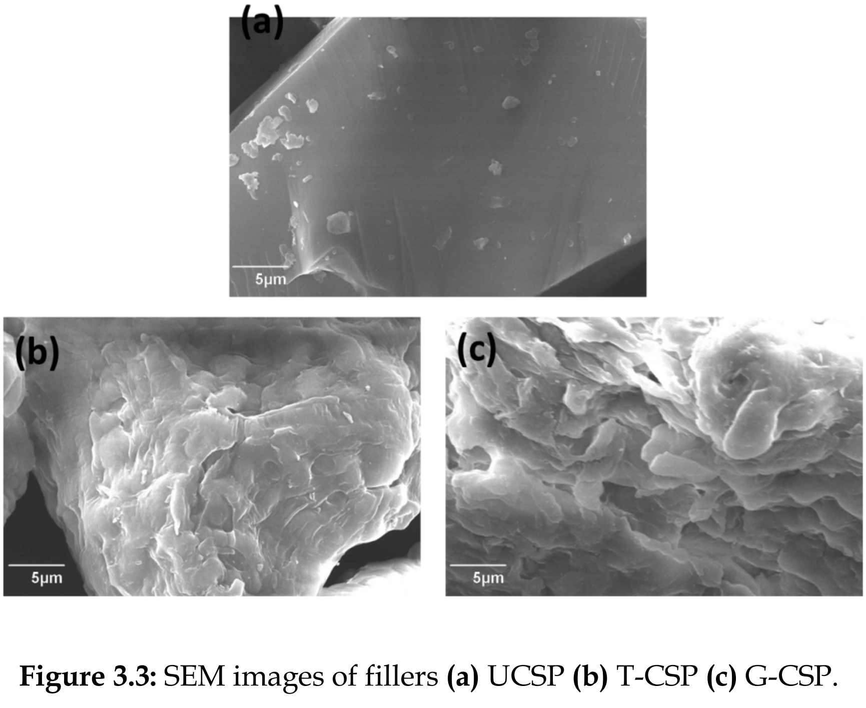


Figure 3.3: SEM images of fillers **(a)** UCSP **(b)** T-CSP **(c)** G-CSP.

TG

TG curves of untreated and treated CSP are shown in **figure 3.4**. Untreated and treated CSP show an initial weight loss at about 100 °C due to the removal of physisorbed water [39]. The decomposition of CSP takes place in three distinct stages like that of other natural fibres such as banana [40]. The initial, second and final degradation were observed at 225, 333 and 480 °C respectively for UCSP. The degradation stages occurred from 225 to 480 °C involves the degradation of hemicellulose, lignin and cellulose respectively [41-42].

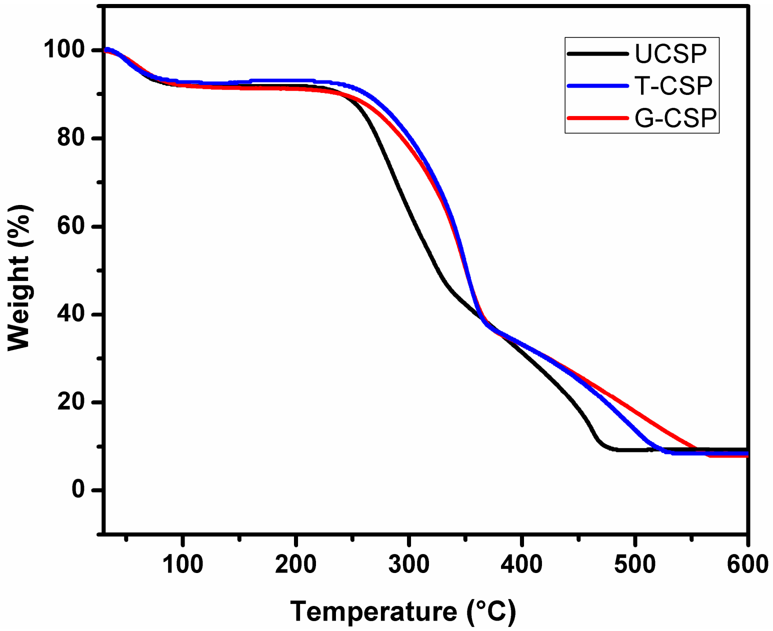


Figure 3.4: Thermogram of UCSP, T-CSP and G-CSP.

Silane treated CSP shows higher degradation temperatures compared with that of unmodified CSP because alkali pre-treatment removes most of the lignin, hemicellulose and other impurities and silane treatment provides hydrophobic coating to CSP surface. T-CSP shows decomposition temperatures at 239, 365 and 533 and G-CSP at 240, 365 and 566 °C respectively. G-CSP exhibits slightly higher maximum degradation temperature than that of T-CSP plausibly due to the higher alkyl chain length in the silyl part grafted to CSP which imparts enhanced hydrophobicity to the fibre. The thermal data obtained from the TG curves are summarized in **table 3.2**.

Table 3.2: TG data for UCSP, T-CSP and G-CSP.

Sample	**T_{onset} (°C)**	**$T_{50\%}$ (°C)**	**T_{max} (°C)**
UCSP	225	325	480
T-CSP	239	350	533
G-CSP	240	350	566

3.2.2 Cure characteristics

The cure characteristics such as maximum torque (M_H), minimum torque (M_L), cure time (t_{90}), scorch time (ts_2), and cure rate index (CRI) of TN–CSP mixes with respect to filler loading are given in the **table 3.3**. The maximum torque (M_H) values give the idea about the reinforcement and cross-link density of the mixes. The presence of CSP in the TN blend increases the rubber compound viscosity. The increment in maximum torque values with increasing filler loadings indicates that as more and more filler dispersed into the matrix, the mobility of macromolecular chains of the matrix decreased, which results in the rigidity of the vulcanizates.

Table 3.3: Cure characteristics of CSP filled TN blend-composites.

Sample code	**M_H (dNm)**	**M_L (dNm)**	**ts_2 (min)**	**t_{90} (min)**	**CRI (min^{-1})**
TN	5.15	0.03	2.13	13.62	8.70
U5	6.45	0.05	1.92	13.25	8.83
U10	7	0.05	1.87	13.15	8.87
U15	7.79	0.07	1.79	13.02	8.90
U20	8.12	0.08	1.67	12.83	8.96
T5	6.83	0.05	1.88	13.18	8.85
T10	7.26	0.06	1.83	13.03	8.93
T15	7.87	0.06	1.75	12.92	8.95
T20	8.21	0.07	1.65	12.78	8.98
G5	7.04	0.06	1.9	13.19	8.86
G10	7.61	0.08	1.81	12.98	8.95
G15	8.15	0.07	1.74	12.9	8.96
G20	8.48	0.08	1.64	12.75	9.00

Similar results for increasing M_H with respect to the addition of fillers in rubber composites were reported [43]. At a given filler loading, silane treated CSP composites show higher maximum torque than untreated CSP composites as shown in **figure 3.5.** This is because of the better rubber-filler interactions achieved by the modification of CSP with silane coupling agents.

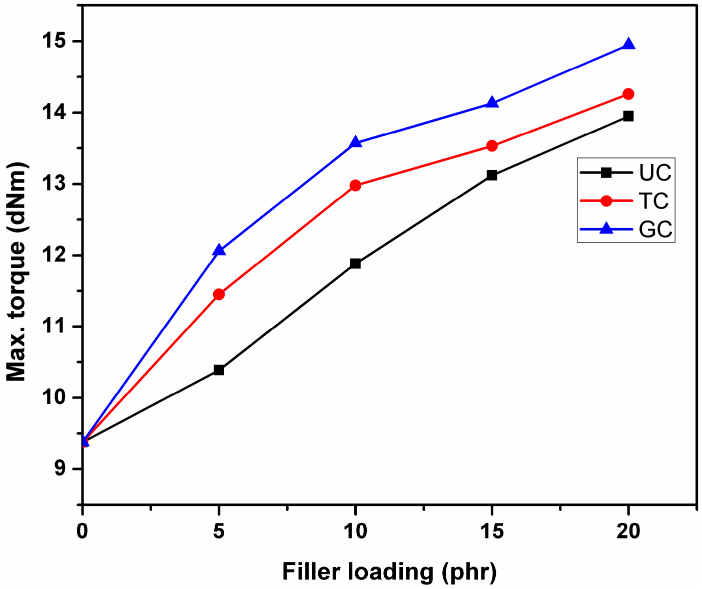


Figure 3.5: Variation in maximum torque of CSP filled TN blend-composites with filler loading.

(UC - UCSP filled TN blend-composites; TC - TCSP filled TN blend-composites; GC - G-CSP filled TN blend-composites)

Minimum torque (M_L) value represents the measure of filler content and the viscosity of the system. Thus, it signifies the extent of filler-filler aggregations [44]. The M_L values for the composites increase with the increase in CSP concentration. At low loading, chances of forming filler-filler aggregates are less compared to the higher loading of filler. Optimum cure time (t_{90}) is the time required to achieve 90 % cross-linking. As CSP loading increases, the optimum curing time exhibits a slight decrease, which confirms the heat generation due to increase in incorporation time of filler and friction which is also supported by the cure rate values as in **figures 3.6 (a** and

b). CRI values imply that CSP fillers accelerate the curing process. As the filler loading increases, the incorporation time of filler into rubber matrix also increases and consequently generates more heat due to additional friction [45]. At a given filler loading, UCSP composites show higher cure time values than that of modified CSP composites.

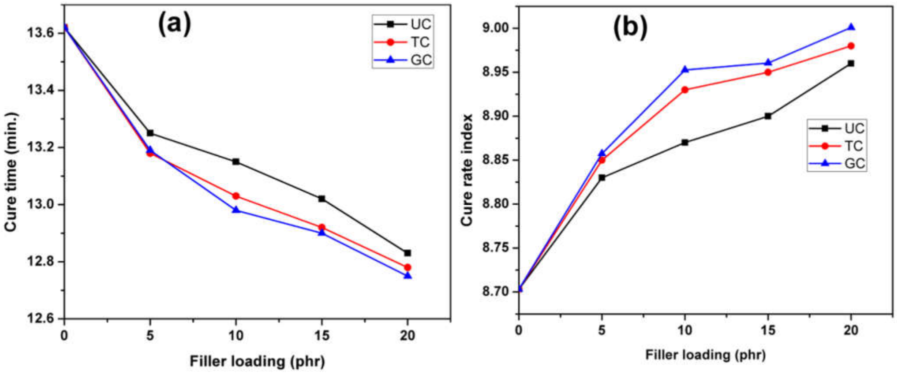


Figure 3.6: Cure characteristics of CSP filled TN blend-composites **(a)** Optimum cure time *vs*. Filler loading **(b)** Cure rate index *vs*. Filler loading.

The good number of hydroxyl groups in UCSP may be able to interfere with the vulcanization process and results in increase in cure time and scorch time [46]. Scorch time decreases with increase in filler loading from 0 to 20 phr, which indicates that increase in CSP accelerates the cure reaction of the composites and further increase in CSP would constitute a potential threat to the scorch safety of rubber composites. Studies carried out by Mathew *et al.*, show a similar trend in scorch time [28].

Table 3.4: Swelling ratio (R %), molar mass between crosslinks (M_c) and crosslink density (v) of CSP filled TN blend-composites.

Sample	**Filler loading (phr)**	**Swelling ratio (R%)**	**M_c (kg/mol)**	**v (mol/kg)**
TN	0	297	4.27	0.1171
U5	5	267	3.99	0.1255
U10	10	199	2.60	0.1923
U15	15	189	2.48	0.2018
U20	20	171	2.23	0.2246
T5	5	251	3.50	0.1430
T10	10	189	2.37	0.2108
T15	15	181	2.30	0.2178
T20	20	167	2.12	0.2361
G5	5	227	3.02	0.1657
G10	10	183	2.27	0.2199
G15	15	170	2.09	0.2389
G20	20	153	1.86	0.2689

Here, it can be seen that, swelling ratio and M_C values decrease and crosslink density increases regularly with increase in filler loading. M_c values are the lowest for samples with 20 phr CSP. This suggests that, these samples contain highest number of crosslinks, and hence the mass occupied by the sorbed solvent is less. Moreover, amount of filler is also responsible for the lowest swelling ratio for 20 phr loaded samples, which decreases the free volume available for solvent occupancy. **Figure 3.6** shows that at a particular loading, silane treated CSP filled samples show lowest swelling ratio and highest crosslink density. This evidently shows better rubber-filler found to be decreasing with increase in filler loading. This implies the filler-matrix interactions. At a particular loading, V_T value is lower for silane treated composites, due to the strong filler-matrix interaction and strengthened interface. As the filler loading and filler-matrix interaction increase, solvent absorptions are getting decreased and hence, volume fraction of rubber in swollen samples (V_r) is found to be higher. This is due to decreased solvent absorption happened as a result of hindrance exerted by the filler loading and interface. Therefore, lower V_T refers to the material with good solvent resisting property, which can be of filler-matrix adhesion or filler loading.

Table 3.5: Values of V_0, V_r and V_T values of CSP filled TN blend-composites.

Sample	**Volume fraction of rubber in dry sample (V_0)**	**Volume fraction of rubber in swollen sample (V_r)**	**V_T**
TN	1.00	0.35	0.64
U5	0.97	0.36	0.63
U10	0.94	0.40	0.58
U15	0.91	0.41	0.55
U20	0.89	0.43	0.60
T5	0.97	0.36	0.63
T10	0.94	0.40	0.57
T15	0.91	0.42	0.54
T20	0.89	0.43	0.51
G5	0.97	0.39	0.60
G10	0.94	0.43	0.53
G15	0.91	0.44	0.51
G20	0.89	0.44	0.50

3.2.4.2 Extent of reinforcement

Lorentz park **equation (3.6)** has been used to determine the extent of reinforcement

$$\frac{Q_f}{Q_g} = ae^{-z} + b \qquad \textbf{(Eq. 3.6)}$$

Where Q_f and Q_g are the amount of solvent sorbed by filled sample and the gum sample, z is the weight of filler per unit weight of the matrix and a and b are the constants. The ratio Q_f/Q_g reflects the restriction to swelling. Higher the ratio, lower will be the extent of interaction between filler and matrix. Q_f/Q_g values of CSP composites are given in **table 3.6**.

Table 3.6: Q_f/Q_g values of CSP filled TN blend-composites.

Amount of filler (phr)	**Q_f/Q_g**		
	UCSP composites	**T-CSP composites**	**G-CSP composites**
5	0.8988	0.8426	0.7646
10	0.6677	0.6337	0.6168
15	0.6349	0.6075	0.5713
20	0.5747	0.5627	0.5136

Value of the ratio decreases with increase in filler loading, which in turn leads to higher extent of reinforcement. From **figure 3.7**, it is clear that, at a particular loading, Q_f/Q_g is lower for silane treated composites. This implies the higher matrix-filler interactions

interactions achieved by the modification of CSP with silane coupling agents and confirms the cure characteristics results.

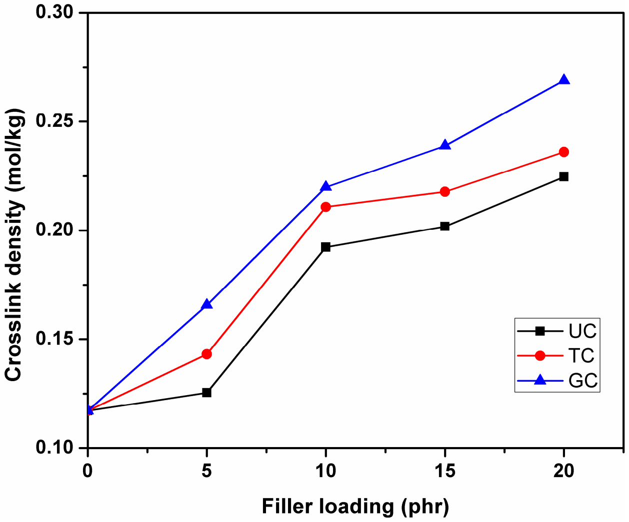


Figure 3.7: Variation in crosslink density of CSP filled TN blend-composites with filler loading.

3.2.4 Rubber-filler interactions

3.2.4.1 Correlation with adhesion

One method of studying the extent of filler adhesion to the matrix is the comparison of volume fraction of dry sample (V_0) to that of swollen sample (V_r) using the **equation 3.5**

$$V_T = \frac{(V_0 - V_r)}{V_0} \qquad \textbf{(Eq. 3.5)}$$

Where V_T is the ratio of change in volume fraction of polymer before and after swelling to the volume fraction of sample before swelling. **Table 3.5** shows the values of V_0, V_r and V_T for the composites in toluene. V_T value is the highest for blend sample and

3.2.4.2 Extent of reinforcement

Lorentz park **equation (3.6)** has been used to determine the extent of reinforcement

$$\frac{Q_f}{Q_g} = ae^{-z} + b \qquad \textbf{(Eq. 3.6)}$$

Where Q_f and Q_g are the amount of solvent sorbed by filled sample and the gum sample, z is the weight of filler per unit weight of the matrix and a and b are the constants. The ratio Q_f/Q_g reflects the restriction to swelling. Higher the ratio, lower will be the extent of interaction between filler and matrix. Q_f/Q_g values of CSP composites are given in **table 3.6**.

Table 3.6: Q_f/Q_g values of CSP filled TN blend-composites.

Amount of filler (phr)	**Q_f/Q_g**		
	UCSP composites	**T-CSP composites**	**G-CSP composites**
5	0.8988	0.8426	0.7646
10	0.6677	0.6337	0.6168
15	0.6349	0.6075	0.5713
20	0.5747	0.5627	0.5136

Value of the ratio decreases with increase in filler loading, which in turn leads to higher extent of reinforcement. From **figure 3.7**, it is clear that, at a particular loading, Q_f/Q_g is lower for silane treated composites. This implies the higher matrix-filler interactions between silane treated CSP and TN matrix. Composites having minimum Q_f/Q_g are associated with maximum cross link density.

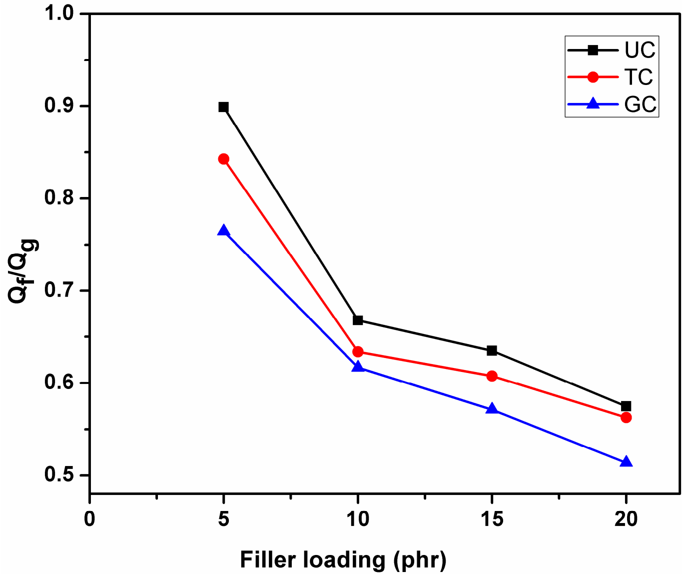


Figure 3.8: The effect of filler loading on rubber-filler interaction (Q_f/Q_g) of CSP filled TN blend-composites.

3.3 Conclusions

Pre-treated coconut shell powder was chemically modified using silane coupling agents TEVS and GPTMS and evaluated using FT-IR, TG and SEM. Results showed that, silyl moiety from the coupling agents were efficiently grafted to CSP and provided sufficient hydrophobicity to the filler. The treated CSP also possessed better filler geometry and thermal stability than unmodified CSP. TN blend-composites using unmodified and different silane treated composites were prepared and examined for the cure properties, crosslink density and rubber-filler interactions. Addition of CSP improved the cure properties such as maximum torque, cure rate, cure time and scorch time, solvent resistance and crosslink density. Sorption of toluene was found to decrease with increase in filler loading and filler treatment. Extent of filler adhesion was evaluated in terms of V_T values. It found to decrease with increase in filler loading, indicated good filler-matrix interactions which led to lower sorption of solvents. Extent of reinforcement was also evaluated from Lorentz-park equation. Silane treatment improved the overall performance of the composites. Comparing the efficiency of different silane treated CSP composites, GPTMS treated CSP filled TN blend-composites showed better cure properties and crosslink properties than TEVS treated CSP filled TN blend-composites.

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Chapter 4

Mechanical properties and thermal analysis of coconut shell powder (CSP) filled thermoplastic polyurethane/natural rubber (TN) blend-composites

Abstract: *The effect of silane treatment and filler loading on the mechanical and thermal properties of coconut shell powder (CSP) filled TPU/NR (TN) blend-composites were studied in this chapter. Density, hardness, tensile strength, elongation at break and abrasion resistance were determined. Results showed that CSP was most effective in TN blend-composite at 10 parts per hundred loading. Silane treated CSPs were efficient than that of unmodified CSP in improving the mechanical properties. Thermal analyses depicted that addition of CSP improved the thermal stability and glass transition temperature of the TN blend.*

4.1 Introduction

Composites possess the properties of an ideal engineering material, such as high strength to weight ratio, stiffness, toughness and lightweight in which other conventional engineering materials like metals and wood do not have. Therefore, composites are considered to be the best candidate as engineering materials, leading to their rapid development and successful use in many applications over the last few decades. Nowadays it plays the pivotal role in automobile industry, aerospace, household furniture industry, and in other engineering applications. The ability to predict the behaviour and limitations of polymers in response to the mechanical stress is important for determining their performance in a variety of applications. Therefore, a thorough knowledge of their mechanical behaviour is inevitable for the application of a polymer material in industries. Reinforcement is primarily the enhancement of strength and related properties, like abrasion resistance, hardness and modulus. Mechanical properties of blend-composites depend markedly on the ability to transfer stress to the matrix through the interface, concentration, shape, size and orientation of the filler and the interfacial adhesion between filler and matrix. In addition to this, nature of polymer matrix, crosslink density, nature of vulcanizing system, miscibility of the components also influences the mechanical properties.

Thermal stability of polymers is another relevant characteristic of materials, especially when potential end use is considered. It is the ability to maintain the required properties at elevated temperatures [1]. It is important to identify the type of information required in order to choose the suitable test methods. Thermo gravimetry (TG) is widely used by most researchers to study the thermal degradation of natural fibre composites. Early decomposition or the start of degradation observed in lower temperature implies less thermal stability and this can be used to compare thermal performance of various composites [2]. Differential scanning calorimetry (DSC) helps to obtain quantitative information about the melting and phase transitions, the heterogeneous nature of polymeric composites and the glass transition temperature (T_g) of the system, which are the relevant information for the designing and processing of the materials with desired properties.

The search for sustainable, non-petroleum based, energy saving, economical and environmental friendly fillers led to various bio-based fillers such as starch, chitin, and natural fibres of plant origin and of animal origin and agricultural wastes and biomass derived from various industries. Coir fibre, sisal, jute, oil-palm, rice husk, kapok fibre, bagassi fibre, chitin and chitosan, protein fibres, *etc.*, are proven to be very efficient in composites [3-9]. Several studies have reported the improvements in tensile strength, Young’s modulus, failure strain, impact strength, fracture toughness and flexural properties of composites as well as thermal stability and long term moisture resistance, the latter of which could be due to the reduced moisture uptake observed with alkali treated natural fibres [10-14]. It has been shown to improve tensile and flexural strength and stiffness as well as impact strength of polypropylene (PP) matrix composites [15-17]. Further, improvement of mechanical performance with MAPP has been explained as being due to its ability to wet fibre and enhance its dispersion [18]. Silane treated fibre composites provide better tensile strength properties than the alkali treated fibre composites [19-21] . The mechanical properties of composites were found to improve with the addition of silane coupling agent. It can be observed that tensile strength of bamboo fibre filled natural rubber composites increased from 7 to 12 MPa due to silane modification [22]. The influence of a number of chemical modifications on oil palm fibre was investigated. The silane-treated fibre exhibited the highest tensile strength among all the treated fibres [23]. Iorga *et al.,* applied different treatments to hemp fibres (HF) and reported the efficiency of treated HF as reinforcement in PP. An increase of 78 % of tensile strength and 61 % of Young's modulus was obtained compared with untreated hemp fibres. Further improvement of tensile strength and modulus, of over 100 %, was obtained for PP composites with treated HF [24]. Several silane treatments were directly applied on HF and their influence on the surface properties and thermal stability of HF was investigated by Panaitescu *et al.* Thermo gravimetry (TG) highlighted the favourable effect of silane treatments on the thermal stability of HF. The HF treatments influenced the mechanical properties of PP/HF composites, as 67 % increase is observed in the tensile modulus of composites of PP with 40 wt % HF– MPS. Nano-indentation results show good modulus and hardness for the composites with silane modified HF [25]. Thermal decomposition processes of different lignocellulosic fibres have very similar TG and DTG curves due to their similar characteristics. Approximately 60 % of the thermal decomposition of most natural fibres occurred within a temperature range between 215 and 310 °C [26]. Ma *et al.,* observed that the T_g and thermal degradation temperature of zinc oxide/polystyrene nanocomposites increased with ZnO content [27].

The enhancement in T_g and improvement in the thermal stability of NBR/Na-MMT nanocomposites were reported by Kader *et al*., [28].

Use of agricultural waste materials as replacement for commercial fillers is of great interest nowadays. The production of coconut generates huge amounts of waste namely coconut shell. Coconut shell is non food part of coconut which is hard lignocellulosic agro waste. The first reported use of coconut shell powder (CSP) as filler was done by Aminabhavi *et al,*. in 1983. They found that CSP and other aggrowaste fibre materials successfully bound with phenol-formaldehyde resin and were efficient to replace the heavy use of asbestos as filler [29]. From that onwards, many researchers investigated the feasibility of utilizing grain by-products such coconut shell as alternative fillers in polymer composites materials such as PVC [30], epoxy [31-34], PE [35-36], PVA [37], PP [38], PLA [39], Polyester [40], NR [14, 41], SBR [42], *etc*. Every result clearly pointed out that, coconut shell waste could be used as alternative biodegradable eco-friendly reinforcement. Hitherto no systematic investigations have been carried out on the mechanical and thermal properties of TN blend-composites using CSP and modified CSP as fillers. Thus, the present chapter deals with the study of different physical properties like density and hardness and different mechanical properties tensile strength, elongation at break, modulus and abrasion resistance of CSP filled TN blend-composites. The miscibility of the blend, the effect of addition of fillers and the effect of filler modification on T_g of the composites were studied using DSC and thermal stability, effect of fillers and effect of filler modification on the thermal degradation were studied using TG.

4.2 Results and discussions

4.2.1 Density and hardness

Density and hardness values of CSP filled TN blend-composites obtained are given in **table 4.1.** It was found that density increases with increase in unmodified and modified CSP loading. This is because of the filling of voids within the matrix with dense and rigid CSP particles. In the case of composites filled with treated CSP, density is found to be lower than that of unmodified composites. During the pre-treatment of CSP with NaOH, most of the lignin, hemicellulose and wax from the fibre is washed off and plausibly led to a decrease in density of the filler and hence, this can be attributed to the decrease in density of the treated CSP composites.

Table 4.1: Density and hardness of CSP filled TN blend-composites.

Sample code	Density (g/cm^3)	Hardness
TN	0.94	46 ± 1.8
U5	0.978	48 ± 1.6
U10	0.996	52 ± 1.5
U15	1.008	53 ± 1.9
U20	1.027	55 ± 2.4
T5	0.968	50 ± 1.6
T10	0.992	55 ± 1.9
T15	1.005	56 ± 1.7
T20	1.02	59 ± 1.8
G5	0.971	51 ± 1.4
G10	0.992	57 ± 2.0
G15	1.006	58 ± 1.6
G20	1.024	60 ± 2.0

Hardness increases consistently with increase in filler loading. Variation of hardness of CSP filled TN blend-composites with increase in filler loading are shown in **figure 4.1.** All fillers used are non-deformable solids and addition of more rigid particles leads to increased rigidity and stiffness of the material. Maximum torque values also support these findings. Similar observations were reported by a number of researchers [10, 14, 43].

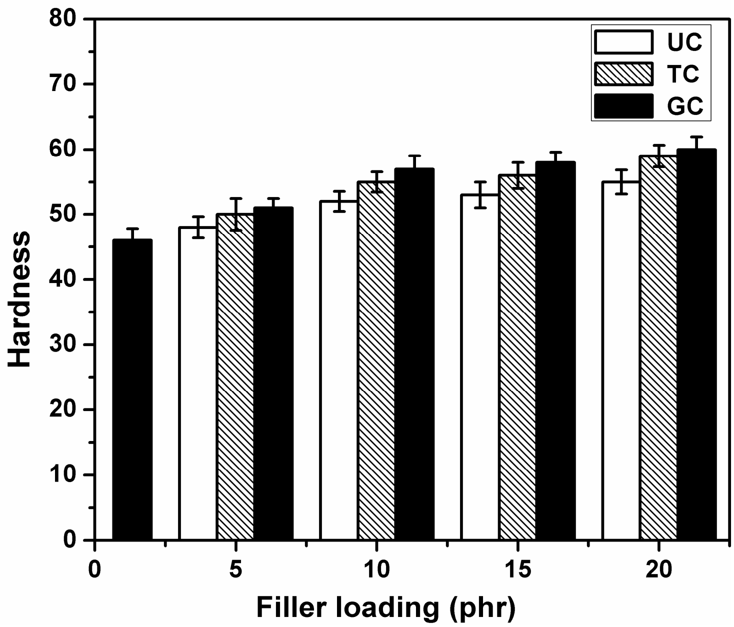

Figure 4.1: Variation in hardness of CSP filled TN blend-composites with filler loading.

(UC - UCSP filled TN blend-composites; TC - TCSP filled TN blend-composites; GC - G-CSP filled TN blend-composites)

4.2.2 Mechanical properties

4.2.2.1 Tensile properties

Stress-strain curves of CSP filled TN blend-composites filled with different filler loadings are plotted in **figure 4.2 (a-c).** All stress-strain curves are of similar in nature which demonstrates somewhat linear behaviour and sharp fracture. The load is increased with increase in filler loading up to 10 phr. Above that, the load is decreased, *i.e.*, the maximum tensile strength is shown by the 10 phr CSP loaded samples.

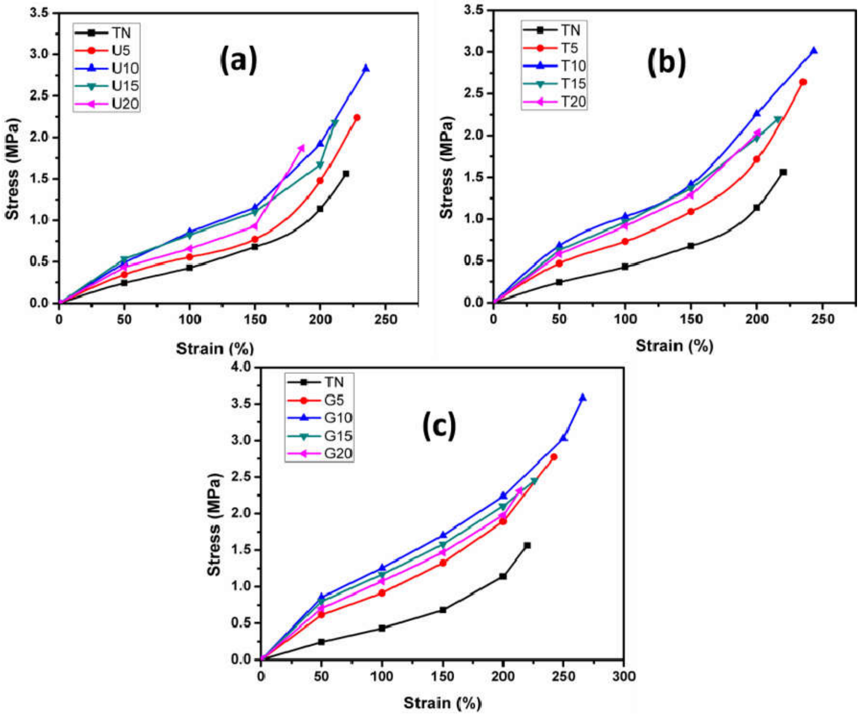

Figure 4.2 (**a**) Stress-strain curve of UCSP filled TN blend-composites; (**b**) Stress-strain curve of T-CSP filled TN blend-composites; (**c**) Stress-strain curve of G-CSP filled TN blend-composites.

The effect of unmodified and modified CSP on the tensile properties of TN blend-composites at room temperature was studied and summarized in **table 4.2.** Results reveal that addition of fillers enhances the degree of reinforcement of the vulcanizates. As shown in **figure 4.3**, the addition of CSP increases the tensile strength up to 10 phr loading and above 10 phr addition, there is deterioration in properties. At 10 phr, CSP shows more uniform dispersion which leads to a large interfacial area and hence better interfacial adhesion between filler and matrix. TN composite with 10 phr UCSP shows 81 % enhancement in tensile strength compared to the gum sample. Most of the researchers, with different fillers, reported the optimum filler concentration as 10 phr [14, 44].

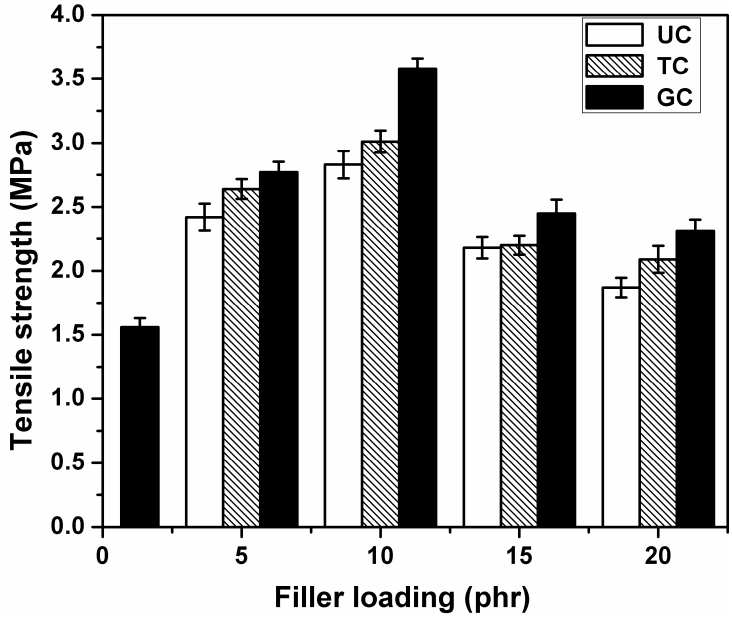

Figure 4.3: Variation in tensile strength of CSP filled TN blend-composites with filler loading.

As the filler concentration increases, agglomeration and hence increased filler-filler interaction occurs which in turn results in weak interaction and bonding between filler and matrix. At a particular filler loading, silane treated CSP composites show better tensile strength than UCSP composites. Both types of silane modifications improve the fibre-matrix compatibility and show enhanced mechanical properties. Researchers suggested that silane coupling agents with bi-functional groups could produce the chemical bonding between filler and matrix and could facilitate the reinforcing effect of filler in matrix [45-46]. G-CSP composites yield higher tensile strength compared to T-CSP composites. This can be explained as, i) the organofunctional group existed in G-CSP promotes the copolymerization with the matrix and has the ability to produce better matrix-filler bonding than that of T-CSP [47] and ii) G-CSP possess longer hydrocarbon in the grafted silyl part than in T-CSP, which generates larger surface spacing to accommodate more matrix molecules to intercalate, so that better dispersion and more homogeneity can be achieved [48]. Both the tensile strength and tensile modulus are important parameters to be determined to designate a composite's structural applications. Variation in tensile modulus M_{100} (stress at 100 % elongation) and M_{200} (stress at 200 % elongation), which is a measure of material stiffness is shown in the **table 4.2**. M_{100} and M_{200} increases slightly with increase in filler loading up to optimum loading. Silane treatment improves the modulus values of the composites, as explained in the case of tensile strength. The most important contribution to the modulus arises from polymer–filler interactions; that can increase when a good dispersion of the filler is achieved with polymer. Hence at same filler loadings, composites with silane treatment exhibit higher modulus than UCSP composites.

Table 4.2: Tensile properties of UCSP, T-CSP and G-CSP filled TN blend-composites.

Sample code	Tensile strength (MPa)	Elongation at break (%)	Modulus at 100% (MPa)	Modulus at 200 % (MPa)
TN	1.56 ± 0.07	221 ± 10	0.43 ± 0.04	1.14 ± 0.06
U5	2.42 ± 0.10	228 ± 15	0.56 ± 0.05	1.48 ± 0.09
U10	2.83 ± 0.10	235 ± 12	0.86 ± 0.04	1.92 ± 0.08
U15	2.18 ± 0.08	210 ± 9	0.82 ± 0.03	1.67 ± 0.08
U20	1.87 ± 0.07	185 ± 9	0.65 ± 0.05	-
T5	2.64 ± 0.08	234 ± 11	0.73 ± 0.06	1.71 ± 0.07
T10	3.01 ± 0.09	242 ± 13	1.03 ± 0.05	2.26 ± 0.09
T15	2.2 ± 0.07	216 ± 11	0.97 ± 0.07	1.97 ± 0.10
T20	2.09 ± 0.11	200 ± 15	0.92 ± 0.03	2.03 ± 0.08
G5	2.77 ± 0.08	241 ± 9	0.91 ± 0.05	1.89 ± 0.09
G10	3.58 ± 0.08	266 ± 11	1.26 ± 0.04	2.23 ± 0.09
G15	2.45 ± 0.11	225 ± 12	1.17 ± 0.05	2.1 ± 0.10
G20	2.31 ± 0.09	213 ± 9	1.07 ± 0.05	1.97 ± 0.06

As expected elongation at break (EB) values reduce with increase in filler loading after optimum loading of CSP, because of the restricted molecular motions of the polymers. At optimum loading, filler is uniformly dispersed and surrounded well by the matrix in which polymer-filler interaction dominates. As the filler concentration increases further, agglomeration occurs and filler-filler interactions increases which offer the lower resistance to break upon stress. It can be seen in the **figure 4.4** that, silane treated composites again shows higher EB values, due to the increased mechanical and chemical interlocking between filler and matrix which assists effective stress-transfer.

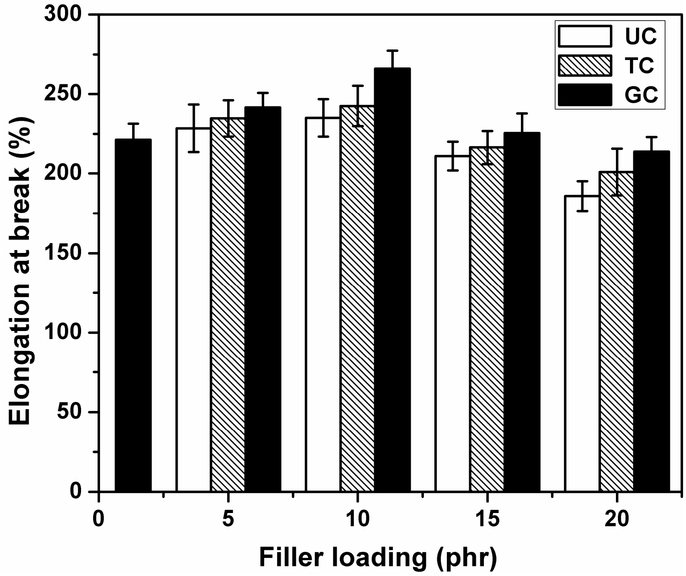

Figure 4.4: Variation in EB of CSP filled TN blend-composites with filler loading.

4.2.2.2 Tear strength

Enhanced filler efficiency is further supported by the improvement in tear strength. Tear strength values of CSP filled TN blend-composites are summarized in **table 4.3**. Filler loading up to 10 phr causes increased value for the tear strength and further loading leads to deterioration in tear property, as shown in **figure 4.5**. The improvement in tear strength is achieved by the effective orientation of molecular chains of the matrix in the direction of strain upon loading.

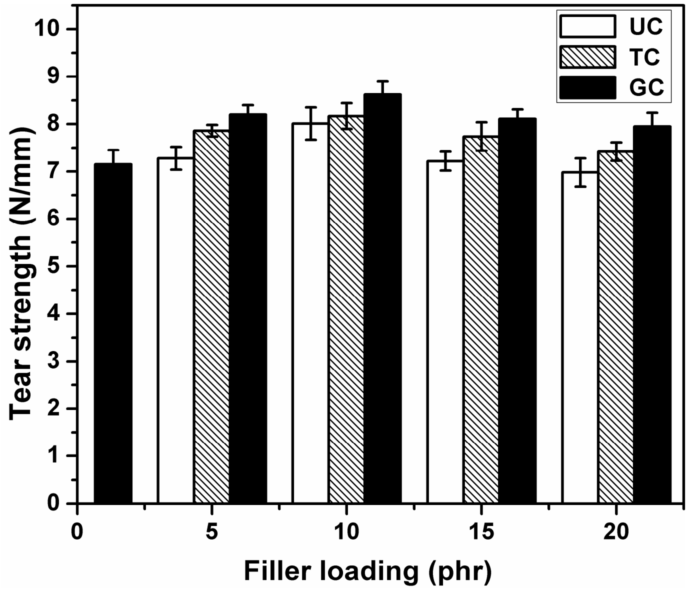

Figure 4.5: Variation in tear strength of CSP filled TN blend-composites with filler loading.

Better interfacial interaction between CSP and matrix improves the ability of polymer to orient around the CSP. Specific surface area and reinforcing ability of the filler control the tear strength of the composites. Modification increases the surface area of CSP. As already discussed in **chapter 3**, the contact surface between matrix and filler is increased, which assists the better stress-transfer and finally results in better tear strength [49]. Above 10 phr loading, agglomeration and filler-filler networks limit the mobility of the polymer chains to slip around the filler and resist the orientation upon strain. Since the filler-filler interactions predominate over polymer-filler interactions, the even distribution of stress throughout the matrix is disrupted and results in the lowering of tear strength at higher loading. Tear strength increases significantly with the efficiency of silane coupling agents.

4.2.2.3 Abrasion resistance

Abrasion resistance values indicate the wear properties of a material. The abrasion is referred to as nominal abrasive power of the test emery paper of 200 mg/40m abrasion distance and calculated as a loss of volume from the following **equation 4.1**

$$\Delta V = \frac{Vm \times So}{D \times S} \qquad \textbf{(Eq: 4.1)}$$

wherein, ΔV = abrasion (volume loss in mm^3), V_m = mass loss in mg, D = density in mg/mm^3 , So = value of nominal abrasive power (200 mg), S = average abrasive power in mg. The results obtained for CSP filled TN blend-composites are given in **table 4.3** as the relative volume loss value.

Table 4.3: Tear strength and abrasion resistance of CSP filled TN blend-composites.

Sample code	**Tear strength (N/mm)**	**Relative vol.loss (mm^3)**
TN	7.15 ± 0.30	0.46 ± 0.01
U5	7.28 ± 0.24	0.42 ± 0.02
U10	8.01 ± 0.34	0.38 ± 0.01
U15	7.22 ± 0.20	0.33 ± 0.01
U20	6.98 ± 0.30	0.27 ± 0.01
T5	7.86 ± 0.12	0.39 ± 0.02
T10	8.17 ± 0.27	0.35 ± 0.02
T15	7.74 ± 0.30	0.31 ± 0.01
T20	7.42 ± 0.19	0.25 ± 0.01
G5	8.2 ± 0.20	0.37 ± 0.02
G10	8.62 ± 0.27	0.31 ± 0.01
G15	8.11 ± 0.20	0.28 ± 0.01
G20	7.95 ± 0.29	0.23 ± 0.01

From the **figure 4.6**, it can be noticed that, eventhough the values are not significantly different; the relative volume loss of CSP filled TN blend-composites decreases with increase in filler loading. This suggests that the abrasion resistance increases with increase in filler loading. This is possibly because of the incorporation of fillers increases the crystalline regions in the composites. Since the filler modifications increase the crystallinity of the filler particles, they are evidently reflected in the abrasion resistance values and hence a decrease on relative volume loss values for TN blend-composites with G-CSP and T-CSP occurred compared to that of UCSP.

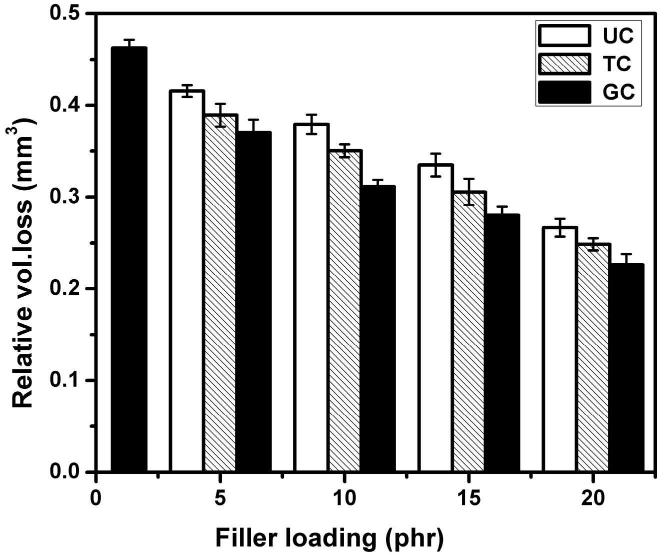

Figure 4.6: Variation in relative volume loss of CSP filled TN blend-composites with filler loading.

4.2.3 SEM

SEM observations provide necessary information regarding the interfacial adhesion between filler and matrix. **Figures 4.7** and **4.8** depict SEM images of the typical tensile fractured surface of TN blend and its composites of unmodified and modified fillers. Two phase morphology is observed in **figure 4.7(a).** The domains of TPU are separated from the continuous phase NR. TN blend is an immiscible polymer blend [50]. The polarity difference between polar TPU and non-polar NR leads to greater interfacial tension which results in the micro voids in the fractured surface. These voids affect the performance of the system as evident from the mechanical data. According to Manoj *et al.*, polymer systems with fillers usually exhibit reduced domain size and a more uniform morphology which leads to lower interfacial tension [51]. Surface tension of the blend is decreased by the introduction of fillers and resulted in improved miscibility of the system. Polymer chains are immobilized on the surface of fillers, and form the constrained regions. This acts as a compatibilizer between fibre and matrix, and improves the interaction of interface between TPU and NR [52-53].

Figures 4.7 (b-d) exhibits the SEM images of CSP filled TN blend-composites. It shows that the fillers could improve the blend compatibility to a certain extent by accelerating the fusion of TPU with NR matrix. The tensile fractured surfaces of CSP reinforced composites generally show the fibre pull-outs, fibre de-bondings, fibre breakage and matrix ruptures after the fracture test. In the image of

U10 composite (**figure 4.7b**), the fracture accompanies pull-out of fibres leaving holes. It indicates the poor adhesion between filler and matrix resulting from the hydrophilic nature of filler. In addition to that, the mechanical interlocking between the filler and matrix is very poor, because the surface of unmodified CSP is very smooth. This results in fast fibre de-bonding and pull-out during the fracture test. The unmodified CSP containing composites as in the **figure 4.7(b)** and **figure 4.8(a)** display a rough morphology with irregular fracture surfaces with cracks and pores. Therefore, the stress applied to the composite is not efficiently transferred from the matrix to the fibre.

Silane modification has changed the nature of filler, as seen in **chapter 3: figure 3.3**. It made the natural filler more compatible with polymer matrix by reducing the –OH group concentration in the hydrophilic filler. It is observed that the gaps and crack lines are thinner and much reduced in T-CSP composites than that of UCSP composites. Roughness in the surface is much lowered and TPU and NR are almost indistinguishable. The fibres are broken off near the surface and do not leave any voids in the surface. This observation gives ample evidence for the improved interfacial adhesion between the phases. The treatment with TEVS changed the morphology of the surface, produced a more homogeneous surface. Better mechanical properties of these composites also can be explained by the improvement in the homogeneity of the composites. G-CSP composites show even better morphology as seen in **figure 4.7 (d)** and **figure 4.8 (c).** The treated fibres, previously having a rougher surface, seemed to have a smoother surface in the composites because they are coated by the layers of matrix material, that reduces the gaps between the fibre and matrix significantly. The treatment with GPTMS further reduces the cracks and the surface appeared to be more homogeneous. The gap between fibre particle and matrix is almost nil in the **figure 4.7 (d).** The improvement in interface substantiates the enhanced mechanical performance of the treated composites. From the **figure 4.8(a-c),** it is clear that, the 20 phr loaded samples possess a rather rougher morphology than their 10 phr loaded counterparts because the uniformity of dispersion is lowered due to the increased filler-filler interactions.

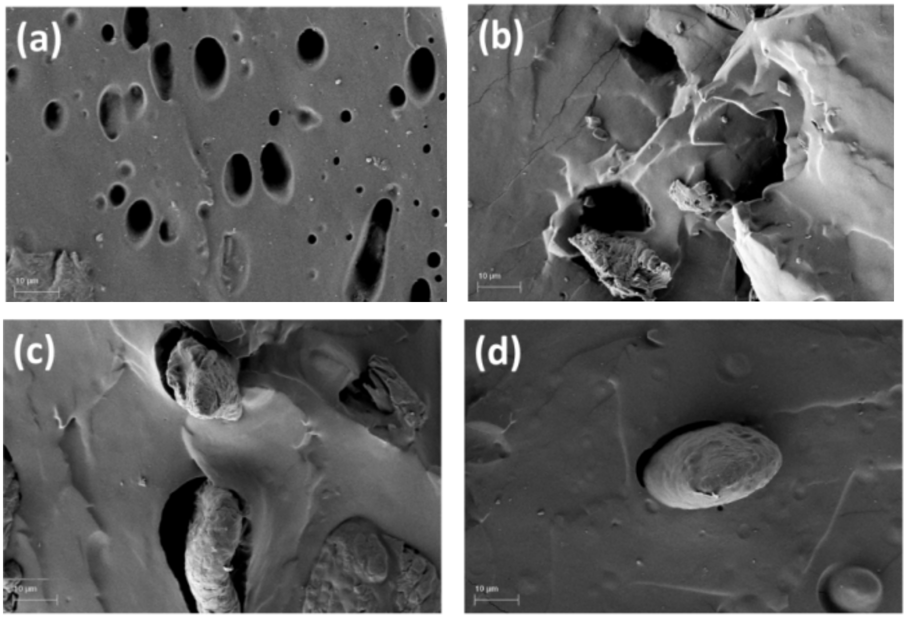

Figure 4.7: SEM images of composites of 10 phr loading (**a**) TN (**b**) U10 (**c**) T10 (**d**) G10.

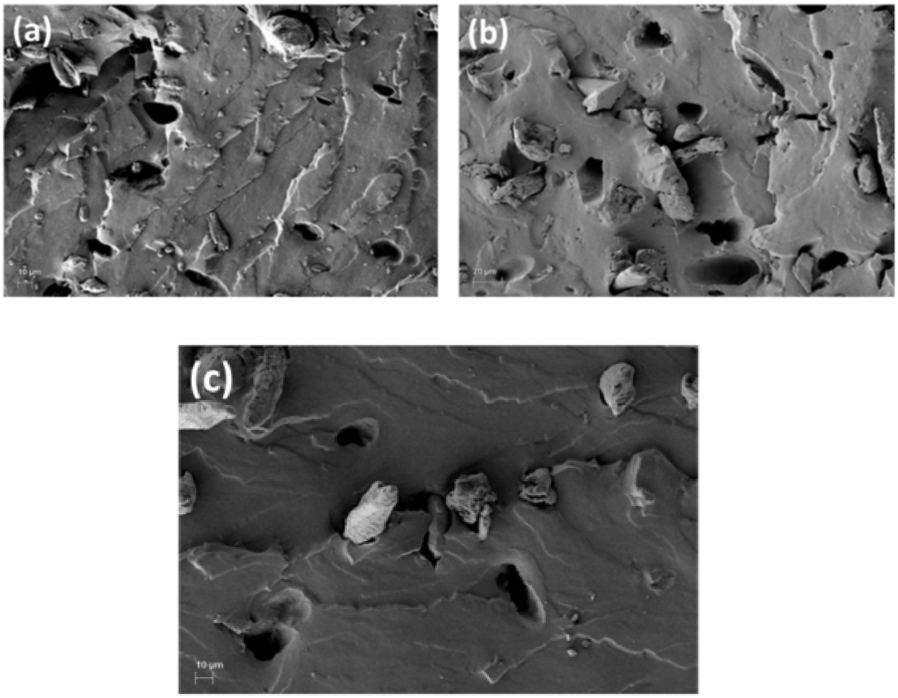

Figure 4.8: SEM images of composites of 20 phr loading (**a**) U20 (**b**) T20 (**c**) G20.

4.2.5 Thermal analysis

4.2.5.1 TG

The effect of unmodified and modified fillers on the thermal degradation of the blend was analyzed using TG. **Figure 4.9** shows the sigmoidal shaped thermal stability curves for TN and 20 phr loaded UCSP, T-CSP and G-CSP composites within the temperature range 30-600 °C.

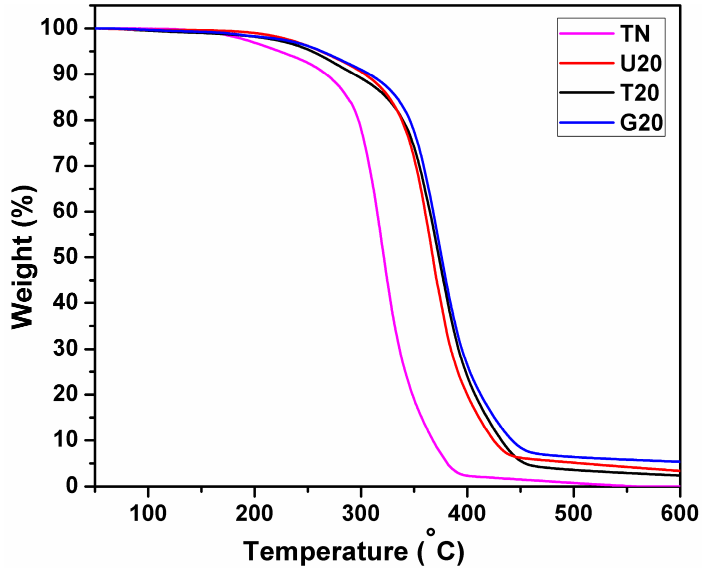

Figure 4.9: TG curves of CSP filled TN blend-composites.

The initial degradation temperature and maximum degradation temperature obtained from the thermogram are shown in the **table 4.4**. The degradation of gum sample TN starts at 168 °C and completes at 386 °C. Addition of fillers (U20, T20 and G20) increased the onset degradation temperature to 238, 233, 234 °C and maximum degradation temperature significantly up to 436, 449, 450 °C respectively. The initial and final degradation temperatures of U20 is 238 and 436 °Cwith a 3.4 % residue at 600 °C. The onset degradation temperature shows 38 % enhancement and maximum degradation temperature 13 % enhancement with the addition of 20 phr UCSP. The chemical treatments on the filler cause a slight increment in onset and maximum degradation temperature values.

Table 4.4: TG data of CSP filled TN blend-composites.

Sample	**T_{onset} (°C)**	**$T_{50\%}$ (°C)**	**T_{max} (°C)**	**Residue %**
TN	168	320	386	0
U20	238	368	436	3.4
T20	233	373	449	2.5
G20	234	376	449	5.5

TG curves further indicate that the gum sample (TN) decomposes quickly with almost no char residue at 600 °C when compared to its CSP filled composites. CSP possess a better thermal stability and it enhances the thermal stability of the composites to a great extent. However, the unmodified and modified composites did not exhibit significant difference in its thermal properties. The increment in the onset and maximum degradation temperature in the composites are attributed to the addition of filler which possess an important role against the gas release during the degradation time that resulted delay in weight loss [54-55].

4.2.5.2 DSC

The thermal behaviour of CSP filled TN composites were analyzed by DSC, which were performed at a temperature range of – 80 °C to 90 °C. **Figure 4.10** describes impact of CSP addition on the glass transition (T_g) values of TN blend-composites.

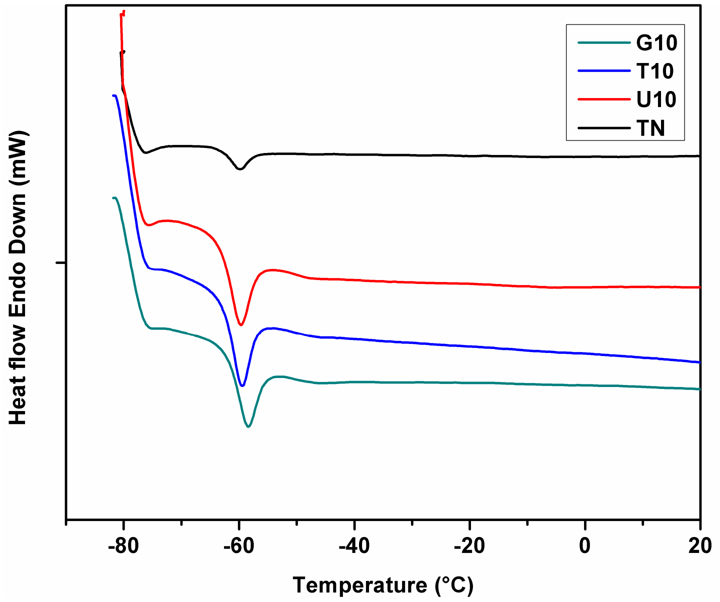

Figure 4.10: DSC curves of CSP filled TN blend-composites.

The DSC curve of blend TN showed the glass transition (T_g) at −65.92 °C whereas the UCSP filled composite showed T_g at a higher temperature −64.22 °C at 10 phr filler loading. The presence of filler influences the glass transition through its impact in free volume. Filler occupies most of the free volume available in the matrix and confinement of polymer chains occurs. Thus, it leads to restriction in segmental mobility [56-57]. The observed T_g values of silane treated CSP filled samples at 10 phr loading are −63.28 °C for T-CSP composites and −62.46 °C for G-CSP composites respectively. Since the T_g values are an indication of segmental mobility of polymer in presence of fillers, the addition of G-CSP restricts the segmental mobility more effectively than T-CSP and UCSP. This observation can be attributed to the effective coupling between G-CSP and the matrix.

Glycidyloxypropyl group in the G-CSP and the filler geometry strengthen the interface between CSP and matrix.

4.3 Conclusions

The effect of concentration of CSP and chemical modifications using different silane coupling agents on the mechanical and thermal properties of the composites were investigated using tensile properties, SEM and thermal analysis in this study. The tensile and tear properties of TN increased with increase in CSP, reached the maximum and then decreased. 10 Phr CSP was observed as the optimum loading. Between the unmodified and modified filler, modified CSP provided better phase morphology, better interfacial adhesion, higher reinforcing efficiency and better mechanical properties. The effect of chemical modification of fillers on the material properties was evaluated in terms of tensile properties, tear strength, hardness, abrasion resistance, TG, DSC and SEM. The composites with GPTMS modified CSP showed better mechanical properties than that of TEVS which were in good agreement with SEM images. Eventhough, addition of CSP improved the thermal stability of the blend, chemical modification did not have a much impact on the thermal stability of composites. Glass transition temperature (T_g) was improved with the addition of CSP through its effect in the free volume of the matrix. Increment in T_g observed with the use of silyl treated CSPs indicated that effective coupling was achieved between CSP and TN blend through the silane treatment which strengthened the interface between CSP and matrix.

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Chapter 5

Transport behaviour of different solvents through coconut shell powder (CSP) filled thermoplastic polyurethane/ natural rubber (TN) blend-composites

Abstract: *The transport behaviour of homologous series of aromatic solvents and petroleum fuels through coconut shell powder (CSP) reinforced thermoplastic polyurethane/natural rubber (TN) blend-composites have been investigated in the temperature range 30- 70 °C. The diffusion and transport properties of solvents through the composites were found to be decreasing with increase in filler loading. The mechanism of transport was found to be Fickian and close to Fickian for aromatic solvents and less Fickian for petroleum fuels. Activation energy for diffusion was calculated from Arrhenius plots and thermodynamic parameters were calculated using vant Hoff's relation. Oil resistant properties were also found to be promising and were well established using morphological analysis.*

5.1 Introduction

The development of fully or partially biodegradable composites plays a crucial role in the current scenario due to environmental concerns. Research is growing on the use of natural fibres for the production of polymer composites all over the world. The applications of natural fibres are encouraged in various fields such as packaging, automobiles, transportation, furniture and construction due to their light weight, low cost, and less environmental pollution at the time of production [1]. An understanding of transport phenomenon of the polymer is essential, as it discloses the information regarding the nature of polymer matrix and its potential for the use in transportation, packaging, *etc*. Applications such as electrodialysis, pervaporation, and reverse osmosis of selectively permeable membranes also can be understood from the study of diffusion process. Since the transport studies of organic solvents, fuels and gases through polymers are of significant technological importance, many researchers have focused on it [2-5]. Hopfenberg and Paul suggested that the transport studies in blend structures provide additional characterizations of blend [6]. Moreover, tailoring of highly efficient end-use products of a polymer blend needs the knowledge of relation between sorption properties and molecular structure also. The mode of transport through polymers depends on various factors such as the nature of matrix, nature of penetrant, temperature, cross-link density, nature of filler, interfacial adhesion between filler, matrix *etc*. Interface between filler and matrix significantly influences the transport of solvent molecules through the polymer membranes [7].

Oil resistance properties were evaluated in applications such as oil-resistant oil handling hoses, seals, and grommets, as they are valuable in predicting the service behaviour of the material. Properties of polymer materials deteriorate during exposure to oils, greases, fuels and other fluids during service affecting the performance of the rubber part, which can result in partial failure. NR products are being used in a variety of environmental applications such as at high temperature or in hot oil or solvent which may lead to crazing or swelling. In order to minimize this, blending and addition of fillers were found to be effective [8-11]. Oil resistant materials are very important to automotive industry as a variety of components may come in contact with a number of fluids.

Our group has studied revealed the properties of TN blend system, which shows promising transport properties [12]. This chapter deals with the diffusion behaviour and oil resistant behaviour of the CSP filled TN blend-composites in aromatic solvents, petroleum fuels and petroleum based IRM oils, with special reference to the effect of filler loading, effect of filler modification, penetrant size and effect of temperature. Studies on the oil resistant properties of natural fibre filled polymer composites are rare in literature. It is expected that CSP filled TN blends will be a cost-effective, eco-friendly, yet a highly useful material for various applications in the fields of packaging and petrochemical industries.

5.2 Results and Discussion

5.2.1 Analysis of swelling data of aromatic solvents and petroleum fuels

5.2.1.1 Mol % uptake

Diffusion of solvents trough the prepared blend-composites were determined in terms of mol % uptake of solvent using the **equation 5.1**

$$Q_t \, mol\,\% = \frac{M_t/_{M_s}}{M_p} \times 100 \qquad \textbf{(Eq: 5.1)}$$

where M_t is the mass of solvent absorbed at a given time 't', M_s is the molar mass of the solvent and M_p is the mass of polymer composite. The mol % uptake (Q_t %) was plotted against square root of time (√t) to get the sorption curves with special reference to the effect of filler loading, effect of filler modification using silane coupling agents, penetrant size and the effect of temperature.

Effect of filler loading

Mol % uptake (Q_t) of xylene and petrol by TN blend and its CSP filled composites at room temperature as a function of square root of time (√t) were shown in **figures 5.1** and **5.2**. All the sorption curves show the same trend, in which, a reasonably high swelling rate initially due to the higher concentration gradient of penetrant with the composites. With the increase in time, it reached at equilibrium solvent uptake where the solvent uptake is counter-balanced by the solvent extraction from the polymer as seen in many other polymer systems [13-14]. It is evident that the equilibrium solvent uptake decreases with the filler loading. The maximum uptake is for TN blend and minimum for 20 phr loaded sample. Each filler particle behaves as an obstacle to the diffusing molecule. As concentration of filler increases in the rubber matrix, more and more obstacles are created to the diffusing molecule and thus reduce the amount of penetrate solvent [15]. Local mobility of polymer gets restricted by the reinforcement of CSP fillers and the better interfacial adhesion between polymer and filler network improves the solvent resistance of the composites. In addition to that, the increase in filler content with good dispersion in matrix increases the surface area of the reinforcing phase. At lower concentrations of CSP, penetrant molecules can easily transport through the matrix. With the increased filler loading, CSP particles form filler-filler networks other than filler-matrix network and offer a higher rate hindrance to the penetrant molecule [16]. The diffusion can also be explained in terms of free volume available in the matrix to accommodate the solvent molecules. The increase in filler content reduces the availability of free spaces and creates a tortuous path for solvent across the matrix [17].

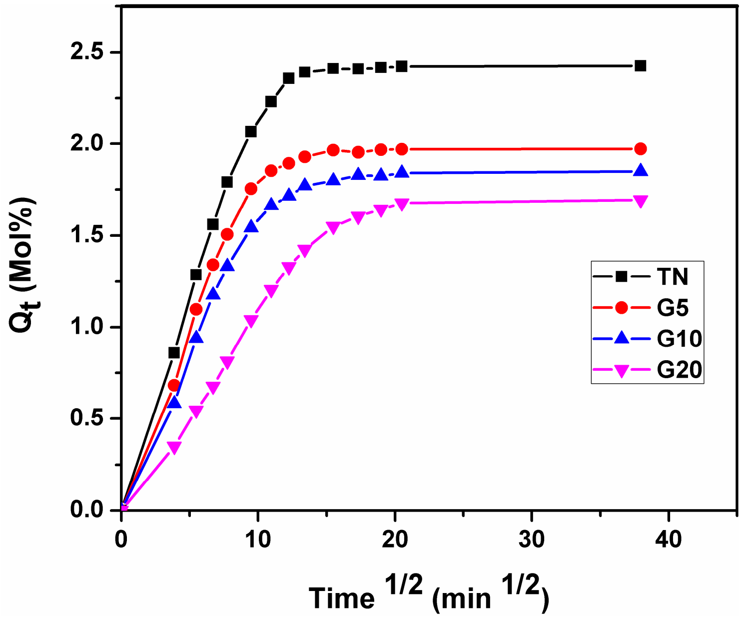

Figure 5.1: Mol % uptake of xylene by TN blend-composites with varying G-CSP loading at room temperature.

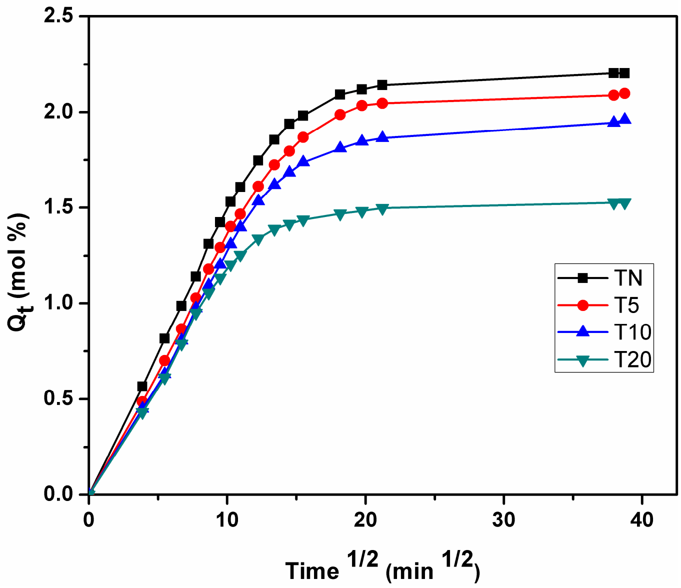

Figure 5.2: Mol % uptake of petrol by TN blend-composites with varying T-CSP loading at room temperature.

Effect of chemical treatment of filler

Effect of chemical treatment of fillers at equilibrium solvent uptake by different types of filler at room temperature is shown in **figures 5.3** and **5.4**, which shows the toluene and petrol uptake on 10 phr loading at room temperature. The diffusion and transport in filled composites depends on the nature of filler, degree of adhesion and their compatibility with polymer matrix [18]. **Figures 5.3** and **5.4** show that the solvent uptake for a particular filler concentration is lower for the treated CSP composites than the untreated CSP composites. It is needless to mention that the chemical treatment enhances the surface properties of fillers with the matrix. Pre-treatment with alkali dissolves the major portions of lignin and hemicellulose and wash out other volatile extractives and impurities, thus results in a rough filler surface. Silane treatment further reduces the enormous number of hydroxyl groups available at the surfaces and leads to a better compatibility between filler and matrix. This compatibility between filler and matrix reduces the free volume within the system consequently results in poor diffusion properties.

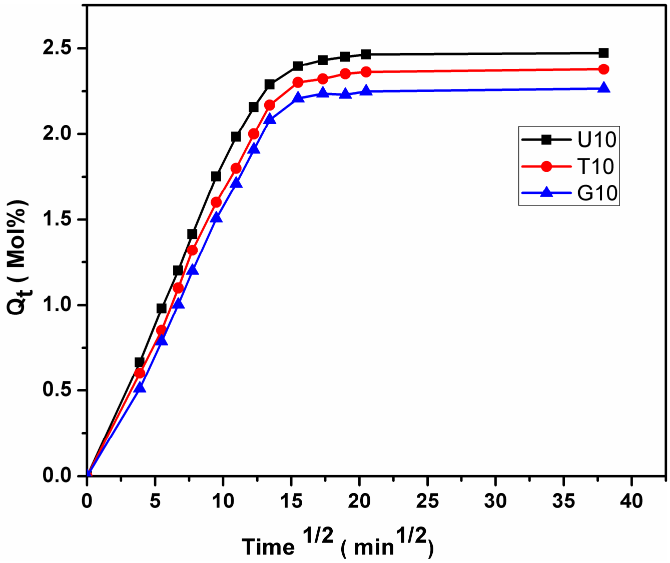

Figure 5.3: Effect of filler modification on mol % uptake of toluene with 10 phr UCSP, T-CSP and G-CSP loaded TN blend-composites.

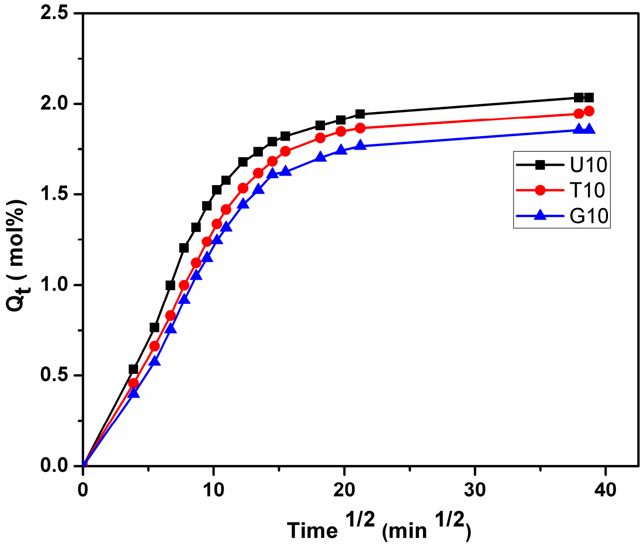

Figure 5.4: Effect of filler modification on mol % uptake of petrol with 10 phr UCSP, T-CSP and G-CSP loaded TN blend-composites.

Effect of penetrant size

Transport properties of composites in a homologous series of aromatic solvents and petroleum fuels are estimated for the sample G20 and G10 respectively are shown in **figures 5.5** and **5.6**. The mol % uptake of composites decrease with increase in the penetrant size; benzene showed highest uptake and xylene showed the lowest and the decreasing order is benzene > toluene > xylene. In case of petroleum fuels, solvent uptake is in the order, petrol > kerosene > diesel. The mol % uptake decreases with increase in the molar volume and length of alkyl chains in the case of petroleum fuels. Higher penetrant size, molecular weight and molar volume of xylene and diesel leads to the lowest uptake. The decrease in diffusivity with the increase in penetrant size has been reported by many researchers [12, 19-20]. This trend can be explained in terms of free volume theory [17]. The diffusion rate of a molecule is primarily depends on the ease with which polymer chains exchange their positions with solvent molecules. As penetrant size or molar volume increases, the ease of exchange become less and leads to the decrease in sorption. Moreover higher activation energy is needed for large penetrant size to diffuse into the matrix [21]. Diesel with C14-C19 may be expected to diffuse slowly and be accommodated in the rubber matrix with highest hindrance.

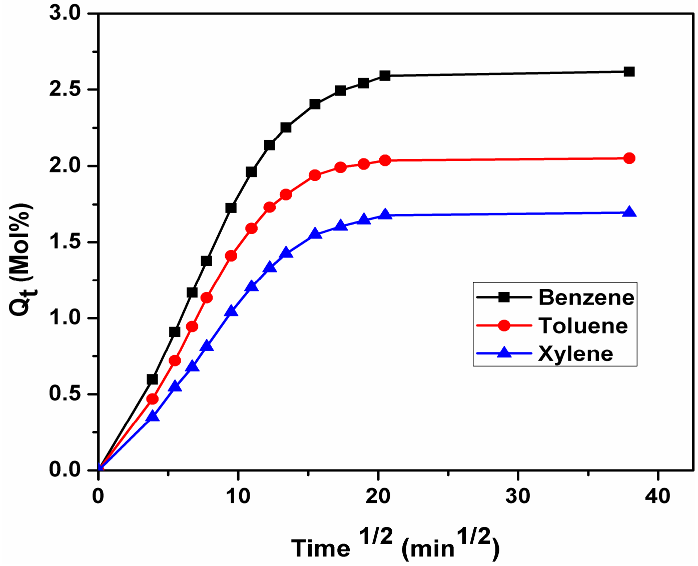

Figure 5.5: Effect of penetrant size on mol % uptake with 20 phr G-CSP loaded TN blend-composite.

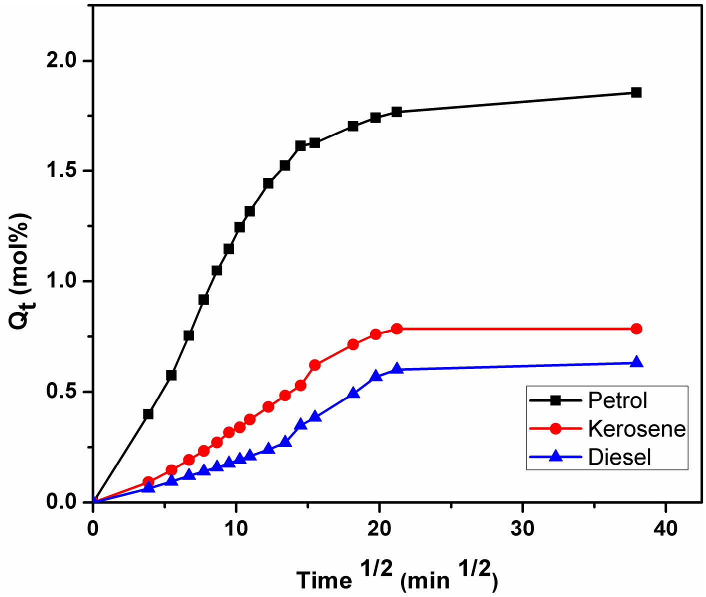

Figure 5.6: Effect of penetrant size on mol % uptake with 10 phr G-CSP loaded TN blend-composite.

Effect of temperature

The effect of temperature on the transport properties has been studied by conducting the experiments at higher temperatures such as 50 and 70 °C for aromatic solvents and 45 and 60 °C for petroleum fuels. **Figure 5.7** shows the change in solvent penetration for G10 in xylene and **figure 5.8** in diesel at higher temperatures. It clearly indicates that the increase in temperature enhances the diffusion process. Q_∞Values significantly increase with the rise in temperature. Similar trend is observed for all other samples in other solvents. It can be explained in terms of the increased segmental mobility and free volume and the gain in kinetic energy by the penetrants at higher temperatures [22].

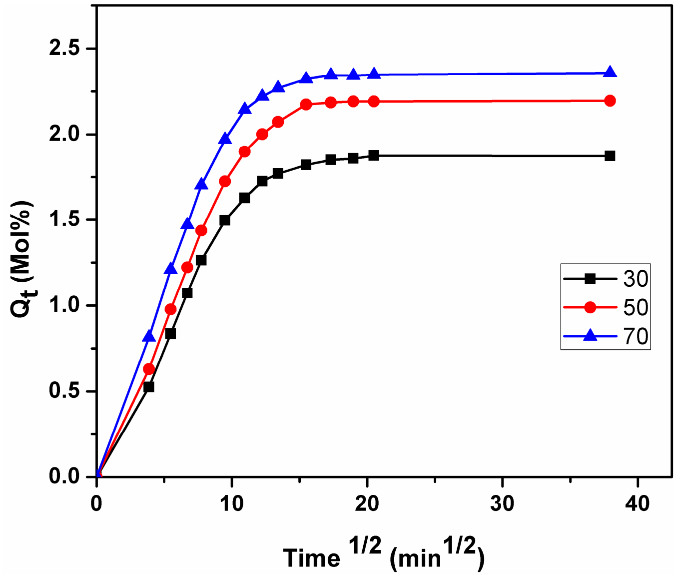

Figure 5.7: Effect of temperature on mol % uptake in xylene with 10 phr G-CSP loaded TN blend-composite.

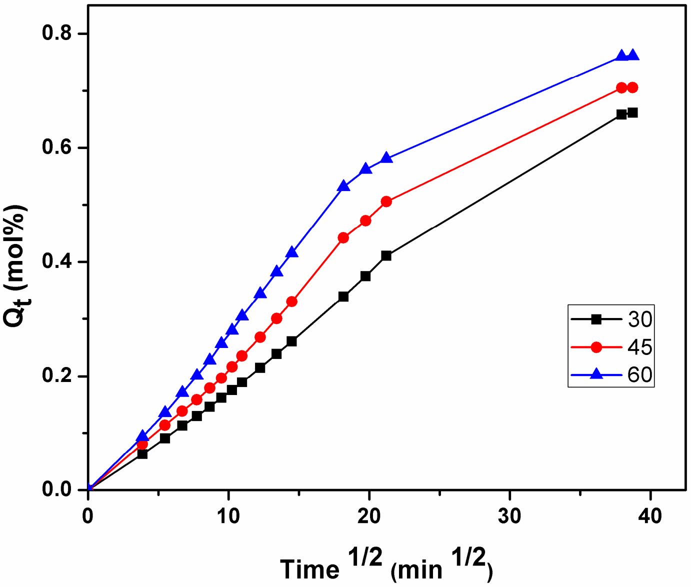

Figure 5.8: Effect of temperature on mol % uptake in diesel with 10 phr G-CSP loaded TN blend-composite.

5.2.1.2 Kinetic parameters

Sorption coefficient (S)

Sorption coefficient S is related to the equilibrium sorption of penetrant and calculated using the **equation 5.2**,[23]

$$S = \frac{w_\infty}{w_p} \qquad \textbf{(Eq: 5.2)}$$

where w_∞ is the mass of the solvent at equilibrium swelling and $w_p$is the mass of the polymer sample. The sorption coefficient (S) obtained from the equilibrium swelling data is presented in **table 5.1** and **5.2**. Both aromatic solvents and petroleum fuels show same trend. From the table, it can be observed that the sorption coefficient decreased with CSP content in the composites for a given solvent. Many other researchers have reported such systems [24-25]. It can also be seen that silane treatment further reduces the sorption coefficient efficiently, indicating that the sorption is somewhat restricted by the filler modification.

Diffusion coefficient (D)

The process of diffusion is a kinetic parameter related to the penetrant size and to the polymer segmental mobility. It can be calculated using the **equation 5.3**.

$$D = \pi \left(\frac{h\theta}{4Q_\infty}\right)^2 \qquad \textbf{(Eq: 5.3)}$$

Where θ is the slope of initial portion of the plot of Q_t *vs.* $t^{1/2}$ and Q_∞ is the equilibrium mol % uptake and h is the initial thickness of sample [26]. **Table 5.1** and **5.2** demonstrate that, for all the three aromatic solvents and petroleum fuels studied, the diffusion coefficient decreases systematically from TN to 20 phr loading in the order TN > 5 phr > 10 phr > 20 phr. The filler modification also shows a decreasing trend in diffusivity as it varies in the order unmodified > modified composites for a particular loading in a given solvent. Blend sample without filler (TN) has flexible chains and can easily adjust with solvent ingression shows highest uptake. In these three solvents, D value decreases with increase in molecular mass and molar volume of the solvent. The decrease in D values are in the order benzene >

toluene > xylene for aromatic solvents and petrol > kerosene > diesel for petroleum fuels.

Upon the addition of fillers, diffusion coefficient reduces due to various factors like reduction in free spaces, restricted chain mobility of polymers, increased surface area of reinforcing phase in the matrix, extended filler-filler network formed at higher loading in addition to the filler-polymer network, *etc*. Filler modification ensures better interfacial adhesion between filler and matrix which further reduces the diffusion coefficient values for a particular filler loading. Penetrant size also plays a significant role in the diffusion coefficient values. For large penetrant molecule, ease of exchange of positions between polymer chains and penetrant molecule is less and higher activation energy is needed for the diffusion. The low solvent diffusion values of petroleum fuels when compared to aromatic solvents are due to their high molar volume [27].

Table 5.1: Diffusion coefficient (D), Sorption coefficient (S) and Permeation coefficient (P) values for 0, 5, 10 and 20 phr UCSP, T-CSP and G-CSP loaded TN blend-composites in aromatic solvents at room temperature.

Sample	Benzene			Toluene			Xylene		
	D×10^{-5} cm^{2}s^{-1}	**S**	**P×10^{-4} cm^{2}s^{-1}**	**D×10^{-5} cm^{2}s^{-1}**	**S**	**P×10^{-4} cm^{2}s^{-1}**	**D×10^{-5} cm^{2}s^{-1}**	**S**	**P×10^{-4} cm^{2}s^{-1}**
TN	6.498	3.1820	2.0676	5.537	2.9747	1.6470	4.293	2.5067	1.0761
U5	5.917	2.8285	1.6736	5.438	2.5056	1.3625	3.995	2.1119	0.8437
U10	5.799	2.6738	1.5505	5.38	2.2744	1.2236	3.873	2.0966	0.8120
U20	5.572	2.5065	1.3966	5.135	1.9351	0.9936	3.698	1.9155	0.7083
T5	5.875	2.7014	1.5871	5.325	2.4267	1.2922	3.903	2.0998	0.8196
T10	5.689	2.4018	1.3664	5.158	2.1864	1.1277	3.816	1.9981	0.7625
T20	5.39	2.3622	1.2732	4.878	1.901	0.9273	3.6	1.8347	0.6605
G5	5.823	2.6319	1.5325	5.212	2.3870	1.2441	3.85	2.0901	0.8046
G10	5.631	2.2623	1.2739	5.075	2.0919	1.0616	3.736	1.9856	0.7418
G20	5.283	2.0422	1.0788	4.641	1.8851	0.8748	3.547	1.7950	0.6366

Table 5.2: Diffusion coefficient (D), Sorption coefficient (S) and Permeation coefficient (P) values for 0, 5, 10 and 20 phr UCSP, T-CSP and G-CSP loaded TN blend-composites in petroleum fuels at room temperature.

Sample	Petrol			Kerosene			Diesel		
	D×10^{-5} cm^{2}s^{-1}	**S**	**P×10^{-4} cm^{2}s^{-1}**	**D×10^{-5} cm^{2}s^{-1}**	**S**	**P×10^{-4} cm^{2}s^{-1}**	**D×10^{-5} cm^{2}s^{-1}**	**S**	**P×10^{-4} cm^{2}s^{-1}**
TN	4.4981	2.1488	9.6658	2.6482	1.7316	4.5856	0.8188	1.2810	1.0489
U5	3.9754	2.0852	8.2896	2.4265	1.7005	4.1263	0.8091	1.2184	0.9858
U10	3.3872	2.0352	6.8935	2.2646	1.6762	3.7961	0.8060	1.1661	0.9399
U20	3.1216	1.7938	5.5995	1.9629	1.2340	2.4222	0.7690	1.0821	0.8321
T5	3.7252	2.0120	7.4950	2.3200	1.5865	3.6808	0.7881	1.2025	0.9477
T10	3.4170	1.9612	6.7014	2.1359	1.4121	3.0161	0.7705	1.1517	0.8874
T20	2.3137	1.5259	3.5306	1.9191	1.1764	2.2575	0.7414	1.0130	0.7510
G5	3.5986	1.9585	7.0481	2.0746	1.4897	3.0905	0.7750	1.1568	0.8966
G10	3.2166	1.8547	5.9658	1.9783	1.3350	2.6410	0.7512	1.0984	0.8251
G20	2.1968	1.4238	3.1278	1.6959	1.0603	1.7982	0.7215	0.9790	0.7064

Permeation coefficient (P)

The permeation process through a matrix is the product of sorption and diffusion. Permeation coefficient gives an idea about the amount of solvent permeated through uniform area of sample per second. It was calculated from the **equation 5.4** [26].

$$P = D \times S \qquad \textbf{(Eq: 5.4)}$$

where D is the diffusion coefficient and S is the sorption coefficient. **Tables 5.1** and **5.2** shows that the permeation coefficient is maximum for sample without any filler (TN) and decreases with the increase in amount of the filler and with the increase in penetrant size. D and P values decrease with increase in filler content. The lower values of diffusion coefficient point to the lower permeation of solvent through the matrix. Sample with filler loading 20 phr shows the minimum sorptivity, permeability and diffusivity and maximum is for sample without filler (TN).

Arrhenius parameters

Activation energy required for the diffusion of solvents through the membranes was calculated using Arrhenius **equation 5.5** [28].

$$X = X_0\, e^{-Ea/RT} \qquad \textbf{(Eq: 5.5)}$$

Where X can be D or P and X_0 is D_0 or P_0 which is a constant. Kinetic parameters of the samples in aromatic solvent increased with increase in temperature, same trend was followed by petroleum fuels also. This can be explained in terms of increase in free volume and gain in kinetic energy. The values of D and P of sample G10 at different temperatures in xylene (for aromatic solvents) and diesel (for petroleum fuels) were used to estimate the activation energy for diffusion and permeation.

In **figure 5.9**, Arrhenius plots of log D or log P *vs.* 1/T for xylene were constructed and the activation parameters were estimated from the slopes of the curve by linear regression analysis. The difference between E_P and E_D values gives the heat of sorption (ΔH_s) values. Higher activation energy values for CSP filled composites when compared with the TN blend indicates that the filler CSP retards the diffusion process of penetrant molecule through the matrix. The presence of filler restricts the free movement of polymer chains and extra energy is needed for the segmental motion which permits the diffusion of xylene.

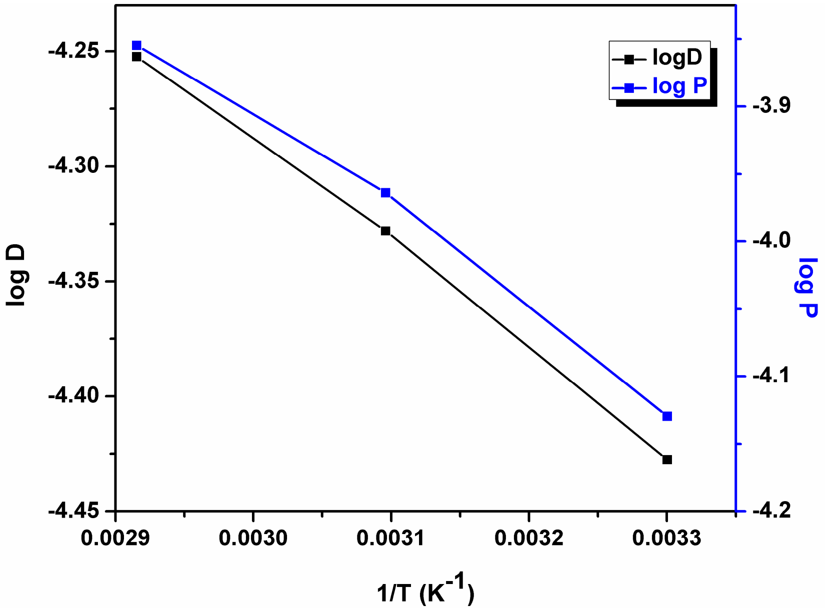

Figure 5.9: Arrhenius plot of log D *vs.* 1/T and log P *vs.* 1/T for 10 phr G-CSP loaded TN blend-composite in xylene.

5.2.1.3 Thermodynamic parameters

In order to determine thermodynamic parameters enthalpy of sorption ΔHs and entropy of sorption ΔS for the solvents in composites, the equilibrium sorption constant (Ks) of the solvents was first determined using the **equation 5.6**

$$Ks = \frac{\text{Number of moles of the solvent sorbed at equilibrium}}{\text{Mass of the polymer sample}} \qquad \textbf{(Eq: 5.6)}$$

The values of Ks were substituted into the van't Hoff's **equation 5.7** to calculate the enthalpy of sorption (ΔH_S) and entropy of sorption (ΔS).

$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H_s}{2.303RT} \qquad \textbf{(Eq: 5.7)}$$

The values of ΔH and ΔS are obtained by the regression analysis of the plots of log Ks versus 1/T.

The change in Gibb's free energy of ΔG for the solvents was obtained using the **equation 5.8**

$$\Delta G_s = \Delta H_s - T\Delta S \qquad \textbf{(Eq: 5.8)}$$

where T is the temperature in Kelvin.

Arrhenius parameters and thermodynamic parameters for xylene and petrol for CSP filled TN blend-composites are summarized in **table 5.3** and **5.4** respectively. From the **table 5.3** and **5.4**, it is observed that ΔH values are positive and ΔS values are negative for both xylene and diesel.

Table 5.3: Arrhenius parameters E_P, E_D and *ΔH* (kJ/mol) and thermodynamic parameters ΔH (kJ/mol), ΔS (J/mol) and ΔG (kJ/mol) for 0 and 10 phr UCSP, T-CSP and G-CSP loaded TN blend-composites in xylene.

Sample	**Arrhenius parameters**			**Thermodynamic parameters**		
	E_D (kJ/mol)	**E_P (kJ/mol)**	**ΔH (kJ/mol)**	**ΔH (kJ/mol)**	**ΔS (J/mol)**	**ΔG (kJ/mol)**
TN	5.86	11.67	5.81	5.85	-13.23	9.86
U10	8.12	13.70	5.58	5.58	-14.22	9.88
T10	8.34	13.72	5.38	5.38	-14.88	9.89
G10	8.73	13.73	4.99	4.96	-16.41	9.93

Table 5.4: Arrhenius parameters *E_P*, *E_D* and *ΔH* (kJ/mol) and thermodynamic parameters ΔH (kJ/mol), ΔS (J/mol) and ΔG (kJ/mol) for 0 and 10 phr UCSP, T-CSP and G-CSP loaded TN blend-composites in diesel.

Sample	**Arrhenius parameters**			**Thermodynamic parameters**		
	E_D (kJ/mol)	**E_P (kJ/mol)**	**ΔH (kJ/mol)**	**ΔH (kJ/mol)**	**ΔS (J/mol)**	**ΔG (kJ/mol)**
TN	7.49	13.4	5.91	5.90	-17.25	11.12
U10	12.38	16.02	3.64	3.69	-25.12	11.31
T10	12.68	16.09	3.41	3.45	-26.17	11.38
G10	12.69	16.09	3.39	3.20	-27.63	11.58

The positive values of ΔH indicate that the sorption is an endothermic process and is dominated by Henry's mode, that is, sorption proceeds through creation of new sites or pores in the polymer [19]. For the filled blends the ΔH value decreases. The ΔS values are negative which implies the retainment of liquid state structure of solvents even in the sorbed state within the polymer. The ΔS value decreases with increase of filler content which reduces the solvent transport. The free energy values are found to be positive and of small magnitude. These results suggest the non-spontaneity of sorption process [29]. ΔG values are higher for TN blend and found to be increasing with addition of filler. It can be understood that the sorption process is more spontaneous for the TN blend sample and spontaneity of the reaction decreases with increasing filler loading. This indicates the increase in tortuosity of the diffusion process through the matrix. Chemical treatment has a slight impact on the thermodynamic parameters. The effect of modification of interface with the chemical treatments influences the solvent diffusion process.

5.2.1.4 Transport behavior

The mechanism of transport phenomenon was analyzed using the **equation 5.8** [30],

$$log\left(\frac{Q_t}{Q_\infty}\right) = \ log\,k \ + n\,log\,t \qquad \textbf{(Eq: 5.8)}$$

where Q_t is the mol % uptake of solvents at time 't' and Q_∞ is the equilibrium swelling and k is a constant which depends on the polymer morphology and polymer-solvent interactions. It is the value of 'n' which determines the mode of transport mechanism of solvent through the matrix. The values of n and k are obtained by the regression analysis of $log\left(\frac{Q_t}{Q_\infty}\right)$ *vs.* log t plot and results were summarized in **tables 5.5** and **5.6**.

If the value of n = 0.5, it is normal Fickian mode of transport , where the rate of diffusion of solvent molecule is lower than that of rate of relaxation of polymer chain [31]. When n=1, the transport become non-Fickian behaviour where the chain relaxation is slower than liquid diffusion. If 0.5 < n <1, the mode of transport is called 'anomalous'. Here, for aromatic solvents, the transport mechanism is Fickian and close to Fickian and for petroleum fuels, it is less Fickian. For both type of solvents, the 'n' values decrease with the addition of filler loading and signifies that, better reinforcement effect at higher filler loading. It is commonly seen among conventional rubber composites and blend-composites [32-33].

Table 5.5: Values of n and k for 0, 5, 10 and 20 phr UCSP, T-CSP and G-CSP loaded TN blend-composites using aromatic solvents.

Sample	n values			k (min^{-1})		
	Benzene	**Toluene**	**Xylene**	**Benzene**	**Toluene**	**Xylene**
TN	0.55	0.6	0.61	0.26	0.27	0.35
U5	0.53	0.58	0.6	0.25	0.26	0.35
U10	0.51	0.59	0.6	0.23	0.28	0.34
U20	0.52	0.56	0.56	0.21	0.25	0.27
T5	0.52	0.57	0.6	0.26	0.25	0.34
T10	0.51	0.58	0.59	0.24	0.25	0.32
T20	0.51	0.56	0.55	0.23	0.24	0.27
G5	0.52	0.57	0.59	0.25	0.26	0.33
G10	0.5	0.56	0.58	0.24	0.25	0.3
G20	0.51	0.57	0.55	0.22	0.24	0.25

Table 5.6: Values of n and k for 0, 5, 10 and 20 phr UCSP, T-CSP and G-CSP loaded TN blend-composites using petroleum solvents.

Sample	n values			k (min^{-1})		
	Petrol	**Kerosene**	**Diesel**	**Petrol**	**Kerosene**	**Diesel**
TN	0.48	0.55	0.59	0.40	0.27	0.23
U5	0.46	0.54	0.58	0.38	0.26	0.22
U10	0.45	0.53	0.56	0.35	0.23	0.19
U20	0.43	0.49	0.54	0.33	0.22	0.18
T5	0.46	0.52	0.58	0.36	0.26	0.22
T10	0.45	0.49	0.55	0.33	0.23	0.19
T20	0.41	0.46	0.52	0.32	0.22	0.19
G5	0.45	0.50	0.56	0.34	0.23	0.20
G10	0.44	0.47	0.54	0.33	0.22	0.19
G20	0.38	0.45	0.51	0.31	0.21	0.18

The magnitude of k signifies the structural characteristics of the polymer and provides an idea about the nature of the interaction between the polymer and the solvent. The higher the *k* value the higher is the interaction between the polymer and the solvent. The values of k in the filled systems are lower than unfilled systems.

Presence of filler can reduce the interaction between the polymer and the solvent [19]. The general trend in decrease in n and k values with the filler addition can be attributed to the better reinforcing effect at higher loading. Filler effectively reduces the chain flexibility, available free volumes and polymer-solvent interactions. Chemical treatment also causes a general decrease in n and k values, which is evidently because of the improved interface could effectively resist the polymer-solvent interactions. When comparing k values of aromatic solvents and petroleum fuels, it is clear that CSP filled composite is less resistant to aromatic solvents than petroleum fuels.

5.2.2 Oil resistance

Oil resistance of CSP filled TN blend-composites were determined using ASTM D 471 with petroleum based industrial reference oils IRM 901, IRM 902 and IRM 903. The % oil swelling is used for estimation of the oil resistance of the material which is calculated using the **equation 5.9**

$$\% \text{ Swelling of oil} = \frac{W_2 - W_1}{W_1} \times 100 \qquad \textbf{(Eq: 5.9)}$$

where W_1 and W_2 are the weights of the samples before and after immersion respectively. Oil-resistance was reported in terms of % mass swell.

The % swelling of TN blend composites filled with UCSP in different oils at varying temperatures are shown in **figure 5.10**, from which we can understand the general behaviour of composites when immersed in oils.

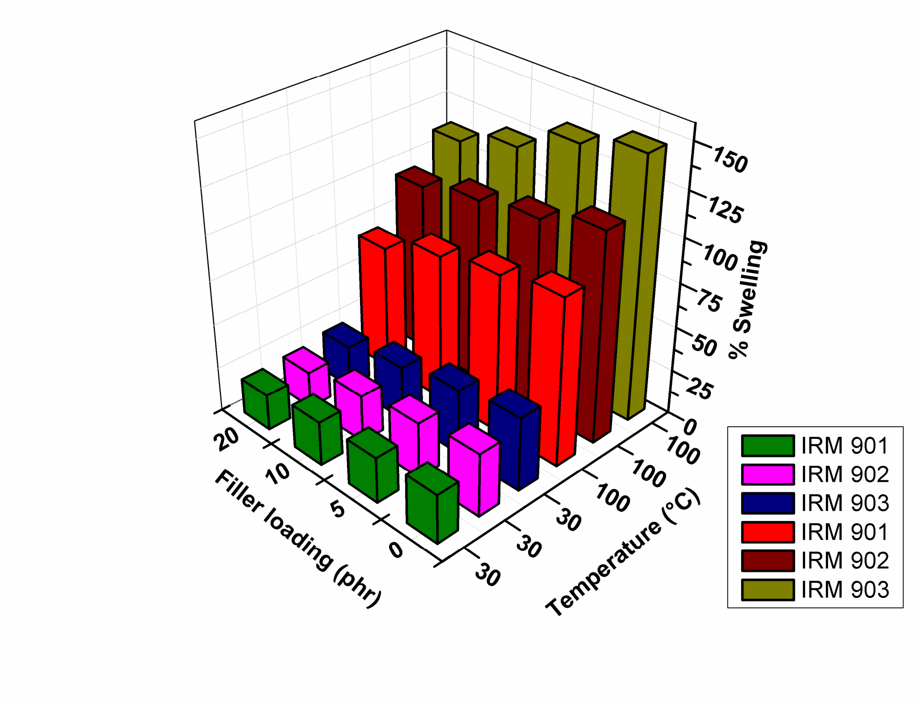

Figure 5.10: IRM oil resistance properties of TN blend-composites filled with 0, 5, 10 and 20 phr loaded UCSP at temperatures 30 and at 100 °C

The vulcanized composite does not dissolve in the oil, but swells due to the effect of cross-linking. The oil-resistance results are consistent with the results of the cross linking density. On the other hand, the incorporation of CSP also makes the penetrant inevitably travel along a tortuous path and decreases the relative permeability in the composites, which improve the oil resistance property [34]. The % swelling of composites are influenced by various factors such as filler loading, nature of fillers, nature of the penetrating oil and temperature.

5.2.2.1 Effect of filler loading

The oil swelling was found to decrease when the CSP was added in the TN blend-composite. This indicated that the presence of CSP enhanced the oil resistance of TN blend. The percentage of oil uptake was considerably decreased for the composites of 5 phr, 10 phr and 20 phr compared to blend as shown in the **figure 5.11**. The reinforcement provided by CSP in the matrix restricts the extensibility of the rubber chains induced by swelling. This makes difficult for oil to penetrate into the gaps between polymer chains and hence decrease the swelling percentage [35-36]. The enhancement of oil resistance is explained by the reasons that the CSP is oil resisting filler and the morphology of the TN blend was improved by compatibilizing effect of CSP. Similar observations are made by Lopattananon *et al.*, [9].

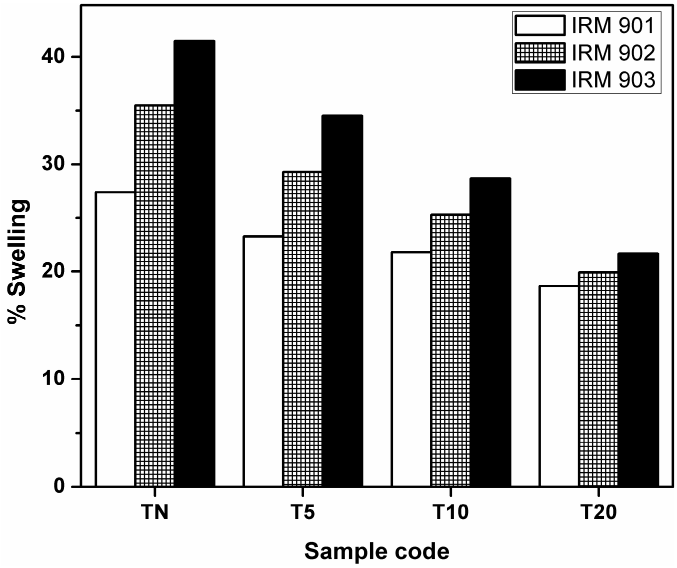

Figure 5.11: % Swelling of IRM oils by TN blend-composites with varying T-CSP loading at room temperature.

5.2.2.2 Effect of chemical modification of fillers

The effect of chemical modification of the fillers in oil resistance of TN blend-composites is shown in the **figure 5.12**. The silane treated CSPs evidently decrease the % swelling and thus, increase the oil resistance of the composites. Here, we can assume that, the interface between the filler and matrix controls the oil uptake. The filler-rubber interaction caused limitations to the ease of penetration of oil into the rubber chains. This also implies that the presence of polarity of the rubber is believed to play a significant role in raising a good filler-rubber interaction which resisted the penetration of the oil into the voids between the rubber chains [37]. In the case of treated CSP containing composites, polarity induced by –OH groups of CSP decreases and hence shows lower swelling than that of unmodified CSP filled composites.

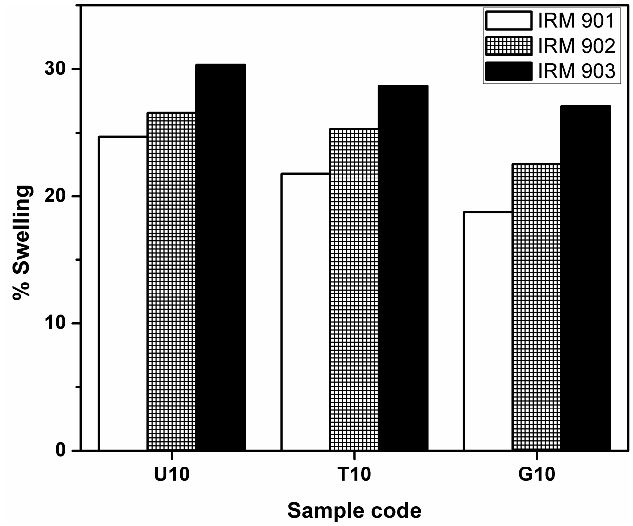

Figure 5.12: Effect of filler modification on oil uptake of TN blend-composites filled with 10 phr UCSP, T-CSP and G-CSP.

5.2.2.3 Nature of penetrating oil

It can be seen that all samples exhibited higher swelling in IRM 903 oil than that in IRM 901 or 902 (**figure 5.13**), means that the samples had less swelling resistance to IRM 903 oil. The IRM 903 oil have lower aniline point (70 °C) than that of the IRM 901 (124 °C), indicating that the aromatic content in the IRM 903 oil is relatively higher. Generally, the lower the aniline point, the greater the tendency for rubber swelling [38].

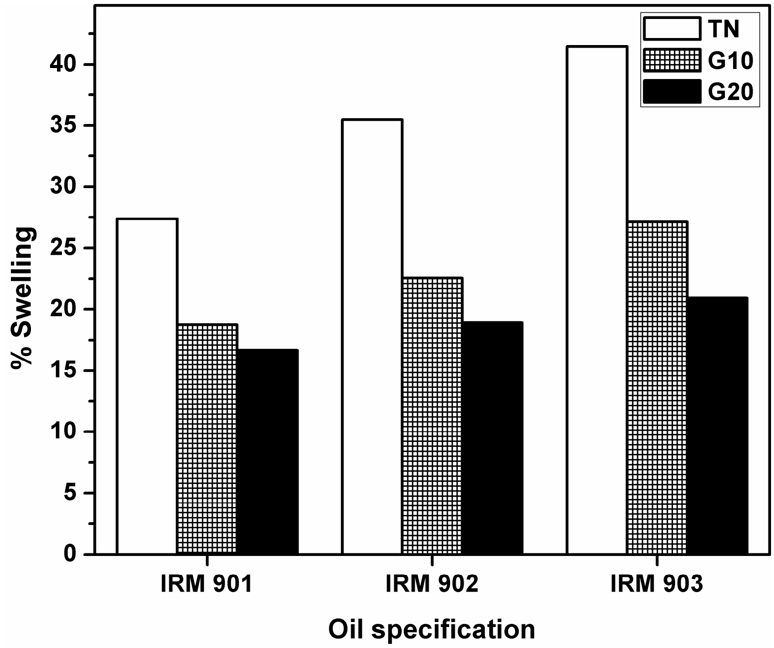

Figure 5.13: Effect of nature of penetrating oil on % swelling of 20 phr G-CSP loaded TN blend-composites.

5.2.2.4 Effect of temperature

The effect of temperature on the swelling properties has been studied by conducting the experiments at temperatures 30 and 100 °C for IRM oils and the results are shown in **figure 5.14**. Temperature plays a prominent role in the oil swelling of TN-CSP composites. It sharply increases when the temperature is raised from 30 to 100 °C. The % swelling at 100 °C is much higher compared to that in 30 °C and hence the oil resistance decreases with increase in temperature. Swelling in IRM 903 at 100 °C shows almost 100 % increase than at 30 °C. But, the effect of temperature is comparably less for IRM 901 oil. Increase in temperature enhances the permeation process of oil through the membranes by facilitating not only the segmental mobility and free volume, but with a gain in kinetic energy by the penetrants at higher temperature.

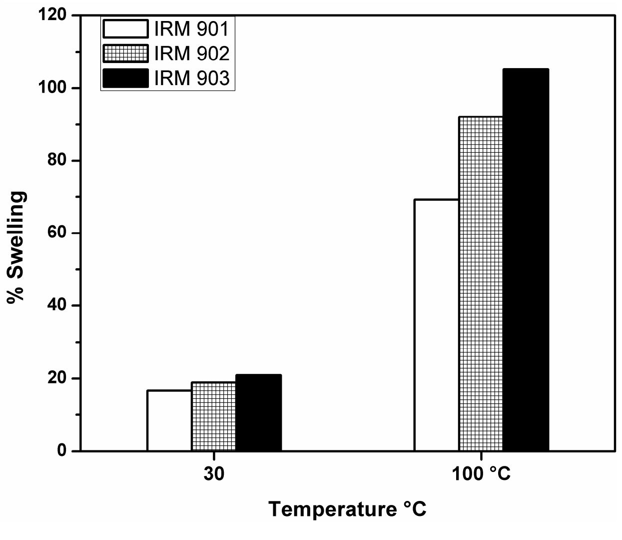

Figure 5.14: Effect of temperature on % swelling in IRM oils with 20 phr G-CSP loaded TN blend-composite.

5.2.3 SEM

Scanning electron microscopy was employed to obtain qualitative evidence on the phase morphology, particle distribution and effect of filler modification. **Figure 5.15** (**a**) shows the SEM image of TN blend, an immiscible blend, where TPU is found to be dispersed as spherical domains in the continuous NR phase and having large number of voids. This happens due to the polarity difference between thermoplastic polyurethane and non-polar natural rubber. With the incorporation of filler particles, as seen in **figure 5.15 (b-d)**, the two phase morphology is found to disappear. According to Manoj *et al.*, polymer systems with filler usually exhibit reduced domain size and a more uniform morphology [39]. **Figure 5.15 (b-d)** shows that the fillers could improve the blend compatibility to certain extent by accelerating the fusion of TPU with NR matrix and they are occupying at every free space within the system. With the addition of UCSP, two phase morphology is transformed into a more or less single phase with a rough morphology. But with silane modified CSPs, T-CSP and G-CSP, as seen in **figure 5.15** (**c** and **d**), smoother surfaces are obtained, which clearly denotes the increase in compatibility of CSP with polymer matrix by reducing the hydrophilicity. The matrix seemed to possess more uniformly dispersed fillers and single phase smoother surface in which TPU and NR were almost indistinguishable. It can be seen that particle distribution is also enhanced upon modification. Thus, we can correlate the morphology with the transport properties of the composites.

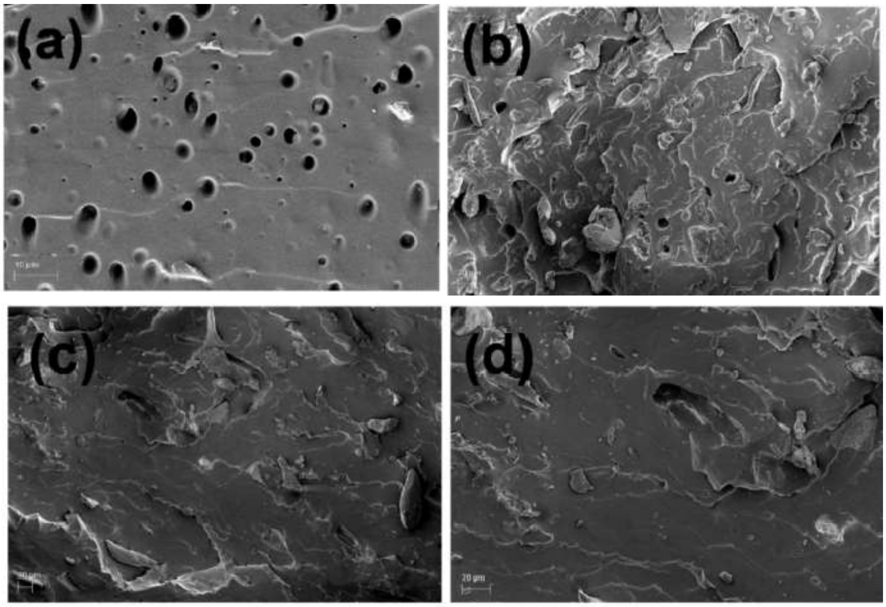

Figure 5.15: SEM of (**a**) TN blend (**b**) 10 phr UCSP loaded TN blend-composite (**c**) 10 phr T-CSP loaded TN blend-composite (**d**) 10 phr G-CSP loaded TN blend-composite.

5.3 Conclusions

The transport behaviour of TN vulcanizates with unmodified and silane treated fillers had been studied using three aromatic solvents benzene, toluene and xylene and three petroleum fuels petrol, kerosene and diesel with temperature variation. Influence of filler concentration, effect of modification, penetrant size and effect of temperature were evaluated using different parameters such as mol % uptake, kinetic parameters, Arrhenius parameters and thermodynamic parameters. Mol % uptake data suggested that as the filler loading increased, the ability of solvent penetration into the matrix decreased, because the filler aggregates effectively screened the penetrant molecules into the bulk. Between unmodified and treated fillers, the latter one showed better solvent resistance evidently because of the enhanced compatibility with matrix obtained after the treatment. All the three kinetic parameters diffusion coefficient, sorption coefficient and permeation coefficient decreased as a function of concentration of fillers. It was observed that, as the size of the penetrant molecule increased, the solvent uptake decreased in the order benzene > toluene > xylene and petrol > kerosene > diesel because the bulky side groups and long carbon chains reduced the ease of exchange of position with polymer chains and penetrant molecule. Temperature was found to be activating the diffusion process. The detailed study of transport mechanism showed that the transport mechanism was Fickian and close to Fickian for aromatic solvents and less Fickian for petroleum fuels. The % swelling of composites in oils were influenced by various factors such as filler loading, nature of fillers, nature of the penetrating oil and temperature. Oil resistance studies in petroleum based reference oils IRM 901, IRM 902 and IRM 903 oils revealed that incorporation of CSP improved the oil resistance property. The modified interface between filler and matrix enhance the oil resistant properties. All samples exhibited higher swelling in IRM 903 oil than that in IRM 901 or 902. The knowledge of behaviour of CSP filled TN blend-composites in an external liquid environment obtained from this study is essential when designing the barrier materials or tubes for the transportation of solvents with these composites. Morphological analysis using SEM affirmed the above findings.

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Chapter-6

Aging and biodegradability studies of coconut shell powder (CSP) filled thermoplastic polyurethane/natural rubber (TN) blend-composites

Abstract: *This chapter discusses the aging and biodegradation of different CSP loaded TN blend-composites under various conditions. Aging studies included oil-aging, thermal aging and water-aging. Addition of CSP to the TN blend improved the aging properties. Chemical treatment with silanes further enhanced the resistance to aging of the samples. The results were well supported with SEM analyses. Biodegradation analysis included soil-burial test and morphological analysis. A significant weight loss and reduction in mechanical strength were observed with CSP filled TN blend-composites. Water-sorption test and water-aging tests supported biodegradation results. The developed natural filler reinforced composites were found to be ecofriendly materials.*

6.1 Introduction

The concept of biodegradability of polymers has achieved an appreciable growth during past decades due to environmental concerns associated with the wide spread use of conventional non-degradable polymers. Modification of synthetic non-degradable polymers with naturally occurring biodegradable materials has been gaining momentum, since they combine the properties such as biodegradability, durability, processability, strength and cost-effectiveness. Biodegradable polymers are so designed that they degrade upon disposal by the action of micro organisms. Lignocellulosic composites degrade easily when exposed to nature, with the action of microbes, chemicals, heat, water, *etc*. However, these composites are supposed to have an effective service life, and after the use, they are capable of undergoing natural degradation.

Aging studies such as oil aging, thermal aging and water sorption are some of the standard methods to define the end-use of a polymer composite. Knowledge of oil-resistance of composites are significant for their applications in many fields, such as automobile, aerospace and machinery industry, since a variety of components may come into contact with oils and greases. In many cases, including hoses, rollers and seals, it is important that they are able to withstand the fluids without losing their properties at elevated temperature [1-2]. Many researchers focussed on the oil-resistant properties of polymer blends and composites [3-5].

Physical properties of polymeric materials are degraded by aging caused by surrounding temperature, humidity or water, or any other environmental factors. During thermal ageing of rubbers, the phenomena like main chain scission, crosslink scission, crosslink formation, *etc.*, take place. It is also possible that the existing crosslinks may break down and a more stable crosslink be formed. The extent of change in properties is governed by the relative ratios and magnitude of the above reactions [6]. Moisture is a known factor of the aging of the composites. In general, aging of composites and interface may cause the failure of properties. Therefore, this chapter mainly focuses on the investigation on the aging effects of the prepared composites by various factors like liquids, heat, water and soil.

6.2 Results and discussions

The aging resistance is expressed as a percentage of retention in tensile properties calculated by the following **equation 6.1**, [7]

$$Retention\ (\%) = \frac{Value\ after\ aging}{Value\ before\ aging} \times 100 \qquad \textbf{(Eq: 6.1)}$$

6.2.1 Oil-aging

6.2.1.1 Tensile test

Oil-aging was mainly studied by noting the changes in tensile strength, elongation at break (EB %), hardness and modulus. Therefore, the results of oil-resistance based on the changes in tensile strength, EB %, modulus and hardness of CSP filled TN blend-composites after oil immersion are represented in **table 6.1**. It can be seen that, all values decrease after oil-immersion. But the extent of decrease tends to go down with increase in filler loading.

Table 6.1: Tensile strength, EB %, modulus and hardness of CSP filled TN blend before and after oil aging for 70 h at room temperature.

Sample	Before aging				After aging			
	TS (Mpa)	**EB (%)**	**M100 (Mpa)**	**Hardness (Shore A)**	**TS (Mpa)**	**EB (%)**	**M100 (Mpa)**	**Hardness (Shore A)**
TN	1.56	221	0.43	46	0.81	140	0.42	41
U5	2.42	228	0.56	48	1.36	151	0.6	43
U10	2.83	235	0.86	52	1.67	162	0.95	47
U15	2.18	210	0.82	53	1.33	152	0.91	48
U20	1.87	185	0.65	55	1.2	141	0.74	50
T5	2.64	234	0.73	50	1.53	160	0.81	45
T10	3.01	242	1.03	55	1.81	177	1.15	50
T15	2.2	216	0.97	56	1.41	164	1.09	51
T20	2.09	201	0.92	59	1.38	161	1.06	55
G5	2.77	241	0.91	51	1.63	169	1.02	47
G10	3.58	266	1.26	57	2.26	200	1.42	53
G15	2.45	225	1.17	58	1.58	176	1.33	55
G20	2.31	213	1.07	60	1.6	177	1.25	57

The effect of oil aging at room temperature for 70 h on the percentage of retention in tensile strength of the composites, after being immersed in hydrocarbon oil (IRM 903) is shown in **figure 6.1**.

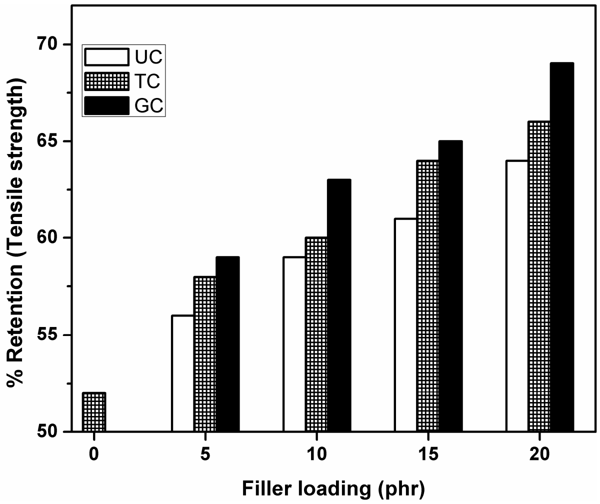

Figure 6.1: Percentage retention in tensile strength of CSP filled TN blend-composites after being immersed in hydrocarbon oil (IRM 903) for 70 h at room temperature. (UC - UCSP filled TN blend-composites; TC - TCSP filled TN blend-composites; GC - G-CSP filled TN blend-composites)

There was a remarkable difference in their retention strength. The percentage retention for silane treated CSP filled TN was higher, whereas it was lower for UCSP filled TN blend-composites and TN blend. The filler-rubber interaction was remarkably improved in the case of the silane treated CSP filled TN (due to the presence of the silyl groups that effectively couple the matrix and filler) compared with UCSP filled TN blend-composite, and thereby the percentage retention of the silane treated CSP filled composites was considerably higher than the UCSP filled composites. The filler-rubber interaction caused limitations in the ease of penetration of oil into the rubber chains [8]. As expected, retention of tensile strength on oil resistance was higher in GPTMS treated CSP (G-CSP) filled TN composites compared with the TEVS treated CSP (T-CSP) filled TN composite due to the better interaction between matrix and filler and made it more difficult for oil to diffuse into the voids between the rubber chains and increased the percentage retention. **Figure 6.2** represents the % retention in EB of CSP filled TN composites, after being immersed in IRM 903 oil for 70 h at room temperature with filler loading. It can be seen that all samples show a decrease in EB after the oil immersion [9].

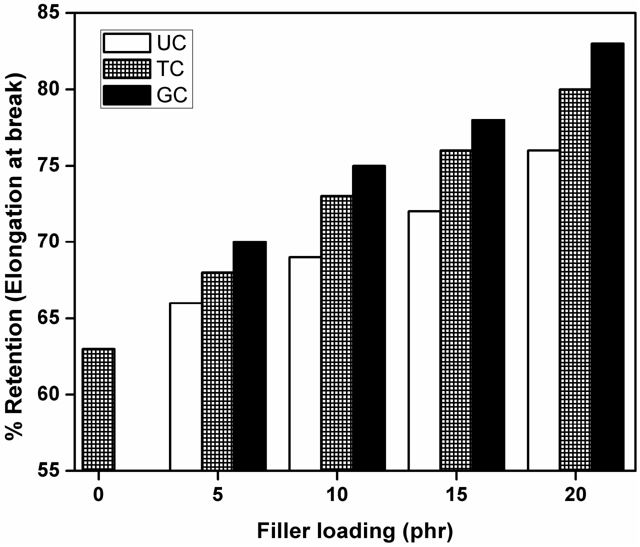

Figure 6.2: Percentage retention in EB of the filled TN blend - composites after being immersed in hydrocarbon oil (IRM 903) for 70 h at room temperature.

Hardness showed a significant decrease as shown in **figure 6.3**. The composites became soft after oil-immersion. The reduction in retention of hardness of the composites, after being immersed in both oils, may be due to the diffusion of oil molecules through the rubber phase.

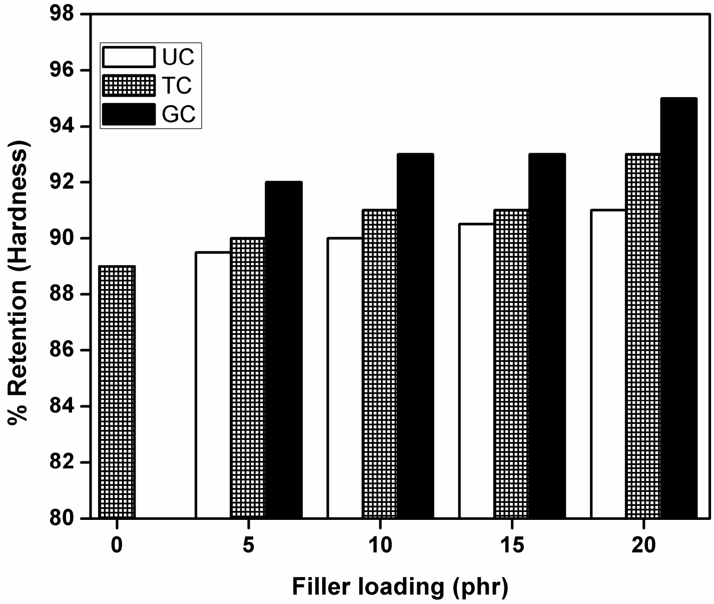

Figure 6.3: Percentage retention in hardness of the filled TN blend-composites after being immersed in hydrocarbon oil (IRM 903) for 70 h at room temperature.

Modulus at 100 % also shows the same trend as that of hardness (**table 6.1**). As expected, the lowest retention of hardness and tensile modulus is found for TN blend and the highest retention value is found for G-CSP filled composites. The order of maximum retention of tensile modulus and hardness was G-CSP filled composites > T-CSP filled composites > UCSP filled composites > TN blend. As discussed before, this is due to the better interaction of filler in the polar rubber matrix, which consequently resulted in less oil penetration into the rubber matrices. Similar results are offered by various researchers [7, 10].

6.2.1.2 SEM

Figures 6.4 and **6.5** represent the SEM images of typical tensile fractured surfaces of oil aged samples of TN blend and its composites of unmodified and modified composites. As shown in **figure 6.4**, TN blend is an immiscible blend, and the polarity difference between polar TPU and non-polar NR leads to greater interfacial tension which results in large number of micro-voids in the fractured surface. Here, not only these voids, but the oil occupied in these voids also affects the performance of the system as evident from the mechanical data. The diffusion of oil is very easier in TN blend due to the micro voids, and hence the oil immersion greatly affects the performance of the blend.

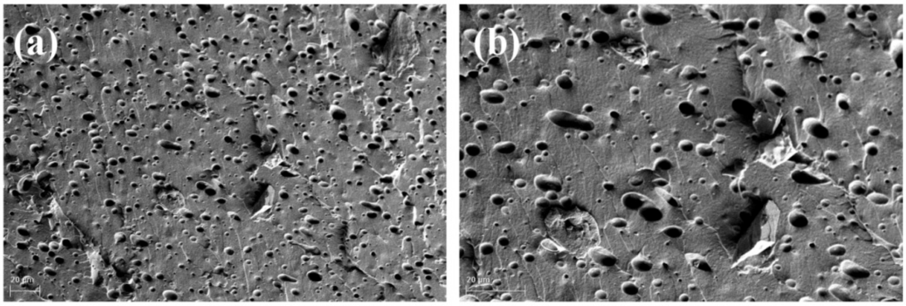

Figure 6.4: Tensile fractured images of oil aged TN blend for 70 h at room temperature at **(a)** magnification 1000 X **(b)** magnification 2000 X.

Figure 6.5 depicts the tensile fractured surface of 10 phr CSP filled TN blend-composites at two different magnifications 1000X and 3000X. It is widely known that, when the vulcanizates is exposed to oil, only the matrix portion is susceptible to degradation or swelling.

Increasing filler loading means the degradable polymer portion is diluted giving rise to higher oil resistances. In **figure 6.5 (a)** and **6.5 (b)**, it can be seen that, micro-voids are present, but with a lesser number than that of TN blend (**figure 4.7 (a)**) and oil is diffused through the voids. The decrease in number of micro voids confirms the improvement in retention of tensile values of UCSP composites after aging. The fibre pull-outs, fibre de-bondings, fibre breakage and matrix ruptures also can be seen, which occurred after the fracture test. The fracture after aging accompanies pull-out of fibres, leaving holes, which is clearly due to the poor adhesion between filler and matrix. The mechanical interlocking between the filler and matrix is very poor, because the surface of unmodified CSP is very smooth. This results in fast fibre de-bonding and pull-out during the fracture test.

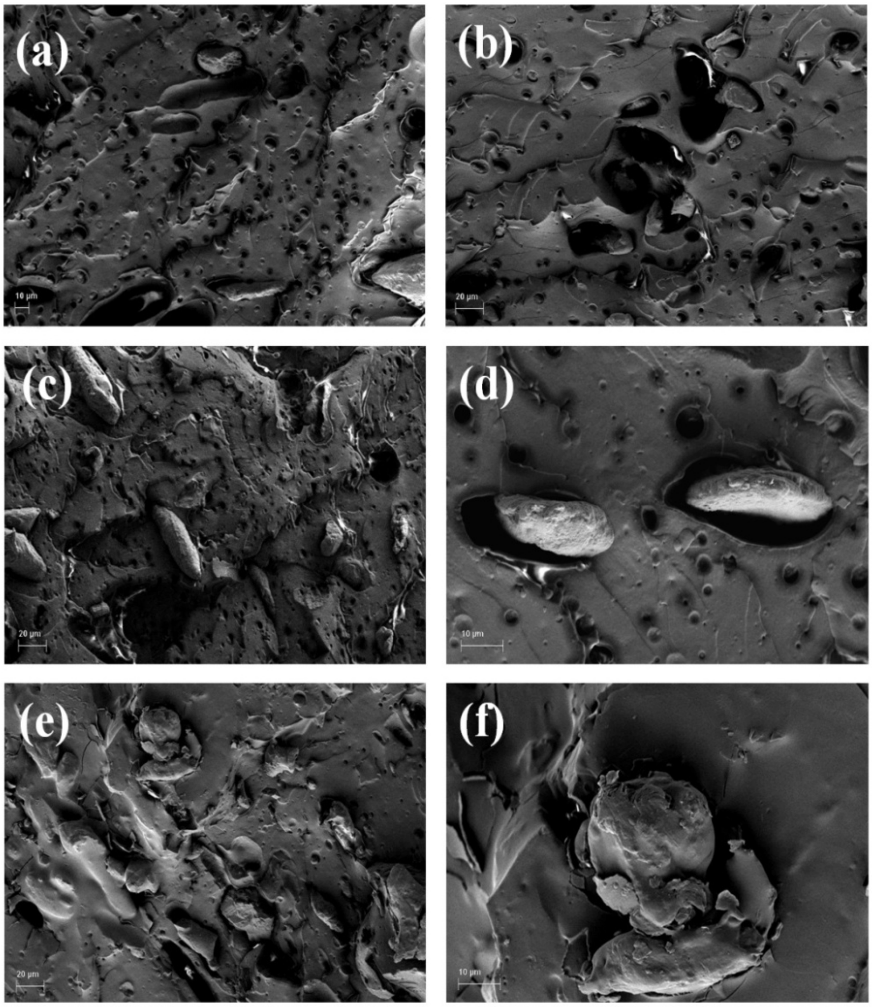

Figure 6.5: Tensile fractured images of oil aged samples for 70 h at room temperature (**a** and **b**) UCSP 10 phr filled TN blend-composite; (**c** and **d**) T-CSP 10 phr filled TN blend-composite; (**e** and **f**) G-CSP 10 phr filled TN blend-composite.

Figure 6.5 (c) describes the improvement in the morphology of fractured surface of T-CSP filled composites. The texture of micro voids is improved in a way to decrease the oil-diffusion through the sample. Fibre pull-outs are less compared to that of UCSP filled composites. Modified interface can be seen in **figure 6.5 (d)**, which helps in the retention of tensile test values of the composites. The surface shown in **figure 6.5 (e)** is a much improved when compared to that of **figure 6.5 (a)** and **6.5 (c)**. Number of micro-voids is almost nil, and hence oil-diffusion through the voids is practically not possible. The fibres are broken off near the surface and do not leave any voids in the surface. This observation gives the evidence for the improved interfacial adhesion between the phases. Filler particles are coated by the layers of matrix material that reduce the gaps between the fibre and matrix significantly. The treatment further reduces the cracks and the surface appeared to be more homogeneous. The gap between G-CSP particle and matrix is almost nil in the **figure 6.5 (f).** The improvement in interface substantiates the improved retention in mechanical performance of the treated composites.

6.2.2 Thermal aging

6.2.2.1 Tensile test

The results of thermal-resistance based on the changes in tensile strength, EB %, modulus and hardness of CSP filled TN blend-composites after aging in an air circulated aging chamber at 100 °C for 24 h are represented in **table 6.2**. It can be seen that tensile strength and elongation values decrease after aging, but M100 and hardness values were found to show a small increase.

Table 6.2: Retention in tensile strength, EB %, modulus and hardness of CSP filled TN blend-composites after thermal aging for 24 h at 100 °C.

Sample	Before aging				After aging			
	TS (Mpa)	EB (%)	M100 (Mpa)	Hardness (Shore A)	TS (Mpa)	EB (%)	M100 (Mpa)	Hardness (Shore A)
TN	1.56	221	0.43	46	0.89	168	0.44	45
U5	2.42	228	0.56	48	1.45	180	0.63	49
U10	2.83	235	0.86	52	1.75	195	0.98	54
U15	2.18	210	0.82	53	1.4	179	0.93	56
U20	1.87	185	0.65	55	1.25	164	0.75	58
T5	2.64	234	0.73	50	1.61	197	0.82	51
T10	3.01	242	1.03	55	1.9	208	1.23	57
T15	2.2	216	0.97	56	1.47	189	1.16	59
T20	2.09	201	0.92	59	1.44	181	1.11	62
G5	2.77	241	0.91	51	1.75	205	1.06	53
G10	3.58	266	1.26	57	2.43	232	1.57	60
G15	2.45	225	1.17	58	1.72	201	1.48	62
G20	2.31	213	1.07	60	1.69	194	1.4	64

Figure 6.6 shows that all the composites, after thermal aging at 100 °C for 24 h in air, exhibited reduction in tensile strength, compared to before aging, indicating thermal degradation of the matrixes of the rubbers. The decline in tensile strength for these materials could be attributed to the natural rubber of 80 % in the TN blend which can react with oxygen, thus leading to chain scission or reduced crosslink formation between the rubber chains [11] . The G-CSP filled TN blend-composite possessed the highest retention in tensile strength; followed by T-CSP filled TN blend-composite, UCSP filled TN blend-composites and TN blend. Furthermore, excessive main chain scissions of NR from TN blend, resulted in a reduced tendency to crystallize with increasing temperature. As discussed earlier, strong interaction between the silyl groups on the silyl treated

CSP provides better distribution and wetting of the fillers in the matrix and leads to good thermal stability.

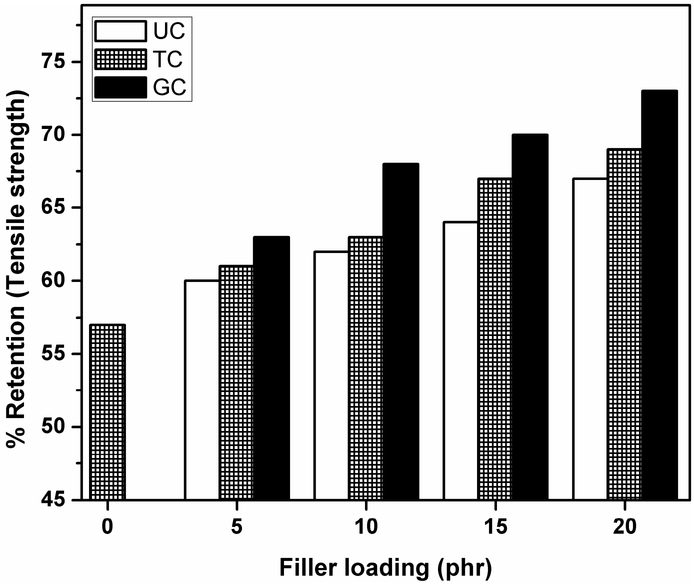

Figure 6.6: Percentage of retention in tensile strength of CSP filled TN blend-composites after thermal aging for 24 h at 100 °C.

Figure 6.7 explains the % retention in EB of CSP filled TN blend-composites after thermal aging for 24 h at 100 °C. As expected, retention of EB increases with increase in filler loading. The matrix portion available for thermal degradation is less for 20 phr loaded sample, and hence, the retention in property is higher for higher filler loaded samples. Chemical modification also has got a significant impact on thermal aging. Silane treated CSP filled composites show better retention than that of unmodified CSP filled composites, which evidently due to the better interactions between silyl modified filler particles and matrix.

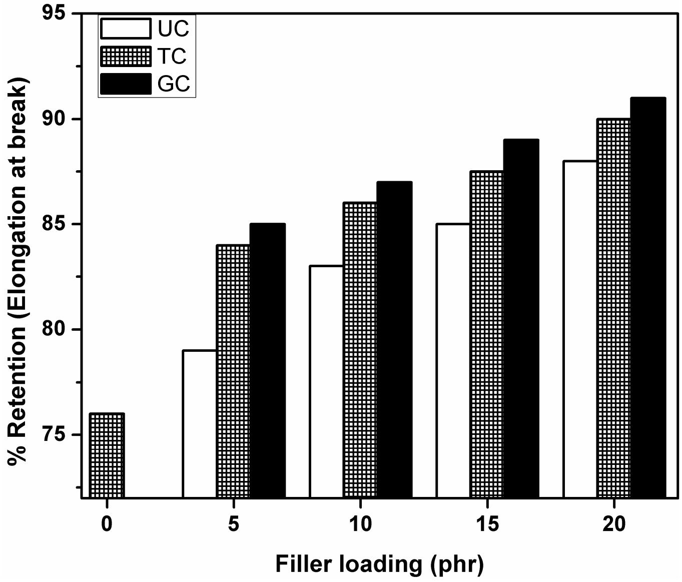

Figure 6.7: Percentage of retention in EB of CSP filled TN blend-composites after thermal aging for 24 h at 100 °C.

On the other hand, all the vulcanizates showed an increase in tensile modulus and hardness after thermal aging, as depicted in **figure 6.8**. Natural rubber from the blend reacted with oxygen resulted in chain scission or the oxidative breakdown during thermal aging. This resulted in the generation of rubber macro-radicals, which on recombination with the rubber macro-radicals form rubber chains with some degree of branching [7]. Thus, the composites would become stiffer resulting in higher tensile modulus and hardness. From **figure 6.8**, it can be seen that the retention of the tensile modulus and hardness of G-CSP filled TN blend-composites showed a higher value than all other composites. This is likely due to the strong interaction between filler and matrix which tends to restrict the flexibility of the rubber chains [12]. It is widely known that, when the rubber vulcanizates is exposed to high temperature or oil, only the rubber portion is susceptible to degradation or swelling. Increasing filler loading means the degradable rubber portion is diluted giving rise to higher thermal aging and oil resistance.

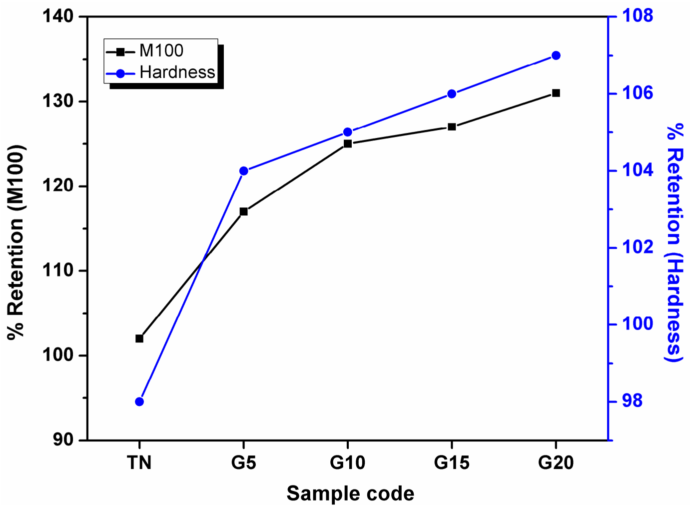

Figure 6.8: Percentage of retention in hardness and M100 of CSP filled TN blend-composites after thermal aging for 24 h at 100 °C.

6.2.3 Water aging

6.2.3.1 Water sorption test

The water absorption of the CSP filled TN blend-composites are shown in **figures 6.9 (a-c)**. In which the effect of filler loading and filler surface treatment on water absorption behaviour of the composites are shown. Basically, the water absorption test provides important information regarding the adhesion property between the fibres and the matrix [13]. In these plots, water absorption is plotted against the number of soaking days. It can be observed that the water absorption of all the composites increases with the growth of time. However, the water absorption of the silane treated CSP filled composites decreases obviously due to the chemical treatments. This is because the higher the adhesion between fibres and matrix, the probability for the water to absorb through the sites becomes limited [14]. The alkaline treatment could remove hydrophilic components (lignin and wax) of the CSP and silane treatment provides hydrophobic coating to the surface of CSP, which prohibited the water infiltration effectively. As a result, the UCSP filled composite shows the highest water absorption as in **figure 6.9 (a)**.

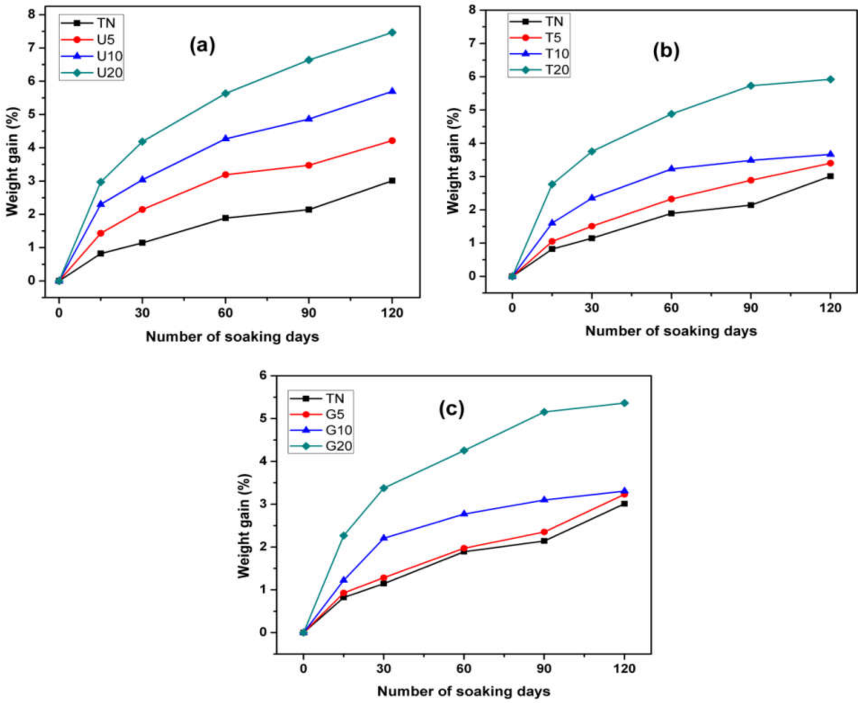

Figure 6.9: Water sorption behaviour of (**a**) UCSP filled TN blend-composites; (**b**) T-CSP filled TN blend-composites; (**c**) G-CSP filled TN blend-composites.

The water absorption behaviour of TEVS treated CSP reinforced composite and GPTMS treated CSP composites are lower than that of untreated fibre reinforced polymer composite, which is shown in **figure 6.10** [15]. After the fibre modification, the applied silane reduces the amount of hydroxyl groups which were free to bind moisture [16]. It can be observed that the surface treatment of fibre reduces the water absorption, but increases wettability of fibre with resin and interfacial bond strength has improved besides increasing the dimensional stability of the composites [17-18].

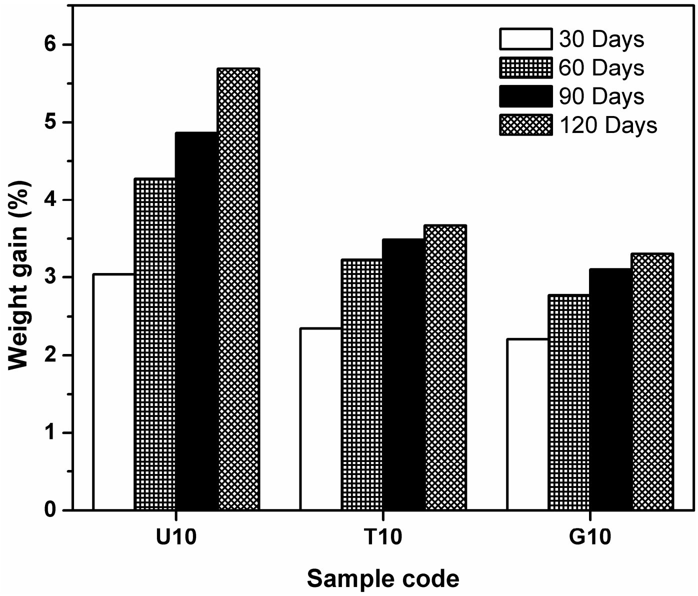

Figure 6.10: Effect of chemical treatments on the water gain (%) of 10 phr loaded CSP filled TN blend-composites.

6.2.3.2 Tensile test

Tensile strength and EB % of CSP filled TN blend-composites before and after aging in water for 30 days at room temperature, were shown in **table 6.3**. Unlike oil or thermal aging, decrease in tensile strength and EB were found to be increasing with increase in filler loading [19-20]. TN was the least affected sample on water aging, which shows 93 % retention after the aging. As explained in **section 6.2.3.1**, hydrophilic nature of filler is responsible for the deterioration in properties with increase in filler.

Table 6.3: Tensile strength (TS) and EB % of CSP filled TN blend-composites before and after aging in water for 30 days at room temperature.

Sample	Before aging		After aging	
	TS (Mpa)	EB (%)	TS (Mpa)	EB (%)
TN	1.56	221	1.45	210
U5	2.42	228	1.89	171
U10	2.83	235	1.98	169
U20	1.87	185	1.22	117
T5	2.64	234	2.22	189
T10	3.01	242	2.26	186
T20	2.09	201	1.44	137
G5	2.77	241	2.44	202
G10	3.58	266	2.86	218
G20	2.31	213	1.64	149

UCSP is highly hydrophilic in nature and absorb more water with time. Mechanical properties were found to decrease as the UCSP loading increased. 20 Phr loaded UCSP filled sample shows the lowest relative tensile strength and relative EB values after immersion in water for 30 days, which is shown in **figure 6.11** and **6.12** respectively.

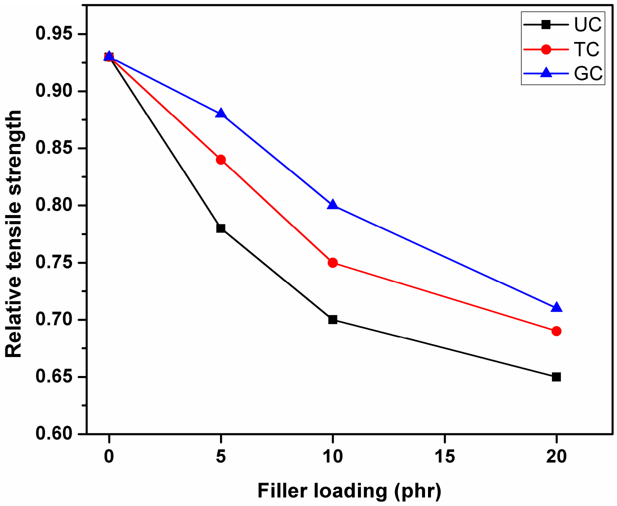

Figure 6.11: Effect of chemical treatment and filler loading in relative tensile strength of CSP filled TN blend composites after aging in water for 30 days at room temperature.

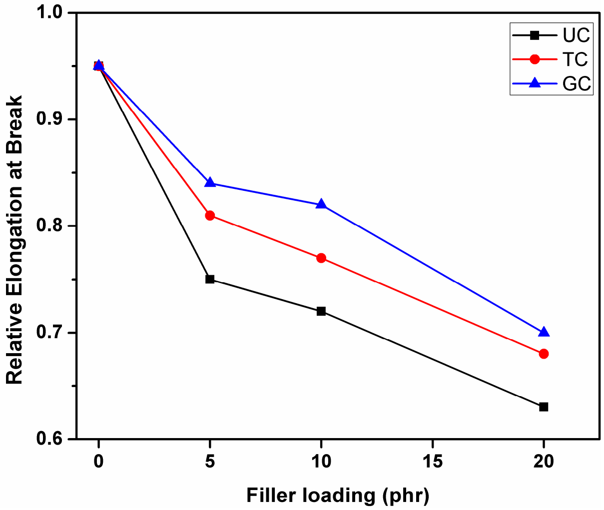

Figure 6.12: Effect of chemical treatment and filler loading in relative EB of CSP filled TN blend composites after aging in water for 30 days at room temperature.

With an increase in water gain, the adhesion between filler and matrix getting poor and leads to a failure in mechanical properties. At higher filler loading, water sorption leads to weak bonding between fillers and matrix. Void formation, adhesion properties, filler distribution, and other factors might also contribute in diminishing the mechanical properties of the composite materials.

Chemical modification shows a significant impact in the aging properties of CSP filled TN blend-composites. 5 Phr G-CSP filled composites show better retention in tensile strength and EB (88 % and 84 % respectively). Chemical treatment reduces the hydrophilicity of CSP and increase the wettabilty of filler with matrix which improves the interfacial bond strength and dimensional stability of composites [21].

6.2.4 Biodegradability

6.2.4.1 Weight loss test

The biodegradability of the samples was assessed by evaluating the weight loss of the samples over time in soil-burial experiment. **Table 6.4** represents the weight of the samples before and after soil-burial for 90 days.

Table 6.4: Weight of various CSP filled TN blend-composites before and after soil-burial for 90 days.

Filler loading	UCSP composites		T-CSP composites		G-CSP composites	
	Initial weight (g)	Weight after 3 months (g)	Initial weight (g)	Weight after 3 months (g)	Initial weight (g)	Weight after 3 months (g)
0	1.7299	1.7083	-	-	-	-
5	1.8241	1.6928	1.8432	1.7363	2.0184	1.9369
10	1.8578	1.6516	1.7906	1.6527	2.0935	1.9511
20	1.8043	1.4669	1.8439	1.6623	2.0041	1.8458

Figure 6.13 represents the % weight loss of CSP filled TN blend-composites after soil burial for 90 days. It can be seen that weight loss depends on the filler content, which facilitates the degradation. TN blend without any filler retains the maximum weight after soil-burial [22]. Maximum weight loss is for sample with 20 phr UCSP loaded TN blend-composite. Due to the microbes present in soil, composites undergo disintegration resulting in reduction of weight loss [23]. Needless to say those other environmental factors also contribute in biodegradation phenomena.

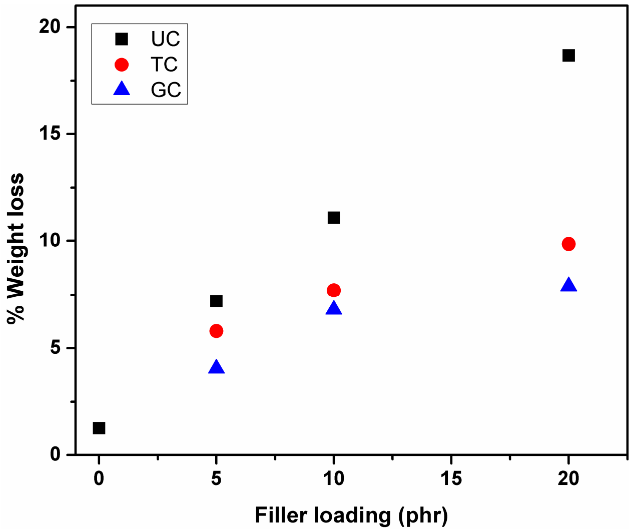

Figure 6.13: % Weight loss of CSP filled TN blend-composites after soil burial for 90 days.

Effect of chemical treatment of CSP on the % weight loss of composites after soil burial is shown in **figure 6.14**. UCSP filled TN blend-composites suffer maximum weight loss. As evident from the **figure 6.14**, silane treated CSPs were more resistant to biodegradation. GPTMS treatment was found to show better resistance than TEVS treatment. This is plausibly because of the difference in hydrophilicity shown by CSP after these treatments. G-CSP was less hydrophilic than T-CSP. Hydrophilicity is an important factor which facilitates the biodegradation [10].

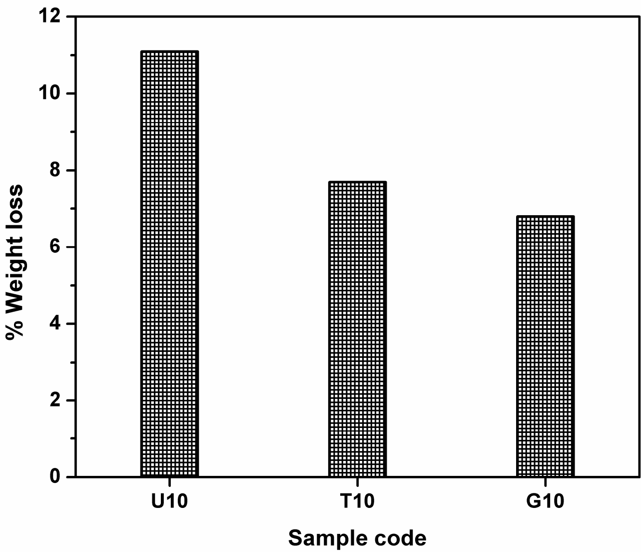

Figure 6.14: Effect of chemical treatment on % weight loss of CSP filled TN blend-composites after soil burial for 90 days.

6.2.4.2 Tensile test

Deterioration in mechanical properties is a well explained indicator of degradation [24-25]. Results of biodegradability test in terms of change in tensile strength and hardness after soil-burial for 90 days are summarized in **table 6.5**. Tensile strength and hardness were found to be decreasing after soil burial.

Table 6.5: Tensile strength (TS) and hardness of CSP filled TN blend-composites before and after soil-burial for 90 days.

Sample	Before soil burial		After soil burial	
	TS (Mpa)	**Hardness (Shore A)**	**TS (Mpa)**	**Hardness (Shore A)**
TN	1.56	46	1.33	45
U5	2.42	48	1.16	44
U10	2.83	52	1.13	47
U20	1.87	55	0.58	49
T5	2.64	50	1.77	47
T10	3.01	55	1.87	51
T20	2.09	59	1.15	54
G5	2.77	51	1.99	49
G10	3.58	57	2.43	54
G20	2.31	60	1.41	56

Figure 6.15 represents the % loss in tensile strength of composites with respect to filler loading. % Loss is minimum for TN blend that means it is the least affected by microbial action. % Loss is higher for UCSP filled composites of TN blend.

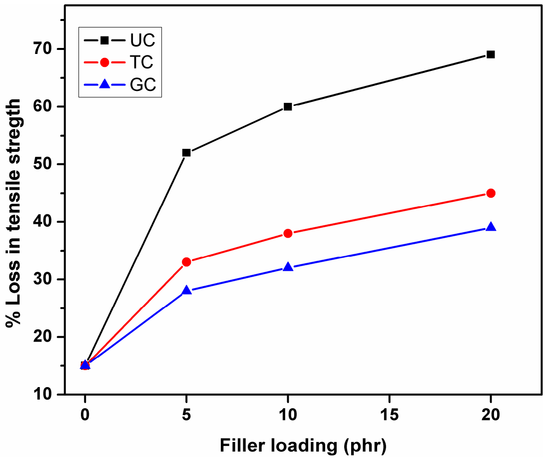

Figure 6.15: % Loss of tensile strength of CSP filled TN blend-composites after soil burial for 90 days.

Effect of filler loading on the biodegradation of composites was shown in **figure 6.16**. As the filler content increases, weight loss and degradation also increase, which results in lowering the tensile strength. Filler content makes the composites more susceptible to microbial action and leads to weakening and disintegration in polymer segments [26-27].

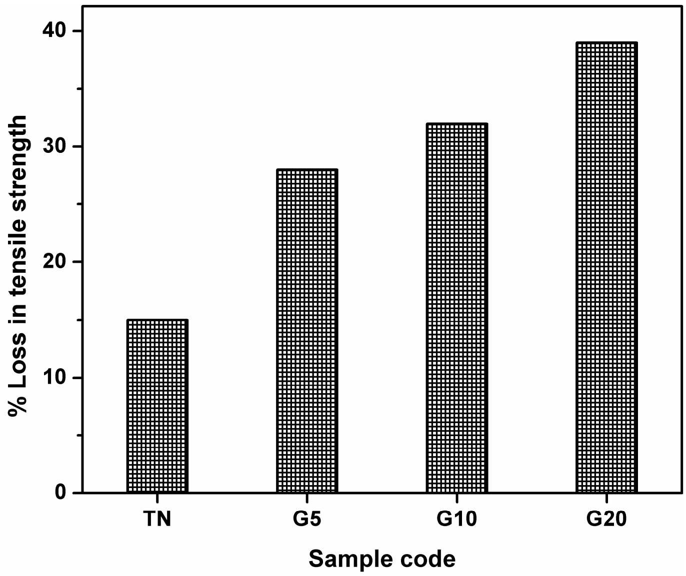

Figure 6.16: Effect of filler loading on % loss of tensile strength of CSP filled TN blend-composites after soil burial for 90 days.

Effect of chemical treatment on % loss of tensile strength of CSP filled TN blend-composites are shown in **figure 6.17**. Chemical modification of filler surface using silane coupling agents improves the interfacial adhesion between filler and matrix and hence, shows a remarkable decrease in % loss in tensile strength.

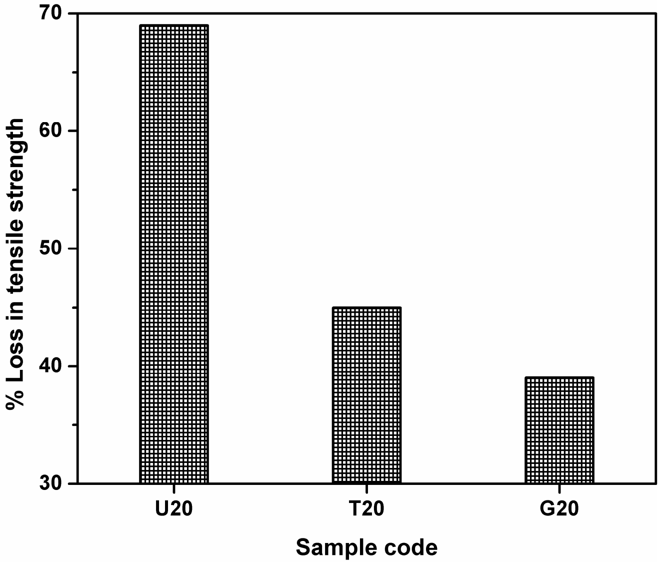

Figure 6.17: Effect of chemical treatment on % loss of tensile strength of CSP filled TN blend-composites after soil burial for 90 days.

% Loss in hardness of CSP filled TN blend-composites after soil burial is depicted in **figure 6.18**. As expected, loss in hardness increases with increase in filler loading. Higher CSP loaded samples are more affected by microbial attack. Silane treatment significantly influences the % loss in hardness after biodegradability because of the efficient interfacial adhesion provided by treated fillers. Similar findings were reported elsewhere [28-29].

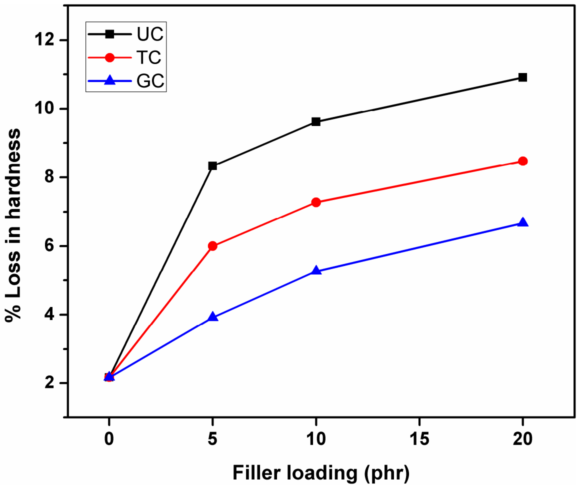

Figure 6.18: % Loss of hardness of CSP filled TN blend-composites after soil burial for 90 days.

6.2.4.3 SEM

Scanning electron microscopy is one of the established methods to analyse the extent of biodegradation [22, 30-31]. **Figure 6.19** shows the SEM images of TN blend before and after soil-burial for 90 days. **Figure 6.19 (a)** shows a relative smooth surface. After soil burial, as seen in **figure 6.19 (b)**, although some cracks, grooves and micro voids were appeared, the microbial attack is not prominent.

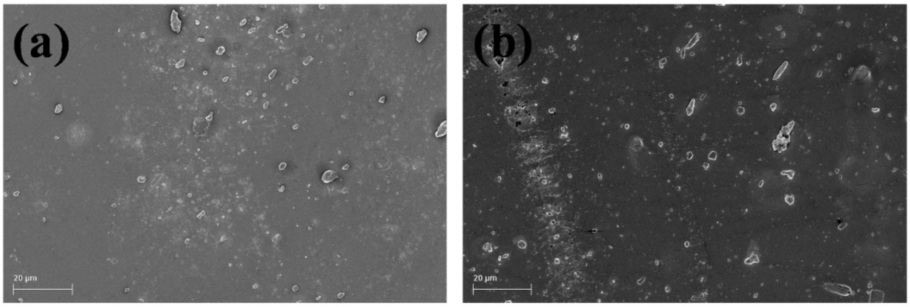

Figure 6.19: Surface images of TN blend (**a**) before soil burial (**b**) after soil burial of 90 days

Figure 6.20 shows the biodegraded surface images of 10 phr UCSP filled TN blend-composite, 10 phr T-CSP filled TN blend-composite and 10 phr G-CSP filled TN blend-composite respectively. Among these, **figure 6.20 (a)** displays severe degradation than the others. Microbial action and surface degradation is visible, which is inevitably due to presence of unmodified CSP. Comparatively less degradation was observed with T-CSP filled composites and G-CSP filled composites [**Figure 6.20 (b** and **c**)]. But, the surface roughness was well observed in all the three cases. It is clear from the figures that, G-CSP filled composites show better resistance to microbial attack than T-CSP filled composites. This is essentially due to the better interfacial adhesion between G-CSP with matrix.

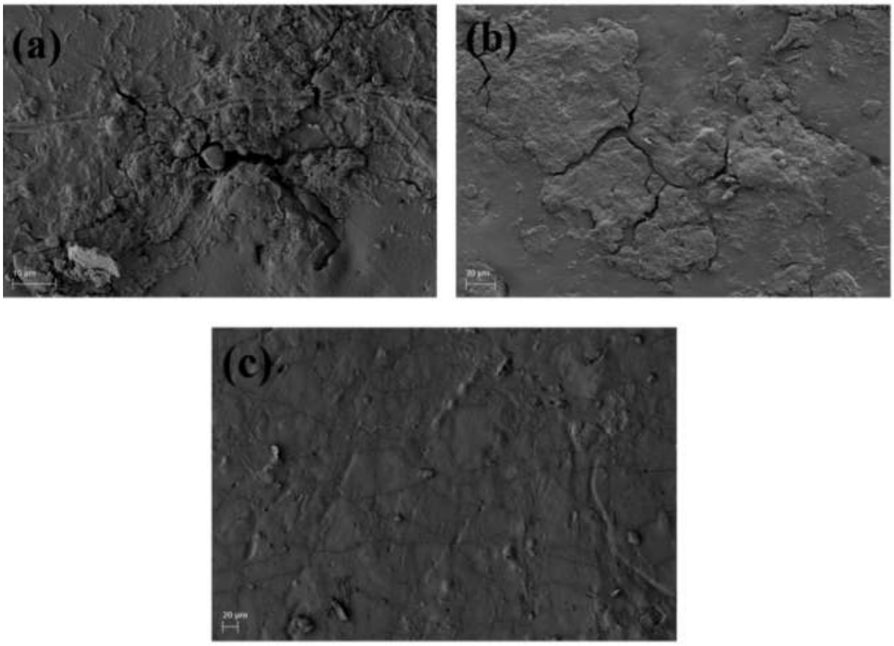

Figure 6.20: Surface images of (**a**) 10 phr UCSP filled TN blend-composite after soil burial of 90 days; (**b**) 10 phr T-CSP filled TN blend-composite after soil burial of 90 days; (**c**) 10 phr G-CSP filled TN blend-composite after soil burial of 90 days.

From the mechanical testing data, it was concluded that, resistance to biodegradation decreases with increase in filler loading. It is well-supported with SEM images of 20 phr CSP loaded TN blend-composites. **Figure 6.21 (a, b** and **c)** represent the surface of 20 phr UCSP filled TN blend-composite, 20 phr T-CSP filled TN blend-composite and 20 phr G-CSP filled TN blend-composite after soil burial of 90 days.

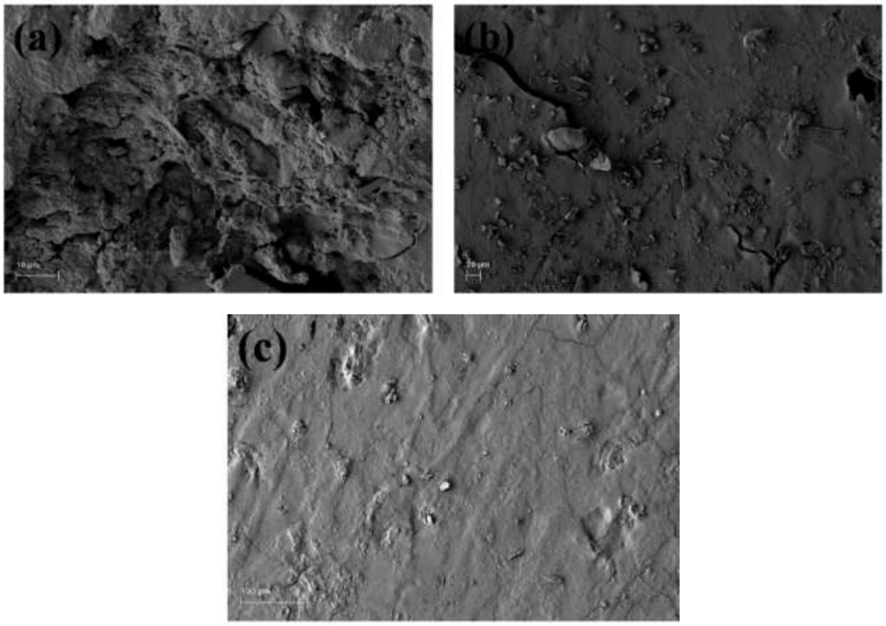

Figure 6.21: Surface images of (**a**) 20 phr UCSP filled TN blend-composite after soil burial of 90 days; (**b**) 20 phr T-CSP filled TN blend-composite after soil burial of 90 days; (**c**) 20 phr G-CSP filled TN blend-composite after soil burial of 90 days.

Surface erosion is higher when compared to that of 10 phr loaded samples. The extent of biodegradation was increased with the addition of natural filler, which is prone to microbial attack. UCSP filled composites were the most affected samples undergoing biodegradation. Chemical modification reduced the extent of biodegradation of fillers not only by acting as a protective covering, but by increasing the strength of interface via coupling with filler and matrix. The SEM micrographs substantiate the results obtained from tensile and hardness studies after biodegradation tests.

6.3 Conclusions

This chapter assessed the aging and biodegradation of different CSP loaded TN blend-composites under various conditions. Oil-aging of samples in IRM-903 oil for 70 h was carried out and the results can be concluded as, mechanical properties such as tensile strength, elongation at break, tensile modulus and hardness decreased after oil-immersion. But the addition of filler and chemical modification of filler with silane coupling agents were found to improve the oil-resistance of composites. This could be explained by (i) dilution effect of filler, *i.e.*, increasing filler content reduced the degradable polymer portion and (ii) strong interaction between filler and matrix restricted the oil diffusion into the matrix respectively. The results were well supported with SEM analyses. Thermal aging of samples at 100 °C for 24 h also gave similar results as that of oil-aging, but with a difference that, tensile modulus and hardness increased after thermal aging indicating an increase in material stiffness.

Water aging and water sorption test showed different results than oil aging and thermal aging studies. From water sorption results, it was found that water sorption increases with addition of hydrophilic filler. At higher filler loading, water sorption led to weak bonding between filler and matrix. Again, chemical treatment of fillers improved the water resistance. Tensile test results of different CSP filled TN composites after the immersion at room temperature for 30 days confirmed the sorption test results. Higher filler loaded samples showed poor retention of tensile strength and elongation at break after aging. TN blend without any filler showed higher resistance to water aging. Since the chemical treatment with silane coupling agents improved the hydrophobicity of CSP, water aging of treated CSP composites also was improved.

Biodegradability of CSP filled TN blend-composites was assessed using weight loss test and tensile test after a soil-burial for 90 days. It was found that degradation was dependent upon filler loading and chemical treatment of fillers. More weight loss and loss in tensile strength were occurred to unmodified CSP filled composites. Increase in filler loading was found to increase the degradation. Silyl treated CSP filled composites were less prone to biodegradation. SEM analyses and hardness test affirmed the results obtained from tensile test after biodegradation.

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Chapter-7

Conclusions and Future Outlook

Abstract: *This chapter deals with the major findings of the investigation on coconut shell powder (CSP) reinforced TPU/NR (TN) blend-composites. The scope for the further studies on these composites has also been discussed.*

7.1 Conclusions

Blends of thermoplastic materials with elastomers are of enormous applications in industry as they possess excellent mechanical properties of conventional vulcanized elastomers together with processability of thermoplastics. Conventional reinforcing fillers such as carbon black, silica, metal oxides, *etc.* have already proven their efficiency as reinforcing agents. The search for sustainable, non-petroleum based, energy saving, economical and environmental friendly fillers led to various bio-based fillers of plant origin and animal origin. Biocompatibility, biodegradability and cost-effectiveness are the unique advantages of natural fillers over conventional fillers. A systematic approach is attempted to study various properties such as cure characteristics, mechanical properties, sorption properties, thermal analysis, aging studies and biodegradation studies of unmodified and modified CSP reinforced TN in the present work.

Pre-treated CSP was chemically modified using silane coupling agents TEVS and GPTMS and evaluated using FT-IR, TG and SEM. Results showed that silyl moiety from the coupling agents were efficiently grafted to CSP. The treated CSP also possessed better filler geometry and thermal stability than unmodified CSP. TN blend-composites using unmodified and different silane treated composites were prepared and examined for the cure properties, crosslink density and rubber-filler interactions. Addition of CSP improved the cure properties, solvent resistance and crosslink density.

The tensile and tear properties of TN blend increased with increase in CSP, reached the maximum at 10 phr loading and then decreased. Between the unmodified and modified filler, modified CSP provided better phase morphology, better interfacial adhesion, higher reinforcing efficiency and better mechanical properties. The composites with GPTMS modified CSP showed better mechanical properties than that of TEVS which were in good agreement with SEM images. Even though addition of CSP improved the thermal stability of the blend, chemical modification did not have a much impact in the thermal stability of composites. Glass transition temperature (T_g) was improved with the addition of CSP through its effect in the free volume of the matrix. Increment in T_g observed with the use of silyl treated CSPs indicates that effective coupling was achieved between CSP and TN blend through the silane treatment which strengthen the interface between CSP and matrix.

The knowledge of behaviour of CSP filled TN blend-composites in an external liquid environment obtained from this study is essential when designing the barrier materials or tubes for the transportation of solvents with this composites. The transport behaviour of TN vulcanizates with unmodified and silane treated fillers had been studied using aromatic solvents and petroleum fuels at different temperatures. Influence of filler concentration, effect of modification, penetrant size and effect of temperature were evaluated using different parameters such as mol % uptake, kinetic parameters, Arrhenius parameters and thermodynamic parameters. Mol % uptake data suggested that as the filler loading increases, the ability of solvent penetration into the matrix decrease. Between unmodified and treated fillers, the latter one showed better solvent resistance evidently because of the enhanced compatibility with matrix obtained after the treatment. Kinetic parameters decreased as a function of concentration of fillers. It was observed that as the size of the penetrant molecule increased, the solvent uptake decreased because the bulky side groups and long carbon chains reduced the ease of exchange of position with polymer chains and penetrant molecule. Temperature was found to be activating the diffusion process. The transport mechanism was Fickian and close to Fickian for aromatic solvents and less Fickian for petroleum fuels. The % swelling of composites in oils were influenced by various factors such as filler loading, nature of fillers, nature of the penetrating oil and temperature. Oil resistance studies in petroleum based reference oils IRM 901, IRM 902 and IRM 903 oils revealed that incorporation of CSP improved the oil resistance property. The modified interface between filler and matrix enhanced the oil resistant properties. All samples exhibited higher swelling in IRM 903 oil than that in IRM 901 or 902.

Aging and biodegradation of different CSP loaded TN blend-composites under various conditions were also investigated. Oil-aging of samples in IRM-903 oil for 70 h was carried out and the results can be concluded as that, mechanical properties such as tensile strength, elongation at break, tensile modulus and hardness decreased after oil-immersion. But the addition of filler and chemical modification of filler with silane coupling agents were found to improve the oil-resistance of composites. The results were well supported with SEM analyses. Thermal aging of samples at 100 °C for 24 h also gave similar results as that of oil-aging, but with a difference that, tensile modulus and hardness increased after thermal aging indicating the increase in material stiffness. Water aging and water sorption test showed different results than oil aging and thermal aging studies. From water sorption results, it was found that water sorption increased with addition of hydrophilic filler. Chemical treatment of fillers improved the water resistance. Tensile test results of different CSP filled TN composites after the immersion in water at room temperature for 30 days confirmed the sorption test results. Higher filler loaded samples showed poor retention of tensile strength and elongation at break after aging. TN blend without any filler showed higher resistance to water aging. Since the chemical treatment with silane coupling agents improved the hydrophobicity of CSP, water aging of treated CSP composites also was improved.

Biodegradability of CSP filled TN composites were assessed using weight loss test and tensile test after a soil-burial for 90 days. It was found that degradation was dependent upon filler loading and chemical treatment of fillers. More weight loss and loss in tensile strength were occurred to UCSP filled composites. Increase in filler loading was found to increase the degradation. Silyl treated CSP filled composites were less prone to biodegradation. SEM analyses and hardness test affirmed the results obtained from tensile test after biodegradation.

7.2 Future outlook

Present work on CSP reinforced TN blend-composites suggests the need of advanced research in this area. Some recommendations include:

- To study the effect of chemical treatments using maleated coupling agents, acetylation and enzymes and physical treatments using corona treatment, plasma treatment and steam explosions on CSP reinforced TN blend-composites.
- To develop nanocomposites of TN blend using nanocellulose and nanolignin extracted from CSP using various methods.
- Fabrication and characterisation of TN blend-composites using other lignocellulosic fibres such as coir fibre, sisal fibres, *etc.*, and seed shell powders such as peanut shell powder and sago seed shell powder.
- Biodegradability studies using advanced methods such as enzyme hydrolysis.
- Pervaporation studies of the blend-composites to be done to examine their efficiency for the use as membranes.
- Comparison of mechanical properties of CSP filled TN blend-composites with composites filled with conventional fillers such as carbon black, silica, and metal oxides.
- Manufacture of products such as oil seals, gasket, cable insulations, *etc.*, can be attempted and tested.

APPENDIX

I. Refereed Journals

1. **Aparna K. Balan**, Sreejith M.P., Shaniba V., Jinitha T.V., Subair N., Purushothaman E. Coconut shell powder reinforced thermoplastic polyurethane/natural rubber blend-composites: effect of silane coupling agents on the mechanical and thermal properties of the composites.***Journal of Materials Science***, 2017;52(11), 6712-6725.

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II. Conference Proceedings

1. **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 Proceedings***, 2017; 1849 (1), 020046.

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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. **Aparna K Balan** and Purushothaman E. Molecular transport of aromatic solvents through filled thermoplastic polyurethane/natural rubber blends. ***Emerging Trends in Chemical Research***, Research & Post Graduate Department of Chemistry, Christ College Iringalakkuda, 28th Feb - 1st March, 2017.

2. **Aparna K Balan**, Sreejith M.P., Shaniba V., Jinitha T.V., Subair N. and Purushothaman E. Transport behaviour of aromatic hydrocarbons through coconut shell powder filled thermoplastic polyurethane/natural rubber blend composites. ***Optics '17-A Conference on Light.*** NIT Calicut, 9-11th January, 2017. **(Best poster award).**

3. **Aparna K Balan**, Sreejith M.P., Shaniba V. and Purushothaman E. Cure characteristics and tensile properties of coconut shell powder reinforced TPU/NR blend-composites. ***Advances in Materials Chemistry (AMC-2014)***.

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4. **Mehar Al Minnath, Aparna K Balan** and Purushothaman E. Biodegradability of TPU/NR and TPU/ENR blends and their chitin reinforced composites. 25th Kerala Science Congress, KSCSTE, 29th January – 1st February, 2013.

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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

Aparna K. Balan[1], Sreejith Mottakkunnu Parambil[1], Shaniba Vakyath[1], Jinitha Thulissery Velayudhan[1], Subair Naduparambath[1], and Purushothaman Etathil[1,*]

[1] *Department of Chemistry, University of Calicut, Malappuram, Kerala 673 635, India*

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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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Address correspondence to E-mail: purushotche@gmail.com

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

M.P.Sreejith, Aparna K Balan, V. Shaniba, E.Purushothaman*
Department of Chemistry, University of Calicut, Kerala, 673635, India
***Corresponding author: E-Mail: epurushot@yahoomail.com**

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.

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ORIGINAL PAPER

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

V. Shaniba[1] · **M. P. Sreejith**[1] · **K. B Aparna**[1] · **T. V. Jinitha**[1] · **E. Purushothaman**[1]

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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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✉ E. Purushothaman
epurushot@yahoo.com

[1] Department of Chemistry, University of Calicut, Malappuram (Dt), Kerala 673635, India

Crystallography: Special Emphasis on Applications in Chemistry
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Mechanical and transport properties of permanganate treated coconut shell powder – natural rubber composites

T.V. Jinitha, M.P. Sreejith, Aparna K Balan and E. Purushothaman*
Department of Chemistry, University of Calicut, Malappuram (Dt), Kerala 673635, India
***Corresponding author: E-Mail: epurushot@yahoo.com**

ABSTRACT

In the present work, modified coconut shell powder has been used as reinforcement material in natural rubber matrix. In order to improve their properties, the coconut shell powder was subjected to chemical treatment using potassium permanganate. Potassium permanganate of two different concentrations was used for chemical treatment. The cure characteristics and mechanical properties of the coconut shell powder (CSP) - natural rubber (NR) vulcanizates were studied at different filler loading of 0, 5, 10, 15 and 20 phr (parts per hundred). The effect of potassium permanganate treatment on the mechanical properties of CSP-NR composites was investigated. The tensile strength of both treated and untreated CSP-NR composites decreased with increase in filler loading. However the values were found to be higher than those of corresponding values of untreated ones. The chemical treatment increases the tensile strength, Youngs modulus, hardness and density. The transport properties of modified CSP-NR composites were studied using aromatic solvents like benzene, toluene and xylene. The effect of filler loading and permanganate treated fibers on the equilibrium swelling was investigated.

KEY WORDS: Composites, modified coconut shell powder, mechanical properties, transport properties.

1. INTRODUCTION

Growing attention is nowadays being paid to natural fiber reinforced composite due to their outstanding properties. Natural filler reinforced materials offer many environmental advantages such as reduced dependence on nonrenewable energy/material sources, lower pollution and green house emission. Natural fibers are hydrophilic in nature as they are derived from lignocelluloses which contain strongly polarized hydroxyl groups. Advantages of natural fillers over traditional ones are their low cost, high toughness, low density, good specific strength properties, reduced tool wear, enhanced energy recovery, CO_2 neutrality when burned and biodegradability (Ismail, 2002). These advantages make natural fibers potential replacement for glass fibers in composite materials.

The drawback of using natural fiber as a reinforcing material is their poor wetability, incompatibility with some polymeric matrices and high moisture absorption (Vazguez, 1999). Treatment of natural fillers is beneficial in order to improve the water resistance of fillers, enhance the wettability of natural filler surface by polymers and promote interfacial adhesion. Chemical modifications of natural fibers aimed at improving the adhesion with a polymer matrix were investigated by a number of researchers (Pual, 1997; Joseph, 1996; Sreekala, 2000; Ray, 2001, Mishra, 2001).

Coconut shell is the one of the most important natural fillers produced in tropical countries like Malaysia, Indonesia, Thailand, Sri Lanka and India. Coconut shell is the nonfood part of coconut, which is hard lignocellulosic agro- waste. Coconut shell is 15-20% of coconut (La Mantia, 2005). Coconut shell powder (*cocos nucifera*) is widely available at very low cost. So it is an ideal filler material in this regard. The utilization of CSP as lignocellulosic fillers in polymer composites becomes more favorable due to their high strength and modulus properties. The present work aims at investigating the prospect of using modified coconut shell powder as reinforcement in natural rubber matrix. The effect of chemical modification and filler loading on the mechanical and transport properties of NR- CSP composites have been studied.

2. EXPERIMENTAL

2.1. Materials: Coconut shell powder (CSP) used as filler obtained from Sip India Exporters Erode. It is reported to contain 29.4% lignin, 27.7% pentosans, 26.6% cellulose, 8% moisture, 0.6% ash, 4.2% solvent extractives and 3.5% uronic anhydride. The NR used was Indian Standard Natural Rubber-5, light colour grade (ISNR-5L). All other rubber chemicals were of reagent grade. Sodium hydroxide and Potassium permanganate used for fiber surface modification were of reagent grade supplied by Merck. The solvents benzene, toluene and xylene used were laboratory reagent grade supplied by Merck.

2.2. Permanganate treatment of coconut shell powder: The coconut shell powder sieved to particle size of 0-53 µm. Here the CSP (1g) was put in a 5% (10mL) NaOH solution for 5h with continuous stirring using a mechanical stirrer and was kept for 24h. The CSP was washed thoroughly with water until the water became neutral. Final washing were carried out with distilled water. The powder was filtered and dried in an air oven at 60^0C. The alkali treated CSP (60g) was soaked with 1L $KMnO_4$ solution in acetone for about 2-3 min. The permanganate solution of concentration 0.01 and 0.05% were used. The treated powder was washed in distilled water and finally dried in air oven at 60^0C.

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

Subair Naduparambath, M. P. Sreejith, T. V. Jinitha, V. Shaniba, K. B. Aparna, E. Purushothaman
Department of Chemistry, University of Calicut, Kerala, 673635, India

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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Correspondence to: E. Purushothaman; e-mail: epurushot@yahoo.com

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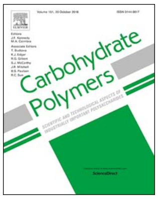

Isolation and characterisation of cellulose nanocrystals from sago seed shells

Subair Naduparambath, Jinitha T.V., Shaniba V., Sreejith M.P., Aparna K. Balan, Purushothaman E.*

Department of Chemistry, University of Calicut, Kerala, 673635, India

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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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* Corresponding author.
E-mail address: epurushot@yahoo.com (P. E.).

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