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INSTITUTE OF MATERIALS ENGINEERING



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CZECH TECHNICAL UNIVERSITY
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Application of Plasma Modified Polyethylene in Composites with Natural Materials

DISSERTATION THESIS

BRANCH OF STUDY

Materials Engineering

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Declaration

I declare that I have developed this Ph.D. thesis on my own, using listed literature and documents and on the basis of consultations and under the guidance of the supervisor.

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Signature

Abstract

This thesis describes detailed investigation on the applications of plasma modified Polyethylene (PPE) powder in combination with natural materials. It is as matrix for natural fiber composite and as fillers in natural rubber compounds. Natural fiber composites were prepared using coir fiber as reinforcement and Plasma modified PE as matrix. Different processing techniques such as compression molding, Injection molding and Rotational molding were used for fabricating the composites. Plasma modified PE based composites showed higher mechanical properties in terms of tensile properties, flexural properties and lower water absorption. Morphology of the composites reveals that there is a good interfacial interaction between treated coir fiber and PPE matrix. Plasma modified PE powder was used as filler in natural rubber matrix and compared the properties (mechanical properties, cure kinetics, morphology and fiber - matrix interaction) with that of unmodified PE composites.

Keywords: Plasma modified Polyethylene, Natural fiber composites, Interface, mechanical properties, water absorption, Natural rubber, morphology

Anotace

Dizertační práce popisuje detailní výzkum aplikace plasmově modifikovaného polyethylenového (PPE) prachu v kombinaci s přírodními materiály. Polyethylen slouží jako matrice pro kompozit s přírodními vlákny a jako výztuž v přírodních sloučeninách na bázi pryže. Kompozity s přírodními vlákny byly připraveny z kokosových vláken sloužících jako výztuha a plasmově modifikovaným PE sloužícím jako matrice. Pro jejich zhotovení byly použity různé zpracovatelské techniky, jako je lisování, rotační tváření nebo vstřikování. Vlákná s modifikovaným PE vykazovaly lepší mechanické vlastnosti ve smyslu pevnosti a ohybu a nižší absorpci vody. Morfologie kompozitních materiálů ukázala dobrou mezifázovou interakci kokosového vlákna a PPE matrice. Plasmou modifikovaný PE prášek byl použit jako výplň do matric na bázi přírodní pryže, jejichž vlastnosti (mechanické vlastnosti, kinetika vytvrzení, morfologie a interakce mezi vlákny a matricí) byly následně porovnávány jejich s nemodifikovanými PE kompozity.

Klíčová slova: Plasmově modifikovaný polyethylen, kompozit s přírodními vlákny, rozhraní, mechanické vlastnosti, absorpce vody, přírodní pryž, morfologie

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CHAPTER I: Introduction

1.1 Background

Plasma modification is an effective, efficient, economic and ecofriendly method to modify the physiochemical properties of a material surface. Plasma, the fourth state of matter contains unique vast variety of components such as excited and ionized particles, photons radicals, etc. When this high energy species comes into contact with the material surface it transfers the additional energy from the plasma, induces consequent chemical reactions on the material surface. These include removal of surface contaminants, polymerization, and crosslinking of polymer chains, etching, functionalizing polymer surface and hydrophilicity of the surface[1].

The principle of the plasma treatment process involves creating active particles by transporting the working gas through the plasma discharge, which changes the surface properties of the material in various ways. The plasma treatment of powders enables modifying the surface properties without altering the bulk material. Plasma-treated polymer powders find wide applications in various industrial sectors. Figure 1.1 illustrates the main application fields and demonstrates that the creation of novel surface functionalities on polymer powders matches the rising need for advanced polymer materials. The list of plasma-treated polymer powder materials is versatile and includes PE (LDPE, HDPE), PP, PS, PA, PMMA, PTFE, PET, POM, ABS, and silicone or tire rubber[2]. PE and PP have received the most attention due to their simple structure and their wide spread. Many researchers investigated the plasma treatment of PE powders with an air or O₂-containing plasma.

Polyethylene has low surface free energy and lack of polar functional groups on their surface, limiting their application in many ways. Plasma modification increases the surface free energy and polarity that improves the adhesion properties which open more applications in polymer technology. These range from the interfacial adhesion between fiber and a polymeric matrix being improved, enhancing the adhesive potential getting improved adhesion of polymer–metal compounds[3], food packaging[4] and biomedical[5,6] industries. Another application is the adhesion of sintered plasma-modified PE powder on PUR foam products for the production of seats in the automotive industry. Another interesting application area is in composites. Initial studies have been reported as matrix for glass fiber composites[7]. The present work investigate

the potential application of plasma modified PE in composite as matrix for natural fiber as well as filler in natural rubber.

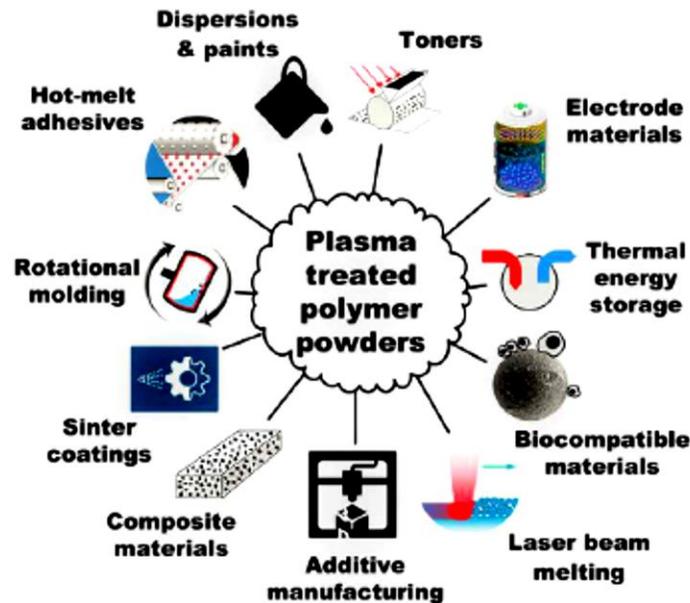


Figure 1.1: Application fields of plasma-treated polymer powders[2].

1.2 Scope of the work

Thermoplastic bio composites reinforced with natural fibers have raised great attention and interest recently due to environmental awareness. Natural fibers have many advantages over synthetic fibers; these include low cost, ease of availability, eco-friendly nature and high specific strength, recyclability, low energy consumption and less abrasive nature. The properties of polymer composites depend not only on the nature of filler and matrix used but also the interaction between the polymer and fiber. Natural fibers are cellulosic fibers which are hydrophilic in nature. The major problem with natural fiber composites is poor compatibility between the hydrophilic natural fiber and hydrophobic polymer matrix. The main scope of this work is to prepare natural fiber – plasma modified PE composites with improved properties and better interphase adhesion.

Plasma treatment generates wide range of reactive species in the treated system (hydroxyl, carbonyl, carboxyl, ether, amine, peroxides etc.) which undeniably depends on the surrounding medium. This also improves its surface micro-hardness and surface roughness due to the

bombardment of high energy radicals and ions. The functional groups present on the modified surface can interact with hydroxyl groups of cellulose fibers which improved interfacial adhesion and properties of the composites.

1.3 Structure of the thesis

This thesis is divided into nine chapters including this introductory chapter and the conclusions. A brief description of each chapter is presented here.

Chapter 1: Introduction

Chapter 2: Review of the relevant literature with the main focus on polymer composite, Interphase in composite, natural fiber composites, Coir fiber and natural rubber composites

Chapter 3: Main goals of the present work

Chapter 4: Provides a detailed description of materials and experimental methods used in the present study. These include the various characterization techniques employed, the fibre surface treatments used, different processing techniques, the mechanical testing and the imaging studies which have been undertaken.

Chapter 5: Presents morphology, mechanical properties, cure kinetics and polymer filler interaction in natural rubber PPE composites and NR PE composites.

Chapter 6: Deals with the results and the detailed discussion of the effect of fibre surface treatments and fibre loading on the morphology, mechanical, water absorption properties of PPE coir fiber composites prepared via hot press method.

Chapter 7: Deals with the results and the detailed discussion of the effect of fibre surface treatments and fibre loading on the morphology, mechanical, water absorption properties of PPE coir fiber composites prepared via rotational moulding.

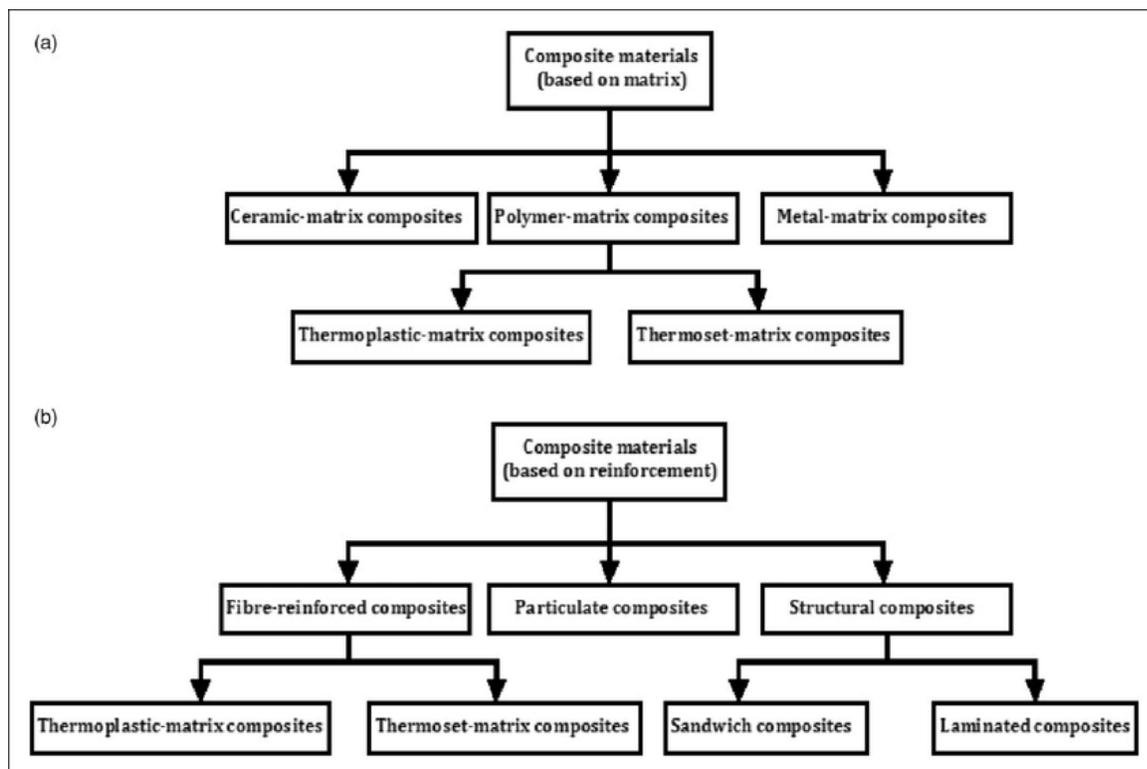
Chapter 8: Deals with the results and the detailed discussion of the effect of fibre surface treatments and fibre loading on the morphology, mechanical, water absorption properties of PPE coir fiber composites prepared via Injection moulding.

Chapter 9: Conclusions and future work.

CHAPTER 2: STATE OF ART

2. 1.Composites

Composite materials comprise two or more constituents with physically separable phases. The properties of composite materials depend on the properties of the constituents and the way in which they are composed. These materials are of great importance in engineering as they are attractive for a wide variety of applications. Composites are generally classified according to type of matrices as well as according to structure of reinforcement. Depending on the matrix used composites are classified as metal matrix composites, ceramic matrix composites and polymer matrix composites. Polymer composite materials are playing an important role in our day-to-day life from aerospace industries to common household applications due to their low density, high specific strength, easy processability, easy availability and more importantly low cost as compared to metal matrix composites.



2.2 Polymer composites

A polymer composite is a complex multi-component, multi-phase system in which reinforcing fillers were integrated with a polymer matrix, resulting in synergistic mechanical properties that cannot be achieved from either component alone. Polymers are giant molecules composed of many (poly) repeat units (mer) called monomers, which have been chemically bonded into long chains. The basic physical phases of polymer composites include matrix phase which is continuous, reinforcement which is scattered and surrounded by matrix and composite interface which is interfaced between reinforcement phase and matrix phase[8]. The reinforcing material provides the structural strength and stiffness to the composite. The function of the matrix is to bond the fibers together and to transfer the loads between them. Polymer matrix composites are very popular due to their high specific strength, high specific stiffness, high fracture resistance, good abrasion resistance, good impact resistance, good corrosion resistance, good fatigue resistance and low cost.

The performance of a composite material is explained on the basis of the combined properties of the reinforcing element, polymer matrix, and the fiber/matrix interface (Figure 2.1). The interfacial adhesion should be strong to meet superior mechanical properties. Matrix molecules can be anchored to the fiber surface by chemical reaction or adsorption, which determine the extent of interfacial adhesion.

2.3 Interface

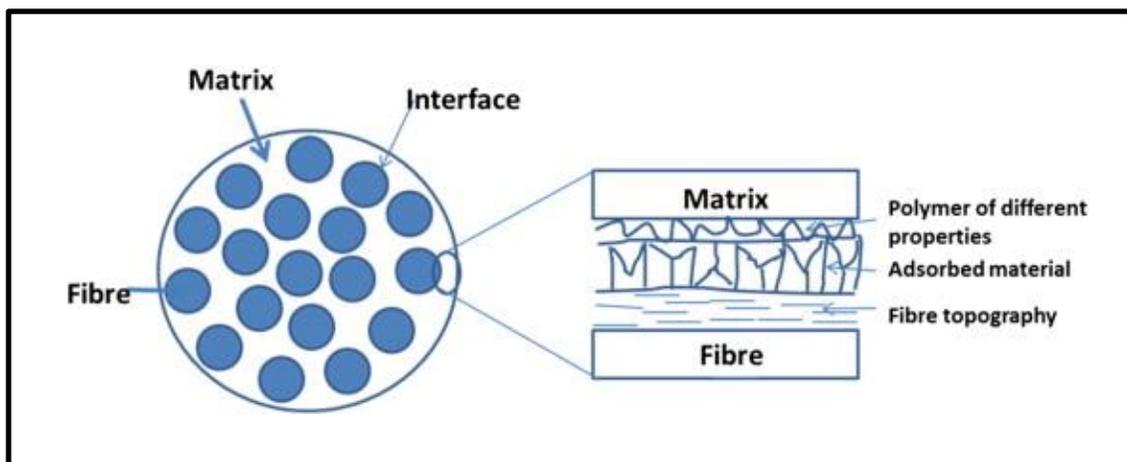


Figure 2.1. Basic components of composites

The primary dimension of any composite is the interface. The interface is the area where the different materials in a composite coincide. In order to have a successful, applicable composite, one must form an interface that is strong and favorable towards maximum compatibility. A good interface is imperative for a material to survive under stress since the interface is the stress concentration points.

The interface region between the fiber and the matrix has been recognized to play a predominant role in governing the global material behavior. The interface in composites, often considered as an intermediate region formed due to the bonding of the fiber and matrix. It is in fact a zone of compositional, structural, and property gradients, typically varying in width from a single atom layer to micrometers[9]. There is a close relationship between the processes occurring on the atomic, microscopic and macroscopic levels at the interface. Interfacial bonding between the fibers and matrix can generally be explained by means of various mechanisms (figure 2.2), namely mechanical interlocking, electrostatic bonding, chemical bonding and inter-diffusion bonding[10].

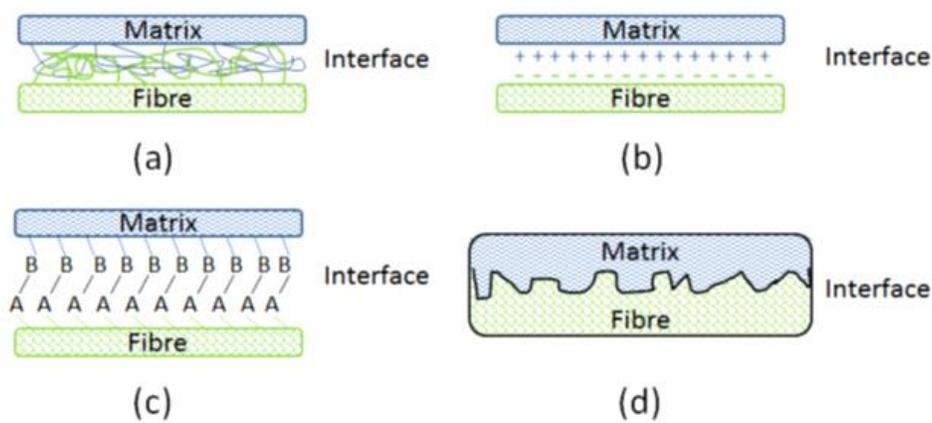


Figure: 2.2 Various mechanisms of interfacial bonding between fiber and matrix (a) mechanical interlocking, (b) electrostatic bonding, (c) chemical bonding and (d) inter-diffusion bonding[10]

Mechanical interlocking at the fiber-matrix interface occurs when the fiber surface is rough, thus increasing the interfacial shear strength. Electrostatic bonding occurs due to negative and positive charges which are only noticeable at metal interfaces and hardly occurs in polymer matrix-fiber systems. Chemical bonding occurs when fiber surface chemical groups react with chemical groups in the matrix to form chemical bonds. The strength of the bond depends on the

type and density of the bond. Inter-diffusion bonding occurs when atoms and molecules of the fiber and matrix were interacting at the interface. For interfaces involving polymers, bonding may take place when polymer chains from each component entangle together and this bonding depends on the distance over which the chains are intertwined, the degree of entanglement and the number of chains per unit area. It should be noted that multiple bonds can occur at the same interface at the same time.¹¹

2.4 Natural fiber composites

The natural fiber composites gained major attention in this era because of the environmental concerns and their specific advantages over synthetic fiber composites. Apart from the lower energy consumption for their production and their relatively low unit cost, compared to synthetic fibers[11], they also have good acoustic, thermal insulation and good specific strength and stiffness properties due to their low density and cellular structure. The lack luster performance of Natural fiber composites has been attributed to a number of factors including poor fiber-matrix interfacial adhesion, low degradation temperature, poor resistance to moisture and variable mechanical properties which are dependent on the growing and harvesting conditions.

The characterization of interface gives relevant information on interactions between fiber and matrix. The mechanical properties of fiber-reinforced composites are dependent upon the stability of interfacial region. Thus, the characterization of interface is of great importance.

However, for natural fiber composites there is usually limited interfacial bonding between the hydrophilic fibers and matrices which are commonly hydrophobic leading to limited mechanical performance. It is shown that, interfacial bonding of natural fiber composites can be improved using physical treatment and chemical treatments¹²⁻²⁰.

Natural fibers have high hydroxyl groups of cellulose content which makes it susceptible to absorb water and thus affects mechanical properties. The water absorption will increase with increase in fiber content and temperature. The evaporation of moisture absorbed may also influence the porosity in the matrix.

2.4.1 Composition and chemical structure of natural fibers

The major constituents of natural fibers are cellulose, hemicellulose, lignin, pectin, and ash. The percentage of each component varies in each different type of fibers. The properties of each

constituent contribute to the overall properties of the fiber. Natural plant fibers have a complex, layered structure consisting of a thin primary wall[12]. The secondary wall is made up of three layers and the thick middle layer determines the mechanical properties of the fiber. The middle layer consists of a series of helically wound cellular micro fibrils formed from long chain cellulose molecules. The angle between the fiber axis and the micro-fibrils is called the micro-fibrillar angle, which affects the fiber property. Bismarck et al. found coir fiber has a high fibrillar angle (45°), which increases the stiffness and reduces the strength[13].

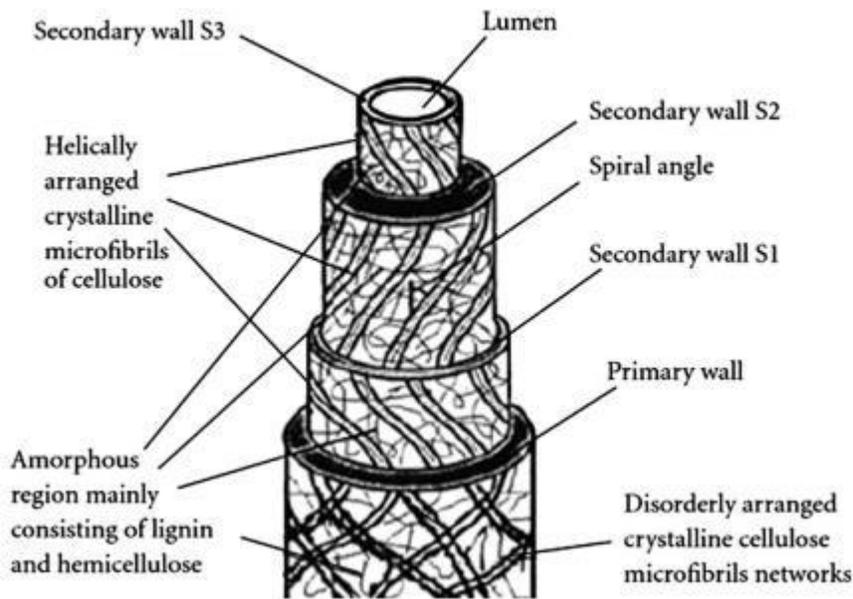


Figure 2.3 Constituents and structural arrangements of plant cell wall[14]

There are lignin and hemicellulose components in the amorphous region between the cellulose micro-fibrils[15]. Lignin is a complex polymer which consists of aromatic alcohols. Khalil et al. found that the content made the fiber tougher and stiffer. Hemicellulose is a group of amorphous polysaccharides. It is said to form hydrogen bonds with cellulose and covalent bonds with lignin. Hemicellulose is responsible for the biodegradation, moisture absorption, and thermal degradation of the fiber as it shows least resistance whereas lignin is thermally stable but is responsible for the UV degradation. The percentage composition of each of these components

varies for different fibers. Generally, the fibers contain 60–80% cellulose, 5–20% lignin, and up to 20% moisture.

Reinforcing efficiency of natural fiber depends upon the nature of cellulose and its crystallinity. Components which are present in natural fibers are cellulose (α -cellulose), hemicellulose, lignin, pectin and waxes. Cellulose is a natural polymer consisting of D-anhydroglucose ($C_6H_{11}O_5$) repeating units which are joined by β -1,4- glucosidic linkage at C1 and C4 position. Hemicellulose is different from cellulose. It comprises a group of polysaccharides compiled by a combination of five and six carbon ring sugars. It differs from cellulose in three aspects, first it has several sugar units, and secondly they show a considerable degree of chain branching containing pendent side groups which give rise to its ion crystalline nature. Third is degree of polymerization because in case of hemicellulose it is 50-30 but in cellulose is 10-100 times more than that of hemicellulose. Hemicellulose is very hydrophilic, soluble in alkali and easily hydrolyzed in acids.

Lignin is a complex hydrocarbon polymer with both aliphatic and aromatic constituents and it is totally insoluble in most of the solvents and can't be broken down into monomeric units. Lignin is considered to be a thermoplastic polymer having a glass transition temperature of around 900^0 C and melting temperature of around 1700^0 C. It is totally amorphous and hydrophobic in nature. It is not hydrolyzed by acids, but soluble in hot alkali, readily oxidized and easily condensable with phenol. Pectin is a collective name for heteropolysachrides. They contribute flexibility to plants. Waxes make up the last part of fibers and they consist of different types of alcohols.

2.5 Coir Fiber

Coir fiber is an important lingo-cellulosic fiber extracted from the fruit husks of coconut tree, which is grown on tropical areas. It is widely used in a variety of applications world wise especially popular for as ropes and matting. Coir fiber is obtained from the fruit by dehusking coconut (figure 2.5). The husks are then subjected to a bacteriological process known as retting which involves soaking the husks in saline backwaters for about 4 to 12 months. Coir fiber measures up to 35 cm in length and 12-25 microns in diameter. Among vegetable fibers, coir has one of the highest concentrations of lignin, making it stronger but less flexible[16].

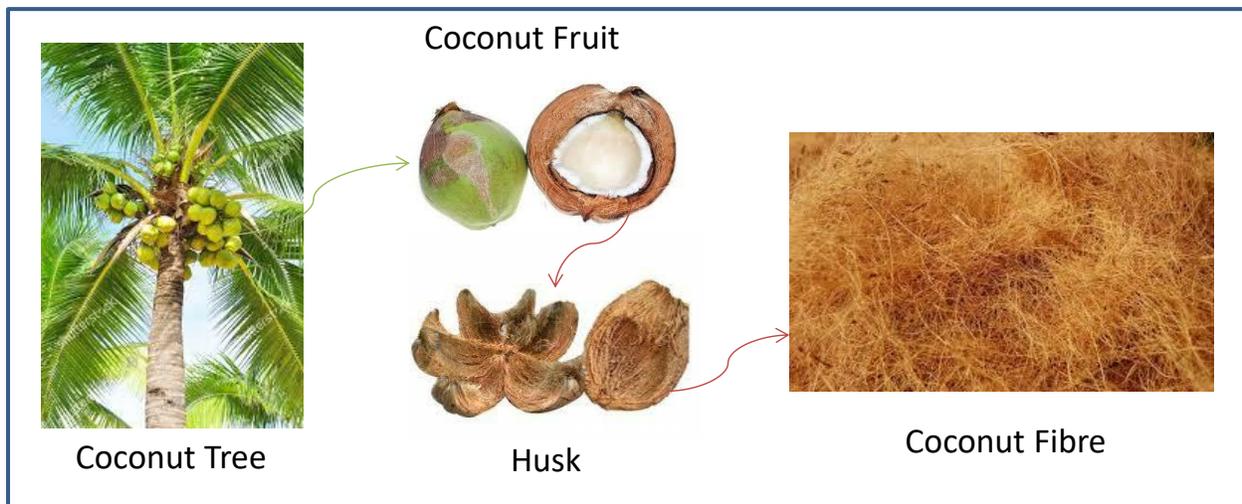


Figure 2.4 Photographs of coconut tree, fruit, husk and coir fiber

2.5.1 Structure of Coir Fiber

Coir is a multicellular fiber that contains 30 to 300 or more cells in its cross section, which is polygonal to round in shape. These cells are 12-14 μm in diameter and are arranged around the central pore that is called lacuna. The cross section of coir fiber is given in figure 2.5. Coir is coated with a waxy cuticle layer made up of fatty acids and their condensation products[17].

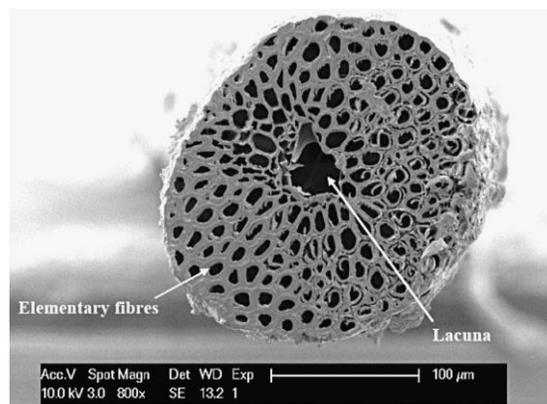


Figure 2.5 Cross section of coir fiber[17]

2.5.2 Chemical modification of Coir fiber

In polymer matrix composites, improvement in interfacial strength can be achieved by modifying the surface characteristics of fibers by means of mechanical, physical and chemical treatments and by modification of the matrix properties using coupling agent. Increased interfacial strength can occur through improved wettability to give more contact and increased bonding between fiber and matrix.

The main disadvantages of natural fibers in reinforcement to composites are the poor compatibility between fiber and matrix and their relative high moisture absorption. Therefore, natural fiber modifications are considered in modifying the fiber surface properties to improve their adhesion with different matrices. By several chemical treatments, natural fibers can improve their interfacial bonding with polymer matrix in natural fiber reinforced polymer composites. The following chemical methods have been used to improve fiber/matrix interfacial adhesion in natural fiber reinforced polymer composites.

1. Alkali treatment:

Alkaline treatment or mercerization is one of the most used chemical treatments of natural fibers when used to reinforce thermoplastics and thermosets. The important modification done by alkaline treatment is the disruption of hydrogen bonding in the network structure, thereby increasing surface roughness. This treatment removes a certain amount of lignin, wax and oils covering the external surface of the fiber cell wall, depolymerizes cellulose and exposes the short length crystallites[18]. Addition of aqueous sodium hydroxide (NaOH) to natural fiber promotes the ionization of the hydroxyl group to the alkoxide. Thus, alkaline processing directly influences the cellulosic fibril, the degree of polymerization and the extraction of lignin and hemicellulosic compounds[19]. Mechanical and thermal behaviors of the composite are improved significantly by this treatment. If the alkali concentration is higher than the optimum condition, the excess delignification of the fiber can take place, which results in weakening or damaging the fibers. Reaction which takes place during this treatment is shown below.



Therefore, when the alkaline treated plant fiber is used to reinforce polar polymer composites, in comparison with the composite filled with untreated plant fiber, the enhanced surface roughness and increased reactive sites exposed on the surface would lead to a better mechanical interlocking and adhesion with the matrix, both of which are in charge of the interfacial strength of the composite[11]. However, it should be pointed out that the superfluous alkali concentration would result in excess delignification of plant fiber, thus weaken or damage the fiber being treated[19].

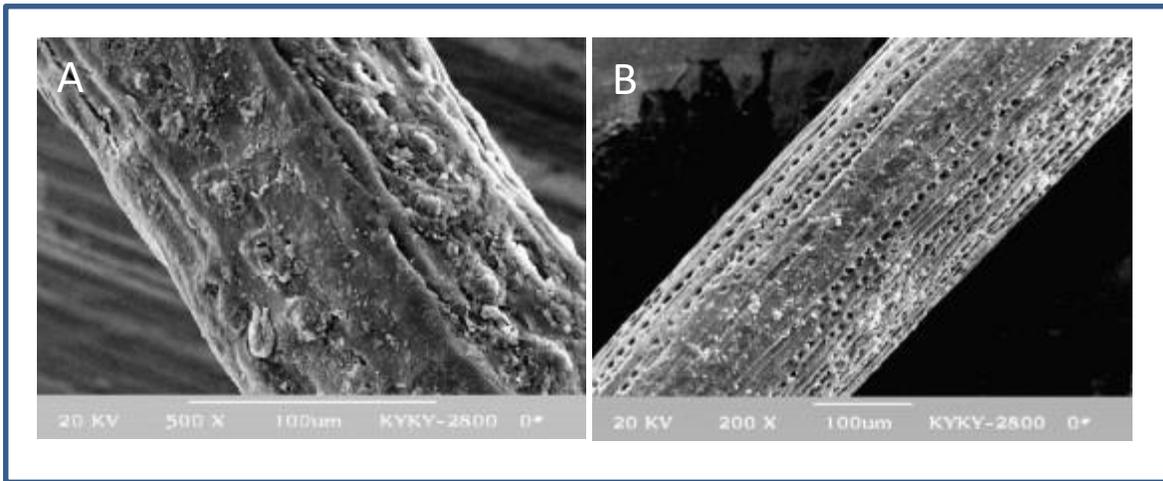


Figure 2.6 images of the appearance of the coir fiber before and after the alkali treatment[20]

2. Hydrogen Peroxide Treatment

Interface properties of fiber and matrix can be improved by peroxide treatment. The peroxide-induced grafting of polyethylene adheres onto the fiber surface. Additionally, peroxide initiated free radicals react with the hydroxyl group of the fiber and with the matrix. As a result, good fiber matrix adhesion along the interface occurs. This treatment also reduced moisture absorption tendency by the fiber and improves thermal stability. The hydrogen peroxide tends to oxidize the hydroxyl groups from cellulose in the fiber surface to carboxyl groups giving the fiber a soft cationic potential.

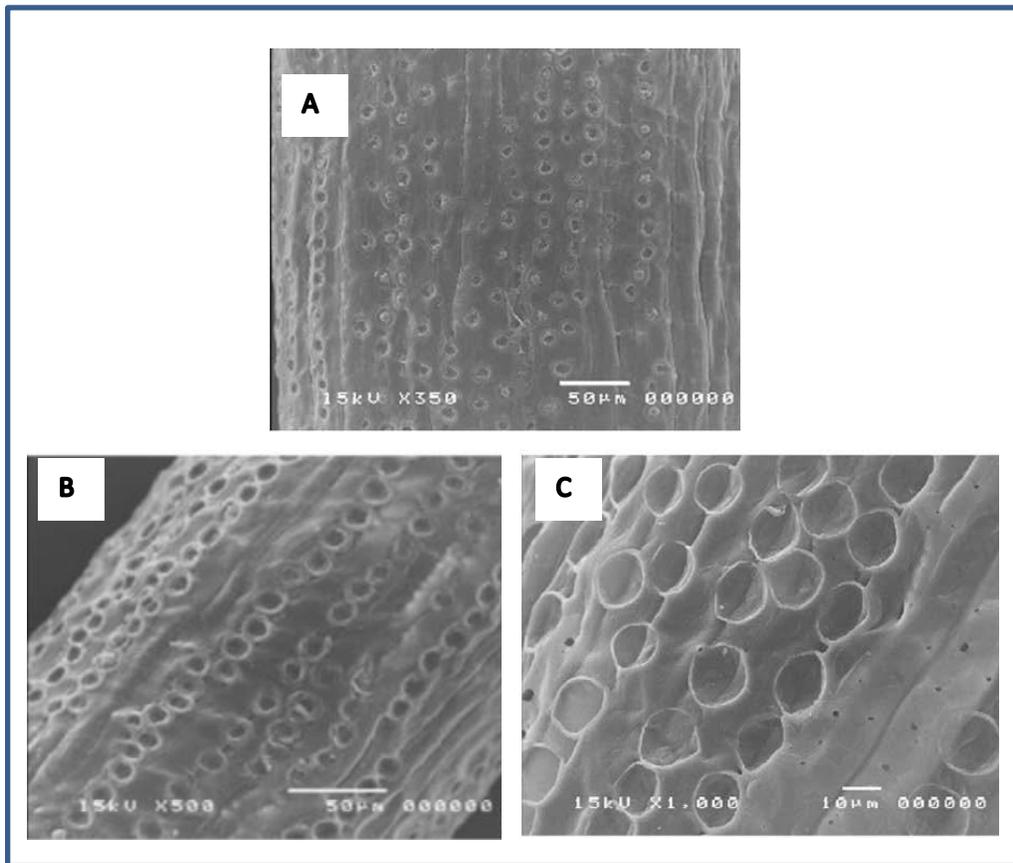


Figure 2.7 a) raw coir fiber, b) H_2O_2 treated fiber, 500 and c) H_2O_2 treated fiber, 1000[21]

The H_2O_2 treatment seems to be the most efficient in the removal of waxy and fatty acids residues (Fig. 2.7b and c) [21]. Although the waxy removal has been observed, pit like openings were preserved (Fig. 2.7b). But, in some parts, where the chemical attack was probably stronger, the fibers appeared to be deformed, with a smoother surface (Fig.2.7c). The treatment of coconut fibers with H_2O_2 promoted an increase in thermal stability. The studies of wettability show that the treatment with H_2O_2 does not modify the hydrophilic/hydrophobic nature of coconut fiber

2.5 Polyethylene Natural fiber composites

In natural fiber-reinforced plastic composite, the processing temperature should remain relatively low to avoid possible degradation of natural fiber when exposed to high temperatures. So PE is a good choice with its lower melting point and lower processing temperatures than other thermoplastics[22]. Table 1 lists some of the physical, mechanical, and thermal properties of PE.

Table 2.1: Properties of Polyethylenes

Polymer Type	Density (g/cm ³)	Degree of Crystallinity	Glass Transition Temperature (°C)	Crystal Melting Temperature (°C)	Tensile Strength (MPa)	Elongation at Break (%)	Flexural Modulus (GPa)
High-density polyethylene (HDPE)	0.95-0.97	high	-120	137	20-30	10-1,000	1-1.5
Low-density polyethylene (LDPE)	0.92-0.93	moderate	-120	110	8-20	100-650	0.25-0.35
Linear low-density polyethylene (LLDPE)	0.91-0.94	high	-74	122-124	20	100-500	0.35

The low energy consumption, low cost, good thermal insulator, and ease of manufacturing of PE are also extra advantages to be considered as matrix in composites. The mechanical properties are influenced by the mechanical properties of both matrix and reinforcement. Only when the composites reinforced with low fiber content, the matrix mechanical properties become more important. So PE is well suited for use as matrix material in natural fiber reinforced composite despite its relatively low mechanical properties. A variety of natural fibers were used as reinforcement in polyethylene composites. Different chemical treatments on natural fibers were also explored in the literature to improve the interfacial adhesion and mechanical properties of the composites.

Herrera-Franco et al. prepared HDPE-henequen fiber composite materials with a 20% v/v fiber content and the tensile, flexural and shear properties were studied[23]. The comparison of tensile properties of the composites showed that the silane treatment and the matrix-resin pre-impregnation process of the fiber produced a significant increase in tensile strength, while the tensile modulus remained relatively unaffected. The increase in tensile strength was only possible when the henequen fibers were treated first with an alkaline solution. It was also shown that the silane treatment produced a significant increase in flexural strength while the flexural modulus also remained relatively unaffected. The shear properties of the composites also increased significantly, but, only when the henequen fibers were treated with the silane coupling agent.

The thermal stability of HDPE was reduced due to the incorporation of bamboo pulp fiber though the mechanical properties improved to a great extent and showed higher stiffness under dynamic load [24]. J.R. Araujo and his group observed that the composites reinforced with curauá fibers have mechanical properties comparable to commercially produced composites of HDPE reinforced with fiberglass[25]. The morphology of the composites showed that the PEMA treated composites presented good interfacial adhesion and that fibrillation occurs, promoting good dispersion of the microfibrils in the composite.

The effects of different fiber treatments such as alkali, isocyanate, permanganate and peroxide on the tensile properties of sisal-LDPE composites were investigated by Kuruvila Joseph as a function of fiber loading, fiber length and orientation[26]. The composites exhibited maximum properties at a fiber length of about 6 mm. Unidirectional alignment of the fiber enhanced the strength and modulus of the composites along the axis of fiber alignment by more than two- fold compared to randomly oriented fiber composites. The electrical properties[27] of the composites were also explored.

Mulinari et al. evaluate the benefits of reinforcing high density polyethylene with cellulose fibers modified with zirconium from sugarcane bagasse[28]. The chemical modification, reduced number of OH bonds in the fiber therefore good adhesion between fiber and matrix observed and the mechanical properties increased to a great extent. Tensile strength increased 47% with the addition of 40 % modified fiber.

Coir fiber was used to reinforce HDPE with the aid of stearic acid as coupling agent [29]. Even though SEM of the fractured samples showed improved adhesion between coir and HDPE matrix upon treatment with SA, tensile strength of the composite was less than pure matrix. Mir et al. investigated the effect of basic chromium sulfate and sodium bicarbonate treatment treatment on the properties of coir fiber reinforced polypropylene and polyethylene composites[30]. Chemical treatment increased the adhesion between the fiber and matrix (figure 2.8). Thus, chemically treated coir fiber reinforced polymer composites had better properties as compared to raw coir fiber reinforced polymer composites (figure 2.9).

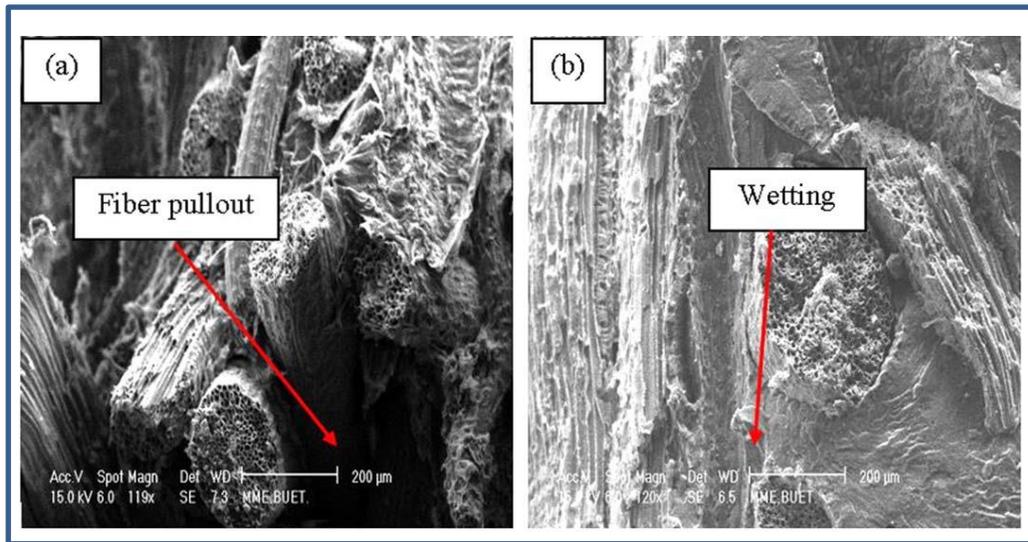


Figure 2.8 SEM micrographs of 20% (a) raw coir reinforced PE, (b) treated coir reinforced PE

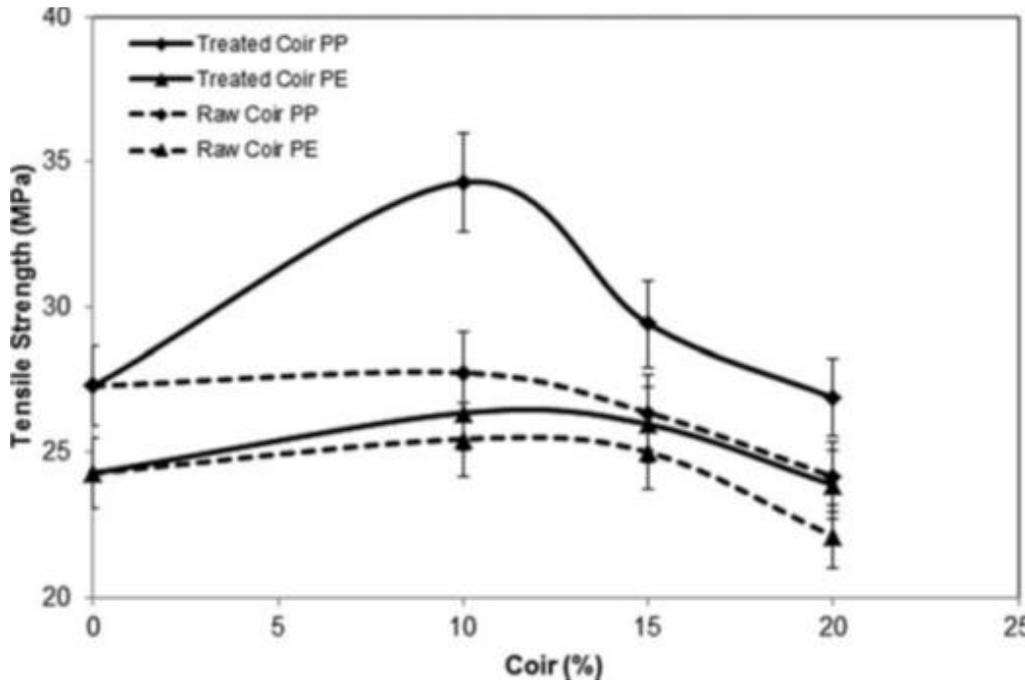


Figure 2.9 Variation of tensile strength of coir fiber reinforced PP and PE composites against fiber loading.

The effect of fiber surface treatments (alkali and acrylic acid) on the thermal degradation behavior of coir fiber (CF)-low-density polyethylene (LDPE) composites with or without compatibilizer (maleic anhydride grafted LDPE, MA-g-LDPE) were evaluated by N Prasad et

al.[31] The composite prepared in the presence of MA-g-LDPE would improve its thermal stability by enhancing the interfacial bonding between LDPE matrix and CFs.

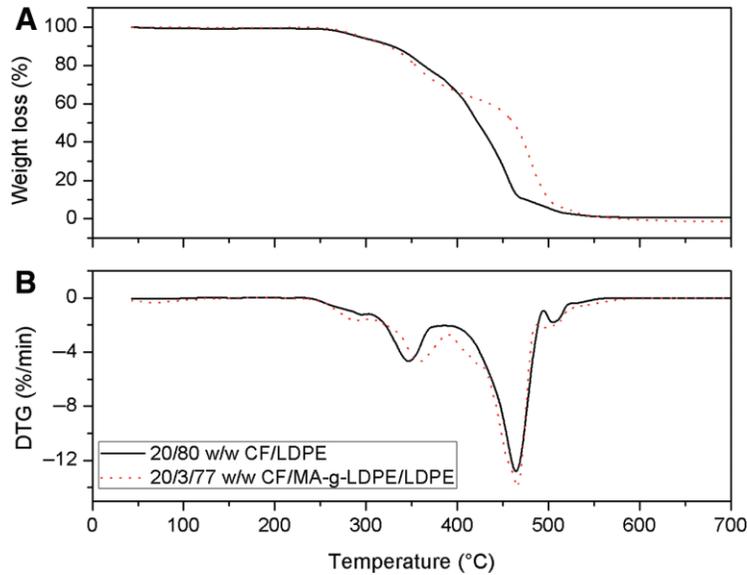


Figure 2.10: Thermal degradation behavior of coir fiber (CF)-low-density polyethylene (LDPE) composites with or without compatibilizer

2.6. Processing Techniques

Fiber-reinforced plastic composite manufacturing is similar with thermoplastic processing. Most thermoplastic processing operations involve heating, forming into the desired shape, and then cooling. These include compression molding, extrusion, injection molding, rotational molding, etc. Selection of a suitable processing method for the generation of fibre reinforced polymer composites is an important task in order to enhance the mechanical, physical and thermal properties of the final product. Temperature, pressure and speed of processing are the major factors which determining properties of the composites. Since the degradation resistance of fiber is low, it has been limited for using it with the thermoplastic matrices with higher melting points.

2.6.1. Compression Moulding

Compression moulding is a frequently used method for the processing of polymer composites, also known as hot press method. Previous studies showed that compression moulding gives composite materials with superior mechanical properties when compared to other processing methods. Polymer fibre mixture is placed between preheated mould cavities and then the mold is

closed, heat and pressure are applied to obtain a homogeneously shaped composite. Applied pressure and heat depend on the thermal and rheological properties of the polymer. A preheating time is needed to reduce holding time. Slow cooling or rapid cooling (quenching) can be applied at the end of holding time. The temperature and applied pressure of the mould cavities are fixed according to the types of matrix and filler materials used and thickness of composite samples[32].

2.6.2. Injection Moulding

Injection molding is commonly used industrial process for manufacturing of thermoplastics, in which high temperature and shear rate are associated with. In injection molding process, the compounded samples are preheated in cylindrical chamber to a temperature at which it can flow and then it is forced into a cold, closed mold cavity by means of quite high pressure, which is applied hydraulically through the ram or screw type plunger. The screw rotates to pick up the polymer and melt it, mix the melt and deliver it to the closed mold. The screw is then moved forward to force a fixed volume of the molten polymer into the closed mold. After melting, polymer is solidified in the cool mold; the screw rotates and moves backward to charge the polymer for the next cycle. Many studies have been conducted on the potential of using natural fibers as reinforcement for polymers to make a composite through injection molding. It is also used with other pressing techniques like extrusion. During the injection molding process for composites, a complex molten polymer flow field is generated and fibers are therefore oriented in the direction of shearing and stretching[33]. A good distribution of fibers is always achieved in this process. However the processing of natural fiber composites is limited via injection molding because of the low thermal stability of the fibers.

2.6.3. Extrusion

Extruder is a versatile machine, which forms thermoplastic items with a uniform cross-section such as pipe, hose, wire and cable. Melting, compression and metering sections are basic sections of an extrusion screw. In melting part, the solid pellets are conveyed from the hopper and converted into molten polymer. In compression section, the molten polymer is compacted and mixed with the additive (if required). The metering section is needed to produce the desired product cross-section. Twin-screw extruder and single screw extruder are basic types of extruders. Twin screw systems have been shown to give better dispersion of fibers and better

mechanical performance than single screw extruders[34]. The processing temperature PE can be in the range of 190–230°C. The mixtures are fed into the hopper of the extruder, compounded, cooled and granulated. The compounded samples are prepared as test specimens by injection molding machine or hot press molding machine.

2.6.4. Rotational Moulding

Rotational molding or rotomolding is one of the most important polymer processing methods for producing stress free, hollow products. Rotational molding involves powder mixing, melting, sintering and melt solidification. In this process, polymer mix is filled up in a half of mold then closed and subjected to biaxial rotation in an oven at a temperature of 200–400°C. Once the polymer has melted, the mold is moved out of the oven with biaxial rotation. For cooling the mold, water or air fan can be used. Rotational molding has particular advantages in terms of relatively low levels of residual stresses and inexpensive molds. Polyethylene can be used in rotational molding because of its low melting point, low cost and good thermal stability. Reinforcements can be incorporated into the rotationally molded components to increase their mechanical properties. Rotational molding is the less explored process for natural fiber thermoplastic composites. The low-shear characteristics of rotomolding limit the amount of fiber that can be added to produce good composite materials as most researchers used fiber contents much less than 30%[35] . Wang et al. prepared linear low-density polyethylene (LLDPE) with treated flax fibers by benzoylation, and their maximum fiber amount was 10%[36]. They found that tensile strength increased from 15.2 to 16.1 MPa, while impact strength also increased from 190 to 220 kJ/m². Lopez-Banuelos et al. prepared LMDPE composites with 5, 10, and 15% of agave fibers[37]. The impact strength decreased with fiber content. Nevertheless, a maximum tensile modulus was achieved at 10% of fiber which was 70% higher than the neat matrix. Raymond and Rodrigue produced LLDPE-wood composites by rotational molding with fiber contents up to 25%. They found a maximum tensile modulus is 17% higher than LLDPE at 20% of wood. But the tensile strength decreased with fiber content from 16 MPa for neat LLDPE to 9.2 MPa at 25% of wood.

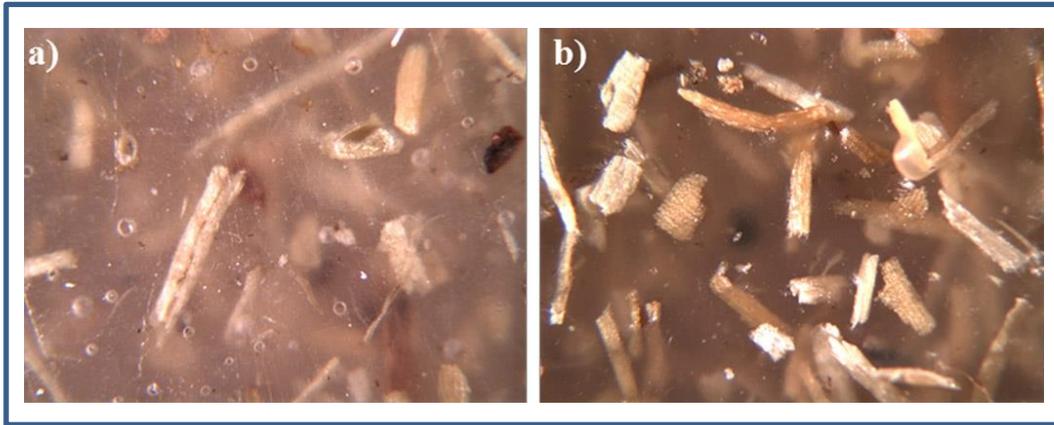


Figure 2.11 (a) External and (b) internal surfaces of the rotomolded composite[38]

Bubbles are one of the most common defects in rotomolded parts[38]. The composites produced had a small amount of bubbles, suggesting that good sintering occurred under these processing conditions as well as an acceptably good dispersion of the fiber without a specific orientation (Figure 2.11). The external surface was smoother than the internal surface, where many fibers stuck out, especially when higher fiber content and larger fibers were used.

Table 2.2: Summary of physical modifications on natural fiber

Composite	Modification	Effects	Outcomes
PE/PP/Jute fiber Compression molding[39] [1]2010	Gamma and UV radiation	Gamma irradiation of PP resulted with increased cross-linked density and active sites inside the matrix. Gamma irradiation affects the polymeric structure of the fiber and produces active site which results in better bonding. UV radiation results in the inter-crosslinking between the neighboring cellulose molecules. It is observed that tensile properties increase with UV pretreatment	For UV treated jute fabrics/PP composites, showed higher mechanical properties than gamma treated composites. The UV treated composite showed an increase of 18% TS and 20% bending strength respectively. SEM images of the fracture sides of the composites were supported that gamma treated jute fabrics/PP composites had poor fiber matrix adhesion than that of the UV treated jute fabrics/PP composites.

PP/ Miscanthus fiber and miscanthus fiber/PLA composites Extrusion and CM[40][2] 2012	Corona treatment	The corona treatment of fibers resulted in a surface oxidation and an etching effect, leading to an improvement of the interfacial compatibility between fiber and matrices.	The mechanical and thermal properties (Young's modulus (68%), stress at yield (34%), glass transition temperature, and decomposition temperature) of the treated composites were greatly enhanced due to the better interaction between the
Polyester / Flax fiber composite[41] [3]2005	plasma treatment		the tensile strength, flexural strength, flexural modulus and interlaminar shear strength of flax fiber-reinforced polyester composites increased by 34%, 31%, 66% and 39% respectively, primarily due to the improved adhesion between the treated fiber and polyester matrix.
HDPE/ Jute Compression Moulding[42] [4] 2011	Oxygen plasma treatments(a low frequency generated cold plasma system and a radio frequency generated cold plasma system)	Better adhesion between the fibers and matrix was observed. At different plasma treatment stage, the mechanism of plasma surface treatment is different. Surface modification is dominant at the beginning, and then is overwhelmed by surface etching at a later stage of the process	The ILSS values of the composites were increased by 65% for 30 W, 84% for 60 W and 189% for 90 W, in comparison with untreated one. The tensile strengths of the composites were increased by approximately 14, 21 and 46% for 30, 60 and 90 W, respectively, in comparison with that of the untreated jute fiber/HDPE composite.
HDPE / flax fibers[43] [5]2013	air atmospheric pressure plasma	Argon plasma treatment predominantly initiates surface activation by generation of free radicals on the surface of flax fiber through chain scission. Air plasma treatment creates mostly oxygen and slightly nitrogen	IFSS values were obtained higher than that of untreated flax fiber.

		containing groups, which are increasing of plasma power until 300 W, on the surface of flax fiber	
PE/ Agava fiber Melt mixing[44][6]2016	plasma polymerization process using ethylene gas	Dispersion evaluation in water confirmed that the AFP treated changed from hydrophilic to hydrophobic behavior	The addition of treated and untreated AFP (200 mesh) at 20 wt% promotes an increase of Young's modulus of the composites of up to 60% and 32%, respectively, in relation to the neat matrix. Also, an increase of crystallinity of LDPE was observed by the addition of treated and untreated AFP
Thermoplastic starch/ coir fiber Melt mixing[45] [7] 2017	plasma treatment (oxygen and air)	partially etching the amorphous layer which covers most of the fibers. This has increased surface roughness and partially exposed the crystalline cellulose underneath.	The best mechanical results have been found for composites made with oxygen plasma treated fibers for 80 W and 7.2 min (teff). Ultimate tensile strength increased 300% and elastic modulus approximately 2000%.
Epoxy / flax fiber[46] [8] 2017	atmospheric pressure plasma jet treatment		Increase in tensile strength in the composite material reached 180%, and the increase in flexural strength was 140%.

Table 2.3: Summary of work on chemical treatment of natural fiber composites

Composite	Modification	Effects	Outcomes
LDPE/sisal Soln mixing& extrusion[26] [1]1996	Alkali Peroxide Permanganate CTDCI	rough surface topography and increased aspect ratio peroxide induced grafting permanganate induced grafting long chain structure of CTDCI linked to	The property increase upon various treatments varies in the order DCP > CTDCI > BP > KMnO4 > alkali. CTDCI and DCP treatments showed the maximum properties. TS increased from 10 to 40 MPa

		the cellulosic fibers makes the fiber hydrophobic, compatible and highly dispersible in the matrix.	
HDPE/henequen fiber[47][2] 1999	Alkaline Silane Surface pre-impregnation with PE dilute solution	partial removal of the hemicelluloses, waxes, and lignin present on the surface of the fiber	12.5% improvement in TS for silane treated fiber composite
PP/ coir & oil palm fiber hybrid[48] [3] 2013	Hybrid fiber at diff ratios (100:0, 75: 25, 50:50, 25:75, 0:100)		No improvement in mechanical properties
HDPE/sugarcane bagasse, thermokinetic Mixer[28] [4] 2016	Zr oxide	Hydrolysis leads to the formation of oxide monolayer, where the metals are incorporated to the surface through Cello-M bond. Reduction of OH bonds	Improvement in mechanical properties. 47% increase in TS with 40% modified fiber.
PP/ coir fiber extrusion[49] [5] 2014	MAPE (5%)		The values of IFSS increased from 2.2 to 3.4 MPa with the addition of 5 wt% MAPP. TS increases to 25% with 30% fiber.
HDPE-curauá fibers, Extrusion[25] [6] 2010	EVA PEMA		Morphology showed that the PEMA treated composites showed good interfacial adhesion and that fibrillation occurs, promoting good dispersion of the microfibrils. TS increased to 100% for EVA and 122% for PEMA
HDPE/ Jute Melt	MAPE	The maleic anhydride	30% fiber loading and 1%MAPE conc. showed

mixing[50] [7] 2006		groups of MAPE covalently links with the hydroxyl groups of the fibers forming an ester linkage. Furthermore, the nonpolar part (PE) of MAPE becomes compatible with the virgin matrix, lowers the surface energies of the fibers, thereby increasing its wettability and dispersion within the matrix.	optimum mechanical strength. 100% increase in TS 95% increase in FS 101% increase in impact strength The damping properties of the treated and untreated composites, decreased in comparison to the virgin matrix and an increase in the thermal stability of HDPE matrix with fiber reinforcement and MAPE treatment.
HDPE/ coir fiber Compression moulding[29] [8]2010	Stearic acid	SA interacted with the hydrophilic coir through its carboxylic group, imparted some extent of hydrophobicity to the coir surface, thus compatibilizing the coir with hydrophobic HDPE.	No improvement in mechanical properties Improved the thermal stability and ageing resistance.
HDPE/ coir fiber, Extrusion[51] [9] 2014	MAPE (1.2%)		29% increase in TS 52% increase in TM 38% increase in FM 23% increase in FS
PP/ hemp fiber Extrusion[52] [10] 2008	Alkali(NaOH, Na ₂ SO ₃) and MAPE	NaOH treatment resulted in fiber dry mass losses of 41.3%, while the NaOH/ Na ₂ SO ₃ treatment resulted in fiber dry mass losses of 32.1%. alkali treatments resulted in decreases in fiber diameter, which can be attributed to the removal of alkali-	40 wt% NaOH/ Na ₂ SO ₃ treated fiber, 4% MAPP and polypropylene had the highest TS(50.5 MPa) and Young's modulus (5.31GPa) Treated fibers have higher thermal stability than untreated one with degradation starting at 240 °C and 205 °C.

		soluble cementing materials from the fiber cell walls	
PP/ PE Coir fiber, layer-by-layer[30] [11] 2015	chromium sulfate and sodium bicarbonate	The chemical treatment of coir reduced the hydroxyl group of the cellulose unit by coupling with basic chromium sulfate salt.	34% improvement in TS and 32% improvement in FS for PP composites. 8% improvement in TS and 18% improvement in FS for PP composites
LDPE/banan a fiber, Compression moulding[31] [12] 2016	alkali and acrylic acid MA-g-LDPE		The addition of compatibilizer to the acrylic acid treated banana fiber composites showed the most effective improvement in the flexural and impact strength and also, exhibited a reduction in the water absorption capacity

2.7 Natural rubber composites

Rubber belongs to a class of polymer called elastomers which are flexible long-chain polymers which are capable of crosslinking. These materials are capable of recovering from large deformations quickly and forcibly and could be stretched rapidly even under small load to about 1000% elongation. Its elastic strain is much higher than that of metal. Hence it can function at high strains. There are different types of rubbers including natural rubber (NR) and a variety of synthetic rubbers.

NR is obtained from rubber tree (*Hevea brasiliensis*) in the form of field latex. Natural rubber (cis-1,4-polyisoprene) is better than synthetic rubbers as they are renewable, inexpensive and creates no health hazard problems. It possesses high tensile strength and modulus due to strain-induced crystallization. It shows superior building tack, which is essential in many products like tires, hoses, belts etc. It possesses good crack propagation resistance also.

Natural rubber (NR) known for its excellent elasticity coupled with extensive availability make it suitable in a wide number of applications. NR has been modified by incorporating various types of fillers such as carbon black, clay, calcium carbonate, metal oxides, CNT, POSS, graphene etc. and other polymers from the time immemorial. When Natural rubber is compounded with

thermoplastic, there exists a special class of material called thermoplastic natural rubber (TPNR). TPNR shows performance properties similar to elastomers and processing properties similar to thermoplastics which make them popular. One of the frequently used thermoplastic materials, which compounded with NR, is polyethylene. TPNRs are generally prepared by melt-mixing techniques using an internal mixer or co-rotating twin-screw extruders. Even though both NR and polyethylene are nonpolar there exists lack of compatibility between them. Lots of studies were reported based on natural rubber polyethylene blends, composites and nanocomposites.

Kurian et al. investigated the morphology of tensile fractured and fatigue fractured surfaces of natural rubber vulcanizates filled with polyethylene[53]. They found that the size and shape of the thermoplastic domains were varying with the thermoplastic content which enhanced their mechanical interaction with the rubber matrix. But there was no much improvement in tensile strength.

Chuan Qin and coworkers studied the effect of compatibilization of natural rubber polyethylene blends by polyethylene-b-polyisoprene diblock copolymers[54]. They found that the compatibilizer localized at the interface with some conformational limitation caused by its embedding into LLDPE and NR phases. Hassan and co-workers studied the effect of HVA-2 (N, N'-m-phenylenebismalimide) on the mechanical and morphological properties of NR/LLDPE blends. They found that the mechanical properties were modified significantly with the addition of HVA.

The curing kinetics and its mechanism are very important in understanding the processing conditions of a material. It is imperative to know the effects on cure behavior of natural rubber when new materials are incorporated into it. Vulcanization of natural rubber has been quite extensively investigated in the literature. Several models have been suggested to describe the curing kinetics of elastomers with reference to the nature of the reaction.

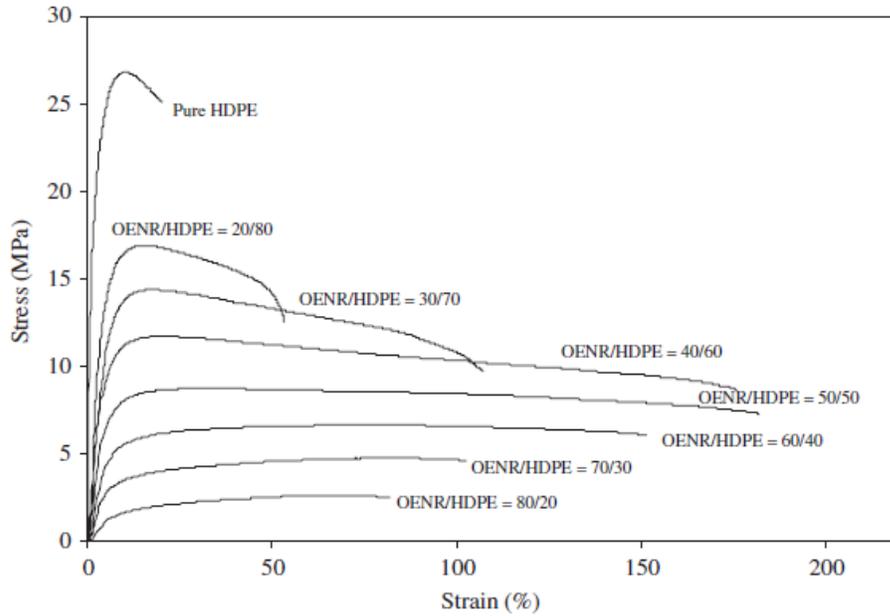


Figure 2.12: Stress–strain curves of OENR/HDPE blends with PhHRJ-PE compatibilizer and various blend proportions[55].

Nakson et al have studied the effect of vulcanization system on properties of thermoplastic vulcanizates based on epoxidised natural rubber/ poly ethylene blends[55]. They found that the mixing torque, shear stress, shear viscosity, tensile strength and elongation at break of the TPVs using mixed curing system exhibited higher values than those of sulphur and peroxide cured systems. In the sulphur cured system only S-S linkages are formed, whilst in the peroxide curing system more stable C-C linkages are formed. However during shearing at high temperature of the peroxide and mixed-cure systems, the peroxide caused degradation of the poly ethylene molecules. Higher level of DCP was used in the peroxide cured system and caused greater influence on properties. In the mixed cure system, lower influence of PE degradation and influence of formation of more stable C-C linkages overcomes the drawback. Therefore they observed the highest values of those properties using the mixed cure system.

Huang and co-workers studied the rheological behaviour poly ethylene/ epoxidised natural rubber blends[56]. The morphology and miscibility of PE/ENR blends were investigated using DMA and SEM techniques. They used the Ozawa kinetics equation to describe the crystallization the crystallization process of the blends.

CHAPTER 3: The Thesis Goals

Thus, the main aim of the present study was to investigate the application of plasma modified Polyethylene powder in polymer composites as matrix for natural fiber composites and as filler in natural rubber composites.

The main objectives set to achieve this aim are as follows:

1. To investigate the effect of plasma modified PE as filler in Natural rubber composites. Analyze the morphology, mechanical properties, cure kinetics and rubber filler interaction. Comparison of properties with unmodified PE natural rubber composites.
2. To investigate the effect of plasma modified PE as matrix for natural fiber composites. Evaluate the interphase properties, mechanical properties and water absorption characteristics.
3. Investigate the effect of chemical modification on coir fiber in Plasma modified PE based composites.
4. Development and optimization of plasma modified PE Natural fiber composites for rotational moulding.
5. Initial studies on Injection moulded natural fiber composites.

Chapter 4

Materials and Experimental Techniques

4.1 Materials used for bio composite

4.1.1 Polyethylene

The polymer used for this study is Linear Low Density Polyethylene (LLDPE). PE powder used in this study was roto moulding (Rotational moulding) grade of Surpass RMS 244-U/UG (particle average diameter 300 μm). The specific gravity and melting point of the polymer are 0.935 g cm^{-3} , 124 ° C respectively.

4.1.2 Plasma modified Polyethylene

The standard plasma-treated powders were obtained from the company named Surface Treat Ltd, Czech Republic. . The specific gravity and melting point of the polymer are 0.935 g cm^{-3} , 124 ° C respectively. Microwave discharge excited in oxygen and/or air was used for the modification. All experiments were performed in air under pressure of 70–100 Pa and room temperature (20–23) ° C. Treatment time was 60–600s. The detailed description of the modification[57] is given below.

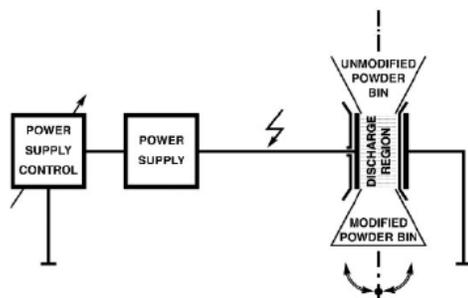


Figure 4.1: Atmospheric-Pressure DBD Plasma Reactor [57]

The atmospheric-pressure DBD reactor consisted of vertically adjustable discharge channel connected with power supply and control units (Figure 4.1). Plasma was generated in the cubical discharge channel confined by two identical large rectangular brass electrodes (inter-electrode distance was set at 11 mm) and two identical glass walls. One of the electrodes was covered with a glass plate which was 2 mm thick.

Powder particles moved along the reactor vertical axis, particle trajectory in this direction was at least 242 mm. The position of the plasma reactor channel was adjustable round its vertical axis. In order to prolong the treatment time of the powder during a single transit through the reactor, the channel vertical axis and the reactor bottom formed a 45 ° angle during all measurements. The plasma reactor was designed as gravity-fed, that is, a continuous stream of powder particles passed through the reactor channel from a hopper at the top of the channel to a collecting bin at its bottom on account of the force of gravity. For simulation of the operation of larger devices (i.e. with longer “active zones” resulting in longer modification times during one transit), every powder batch was repeatedly thrown through the discharge channel of the plasma reactor, the number of transits through the plasma reactor being one of the investigated parameters. Precise measurement of the particle transition time through the reactor, i.e. modification time, was hardly achievable because of indirect powder grain trajectories through the discharge channel; nevertheless the modification time corresponding to one transit through the reactor could be estimated as being less than one sec. Thus, the total modification time can be estimated by using the product of the modification time corresponding to one transit and number of transits through the reactor. Modification in atmospheric pressure DBD reactor was performed in stationary air.

4.1.3 Coir fiber

Coir fiber was obtained from Coir board of India in Kerala, India. Its constituents are given in table 3.1. The average diameter of coir fiber will vary from 100 to 400 µm and density of 1.15g/cc. The fibers were thoroughly washed and chopped into short fibers having an average length of 6 mm to ensure easy blending with polymer matrix. The chopped fibers were dried at 120 °C for 24 h. The dried fibers were subjected to various chemical treatments as described below.

Table 4.4 Chemical composition of coir fiber[16]

Properties	Value
Cellulose	36–43%
Lignin	41–45%
Hemicellulose	0.15–0.25%
Pectin	3–4%
water-soluble materials	7-8%

4.1.4 Chemical treatments for coir fiber

4.1.4.1 Alkali treatment

The dry fiber was treated with 5% of NaOH solution for 2 hour to remove unwanted soluble cellulose, hemicelluloses, pectin, lignin, etc.[19] from the fiber. The fiber to solution weight ratio was maintained as 1: 25. After 2hr the fibers were washed thoroughly in distilled water to remove excess of NaOH and then dried at 60 ° C for 24 hr.

4.1.4.2 Treatment with hydrogen peroxide

Coconut fibers were subjected to oxidation using 40 ml of hydrogen peroxide solution in basic medium (0.05 g NaOH and 18 mL of hydrogen peroxides 30% v/v for 100 mL of solution) at 85 ° C for 2 hr. During this process the fibers were cooked under gradual rise of temperature. Finally the cooked fibers were taken out from the mixture. The fibers then washed with distilled water thoroughly and were dried and chopped to 6 mm length. It is again dried in an air oven at temperature of 60 ° C for 24 hr. Then these fibers were designated as bleached fibers.

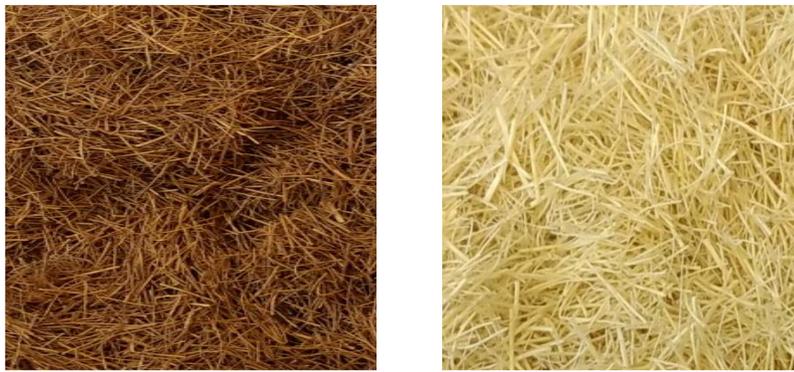


Figure 4.2: coir fiber after a) alkali treatment and b) treatment with hydrogen peroxide (bleached)[58]

4.2. Preparation of Natural Fiber PE composites.

Various methods were followed to manufacture the composites include melt mixing, compression moulding, Injection moulding, Rotational moulding and Pressure less moulding in an air oven.

4.2.1 Mechanical mixing and hot press method (Compression moulding)



Figure 4.3: Procedure for the fabrication of bio composites via hot press method[59]

PE and heated coir fiber were taken in a beaker, mixed thoroughly using a glass rod. After proper mixing, the mixture was kept for 24 hr. Then it was moulded using hydraulic press. Compression

mould temperature and pressure are set at 130° C and 120 psi respectively. Procedure for the fabrication of PE biocomposite is shown in Figure 15.

4.2.2 Injection Moulding

The injection molding machine (ARBURG ALLROUNDER 570 C 2000-675) used for the fabrication of PE biocomposites is shown in Figure 3.6. Dumbbell shaped dies were used for the moulding according to ISO527 to make it easy for further tensile testing on biocomposites.

PE powder and short coir fibers were preheated and mixed together before injection moulding process. Parameters for Injection moulding is given in the table 3.2.

Table 4.5: Processing parameters of Injection moulding

Parameters	Values
Melt temperature	185 ° C
Injection rate	35 cm ³ / s
Impact size	500 bar
Back pressure	30 bar
Cycle time	60 s

4.2.3 Rotational Moulding

A laboratory-scale rotational molding machine was used for composite processing (Fig.17). The oven was heated by electrical resistances. The machine controls the temperature in the oven, tilts the furnace and rotates the mold. Temperature sensors are pt100. One is located in the furnace and the other inside the mold. Position sensors detect the position of the machine for only a few points. The current position is counted from stepper motor control. One position sensor is used to detect the rotation of the mold. The second position sensor is used to detect the zero tilt of the furnace. The third position sensor is used to detect furnace tilt beyond the safe limit. The mold cooling is activated with two fans.



Figure 4.4: Rotational moulding machine

A rectangular shaped box made up of aluminium with dimensions 25cm x 10cm x 10cm was used to produce the rotationally molded parts (Fig. 4.4). Before loading the material, the demolding agent was applied to the internal surface of the mold. In all cases, a weight of 400 g of material (mixture of fiber and LMDPE) was loaded into the mold to produce parts with an approximate wall thickness of 4 mm. The charged mold was then closed and mounted on the rotating arm and introduced into the oven. Then, heating started and the mold was kept rotating. The oven temperature kept at 260 °C. The internal air temperature (IAT) was monitored with a thermocouple during the process. When the IAT reached for example 210 °C, the cooling started. After the heating cycle, forced air for cooling was started until the IAT dropped to 100 °C, and the part was demolded. The rectangular mould used for rotational moulding and rotomoulded PE and composite boxes are shown in figure 4.5



Figure 4.5: Mould used for Rotational moulding and Rotomoulded PE and composite samples

4.3.4 Pressure less Moulding

Pressure less moulding was done in an air oven using rectangular shaped moulds. Sufficient quantities of PE powder and short coir fiber with required proportions were taken in a closed jar and shake well. Rectangular mould with size 10cm length, 1cm width and 4cm depth was used for the moulding process. It was then cleaned properly and mould releasing agent was uniformly applied by wiping it with cotton cloth. PE coir fiber mixture was filled into the mould and then kept in air oven for 30 minutes at 200 °C. Then the samples were taken out and cooled at room temperature.



Figure 4.6: Mold used for pressureless moulding and prepared PE and composite samples

4.3 Characterization

4.3.1 Infra-Red Spectroscopy

Surface chemical properties of coir fibers and polyethylene were analyzed by infrared spectroscopy using Perkin Elmer FTIR spectrometer spectrum R-X-1 in the mid IR range, i.e. from 400 and 4000 cm^{-1} .

4.3.2 Contact angle Measurements

Contact angle measurements were carried out in a SEO Phoenix instrument with water (triple distilled), on samples of size 1x1x0.2 cm^3 at room temperature. The contact angle was measured within 45–60 sec of the addition of the liquid drop with an accuracy of 1°. The volume of the sessile drop was maintained as 5 μL in all cases using a micro syringe. Measurements were repeated for ten times with different test pieces of the same sample to check the accuracy. Also contact angles were measured with definite time intervals for a single drop and the measurements were recorded as snap shots.

4.3.3 Mechanical testing

Tensile Properties

Tensile properties of short coir fiber polyethylene and plasma modified polyethylene with different fiber contents were measured according to ASTM D638 using universal testing machine Tinius Olsen H50KT at a gauge length of 60 mm and speed of 50 mm per minute. Reported values are the average of 5 specimens.

Flexural properties

The flexure properties were measured by the three point bending method according to ASTM D790 using universal testing machine. The flexure properties were carried out at room temperature with a cross head speed of 2 mm per minute. Reported values are the average of 5 specimens.

4.3.4. Water absorption characteristics

Water absorption characteristics of the composites have been studied at room temperature. Square specimen having 2 mm side length and 2 mm thickness were immersed in distilled water and the percentage weight change was determined until the equilibrium values were reached. After immersion in water, samples were removed at different times, wiped with tissue paper to remove surface water and weighed with an analytical balance with 1gm resolution. The morphology of the bio composite was investigated by using a stereo microscope with deep image sharpness. The molar absorption Q_t (mol percent) of water by the composite at time 't' was calculated from the equation given below;

$$Q_t (\%) = \frac{(W_2 - W_1)}{18 \times W_1} \times 100$$

Where W_1 is the weight of dry specimens and W_2 is the weight of the wet specimen. The molar absorption at equilibrium (infinite time) is represented by Q_N . The weight gains maximum moisture contents and diffusivity of such materials during immersion in distilled water was also estimated.

4.3.5 Morphology

The morphology of the bio composite was investigated by using a stereo microscope with deep image sharpness.

Scanning Electron Microscopy

The morphology of the composite surface was studied by Scanning Electron microscope JSM-7600F (JEOL, JP). Impact fractured surface of the composite were selected for analyzing microscopy. The samples were coated with silver sputtering to avoid the sample becoming charged under the electron beam. SEM images were taken at 5 kV.

4.4. Preparation of Natural Rubber PE compounds

4.4.1 Materials

Natural rubber (ISNR 5) was obtained from Rubber Research Institute of India, Kottayam. PE and PPE having melting point 124°C were supplied by Surface treat a. s., Czech Republic. The rubber chemicals such as zinc oxide, stearic acid, tetra methyl thiuram disulfide (TMTD), cyclo hexyl benzo thiazyl sulphenamide (CBS) and sulfur used were of commercial grade obtained from Sigma Aldrich.

4.4.2 Sample preparation

In this work the compounding was done by using two roll mill mixing method as per ASTM D3182 at a friction ratio of 1:1.25. The raw NR was masticated in the laboratory two roll mill for 2-3 minutes to reduce the viscosity followed by the addition of compounding ingredients. The formulations are given in Table 4.3.

Table 4.3. Compounding recipe for the composite

Ingredients	Phr
NR	100
PE / PPE	0,5,10,20,30,50
Zinc oxide	5.0
Stearic acid	2.5
CBS	0.8
TMTD	0.2
Sulphur	2.5

Zinc oxide and Stearic acid were added and mixed for a few minutes followed by filler material. After thorough mixing of the filler, CBS and TMTD were added and mixed. Sulphur is added at later stage and mixed properly. The rubber was first masticated by careful control of temperature, nip gap, time and uniform cutting operation. The nip-gap, mill roll speed ratio and the number of passes were kept same in all mixes. Then the process is completed by increasing the nip gap and rolling the mix out. The whole mixing process should be completed within 20 minutes.

Curing

The samples were then compression moulded at 160 °C with a cure time of t_{90} obtained from an oscillating disc rheometer according to ASTM D2084. The compounds were cured at their respective cure times using a hydraulic press under a pressure of about 120 bar. The specimens for various tests were taken in accordance with ASTM standards.

4.5 Characterization Techniques

4.5.1 Curing characteristics

Curing behavior was studied at 140°C, 160°C and 180°C on a Monsanto Oscillating Disc Rheometer, according to ASTM D1646.

4.5.2 Field Emission Scanning electron microscopy (FE-SEM)

Microscopic observations were done by means of FESEM with the samples broken after immersing into liquid nitrogen.

4.5.3 Mechanical properties

Tensile properties of the samples were measured using universal testing machine (Tinius Olsen) with a cross-head rate at 500 mm/min according to ASTM D 412 at a room temperature (25 ± 2 °C). Five dumbbell shaped samples of each system were used to determine the Young's modulus, tensile strength and elongation at break. Tensile modulus was taken as the slope of the initial linear region of the stress-strain curve.

Results and Discussion PART I

Chapter 5 : Plasma Modified and Unmodified Polyethylene as Filler in Natural Rubber Compounds

Introduction

Natural rubber (NR) known for its excellent elasticity coupled with extensive availability make it suitable in a wide number of applications. NR has been modified by incorporating various types of fillers such as carbon black, clay, calcium carbonate, metal oxides, CNT, POSS, graphene etc. and other polymers from the time immemorial. The present chapter investigates the influence of polyethylene (PE) and plasma modified polyethylene (PPE) as fillers in natural rubber (NR) compound. The NR/PE and NR/PPE composites were prepared through mechanical mixing using two roll mill by varying their compositions. The morphology of the compounds was analyzed in detail using field emission scanning electron microscopy (FESEM) to understand the dispersion of PE and PPE in the NR matrix as well as its interfacial adhesion. The vulcanization kinetics and cure characteristics of natural rubber compounds containing PE and PPE were examined using an oscillating disc rheometer. The cure behavior of the composites were studied at different temperatures (140°C, 160°C and 180°C) using conventional sulphur vulcanization system. This chapter has been published in an international journal Macromolecular Symposia[60].

5.1 Effect of Plasma Treatment on PE

5.1.1 FTIR spectrum

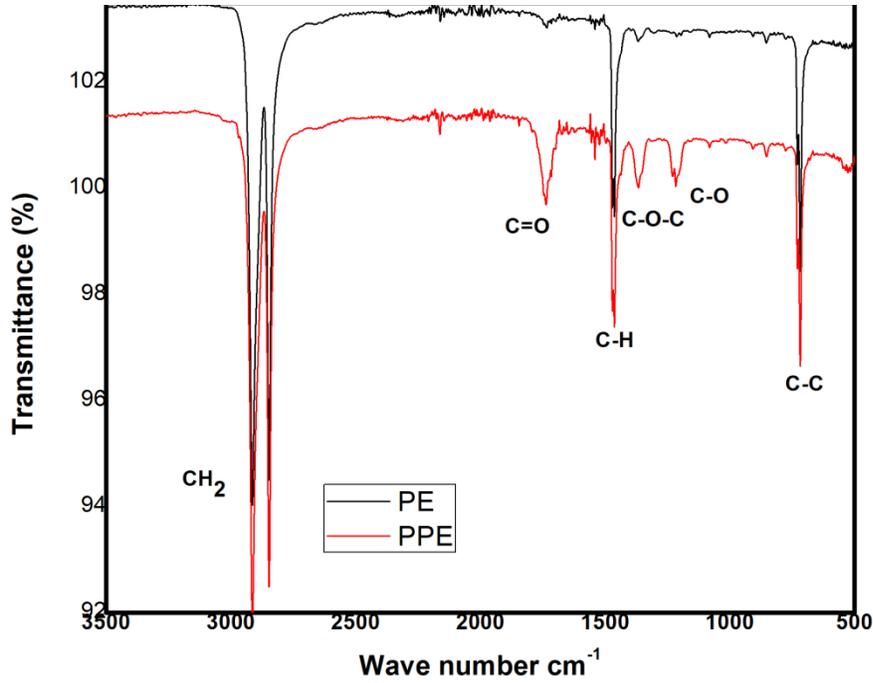


Figure 5.1: FTIR spectra of untreated PE and plasma treated PE

The influence of plasma treatment on PE was studied by FTIR measurements and showed in Figure 5.1. The spectrum of the untreated PE is a typical polyethylene spectrum as reported[61]. After plasma exposure of the pristine material, the characteristic oxygen functional groups were introduced and therefore significant changes in the measured spectrum have been observed. These changes seem to be caused by the incorporation of some polar groups by plasma treatment with the appearance of peaks at 1741 cm^{-1} (C=O stretch in carboxylic acid) and 1168 cm^{-1} (C-O stretch in alcohol).[62]

5.2. Morphological Analysis

The morphology of the cryo fractured surface of both NR/ PPE composites and NR /PE composites were analyzed using FESEM.

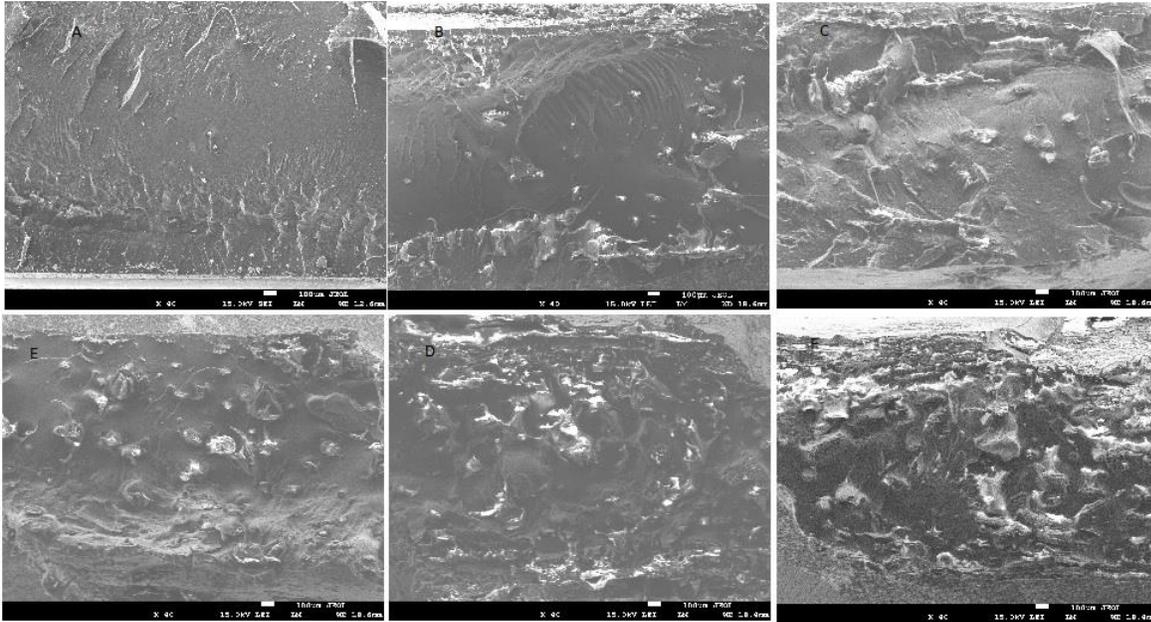


Figure 5.2: SEM images of a) Neat NR, b) NR with 5phr PE, c) NR with 10phr PE, d) NR with 20phr PE, e) NR with 30phr PE, f) NR with 50phr PE[60]

Low magnification SEM images of fractured surface of NR filled with varying amount of PE are given in figure 5.2. It is clearly observed from the figure that neat NR shows comparatively smooth surface. The roughness of the surface also increases with the addition of thermoplastic filler. A similar kind of observation has been noticed by Kurian et al.[53]. Low magnification SEM images of fractured surface of NR filled with varying amount of PPE are given in figure 5.3. The surface of NR containing PPE compounds has become rougher with the increasing amount of PPE content in a similar way.

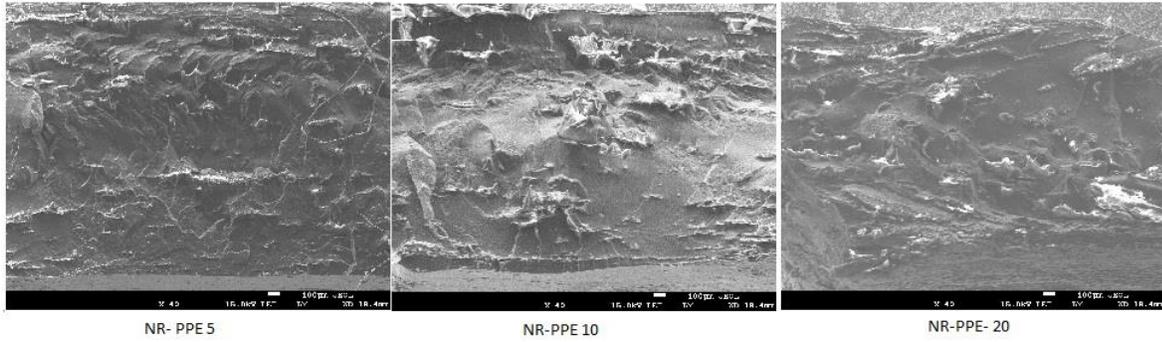


Figure. 5.3. SEM images of a) NR with 5phr PE, b) NR with 10phr PE, c) NR with 20phr PE[60]

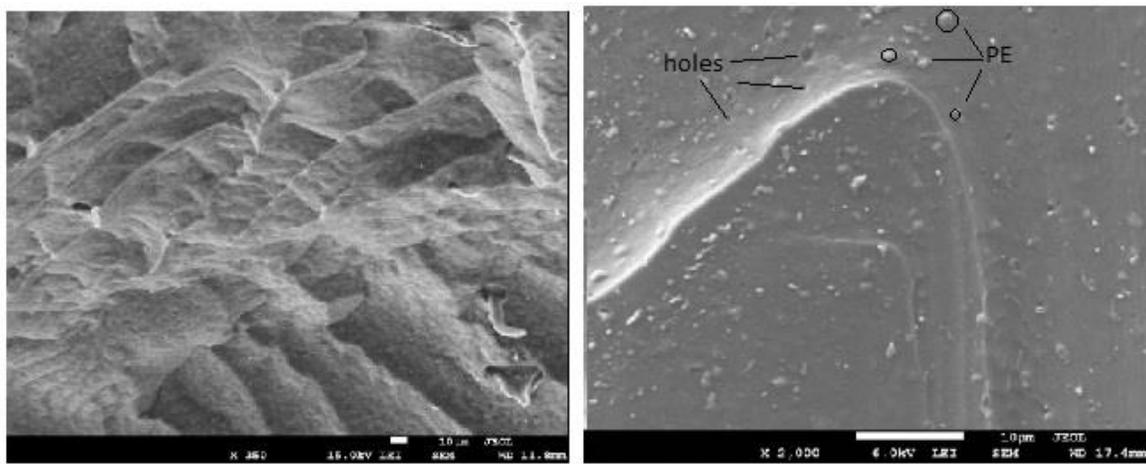


Figure 5.4: SEM image of NR with 5phr PE at higher magnifications[60]

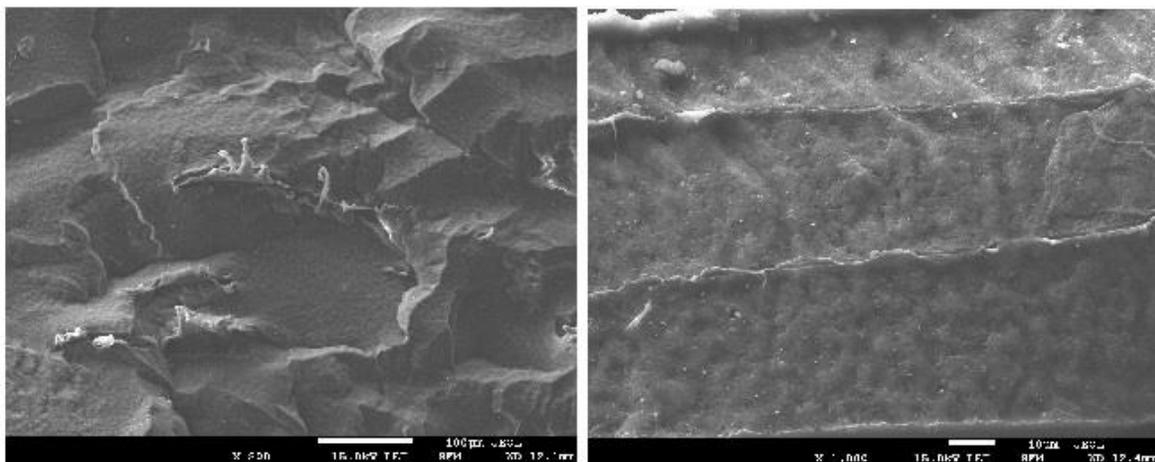


Figure. 5.5. SEM image of NR with 5phr PPE at higher magnifications[60]

For a better understanding of the morphology, the compounds were analyzed at higher magnifications. The SEM images of NR compound with 5phr PE are shown in figure 5.4. We can observe from the SEM images that there are different structures present in the NR matrix. It is noticeable that the PE powder is nicely dispersed in the NR matrix as small particles. It can be seen from the second image that some holes are also present due to the detachment of these polyethylene powder during fracture. We could also observe some protrusions in the third image due to the ductile behavior of PE. In the case of plasma modified polyethylene filled compound the morphology was entirely different. The SEM images of NR containing 5phr PPE are given in figure 5.5. Here the polyethylene particles were agglomerated and were seen as a separate phase. This was because of the polar-polar cohesive interaction between the modified polyethylene surfaces due to the presence of polar groups [63]. In the case of unmodified polyethylene, even though there was no chemical interaction with natural rubber matrix, the polyethylene particles could be easily dispersed in the NR matrix due to similarity in structure (both NR and PE are non-polar), their powdery form and also the sample preparation method. But the modified polyethylene particles had a tendency to come closer to form aggregates owing to the polar-polar cohesive interaction. Since natural rubber was non polar, the modified PE tried to move apart from the rubber hydrocarbon chain. This could be seen from the figure 5.6, where NR/PPE system is showing a clear and sharp interface.

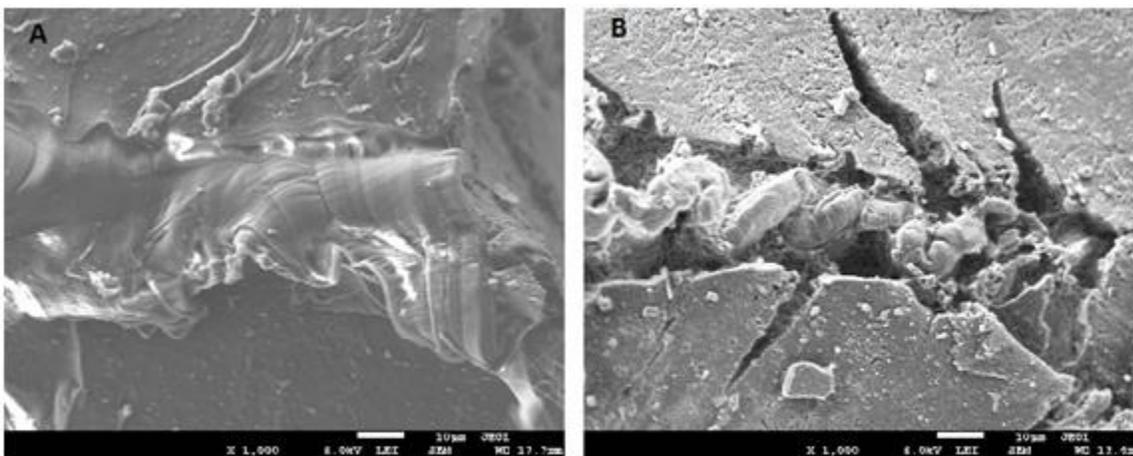


Figure 5.6: SEM image of a) NR with unmodified PE and b) NR with modified PE[60]

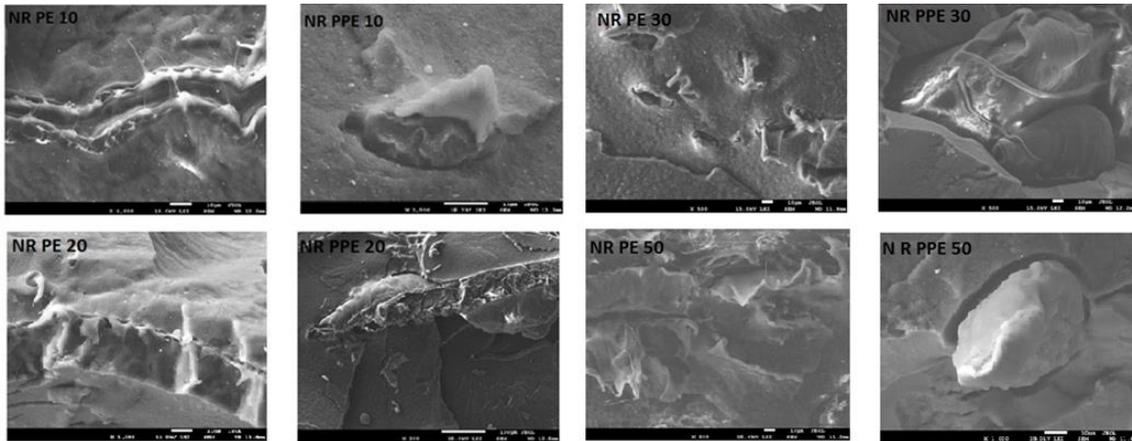


Figure 5.7: SEM image of NR/PE and NR /PPE with varying amount of PE (10 to 50phr) at higher magnification[60]

Scanning electron micrographs of the composites at higher magnification showed a clear picture about the dispersion of PE as well as PPE in the NR matrix which is given in figure 5.7. The unmodified PE was dispersed in the NR matrix at lower concentrations and also at increasing concentrations. The composite with 5phr PE showed a nice dispersion. Both NR and PE are non-polar in nature and the similarity in structure facilitates the excellent dispersion of PE in NR matrix, even though there was no chemical interaction between NR and PE. But plasma modified PE was showing a different morphology. PPE exists as aggregates irrespective of its concentration in NR matrix. This was attributed to its polar nature, which causes strong phase segregation from the NR phase leading to coarse structure.

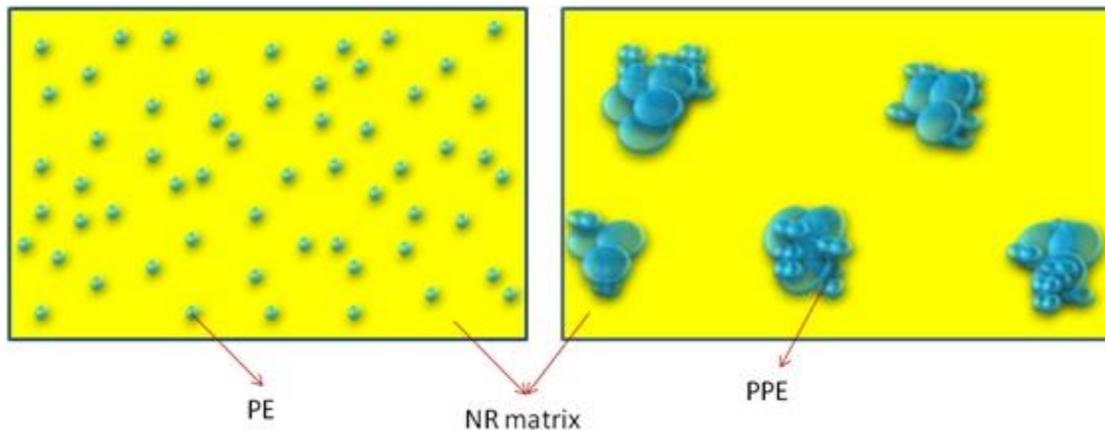


Figure 5.8: Schematic representation of the morphology of a) NR/PE and b) NR/PPE composites

Figure 5.8 illustrates the schematic representation of the morphology of PE and PPE filled NR matrix. Figure 5.8a demonstrates the fine dispersion of unmodified PE in the NR matrix and figure 5.8b demonstrates the agglomerated structure of modified PE. The polar nature of the modified PE was responsible for this agglomeration in the non-polar NR matrix. The modification made PE more incompatible with NR phase.

5.3 Cure Characteristics

To explore the curing behaviour as a function of the polyethylene loading for both plasma modified and unmodified, the curing characteristics were studied at different temperatures. The curing characteristics at a particular temperature (160°C) are listed in table 2. The effect of PE loadings on the cure profile obtained at 160°C was shown in figure 5.9.

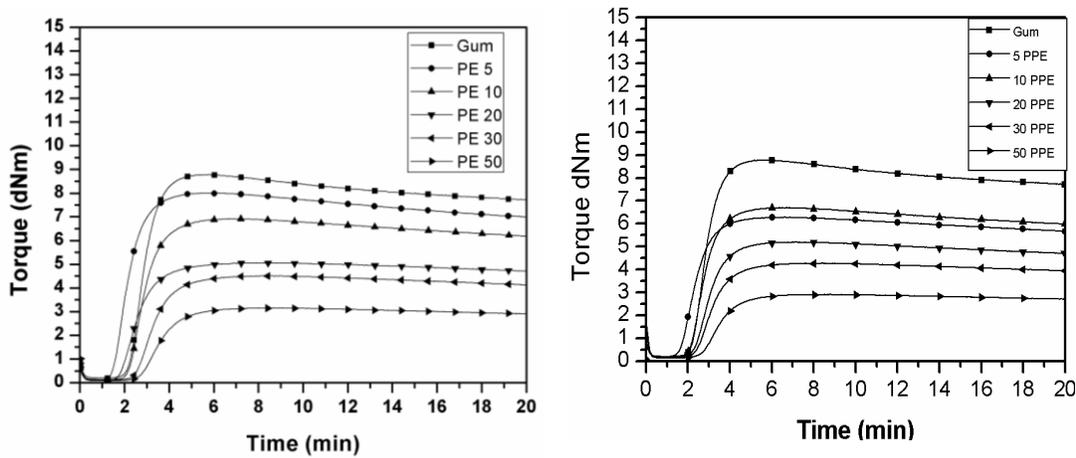


Figure 5.9: Cure behaviour of a) NR/PE and b) NR/PPE at various PE content at 160°C[60]

Table 5.1. Cure characteristic of NR/ PE and NR/ PPE compounds at 160 °C

Amount of PE /PPE (phr)	Min. Torque ML (dNm)		Max. Torque MH (dNm)		MH-ML (dNm)		Scorch time (min)		Cure time (min)	
	NR/ PE	NR/ PPE	NR/ PE	NR/ PPE	NR/ PE	NR/ PPE	NR/ PE	NR/ PPE	NR/ PE	NR/ PPE
0	0.19		8.78		8.59		2.48		3.74	
5	0.10	8.01	8.01	6.28	7.91	6.10	1.78	2.08	3.18	3.44
10	0.12	0.15	6.92	6.70	6.80	6.55	2.48	2.55	3.81	4.00
20	0.09	0.17	5.06	5.20	4.97	5.03	2.37	2.80	3.93	4.16
30	0.10	0.14	3.50	4.27	3.40	4.13	3.18	3.08	4.58	4.47
50	0.08	0.13	3.15	2.91	3.07	2.78	3.87	3.93	4.85	4.98

The curing characteristics of the studied material were expressed in terms of minimum torque (M_L), maximum torque (M_H), scorch time (t_{s2}), and cure time (t_{c90}). The minimum torque was related to the viscosity of the uncured compound at a given temperature. The addition of thermoplastic polyethylene reduced the viscosity of the compound. So the minimum torque value decreased with increasing amount of polyethylene. By the addition of PE to the NR matrix minimum torque, maximum torque and difference between them (ΔS) were tend to decrease in both cases. This was because polyethylene was in the molten state at this high temperature since the melting point of PE is 124°C. The melted PE had a plasticising effect which lowers the ultimate torque values[64]. The scorch time and cure time were tending to increase with increasing the PE content. Plasma modified PE showed comparatively higher values for scorch time and cure time. It is clear from the figure 8 that the slope of the rheographs decreases with the addition of polyethylene. This indicates that the rate of curing reaction was lowered in the presence of polyethylene as it restricts the cross linking site of rubber chains.

Effect of Temperature on Cure Behaviour

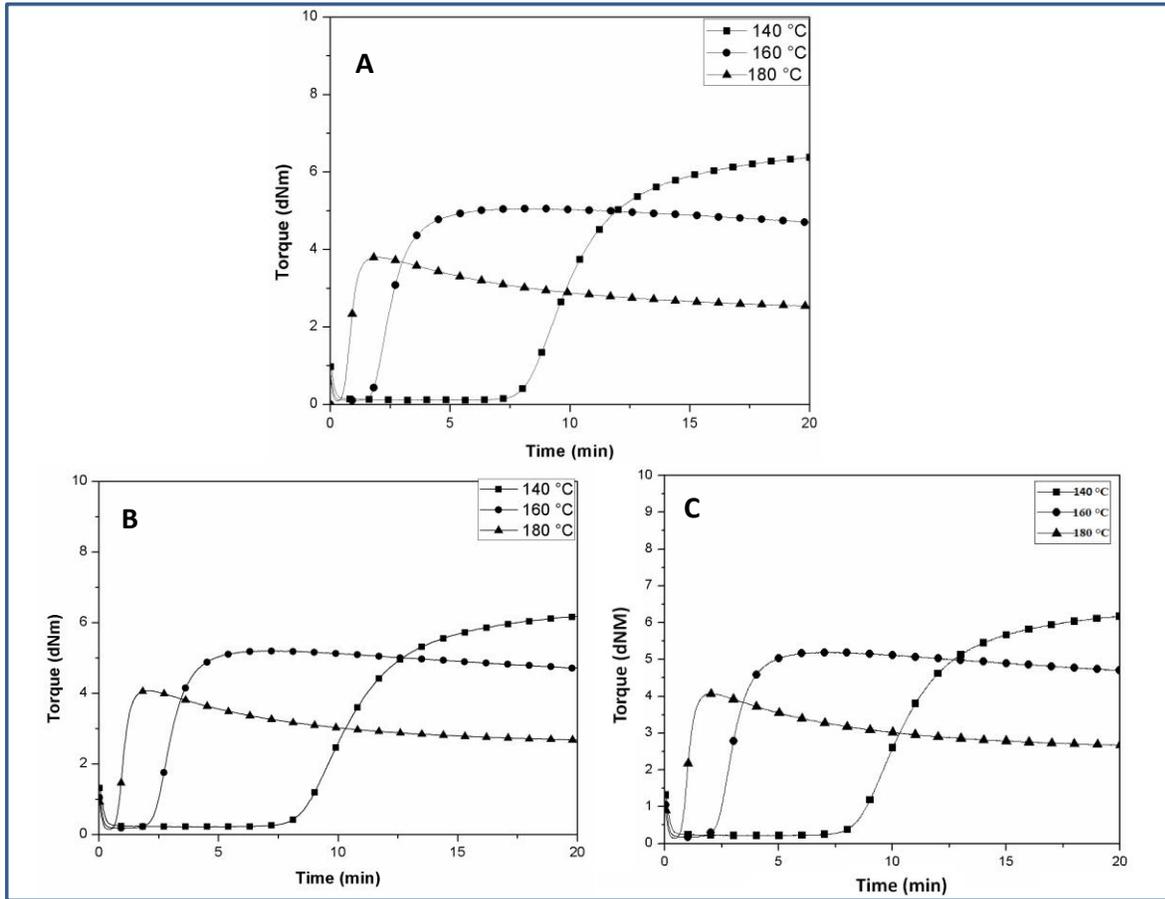


Figure 5.10. a) cure behaviour of pure NR at different temperatures, b) cure behaviour of pure NR-PE 20 at different temperatures and c) cure behaviour of pure NR-PPE 20 at different temperatures

The cure behaviour of all the compounds was studied at 140°C, 160°C and 180°C to understand the cure kinetics. Rheographs of neat NR and composites containing PE and PPE were given in figure 28. Maximum torque, scorch time and cure time decreased with increasing temperature as expected. The reversion phenomenon was more pronounced at 180°C. It was observed from the figure that there was a decrease in reversion when polyethylene was incorporated to the NR matrix.

5.4 Vulcanization Kinetics

It is believed that the torque obtained from the rheograph, which is a measure of stiffness, is proportional to the cross link density of the system. Thus extent of cross-linking reaction (α) is calculated from the torque values as follows:

$$\alpha = \frac{M_t - M_0}{M_\infty - M_0} \quad (2)$$

where M_0 , M_t and M_∞ , are the torque values at time zero, t and at the end of the reaction respectively.

Regardless of the reaction mechanism, the kinetics of the cross linking reaction is described by a differential equation related to time and temperature as follows:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (3)$$

where t is the time, T is the temperature; K is the kinetic constant at temperature T and the function $K(T)$ is described by the Arrhenius equation:

$$K(T) = K_0 e^{-E_a/RT} \quad (4)$$

Where K_0 is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the temperature.

The function $f(\alpha)$ is defined as follows for an autocatalytic curing reaction[65,66]

$$f(\alpha) = \alpha^m (1-\alpha)^n, 0 \leq m \leq 1, n \geq 1 \quad (5)$$

where m and n denote the reaction orders that depends on temperature.

Effect of Temperature on the Conversion rate

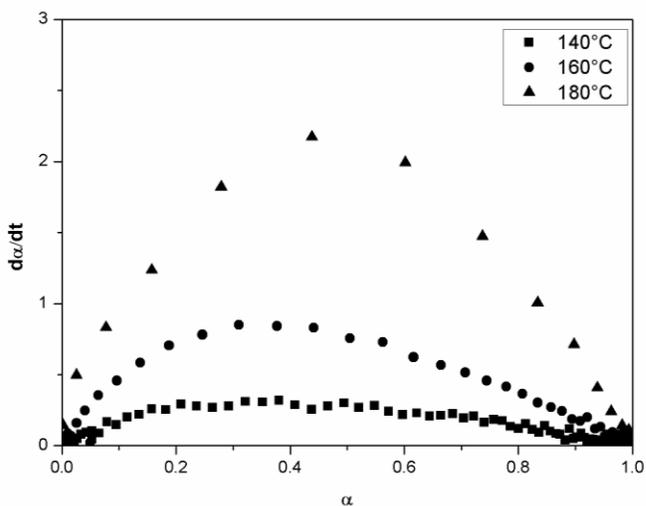


Figure 5.11: Rate of conversion as a function of degree of conversion plot of neat NR compound at different temperature

A plot of rate of reaction vs. degree of conversion for NR compound at different temperatures is given in figure 5.11. As the rate of curing reaction increased, the rate of conversion increased, passed through a maximum and then decreased. All compounds followed similar behavior for all the curing temperatures. This indicated that the curing reaction of NR compounds exhibited autocatalytic characteristics, which means the maximum reaction rate occurs at the beginning followed by a decrease at longer time. It was seen that the shape of the conversion curve depended on temperature. As the temperature increased, the peak height of the conversion rate curve also increased with a shift in peak position toward higher α value.

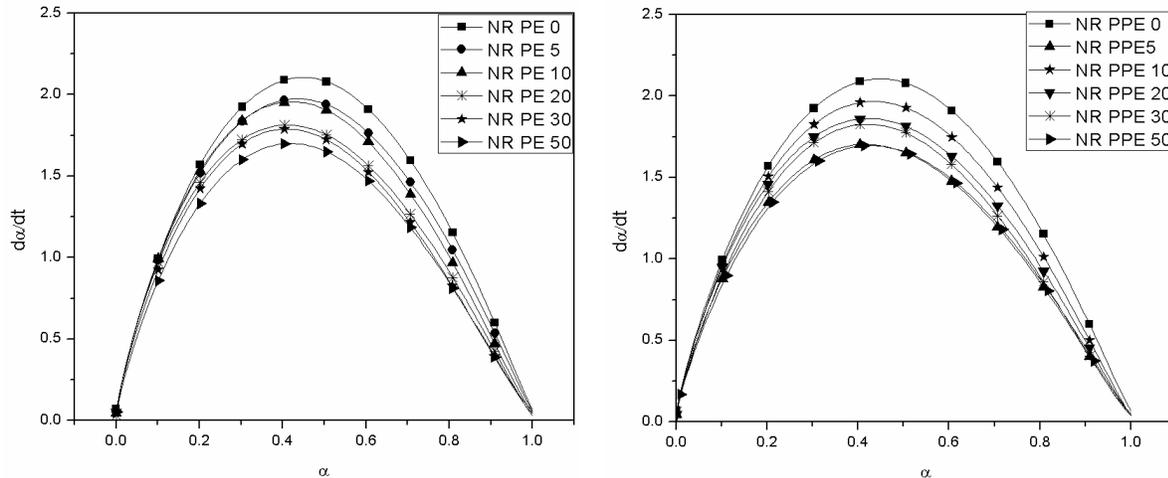
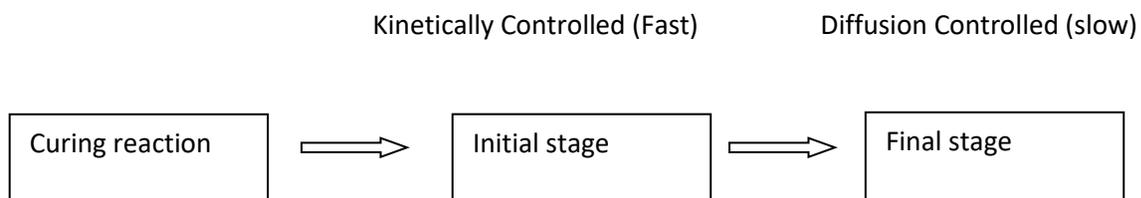


Figure 5.12: Rate of conversion as a function of degree of conversion plot at 180°C of a) NR/PE and b) NR/PPE[60]

A plot of rate of conversion $d\alpha/dt$ versus the degree of conversion α of NR /PE compounds and NR /PPE compounds at three different temperatures obtained from the rheograph curves are represented in figures 5.12a and 5.12b. For all compounds, the maximum rate of conversion occurred at α value between 0.4 and 0.5. The addition of thermoplastic did not alter the reaction mechanism but the rate of reaction was found to be decreasing with increasing PE content. This is due to the phase separation of the thermoplastic component as the curing reaction proceeded[67]. It could be better said that the possibility for the reaction between natural rubber chain and curing agents decreased with increasing PE content. It is very important to add that cure reaction was initially very fast and was kinetically controlled. As the curing proceeded, the reaction rate was lowered due to the cross linking of the rubber phase which decreased the mobility of the chains[68]. At this stage reaction became diffusion controlled. This could be better explained as shown below.



Kinetic Parameters of Vulcanization Reaction

The kinetic parameters of vulcanization, such as order of reaction n and m and temperature dependent specific rate constant, $K(T)$ were estimated from the generic kinetic model expression of Eqn. (5). The fitted curves are shown in figure 5.13. In this figure, a comparison was made between the experimental curves (points) and the model curves (solid lines). The experimental values were closely fitted with the conversion rate curve obtained from model parameters all the way through the entire degree of conversion for all the systems. The values of n and m were calculated at three different temperatures using non-linear regression analysis using ORIGIN 8.0 computer software and are given in Table 4 and figure 5.14. From the kinetic analysis it was observed that the order of reaction did not follow the n th order kinetics. The reaction order was the sum of the of n and m values, which changed with temperature, amount of thermoplastic component and PE modification. The total order of curing reaction ($n + m$) was decreasing with increasing the curing temperature.

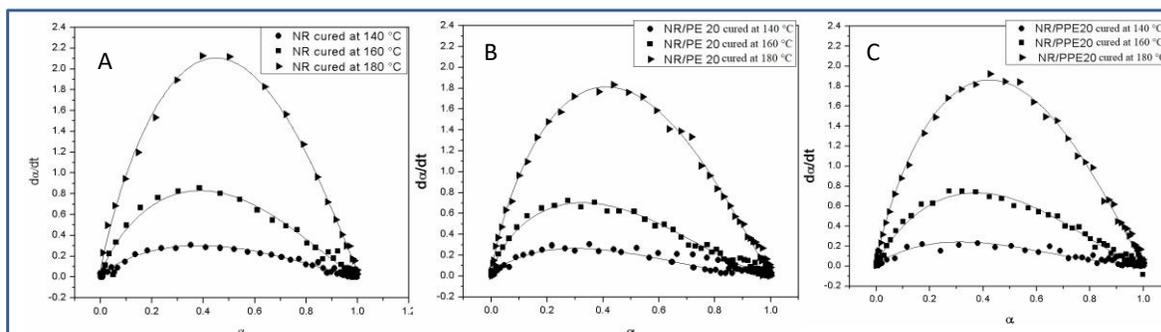


Figure. 5.13. Reaction rate vs. conversion plot for experimental (points) and autocatalytic fit (solid line) cured at temperatures 140°C, 160°C and 180°C for a) neat NR b) NR/PE 20 and c) NR/PPE 20

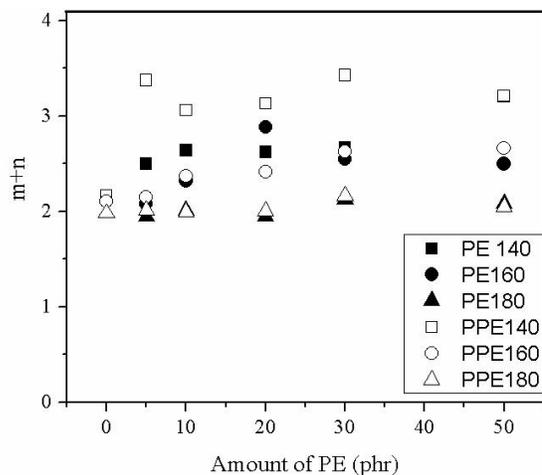


Figure 5.14. Order of curing reaction of NR/PE compounds and NR/PPE compounds at different temperature

The total order of reaction $m+n$ mainly shows an increasing trend by adding plasma modified polyethylene, which indicates that the reaction order is slightly changed when PPE takes part in the curing reaction of NR. PPE shows a retarding effect on the curing of NR compound. The $m+n$ values also suggest that the polar functional groups are acting as a hindrance for the curing reaction.

5.5. Mechanical properties

a) Effect of plasma modified PE on the mechanical properties of NR

The addition of plasma modified PE improves the modulus but improvement in tensile strength is marginal. This may be due to the fact that the presence of functional groups present on the surface of the polyethylene after the plasma treatment reduces the interaction between NR and PE.

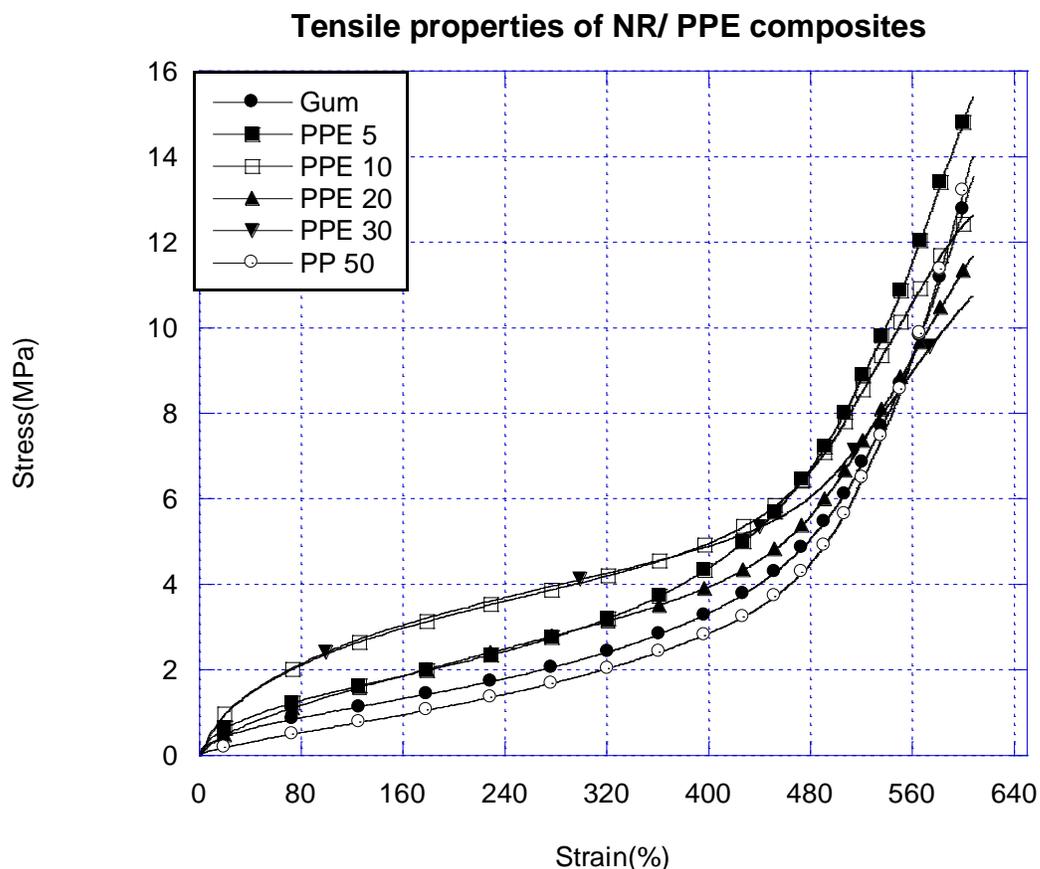


Figure 5.15. Stress Strain curves for NR/PPE system[69]

b)Effect of unmodified PE on the mechanical properties of NR

Stress strain curves of NR and NR/PE composites have been shown in figure 34. The addition of PE increases the mechanical properties. The composite with 10 phr PE shows the highest tensile strength. But on further increase in PE tensile strength decreases gradually. This may be because at higher loading PE can accumulate together and act as a hindrance for stress transfer. The vulcanizate with 50 phr PE shows remarkable increase in modulus. The decrease in mechanical properties at 5 phr may be because of the fact that at extremely low loading, PE acts as a hindrance for stress transfer. The increase in modulus at higher filler loading is due to the thermoplastic nature of PE and PPE and this is confirmed from the percentage of thermoplasticity obtained from the rheograph .

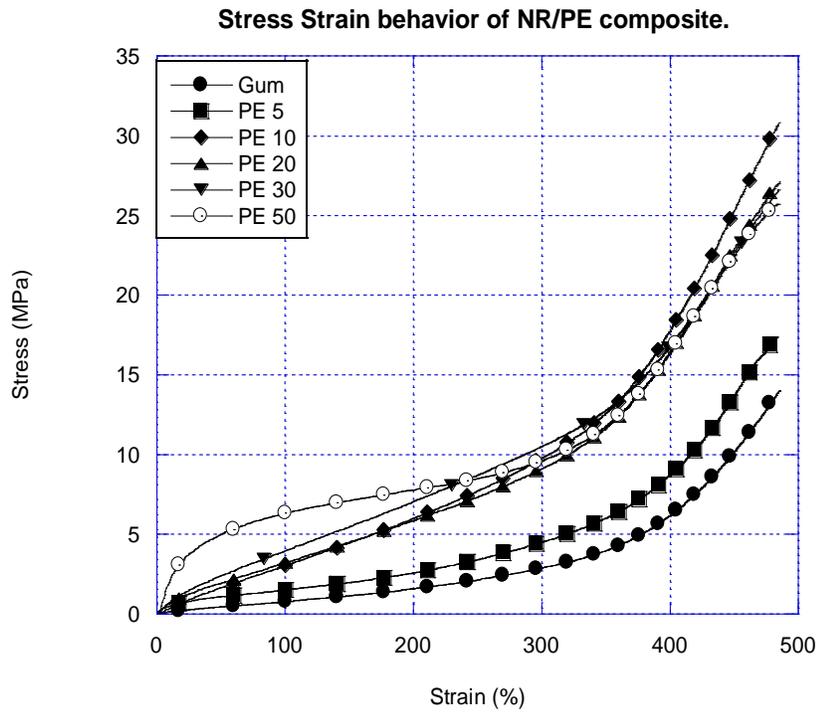


Figure 5.16. Stress Strain curves for NR/PE system[69]

c) Comparison of mechanical properties of NR/PE and NR/PPE composites

The plasma modification was found to reduce the mechanical properties may due to the decrease in interaction caused by the functional groups present on the surface which made less hydrophobic.(Table 5.2).

Table 5.2. Tensile properties of NR/PE and NR/ PPE vulcanizates.

Filler loading (phr)	Tensile strength (MPa)		Mod @ 300% (MPa)		Elongation at break (%)	
	PE	PPE	PE	PPE	PE	PPE
0	14.00± 0.7	14.00 ± 0.7	3.42 ± 0.14	3.42± 0.14	485 ± 15	485±15
5	17.37 ±1.1	13.53 ± 1	2.53 ± 0.1	1.95 ±0.5	573 ± 13	608±12.16
10	30.80±0.77	15.40 ± 0.77	14.58± 0.25	3.61± 0.58	388 ±7.1	571 ±9.6
20	27.10 ±0.64	12.63±0.6	10.61± 0.42	3.77± 0.42	437 ±12.1	545 ± 10.9
30	26.60 ±0.5	11.67±0.4	11.75± 0.47	3.88 ± 0.5	452 ±13.7	548 ±10.96
50	25.70 ±0.9	10.73± 1	12.33± 0.56	5.12 ± 0.49	573 ±20	535±20

5.6 Filler polymer interaction

The concept of ‘‘bound rubber’’ at the particle– elastomer interface has been put forth to describe interfacial interaction between filler and polymer[70]. Bound rubber is a film that is stabilized around the filler via van der Waals interactions, and is thus resistant to dissolution in solvent. It is also understood that the motion of macromolecular chains within the bound rubber phase is restricted by interaction with the filler particle surfaces. Analysis of bound rubber content gives the extent of filler polymer interaction.

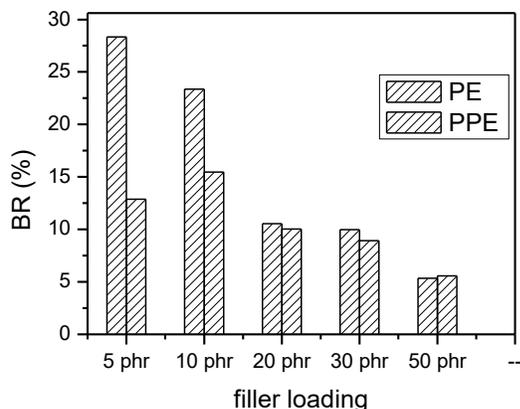


Figure 5.17. Effect of filler loading on bound rubber content [69]

The bound rubber content was found to be higher for unmodified PE. The comparatively lesser bound rubber content for PPE for all the compositions may be due to the lesser interaction between PPE and NR as explained earlier. Also as we increase the loading, for both PE and PPE, a general trend of decrease in bound rubber content was observed. (Figure 5.17)

Kraus plot

An attempt has been made to apply the Kraus[34] equation to find the extent of reinforcement of fillers in the matrix. According to Kraus equation

$$\frac{V_{r0}}{V_{rf}} = 1 - m \left(\frac{f}{1-f} \right)$$

where V_{r0} and V_{rf} are the volume fraction of solvent swollen rubber in the fully swollen unfilled sample and in the fully swollen filled sample respectively. f is the volume fraction of the filler and the slope m will be a direct measure of the reinforcing capacity of the filler in the elastomer matrix. V_{r0}/V_{rf} values of all the composites have calculated using toluene as the solvent and it was plotted against corresponding $f/(1-f)$ values. Reinforcing ability and swelling resistance caused by the filler is directly related.

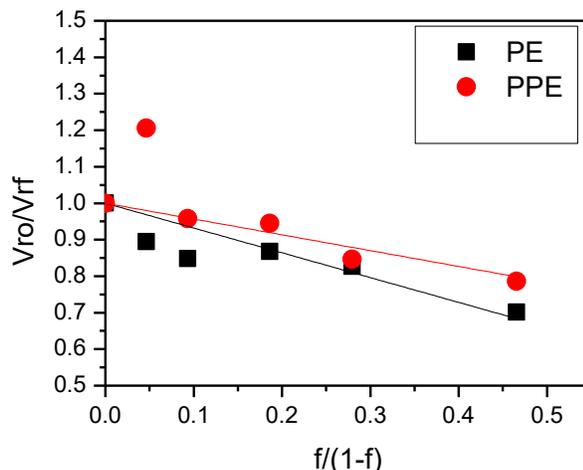


Figure 5.18. Kraus plot NR/PE and NR/PPE composites

Higher the slope in the Kraus plot more interaction between filler and polymer. Kraus plot which also gives the degree of filler polymer interaction also confirms that for modified there is lesser interaction between filler and polymer.(Fig5.18)

5.6 Conclusion

The plasma modified polyethylene and unmodified polyethylene were successfully incorporated into natural rubber matrix as fillers by mechanical mixing using two roll mill. Both polyethylene and plasma modified PE enhanced the mechanical properties of NR. The interaction between the filler and matrix is highlighted and was found to be more in the case of polyethylene/NR composites. Plasma modification can impart some polar groups on PE but this reduced the interaction between NR and PPE compared to PE. The interaction between NR and plasma modified PE, which has some functional group on it can be improved if we add compatibilizer like modified NR.

In all compositions the unmodified PE was nicely dispersed in the rubber matrix whereas the plasma modified PE (PPE) showed high degree of phase separation and a tendency to agglomerate due to the polar- polar cohesive interactions among them. The vulcanization kinetics and cure characteristics were studied by using multi-functional rheometer. The torque values were found to decrease with the addition of PE because of the thermoplastic nature of polyethylene. The curing reaction became slow when the plasma modified PE was added to the natural rubber matrix due to its polar nature. This was evidenced from the morphological images and $m+n$ values. The curing reactions of all the composites were autocatalytic in the beginning and very fast. The reaction was kinetically controlled. The rate of the reaction reached a maximum followed by a decrease due to the cross linking of NR phase. This is due to the fact that as the degree of cross linking increase, the reaction rate becomes slower. At this stage the reaction was controlled by the diffusion mechanism. The experimental kinetics of curing reaction gave excellent fitting with the theory.

Part II: Plasma modified PE as a matrix for natural fiber composites

Chapter 6: Thermoplastic biocomposite prepared via compression moulding

This chapter described development of new type of thermoplastic bio composite with coir fibre derived from coconut was fabricated by means of plasma modification of the polymer surface. Plasma modified polyethylene (PPE) was used as the matrix for coir fibre reinforced composites. Here, plasma modification of PE was introduced as a new method to improve the compatibility. The present study involves and characterization of plasma modified PE (PPE) and coir fibre composites prepared via hot press method or compression moulding. The detailed description of preparation method is given in chapter 3. This chapter has been published in RSC advances.

6.2 Effect of chemical treatment on coir fibres

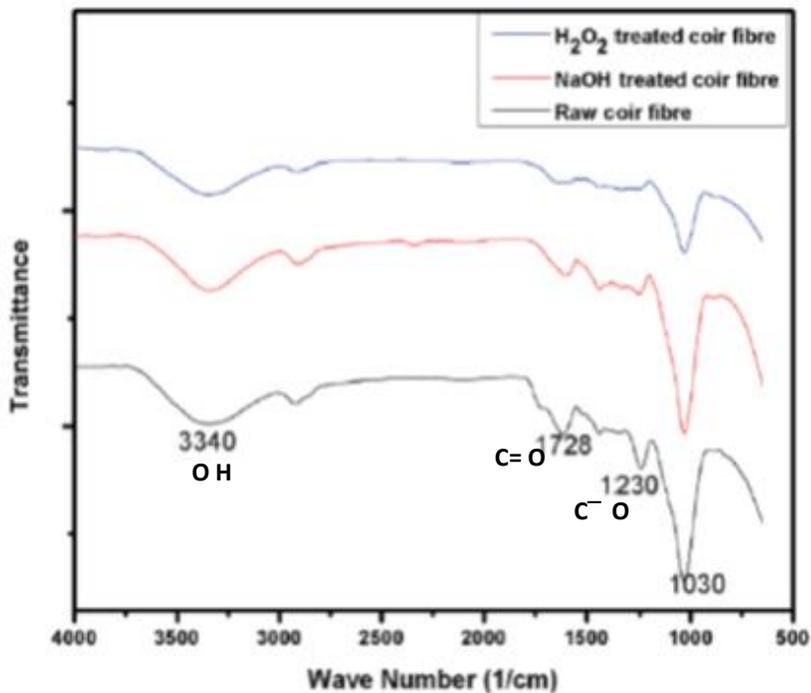


Figure 6.1:FTIR spectra of raw coir fibre, NAOH treated coir fibre and H₂O₂ treated coir fibre[71].

The FTIR spectra of natural and treated coir fibers are shown in Fig.6.1. All these spectra reveal a broad and intense peak at 3340 cm^{-1} suggesting hydrogen-bonded (O–H) stretching vibration from the cellulose and lignin structure of the fibre. The band at 1728 cm^{-1} corresponds to axial vibration of C=O (which is the characteristic band of hemicellulose, observed in the natural coir fibre) disappeared after chemical treatments. The band at 1238 cm^{-1} is related to the vibration (C–O) of esters, ethers and phenols groups attributed mainly to a presence of waxes in the epidermal tissue[21] and the disappearance of this band in the treated fibers results from the removal of those waxes. The H_2O_2 treatment seems to be the most efficient in the removal of waxy and fatty acid residues. The bleaching process resulted in removal of waxy layer and partial removal of pectin and lignin and hence more hydroxyl groups on cellulose were exposed. The pectin and waxy substances in plant fibre acting as a barrier to interlock with nonpolar polymer matrix, hence the removal of these components will improve the interaction with PE matrix. So this chemical treatment were used for further studies as treated fibers or bleached fibers.

6.3 Effect of Fiber loading

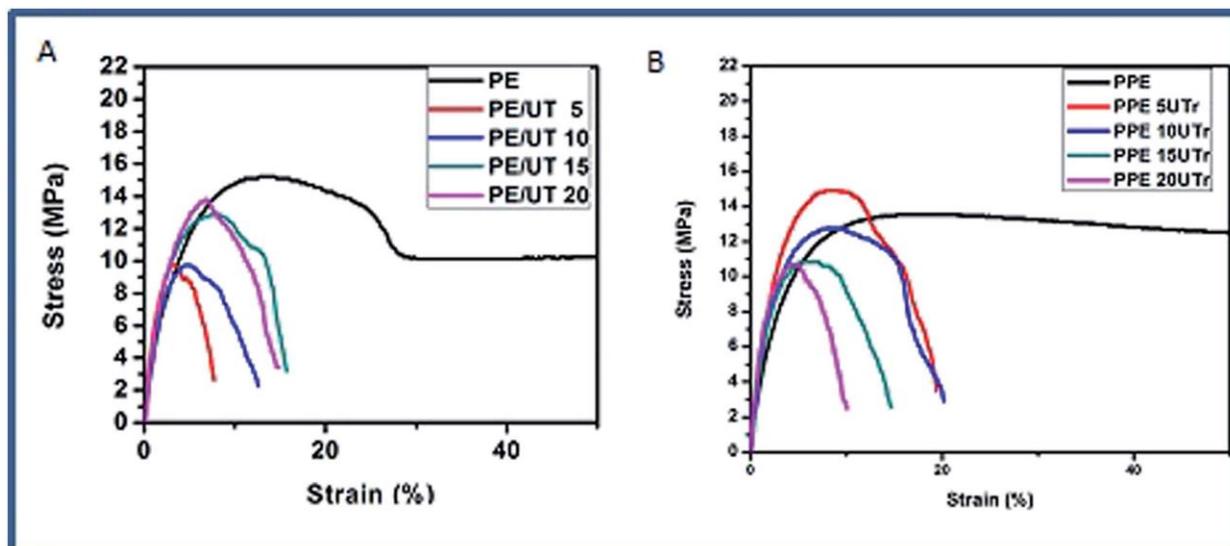


Figure 6.2: Stress–strain plot of bio composites with varying amount of coir fibre (a) PE and (b) PPE.[71]

Stress– strain behaviour of thermoplastic bio composites prepared from PE and PPE is shown in Fig. 6.2. The plasma modification did not alter the stress– strain behaviour of PE but a small reduction in the tensile strength was observed. This could be due to the chain scission came

about during plasma treatment[72]. The addition of coir fibre completely modifies the stress–strain behaviour of the system. The thermoplastic biocomposites were not showing any plastic deformation because of the presence of rigid coir fibres[73]. The modulus of the system tremendously increased with the addition of fibre in both cases. But the tensile strength of the PE biocomposite is lower than the neat polyethylene. This is mainly due to the lack of proper interfacial adhesion between the polymer matrix and coir fibre and inefficient dispersion of fibre. Tensile strength of the composites increased with the amount of coir fibre added into it. Fig. 6.2b describes the stress–strain behaviour of thermoplastic bio composites prepared from PPE. In this case the biocomposite with 5 phr coir fibre showed higher tensile strength which is higher than that of neat polymer and further addition of fibre decreases the tensile strength. This means that there is interaction between the coir fibre and PPE matrix which improves the interfacial adhesion[73].

6.4 Effect of chemical treatment of coir fibre on the properties of bio composites

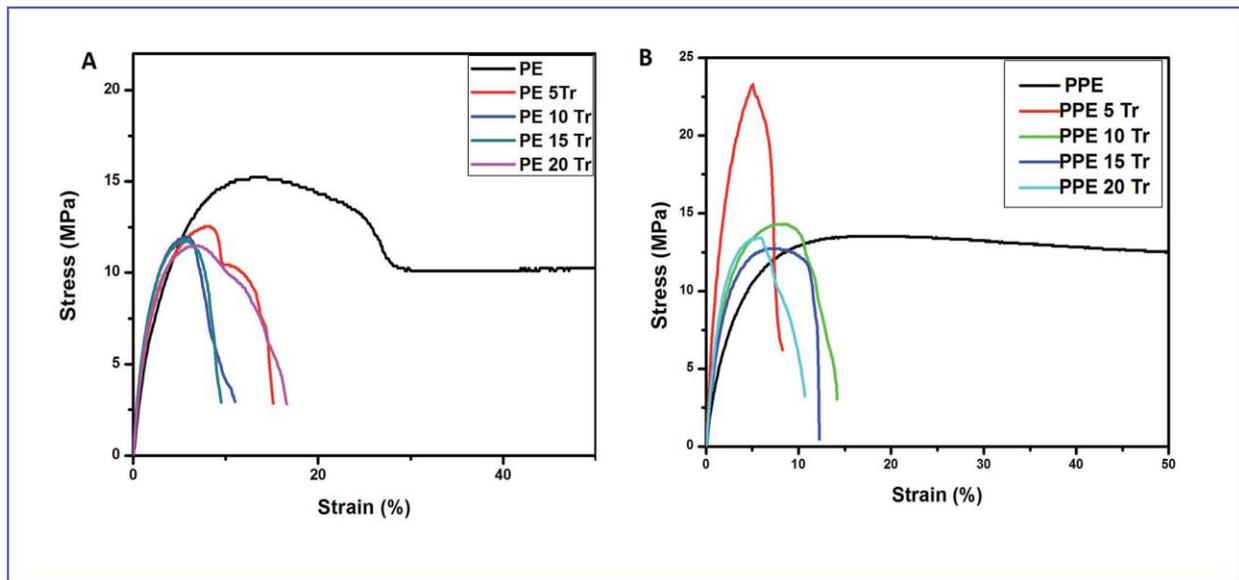


Figure 6.3: Stress–strain plot of bleached coir fibre composites with varying amount of coir fibre (a) PE and (b) PPE.[71]

Stress–strain behaviour of thermoplastic bio composites prepared by bleached coir fibre is shown in Fig. 6.3. The biocomposite with bleached fibres were also showing the same trend for stress–strain plot. But the tensile properties such as tensile strength and tensile modulus were increased.

Bleaching with hydrogen peroxide improves the quality and the aspect ratio of the coir fibre by partially removing the lignin and hemicelluloses[21]. That might be the reason for the improvement in tensile properties of biocomposite with bleached fibre. In this case also the composite with 5 phr fibre were showing better properties and higher loading of fibre show a small decrease in the tensile strength as well as tensile modulus. PPETr biocomposites has been showed better properties compared to that of PETr biocomposites. The maximum tensile strength and modulus was shown by composite with 5 phr loading of treated coir fibre. At this composition there may be good interfacial adhesion between the fibres and matrix that could be further explained from morphology and water absorption studies. The increased aspect ratio of coir fibre after bleaching helped to improve the dispersion and also the partial removal of lignin and hemicellulose from the surface made cellulose more interactive with the plasma modified PE matrix.

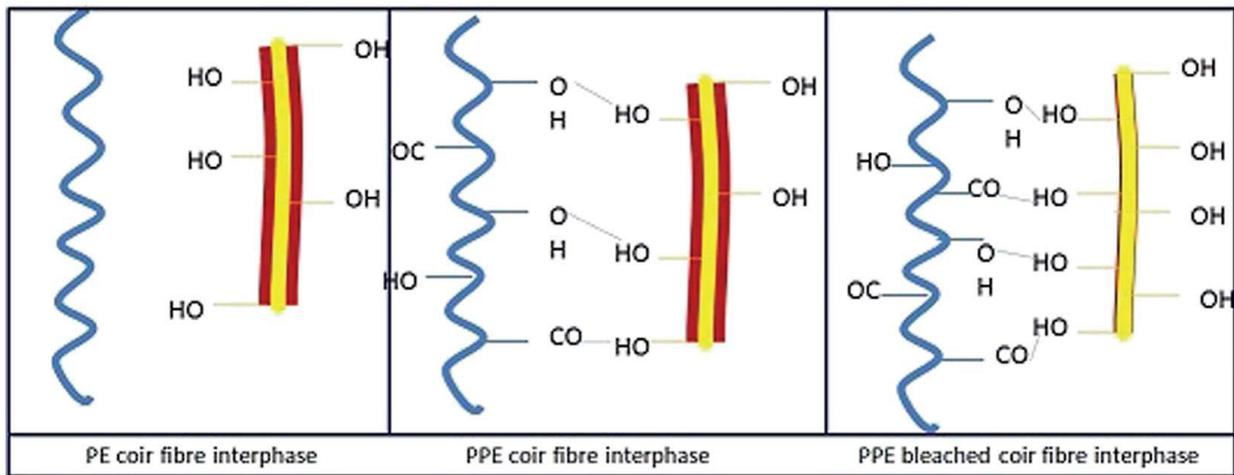


Figure 6.4: Schematic representation of biocomposite interphases.[71]

The interphases of three different types of biocomposites are represented schematically in Fig. 6.4a illustrates the untreated PE coir fibre interphase in which no interaction between the nonpolar matrix and polar cellulosic fibre is observed. So this kind of composites showed sharp interphase that was the reason for poor mechanical properties. The interphase of plasma modified PE and coir fibre is given in Fig. 6.4b. The presence of polar functional groups on modified PE facilitates more interaction between the fibre and matrix. In the third case, coir fibres were bleached and so most of the lignin and hemicelluloses were removed during bleaching therefore more hydroxyl groups were available for the interaction.

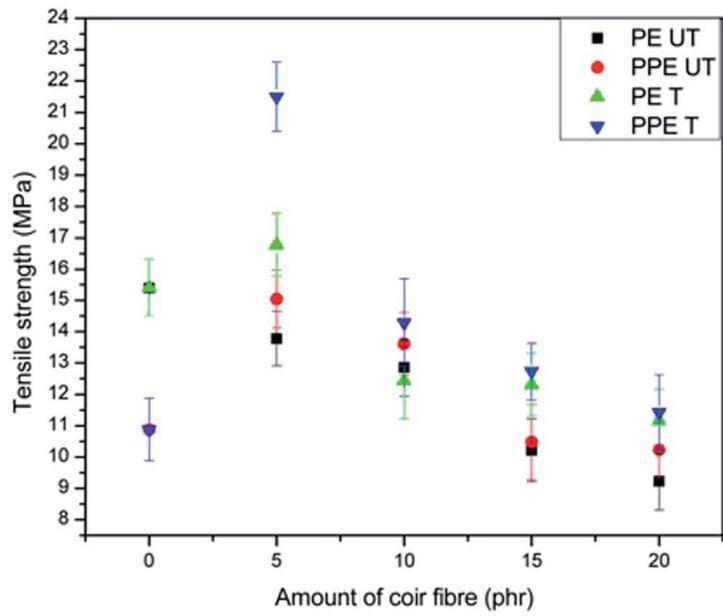


Figure 6.5: Tensile strength vs. amount of filler[71]

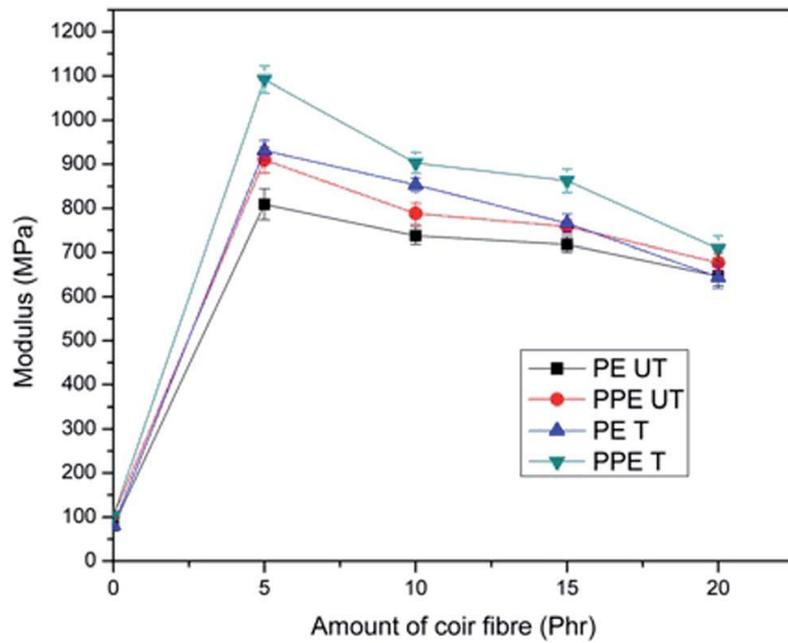


Figure 6.6 Tensile Modulus vs. amount of filler[71]

Fig. 6.5 and 6.6 describe the tensile strength and tensile modulus of all bio composites with varying amount of coir fibre respectively. The tensile strength was increased by around 100% in the case of PPETr biocomposite where as it was only 10% for PETr biocomposite than neat polymer. Even though the tensile moduli increased to a great extend for both cases, PPETr biocomposites showed higher modulus than PETr biocomposites. The composite prepared from PPE and bleached fibres showed the best properties. This is because of the interaction between the polar groups on the polymer surface and hydroxyl groups of the cellulose fibre. This new biocomposite showed better interfacial adhesion, good dispersion of fibres and proper wetting of fibers. As a result of the high degree of interfacial interaction, the stress transfer from the matrix to the reinforcement is very efficient. The good interfacial adhesion and proper wetting of fibre was further confirmed from the morphological analysis. In all the compositions 5 phr fibre loading showed better properties and at higher loadings agglomeration of fibers adversely affect the mechanical properties. But compared to other samples, the unusual trend observed in the tensile strength of 10 phr samples is within the acceptable range of statistical error.

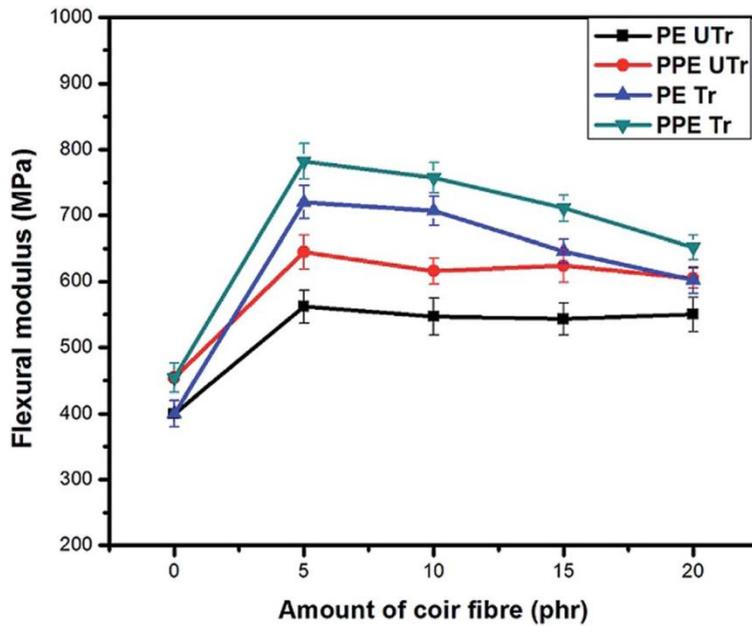


Figure 6.7: Flexural Modulus vs. amount of filler[71]

The variation of the flexural modulus of both raw and treated coir reinforced PE biocomposites at different fiber loading is shown in Fig. 6.7. The flexural modulus of coir fiber reinforced composites increased with the fiber loading[74]. Since the coir fiber is of higher modulus, higher

fiber concentration demands higher stress for the same deformation. So the incorporation of the coir fiber into the soft polyethylene matrix resulted in increase of the modulus. The flexural modulus of PPETr biocomposites was the highest. This is because treated fiber composite provides evidence of homogeneous distribution of Fig. 6.4 Schematic representation of biocomposite interphases.

6.5 Morphology



Figure 6.8: Microscopic images of biocomposites with untreated coir fibre (a) PE and (b) PPE.[71]

Morphology of the fractured composites surface was studied by using a stereo microscope. The Fig. 6.8a and b illustrate the images of PE biocomposite and PPE biocomposite respectively. In Fig. 6.8a a visible gap is clearly observed between the fibre and matrix, which can be attributed to the poor interfacial adhesion between PE and coir fibre. But in the case of PPE biocomposite there is no micro voids and we can see nice wetting of polymer matrix on the fibre surface (Fig. 6.8b). All these observations can be evidence for good interfacial adhesion between PPE matrix

and coir fibre, which can be evidenced in the improvement in mechanical properties. The strong adhesion and fibre wetting was the result of the formation of polar interactions between the plasma modified polymer surface and cellulosic fibres.

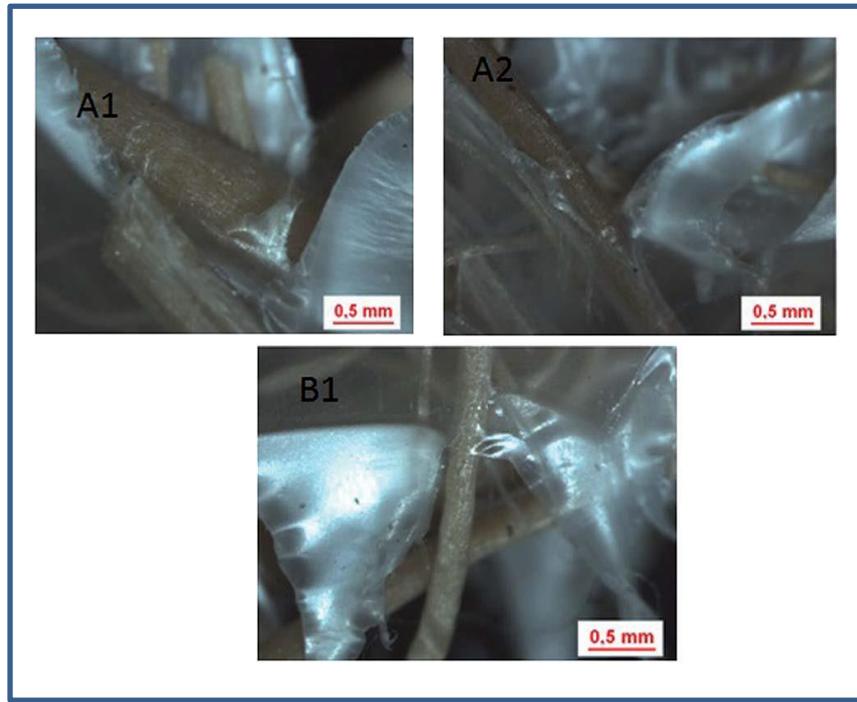


Figure 6.9: Microscopic images of biocomposites with treated coir fibre (a) PE and (b) PPE.

The morphology of biocomposites prepared by treated coir fibres also showed the same behaviour (Fig. 6.9). Morphology reveals that good wetting of coir fibre was observed by PPE matrix where as we can clearly see the interface in the case of PE biocomposite. A good fibre/matrix interfacial adhesion was established in PPE coir fibre composite in place of PE coir fibre composite.

6.6 Water absorption behaviour of bio composites

The study of water absorption characteristics is significant in the case of natural fibre composites, due to their intense sensitivity to water, which affects the performance of the material. Water absorption studies of PE and PPE based biocomposites were conducted at room temperature. The water uptake evolution by the composites as a function of time at various filler loading is given in Fig. 6.10.

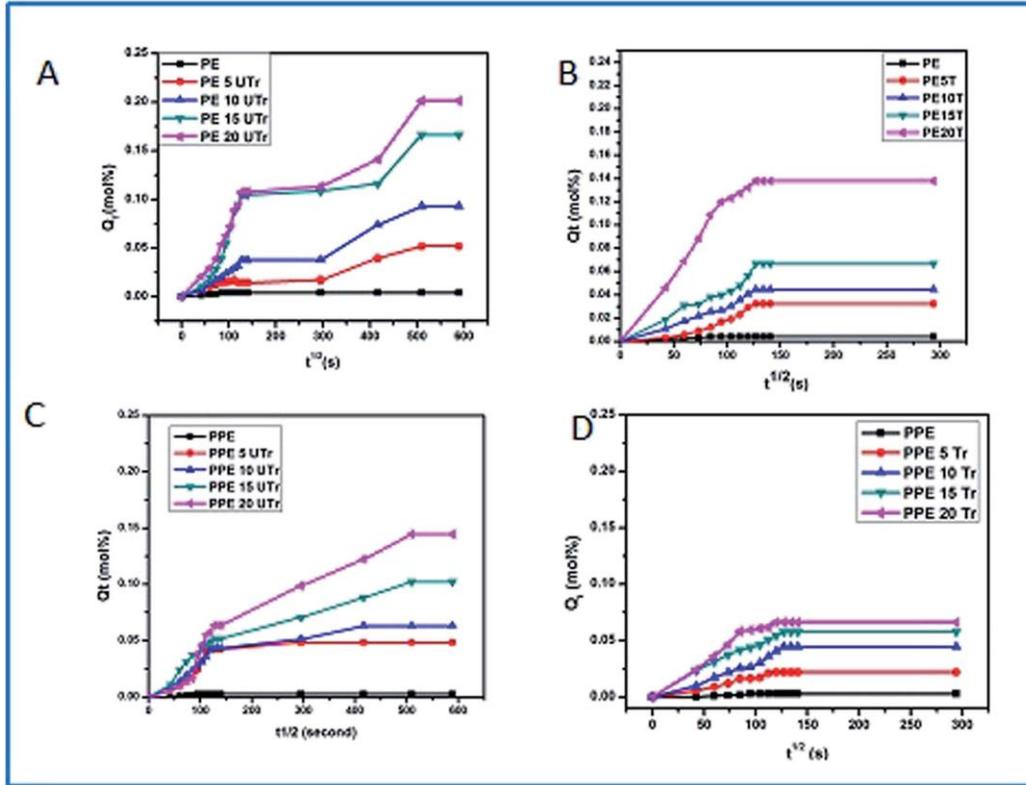


Figure 6.10: Q_t vs. $t^{1/2}$ plot of bio composite with varying amount of fibre (a) PE UTr, (b) PPE UTr, (c) PE Tr and (d) PPE Tr.[71]

The polyethylene matrix did not absorb any water given that it is nonpolar / hydrophobic material. We can understand from the figure Fig. 6.10 that neat PPE sheet has slightly higher water absorption behavior than PE due to the polar functional groups introduced on the surface of polyethylene. Interestingly as shown earlier the water contact angle was lower for PPE samples. It is obvious from the figure that amount of water absorbed by the composite increased with the addition coir fibre in all the cases as we expected. The water absorption of thermoplastic natural fibre composite happens mainly due to the presence of hydroxyl groups in the cellulose fibre, several porous tubular structures associated with lignocellulosic fibres and also the micro voids in the composites because of the lack of interfacial adhesion[75]. So the water absorption increased with the amount of fibre in the composites increased in all the cases. Interestingly, as expected the chemically treated coir fibre reinforced composites showed much lower water absorption compared to the raw ones. This is due to the fact that after treatment the number of hydroxyl groups, responsible for the water absorption are reducing. In the beginning, all the bio

composite samples showed a very quick increase in percentage of water absorption. As the time of immersion increased, the absorption curve reached a maximum value and attains the equilibrium point.

The time to reach equilibrium value and the amount of water absorbed were not same for all the bio composites. Compared to other bio composites PPETr composites showed lower percentage of water absorption and reached the equilibrium at shorter time of immersion. From this we can understand that PPETr bio composites possess higher resistance to water absorption.

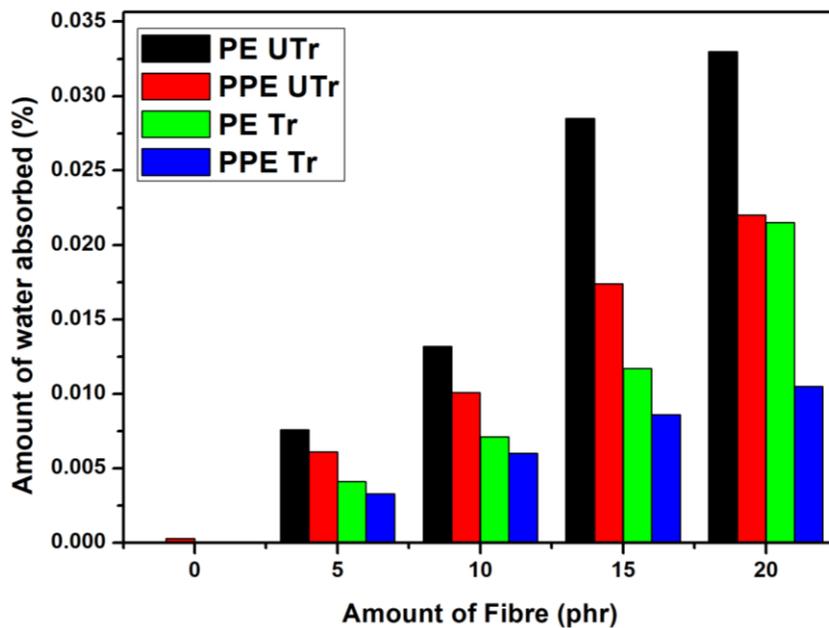


Figure. 6.11 Amount of water absorbed Vs Amount of fiber

Figure. 6.11 describes the Q_N , molar absorption at equilibrium (infinite time) of all biocomposites. It is very clear from the figure that PPETr biocomposites show the lower absorption of water at any filler loading. PEUTr composites show the higher absorption of water. Even though neat PPE was showing small absorption than neat PE, the water absorption was very less in PPE biocomposite compared to PE biocomposites irrespective of the fibre loading. This is because a considerable amount of accessible OH groups, those are responsible for water absorption disappeared to become bonded to the polar groups on the plasma modified PE surface. And also the lack of micro voids present in the composite due to better polymer fibre

interaction will help to reduce the water absorption[76]. This can be well explained from the microscopic images of the composites. The coir fibers were effectively wetted by PPE matrix which cannot be seen in PE coir fibre biocomposites. Chemical treatment of coir fibre substantially reduces the water absorption of both PE composites and PPE composites.

6.7 Conclusions

A new kind of thermoplastic bio composite reinforced with coir fibre can be successfully fabricated by means of plasma modified thermoplastic polymer with improved properties. The preparation method we adopted was mechanical mixing and hot press method, which is simple, energy saving and more cost effective than other methods like melt mixing. Plasma treatment modifies the surface of powder polymer surface to become more hydrophilic by imparting functional groups on it. This could improve the compatibility between the polymer matrix and natural fibre. The new biocomposites showed higher mechanical properties in terms of tensile and flexural properties. Plasma modified polyethylene biocomposites with H₂O₂ treated fibres at 5 phr loading showed the best properties. The increase in tensile strength was 100% whereas that of PE treated fibre biocomposite was only 10%. The lower water absorption characteristics of the new biocomposites disclose that there is good wetting of the polymer on the natural fibre. The morphology confirms that good wetting of fibre was obtained by plasma modified polyethylene matrix which is very essential to have good interfacial adhesion⁶⁸.

Chapter 7: Rotational Moulding of PE coir fiber composites

7.1 Introduction

Pressureless Moulding

Composites samples were prepared by heating PE powder- coir fiber mix at atmospheric pressure and cooled in room temperature. This process can be considered as an initial step for rotational moulding, in which no pressure is involved. Consequently composites prepared via this method lack mechanical interlocking between fiber and polymer matrix, which could be the main interfacial adhesion mechanism in composites prepared via molding involved high pressure.

7.2 Mechanical properties of pressureless molded composites

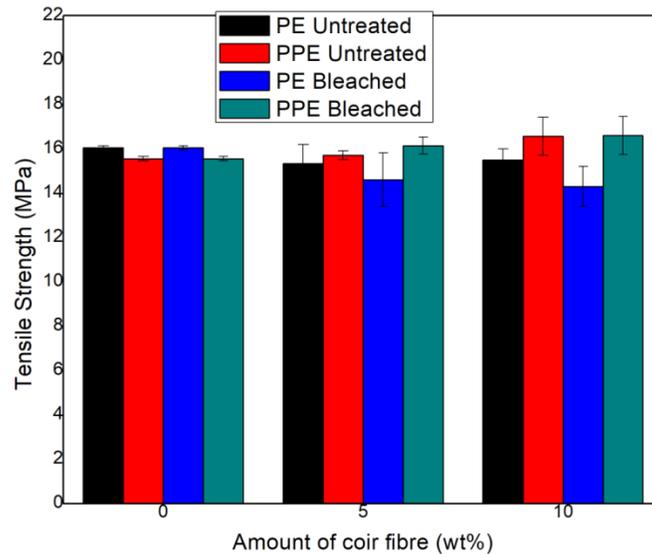


Figure 7.1 Tensile strength of Pressureless molded composite

Tensile strength of all composites prepared via pressureless molding has summarized in figure 7.1. The addition of coir fiber into unmodified PE matrix showed slight decrease in tensile strength whereas with plasma modifies PE tensile strength increased. Mechanical interlocking is not possible in composites prepared via pressureless molding. So the increase in tensile strength is mainly due to good interfacial adhesion between plasma modified PE and coir fiber. Plasma modification introduced functional groups on the surface of PE which can interact with hydroxyl group of the cellulose fibers. Composites with bleached fibers showed better properties than

untreated fibers. In treated fibers more hydroxyl groups were available for the interaction so interfacial adhesion is improved.

Flexural Strength

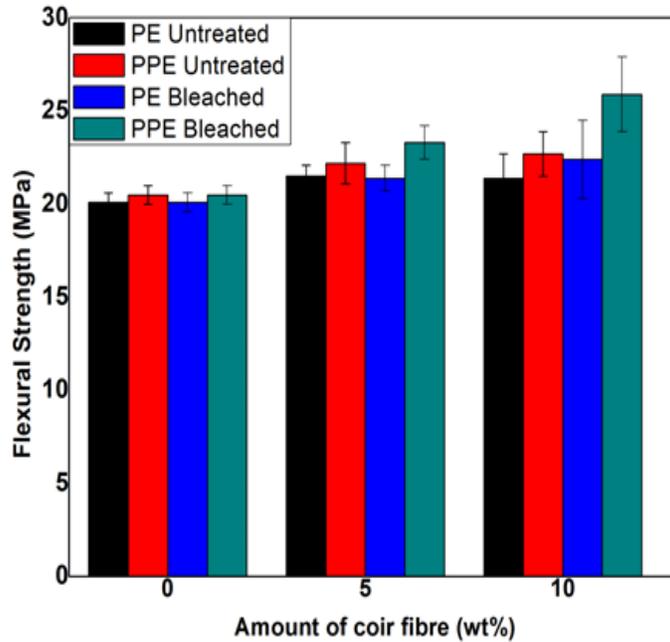


Figure 7.2 Flexural strength of Pressureless molded composite

The flexural strength increased with fiber loading (figure 7.2). Plasma modified PE -treated fiber composites showed higher flexural strength for all composition. PPE treated fibers with 10 wt% loading has improved flexural strength 24% higher than that of neat PE. This result is also in agreement with tensile properties.

Impact Strength

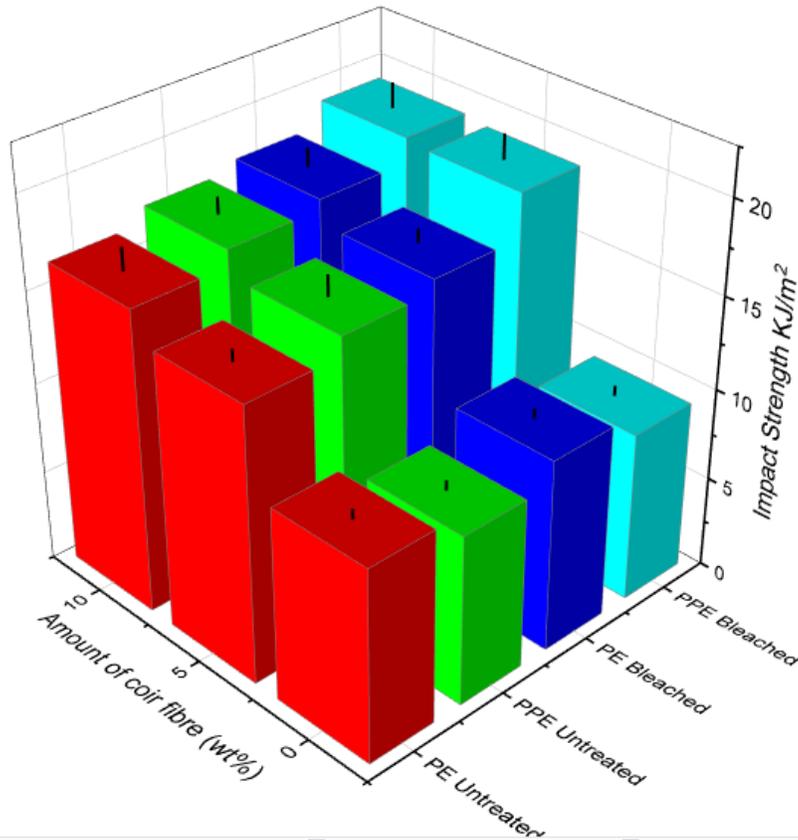


Figure 7.3 Impact strength of Pressureless molded composite

Impact strength has increased with the addition of coir fiber into PE matrix irrespective of any modification. It is found from the figure 7.3 that plasma modified PE based composites required more impact energy for breaking compared to that of unmodified PE composites. This is attributed to good interfacial adhesion improved wetting of the fiber by modified PE.

7.3 Rotational moulding

7.3.1 Single layer Experiment

In single layer process, the PE powder and short coir fibre (5 wt%) were premixed before molding. The total mixture (400g) was loaded into the mold and kept in the oven. The oven temperature was 260 °C and peak internal air temperature was set at 200 °C. Rotation was started when the oven temperature reached 100 °C. Both the oven temperature and the peak internal

atmosphere temperature (PIAT) were monitored during the process. When PIAT reached 200 °C, the set temperature heating stopped and cooling started. Approximately 30 min was taken for heating cycle and 30 min for cooling cycle for this particular PIAT. The composites were prepared at 240 °C and 260 °C respectively. The same procedure was used to prepare composites from plasma modified PE. This experiment was conducted to optimize the conditions for PPE coir fibre composite via rotomolding technique.

Single layer composites

The images of inner surface of single layer composite are shown in the figure 7.4. When introducing polymer and fiber together at the beginning of the process, it was found that most of the fibers tend to remain close to the inner surface of the molded specimen. In order to obtain an adequate fiber distribution in the thickness of the rotationally moulded specimen, it was necessary to produce a second layer of unreinforced polymer that covers and sinters on the inner specimen surface. In this way the fibers ended up well distributed across the specimens thickness.

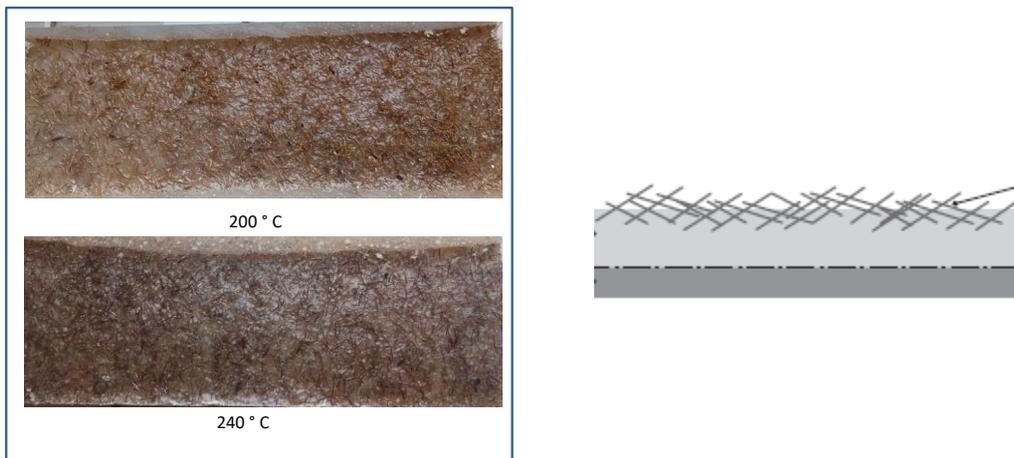


Figure 7.4: The inner surface of single layer composite processed at 200 °C and 240 °C

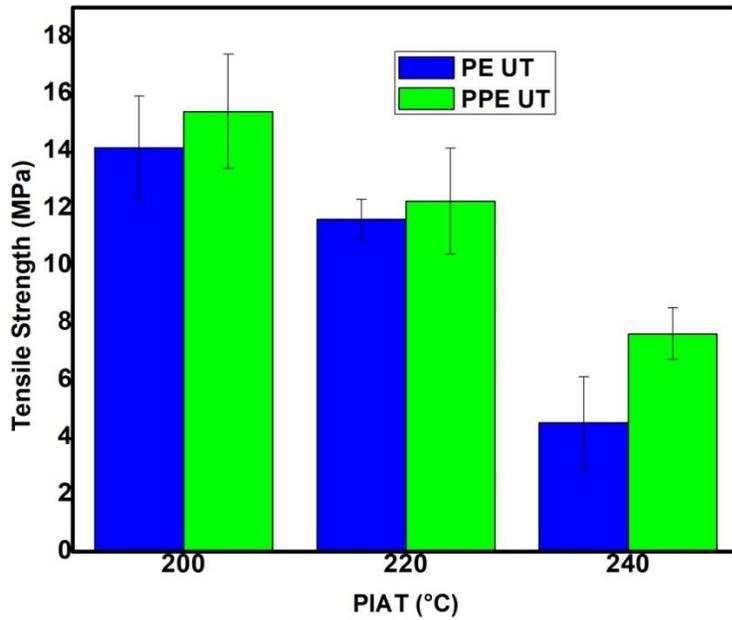


Figure 7.5: Tensile strength of untreated fiber (5%) composites with PE and PPE prepared at varying temperatures[77]

Tensile strength of the composite decreased with increasing processing temperature. This might be due to degradation of both fiber and PE matrix. Natural fiber is less thermally stable and there was color change observed for composite processed at 240 °C (figure 7.4). However the plasma modified PE based composite showed higher values compared to the unmodified PE composites.

Table 7.1 : Molding temperature vs molding cycle time

PIAT (°C)	Time of Heating (min)	
	PE	PE + 5% fiber
200	28	36
220	32	40
240	37	44

The increase in molding temperature resulted in increase in molding cycle time for neat PE as well as composites. This is because more energy required to achieve higher temperature since the rate of heating is same for all the molding. This resulted in degradation of coir fiber which

reduced the mechanical properties of the composites. The addition of coir fiber also increased the time of heating. This might be due to the increased melt viscosity of the composite material.

7.3.2 Double layer Experiment

In this process one half amount of the PE powder and full amount of coir fiber were premixed and this mixture was loaded into the mould. The oven temperature was 260 °C and PIAT was set 190 °C, since this process took more time. When the PIAT reached 140 °C other half of PE powder was added into the mould. During this time heating and rotating was going on. At this time PIAT was drop into lower temperature and finally when it reached 190 °C cooling was started. The final products are showed in the Fig.7.6.

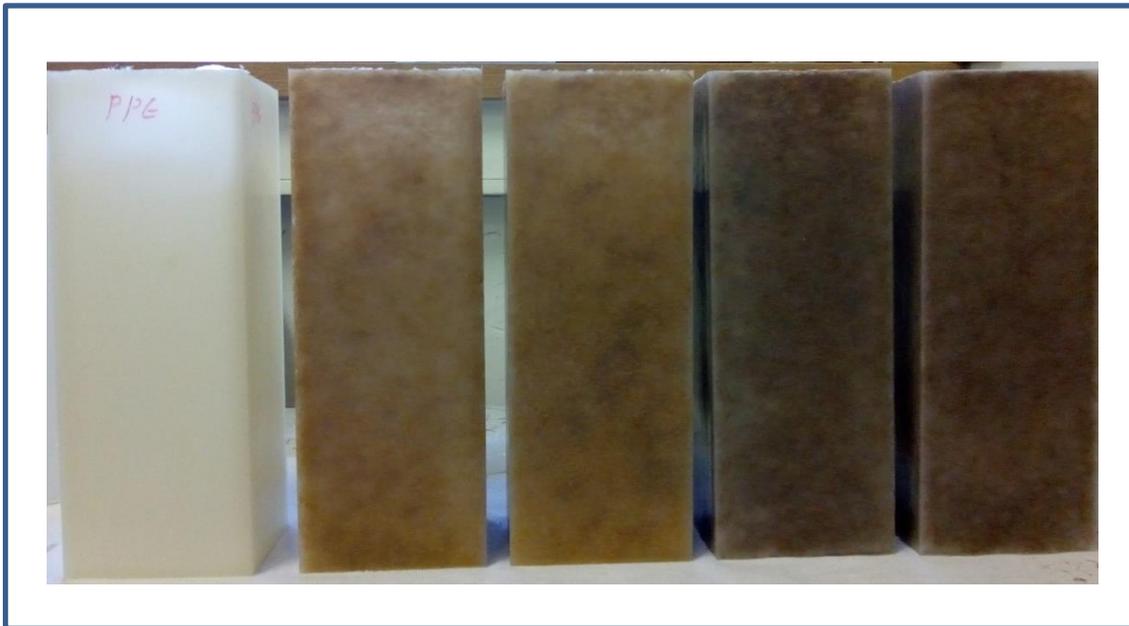


Figure 7.6: Rotomoulded products of PPE and other composites

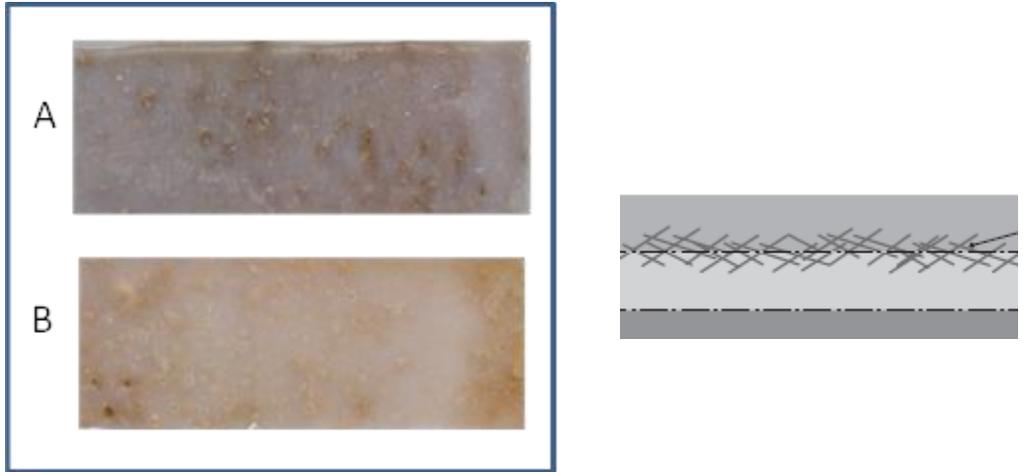


Figure 7.7 : Inner surface of double layer composite part a) untreated fibre composite and b) treated fiber composite

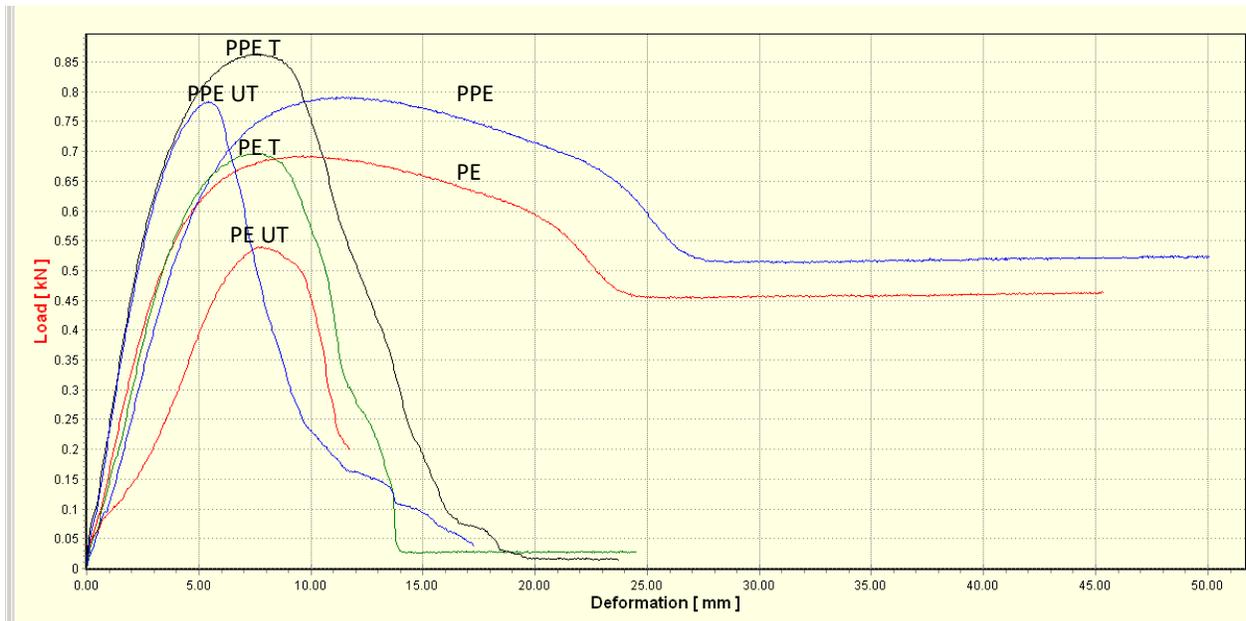


Figure 7.8: Load Deformation plot of composites[77]

Figure 7.8 describes the load displacement plot of rotomolded PE, PPE and their composites with 5 wt % fiber loading. Plasma modified PE showed higher strength than unmodified PE processed in rotomoulding technique. Incorporation of both treated and untreated fibers to unmodified PE matrix has a negative effect in tensile properties because of the lack of interfacial

bonding. On the other hand there is an increase in tensile properties like tensile strength and modulus with addition of fibers into PPE matrix. This may be due to better interfacial bonding between modified PE and cellulosic fibers and enhancement in fiber wetting. Elongation-at-break of the composites decreased as compared to that of neat PE which indicates that addition of coir fibers in PE increases its brittleness[78].

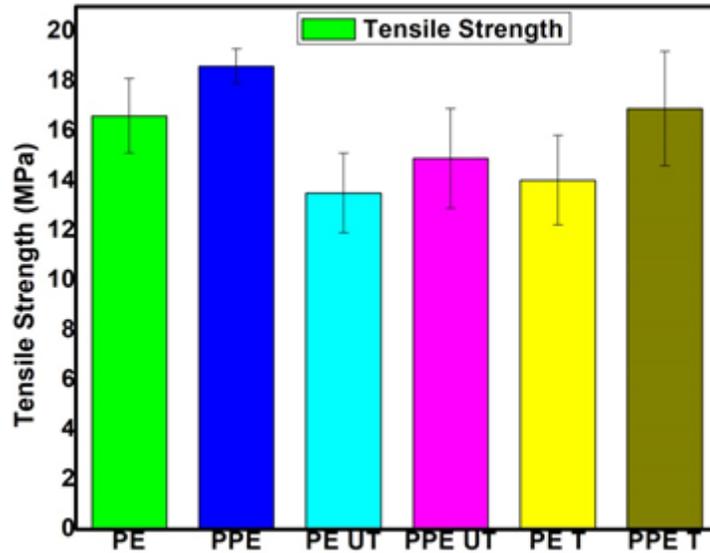


Figure 7.9: Tensile Strength of Rotational molded composites[77]

Tensile strength of the composites is shown in figure 7.9. Plasma modified PE showed the highest value for Tensile strength. There is a trend of decreasing tensile strength with the introduction of fiber in all cases as reported in previous studies rotomolded composites. But comparing the values of composites PPE treated fiber composite has showed highest value even higher than unmodified PE. Unmodified PE composites are showing lower values than plasma modified PE composites. This improvement in tensile strength is due to the strong interfacial adhesion between fiber and polymer matrix which was evidenced in SEM images. Generally the tensile strength depends on the weakest part of the composites and fiber-matrix interfacial adhesion. The presence of bubbles is also being the reason for lower tensile strength. The treated fibers are showing better properties due to higher aspect ratio and improved adhesion with the matrix. This behavior is also showed in our previous studies[71].

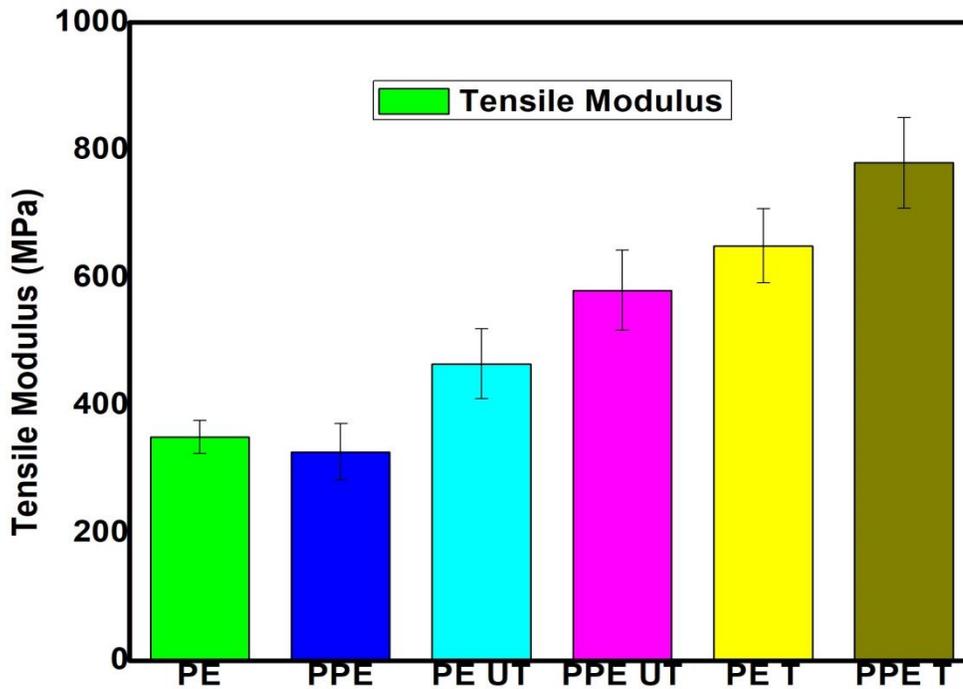


Figure 7.10: Tensile Modulus of Rotomolded composites [77]

Tensile Modulus of the composites were described in figure 7.10. Addition 5 wt % of coir fiber increased the modulus for all kind of composites. The highest modulus was reported by Plasma modified PE treated fiber composites, which was 122% higher than pure PE. Improvement in modulus of other composites are 33%, 66% and 71% for PE untreated fiber composites, PPE untreated fiber composites and PE treated fiber composites respectively. Plasma modified PE based composite showed a significant increase in tensile properties because of the interaction between polar groups on the surface of PE with hydroxyl groups of cellulose in the natural fiber. Treatment with H_2O_2 on coir fiber has also positive effect on the improvement in properties, since more hydroxyl groups were exposed for better interaction as a result of chemical treatment.

Impact Strength

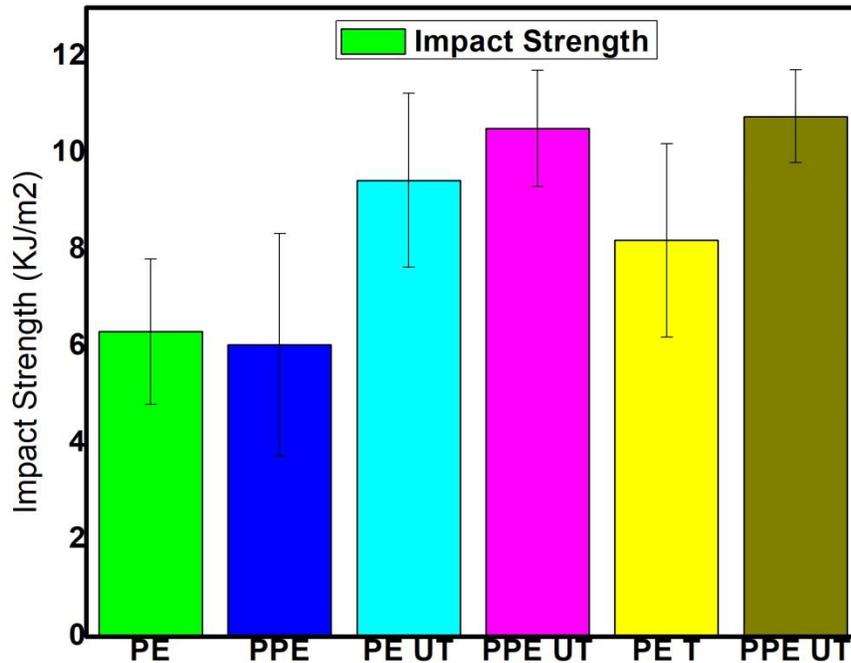


Figure 7.11: Impact Strength of Rotational molded composites[77]

Figure 7.11 summarizes the Impact properties of all composites. Impact strength of the composite was higher than neat polymer. Also plasma modified PE composites showed better properties similar to tensile properties. Previous studies reported that composite impact strength can increase because of higher mechanical energy dissipation during failure (longer fiber pullout distance) and possible fiber–fiber interaction (entanglements), as long as no fiber breakup occurs[79]. When longer fibers are used as reinforcement in polymer matrices, the impact strength greatly increased due to a high number of long fiber pullouts[37]. This result also give indication that plasma modified PE has an effective interaction with natural fiber.

7.3.3 Morphology

Impact fractured surface of the samples were analysed by scanning electron microscope to understand the morphology. SEM images of pure PE and plasma modified PE double layered samples prepared by rotational moulding are given in figure 6a and 6b

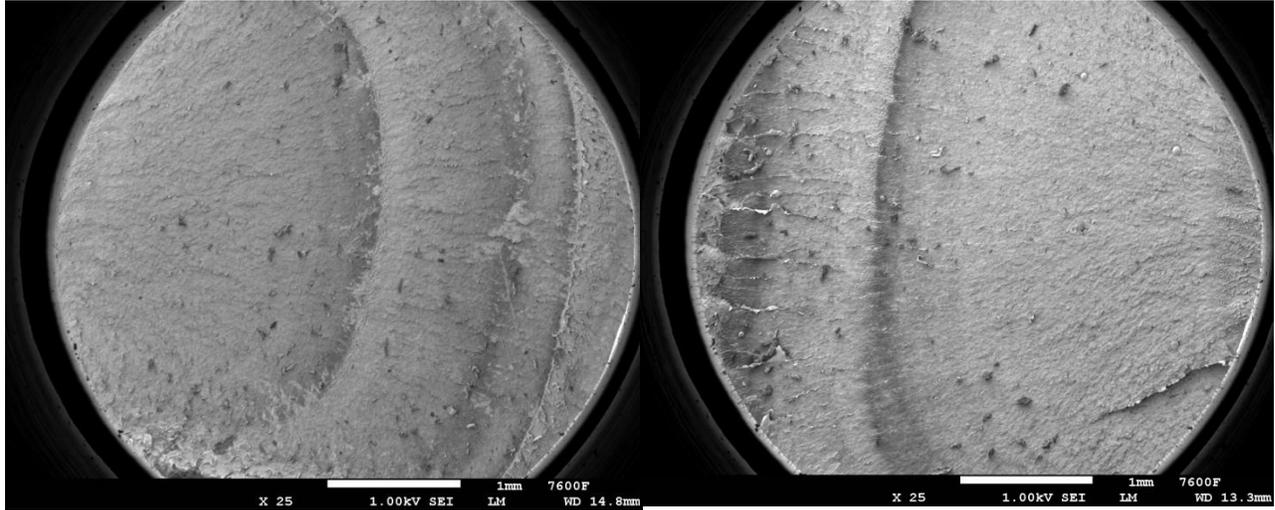


Figure 7.12: SEM images of a) PE and b) PPE

Figure shows the SEM micrographs of fractured surfaces of all composites at lower magnification. In figure 7.12(a) and 7.12(c) images of unmodified PE based composites are given. Whereas, Figure 7.12(b) and 7.12(d) are the images of plasma modified PE based composites.

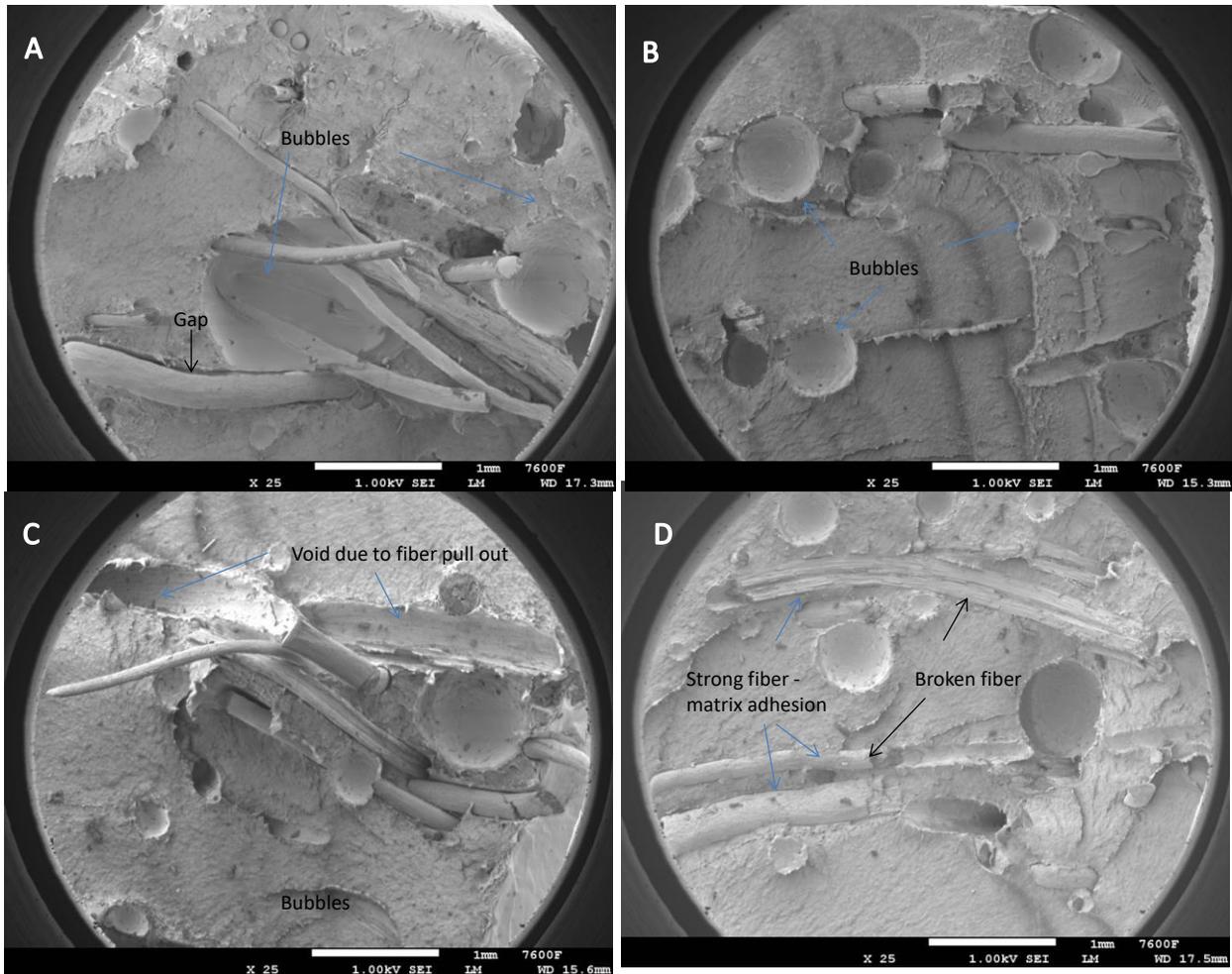


Figure 7.13: SEM image of a) PE -untreated fiber composite, b) PPE-untreated fiber composite, c) PE -treated fiber composite and d) PPE- treated fiber composite[77]

Broken fibers are visible in figure 7.13(d) which attributed to strong interfacial adhesion between treated fibers and plasma modified surface. Besides that fiber pull outs are very less and strong fiber matrix adhesion can be observed in this image. However in the images of unmodified PE composites we can see many fiber pull outs and void due to fiber pull outs. Evidence for poor fiber matrix interaction also observed in figure 7.13(a) and 7.13(c) as gap between fiber and PE matrix. The interface between polar natural fiber and non-polar polyethylene matrix is weak as expected. The plasma modification improves the polarity and surface energy of polyethylene matrix that greatly contribute to increase the interfacial adhesion. There are presences of bubbles in all the composites which are inevitable defects in rotomolding of composites.

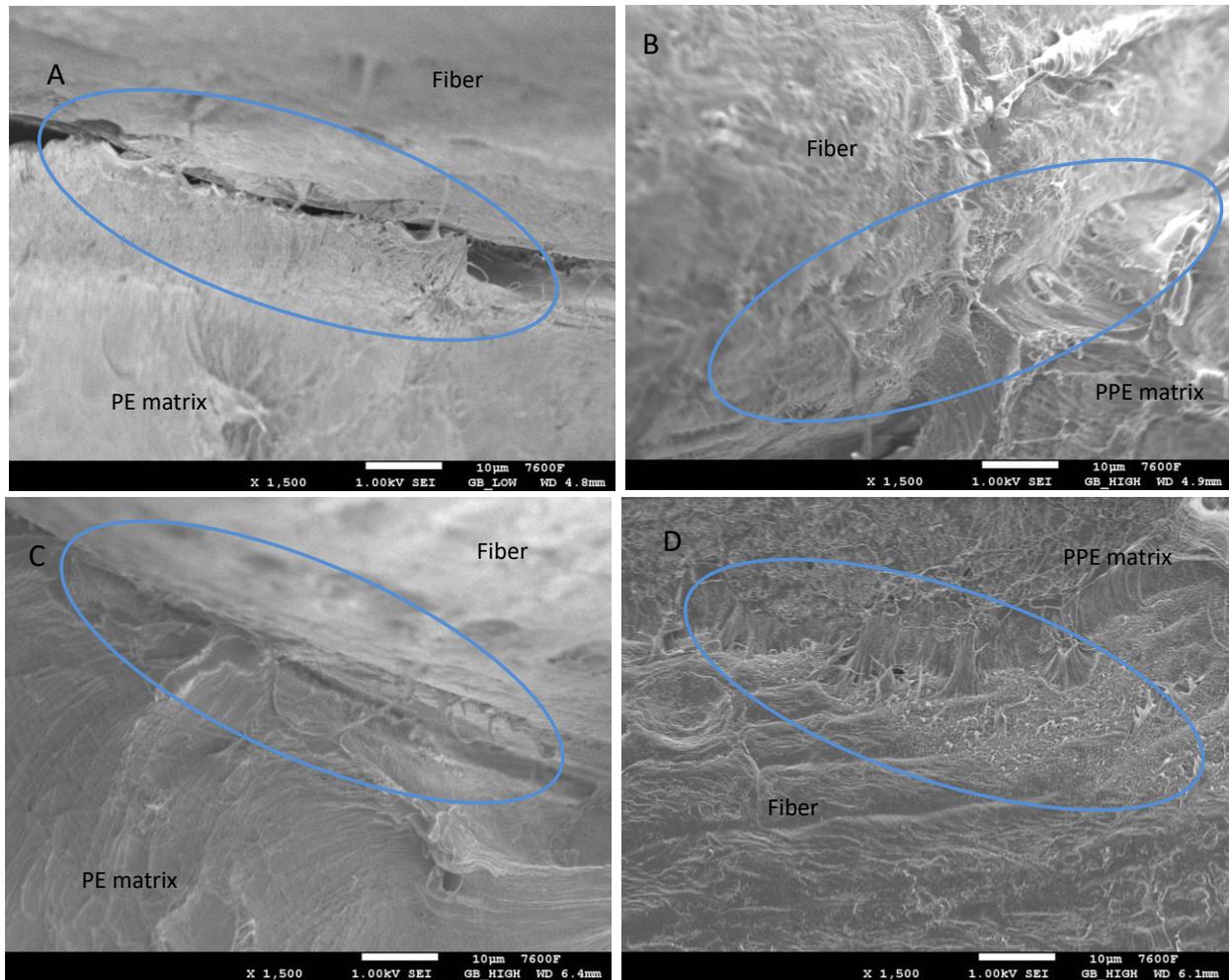


Figure 7.14 : SEM image of a) PE -untreated fiber composite, b) PPE-untreated fiber composite, c) PE -treated fiber composite and d) PPE- treated fiber composite[77]

In order to probe the effect of the plasma modification of PE on the interfacial bonding in the composites, their fractured surface were closely examined by SEM. Scanning electron micrographs of the fractured surfaces of all composites at higher magnification are shown in Figure 7.14. From these micrographs, we can see very good interfacial adhesion between fiber and matrix for plasma modifies PE composites. The interface is not distinguishable as the matrix is nicely coated over the fiber surface. It is clearly observed in figure 7.14(c) that the matrix is attached to the fiber surface and in figure 7.14(d) that the fiber surface is fully covered by polymer matrix. However in unmodified PE composites there is no interfacial adhesion found. We can prominently see a gap between fibre and matrix in figure 7.14(a).

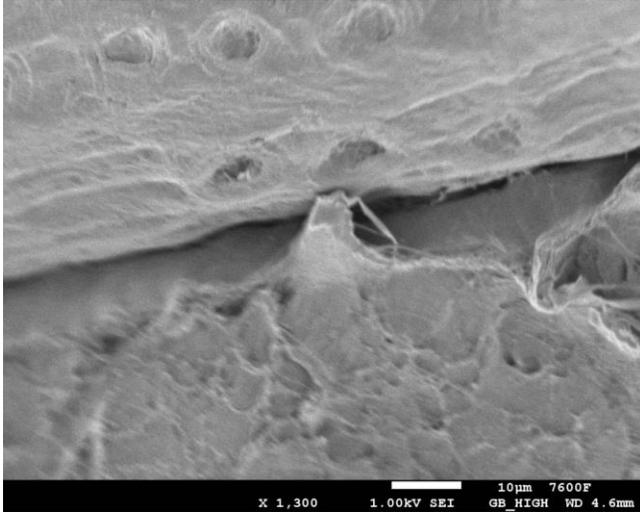


Figure 7.15: SEM image of untreated PE coir fibre composite[80]

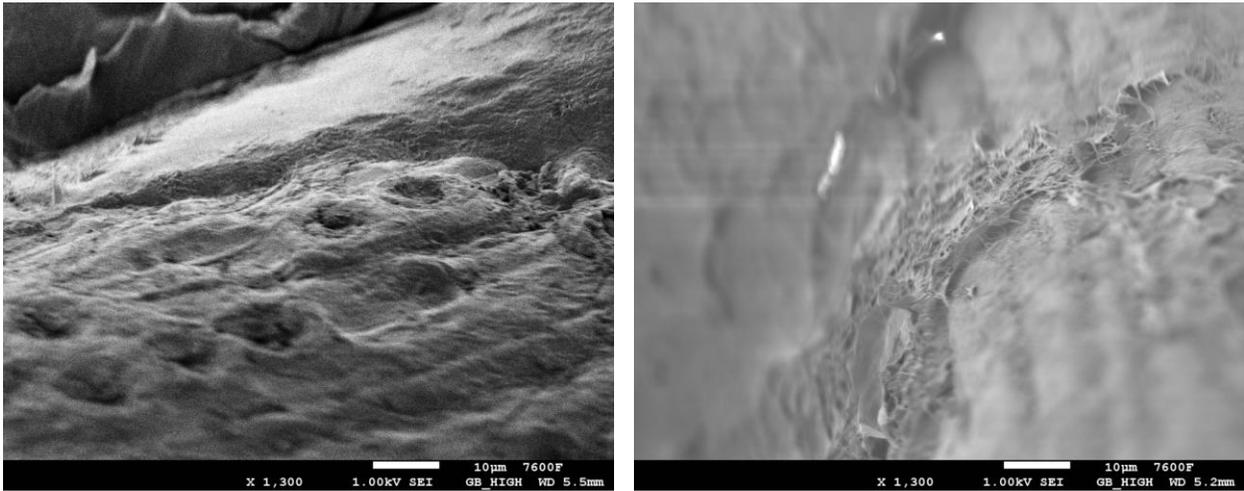


Figure 7.16: SEM image of Plasma modified PE coir fibre composite[80]

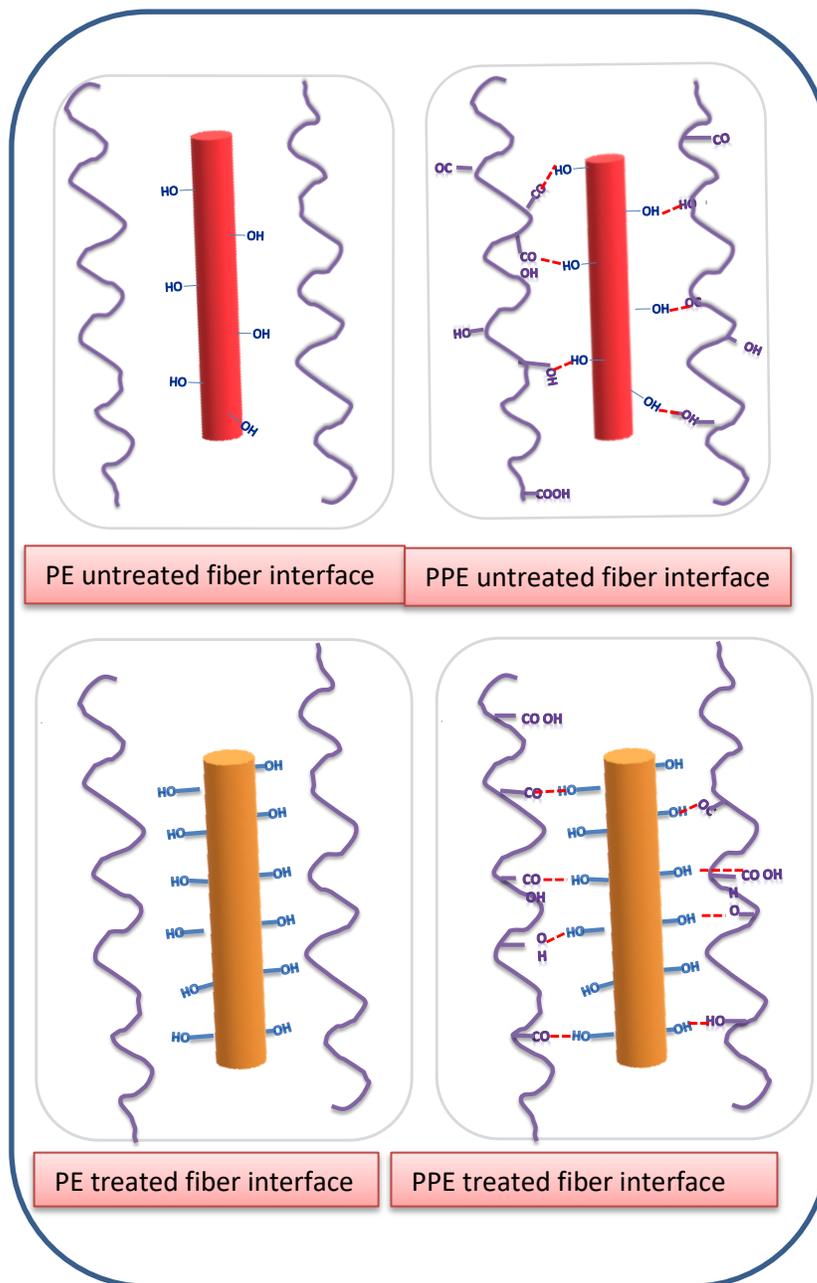


Figure 7.16 : Schematic representation of composite interface[77]

The interphases of different types of composites are represented schematically in Figure 7.16. First one illustrates the PE untreated coir fibre interphase in which no interaction between the nonpolar matrix and polar cellulosic fibre is observed. So this kind of composites showed sharp interphase that was the reason for poor mechanical properties. The interphase of plasma modified PE and coir fibre is given in second figure. The presence of polar functional groups on modified PE facilitates more interaction between the fibre and matrix. In the last two pictures coir fibres were bleached and so most of the lignin and hemicelluloses were removed during bleaching therefore more hydroxyl groups were available for the interaction.

7.3.4 Water Absorption studies

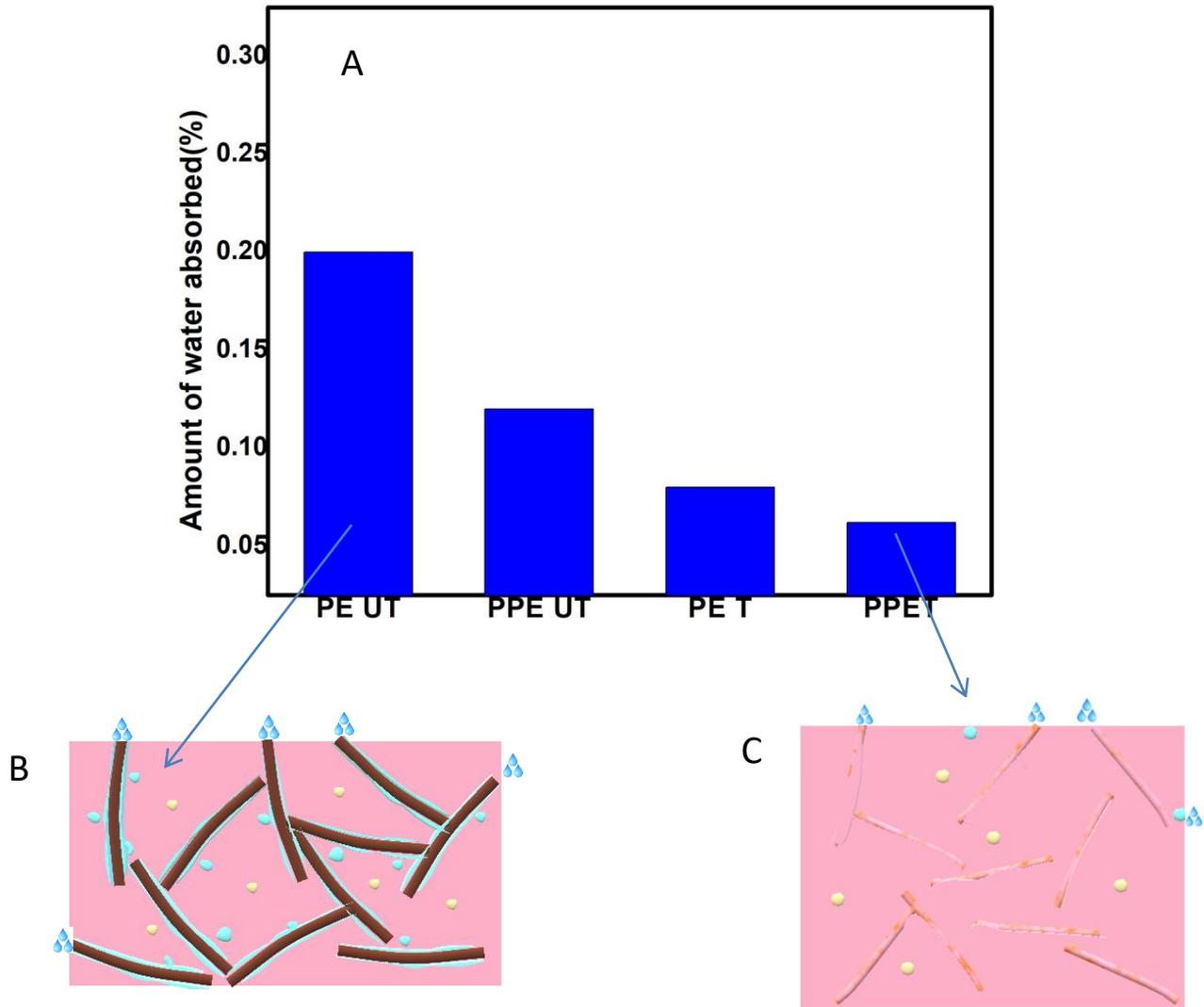


Figure 7.17: a) Amount of water absorbed by the composites, b) Schematic representation of water absorption (higher) by PE untreated fiber composite and c) Schematic representation of water absorption (lower) by PPE treated fiber composite[77]

Water absorption studies are very important for natural fiber composites, since due to the hydrophilic nature of natural fibers absorb moisture. Since natural fibers and polymer matrix exhibit different properties in terms of moisture absorption, the fiber distribution in polymer matrix and interface interaction are key to the overall moisture absorption of composites[81],[82]. Both plasma modification on PE matrix and chemical treatment on coir fiber have positive effect on the resistance to water absorption. The lowest absorption was

showed by plasma modified PE treated fiber composite. This is because a considerable amount of accessible OH groups, those are responsible for water absorption disappeared to become bonded to the polar groups on the plasma modified PE surface. And also the lack of micro voids present in the composite due to better polymer fiber interaction will help to reduce the water absorption[83]. This can be well explained from the SEM images of the composites. It could be also explained by the formation of small capillary between the PE and the fibers whereas good adhesion between the PPE and fibers such capillary was not built. The coir fibers were effectively wetted by PPE matrix which cannot be seen in PE coir fiber composites. Chemical treatment of coir fiber substantially reduces the water absorption of both PE composites and PPE composites[84].

7.4 Conclusion

Rotomoulding is an important pressureless processing method in the polymer industry which can produce stress free products. Use of composite material in rotomoulding is facing a lot of issues because of the filler aggregation and lack of good adhesion with polymer matrix. We successfully prepared plasma modified PE natural fiber composites with improved properties. SEM images showed that a strong interfacial interaction between natural fiber and polymer matrix is possible with plasma modification of PE matrix. Plasma treatment modifies the surface of powder polymer surface to become more hydrophilic by imparting functional groups on it. This could improve the compatibility between the polymer matrix and natural fiber.

Chapter 8: Injection molding

8.1: Injection Molded composites

Preliminary experiments were also performed in order to investigate whether the plasma modification of PE can influence the mechanical properties of natural fibre composite prepared by injection molding process since it is the most common processing method used in thermoplastic industry. The injection molded samples of all composites were shown in figure 8.1. It was observed that color of the composite has changed because of the degradation of coir fiber especially in composites with high amount of fiber. Injection molding has also reduced the average fiber length[85].



Figure 8.1: Injection molded samples of all composites

8.2. Tensile Properties of Injection molded composites

Tensile Modulus

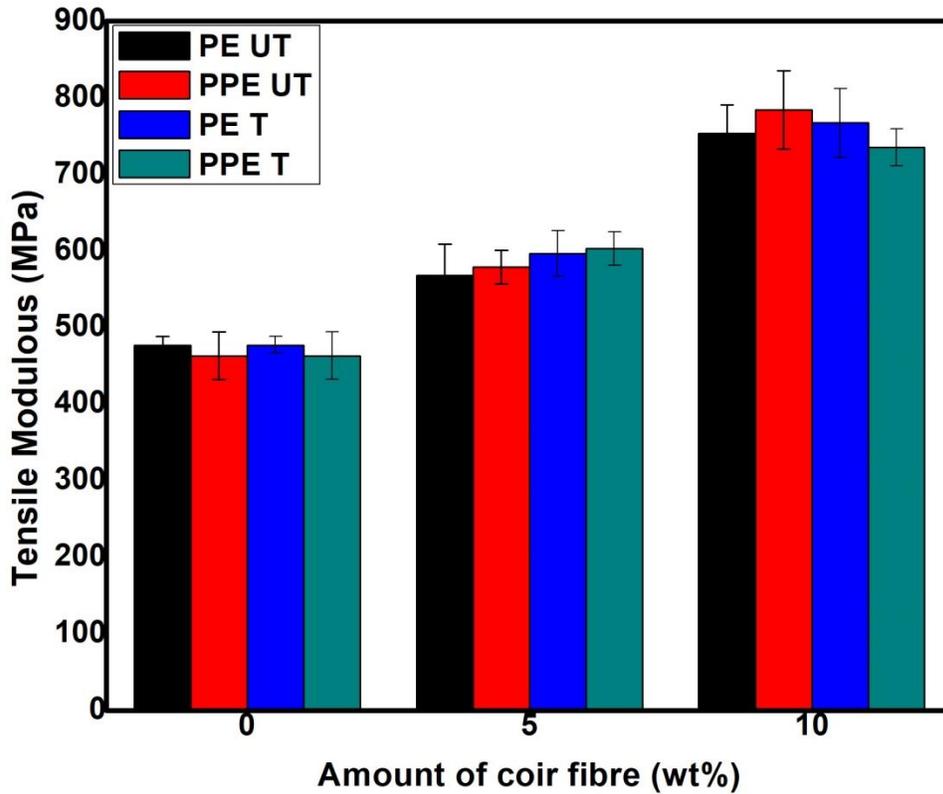


Figure 8.2: Tensile Modulus of Injection molded composites

Tensile modulus of injection molded composites was shown in figure 8.2. The stiffness of the composites, which are characterized by the Young's modulus, significantly increase with an increase in the filler content in the entire concentration region. Addition of coir fiber increased the tensile modulus gradually due to the rigidity of fiber. This kind of behavior is very common in natural fiber polymer composites[73]. But there was no significant difference observed between tensile modulus of plasma modified PE composites and unmodified PE composites.

Tensile Strength

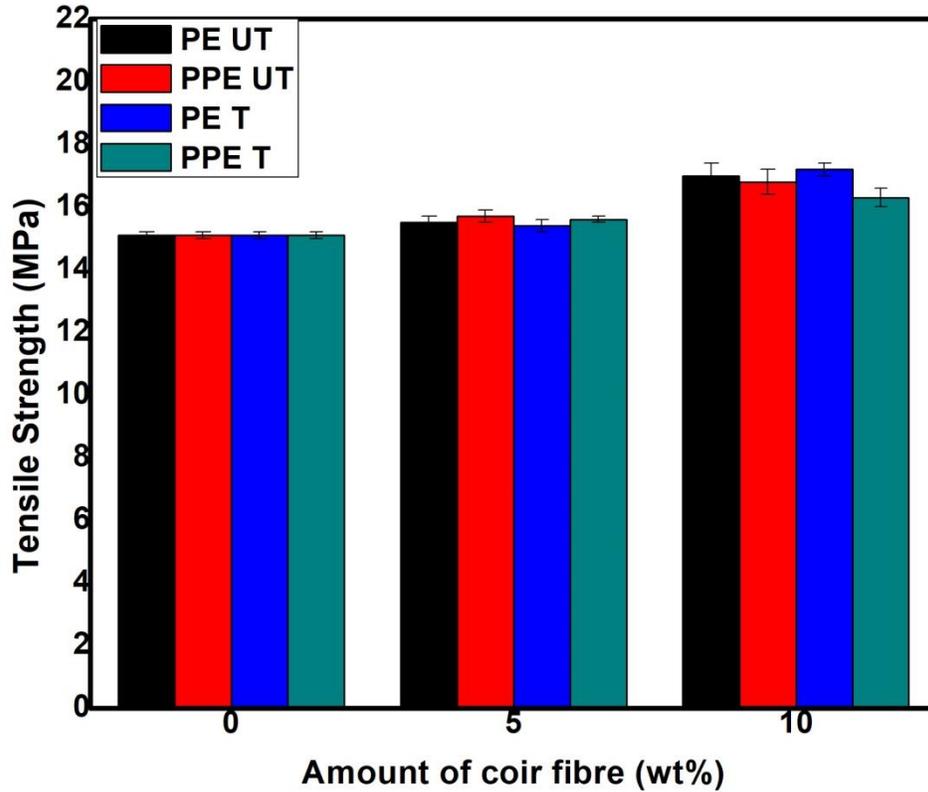


Figure 8.3 Tensile strength of Injection molded composite [80]

Figure 8.3 describes the tensile strength of all composites prepared via injection molding. Composites with 5 % coir fiber showed same value that of neat PE. However there was a slight increase in tensile strength with the addition of 10% coir fiber. The slight increase in the stress at break at higher filler contents is caused by the reinforcing effect of the filler[86]. It is also found that there is no effect by either plasma modification of PE or chemical modification of coir fiber. This might be due to the degradation of fiber during injection molding. And also PE powder and fiber were mixed at the time of molding, which did not allow enough time for any interaction between modified PE and cellulose fiber.

8.3 Flexural Properties of Injection moulded Composites

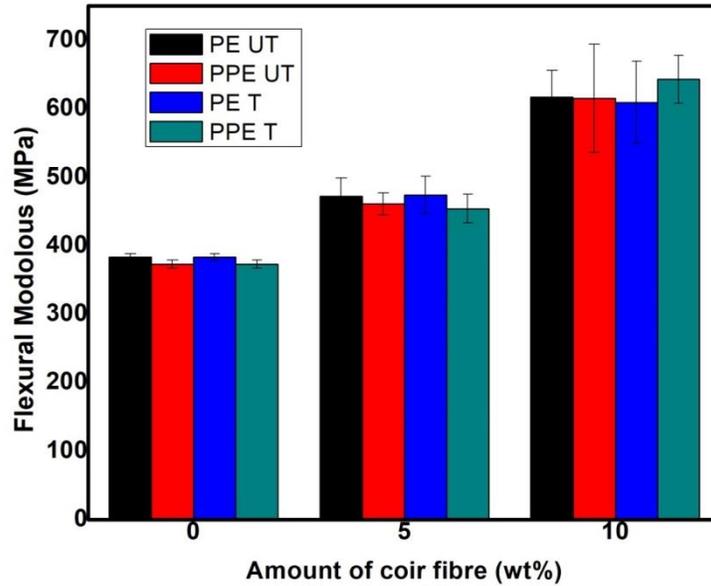


Figure 8.4 Flexural Modulus of Injection molded composite[80]

Flexural modulus of all composites has shown in figure 8.4. There is an increasing trend for flexural modulus with the addition of coir fiber in both plasma modified PE and unmodified PE composites. Composites with 10 wt% showed highest value irrespective of the modification on PE and coir fiber. Plasma modified PE with 10 wt% treated fiber showed the highest value 80% of neat PE. However composites with 5 wt% fiber showed same value of flexural modulus for all kind of composites.

Flexural Strength

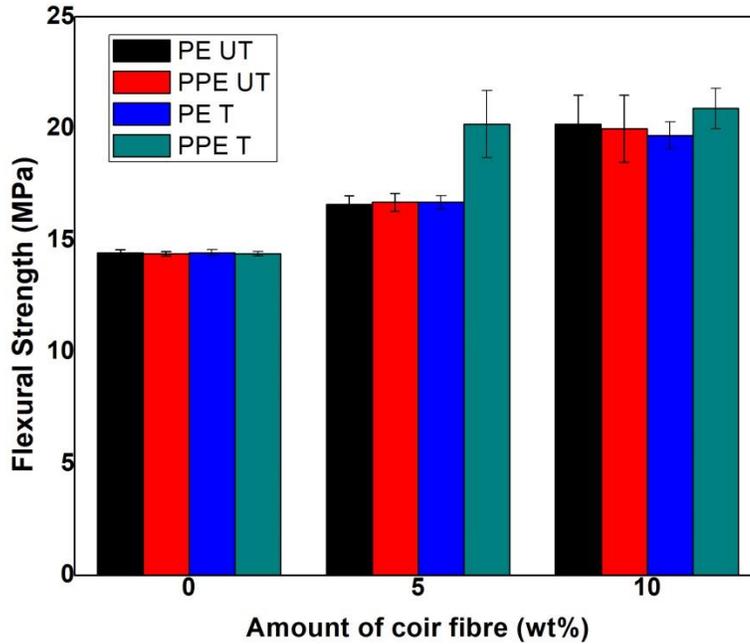


Figure 8.5 Flexural strength of Injection molded composite

It is observed from the figure 8.5 that flexural strength of injection molded composite increased with the addition of coir fiber for all composites. Nevertheless plasma modified PE- treated fiber composite showed better properties (43% higher than neat PE) compared to other composites. Flexural strength of composite is indirectly a measure of interfacial adhesion between fiber and polymer matrix[87]. This result reveals that there is interfacial interaction between plasma modified PE and lignocellulose fibers even though other mechanical properties are not increasing to a great extent.

8.4 Impact Strength of Injection moulded Composites

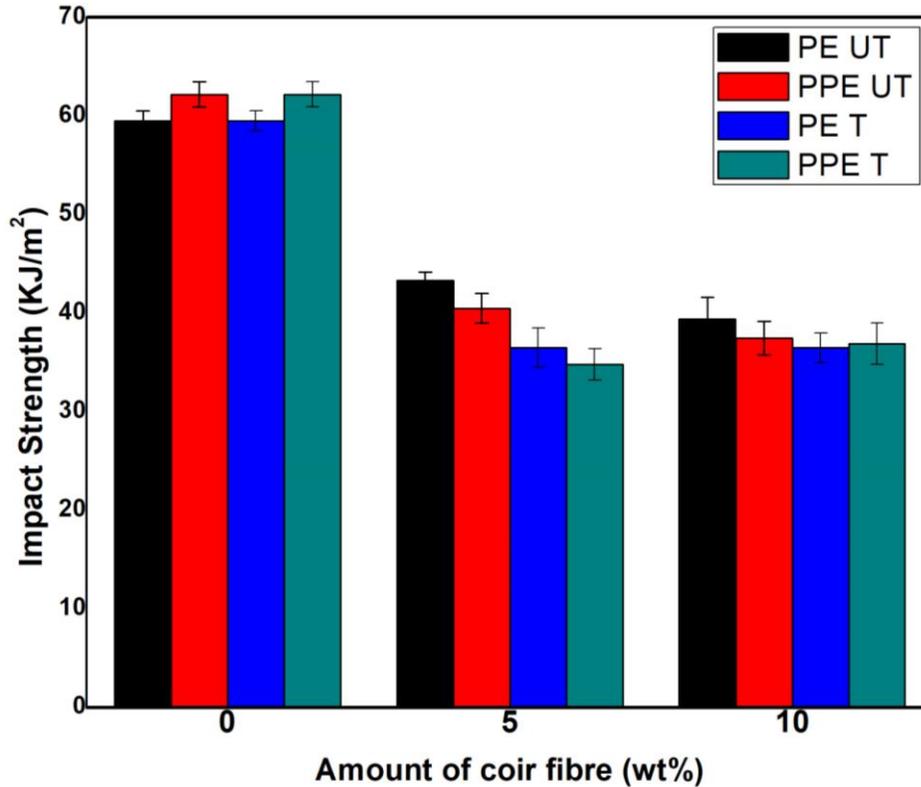


Figure 8.6 Impact strength of Injection moulded composite[80]

Composite toughness is usually affected by interlaminar and interfacial parameters and failure is observed due to the matrix fracture, fiber debonding and fiber pullout. Among these, fiber pullout is found to be an important energy dissipation factor in fiber reinforced composites. Impact strength was decreasing with the addition of fiber as summarised in figure 8.5. The low value at higher fiber content might be due to the presence of too many fiber ends within the body of the composites, which could cause crack initiation and hence potential composites failure[88]. It was also found that plasma modification has no effect in this case.

8.5 Water Absorption

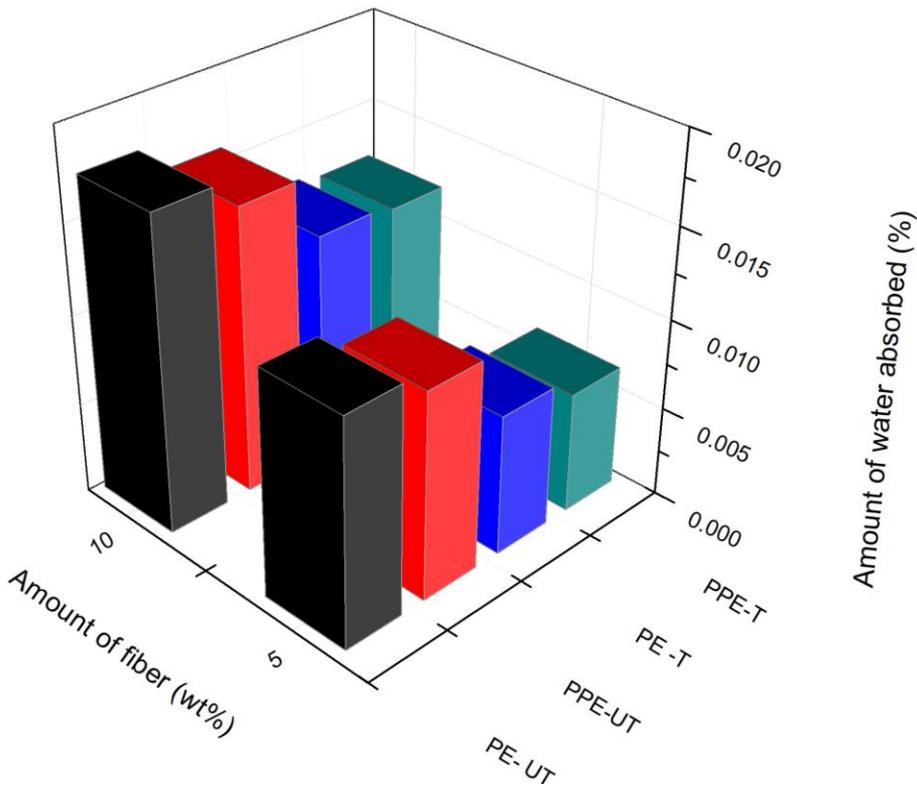


Figure 8.7 Water absorption behavior of Injection molded composite

The total amount of water absorbed at equilibrium by composite samples are given in figure 8.7. Amount of water absorbed by injection molded composites was less compared to composites prepared via other processing techniques. It is due to less number of fiber ends presented on the surface and lack of air bubbles[89]. Composites with treated fiber showed lower absorption of water compared to untreated fibers as observed in other cases. However no difference was found between plasma modified PE and unmodified PE based composites. With increasing amount of coir fiber in the composite water absorption increased[82].

Chapter 9: Conclusions and future works

The present thesis covers a systematic and detailed investigation on the applications of plasma modified Polyethylene powder in combination with natural materials. Plasma modified Polyethylene has been used in two different purposes. One is as matrix for natural fiber composite and other is as fillers in natural rubber. Plasma surface modification makes the polymer more polar and active, which increase its applications in many ways.

Natural fiber composites were prepared using coir fiber as reinforcement and Plasma modified PE as matrix. Different processing techniques for the composites such as compression molding, Injection molding, Rotational molding and pressure less molding were used for fabricating the composites. All properties were compared with that of unmodified PE based composites prepared in the same way. Effect of chemical treatment on coir fiber was also investigated. Coir fiber was treated with alkali and then with hydrogen peroxide (bleaching). Treated fibers were analyzed by FTIR spectroscopy and found that waxy layer, pectin, lignin and part of hemicellulose were removed and more hydroxyl groups on the cellulose are active. Effect of plasma modification on PE powder was analyzed by contact angle measurements and FTIR spectroscopy. Contact angle has reduced due to presence of polar functional groups on the surface of modified PE. The presence of groups such as CO, COOH, OH, etc. was confirmed from FTIR spectra of both modified and unmodified PE.

9.1 Meet the thesis goal

- To investigate the effect of plasma modified PE as filler in Natural rubber composites.

Plasma modified PE powder was used as filler in natural rubber matrix and compared the properties (mechanical properties, cure kinetics, morphology and fiber - matrix interaction) with that of unmodified PE composites. In all compositions the unmodified PE was nicely dispersed in the rubber matrix whereas the plasma modified PE (PPE) showed high degree of phase separation and a tendency to agglomerate due to the polar- polar cohesive interactions among them. Both polyethylene and plasma modified PE enhanced the mechanical properties of NR. The interaction between the filler and matrix is highlighted and was found to be more in the case of polyethylene/NR composites. Plasma modification can impart some polar

groups on PE but this reduced the interaction between NR and PPE compared to PE. The interaction between NR and plasma modified PE, which has some functional group on it can be improved if we add compatibilizer like modified NR.

- To investigate the effect of plasma modified PE as matrix for natural fiber composites.

Short fiber composite based on PPE and PE matrix were prepared via compression molding with varying the fiber content from 5 to 20 wt%. The mechanical properties and water absorption behavior studied in detail. The interfacial adhesion and fiber wetting were examined by stereo microscope. Plasma modified PE based composites showed higher mechanical properties in terms of tensile strength, tensile modulus and flexural modulus than unmodified PE composite. Morphology of the composites reveals that there is a good interfacial interaction between coir fiber and PPE matrix. In the plasma modified one, a good wetting of fiber by the matrix eliminated the possible micro voids.

- Development and optimization of plasma modified PE Natural fiber composites for rotational moulding.

Natural fiber composites were successfully manufactured via rotational molding with improved mechanical properties and reduced water absorption. Morphology of composites revealed the good interfacial adhesion between coir fiber and plasma modified PE which was absent in unmodified PE composites. Single layered composites and multilayered composites were prepared with this technique.

- Initial studies on Injection moulded natural fiber composites.

Injection molding technique was also explored for the manufacturing of PPE coir fiber composite. It was found that it is not as good as other processing techniques concerning plasma modified PE natural fiber composites because of the processing conditions like high temperature and high shear rate.

9.2 Comparison of Processing Methods for PPE/Natural fiber composites

In this study natural fiber composites were prepared using different polymer processing techniques including compression moulding, Injection moulding and rotational moulding. Compression moulding and injection moulding were used quite often for the manufacturing of natural fiber thermoplastic composites. Rotational moulding is the less explored process for natural fiber thermoplastic composites. The low-shear characteristics of rotomolding limit the amount of fiber that can be added to produce good composite materials. Injection moulding is commonly used as a secondary shaping method after other processing methods like extrusion.

The drawbacks of natural fiber which are to be considered in selecting processing method for composites are poor temperature stability and moisture absorption. Processing parameters such as temperature, pressure and time of processing are the major factors which determining properties of the composites. Different processing parameters used for this work is summarized in table 9.1.

Table 9.1. Processing Parameters

	Compression Moulding	Rotomoulding	Injection Moulding
Temperature	130 °C	200 °C	185 °C
Pressure	8 bar	No pressure	30 bar
Cycle time	5 min.	60 min.	60 s
Cooling	Water Cooling	Air cooling	Air cooling

Due to very high pressure and temperature, injection molding damaged the properties of natural fibers as well as traditional fibers, which result in changes in length and diameter distribution of the fibers. Consequently, the properties of the composite materials are affected [16]. In contrast, compression molding neither damages, nor orients the fibers during processing, which preserves the isotropic properties of the composites and reduces the changes in physical properties that

derived from the molecule relaxation of the materials during usage. In addition, the properties of the compression molded composites are related to consolidation of the composites, which depends on the processing conditions as well as the molder used in the processing. For instance, more pressure is transfer to the composite in a closed mold process than in a frame mold process.

One of the main advantages of melt mixing is the superior mixing of fiber and matrix, but at the cost of high shear forces, which may lead to fiber damage. The mechanical mixing and compression molding process, allows for these forces to be avoided.

Rotational moulding is a pressureless moulding even though high temperature is involved. It is used for making stress free products. The main problems that arise are the bad mixing and bad adhesion of the filler to the thermoplastic matrix which results in segregation of the reinforcement, and agglomeration and poor distribution of reinforcement. It is difficult incorporate more amounts of filler in composite prepared via rotational moulding process. Since there is no pressure involved there is no chance of mechanical interlocking between fiber and matrix. This attributed to the formation of bubbles in the final product. The moisture absorption of natural fiber is also a reason for air bubbles.

Properties of the composites

The properties of composite are depended on the processing condition and method. Compression moulded composites showed higher values for tensile modulus and tensile strength. It was used lower temperature, pressure and time for molding. So there is no degradation of natural fiber occurred. The tensile properties of composites varies in the order Compression molding > Rotational moulding > Injection moulding. Nevertheless for neat PE matrix injection moulded samples showed highest value for tensile modulus. Even though Injection moulding ensured good dispersion of fiber, the mechanical properties are not improved because of the lack of interfacial adhesion between PE matrix and natural fiber.

Injection molded samples showed high values for Impact strength. The main explanation for the higher toughness of IM specimens is probably the higher density of tie-molecules and chain entanglements, due to the higher cooling rate[90]. Flow-induced orientation in the IM specimens may also play a role. Rotational molded samples showed lowest value for Impact strength. This

might be due to the presence of voids or air bubbles present in the composites. There was no much difference in flexural properties of the composites due to difference in processing methods.

The factors affecting water absorption characteristics are presence of voids, the gap between fiber and matrix (interfacial adhesion) and nature of fiber. Compression moulded composites showed lowest rate of water absorption, since it offered samples with good interfacial adhesion and lower void content. Two kinds of interfacial adhesion are possible in Compression moulded composites, ie, mechanical interlocking and chemical interaction. In Rotational molded composites mechanical interlocking is not possible due to pressureless molding. Presence of voids also increased the water absorption.

9.3 Suggestions for Future work

- More studies will be done on the injection molding of plasma modified PE coir fiber composites.
- In rotational molding, special focus will be given to reduce bubble formation like two stages mixing or in-situ plasma modification of PE powder and natural fiber.
- Even though few fibers were exposed to atmosphere in double layered rotomolded composites, three layered composites can be manufactured.
- In rotational molding process higher length of fiber reduces dispersion. So studies can be done on composites with different length of fiber from macro to nano.
- Thermal properties and aging behavior of plasma modified PE coir fiber composites can be studied in detail.
- This new composite material can be used for 3D printing technology, which is also a pressure less processing method.

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- [71] **Sari P. S.**, Petr Spatenka, Zdenka Jenikova, Yves Grohens, and Sabu Thomas. "New type of thermoplastic bio composite: nature of the interface on the ultimate properties and water absorption." RSC Advances 5, no. 118 (2015): 97536-97546.
- [60] **Sari P. S.**, Petr Spatenka, Evgeny Anisimov, and Sabu Thomas. "Plasma Modified and Unmodified Polyethylene as Filler in Natural Rubber Compounds: Morphology, Cure Behavior and Vulcanization Kinetics." In Macromolecular Symposia, vol. 381, no. 1, p. 1800135. 2018.
- [80] **Sari P. S.**, Zoya Ghanem, Zdenka Jenikova and Petr Špatenka, "Composite with short fibers and plasma-treated polyethylene matrix prepared by rotomolding technology " submitted to SAMPE 2019 - Charlotte, NC.(under review)
- [77] **Sari P.S.**, Petr Spatenka, Zdenka Jenikova, Zoya Ghanam, and Sabu Thomas. "Effect of plasma modification of Polyethylene on natural fiber composites prepared via rotational moulding" (submitted to Composites Part B: Engineering)

Conference Papers

- [69] Presented a poster, Sari, P. S., Spatenka, P., Jenikova, Z. and Sabu Thomas, Conference proceedings, "Influence of plasma modified polyethylene on the mechanical properties of natural rubber" National Conference on Recent Trends in Materials Science (NCMST 2013) and Technology at Indian Institute of Space Science and Technology Kottayam, (2013), 24
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- **Sari P.S.**, T. Sharika, K. Bicy, and Sabu Thomas. "Recycling of Polyolefin Materials." In Polyolefin Compounds and Materials, pp. 315-339. Springer International Publishing, 2016.
- Ajitha A.R., **Sari P.S.**, Maria H.J., Thomas S. "Multilayer Nanowires and Miscellaneous Multilayer Products". In Multicomponent Polymeric Materials. Springer Series in Materials Science, vol 223. 2016.

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11.3 List of the abbreviations

ABS	Acrylonitrile butadiene styrene
BP	Benzoyl Peroxide
BR	Bound rubber
CNT	Carbon nanotube
DBD	Dielectric barrier discharge
DCP	Dicumyl peroxide
DMA	Dynamic mechanical analysis
ENR	Epoxidised Natural rubber
EVA	Ethylene-vinyl acetate elastomer
FM	Flexural modulus
FS	Flexural strength
FTIR	Fourier transform infrared
H ₂ O ₂	Hydrogen Peroxide
HDPE	High density Polyethylene
IFSS	Interfacial shear strength
ILSS	Interlaminar shear strength
LDPE	Low density Polyethylene
LLDPE	Linear low density Polyethylene
MA-g-	Maleic anhydride grafted
MAPP	Maleic anhydride grafted Polypropylene
MDR	Moving Die rheometer
Na ₂ SO ₃	Sodium sulfite
NaOH	Sodium hydroxide
NR	Natural rubber
PA	Polyamide
Pa	Pascal
PE	Polyethylene
PET	Poyethylene terephthalate
PLA	Poly lactic acid
PMMA	Poly(methyl methacrylate)

POM	Polyoxymethylene
POSS	Polyhedral oligomeric silsesquioxanes
PP	Polypropylene
PS	Polystyrene
PTFE	Poly tetra fluoro ethylene
PUR	Polyurethane
SA	stearic acid
SEM	Scanning electron microscopy
Tg	Glass transition temperature
Tm	Melting temperature
TGA	Thermogravimetric analysis
TM	Tensile modulus
TPNR	Thermoplastic natural rubber
TS	Tensile strength