PHYSICO-MECHANICAL PROPERTIES OF RECYCLED POLYETHYLENE COMPOSITES REINFORCED WITH CHEMICALLY TREATED SAW-DUST

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Declaration

This thesis work has been done by the candidate himself and does not contain any material extracted from elsewhere or from a work published by anybody else. The work for this thesis has not been presented elsewhere by the author for any degree or diploma.

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Dedication

This Thesis Work is Dedicated

To My

Almighty Allah, Beloved Parents and Teachers

DEPARTMENT OF CHEMISTRY

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THESIS APPROVAL

This thesis titled" Physico-Mechanical Properties of Recycled Polyethylene Composites Reinforced With Chemically Treated Saw-Dust" Submitted by Mr. Md. Sakinul Islam (Roll No:100603213F, Session: October, 2006) has been accepted as satisfactory in partial fulfilment of the requirement for the degree of Master of Philosophy in Chemistry on 25 September, 2011.

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ABSTRACT

Plastic wastes have been a major environmental concern not only in Bangladesh but also worldwide. In the present work, the wood waste and the rejected plastic were recycled to produce new useful product; Wood Plastic Composite (WPC), having characteristics similar or close to commercial wood. An innovative, clean, cheap, and effective yet simple technology with different procedures was introduced in this work to demonstrate the suitability of wood plastic composites' techniques for developing countries. Testing was done for some important mechanical properties; flexural strength and modulus, and physical properties; water absorption and thickness swelling, which has proven an acceptable final product and promising results; especially regarding the physical test. Wood plastic composites (WPCs) were made using matrices of recycled polyethylene (rPE) and sawdust or wood fiber as filler. Corresponding WPCs were also made using virgin plastics (HDPE and LDPE) for comparison with the recycled plastic based composites. WPCs were made through extrusion moulding and injection moulding machine with varying formulations based on the plastic type, plastic form (recycled and virgin), sawdust content. The chemical compositions of sawdust were determined in this experimental work. It was found that wood also have sufficient % of cellulose, hemicelluloses and lignin; so it can be defined as lignocellulosic materials. In this present work, sawdust is used as filler but before using it as filler several chemical treatment were conducted to prevent the water absorption properties because the water absorption is only one of the negative side which affect the mechanical properties of composites materials. As a chemical treatment, sawdust or wood fiber is treated by three categories of single and double pretreatment i.e. NaOH, NaOH+Benzoyl Chloride and NaOH+CTAB. FT-IR was conducted for observing the change in sawdust flour by chemical treatment. In this work the recycled PE is used after recycling the polyethylene bags successfully.

Polyethylene shopping bags manufactured from both HDPE and LDPE these are collected as wastage from various sources then it was sorting, washing, drying, cutting, grinding and finally pelletizing. This pellet and saw dust were mixed with together in varying composition and composites were manufactured by using extruder and injection moulding machine. During the preparation of composites the raw and treated sawdust was taken 20%, 25%, 30% and 35% with recycled polyethylene. The prepared composite sample was then taken for various physical and mechanical tests for as example the mechanical tests are hardness test, tensile test, flexural test, impact test. The physical tests are SEM, Water absorption and FT-IR. The chemical treatments of the saw dust were conducted by surfactant and followed effect of chemical treatment on mechanical properties of WPCs. It was found from the experiment that the sawdust treated by NaOH+Surfactant showed better mechanical properties and better resistance to hydrophilic nature. The sample prepared from single pretreatment saw dust shows higher water absorption and low mechanical properties. In between the NaOH+Benzoyl chloride and NaOH+Surfactant treated sample the NaOH+Surfactant treated sample shows better mechanical properties and greater resistance to water absorption. On the other hand, FESEM result was also found very excellent for treated sample than raw sample. To justify the mechanical properties of recycled rPE composites with virgin PE both composites were prepared and it was also found that rPE have the excellent characteristics for engineering materials. So, recycled PE matrix based composites exhibited excellent durability and mechanical properties, which were comparable to those made from virgin plastics. The results from this work clearly show that rPE (rHDPE and rLDPE) can be successfully used to produce stable and strong WPCs, with properties and performances similar to or comparable to composites made of wood and virgin plastics. Therefore, WPCs based on recycled LDPE and HDPE matrix could have potential to use as engineering and construction materials.

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ABBREVIATION

SD	Sawdust
WF	Wood flour or Wood fiber
UT	Untreated
AT	Alkali Treated
BT	Benzoyl Chloride Treated
ST	Surfactant Treated
UTC	Untreated Composites
ATC	Alkali Treated Composites
BTC	Benzoyl Chloride Treated Composites
STC	Surfactant Treated Composites
RPE	Recycled Polyethylene
VPE	Virgin Polyethylene
FESEM	Field Emission Scanning Electron Microscopy
FT-IR	Fourier Transform Infrared Spectrometer
WPCs	Wood Plastic Composites
ASTM	American Society for Testing and Materials
BCl	Benzoyl Chloride
CTAB	Cetyltrimethylammonium Bromide
PVC	Polyvinyl Chloride
PS	Polystyrene
MFI	Melt Flow Index
UTSD	Untreated Sawdust
ATSD	Alkali Treated Sawdust
BTSD	Benzoyl Chloride Treated Sawdust
STSD	Surfactant Treated Sawdust

CHAPTER 01

INTRODUCTION

1.1 INTRODUCTION

Over the last few years a large number of reports have appeared in the literature on recycled thermoplastic polymer composites reinforced with natural fiber [1-6]. Natural fiber reinforced polymer composites have attracted much attention as they are cheap, lightweight and environment friendly. Furthermore incorporation of natural fibers with synthetic polymers not only show strong promises for using the agro based natural resources but also has an added advantages of showing desired performance properties from a more sustainable materials that would otherwise cause environmental pollution if thrown away or burnt down [7]. Wood-plastic composites (WPCs) are emerging as one of the dynamic growth materials in the building industry. WPC is manufactured by dispersing wood particles into molten plastic with coupling agent or additives to form composite material through various techniques of processing such as extrusion, compression or injection moulding. It was first made commercially from phenol-formaldehyde and saw-dust that was used for Rolls-Royce gearshift knob in 1916, and it was reborn as a modern concept in Italy in the 1970s, and popularized in North America in early 1990s [8]. Wood-thermoset composites date back to early 1900s; however, thermoplastic polymers in WPC are a relatively new innovation. In 1983, an American Woodstock company (Lear Corporation in Sheboygan, WI) began producing automotive interior substrates by using extrusion technology from the mixture of polypropylene (PP) and saw-dust [9].

Since then production and markets demand for the WPCs have been growing rapidly worldwide. The share in North American decking market has grown considerably, from 2% in 1997 to an estimated 18 % in 2005, with total sales of US$3.9 billion in 2005 for residential, industrial deck-boards and railing market in USA [10]. It is expected to increase to about 500 million to 1 billion pounds over the next five years in the UK and other European markets [11].

Currently WPCs are mainly used for building products like decking, fencing, siding, garden furniture, exterior windows and doors [10, 11], although other applications can also be found in marine structures, railroad crossties, automobile parts and highway structures such as highway signs, guardrail posts, and fence posts [12]. WPCs possess many advantages over the raw materials of polymers and wood filler. WPC had better dimensional stability and durability against bio-deterioration as compared to wood. In addition, WPC also reduces the machine wear and tear of processing equipment, and lowers the product cost significantly against inorganic fillers when waste streams such as SD are used [11]. Compared to the polymers, WPC had higher mechanical properties, thermal stability, and more resistance to the ultraviolet light and degradation [11].

Due to growing production and consumption, plastics worldwide is currently resulting in a significant contribution to the municipal solid waste management [13]. According to the Solid Waste Management (SWM) division of Dhaka City Corporation (DCC), 3000 to 4000 tons of waste is generated everyday in the city [14]. In this, 50 tons are hospital waste, one-fifth of which is hazardous to health. About half of the total waste is collected and dumped for landfills and the rest is scattered and left unattended all over the city. About 80% of the garbage is food waste, the rest are metal, glass, paper, polyethylene bags, cloth, etc. Polyethylene used for various purposes ranging from commodity wrappers to shopping bags is usually thrown away after use. These accumulate in the rivers, ponds, cannels, municipal drainage systems and agricultural land, causing environmental pollution and disrupting soil fertility. Furthermore, accumulation of these synthetic wastages in cannels and municipal drainage systems disrupts normal water flow through them. In Bangladesh we have 18% forest of total land area, a lot of timber houses are spreading all over the country. A lot of saw-dust generated from this timber houses but these are burnt out or considered as useless. These valuable assets are diminishing day by day without proper utilization from undeveloped countries.

Due to their unregulated and careless disposal, they are creating secondary pollution to the environment. It was reported that waste wood in the form of saw-dust, fibers or pulp are suitable as a filler for polyolefin's matrix composites [15, 16]. Wood fibers possess physical and mechanical properties suitable for reinforcement in plastics [17]. Hence, increased usage of the recycled plastics and the waste wood for WPCs offers the prospect of lessening waste disposal problems and lowering production costs. Virgin thermoplastics such as HDPE, LDPE, PVC, PS and polypropylene (PP) are widely used for the production of WPCs, and significant numbers of papers have appeared in the literature regarding mechanical properties, dimensional stability, interface adhesion and durability [18-24]. However, published reports on recycled HDPE, PP and LDPE based WPCs are rather limited [25-29]. Most of the studies were focused on the use of a single type/or grade of plastic from the waste stream, or simulated recycled plastic, or mixing of recycled plastic with virgin plastic for use in WPCs. Increased moisture content in the composites reduces mechanical properties, dimensional stability, and tends to lead to biodegradation [30].

The main disadvantages of using lignocellulosic fibers as fillers in thermoplastics is their affinity to absorb moisture (which can be as high as 3-13%) and consequent deformation of furnished products [31]. Another problem of using natural fiber in thermoplastic composite is the poor interfacial adhesion between the filler and the polymer matrix [32]. However, surface modification of lignocellulosic materials by suitable chemicals has shown to be capable of improving the water resistance and mechanical properties through improved compatibility between the hydrophilic wood filler and hydrophobic polymer matrix [19, 33-35]. Several studies were conducted to examine the effect of moisture content on mechanical properties and stability of the natural fiber and thermoplastics composites [30, 36, 37]. In recent research in our laboratory it has been shown that interfacial adhesion can be significantly improved by suitable chemical treatment of fiber [38, 39].

However, this study was conducted only for recycled PE (RPE) reinforced composites where saw-dust was used as filler; briefly it is called wood plastic composites (WPCs). As dimensional stability of the WPC is the important property in exterior applications, understanding and quantification of the moisture absorption and dimensional changes of WPC is focused in the present work. Due to the uncertainties regarding WPC stability in exterior conditions, their use is mostly limited to non-structural interior applications. Exposure to varying ambient conditions such as humidity, temperature and sunlight alters the chemical and physical properties of WPCs. Previous studies have shown that changes in ambient humidity and temperatures may have an adverse effect on physical and mechanical properties of the WPCs [40-43].

The processing method can also affect the moisture absorption and extruded WPCs trend to absorb greater moisture than compression or injection moulded products [44]. In addition to stability, durability is also an important property of WPC for the exterior applications and this is gaining more attention recently. Durability of the WPC made from virgin thermoplastics with organic fillers (such as wood, natural fibers and rice hull) exposed to biological organisms [45, 46] and ultraviolet radiation (UV) have been investigated [47-50]. There are limited reports available for the WPCs made from virgin or recycled thermoplastic and wood or natural fibers [51-53]. If WPCs are to be used in different environmental conditions, it is essential to investigate the physic-mechanical properties like tensile strength, flexural strength, hardness, water absorption, various chemical treatments, impact strength for product stability and durability.

In conclusion, stability and durability performance of WPCs based on post-consumer thermoplastic are not fully understood and the affecting factors are not known, leaving open research opportunities for the optimization of formulation and processing. WPCs performance can be optimized by investigating a wide range of composite formulations and processing techniques. Considering the potentials for applications and resource availability RPE was chosen as the matrix materials to produce the WPCs with saw-dust through the injection moulding technique. Subsequently, dimensional stability, durability, mechanical and thermal properties need to be investigated.

1.2 OBJECTIVES

The main objective of this project is to prepare reinforced composites from law cost renewable natural fiber and recycled polyethylene which may replace the use of costly metals, mineral fillers and wood traditionally used as engineering materials. Another aim of the present study is to look for better use of saw dust which may offer economic benefit of the country.

Furthermore, if polyethylene is recycled and reused Bangladesh will be economically benefited by reducing the import cost of polyethylene from abroad.

In order to achieve the overall objective, specific targets are defined as follows:

- To prevent environmental pollution and ecological imbalance by recycling synthetic polymeric materials.
- To get reinforced materials from SD and recycled synthetic polymeric materials.

- To develop better resistance to water absorption, high mechanical properties of the composites by chemical treatment of SD.
- To investigate the long-term water absorption and thickness swelling behavior of WPCs by water immersion.
- To show better use, applications and renewable properties of polymeric wastage materials.

The overall objective of this study is to develop and investigate the performance of WPCs product made of post-consumer recycled plastics and SD with focus on stability and durability at differ filler-matrix mixing ratios. The performances of WPCs made from the recycled polyethylene (RPE) reinforced with raw and chemically treated saw-dust is to be compared for the same composite formulations and various chemical treatments.

CHAPTER 02

REVIEW OF LITERATURE

This chapter will cover the discussion about the concept of cellulosic fiber, structure and composition of saw-dust, concept of polymer composites materials, polyethylene and environmental pollution and recycling aspect of polyethylene.

2.1 General Background

Composite is a material formed with two or more components, combined as a macroscopic structural unit with one component as continuous matrix, and other as fillers or reinforcements. Normally, the matrix is the material that holds the reinforcements together and has lower strength than the reinforcements. In the plastic based composites, the polymers, either thermoplastics or thermoset, act as a matrix and fibers of wood or other natural fibers are fillers. The reinforcing fibers are the main load-carrying component in the composites. It provides high strength and stiffness as well as resistance to bending and breaking under the applied stress. Interface bonding between the fillers and the matrix is the key to transfer the stress from the matrix into the fillers across the interface. The interface adhesion between the polymer matrix and wood fillers can be improved using coupling agents. The coupling agents will form a bond between the fibers and the matrix through improved compatibility (wettability) and developing a mechanical or chemical bonding (details given in 2.3.7). To achieve the required properties of the composites, properties of both the fibers and the matrix are important although the extent of the influence of the fibers and the matrix may vary depending on the required properties of the composite. The tensile strength of short fiber composite is more sensitive to polymer matrix properties, whereas elastic modulus is more strongly dependent on the fiber properties [54]. As WPC contained a low density plastic matrix reinforced with stiff wood fibers, polymer matrix is stretched more under the same stress as to the fibers due to lower modulus than the fibers. Therefore, stiffness of the matrix has impact that is more significant on the overall stiffness of the composite and the stiffness of the composite is more sensitive to the properties of the matrix than the fillers.

2.2 Concept of Composites and Classification

The composite material contains a matrix and fillers. Polymer may be used as formaldehyde, teflon, phenol formaldehyde, etc. Like matrix, fibers are mainly two types one is natural fiber and another is synthetic these are used as filler content. Composites materials are broadly classified by Kundu [55] which examples are given below.

Natural composite materials: The typical example of natural composites materials are wood, bone, bamboo, muscle natural composite and other tissue materials. Usually, all types of natural fibers are classified in three categories.

- Mineral Fibers
- Animal Fibers
- Plant Fibers

Among these three types of fibers plant fibers (hard wood fiber) in particular are described in this chapter. Concerning vegetable fibers, these are classified depending on the place of the plant (stem, leaves, seeds, grass etc) from where they are extracted. Fig. 2.1 shows the classification of plant fibers according to their origin.

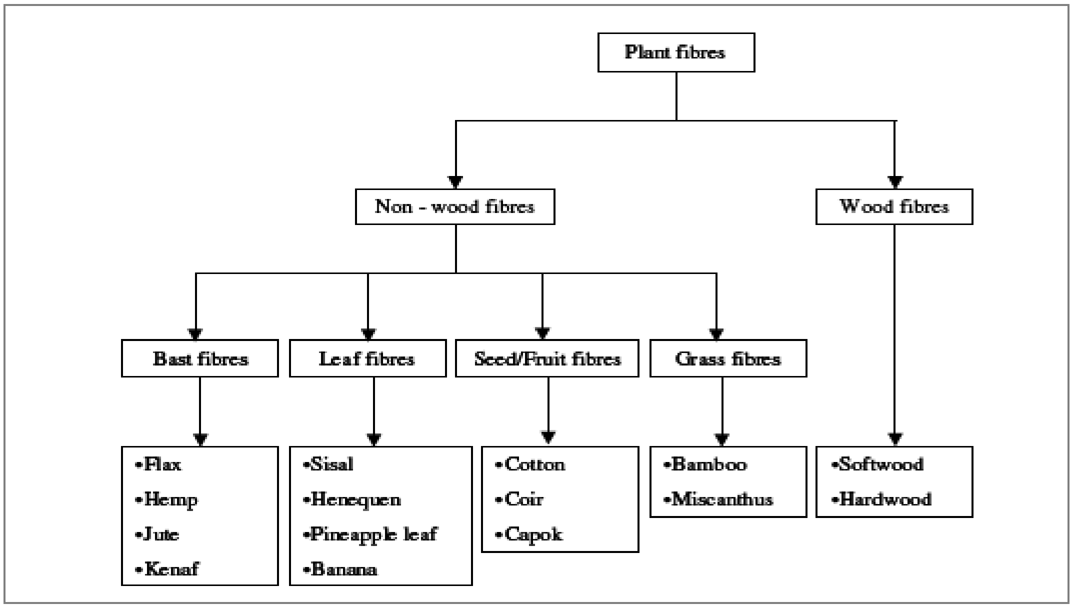


Figure 2.1: Classification of plant fibers according to their origin [56].

2.3 SD Filler in WPCs

Wood has been used as reinforcing filler in thermoset polymer for decades, however, its use in thermoplastics is a relatively new spurred by improvement in processing technology and development of coupling agents. Use of wood as the filler in WPCs has advantages such as low-cost, renewable nature, biodegradability, low specific gravity, and low abrasive to pr0cessing equipment as compared with inorganic fillers (e.g. glass fibers and clay). Commonly used wood species for WPCs manufacturing are pine, maple and oak, although other species can also be used. As the physical, chemical and micro-structural properties of wood species depends on the type of species such as for softwood and hardwood. Hence selection of wood species for the use in WPCs could have a significant influence on the microstructure and properties of WPCs [27]. The wood may have the forms of sawmill chips, SD, saw-dust, wood fibers, wood powder, or pulp are available for WPCs production [57].

However, for the plastic based composites, the wood should be grounded to fine flour or refined to fibers. When saw-dust is used, the saw-dust reinforcement to the plastic is not through individual fibers but through particulates consisting of broken fiber bundles of wood. Maiti and Singh [15] examined influence of saw-dust size that was compounded with HDPE followed by extrusion moulding. They found that the extruded samples displayed an increasing Young's modulus with the saw-dust particle size in the range of 180-425Mm. Tajvidi et al. [58] studied extruded composite made from Reed flour-PP with particle sizes ranged from 20-40 mesh to smaller than 100 mesh sizes. It was reported that lowest water absorption and thickness was found with smallest particle size. Stark NM et al. [59] had reported the composites made from saw-dust-PP with various sizes of wood particles (35, 70, 120, and 235 mesh) showed that aspect ratio, not particle size, had the greatest effect on strength and stiffness. However in case of wood fiber, the tensile strength and Young's modulus was found to decrease and failure strain increased with decreasing of average fiber length in composites with the aspect ratio of wood fiber calculated to be between 16 and 26. This higher aspect ratio enhanced stress transfer from the matrix to the fiber. The use of wood fiber had little effect on impact energy. Most commercially manufactured saw-dusts used as fillers in thermoplastics are less than 0.425mm (40 mesh size), which has the aspect ratio of 3.4 [60]. Very fine saw-dusts can cost more and increase melt viscosity more than coarser saw-dusts, but composites made with them typically have more uniform appearance and a smoother finish. If ground too finely, fiber bundles become wood dust, fragments that no longer resemble fibers or fiber bundles.

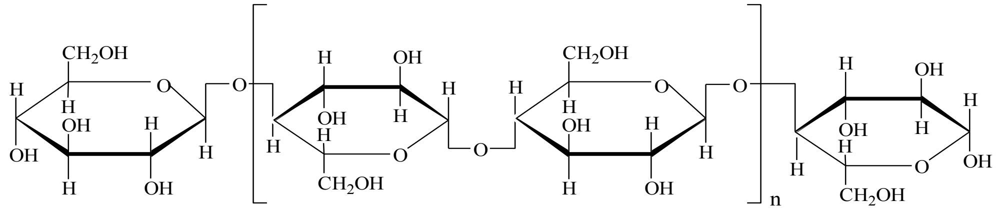
2.4 Chemical Composition of Hard Wood

Wood is classified as a lignocellulosic material and made up of three major chemical constituents (cellulose: 45-50%, hemi-cellulose: 20-25%, and lignin: 20-30%) and other minor constituents (ash: 0-0.5% and extractives: 1-10%) [61, 62]. The chemical composition of wood varies between wood species. The major constituents of wood are briefly explained below.

- ***Cellulose***

Cellulose is the most abundant and the main structural component of wood. The cellulose molecule is long, straight linear chain of homo-polymer consisting of three elements namely carbon, hydrogen, and oxygen, which are organised into anhydro dglucopyranose linked via N1, 4 glycosidic bonds (Fig. 2.2). It is a highly crystalline, linear polymer of anhydroglucose units with a degree of polymerization of around 10,000. It is the main component providing the wood strength and structural stability. Cellulose is typically 60-90% crystalline by weight. The arrangement of molecular cellulose is due largely to the surface hydroxyl groups. A high portion of cellulose is crystalline, held together by intermolecular hydrogen bonding. The hydroxyl groups can be between glucose units in the same molecule (intra-molecular) or between two adjacent molecules (intermolecular linkages). The hydroxyl groups on cellulose are largely responsible for its reactive nature. The cellulose is hygroscopic because it consists of polar molecules and easily undergoes hydrogen bonding [61]. Water absorption by cellulose depends on the number of free hydroxyl groups, not those linked with each other. The water molecules cannot enter the crystalline region but can reside in the amorphous regions.

The structure of cellulose :



Cellobiose residue = repeating unit of cellulose

Fig. 2.2: Segment of a cellulose molecule showing linear and unbranched structure [63].

As early as 1920, Herzog and Janeke [64] recognized that cellulose from such widely different sources as cotton, ramie, wood, jute and flax gave identical X-ray diagram and concluded that the these fibers had identical crystalline structures.

- ***Hemicelluloses***

Hemicellulose consists of a collection of polysaccharide with lower degree of polymerization than cellulose. Its structure is similar to that of the cellulose in the way that the hemicelluloses are arranged in 5 or 6 carbon sugars in chains. However, chains are relatively short and less regular compared to the cellulose, therefore, the hemicelluloses are soluble or easily degraded. The degree of polymerization is only tens or hundreds of repeating units.

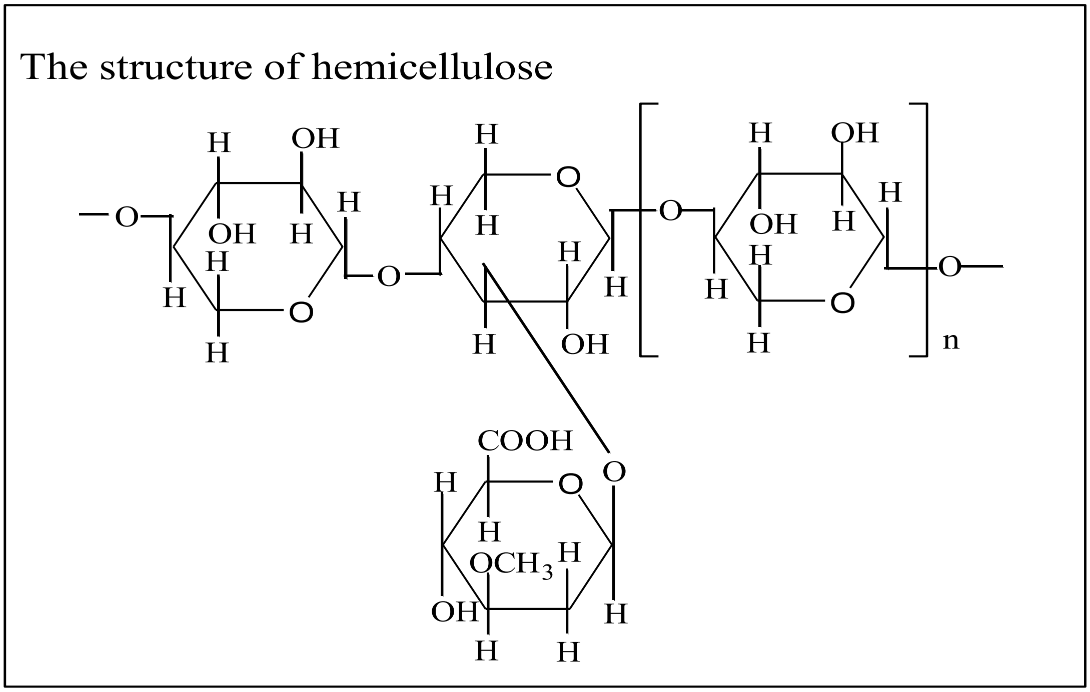
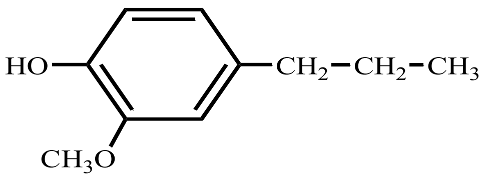


Fig. 2.3: The structure of hemicellulose

- ***Lignin***

Lignin is an insoluble, resin like substance of phenolic character. It is built up to a large extent, of phenyl propane building stones, often having a hydroxyl group in the para position and methoxyl group/groups in meta position/positions to the side chain [65-67]. Besides, there may be carbon to carbon or carbon to oxygen bonds joining the aromatic ring to the portions of structure. The lignin molecule, thus being polyfunctional due to the presence of alcoholic and phenolic hydroxyl groups, may exist in combination with two or more neighboring chain molecules, cellulose or hemicellulose, serving the function of a cross-linking agent. Postulated monomer in lignin [68] as shown in the figure 2.4.

Structural unit of lignin:



4-hydroxy-3-methoxy phenyl propane.

Fig. 2.4: Structural unit of lignin molecule

Lignin is a binding agent that holds cellulose fibers together. This is a brittle and relatively inert material acting as both bonding and stiffening agent. Diffusion of lignin into the fiber wall increases the stiffness of the wood cell and allows for stress transfer between matrix and fillers in the WPCs. It is comprised of carbon, hydrogen and oxygen. Lignin is not as active as cellulose due to low occurrence of hydroxyl sites.

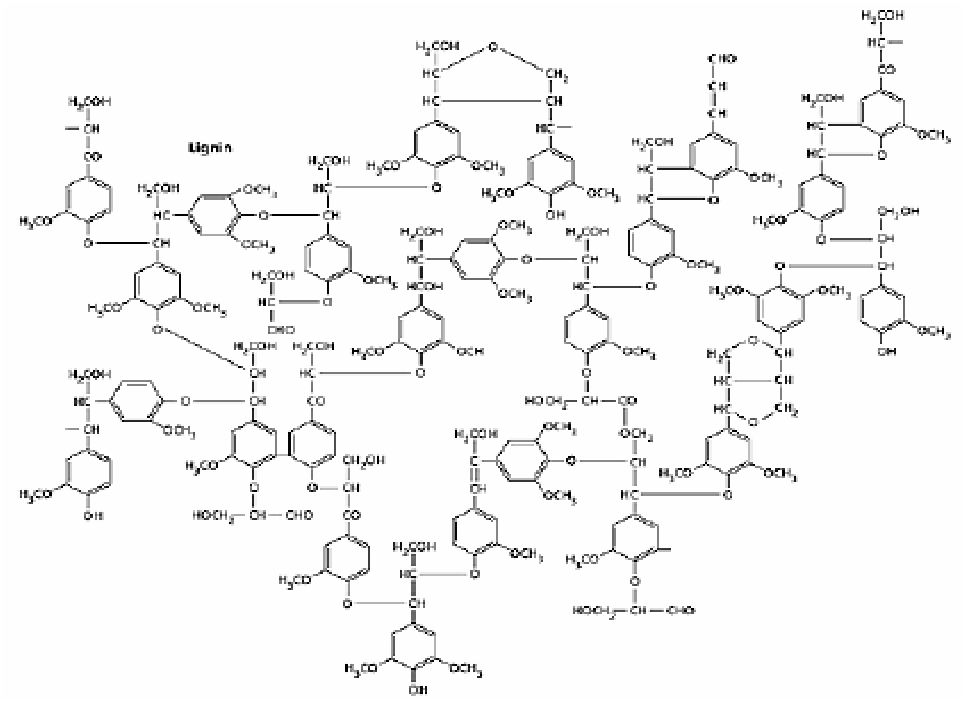


Figure 2.5: Partial polymeric structure of lignin molecule from beech wood [69].

Most plant tissues contain, in addition to carbohydrate and extractives, an amorphous polymeric gummy material is called lignin [66, 67]**.** The nature of lignin and its relationship to cellulose and other constituents of fiber are still uncertain. Unlike cellulose and hemicellulose, lignin gives a series of colour reaction [70] that indicate the presence of compounds for which these reactions are typical. Isolated lignin is generally an amorphous material having average high molecular weight.

2.5 Waste Wood for Reinforcing Filler

The large amount of wood waste is generated at different stages in the wood processing and a proportion of this waste is mainly destined for landfill although major part of the wood processing waste used for energy. About 1,038,996 m^3 round wood equivalents of wood chip residuals (wood off-cuts, slab wood, planer shavings and SD) was produced by New Zealand forest industry in 2002, which are mostly from radiata pine forest [71]. The use of waste wood in

WPCs helps to offset these disposal costs. The waste wood in the form of SD, fibers or pulp are suitable filler for polyolefin's matrix composites [15, 16]. The Pinus radiata fiber possesses physical and mechanical properties suited to the reinforcement of plastics [17]. According to Lightsey et al. [72] there was little difference in tensile modulus of composites made from either saw-dust or pulp mill wood residue with HDPE matrix. Wood particles for the use in WPCs need to be dried to 0-2% moisture content to process adequately with thermoplastic polymers. Due to the thermal stability of wood under temperature of 200ºC, most common thermoplastics (PE, PP, PS, and PVC) are easily processed with wood below this thermal decomposition temperature [12].

2.6 Polymers in WPCs

In the production of WPCs, both thermoplastics and thermosetting plastics can be used. Thermoplastics are based on linear or slightly branched polymers in which the molecular chains flow over each other. This type of plastics is in solid form at ambient temperature and becomes deformable at elevated temperatures, and the process of hardening at low temperatures and softening at high temperatures is reversible. It can go through a number of melting-freezing cycles without appreciable chemical changes, which makes it suitable for recycling [73]. On the other hand, thermosets are network polymers formed by cross-linking reactions and cannot be re-melted. Thermoset resins such as phenolics and epoxies are generally used in structures that require higher mechanical properties or integrity at higher temperatures. Polyethylene (PE) is one of the thermoplastic polymers consisting of long chains of the monomer ethylene ($CH_2=CH_2$), and is produced through polymerization of ethylene, and contains small proportions of additives. There are two major categories in PE: high density polyethylene (HDPE) and low-density polyethylene (LDPE). HDPE has a density of greater than or equal to 0.941 g/cm^3 and low degree of branching and thus demonstrates strong intermolecular strength. It exhibits greater rigidity and physical strength and has a higher melting point (130-135 ^{o}C) than the LDPE, but the HDPE has lower resistance to stress cracking. The HDPE is commonly used as containers and packaging such as milk jugs, detergent bottles, garbage containers and water pipes. The mechanical properties of PE depend strongly on variables such as the extent and type of branching, the crystal structure and the molecular weight.

Polypropylene (PP) is also one of the thermoplastics with a semi-crystalline polymer structure similar to PE and is produced through polymerization of propylene gas. PP has an excellent resistance to stress, low specific gravity, and good mechanical properties such as excellent impact strength. It has a melting point of 160-165 ^{o}C, and has low density (0.85 g/cm^3 with amorphous, 0.95 g/cm^3 with crystalline) and higher stiffness and strength than HDPE. It is used in a wide range of applications, including food packaging, plastic parts and reusable containers of various types. There are three different types of PP: homo polymer, random copolymer and impact or block copolymer. The co monomer used is typically ethylene. Ethylene-propylene rubber added to PP homo polymer increases its low impact strength at low temperatures. Randomly polymerized ethylene monomer added to PP homo polymer decreases the polymer crystallinity and makes the polymer more transparent. Impact copolymer PP is expensive than homo polymer polypropylene. Random copolymer PP is more expensive than the impact copolymer PP. The melt flow rate (MFR) or melt flow index (MFI) is an indicator of thermoplastic molecular weight. It is used to determine how easily the melted raw material will flow during processing. Higher MFI or MFR plastics fill the plastic mould more easily during the injection or blow moulding production process. As the MFI increases, however, some physical properties, like impact strength will decrease. Thermoplastics are commonly used as matrix materials for wood or other natural fiber composites. The thermoplastics in these composites should have a processing temperature less than the thermal degradation temperature of wood (~200oC). Due to the limited thermal stability of wood, thermoplastics that meet this requirements include LDPE, HDPE, PP, PS and PVC, which are suitable for use in WPCs in both virgin and recycled form [12, 74]. Although PVC was the first thermoplastic commercially used in WPC manufacturing [9], PE is now the most commonly used type followed by PP for WPCs among the entire thermoplastics [74]. The WPCs made from PE are widely used for exterior building components such as decking, fencing, and infrastructure, while PP composites are mainly for transportation applications. In this study RPE is used to fabricate WPCs composites so the following discussion mainly focused on PE and RPE.

2.7 An Overview of Polymers and Polyethylene

2.7.1 Definition and Classification of Polymer

Polymer is a large molecule composing, hundreds of thousands of atoms formed by successive linking of one or two, occasionally more types of small molecules into chain or network structures. There are mainly two types of polymer depending on the thermal properties which as follows.

- Thermoplastic Polymer
- Thermosetting Polymer

Thermoplastic Polymer

The term “thermoplastics” indicates that these materials melt on heating and may be processed by a variety of moulding and extrusion techniques. The most common thermoplastics are polyethylene, polyethylene, polystyrene (PS) and polymer chloride together with a number of more specialized engineering polymers. Thermoplastic polymer matrix (RPE) is used in this work.

Thermosetting Polymer

Thermosetting polymers are those polymers, which are incapable of melting or of truly dissolving. These are naturally branched structures formed by step polymerization processes of at least two functional groups. As these functional groups intercombine, random three-dimensional networks are developed. Ultimately the network extents throughout the mass of polymerized material, which therefore in effect constitutes a single joint molecule. Important thermosets are phenolic and amino resins. The most common thermosets are epoxy, melamine formaldehyde urea formaldehyde unsaturated polyester, phenolic, alkane and polyurethane.

2.7.2 Importance and Applications of Polyethylene

Polymer science has made tremendous strides in the last century. From the earliest attempts at synthetic reproduction of natural fibers and rubber to the most technically advanced engineering plastics today, scientists worldwide endeavor to make advancements in stronger, more versatile polymers. Polyethylene (PE) is one such very important economic raw material. This is used for the various industrial and house hold applications. Globally 500 billion to 1.0 trillion plastic bags are used annually [75, 76] or 1 million plastic bags every minute [76], while more than 200,000 plastic bags are dumped in landfill sites every hour [77]. More than 4-5 trillion bags were manufactured globally in 2002 [78].

In Western Europe alone approximately 21.37 million tonnes of LDPE, HDPE and PP are consumed each year (data of 2003), representing an amount of 56% of the total thermoplastics [79]. The United States plastics industry produces 15 billion pounds PE annually. There were 4.2 million tons of HDPE produced in the United States in 1990. So the plastic pollution is becoming an increasing environmental problem [75, 80-85] and it is creating major concern among the researcher for last two decades. The most common uses of PE are shopping bags, industrial wrapping, coating, vehicles tires and tubes, films, coating, cables insulation, food and beverage packaging, thin film, medical products, pharmaceuticals products and marine application. Among these all products, PE shopping bags are become most descriptive issue. Every year, more than 500 billion plastic bags are distributed, and less than 3% of those bags are recycled. All plastics bags are typically made of PE and can take up to 1,000 years to biodegrade in landfills that emit harmful greenhouse gases [86]. Hence the use of PE shopping bags created public concern worldwide for its enormous environmental and ecological imbalance.

Bangladesh is the first listed country of this world banded PE shopping bags of 20μ or >20μ thickness in January, 2002. Last year (October, 2010) information was reported in the open literature by Shanna Foley, where survey reports showed about 10 million plastic bags were still used every day [87, 88] in Bangladesh. One could easily find the polyethylene bags everywhere i.e. in the street, dumpsites, drains, ditches, open-fields, roof tops, hanging from trees and overhead cables, floating on ponds, canals, rivers [88]. So in this point of view several questions may come out i.e. the government banned the PE shopping bags but why these are located at the supermarket and public places? Is it possible to prohibit PE in medical and pharmaceutical industries? Is it possible to prohibit PE as industrial wrapping, vehicles tires and tubes, films, coating, cables insulation, food and beverage packaging? No it is quite impossible to prohibit these applications of PE completely.

Actually the government banned only one application of PE i.e. shopping bags of 20 or >20μ thickness otherwise other several hundred of PE application such as low thickness polyethylene bags, vehicles seat cover, rain coat, industrial wrapping, coating, electric devices, cable coating, marine application, water protector, medical and pharmaceutical products, food and beverage packaging extremely using every day. These applications are daily needs we cannot do our everyday's work without PE today. At these circumstances the government of every country should emphasize on the solid waste management and public concern on the reuse and recycling of thermoplastics. Otherwise no nations can solve these problems. Nevertheless, PE is a very important economic raw material and extremely suitable for reuse so it is not wise to treat as only problematic materials. Very clean and efficient production is possible from recycled PE also can be used as replacement of energy recovery. Proper utilization and extensive research can bring a golden future for a nation by novel invention. We should not blame PE as problems in fact all synthetic materials have positive and negative sides so this is better and wise for thinking about alternative technology for reuse and recycling not banned these materials. Some sensitive application of PE is still using by all nations where we cannot think alternative without PE. So it is concluded that PE is a very essential part of our daily need, it is not possible to prohibit totally. For this reason in the developed countries plastics bags are not prohibited these are recycled and converted into valuable products like flower pot, garbage bags, dust bin, composites, energy recovery, respective monomer and house hold materials. Due to the superior properties of polyethylene, PE cannot be treated as an environmental problem this is the large asset of every nations. Everything points to the fact that we can expect a lot of valuable products from this material in the future.

2.7.3 Definition and Structure of PE

Polyethylene is a thermoplastic polymer consisting of long chains produced by combing the ingredient monomer ethylene (IUPAC name ethene), the name comes from the ingredient and not the actual chemical resulting. The ethylene actually converts to ethane as it takes its place in a polymer and straight sections of the polymer are the same structure as the simple chain hydrocarbons, e.g., propane, decane and other straight single-bonded carbon chains. As with any polymer, the structure of the resulting substance defies molecular description due to cross branching of the chains. The recommended scientific name polyethene is systematically derived from the scientific name of the monomer [89, 90]. In certain circumstances it is useful to use a structure-based nomenclature; in such cases IUPAC recommends poly(methylene) [90] (poly(methanediyl) is a non-preferred alternative [91, 92]). The difference in names between the two systems is due to the opening up of the monomer's double bond upon polymerization. The name is abbreviated to **PE** in a manner similar to that by which other polymers like polypropylene and polystyrene are shortened to PP and PS respectively. In the United Kingdom the polymer is commonly called **polythene**, although this is not recognized scientifically.

$$\boxed{\text{—}[CH_2\text{-}CH_2]_n\text{—}}$$

Polyethylene contains the chemical elements carbon and hydrogen. Polyethylene is created through polymerization of ethene. It can be produced through radical polymerization, anionic addition polymerization, ion coordination polymerization or cationic addition polymerization. This is because ethene does not have any substituent groups that influence the stability of the propagation head of the polymer. Each of these methods results in a different type of polyethylene.

2.7.4 Polymerization Reaction of PE

Polyethylene is a chain-growth polymer, in which the double bond of the alkene monomer gets broken as new bonds are formed between monomer molecules. Can you predict the basic structure of polyethylene? As you might imagine, it simply consists of $–CH_2CH_2-$ units repeated again and again. The most common type of chain-growth polymerization uses “radical initiation,” in which a small amount of a compound with only seven valence electrons ($R^{\bullet}$, called a free radical) begins the polymerization by adding to an alkene monomer and generating a new radical that then adds to another alkene and so on. The polymer is “terminated” by reaction with another radical, either another initiator or another growing chain.

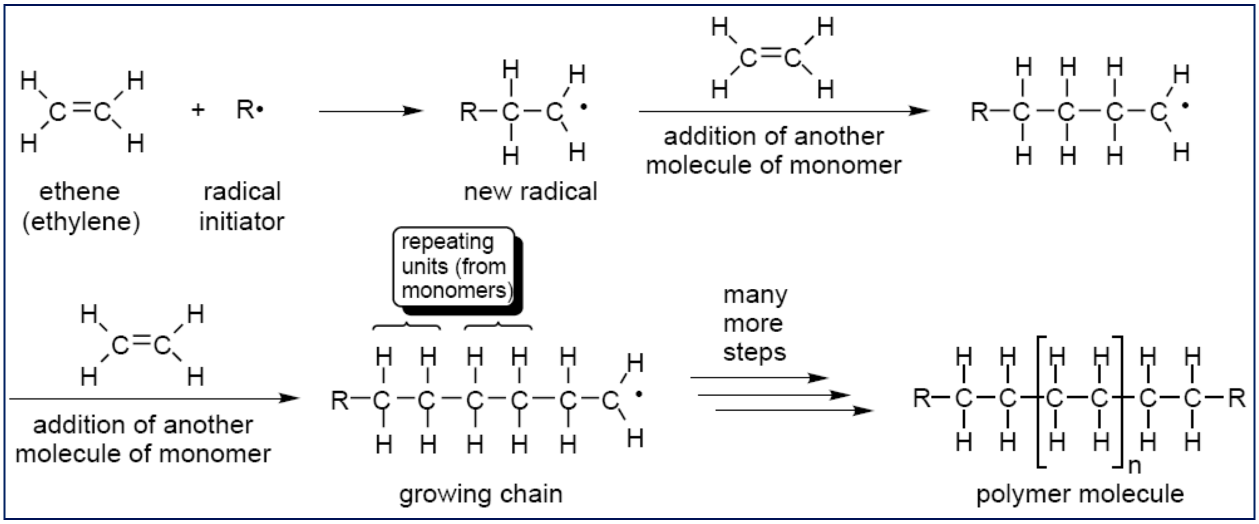


Fig. 2.6: Polymerization of ethylene to form polyethylene

2.7.5 Classification of PE and Application

Polyethylene is classified into several different categories based mostly on its density and branching. The mechanical properties of PE depend significantly on variables such as the extent and type of branching, the crystal structure and the molecular weight. With regard to sold volumes, the most important polyethylene grades are HDPE, LLDPE and LDPE.

- Ultra high molecular weight polyethylene (UHMWPE)
- Ultra low molecular weight polyethylene (ULMWPE or PE-WAX)

- High molecular weight polyethylene (HMWPE)
- High density polyethylene (HDPE)
- High density cross-linked polyethylene (HDXLPE)
- Cross-linked polyethylene (PEX or XLPE)
- Medium density polyethylene (MDPE)
- Low density polyethylene (LDPE)
- Very low density polyethylene (VLDPE)

UHMWPE (ultra high molecular weight PE) - because of its outstanding toughness, cut, wear and excellent chemical resistance, UHWMPE is used in a wide diversity of applications. These include can and bottle handling machine parts, moving parts on weaving machines, bearings, gears, artificial joints, edge protection on ice rinks, butchers' chopping boards., HMWPE (high molecular weight polyethylene), HDPE (high density PE) - is used in products and packaging such as milk jugs, detergent bottles, margarine tubs, garbage containers and water pipes, HDXLPE (high density cross-linked PE), PEX (cross-linked PE), MDPE (medium density PE) - is typically used in gas pipes and fittings, sacks, shrink film, packaging film, carrier bags, screw closures, LDPE (low density PE), LLDPE (linear low density PE) - is used predominantly in film applications due to its toughness, flexibility, and relative transparency., VLDPE (very low density PE) - used for hose and tubing, ice and frozen food bags, food packaging and stretch wrap.

2.7.6 Statistical Overview of PE Production in Bangladesh

Survey report showed that near about 10 million polyethylene bags were used every day and every year about 3000 million bags were dumped in Dhaka City alone. The number of factories which produced polyethylene shopping bags, as perceived, widely varied from 800 to 1,700 by different categories of respondents/participants. In Bangladesh HDPE factories were started in 1982, but about 75 percent were established in the last decade, i.e. during 1990-2000. The total number of workforce employed in polyethylene factories of Bangladesh were estimated at 18,000 and another 7,000 workers are engaged in different stages of recycling. Thus, about 25,000 workers were related to polyethylene industry. The monthly average salary/wages of polyethylene workers ranges from Taka 2000-3200 per person. On an average, work more than 8 hours a day. It appeared from the study that total number of polyethylene bags produced in the country had been 47 billion annually or 130 million per day for domestic and commercial use. Taking population at 129 million (The 2001 Population Census), per capita daily polyethylene production had been one bag. In terms of weight, only 20 percent of the total production was thinner and smaller, the remaining 80 percent were thick and big bags. It was estimated that about 14.1 billion bags were used annually at household levels in Bangladesh [93].

2.8 PE and Environmental Pollution in Bangladesh

Polyethylene industries for shopping bag production emerged in Bangladesh in early 80's and within a decade the industry reached in such a level that the jute bag production forced to be almost closed. It was revealed that polythene bags used and dumped in Dhaka City was causing extreme health hazards like soil degradation, loss of agricultural land fertility, blocking up of the cities' drainage and sewerage systems, water logging and the spread of harmful microbes and bacteria giving rise to epidemics. Other cities were also experiencing similar problems, but with lesser gravity. The country side was also experiencing polyethylene menace as people were no more using traditional bags made from jute or other sources. The worst example of adverse effect caused due to polyethylene bags was the delaying process of recession of flood water in Dhaka city during 1998. In the following some practical view of environmental pollution in Bangladesh were discussed below.

2.8.1 Pollution in Market Area

In Bangladesh so many unplanned and unregulated shopping complex, shopping center, bazaar and shops are made everywhere as a result extremely increasing environmental pollution. Here the waste management is so poor and in the rural area no waste management. In these areas normally wastage products are thrown beside the road, near able lake or pond, free space and backward place of market. A lot of synthetic wastage materials were produced every day from these market areas and directly mixed into soil and finally causing pollution. A picture was taken from village market from here we can easily assume the pollution of our country.

Figure 2.7: Back word place of market area covered by PE

2.8.2 Effect of Land Filling

Forecasts concerning the production of resins indicate that the economies of many developed and developing countries are increasingly relying on the use of plastics. In this regard the most intractable problem relating to plastics and the environment has been so far their disposal. Land filling on one hand is increasingly seen to pose problems of environmental impact, because the availability of suitable sites is decreasing day by day. A typical picture of land filling was taken from Amin Bazaar, Gabtoli, Dhaka which are as follows.

Figure 2.8: Land filling by PE

Polyethylene materials are not bio-degradable. Whenever a polyethylene bag is thrown away, it does not decompose through natural process. It remains interact in the soil and disturbs the flow of nutrients to the soil and hinders entering sunlight. It destroys the beneficial bacteria of soil and losses soil fertility. It hinders the way of soil compaction, which in the long run effects the construction of foundation of the different structure.

2.8.3 Water Pollution

Bangladesh is a land of rivers, so many rivers are going through the country but most of the rivers water extremely polluted by PE shopping bags and municipal wastage. Turag and Buriganga rivers are flowing through the capital city Dhaka also so many small rivers flowing through the Dhaka city. The water surface of these rivers is covered by PE products also covered the rivers bottom. The bank of this rivers totally covered by various color PE products and municipal wastage. As a result aquatic lives become danger and decreasing rivers deepness. Moreover, the leaching of the plastic additives into the ground waters is now being questioned.

Figure 2.9: Rivers water contamination by PE and other municipal wastage [94].

2.8.4 Air Pollution from PE

During incineration uncontrolled burning of plastics including polyethylene in the dumping sites and other areas is not acceptable environment-wise. The controlled incineration of plastic waste is also raising concerns in some cases. One of the effective ways of management of polyethylene bags is recycling or reuse of post-consumer polyethylene bags for other useful purposes. But the state of recycling in Bangladesh again posed some other environmental hazards and some means of transmission of diseases. The burning of polythene in open air produces the threat of poisonous gas like carbon mono-oxide, carbon dioxide hydrogen cyanide those causes health hazard to the people. The people who are involved in collection of polythene bags are the most vulnerable group.

2.8.5 Water Circulation Problems

Wild life is also highly hampered by PE, most of the food packages are contain food or sweet meat then animals are taken with food and affected by diseases because plastics are not digestive. Plastics are also throwing in the forest, zoo and park where plant, crops and grass cannot grow properly. Day by day forest area covered by plastics waste and creating complexity for wild life. Plastics are non biodegradable materials so always clogging the drainage system and workers are always working for water circulation.

Figure 2.10: Clogging drainage system [95] in Bangladesh.

2.8.6 Unhygienic Problem of PE

Medical reports find it as an agent of cancer, skin diseases and other health problems. The users are more exposed to these types of health hazards when polyethylene is used to pack bread, biscuits, potato chips or other food items. In the developed countries, food is wrapped in food graded plastic or polyethylene, but in Bangladesh this was not strictly followed and sometimes colorants are used, some of which may be carcinogenic.

2.9 Anti-polyethylene Campaign

Environment and Social Development Organization (ESDO), an environmental NGO for the first time started campaign against polythene shopping bags in Bangladesh in 1992. It was supported by many government and nongovernment organization such as school, college, NGO etc. Based on the popular demand on 1993, Ministry of Environment and Forest (MOEF) took an initiative to ban the production and trade of polythene bags outside Export Processing Zone (EPZ) with the approval of the cabinet, but it was not materialized. In 1998, 2/3 part of Dhaka capital city was flooded for 2-3 month and the water circulation was clogging by PE shopping bags. In 1999, Ministry of Environment again started campaign against polyethylene through its Sustainable Environment Management Programme (SEMP) that led to the formation of a Task Force by the Government under the Ministry to work towards framing a Strategy for phasing out of polythene shopping bags. After a land slide victory in the Parliamentary Election in 2001, with a two third majority in the parliament, the Four Party Alliance Government under the leadership of Begum Khaleda Zia undertook a crash programme for 100 days. All the Ministries were asked to develop their own priority programmes for implementation within first 100 days of the government. The Ministry then held a series of meetings under the leadership of Minister Mr. Shajahan Siraj with the jute and paper bag producers including Bangladesh Jute Manufactures Exporters Association (BJMEA) and Bangladesh Garments Manufacturers Exporters Association (BGMEA) for banning plastics bags. All the associations, more importantly the BJMEA responded positively and promised that they would produce jute shopping bags to fill the gap and sell at a competitive price. The paper bags producers and the cloths bag producers also responded positively. Finally the government banned PE shopping bags of thickness 20μ or greater than 20μ from first January, 2002.

Plastic materials play an important role in our daily life in the form of a wide variety of household articles. As a result, in municipal solid waste all over the world plastics account for a significant amount made up of mostly polyethylene and polypropylene. Unregulated dumping, open burning and uncontrolled land filling are their common disposal methods particularly in developing countries. The utilization of this enormous quantity of waste from an environmentally friendly and energetically affordable way has not yet been developed. The problem has stirred the policy makers around the world and is not confined within the territorial frontiers of a country. They have now understood that unregulated dumping or burning can no longer be continued as the environmental devastation already caused by these processes is enormous and that recycling and reuse of polymer based solid waste can assuage this problem [96-98].

2.10 Plastics in Municipal Solid Waste and Prospect

Growing production and consumption of plastics worldwide has resulted in significant contribution to municipal solid waste as described in the first section of this chapter. Recycling of the waste plastics has benefits of minimizing solid waste disposal problem, reducing the virgin plastics consumption and lowering the production costs. A number of reclamation techniques have been developed to obtain well sorted plastics that can be used or substitute for the virgin plastics in many applications [73]. Past studies were shown that the recycled plastics possess similar mechanical properties and are cheaper than in the virgin form. Pattanakul et al. [99] found that the mechanical properties of recycled HDPE from the post-consumer milk bottles were not largely different from those of virgin resin. Recycled HDPE pellets and flakes are 31-34% less expensive than the virgin HDPE [100]. About 40% of all recycled plastics products were used in distribution products such as film and bags, and ~30% were used in building applications such as pipes, windows and tiles in Western Europe [101]. There is a greater potential to use recycled plastics to produce WPC products in low cost without reduced properties.

2.11 Recycling Aspect of PE

During last decades, the great population increase worldwide together with the need of people to adopt improved conditions of living led to a dramatically increase of the consumption of polymers (mainly plastics). Materials that appears interwoven with the consuming society where we live. According to the Solid Waste Management division of Dhaka City Corporation (DCC), 3000 to 4000 tons of waste is generated everyday in the city. In this, 50 tons is hospital waste, one-fifth of which is hazardous to health. About half the total waste is collected and dumped for landfills and the rest is scattered and left unattended all over the city [14]. Currently, 9.3 million plastic bags are dumped in the city every day, with only 10-15% put in dustbins. The rest are left go into drainage and sewage lines, causing blockages [102]. Disposing of the waste to landfill is becoming undesirable due to legislation pressures (waste to landfill must be reduced by 35% over the period from 1995 to 2020) rising costs and the poor biodegradability of commonly used polymers. The approaches that have been proposed for recycling of waste polymers [103, 104]. Mechanical recycling where the polymer is separated from its associated contaminants and it is reprocessed by melt extrusion. Chemical recycling leading in total depolymerization to the monomers or partial degradation is applied to other secondary valuable materials. Energy recovery is an effective way to reduce the volume of organic materials by incineration. Among the recycling techniques, incineration meets with strong societal opposition and mechanical recycling can be carried out only on single-polymer waste streams. However, the most attractive method is tertiary recycling. According to this method, waste polymers can be either converted into original monomers or other valuable chemicals. These products are useful as feedstock for a variety of downstream industrial processes or as transportation fuel. The Mechanical recycling is very attractive technology PE is melted with filler and produced reinforcing materials. The resultant products are very good in quality, no emission of hazard gases during production. Few example of waste PE application are shown in the following.

2.12 Recycled Thermoplastic in WPCs

In a similar way as for the virgin plastics, any recycled plastics that can melt and be processed below the degradation point of wood can be used for manufacturing WPCs [105]. However, limited studies were conducted to evaluate the performance of the WPCs made from recycled HDPE [25, 27, 29, 106-108] and PP [28, 109] with saw-dust. Kamdem et al. [25] studied the properties of compression moulded composites made from the rHDPE and saw-dust. Selke et al. [27] and Yam et al. [65] studied the rHDPE (simulated milk gallon) and wood fiber composites using extrusion moulding. Li et al. [108] studied compression moulded composites based on a combination of virgin HDPE and recycled HDPE with waste pine wood flakes. The mechanical properties of the compression-moulded composites made from SD and virgin PP and recycled PP was studied by Najafi et al. [28] who reported that the composites containing PP (25% each of virgin and recycled) were exhibited statistically similar mechanical properties to those of composites made from virgin plastics. Li et al. [109] examined the impact strength for the composite made from pine SD and recycled PP with coupling agent Epolene E-43. Sellers et al. [106] studied the WPC panels using recycled PE or polystyrene (PS) and pine wood fibers at a ratio of 50:50 through high pressure pressing moulding. They reported that the products had good mechanical properties suitable for construction materials. A study by Jayaraman et al. [29]

showed that the tensile strengths of WPCs made from wood fibers (pine) and recycled HDPE are about 25% higher than those of the entirely virgin HDPE panel.

2.13 Improvement of Interfacial Bonding Between Sawdust and RPE

The processing and desired properties of SD can be improved by using additives such as lubricants, coupling agents, antioxidants, UV-absorbers and antimicrobial agents among others [35]. Properties of SD depend on many factors including the species and forms of the wood filler, types and forms of polymer matrix, compatibility and chemical bonding of the wood fillers and polymer matrix, and processing methods used. The mechanical properties of WPCs depended on the interfacial bonding between the wood fillers and polymer matrix [110]. Therefore, the interface bonding between the wood filler and polymer matrix has to be strong enough to transfer stress from the polymer matrix to wood fillers. However, interface between the wood filler and polymer matrix is weak due to the incompatibility between the hydrophobic wood filler and the hydrophilic polymer matrix. In this case, addition of coupling agent is necessary to improve the compatibility and interfacial bonding between the wood filler and polymer matrix [35, 111]. Functionalised polyolefin's coupling agents with maleic anhydride grafted polymer (LLDPgMA, HDPEgMA, HDPEgAA, and PPgMA) has been using in WPCs to improve the compatibility and bonding between hydrophilic wood filler and hydrophobic polymer matrix [34]. The maleated polypropylene (MAPP) and maleated polyethylene (MAPE) are more commonly used in WPCs and highly regarded as the effective coupling agents [34, 110, 112, 113]. These coupling agents improved the overall performance of the WPCs through the improved compatibility (wettability) and chemical bonding between the wood filler and polymer matrix. The coupling agents are acting as hydrophobic wetting agents, which displace the water and air to give a more stable and uniform dispersion of particles.

The melt viscosity, which increases with the filler loadings is lowered when coupling agents used in the processing. Furthermore, wood dispersion and wettability in plastic matrix can be improved by the wetting agents (lubricants) such as metallic stearates, fatty acids, and paraffin wax [114]. The wetting agents forms protective layers around the filler thereby improved the dispersion. It also promotes bonding by allowing the polymer melt to wet the solid surface more efficiently. The essential difference between a wetting agent and a coupling agent is that coupling agent forms a chemical bond with the solid inclusion whereas a lubricant does not. In addition, the coupling agent improved the bonding between hydrophilic wood fiber and hydrophobic polymer matrices by forming bridges of chemical bonds between the fiber and the matrix. Fundamentals on the influence of the coupling agents have been investigated and it is widely believed that the functionalized polyolefin coupling agents in WPCs formulation improved interface bonding between the polymer and saw-dust through the esterification mechanism [63, 115]. Such improvement is due to the formation of ester bonds between the anhydride moieties of coupling agents entered into an esterification reaction with the surface hydroxyl groups of saw-dust (Fig. 2.11).

The MAPP coupling agent improves the dispersion and adhesion of the wood filler in the polymer matrix and enhances the stiffness and the flexural strength for a wide range of wood contents, with 2-5 wt. % providing the best results [110]. Succinic acid is the byproduct thorough the hydrogenation of maleic anhydride. It is believed that succinic anhydride residues in MAPP serve as a wood-bonding domain and polymer (PP or HDPE) chains co-crystallize or form entanglements with the polymer matrix.

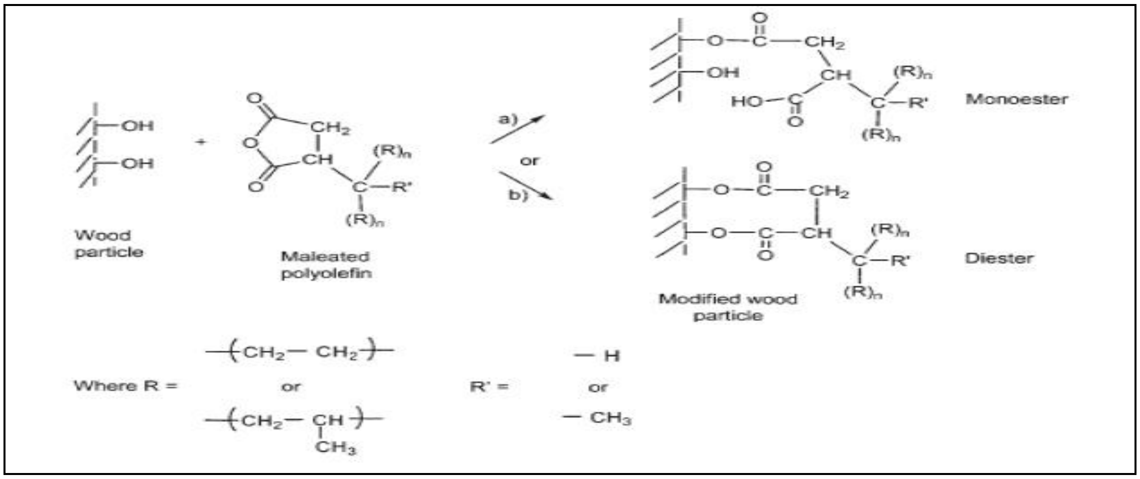


Fig. 2.11: Modification mechanism for esterification reaction between wood particles and maleated polyolefin's: (a) monoester; (b) diester formation [74].

2.14 Fabrication of Sawdust Reinforced Polymeric Composites

The manufacturing of the thermoplastic based composites is usually through a two-step process: (1) compounding of the wood filler and the plastic with coupling agent or other additives, and (2) extrusion moulding, injection moulding or compression moulding of the compounded mixture to produce a panel type product [105]. Proper mixing of wood filler with polymer and additives are important to manufacture consistent composites. Compounding is a process of feeding and dispersion of fillers and additives in the molten polymer either using batch or continuous mixtures. The compounding process produces compounded wood plastic pallets with coupling agent or other additives, and the compounding process directly affects the properties of the resultant composite [116, 117]. An appropriate compounding time, mixing temperature and moderate intensity of the mixing improve the compounding quality and the composite properties.

The compounding step also reduces the time for extrusion moulding thus reducing the possibility of wood degradation in the moulding. Furthermore, moisture is removed from the wood during compounding, which also improves the quality of final product. Compounding can be carried out in specially designed equipment such as Gelimat mixture, single or twin screw extruder. Mixing of wood filler and plastic can be done in different way depending on the type of equipment, such as pre-drying of the wood and pre-mixing with polymer/or additives, or pre-drying and split feeding the material into an extruder [62]. The compounded materials can be immediately shaped into product (in extrusion moulding and injection moulding) or formed into pellets for future press moulding. Extrusion, injection and compression mouldings are common processing methods for WPCs manufacturing. The processing methods and operation conditions influence the morphology of the composites and their properties. In large scale production, the WPCs can be produced with flat platen pressing through initial fast press closing, lateral confinement and final cooling under pressure [118]. The previous studies show that the hot platen press system is suitable for producing flat and curved composite panels using thermoplastic and wood filler.

CHAPTER 03

EXPERIMENTAL METHODS AND APPARATUS

3.1 Collection and Processing of Sawdust (SD)

The SD is collected from the timber house and processed it by using several physical methods like shaking, sieving, meshing and washing. Initially the SD sample was shaken on a large shaker and separated large particle such as stone, concrete, bark etc then sieving for removing all undesirable particles and confirmed these are 100% SD. This 100% SD exist many particle sizes so it this experiment the specific meshes are used. The used meshes in these experiments are mesh70+, mesh100+, mesh140+ and mesh120+. The predetermined particle sized SD is taken which as above mentioned then these are mixed thoroughly and make it homogeneous by using a grinding machine. Previously we have investigated that the large particle sized SD reinforced composites badly affect the composites physic-mechanical properties so no large sizes SD and bark is expected in the processed SD. After that the pure SD washed with distilled water for separating soil and mud in dust form then dried at open atmosphere in sunny place finally dried at 105^{o}C in an air oven and stored. The following diagrams (Fig. 3.1) will insight overall processing of SD.

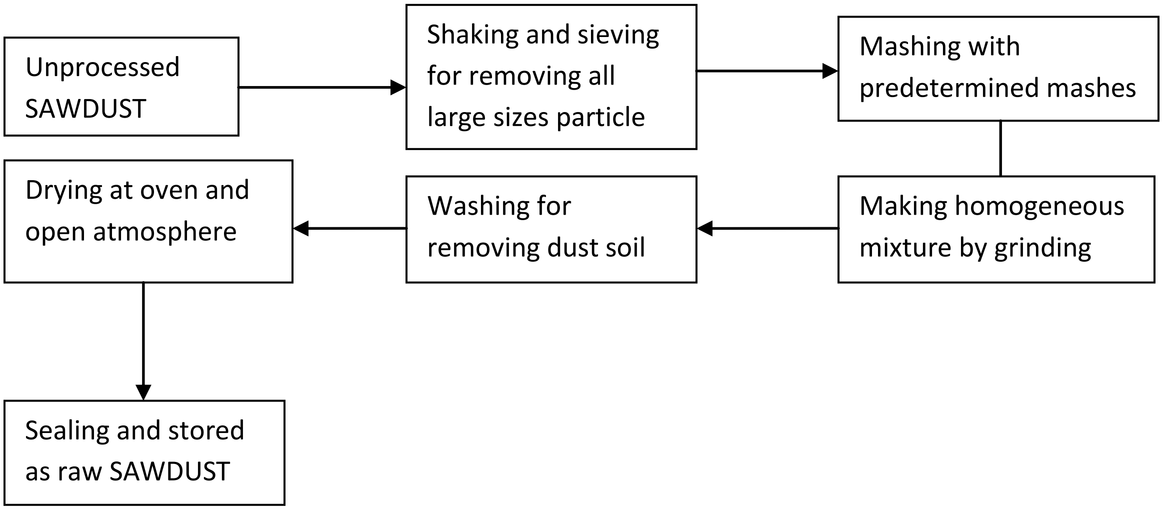


Fig 3.1: Schematic flow diagram of processing raw sawdust (SD)

3.2 Estimation of Sawdust Constituents:

The main constituents of sawdust (SD) were isolated according to TAPPI standard method [119-121]. SD is considered as cellulosic or lignocellulosic materials because the main and major constituents are cellulose, hemicellulose and lignin. These constituents have a viable effect on the physic-mechanical properties of composites materials. Hence, the estimation of SD constituents is emphasized in this research work which explained below.

Estimation of Aqueous Extract:

Certain amount of SD dried at 105°C, is heated with distilled water at 60^{O}C for two hours and the fiber is separated by filtration, dried at 105^{0}C for constant weight. The loss in weight gives the amount of aqueous extract in the fiber. The amount of aqueous extract was found about 3.32%. The calculation was given below.

$$\%\text{ of Aqueous Extract} = \frac{\text{Wi} - \text{SD}}{\text{Wi}} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(3.1)$$

Where, Initial Weight of SD=W_i ; Final Weight of SD=SD

Estimation of Fatty and Waxy Matters:

The SD at 105^{0}C is immersed in a benzene-alcohol mixture (2:1 by volume) contained in a beaker in the ratio 1 gm dried SD per 100 ml of the mixture and then allowed to stand for 10 hours with occasional stirring. The SD is separated from the mixture by filtration, subsequently washed several times with fresh benzene-alcohol mixture and finally with alcohol and then the SD is dried at 105^{0}C for constant weight. The loss in weight on extraction with the solvent mixture gives the amount of fatty and waxy matters in the SD.

$$\%\text{ of Fatty and waxy matter} = \frac{\text{Wi} - \text{SD}}{\text{Wi}} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots\ldots.(3.2)$$

Where, W_i is the initial Weight of SD and SD is the final Weight of SD

Estimation of Pectic Matters:

Among the several methods for the estimation of pectic matters, A.G. Narman method is the best method which is given below. The saw-dust (SD) dried at 105^0C is taken in a beaker and heated with a 0.5% ammonium oxalate solution in the ratio of 1 gm SD per 100 ml solution at $70\text{-}80^0$C for three days in a heating mantle. As evaporation goes on the loss of water is compensated by adding hot distilled water to keep the level of the solution constant throughout the process. The SD is then filtered, washed thoroughly with hot distilled water then dried at 105^0C for constant weight. The loss in weight gives the amount of pectic matters in the SD.

$$\% \text{ of Pectic matters} = \frac{\text{Wi} - \text{SD}}{\text{Wi}} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.3)$$

Where, Initial Weight of SD= W_i g; Final Weight of SD =SD

Estimation of Lignin:

Isolation of Lignin is achieved in two principally different ways:

◙ Dissolution or destruction of carbohydrates by means of suitable solvents such as 72% sulphuric acid, supersaturated hydrochloric acid (42%) or cupramonium to level the lignin as an insoluble residue.

◙ Dissolution of the lignin either in a more or less unchanged form or as a derivative forms. In both cases, removal of the components extractable with benzene-alcohol mixture (2:1) is essential to avoid contamination of the lignin.

Numerous method have been proposed for the quantitative determination of lignin in cellulosic materials, the most common being based upon the assumption that lignin remains as the unsaccaharidable residue when the carbohydrate dissolves in strong mineral acids.

Dewaxed and depectic SD dried at 105^0C treated with 72% sulfuric acid 15 ml for 1 gm of the SD with frequently stirring at ordinary temperature. The mixture is allowed to stand for 2 hours and then diluted to 3% acid concentration. After refluxing the mixture for 4 hours it is allowed to stand for overnight and filtered through a sintered glass funnel and washed thoroughly with hot distilled water. The constant weight of the residue in the sintered funnel dried at 105^0C gives the amount of the lignin content of the SD.

$$\% \text{ of Lignin} = \frac{\text{SD}}{\text{Wi}} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (3.4)$$

Where, Wi= Initial Weight of dewaxed and depectic SD

SD= Final Weight of dewaxed and depectic SD as residue

Estimation of α-cellulose and Hemicellulose:

In this step all non cellulosic matters of SD are removed by the treatment of the bleaching agent, such as sodium chlorite when chlorite holocellulose, a combination of α-cellulose and hemicellulose is obtained.

Preparation of Chlorite Holo-cellulose:

A suitable amount of dewaxed and depectinised fiber dried at 105^0C is treated with 0.7% sodium chlorite solution buffered at pH = 4 in the ratio 1 gm SD per 80 ml liquor at $90\text{-}95^0$C for 90 minutes; 1 ml buffer solution of sodium acetate and acetic acid of pH = 4 is added for every 10 ml of chlorite solution to stabilized the constant pH. The SD is then filtered, washed thoroughly with distilled water, then treated with 2% sodium metabisulphite solution for 15 minutes again filtered and washed thoroughly. The cellulosic materials obtained in the sintered funnel are called the chlorite holo-cellulose, which is dried at 105^0C till constant weight is obtained.

$$\text{\% of chlorite holocellulose} = \frac{W_{chc}}{W_i} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . (3.5)$$

Where, Initial Weight of dewaxed and depectic SD sample= W_i

Final Weight of chlorite holocellulose in SD sample= W_{chc}

Separation of α-Cellulose from Hemicellulose:

Chlorite holo-cellulose dried at 105^0C and 5.00 gm of holocellulose sample which obtained from the above conducted experiment treated with 24% KOH solution for 4-hours with occasional stirring, the ratio 1 gm SD per 100 ml of alkali solution. By this treatment hemicellulose goes into solution and α-cellulose remains undissolved. The α-cellulose is separated by filtration, washed throughly with 2% acetic acid solution, finally with distilled water and then dried at 105^0C for constant weight. The amount of α-cellulose thus obtained is deducted from the weight of holo-cellulose taken gives the amount of hemicellulose.

$$\text{\% of cellulose in WF} = \frac{W_c}{W_{chc}} \times \text{CHC (\%)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . (4.6)$$

$$\text{\% of hemicellulose in WF} = \frac{W_{chc} - W_c}{W_{chc}} \times \text{CHC (\%)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . (4.7)$$

Where, Initial weight of depectic and dewaxed SD sample= W_i gm

Weight of the chlorite holocellulose of SD sample= W_{chc} gm

Weight of the residue as cellulose form =W_c gm

Estimation of Ash Matters:

Certain amount of SD dried at 105°C and then burned it in high temperature resistant ceramic porcelain in the presence of oxygen till to get final products as ash matters. The residual part of the burned SD measured again and these are considered as ash matters. The amount of ash matters was found about 1.09634%. The calculation was given below.

$$\% \text{ of Ash contents} = \frac{W_f}{Wi} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (4.8)$$

Where, Initial Weight of SD =W_i g, Final Weight of SD =W_f g

3.3 Surface Modification of Sawdust by Chemical Treatment

The chemical modifications of SD were conducted with single and double pretreatment by 5% NaOH, benzoyl chloride and hexadecyl trimethyl ammonium bromide surfactant. The all chemical reaction between SD and above mentioned chemicals was accomplished in our well decorated polymer laboratory in the Department of Chemistry, BUET, Dhaka, Bangladesh. The overall process and chemical modification explained by the following representation.

3.3.1 Chemical Modification of Sawdust by Sodium Hydroxide (NaOH)

Required amount of SD was taken and heated at 105˚C for one to two hours till to get constant weight then transferred to large volume of glass or plastic vessel. Previously prepared 5% NaOH solution added into the SD reaction vessel for 45 min to 1 hour to accomplish the alkali modification of SD at constant pH >9. The reaction between SD and NaOH was carried out with occasional stirring by glass rod and carried out at atmospheric condition no external heat was applied. At the end of the experiment SD color transferred golden to blood red also the solution become deep blood red color. At this moment SD is separated from the solution by filtration and dried at sunlight at first then finally in oven at 105˚C till to get constant weight.

This chemical modification basically separated lignin molecule from SD as a result finally SD become softer than raw. In this chemical treatment NaOH react with OH radical at 2, 5 position of cellulose unit and reduced its affinity to react with moisture content. Alkali modified SD then taken for further double pretreatment and fabrication for manufacturing composites specimen with virgin polyethylene and recycled polyethylene. For further double pretreatment of SD were conducted by benzoyl chloride and surfactant (Hexadecyl trimethyl ammonium bromide). The basic chemical reaction between SD and NaOH is given below.

3.3.2 Chemical Modification of Sawdust by Sodium Hydroxide and Benzoyl Chloride

The chemical modification of SD by NaOH already shown in the above mention chemical reaction so in this step required amount of alkali (NaOH) treated SD was taken for this chemical modification by benzoyl chloride. The certain amount of SD were taken in the reaction vessel and previously prepared 0.5 M benzoyl chloride solution of pH>9 added into the SD with constant stirring at normal atmospheric condition. The reaction was carried for 45 minutes to 1 hour with occasional stirring in each five to ten minutes difference. At the end of this treatment alkali treated dried SD transferred brick color to light brick color then separated by filtration and dried at sunlight first then finally in the oven at 105˚C. The occurred chemical reaction between SD and benzoyl chloride is given in the fourth chapter (Scheme-II). This dried SD was taken for the fabrication of manufacturing composites specimen with virgin polyethylene and recycled polyethylene and finally measured various engineering properties.

3.3.3 Chemical Modification of Sawdust by Sodium Hydroxide and CTAB

Chemical modification of SD by NaOH already shown in the above mentioned representation (3.3.1) so during this treatment required amount of alkali (NaOH) treated SD was taken in the reaction vessel for this double pretreatment by surfactant. Previously prepared 0.5 M surfactant solution of pH>9 added into the SD with constant stirring at normal atmospheric condition. The reaction was carried for 45 minutes to 1 hour with occasional stirring in each five to ten minutes difference. At the end of this treatment alkali treated dried SD transferred brick color to dark brick color then separated by filtration and dried at sunlight first, then finally in the oven at 105˚C. The occurred chemical reaction between SD and surfactant is given in the fourth chapter (Scheme-III). Surfactant modified dried SD was taken for the fabrication of manufacturing composites specimen with virgin polyethylene and recycled polyethylene and finally measured various engineering properties.

3.4 FT-IR Analysis of Raw and Chemically Treated Sawdust (SD)

3.4.1 Principle

Light from the source is split into two beams. One of the beams is passed through the sample (α-cellulose and lignin extracted from SD) under examination and is called the sample beam. The other beam is called the reference beam. When beam passes through the sample, it becomes less intense due to the absorption of certain frequencies. Let I_0 be the intensity of the reference beam and I be the intensity of the beam after interaction with the sample respectively [122]. The absorbance of the sample at a particular frequency can be calculated as [123]:

$$A = \log (I_0/I) \quad \ldots\ldots\ldots (3.9)$$

$$\text{Transmittance } (T) = I/I_0 \quad \ldots\ldots\ldots (3.10)$$

$$\text{Or, } A = \log (1/T)$$

3.4.2 FT-IR Spectrophotometer

The infrared spectra of the raw SD and chemically treated SD were recorded on a Shimadzu FT-IR-8101 spectrophotometer. The sample pellets for FT-IR spectroscopy were prepared as follows. Approximately 0.5 mg of powdered SD samples was mixed thoroughly with approximately 100 mg of dried powdered potassium bromide in a small agate mortar pestle. The mixture was taken in a dice of specific dimensions. Pellets were made by applying vacuum pressure. IR spectra obtained in this study are presented in the result and discussion section.

3.4.3 Sampling Techniques

Various techniques can be employed for placing the sample in the path of the infra red beam depending upon whether the sample is a gas, a liquid or a solid. The intermolecular forces of attraction are most operative in solids and least in case of gases.

Thus, the sample of the same substance shows shifts in the frequencies of absorption as we pass from the solid to the gaseous state. In some cases, additional bands are also observed with the change in the state of the sample. Hence it is always important to mentioned the state of the sample on the spectrum which is scanned for its corrects interpretation [123]. Solids for the infra red spectrum may be examined as an alkali halide mixture. Alkali metal halides, usually sodium chloride, which is transparent throughout the infra red region is commonly used for the purpose. Potassium bromide also serves the purpose well.

3.5 Molecular Weight Determination of Sawdust (raw and treated) [124]

Direct and Indirect methods are used for the determination of molecular weight of SD or cellulosic materials. Here direct method is explained below.

3.5.1 Preparation of Sawdust Solution

A certain amount of SD was dissolved in phosphoric acid at 55 ± 2ºC in a 250 mL conical flask with continuous stirring. When the solution became clear, it was suddenly cooled to 30ºC in a cold water bath. Finally, the solution was filtered with a Buchner funnel [125].

3.5.2 Experimental Technique

Measurement of viscosity is carried out in an Ubbelohde suspended viscometer at 30^0C in a water bath. The bath temperature thermostatically controlled at 30^0C±0.2^0C. The viscometer is placed vertically in the water bath in such a way that the highest level of the liquid in the viscometer is at least 1 cm below the water level in the bath. Special precautions are taken to keep the viscometer free from grease and dust. Before each measurement the viscometer containing experimental solution is allowed to stand for 5 minutes in the water bath to attain the temperature of the bath. The SD in phosphoric acid solutions of different concentrations is then prepared by dilution of the original solution. The concentrations of SD solutions were taken according to predetermined method.

For each SD solutions the viscometric flow times are measured. The viscosity of phosphoric acid is also determined at 25^0C solution. The relative viscosity (Eq. 3.11) of the cellulose in phosphoric acid solution is obtained by dividing the viscosity of the solution [126].

$$\eta_r = \frac{\eta_{solution}}{\eta_{solvent}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.11$$

Then the specific viscosity of the solution is

$$\eta_{sp} = \eta_r - 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.12$$

Intrinsic viscosity $[\eta]$ is then obtained from the intercept of straight-line by plotting η_{sp}/C against C and extra plotting to zero concentration, where C is the concentration in $\frac{g}{100\ ml}$ of the solution.

From the measured intrinsic viscosity the molecular weight of SD calculated by the equation.

$$[\eta] = KM^a \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.13$$

From the intercept of the plot log $[\eta]$ against log [M], value of k and from the slope, value of “a” are found to be 1.78 x 10^{-5} and 1 respectively. The molecular weight of SD is then calculated by putting the obtained value a, k and $[\eta]$ in equation 3.13.

3.5.3 Calculation of Molecular Weight:

$$[\eta] = KM^a \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.13$$

By taking logarithm in both side then we have

$$\text{or } \log[\eta] = \log[KM^a] \qquad 3.14$$

$$\text{or } \log[\eta] = \log K + \log M^a \qquad 3.15$$

$$\text{or } \log[\eta] = \log K + a\log M \qquad 3.16$$

$$\text{or } a\log M = \log[\eta] - \log K \qquad 3.17$$

$$\text{or } \log M = \log\frac{[\eta]}{K} \div a \qquad 3.18$$

$$\text{or } M = \{\frac{[\eta]}{K}\}^{1/a} \qquad 3.19$$

$$\therefore M = \text{Anti}\log[\log\frac{[\eta]}{K} \div a] \qquad 3.20$$

3.6 Recycling of Wastage PE From Various Sources

Step I- Collection of plastics wastage materials

There are several and simple tests that can be used to distinguish between the common types of polymers so that they may be separated for processing. Polymeric wastage materials obtained from agricultural, commercial, industrial, and municipal sources were collected and then PE was sorted out by scratching test, burning test and water floating test.

Step II- Manuals of sorting plastic wastage materials

At this stage nails, papers, labels and stones are removed, and the plastic is sorted into four types like PE, PP, PS and PVC. Details manuals for sorting plastics materials discussed below.

- **The water test:** After adding a few drops of liquid detergents to some water in a bowl a small piece of plastic was put in the bowl and was seen if it floats or not. Only PE based materials were found to float while others were not.
- **Burning test:** A piece of the plastic material was placed on the tip of a knife and applied to a flame. In the case of plastic bags it was found that they melts and show reversibility. Finally PE is confirmed by further tests given below:
- **Fingernail test:** To confirm that the collected plastic bags are made of PE fingernail test was carried out. It was observed that only PE shows signs of scratches easily. Then those were separated for further experiments.

To determine if a plastic is a thermoplastic or a thermosetting, take a piece of wire just below red heat and press it into the material. If the wire penetrates the material, it is a thermoplastic; if it does not it is a thermosetting. This test is also implemented during this identification and confirmed that PE is thermoplastic polymer.

Step III – Washing and drying

At this step PE wastages are then washed to remove glue, paper labels, dirt and any remnants of the product they once contained. PE which has a much lower melting point so must be washed below 40 °C to prevent any discoloration. Required amount of PE wastage are taken in the large size washing tank which is designed with stirrer of automated controller system for washing. In case of PE, washing is continued for thirty minutes minimum. The wash solution consists of an alkaline detergent in water, which removes dirt and grease and degrades protein. The detergent used is an alkaline, cationic detergent (i.e. an alkaline solution containing a cationic surfactant). Dishwashing detergents are usually anionic, because glass, china etc. usually build up a negative surface charge. This means that positively charged dirt particles are attracted to them, so an anionic detergent is needed to remove the dirt. If a cationic surfactant were used it not only would be incapable of removing the dirt, but it would itself stick to the surface to be cleaned, making it greasy.

However, plastics acquire a positive surface charge, meaning that a cationic detergent is needed to clean them. Cationic surfactants are much less common than anionic ones, but they are used for shampoos and for fabric softeners [127]. During washing the agitator in the wash tank acts as an abrasive, grinding off the glue of the labels and reducing any paper labels to fibers. The plastics are then separated from the glue, paper, dirt etc. in a spinning tower in which this very fine material is forced out through small holes, while the plastic itself remains inside. In this way waste PE cleaned and washed properly and finally dried at sunlight. The final product at this step transferred to chipper and cutter for further processing and size reduction.

Step IV- Chopping of washed plastics wastage

All sorted and cleaned plastic is then sent separately to a cutter and chipper. The cutter cuts the plastics into small pieces and reduces its size for chipping. The chipper is a cylinder of blades somewhat like an old-fashioned lawnmower in a vessel with a 10 mm grill floor. The blades cut the material until it is small enough to fall through the grill. At this step PE sheets and bags are converted into dust like particle sizes that can be easily converted into PE pellets.

Step V- Pelleting

This is done by melting the chips and extruding them out first through a fine grill to remove any solid dirt or metal particles that have made it through the treatment thus far and then through a die of small holes. If the plastic was simply allowed to extrude from these holes it would come out as spaghetti-like strings and quickly tangle together. However, it is sprayed with water as it comes out (to prevent the plastic from sticking together) and cut off by rotating knives to give small pellets.

Step VI- Fabrication

Finally PE pellets were mixed with raw and chemically treated saw-dust in different weight fraction for the preparation of composites by extruder machine. The composites specimen is prepared by injection moulding method. Finally the composite specimen was taken for mechanical and other various testing. Now the overall recycling of PE was given by the following flow diagram (Fig. 3.2).

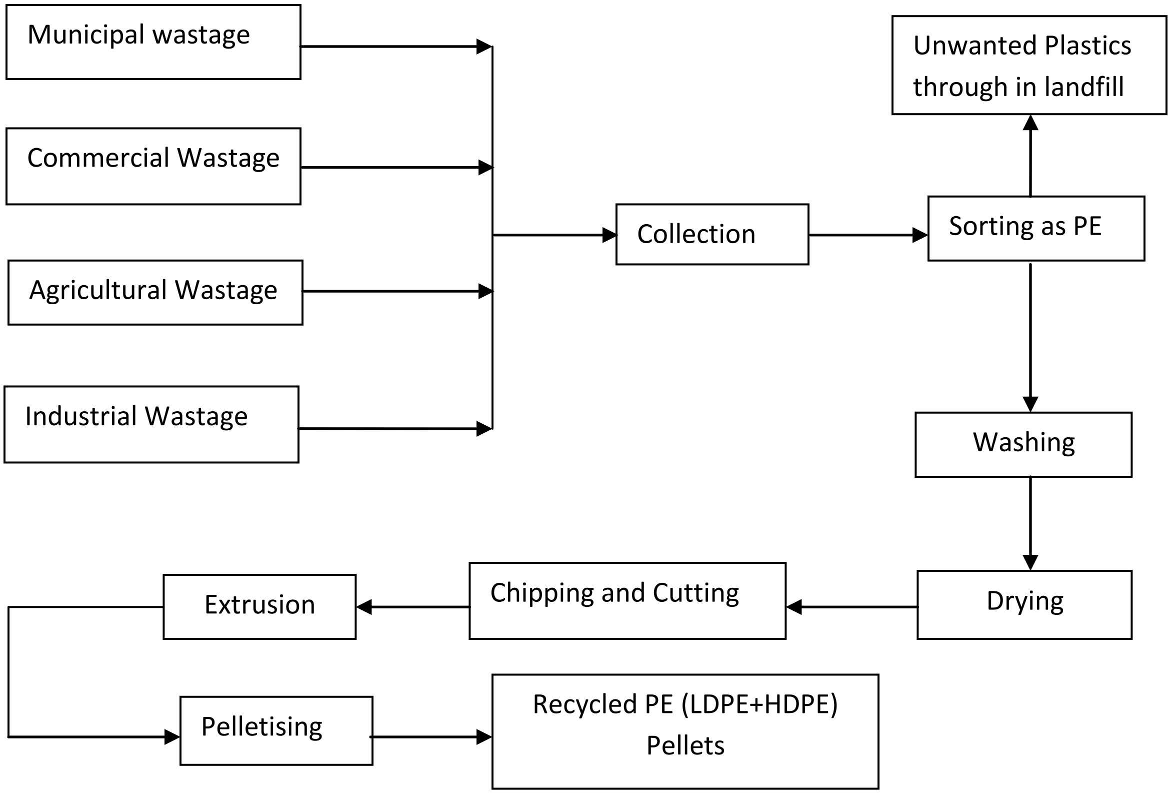


Fig. 3.2: Flow diagram of recycling plastics wastage materials

3.7 Preparation of Composites Specimen

3.7.1 *Materials*

3.7.1.1 Filler- SD (*Switenia mehogoni*, *Tectona grandis, Shorea robusta*
Pinus roxburghii, Acacia nilotica)

3.7.1.2 Resign- Recycled polyethylene (RPE) and Virgin polyethylene (VPE)

3.7.1.1 SD (SD)

SD of the above mentioned hardwood was collected from a local timber house company (Mazar road, Mirpur -1, Dhaka -1216). The fresh SD received was dried at 103°C for 24 h to a m ıe

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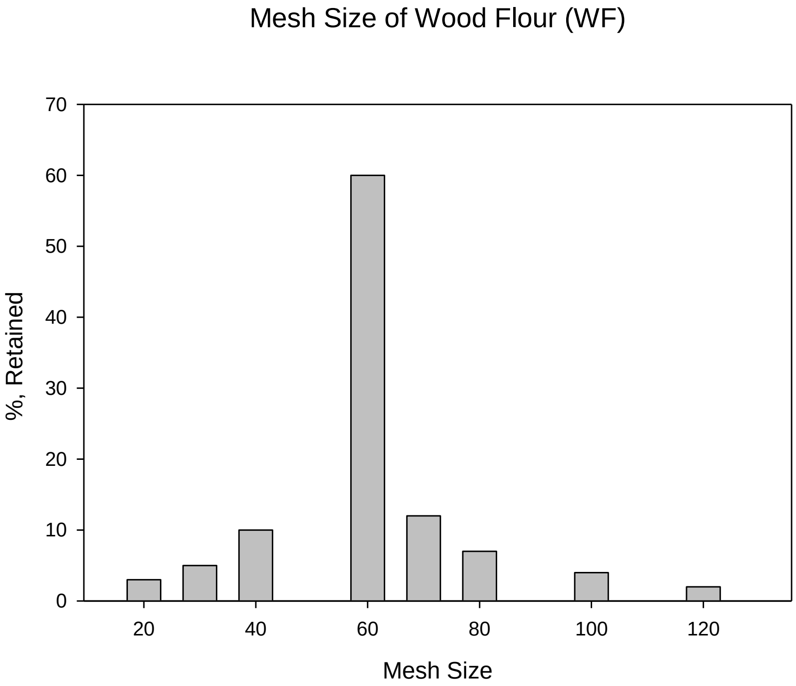

Fig 3.3: Size Distribution of Experimental Saw-dust Mixture

3.7.1.2 *Resin: Recycled polyethylene (RPE) and Virgin polyethylene (VPE)*

Both virgin and recycled thermoplastics resin of PE and VPE were used in this study. The recycled polyethylene (RPE) granules were produced and procured jointly in the polymer laboratory at BUET, Dhaka and local plastic recycling plant (Dhaka Plastics Recycling Ltd., Chakbazar, Dhaka 100, Bangladesh). A commercial grade of virgin polyethylene (PE) was used in this study. It was manufactured by the Polyolefin Company, Pvt., Ltd., Singapore; and its commercial name is Cosmoplene. Melting point of this PE was measured and found to be 140°C. Melting point and FT-IR spectroscopic observations indicated that the used PE was an isotactic polyethylene and commercial grade. In the literature it is mentioned that the melting point of commercial grade PE lies in the range 120-130°C but Pure PE melts at 140 °C[128]. The properties of the virgin and recycled PE are given in Table 3.1.

Table 3.1: Physical and Mechanical properties of recycled and virgin polyethylene

SI No	Properties	RPE	VPE
1	Density (g/cm^3)	0.682500	0.654230
2	MFI (g/10Min)	0.136	0.302
3	Tensile Strength (MPa)	12.425	10.575
4	Youngs Modulus (MPa)	579.48	553.96
5	Flexeral Strength (MPa)	16.9218	14.1703
6	Flexeral Modulus (GPa)	0.819	0.802
7	Hardness (Shore D)	45.932	45.00
8	Izode impact strength (KJ/m^2)	21.4	17.9
9	Molecular Weight (M_v)	1,45,182.00	1,28,165.00
10	BP ˚C	N/A	N/A
11	MP ˚C	145-155	120-130

3.7.2 Preparation

3.7.2.1 Mixing and compounding of the saw-dust and plastics

The prepared raw and chemically modified saw-dust was further dried in an oven to remove the moisture gained during the grinding, handling and preservation to maintain the moisture content of about 2-3%. Similarly, the plastic granules (both virgin and recycled PE) were also dried at 65°C for 12 h to remove all of the moisture during washing. Then the saw-dust was compounded, respectively, with the recycled and the virgin plastic granules (VPE and RPE) by using single screw extruder machine. The typical experimental run of composites formulations were given in the Table 3.2.

The single screw extruder machine (Fig. 3.4) equipped with a single die of two temperature zone connected with two thermocouple and automated temperature controller ranges from 0˚C to 1000˚C temperature. Composites were prepared by passing the mixtures through a single screw extruder machine at a constant temperature of 135°C ± 5°C. The extruded composites were cut into 2-3 cm long small pieces. All the pieces were then crashed into smaller granules using a grinding machine (Model FFC-23, Machinery Company Limited, India). The granules were dried in a vacuum oven at 65°C for one hour.

Table 3.2: Typical experimental run of WPCs formulations with RPE and VPE (percent by weight fraction)

Sample Code	**Type of Resign**	**SD Type**	**Resign Contents (%)**	**SD Contents (%)**
VPE100	VPE	n/a	100	0
RPE100	RPE	n/a	100	0
RPEUTSD20	RPE	Untreated	80	20
RPEUTSD25	RPE	Untreated	75	25
RPEUTSD30	RPE	Untreated	70	30
RPEUTSD35	RPE	Untreated	65	35
RPEATSD20	RPE	Alkali Treated (AT)	80	20
RPEATSD25	RPE	Alkali Treated (AT)	75	25
RPEATSD30	RPE	Alkali Treated (AT)	70	30
RPEATSD35	RPE	Alkali Treated (AT)	65	35
RPEBTSD20	RPE	Benzoyl Chloride Treated (BT)	80	20

RPEBTSD25	RPE	Benzoyl Chloride Treated (BT)	75	25
RPEBTSD30	RPE	Benzoyl Chloride Treated (BT)	70	30
RPEBTSD35	RPE	Benzoyl Chloride Treated (BT)	65	35
RPESTSD20	RPE	Surfactant Treated (ST)	80	20
RPESTSD25	RPE	Surfactant Treated (ST)	75	25
RPESTSD30	RPE	Surfactant Treated (ST)	70	30
RPESTSD35	RPE	Surfactant Treated (ST)	65	35

Fig. 3.4: Single Screw Extruder Machine for Compounding

3.7.2.2 Preparation of test specimen

The dried composites granulates were molded according to DIN EN ISO 572-2 (Type 1A) and DIN EN ISO 179 (Type 1) using the injection molding machine at a molding temperature of 165°C in order to prepare tensile, flexural and all test specimens according to the individual ASTM. All specimen samples were prepared manually by using several dimensional specimen dishes. Molds with single cavity were used during the process. This machine is equipped with single die and single temperature zone connected with temperature controller ranges from 0˚C to 1000˚C. There is a cylindrical metallic sample container which down part is designed with heating surface and sample outlet product as well as the upper portion is open for sample inlet. A moving metallic piston is also equipped with this machine that can be moved up and down easily inside the cylindrical sample container. When the sample melted inside the machine then the specimen dish fitted strongly at the right position of sample outlet and created enormous pressure by using rotary piston to fill the dish void place. In this way all typical experimental run in the Table 3.2 were completed to get specimen sample.

Fig. 3.5: Injection moulding machine operated by manually

In this experiment mainly SD is screened for specific meshes then modified by chemical treatment for considering as filler and resign is prepared by recycled polyethylene bags resign. Finally SD and RPE compounded by extruder machine to get the composites. At last composites test sample were prepared by injection moulding machine. In this way SD reinforced recycled polyethylene composite specimen were produced in this research work. A schematic diagram of the whole procedures is given in the following diagram (Fig. 3.6).

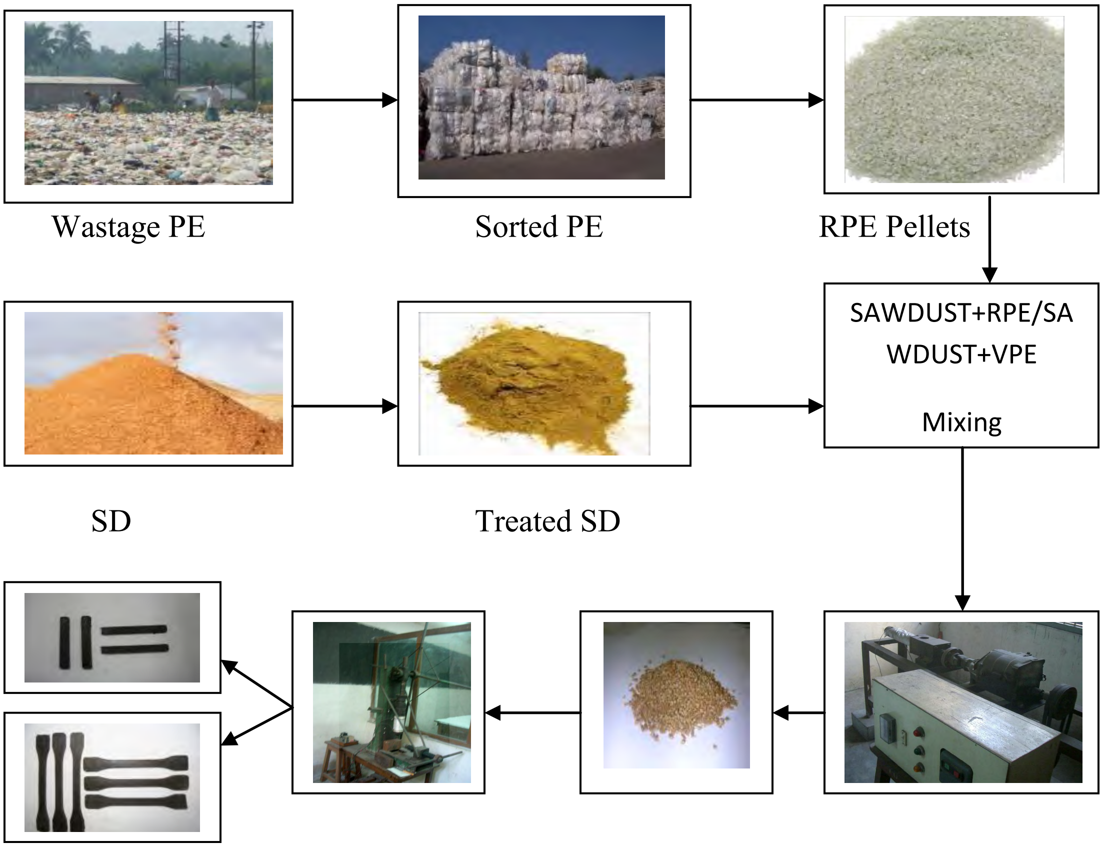

Fig. 3.6: Schematic flow diagram of overall procedure for preparing composites specimen

3.7.2.3 Dimension of sample:

In this research work, we worked with a type of mold which have the upper and lower halves but have no cavity in any half in the mold. These two halves are completely plane with smooth surface platens which also acts as heater and cooler simultaneously. In this of molding process one have to make die for casting with his desired size. We made a die, which has a ring of inside diameter 148 mm and outside diameter 158 mm, and have two disc (or plates) on each side, each of 7.5 mm in thickness.

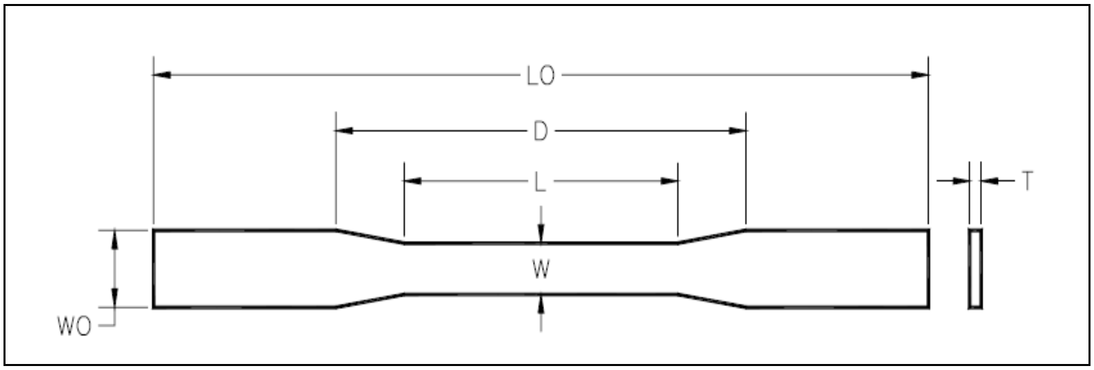

Fig. 3.7: Dimensions of fabricated composite's specimen

Here,

Overall length of the sample (LO)	145.00 mm
Wide of narrow section (W)	10.00 mm
Overall wide (WO)	20.00 mm
Length of narrow section (L)	67.00 mm
Thickness of the sample (T)	04.00 mm
Gauge Length (G)	65.00 mm
Distance between grips (D)	105.00 mm

3.8 Testing of Composites Sample

Testing of the fabricated composite specimen was done for the following physic-mechanical properties. These are listed below.

3.8.1 Methods for the determination of Physical properties

3.8.2 Methods for the Testing of Mechanical Properties

3.8.3 Miscellaneous Methods

3.8.1 Methods for the Determination of Physical Properties

3.*8.1.1 Field Emission Scanning Electron Microscopy (FESEM)*

The fracture surfaces of the Impact or tensile test specimens were characterized with high resolution field emission scanning electron microscopy (FESEM). The FESEM was operated at an accelerating voltage of 1-5 kV and emission current of 47 μA.

The fracture surfaces were sputter-coated with gold of approximately 50 nm in thickness. The scanning data were analyzed at magnifications of 100× and 200×. Approximately about 8-10 SEM images were taken and analyzed for each composite formulation. The FESEM analysis was carried out at the faculty of engineering of University of Malaya, 50603 Kuala Lumpur, Malaysia. The photographs are presented in the result and discussion section.

Fig. 3.8: FE-SEM Machine for microstructure investigation

3.8.1.2 Melt Flow Index (MFI) Test

The melt flow rate (MFR) or melt flow index (MFI) is an indicator of thermoplastic molecular weight. It is used to determine how easily the melted raw material will flow during processing. Higher MFR plastics fill the plastic mould more easily during the injection or blow moulding production process. As the MFI increases, however, some physical properties, like impact strength will decrease.

Fig. 3.9: MFI Machine for thermal properties

The rheological analysis was done to study the flow behaviour of the composite material. The correlation between the size of filler and the concentration can be developed to choose the best flowable material for injection moulding. The SD reinforced RPE composite melt flow rate was measured by using S.A. Associates Melt Flow Indexer in accordance with ASTM D 1238 procedures. According to the standard, loads weighing 1.05 kg, 2.16 kg, 3.80 kg, 5.00 kg and 10.00 kg were applied at barrel temperature of 190ºC. The material was loaded in a heated barrel (190ºC) and forced by the selected load using a piston to flow through a die of internal diameter 2.095 mm. The amount of material extruded through the die in 10 minutes, measured in grams, defined as the melt flow rate or MFR (see equation 3.21).

The melt flow rate of polymer depends on the rate of shear. The shear rate in this test was much smaller than those in actual process behaviour. Therefore, data obtained by this method may not always correlate with their behaviour in actual application. Eq. 3.21 as follows

$$\text{MFR} = \frac{\text{Mass of Extrudate (g)} \times 600}{\text{Extrudate time (s)}} \text{ (g/10 minutes)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ (3.21)}$$

3.8.1.3 Water Absorption Test

In order to measure the water absorption of the composites flexural tested rectangular specimens were cut from each sample having dimensions of 39mm x 1Omm x 4mm. The samples were dried in an oven at 105°C for 2 h, cooled in a desiccator using silica gel and immediately weighed to the variation of 0.0001 g. Denver Instron balance was used for this test. The dried and weighed samples were immersed in distilled water and kept for about 24 h at room temperature and in boiling water for about 2 hours as described in ASTM procedure D570-99 (ASTM 2002) [129]. Excess water on the surface of the samples was removed by using a piece of soft cloth. Then the weights of the samples were taken. Three replicate specimens were tested and the results were presented as average of the tested specimens. The percentage increase in weight during immersion was calculated as follows [129]:

$$\%\text{ of Water absorption} = \frac{W_f - W_i}{W_f} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.22$$

Here, SD is the final weight of composites specimen (After absorption)

W_i is the initial weight of composites specimen (Before absorption)

3.8.2 Methods for the Testing of Mechanical Properties

3.8.2.1 Tensile Strength Test

Type-I tensile bar specimens with dimensions of 165mm × 19mm × 6.4mm (thickness) were prepared from injection moulding machine. The tensile tests were performed in accordance with ASTM D638-99 [130] using a standard Material Testing System (MTS-810 load frame with 5 KN load cell) at a crosshead speed of 5 mm/min. Elongation (strain) of the specimen was measured over a 25 mm gage length using an extensometer. Prior to the tensile test, the specimens were conditioned at 23±2°C and 50% RH for at least 40 h according to the ASTM D638-99 [131].

All measurements were performed at ambient conditions (23±2°C and 50% RH), and five replicates were tested for each composite formulation. The tensile strength was calculated by dividing the maximum load in Newton by the original minimum cross sectional area of the specimen in square meters. The Young's modulus of elasticity (MOE) was calculated from the load-elongation curves by using the initial linear part. The MOE is equal to the stress increase over this linear period divided by the corresponding increase in the strain. The following two equations 3.23 and 3.24 are used to calculate tensile strength and tensile modulus.

$$\sigma_T = \frac{F}{A} \quad \ldots\ldots \quad (3.23)$$

$$E_M = \frac{FL}{A\Delta L} \quad \ldots\ldots \quad (3.24)$$

In the above two equations 3.23 and 3.24

σ_T = Tensile strength

F = Maximum load

A = Area (width × thickness)

E_M = Modulus of elasticity

L = Original length of specimen sample

ΔL = Stroke or length of the object changes

Fig. 3.10: Universal testing machine for TS and MOE

3.8.2.2 Flexural Strength Test

The flexural properties were measured in three-point bending tests using a standard Material Testing System (MTS-858 load frame with 2.5 kN load cell) at a crosshead speed of 2.8 mm/min in accordance with ASTM D790 [132]. The flexural test specimens were also prepared by using right sample dishes during injection moulding machine operation with dimensions of 130 mm × 12.7 mm × 6.4 mm (thickness). The bending measurements were also performed at the ambient conditions of 23±2°C and 50± 5% relative humidity. Five replicates of each composite formulation were tested. The experimental setup used for the three point bending test was shown in Fig.3.11.

The flexural strength (FS) is calculated for the load-deflection curve by using the following equation [133].

$$\sigma_f = \frac{3PL}{2bd^2} \quad \text{...} \ (3.25)$$

The flexural modulus of the elasticity (FMOE) in the bending tests is calculated within the linear limit by using the following equation [133]:

$$E_B = \frac{L^3 m}{4bd^2} \qquad (3.26)$$

In Equations (3.25) and (3.26),

σ_f is the flexeral Strength or the stress in the outer layer at mid-length point of the specimens

E_B is the flexural modulus of elasticity of the specimens in bending tests

P is the load at the loading point (mid-length)

L is the supporting span of the specimen, mm

b is the width of the specimens in perpendicular to the loading direction, mm

d is the depth of specimens tested in parallel to the loading direction, mm

m is the slope of the initial linear portion of the load deflection curve

Fig. 3.11: Universal testing machine for FS and FM

3.8.2.3 Izode Notched Impact Strength Test

Notched Izod Impact is a single point test that measures a materials resistance to impact from a swinging pendulum. Izod impact is defined as the kinetic energy needed to initiate fracture and continue the fracture until the specimen is broken. Izod specimens are notched to prevent deformation of the specimen upon impact. This test can be used as a quick and easy quality control check to determine if a material meets specific impact properties or to compare materials for general toughness.

The specimen is clamped into the pendulum impact test fixture with the notched side facing the striking edge of the pendulum. The pendulum is released and allowed to strike through the specimen. If breakage does not occur, a heavier hammer is used until failure occurs. Since many materials (especially thermoplastics) exhibit lower impact strength at reduced temperatures, it is sometimes appropriate to test materials at temperatures that simulate the intended end use environment.

In the reduced temperature test procedure the specimens are conditioned at the specified temperature in a freezer until they reach equilibrium. The specimens are quickly removed, one at a time, from the freezer and impacted. Neither ASTM nor ISO specify a conditioning time or elapsed time from freezer to impact - typical values from other specifications are 6 hours of conditioning and 5 seconds from freezer to impact.

The standard specimen for ASTM is 64 x 12.7 x 3.2 mm (2½ x ½ x 1/8 inch). The most common specimen thickness is 3.2 mm (0.125 inch), but the preferred thickness is 6.4 mm (0.25 inch) because it is not as likely to bend or crush. The depth under the notch of the specimen is 10.2 mm (0.4 inches). The standard specimen for ISO is a Type 1A multipurpose specimen with the end tabs cut off. The resulting test sample measures 80 x 10 x 4 mm. The depth under the notch of the specimen is 8mm. The specimen size and notching machine is given below (Fig. 3. 12 and Fig. 3.13).

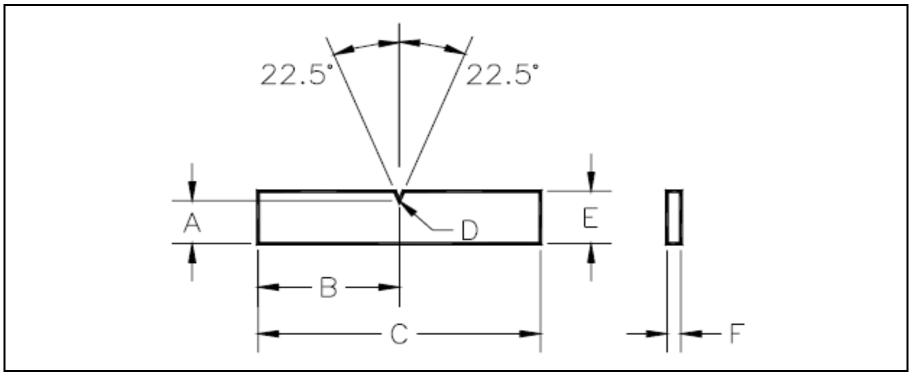

Fig. 3.12: Dimension of notched WPC for IIS test

Where, Width of notched section (A) = 8.00 mm

Notch location (B) = 34.00 mm

Overall length (C) = 68.00 mm

Depth of notch (D) = 2.00 mm

Overall width (E) = 10.00 mm

Thickness (F) = 4.00 mm

Notch Angle = 45˚ (22.5˚ + 22.5˚)

Fig. 3.13: Motorized Notching Cutter Machine

ASTM impact energy is expressed in J/m or ft-lb/in. Impact strength is calculated by dividing impact energy in J (or ft-lb) by the thickness of the specimen. The test result is typically the average of 5 specimens. ISO impact strength is expressed in kJ/m^2. Impact strength is calculated by dividing impact energy in J by the area under the notch. The test result is typically the average of 5 specimens. Custom Scientific Instruments (CSI) Impact Tester is used to test the specimen (figure 3.14).

Fig. 3.14: Custom Scientific Instruments (CSI) Impact Tester

3.8.2.4 Hardness Test

Rockwell hardness test of the composites were carried out following ASTM D 785-98 [134]. A Rockwell hardness number is a number derived from the net increase in depth impression as the load on an indenter increased from a fixed minor load to a major load and then returned to a minor load [134]. Specimen samples used in flexural test were used to conduct this experiment. Procedure A was followed using L scale with a 6.35 mm diameter indenter and 490 N major loads. Rockwell hardness testing instrument and Durometer (Type D) were shown in Figure 3.15

and 3.16 respectively. To be more accurate the samples were also conducted this hardness test by durometer hardness tester (Type D, ASTM 2240). Five measurements were taken for each type specimen and the results were averaged.

Fig. 3.15: Wilson instron rockwell hardness tester

Fig.3.16: Hardness testing by Durometer (Type D)

3.8.3 Biodegradability Test

Disintegration test (part of biodegradability test) was done following ASTM D5338-98 methods. After three months, weight loss (disintegration) occurred in the experimental sample which is determined by using the following equation 3.27. These results are described elaborately in the chapter 04. Biodegradability test is conducted for composites and both 100% recycled and virgin polyethylene.

$$\% \text{ of Biodegradability} = \frac{W_i - W_f}{W_i} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.27)$$

Where, W_i = Initial weight of specimen before degradation

SD = Final weight of specimen after degradation

CHAPTER 04

RESULTS AND DISCUSSION

4.1 Performance of Untreted, Alkali Treated and Benzoylchloride Treated Saw-Dust Reinforced Recycled Polyethylene Composites

This part of the study investigated the thermal, mechanical, physical properties and the microstructure of three different class of wood-plastic composites (WPCs), which were made through injection moulding machine using recycled PE with saw-dust (Mehogoni, shal, shagun, korai) as filler. The three different classes of composites are UT, AT and BT. The recycled PE (RPE) was collected from a local plastics recycling plant and pine SD was obtained from a local sawmill. The composite made from RPE and chemically treated SD exhibited excellent physico-mechanical property as compared to those made from raw SD and RPE. Several chemical treatments were conducted for SD but benzoyl chloride treated composite formulation significantly improved both physical and mechanical properties compared to untreated (UT) and alkali treated (AT) composites. Microstructure analysis of the fractured surfaces of the raw and treated SD composites and confirmed that chemical modification of SD improved interfacial bonding between filler and matrix. Water absorption and strength properties of the composites can be improved by increasing the plastic content or by the chemical modification of SD filler. The final result were found to follow this trends BT>AT>UT by considering all conducted test.

4.1.1 Introduction

There are a number of published studies on the reinforcement of vHDPE with wood fiber with regard to resulting mechanical properties, dimensional stability and interfacial bonding and durability [135-138]. However, studies on WPCs based on RPE are very limited. Yam et al. [139] and Selke et al. [27] studied rHDPE (simulated milk gallon) and wood fiber composites using extrusion moulding and reported that the performance of these composites was at least as good as the composites based on virgin plastic. Li et al. [109] studied hot-press moulded composites based on a combination of vHDPE and rHDPE, and pine wood flakes. It was found that the initial particle geometry of HDPE played an important role in the quality of the composites. Kamdem et al. [25] studied the properties of compression moulded composites made of rHDPE and saw-dust from untreated or CCA treated pinewood, respectively. It was observed that composites with particles from recycled CCA treated pine exhibited higher flexural strength compared to composites from untreated pine. Sellers et al. [107] demonstrated that for hot-pressed composites of recycled pine wood fibers and recycled polyethylene, these composites had mechanical properties suitable for construction applications. Youngquist et al. [12] had shown that composites made from demolition wood waste and waste plastics from milk bottles by thermoforming method exhibited a broad range of properties similar to those made of virgin ingredients. Jayaraman et al. [29] studied the performance of melt blending and injection moulding composites made from Pinus radiata fibers and rHDPE, and found that the tensile strength was 25% higher than those of panel made of entirely using vHDPE. Chen et al. [140] investigated the influence of wood particle size in hot-pressed composites based on construction wood waste and rHDPE, and found that smaller sized wood particles improved water absorption and thickness swelling. Most of the research reported above on wood and rHDPE composites has concentrated on the use of either a single type of plastic from the waste stream, or a simulated mixing of waste plastics or mixing of recycled and virgin plastics.

The post-consumer recycled polyethylene waste stream may contain many different grades, colors and contaminants, leading to varying performance when these plastics are combined with wood fillers (fibers or flour). SD constituents affect the composites properties or even its surface modification also caused sustainable change of the resultant product. But the information about the chemical modification of SD in the open literature was found inadequate so to overcome this situation further research to be done. The impact of post-consumer RPE in WPCs is still not fully understood, leaving open research opportunities for the optimization of the products and processing. This part of study aims to explore the use of SD and post-consumer RPE for the production of the saw-dust-RPE composites. The effect of the saw-dust loadings and chemical modification of SD mechanical properties and microstructure was investigated. The test results for the raw and chemically treated SD reinforced RPE composites were presented and discussed in this chapter.

4.1.2. Chemical Modification

This part of this chapter is mainly discussing the following test analysis and the chemical reaction occurred between SD with NaOH and benzoyl chloride. FT-IR analysis confirmed the occurred chemical reaction with SD by giving right peak of relevant functional groups.

4.1.2.1 Chemical Modification of SD by Sodium Hydroxide (NaOH)

Upon chemical treatment of SD by alkali, NaOH breaks the OH groups at C_2 and C_6 positions of the cellulose in the SD, producing 2,6-disodium cellulose [141] as shown in the figure 4.1. Maybe due to the steric effect, the hydroxyl group at C_3 does not undergo chemical reaction with the Na^+ ion of alkali NaOH.In this chemical treatment NaOH react with OH radical at 2, 5 position of cellulose unit and reduced its affinity to react with moisture content.

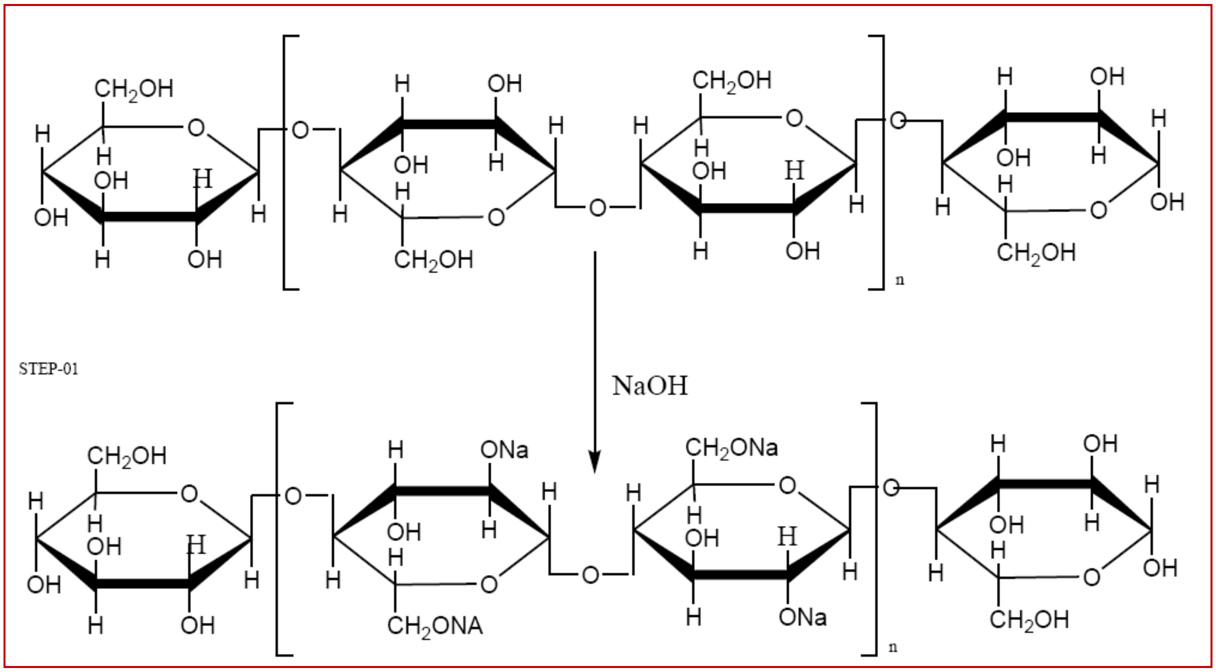

Figure 4.1: Single pretreatment coupling reaction of SD by alkali.

4.1.2.2 Chemical Modification of SD by Sodium Hydroxide and Benzoyl Chloride

The chemical modification of SD by NaOH already shown in the above mentioned chemical reaction so in this step required amount of alkali (NaOH) treated SD sample was taken for this chemical modification by benzoyl chloride. At the end of this treatment alkali treated dried SD transferred brick color to light brick color then separated by filtration and dried at sunlight first then finally in the oven at 105˚C. The occurred chemical reaction between SD and benzoyl chloride is given below (Figure 4.2). This dried SD was taken for the fabrication of manufacturing composites specimen with virgin polyethylene and recycled polyethylene and finally measured various engineering properties.

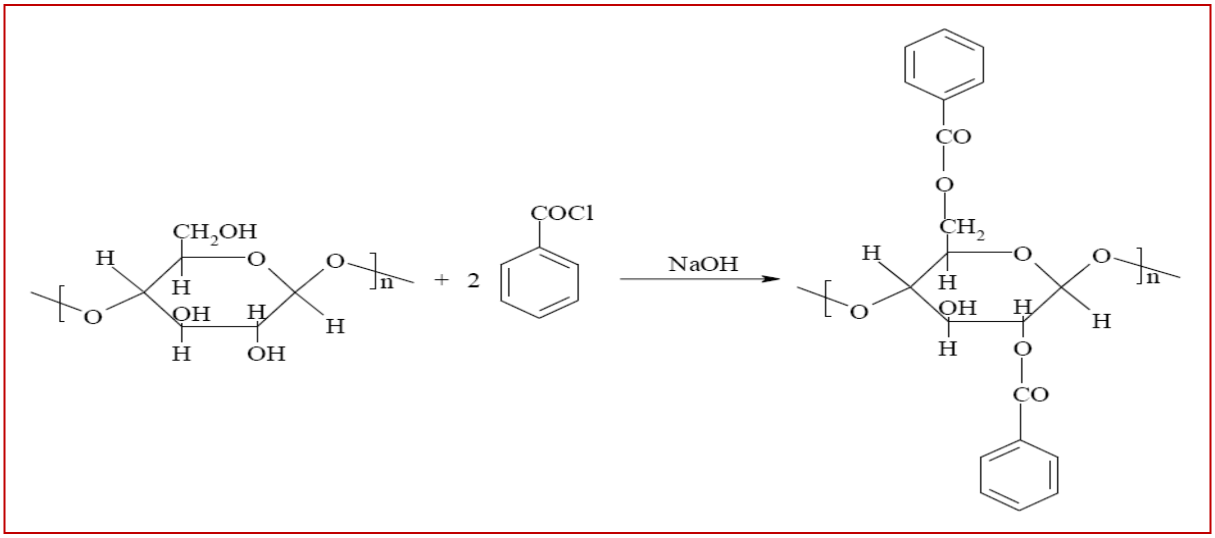

Figure 4.2: Double step pretreatment coupling reaction of SD by alkali and benzoyl chloride.

4.1.2.3 FT-IR spectroscopic analysis of raw SD

The FT-IR spectrum of raw SD is shown in Figure 4.3. The peak assignments of the absorption bands corresponding to various groups are summarized in Table 4.1, which are quite similar to the literature value [142-145]. The FT-IR spectrum of raw SD shows a band in the region near 1636 cm^{-1}, which is probably due to the CO group of acylester in hemecellulose or of aldehyde group in lignin [115]. On the other hand absorption bands of raw saw-dust give clear peak of cellulose, lignin and hemicelluloses. It was also found that the existence of aromatic ring with desired functional group spectrum.

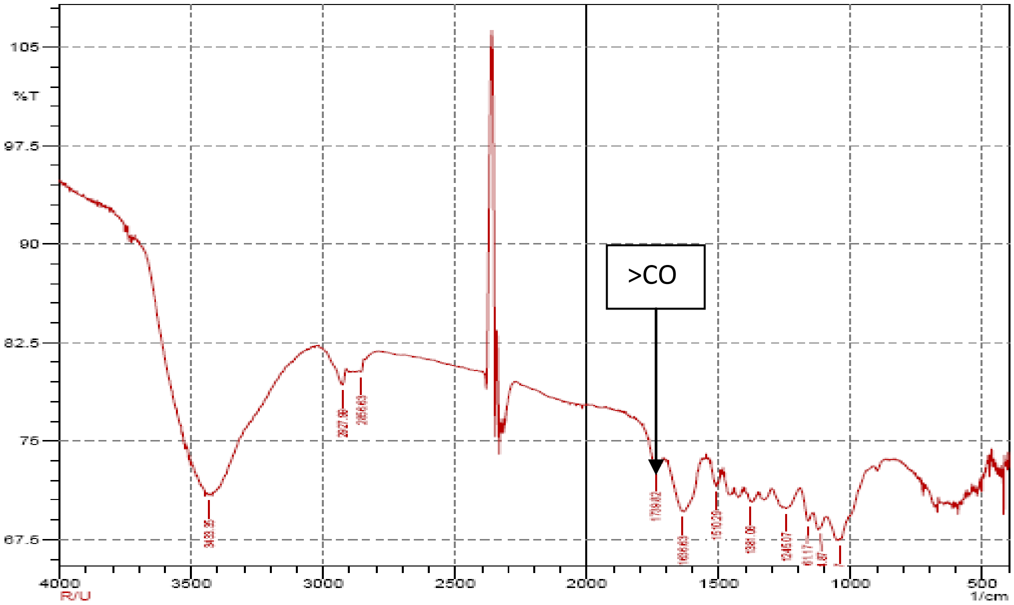

Fig. 4.3: FT-IR spectrum of untreated saw-dust

Table 4.1: FT-IR spectral data of untreated saw-dust

Peak	Intensity	Position/cm^{-1}	Assignment
1044.47	67.494	~ 1050	ν(C-OI >CO cohol
1114.87	68.391	~ 1114.8	V (C-O-C) glycosidic, AntisymZmetrical in phse ring stretching.
1161.17	68.918	~ 1155	ν(C-C) ring breathing, asymmetric
1245.07	69.858	~ 1255.6	δ(C-OH) out-of-plane
1381.06	70.403	~ 1377.3	Methyl symmetric deformation vibration
1510.29	71.534	~ 1508.2	ν(C=C) aromatic skeletal ring vibration due to lignin
1636.63	69.615	~1650-1630	possibly aromatic ring
1739.82	72.954	~ 1750-1710	ν(C=O) most probably from the lignin and hemicelluloses
2856.63	80.28	~ 2854.5	CH_2 symmetrical stretching.
2927.99	79.276	~ 3000-2900	ν(C-H) in aromatic ring and alkanes

3433.35	70.88	~ 3600-3200	v(OH) broad, strong band from the cellulose, hemicellulose and lignin of rice husk

4.1.2.4 FT-IR Spectrum of α - Cellulose and Lignin

FT-IR analysis of lignin and cellulose were individually conducted to ensure the raw SD absorbance. The Infrared spectrum of α - cellulose and lignin by FT-IR is given in the Figure 4.4 and Figure 4.5 represents the spectrum of α - cellulose and lignin which is extracted from SD. Lignin extracted from different sources has different structure. So, the spectrum peak can be changed signal, if it is extracted from different sources. From the analysis, spectrum of α - cellulose and lignin extracted from SD we have the following conclusions.

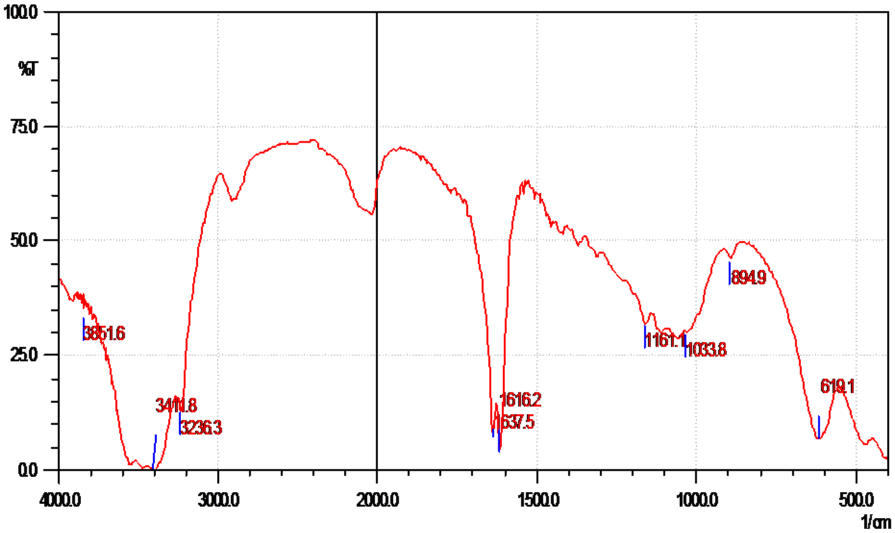

Fig. 4.4: FTIR spectrum of α -Cellulose.

From the Table 4.2, it is evident that cellulose gives two main peak 3236.3 cm^{-1} for hydroxyl aldehydes and ketones. This gives the sufficient information for the functional group of cellulose.

Table 4.2: FT-IR spectral data of α -cellulose

Wave number (cm^{-1})	Interpretations
3411.8	OH stretching (Intermolecular hydrogen bonding)
3236.3	OH stretching (Intermolecular hydrogen bonding)
1637.5	Hydroxy aldehydes, in which hydrogen bonding is possible, C= O str.
1616.2	Ketones in which hydrogen bonding is possible, C = O
1161.1	Antisymmetrical bridge oxygen stretching.
1033.8	CO stretching
894.9	Cl group frequency
619.1	OH out of plane bending

Lignin gives the same absorption of 3236.3 cm^{-1} for hydroxyl aldehydes and ketones but it gives another broad peak at 2854.5 cm^{-1}, which gives the evident that methoxy group present in lignin.

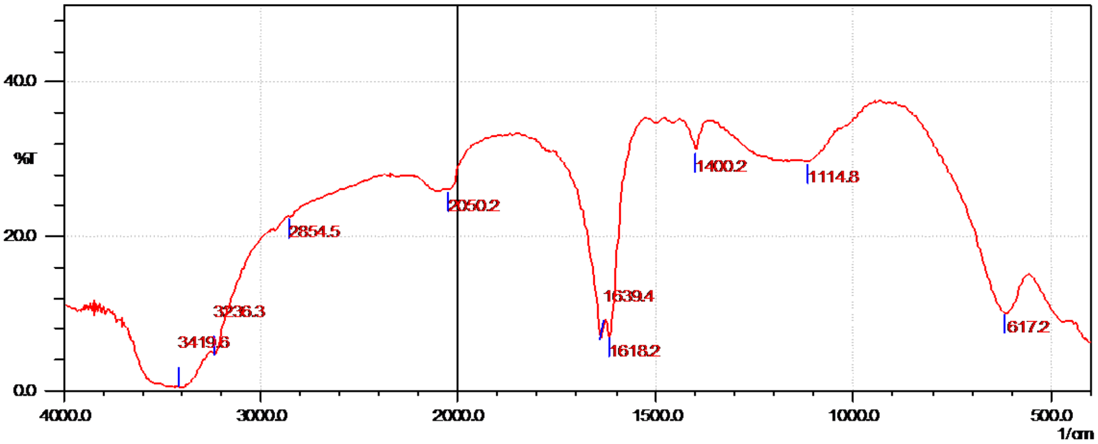

Fig. 4.5: FTIR spectrum of lignin.

Table 4.3: Shows the FTIR spectral data of α -cellulose.

Wave number (cm^{-1})	Interpretations
3419.6	OH stretching (Intermolecular hydrogen bonding)
3236.3	OH absorption gives a broad bond
2854.5	CH_2 symmetrical stretching.
1618.2	Hydroxy aldehydes and ketones in which hydrogen bonding is possible, C = O str.
1400.2	CH_2 bonding
1114.8	Antisym Zmetrical in phase ring stretching.
617.2	OH out of plane bending

4.1.2.5 FT-IR Spectrum of Alkali Treated Sawdust

Fig. 4.6 shows the FT-IR spectra of alkali treated sawdust. It is clear in the spectrum that untreated SD shows presence of absorption band near 1734 cm^{-1}, which is assigned to CO group of acyl ester of hemicellulose and aldehyde group in lignin [115]. Several additional absorption bands for the common functional group present in cellulose, hemicelluloses and lignin unit of saw dust were found in this analysis. These results suggest that chemical modification of SD has occurred upon treatment with alkali.

Table 4.4: FT-IR spectral data of alkali treated Sawdust.

Peak	Intensity	Position/cm^{-1}	Assignment
985.64	86.893	~ 985	ρ(-CH-)
1049.29	86.457	~ 1050	ν(C-OH) 2º alcohol
1115.84	86.496	~1260-1000	OH, -O-, COOR, COOH
1164.06	86.661	~ 1155	ν(C-C) ring breathing, asymmetric
1328.98	87.02	~ 1315	δ(C-H)
1374.3	86.889	~ 1365	δ(C-H)
1426.38	86.333	~ 1419.5	δ(C-H)
1467.85	85.77	~ 1455	δ(C-H); δ(C-OH), 1° & 2° alcohol
1587.44	84.846	~1650-1580	N-H
1639.52	85.083	~ 1700-1600	>CO
2333.91	86.151	~ 2360-2100	Si-H silane
2850.84	80.779	~ 2960-2850	C-H
2919.31	79.215	~ 3000-2900	ν(C-H) in aromatic ring and alkanes
3445.89	71.355	~ 3600-3200	ν(OH) broad, strong band from the cellulose, hemicellulose and lignin of rice husk

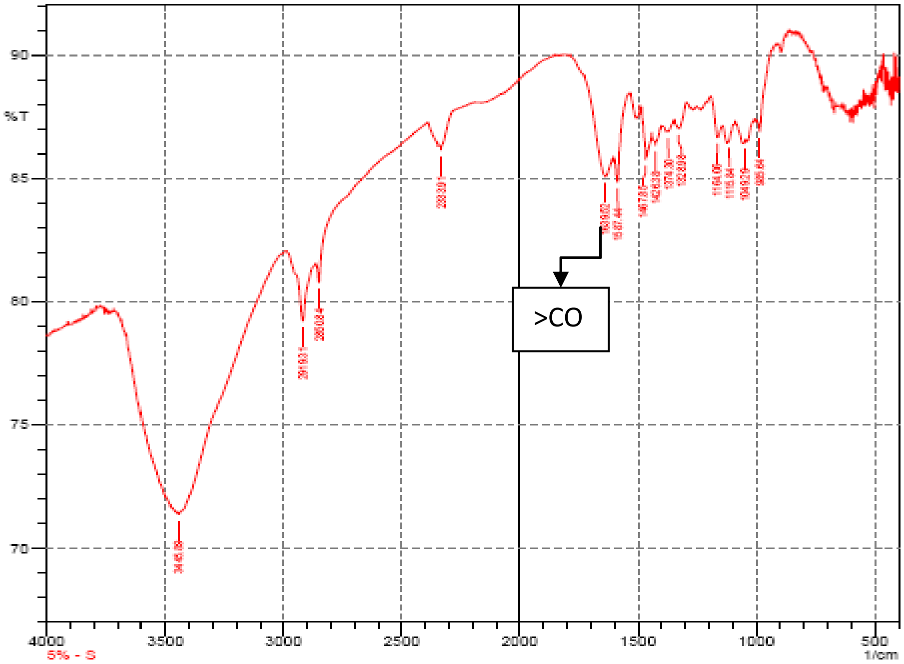

Figure 4.6: FT-IR spectrum of alkali treated Sawdust.

4.1.2.6 FT-IR Spectrum of Alkali and Benzoyl Chloride Treated SD

Scheme-II shows the chemical changes of the cellulose in SD upon a two-step pretreatment with sodium hydroxide and benzoyl chloride. Upon treatment with alkali, the hydroxyl groups at C_2 and C_6 are transformed into -ONa, which further undergoes coupling reaction with benzoyl chloride. The corresponding FT-IR spectra of alkali and benzoyl chloride treated SD are shown in Figure 4.7. The FT-IR spectrum of raw SD shows a band in the region near 1646 cm^{-1}, which is probably due to the CO group of acylester in hemecellulose or of aldehyde group in lignin [115]. The IR spectrum of NaOH treated SD shows a band near 1617 cm^{-1}, which is maybe due to the carbonyl groups produced from the oxidation of the hydroxyl groups of cellulose. On the other hand, Benzoyl chloride treated SD shows a clear band in the region near 1374.3 cm^{-1} and 896.91 which is maybe due to the stretching frequency of nitro group present in the aromatic ring of Benzoyl chloride. There is a another absorption band 896.91 cm^{-1} was found which proved the presence the -O- group of chemical modification. Several additional absorption band were also obtained for C-H, -OH, CH_2 and $-CH_3$ functional radical for most probably in cellulose, hemicellulose and lignin unit of SD. These results suggest that chemical modification of the cellulose has occurred upon treatment with NaOH and Benzoyl chloride.

Table 4.5: FT-IR spectral data of alkali and Benzoyl Chloride Treated SD

Peak	Intensity	Position/cm^{-1}	Assignment
675.1	81.669	~ 675-870	C-H (Aromatic ring)
896.91	86.158	~ 895	ν(C-O-C) in plane, symmetric; -Cl
1044.47	81.132	~ 1050	ν(C-OH) 2º alcohol
1114.87	82.011	~1000-1260	OH, -O-, COOR, COOH
1162.13	82.803	~1000-1260	OH, -O-, COOR, COOH
1432.17	84.689	~1350-1470	C-H (Alkanes)
1467.85	84.756	~1350-1470	C-H (Alkanes)
1588.41	84.674	~1580-1650	N-H (Amines)
1617.00	86.324	~1580-1650	>CO
2850.84	88.931	~2850-2960	C-H (Alkanes)
2918.35	87.671	~2850-2960	C-H (Alkanes)
3446.85	81.205	~3400-3500	N-H(1˚Amines)
3746.79	91.75	~na	na

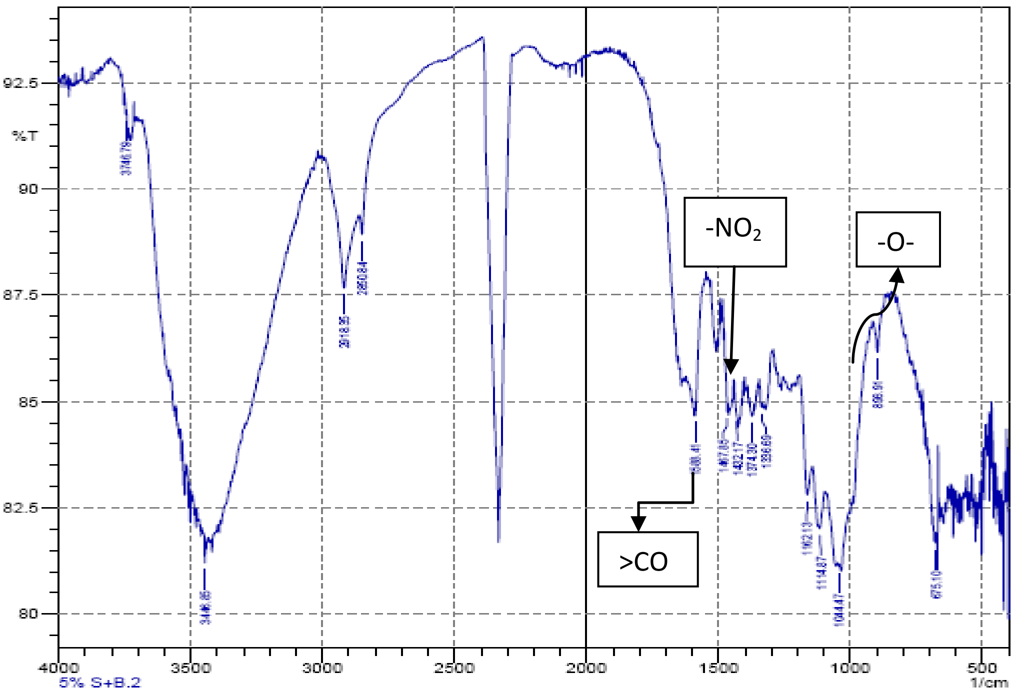

Figure 4.7: FT-IR spectrum of alkali and benzoyl chloride treated SD

4.1.2.7 FT-IR Spectrum of VPE and RPE

Polyethylene is a semicrystalline polymer. The crystallinity of a semicrystalline polymer depends on the content of the ordered phase, which is defined as the molar fraction of chain atoms which possess a specified steric configuration related to their immediate neighbors along the chain. To investigate the structure of VPE, an IR spectrum was taken which has been presented in Figure 4.8.

FT-IR spectroscopic observation was used to identify the crystalline and amorphous domains in the PE structure. Absorptions near about 1167.1, 997.3, 898.9, 842 and 808.3 cm^{-1} are due to the crystalline phase of PE and absorption at 974.2 cm^{-1} is due to the amorphous or irregular phase of PE. The peak assignments of the absorption bands of VPE are summarized in Table 4.6 which is quite similar to the literature value [146-149]. The main peaks, their associated vibrational modes, associated microstructures, and dipole moment orientation angles with respect to the main chain are listed below.

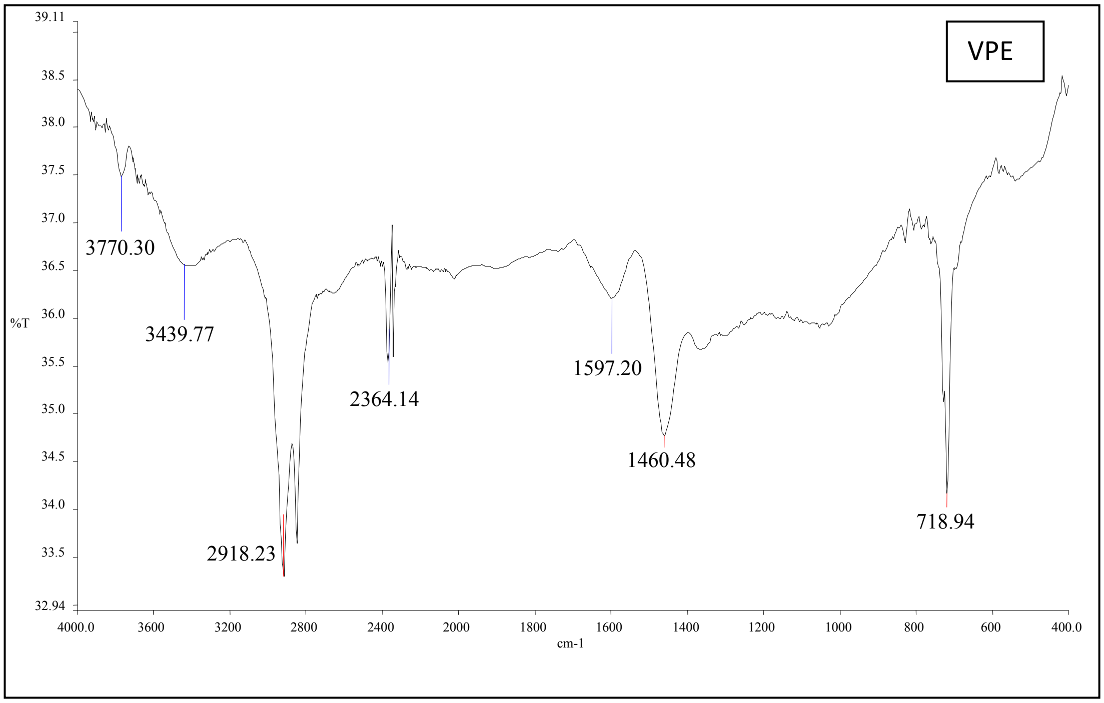

Figure 4.8: FT-IR spectrum of virgin PE

Table 4.6: FT-IR spectral data of virgin PE

Wave Number (cm^{-1})	Possible Assignment
~ 3770.30	O-H of alcohol
~ 3439.77	O-H vibration hydroxyl group
~ 2918.23	C-H stretching
~ 2364.14	C=C stretching vibration
~ 1460.48	In plane OH bending, C-O stretching of dimers
~ 718.94	C-H out of plane bending

The FT-IR spectroscopic data analysis results of RPE were given in the table 6.7 which is very similar to VPE. A little bit variation of this result were also followed in this experiment, this is mainly due to the presence of impurities present in RPE sample. FT-IR spectrum of RPE was given in the figure 4.9.

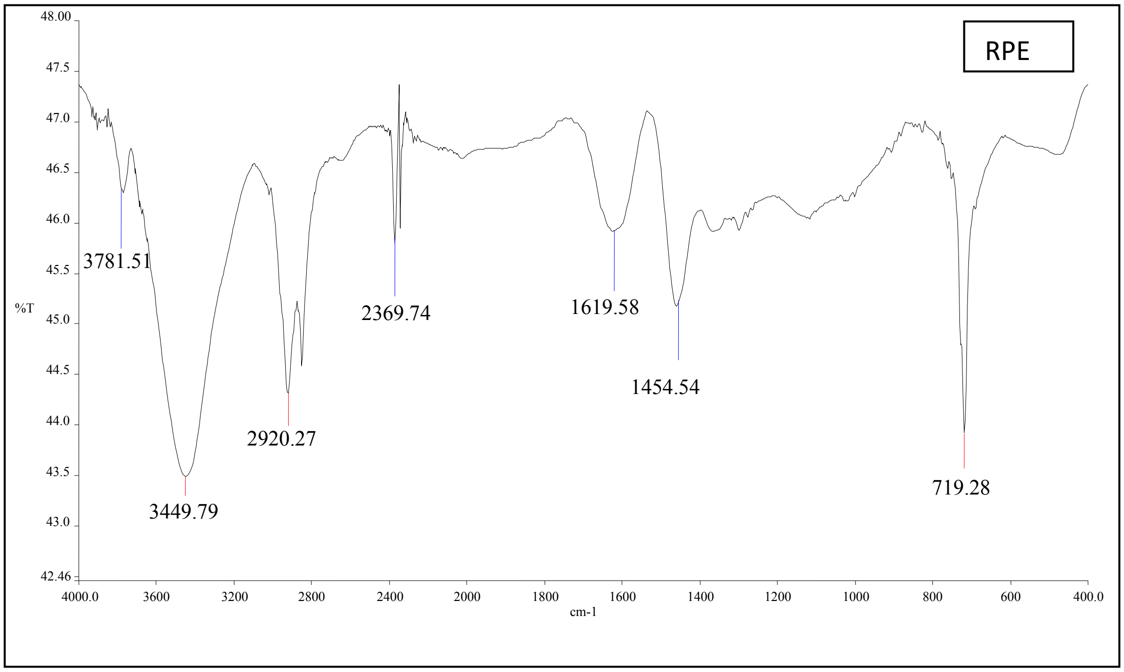

Figure 4.9: FT-IR spectrum of RPE

Table 4.7: FT-IR spectral data of recycled PE

Wave Number (cm^{-1})	Possible Assignment
~ 3781.51	O-H of alcohol
~ 3449.79	O-H vibration hydroxyl group
~ 2920.27	C-H stretching
~ 2369.74	C=C stretching vibration
~ 1619.58	C=O stretching
~ 1454.54	In plane OH bending, C-O stretching of dimers
~ 719.28	C-H out of plane bending

4.1.3 Physical Properties of Fabricated Composites

The water absorption and thickness swelling behavior of fabricated composites are briefly explaining according to the standard ASTM methods in the following representation.

4.1.3.1 Water Absorption Test

Water absorption test were conducted for WPC in both cool and hot water. Basically this test gives us the preconception about the stability and engineering properties of any composites. High water absorption means higher swelling, low stability and poor engineering properties. By considering all sides water absorption test was conducted in hot and cool water. In both cases water absorption of untreated sample is greater than chemically treated sample. On the other hand water absorption of all WPC in hot water is greater than cool water. This absorption is also increased with time but decreased with surface modification of SD. These results are consistent with previous studies with chemically modified filler reinforced composites which showed higher water absorption resistance with lower porosity and thus had better interfacial strength as compared to the composites without chemical modification [150-154].

4.1.3.1.1 Cool water absorption test

Cool water absorption tests are classified into two types i.e. **short term** cool water absorption for 24hr (figure 4.10) and **long term** cool water absorption for 72hr (figure 4.11). Water absorption for three categories of composites were illustrated in this section these are untreated (UT), alkali treated (AT), benzoyl chloride treated (BT). Each composite are also designed with specific sample code which as follows. Among these designated composites RPEUTSD35 showed greater water absorption than others composites but RPEBTSD20 showed lower absorption. The RPEUTSD35 composites are fabricated by untreated SD so it contains more OH groups. For this reason it has higher water absorption. Benzoyl chloride (BT) treated composites specimen are RPEBTSD20, RPESTSD20, RPEBTSD20 and RPEBTSD20 these are having better water resistance properties than untreated (UT), alkali treated (AT). Alkali treated samples (RPEATSD20, RPEATSD25, RPEATSD30, RPEATSD35) and Benzoyl chloride treated samples (RPEBTSD20, RPESTSD20, RPEBTSD20, RPEBTSD20) are better than untreated samples but bezoyl chloride samples are better than alkali treated and untreated by considering this test analysis.

From the graph it is clear that water absorption depends on the filler contents, resign contents and chemical modification of SD. We have already explained the effect of filler contents and resign contents. Chemical modification of SD dramatically reduced the water absorption properties but not inhibited 100%. In the case of all treated sample water absorption reduced comparatively with raw filler but increased with wood filler contents. This experiment has proved that chemical modification of SD by alkali and benzoyl chloride has significantly reduced the hydrophilic nature of sawdust. Now it is necessary to know among the three chemical modifications of SD filler which one is the best and why. The cool water absorption behaviors of composites were shown in the figures 4.10 and 4.11 for 24h and 72h respectively.

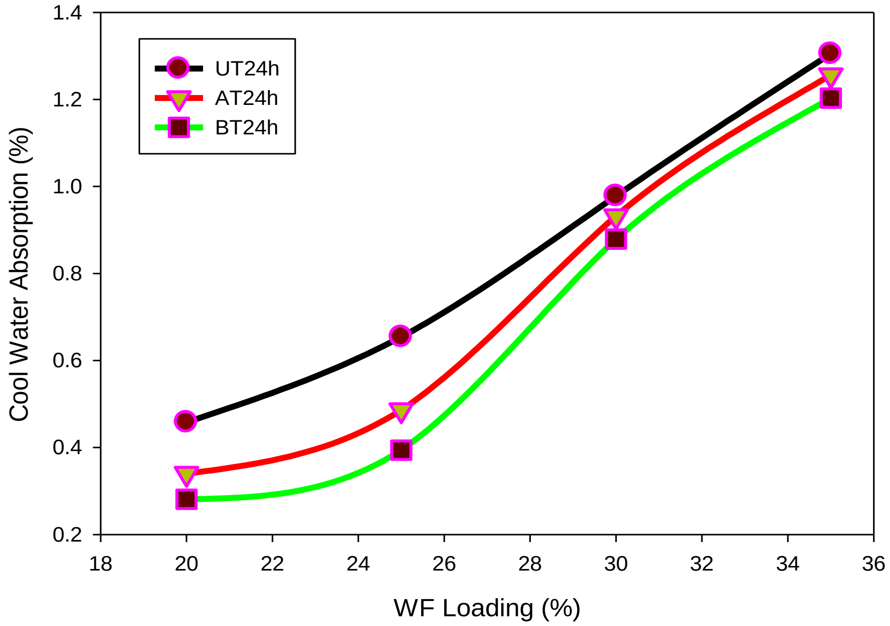

Fig. 4.10: Variation of short term cool water absorption behavior of RPE composites with untreated (UT), alkali treated (AT) and benzoyl chloride treated (BT) for 24h.

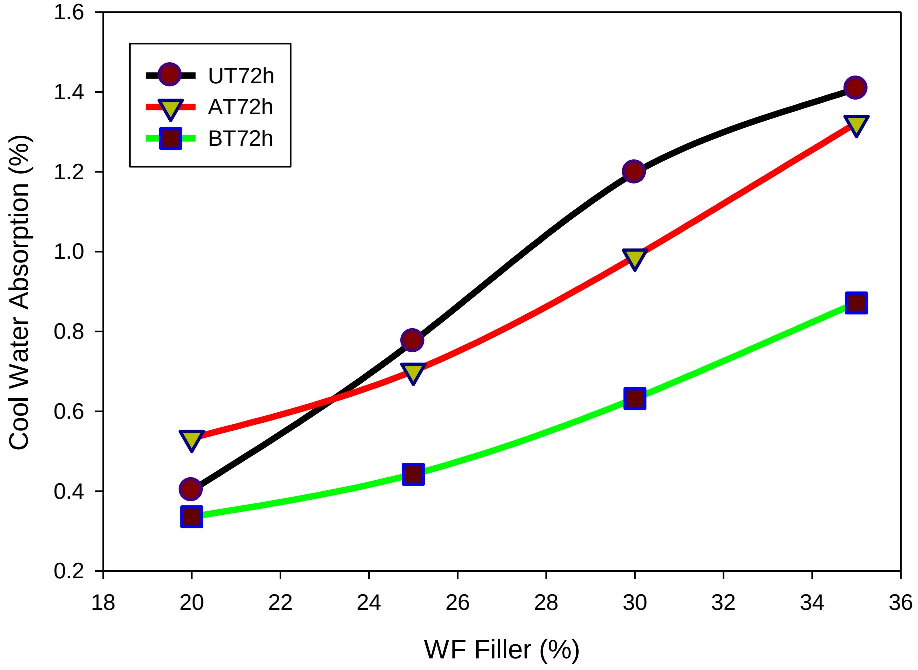

Fig. 4.11: Variation of long term cool water absorption behavior of RPE composites with untreated (UT), alkali treated (AT) and benzoyl chloride treated (BT) for 72 h.

The water absorption of the entirely VPE samples was only 0.06 to 0.09% after 24 h and 72 h respectively. For the 100 % RPE samples are about same with VPE i.e. 0.07 to 0.13% at the same immersion condition. RPE is little bit high absorption because its consistency is not pure, some dust or foreign elements added during recycling. This is the reason for discriminating of water absorption of RPE and VPE.

Now the possible reason for the variation of water absorption is explained below. Water absorption increased with the increasing of wood content in the composites a trend that is true for both the 24 h and 72 h water immersion tests. However, after 72 h water immersion, the water absorption by the composites was almost doubled. With the increase in wood content, there are more water-residence sites thus more water was absorbed. On the other hand, the composites made with higher plastic content had less water-residence sites and thus lower water absorption.

On the other hand, NaOH treated sawdust reinforced RPE composites are found to exibit lower degree of water absorption compared to those prepared from untreated sawdust. This is due to the replacement H^+ ion by the Na^+ ion. On the other hand, benzoyl chloride treated sawdust reinforced RPE composites showed lower amount of water compared to those prepared from NaOH treated sawdust which is due to the coupling reaction of cellulose is sawdust with benzoyl chloride.

4.1.3.1.2 Hot Water Absorption Test

Hot water absorption test are also conducted for short term duration and long term duration in case of fabricated composites and resin. For RPE based untreated or raw composites, the hot water absorption with 20 wt. % saw-dust content was found lower than 35 wt. % of SD content after 24h-72h immersion same as cool water absorption behavior. Hot water absorption is greater than cool water absorption it follows the same trends like cool water.

In the figure 4.12 the composites RPEUTSD35 and RPEUTSD30 showed greater absorption than other composites like AT (RPEATSD225, RPEATSD30, RPEATSD35) and BT (RPEBTSD25, RPEBTSD30, RPEBTSD35) types composites. In these three composites at 25 % wood content absorption is not clearly understand so in this case the experiment to be conducted for 72h to avoid this problem. It was assumed that BT composites lower absorption than UT and AT because when the wood contents are 30 % to 35 % then it showed better properties. In hot water all chemical is not same in behavior that’s why affected by experimental condition. During the water absorption test the different experimental condition should be emphasized to get better composites properties.

Hot water absorption test were conducted for 72h, the result of this test was given in the figure 4.13. From this figure it is clearly understand the absorption between AT and BT types of composites. Three composites RPEUTSD30, RPEATSD30 and RPEBTSD30 are showed very close absorption but distinguishable between each other. In these three composites at 20% wood content shows disproportionate but considering all sides it is concluded that BT type of composite had better resistance to water than UT and AT types of composites.

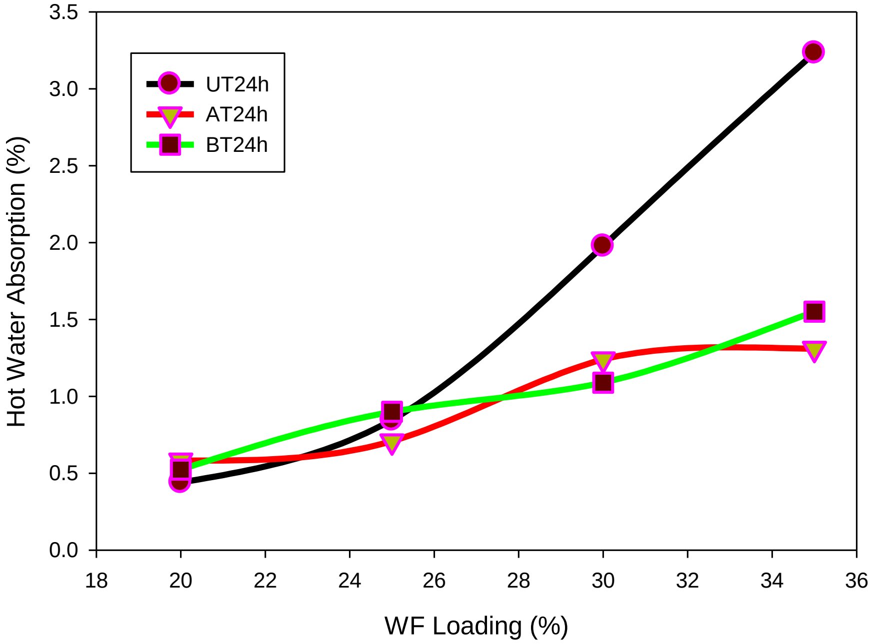

Fig. 4.12: Variation of hot water absorption of RPE composites reinforced with untreated (UT), alkali treated (AT) and benzoyl chloride treated (BT) SD for 24h.

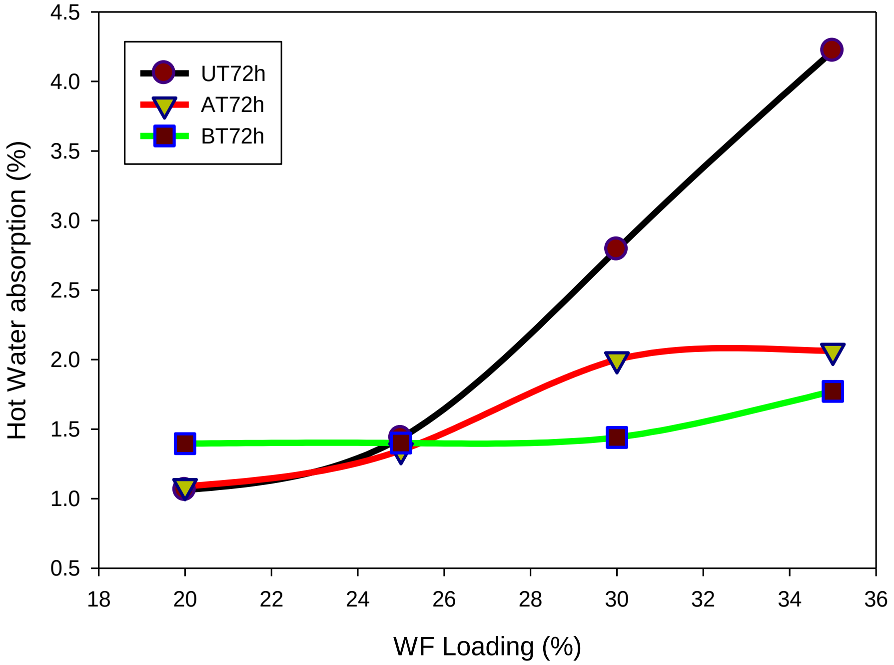

Fig. 4.13: Variation of hot water absorption behavior of RPE composites reinforced with untreated (UT), alkali treated (AT) and benzoyl chloride treated (BT) SD for 72 h.

Hot water absorption test given one additional information i.e. the stability of chemical treatment. Among the three treatments which one is high temperature resistant or stable? Benzoyl chloride treated SD is very stable in both duration. Alkali treated and benzoyl chloride treated SD reinforced composites at hot water shown divergent result (Fig. 4.12) but in the case of long immersion time (figure 4.13) it was found that benzoyl chloride treated composites are better water resistant than alkali treated and untreated sample. Finally the absorption resistance was found to follow this order BT>AT>UT.

Here some possible reasons for variation of water absorption are explained below. Water absorption of composites is mainly due to the presence of lumens, fine pores and hydrogen bonding sites in the saw-dust, the gaps and flaws at the interfaces, and the micro-cracks in the matrix formed during the compounding process [63]. The presence of hydroxyl and other polar groups in various constituents of the saw-dust resulted in poor compatibility between the hydrophilic saw-dust and the hydrophobic plastic, and thus weakened the interfacial bonding. Therefore, the water absorption increases with increasing the sawdust content in the composites. Water absorption by cellulose and hemicelluloses depends on the number of free hydroxyl groups thus the amorphous regions are accessible by water. On the other hand, plastic is water repellent and had much lower water sorption capability than the fiber.

The recycled PE and treated sawdust based composites absorbed less water compared with RPE and untreated SD based composites for the same wood plastic content. The possible reason could be the enhanced interfacial bonding due to the chemical treatment and different molecular differences between SD and recycled plastics. The interfacial bonding of benzoyl chloride treated SD reinforced composites was found stronger than another. The sequence of interfacial bonding of WPCs followed the trends BT>AT>UT.

4.1.3.2 Thickness Swelling Test (TST)

Thickness swelling of the SD-RPE composites increased with the water absorption and thus had similar trend to the water absorption regarding the impacts of wood to plastics ratio and chemical modification. Samples made with lower content of saw-dust had lower thickness swelling and this is true both for the composites made from untreated and treated SD reinforced RPE composites. In general, the composite made of virgin and recycled plastics had similar dimensional stability properties without adding the coupling agent which is consistent with previous findings by Chen et al. [140].

The impact of wood to plastic ratio on the water absorption and thickness swelling can be explained by the differences in water absorption between wood and plastic. Water absorption in composites is mainly due to the presence of lumens, fine pores and hydrogen bonding sites in the saw-dust, the gaps and flaws at the interfaces, and the micro-cracks in the matrix formed during the compounding process [63]. The presence of hydroxyl and other polar groups in various constituents of the saw-dust resulted in poor compatibility between the hydrophilic saw-dust and the hydrophobic plastic, and thus weakened the interfacial bonding. Therefore, the water absorption increases with increasing the wood content in the composites. Water absorption by cellulose and hemicelluloses depends on the number of free hydroxyl groups thus the amorphous regions are accessible by water. On the other hand, plastic is water repellent and had much lower water sorption capability than wood. With the addition of chemically modified filler the interface bonding between sawdust and RPE was improved because of replacement of –H of the cellulose by the benzoyl mainly [115]. This lowered the water absorption sites and reduced the water absorption by chemically modified composites.

The graphical representation of thickness swelling was presented in the figure 4.14 where the order of thickness swelling is UT>AT>BT. The untreated composites RPEUTSD35 showed higher thickness swelling which is 3.95348 % but the same sawdust content alkali treated and benzoyl chloride composites showed 3.25 % and 2.22% respectively. From this thickness swelling behavior it can be concluded that the dimensional stability of the benzoyl chloride treated SD reinforced composites is better than sawdust RPE-composites. Actually the dimensional stability of these three composites is the opposite order of thickness swelling i.e. BT>AT>UT.

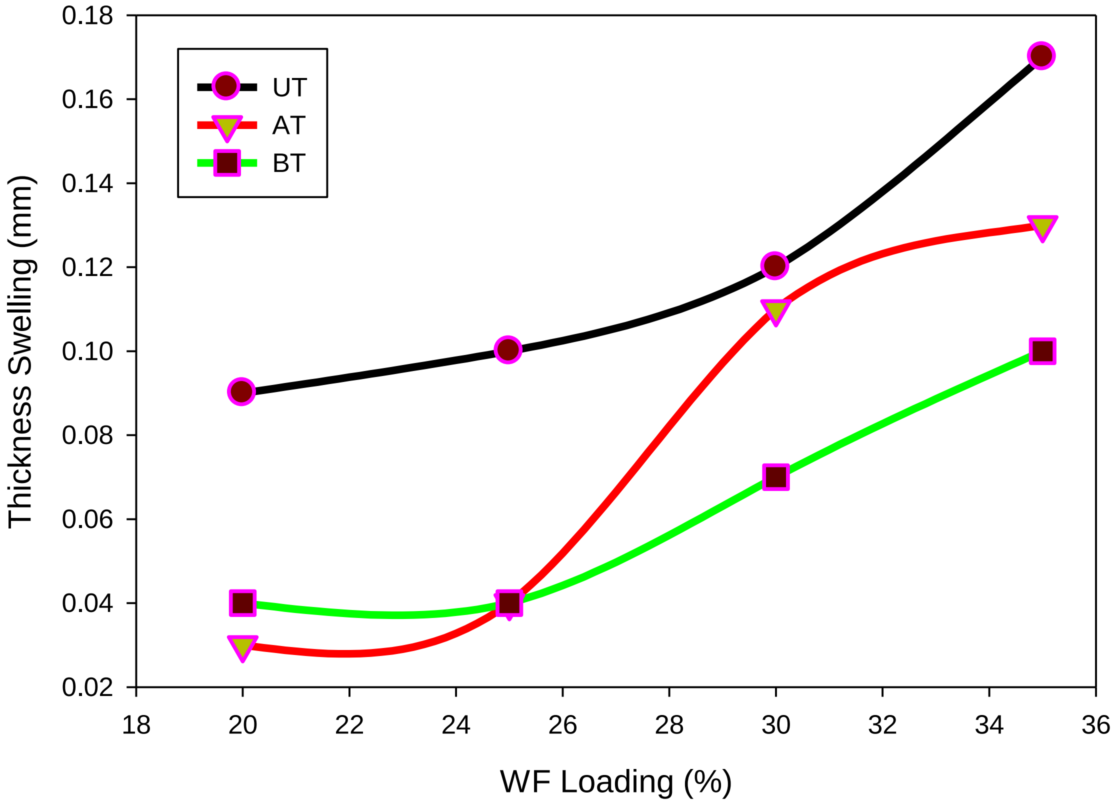

Fig. 4.14: Variation of thickness swelling of RPE composites reinforced with untreated (UT), alkali treated (AT) and benzoyl chloride treated (BT) SD filler.

Now the possible reasons of lowering and increasing the thickness swelling behavior of composites can be said that the surface modification of filler by chemical reagent significantly decreased up to 8O%. The molecular weight of resin, degree of crystalinity of resin, MFI and interfacial bonding between filler and matrix also related with this result. Fiber dispersion into the matrix is another reason of composites dimensional stability. The other possible reason for less water absorption by the treated filler reinforced composites could be the change in crystallinity (Xc) of WPCs upon treatment .

4.1.4 Mechanical Properties

The standard ASTM methods were followed to test specimens. The result and discussion of mechanical properties are briefly explained below.

4.1.4.1 Tensile Properties

Tensile strength values of both untreated, alkali treated and benzoylchloride treated SD reinforced RPE composites at different filler loading (20%-35%) are shown in Figure 4.15. For raw and treated filler reinforced composites, the tensile strength decreased with an increase in fiber loading [151-153, 155]. As the filler load increased, the weak interfacial area between the filler and the matrix increased, which in turn decreased the tensile strength.

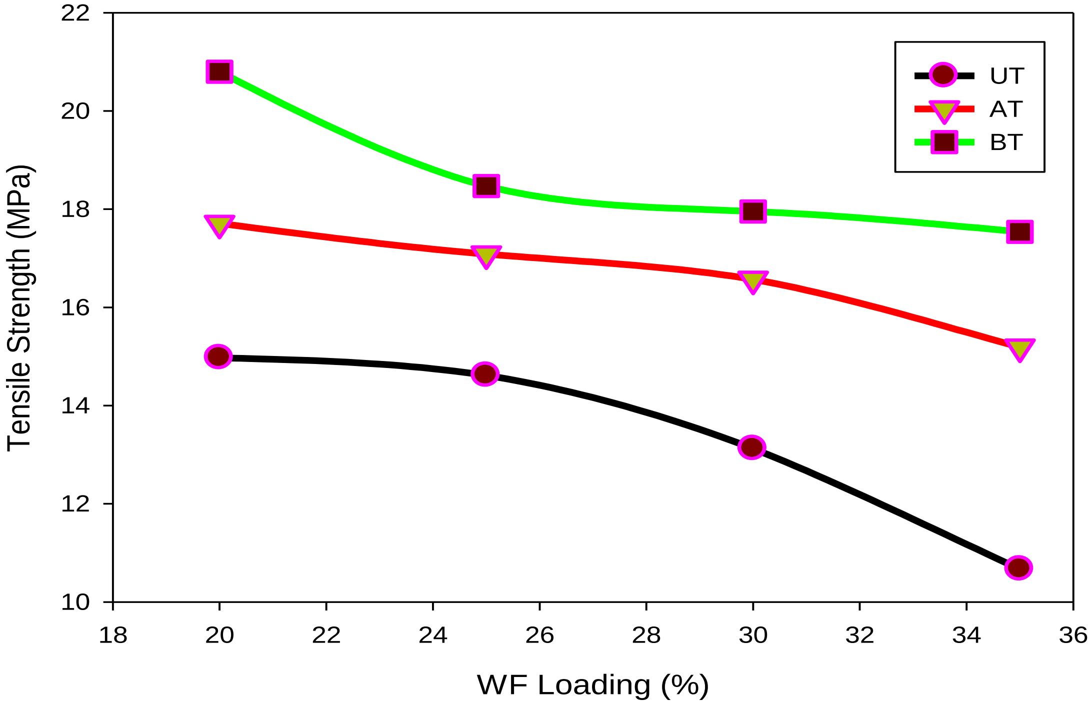

Fig. 4.15: Variation of tensile strength of RPE composites reinforced with untreated (UT), alkali treated (AT) and benzoyl chloride treated (BT) SD filler.

Untreated composites RPEUTSD20, RPEUTSD25, RPEUTSD30 and RPEUTSD35 in the fig 4.15 showed lower tensile strength than alkali and benzoyl chloride treated sample. The tensile strength values of the composites followed the order BT>AT>UT. All composites showed a sequence in fig 4.15 i.e. with an increase in SD loading the tensile strength is decreased. At the filler content 20% it showed higher tensile strength. From figure 6.16 it can be concluded that tensile strength increased significantly by the chemical modification and benzoylchloride treated SD reinforced composites is the highest in properties. The improved tensile strength of the treated SD reinforced RPE composite may be attributed to the interfacial bonding between the fiber and the matrix.

The following figure 4.16 is focused the variation of MOE between raw and chemically modified SD reinforced composites.

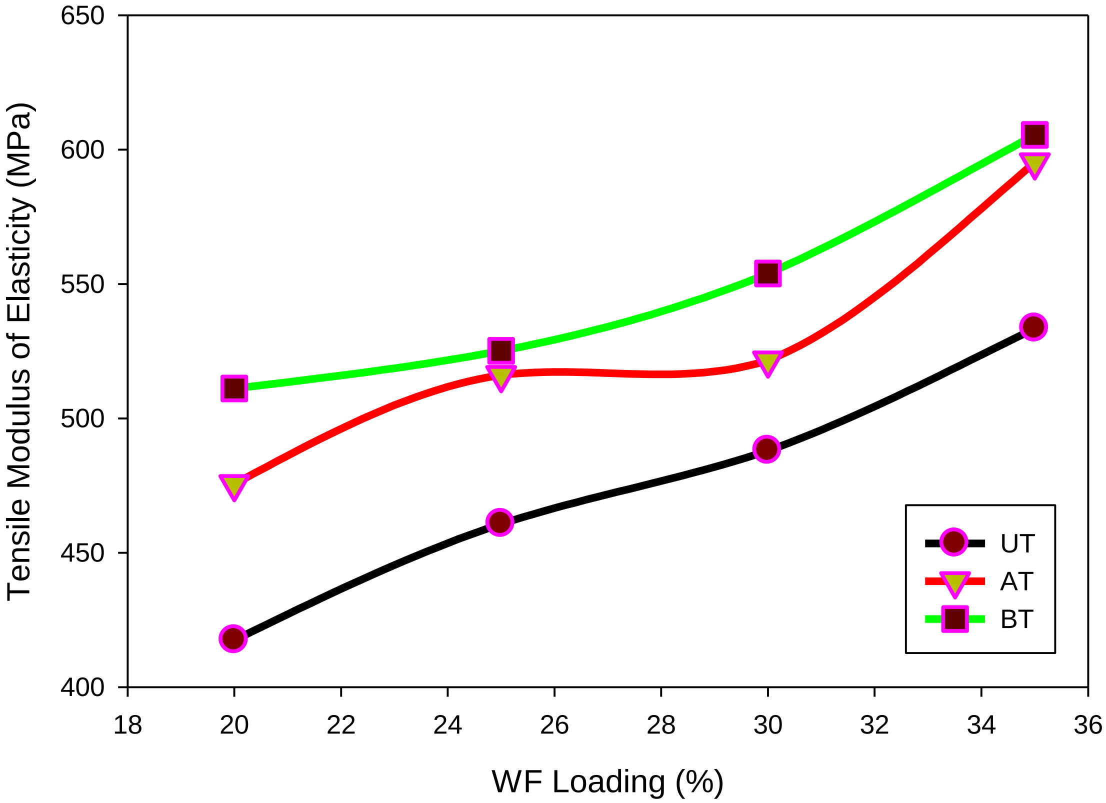

Fig. 4.16: Variation of MOE of RPE composites reinforced with untreated (UT), alkali treated (AT) and benzoyl chloride treated (BT) SD filler.

Figure 4.16 shows the variation of the Young's modulus at different filler loading. The Young's modulus increased with an increase in filler loading [151, 152, 156-160]. During tensile loading, partially separated micro-spaces are created, which obstructs stress propagation between the filler and the matrix [161]. As the fiber loading increases, the degree of obstruction increases, which in turns increases the stiffness. Again there is a slight increase in stiffness in treated SD reinforced composites compared to the untreated ones.

Variation of elongation at break with filler loading is shown in Figure 4.17. The elongation decreased with an increase in filler loading due to the increase in stiffness of the corresponding composites. Chemically treated SD reinforced composites are found to show greater elongation compared to the raw ones due to the same reason but here also due to the filler loading elongation properties decreases for increasing stiffness.

Figure 4.17 showed elongation properties of untreated (UT), alkali treated (AT) and benzoyl chloride treated (BT) composites where as the three composites are very close to each other. In this figure elongation properties of untreated composites RPEUTSD20, RPEUTSD25, RPEUTSD30 and RPEUTSD35 showed lower than other two composites i.e. alkali treated (AT) and benzoyl chloride (BT). Among the alkali treated and benzoyl chloride treated composites, benzoyl chloride showed slight greater elongation properties than alkali treated composites. The RPEUTSD30 and RPEATSD30 two composites showed much closed elongation properties on the other hand RPEATSD25 and RPEBTSD25 these two composites showed about same properties. Among these three composites the variation of elongation properties were found to follow this order BT>AT>UT.

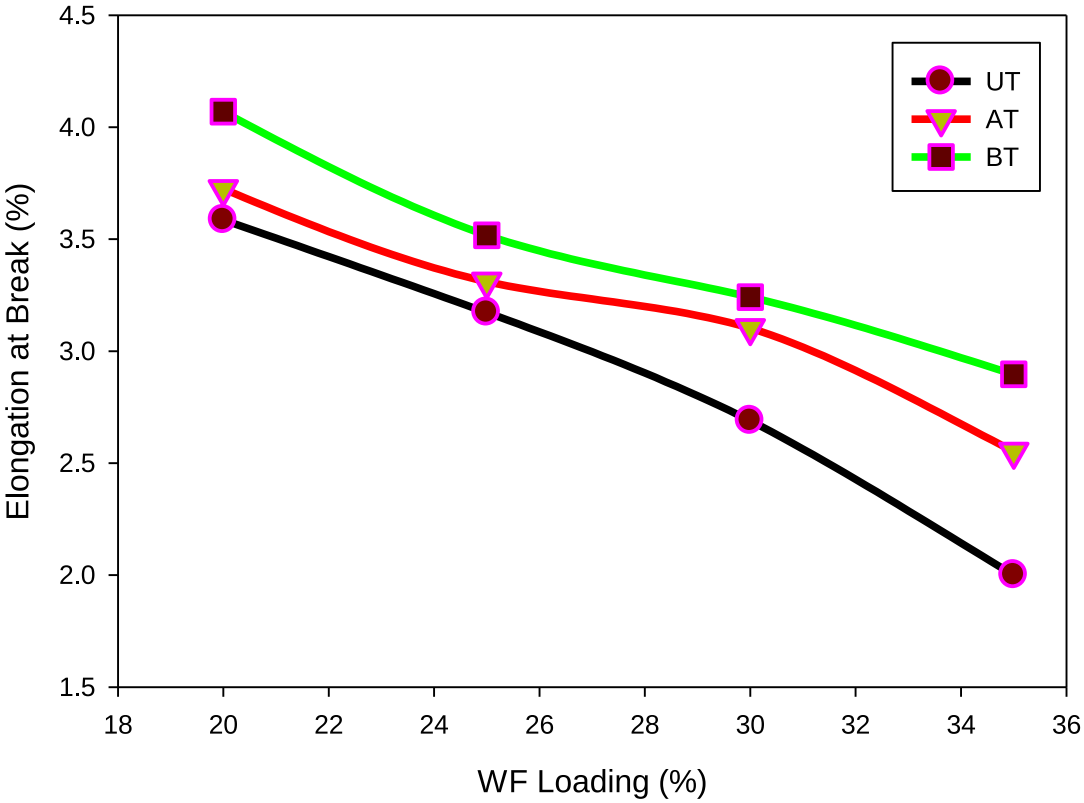

Fig. 4.17: Variation of EAB of RPE composites reinforced with untreated (UT), alkali treated (AT) and surfactant treated (BT) SD filler.

The elongation properties of composites can be explained in such a way that in the case of untreated composites the interfacial bonding between fiber and matrix is poor than the treated sample. Chemically treated SD reinforced composites showed relatively greater elongation properties due to improved interfacial bonding between filler and matrix. Chemically modified SD dispersed in to the matrix properly. As a result the ductility and stiffness are found to be better than untreated one. In the case of raw composites ductility decreased but stiffness is increased. On the other hand, for the treated one the ductility and stiffness is increased homogeneously for good interfacial bonding between fiber and matrix.

The tensile properties variation of composites based on recycled RPE can be explained differently. It was found that composites prepared from RPE and chemically modified SD exhibited higher tensile strength and modulus than those based on RPE and untreated SD for the same plastic to wood ratio. This is probably due to the better fiber dispersion within the recycled PE matrix by the increased wettability induced from the chemical modification. Although, recycled PE had lower MFI than that of virgin PE, the better wettability could be possible for RPE processing due to chemical impurities during processing.

The other possible reason could be the change in Xc of RPE matrix with the incorporation of saw-dust. It was found that with the addition of saw-dust in the RPE matrix, the Xc of the composites reduced for the resultant composites. The observed increase in the tensile strength and stiffness is attributed to the improved interfacial bonding between the saw-dust and the matrix as well as the modification of individual components [2, 138].

4.1.4.2 Flexural Properties

Results of flexural strength of both raw and treated SD reinforced RPE composites at different filler loading (20%-35%) are shown in Figure 4.18. This figure focused flexural strength of UT, AT and BT types of composites where the BT treated composites had higher values than two. The order of the flexural strength of these three types of composites is BT>AT>UT. In this figure three different composites had same ratio SD to RPE. The maximum flexural strength were found for 35 wet. % of SD reinforced composites and 20 wet. % SD loaded composites had lowest flexeral strength. Figure 4.18 gives clear concept about the variation of flexural strength with different filler loading i.e. 20 % to 35%.

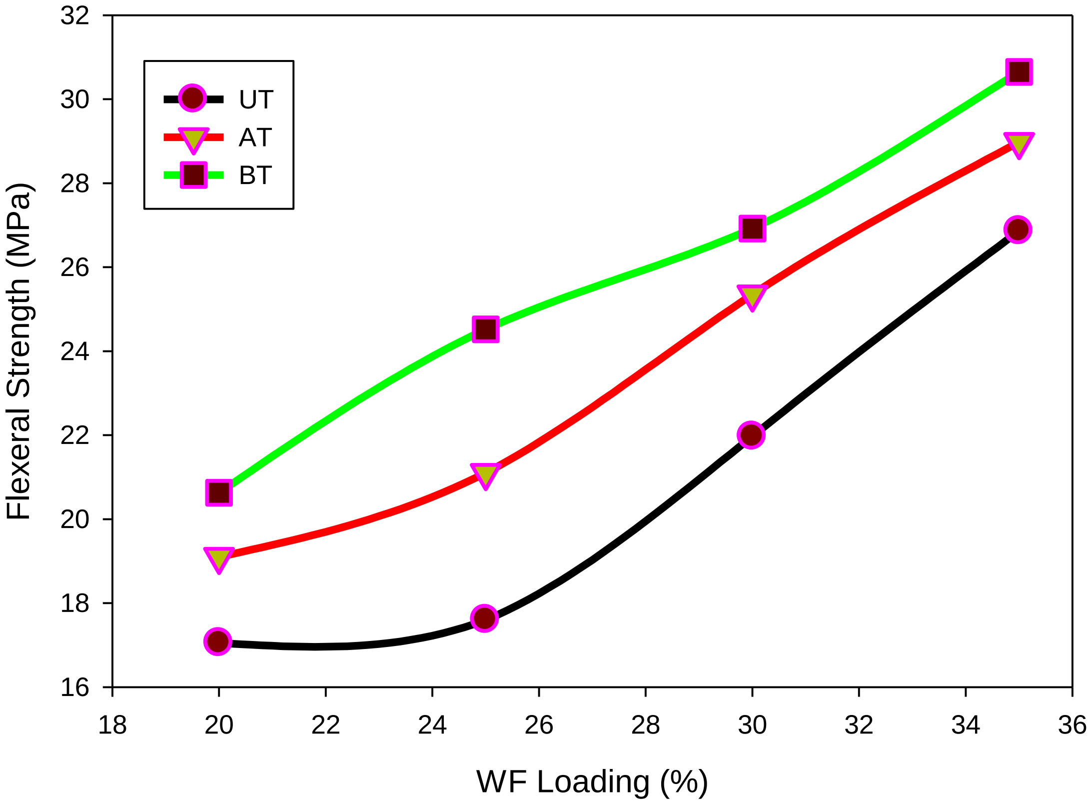

Fig. 4.18: Variation of flexural strength of RPE composites reinforced with untreated (UT), alkali treated (AT) and benzoyl chloride treated (BT) SD filler.

The flexural modulus of elasticity is given in the figure 4.19, as shown in the figure, the flexural modulus of SD-RPE composites increased with filler loading. In figure 4.19 flexural modulus of UT, AT and BT composites presented each of these had same trends and their found order is BT>AT>UT. Similar results were also reported in the literature by many researchers [151-153, 157-160].

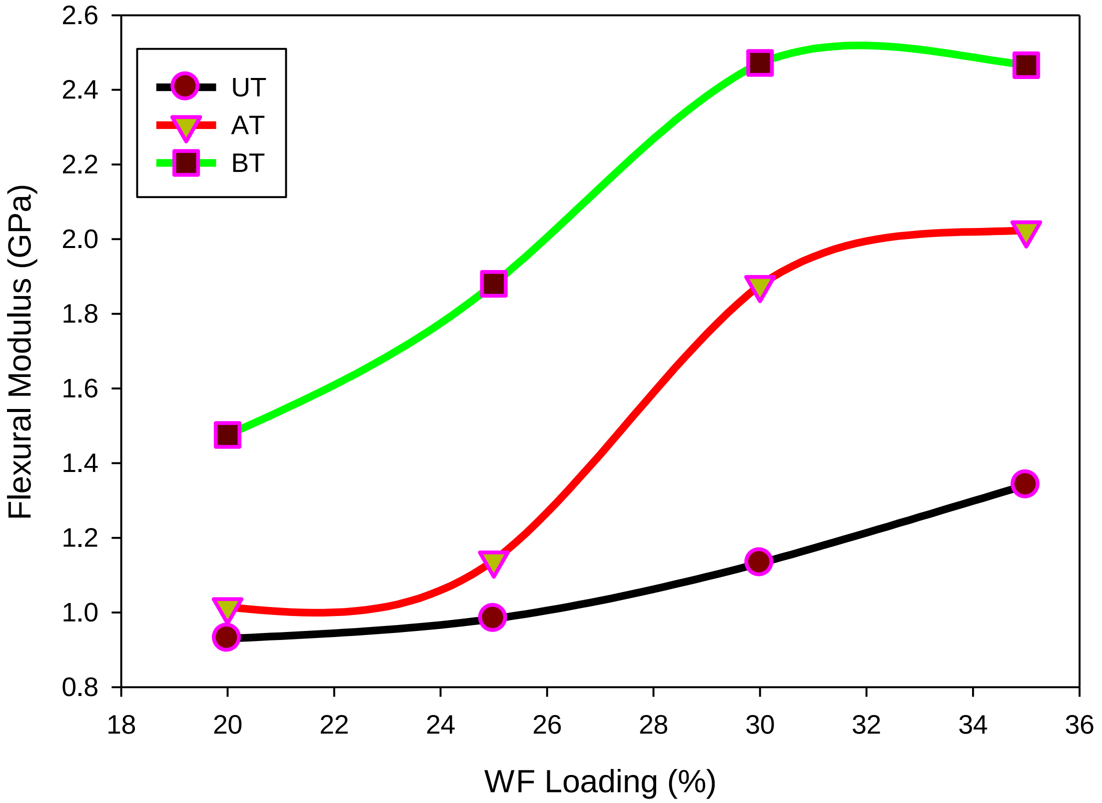

Fig. 4.19: Variation of flexural modulus of RPE composites reinforced with untreated (UT), alkali treated (AT) and benzoyl chloride treated (BT) SD filler.

From the experimental results presented here, it was found that effect of sawdust is notable in material properties of the composites. Wood is a lignocellulosic material made up of three major constituents (cellulose: 42-44%, hemicelluloses: 27-28%, and lignin: 24-28%) with some minor constituents (extractives: 3-4%) [62, 63]. The major portion of sawdust is crystalline cellulose. The aligned fibril structure of cellulose along with strong hydrogen bond has high stiffness thus addition of the saw-dust can increase the stiffness of the polymer based composites.

Lignin as an amorphous polymer does not greatly contribute to the mechanical properties of saw-dust but plays an important role in binding the cellulose fibrils that allows efficient stress transfer to the cellulose molecules. Hence, wood filler increased the stiffness of RPE without excessively increasing the density.

Furthermore, these composites have potential to take up water under humid conditions due to the presence of numerous hydroxyl groups available for interaction with water molecules via hydrogen bonding. The surface modification of sawdust improved the compatibility between the wood filler and RPE through esterification and thus reduced the water absorption and improved the stability and mechanical properties.

4.1.4.3 Izode Notched Impact Energy and Strength

Impact strength is a measure of the tolerability, when the composite is subjected to a sudden impact that results in crack propagation through the material. For fiber-reinforced polymeric composites, it depends on a number of factors, such as the nature of the fiber, polymer matrix, and the polymer-matrix interfacial bonding [162]. Sanadi et al. reported that high fiber content increases the possibility of fiber agglomeration, which results in regions of stress concentration that require less energy for crack propagation and that an increase in the resistance of crack propagation occurs if fiber bridges the crack in the composites [163].

As shown in Figure 4.20, impact strengths of both treated and untreated RPE-Sawdust composites show a slight increasing trend with an increase in the filler loading, indicating that the filler is capable of absorbing energy because of strong filler-matrix interfacial adhesion. It has been reported that improved interfacial bonding provides an effective resistance to crack propagation during impact tests [162, 164]. Thus, higher impact strengths of the treated SD-RPE composites suggest a better interfacial bonding compared to those of untreated ones. This could be due to better kneading of the matrix-filler system during the preparation of composites, their grinding and then specimen fabrication in the injection molding method. Slightly higher impact strength for AT and BT types of Sawdust-RPE composites is probably due to the favorable interaction between the treated coir and the hydrophobic RPE chain of the matrix. So-called fiber pullout and fiber agglomeration could be responsible for lower impact strengths of untreated sawdust reinforced RPE composites.

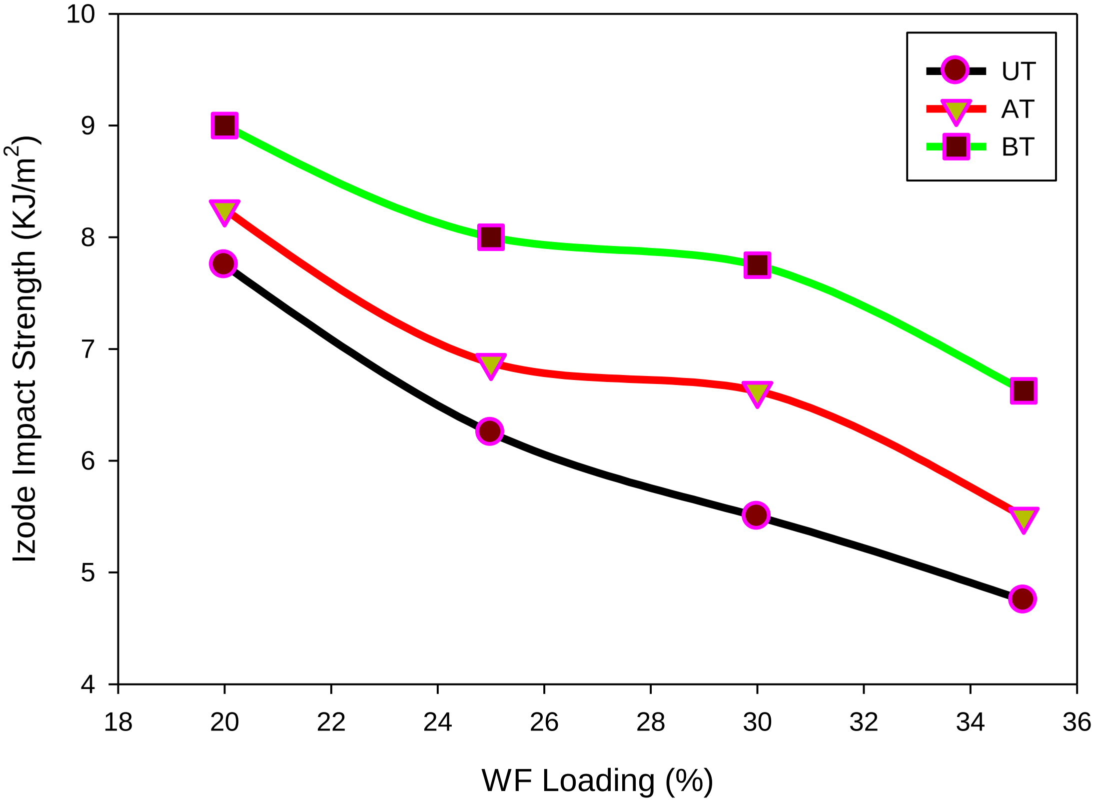

Fig. 4.20: Variation of izode notched impact strength of RPE composites reinforced with untreated (UT), alkali treated (AT) and benzoyl chloride treated (BT) SD filler.

Figure 4.21 shows the variation of impact energy of sawdust reinforced RPE composites at the same filler loading which also followed the same trends as impact strength. The possible reason for the variation of result is the filler-matrix ratio in fabricated composites, chemical treatment of filler, interfacial bonding between the filler and the matrix and filler dispersion into the matrix. Saw dust is notable fibril in nature that can be properly homogenate into the matrix than any other fiber. As a result fabricated composites showed greater hardness than RPE matrix. Raw and chemically treated filler reinforced composites in this hypothesis showed relatively lower impact energy than 100% RPE matrix and VPE but treated composites showed higher impact energy than untreated one. Finally order of impact energy were found BT>AT>UT which is mentioned in the figure 4.21 graphically.

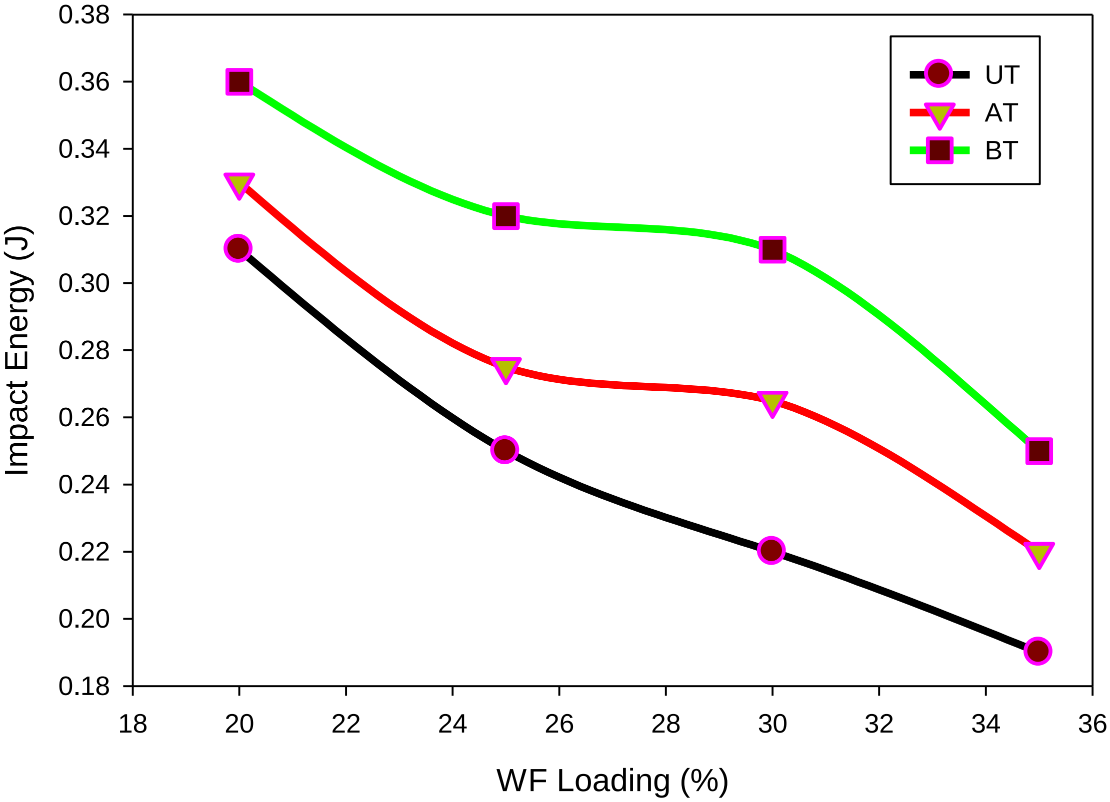

Fig. 4.21: Variation of izode notched impact energy of RPE composites reinforced with untreated (UT), alkali treated (AT) and benzoyl chloride treated (BT) SD filler.

4.1.4.4 Hardness

Hardness of a composite material refers to its resistance to shape changes when force is applied on it. For composites, it depends on the distribution of the filler into the matrix [162]. Usually the presence of a more flexible matrix causes the resultant composites to exhibit lower hardness [165]. As shown in Figure 4.22, incorporation of both treated and untreated SD into the RPE matrix has reduced the flexibility of the matrix, resulting in more rigid composites. The hardness of both treated and untreated composites is found to increase with an increase in the filler loading. The incorporation of filler particles into the RPE matrix has reduced the mobility of the polymer chain in the rigid composites. The treated saw-dust composites seem to have better hardness compared to untreated ones. This could be attributed to both better dispersion of the fiber into the matrix with minimization of internal voids and stronger interfacial adhesion between the matrix and the filler.

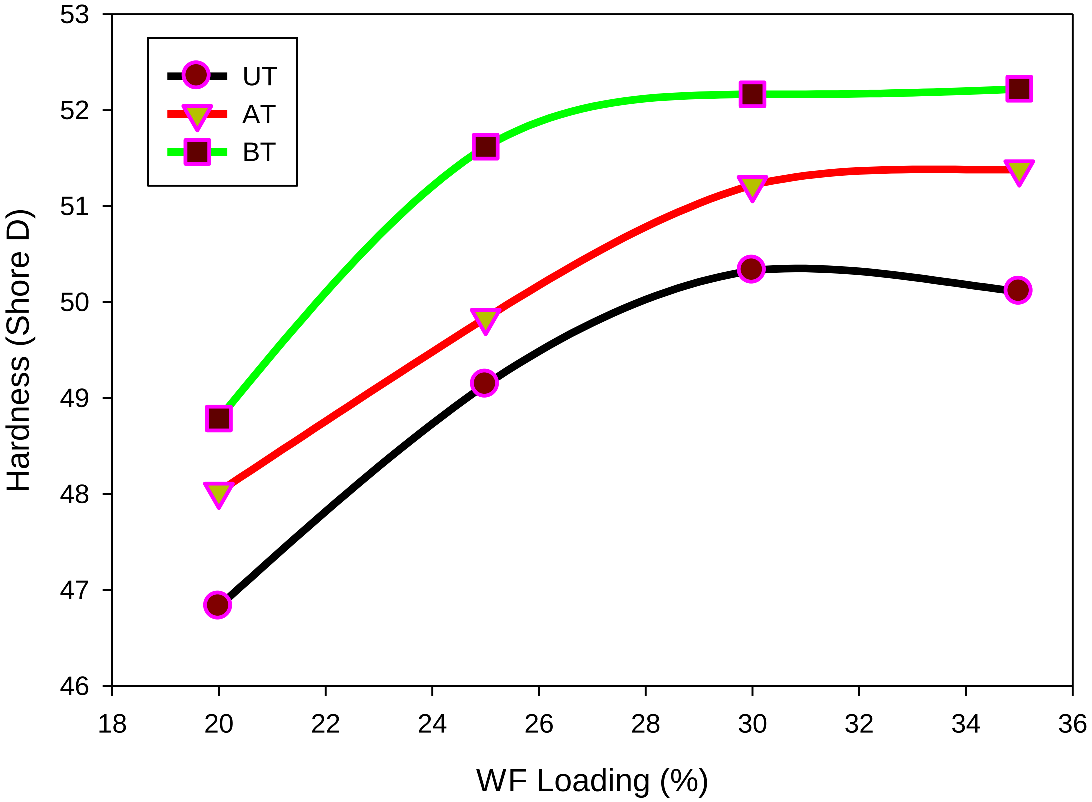

Fig. 4.22: Variation of hardness of RPE composites reinforced with untreated (UT), alkali treated (AT) and benzoyl chloride treated (BT) SD filler.

4.1.5 Characterization of Surface Morphology

The morphology of the tensile fractured surface gives information as to why mechanical properties of the composites prepared under different treatment conditions are different. The tensile fractured surface morphologies of untreated and treated SD-RPE composites prepared with 35 wt. % SD are shown in the following figures. The FESEM image of the untreated SD reinforced RPE composite (figure 4.23) shows a number of fiber agglomerations and fiber pullout traces in the composites (image A).

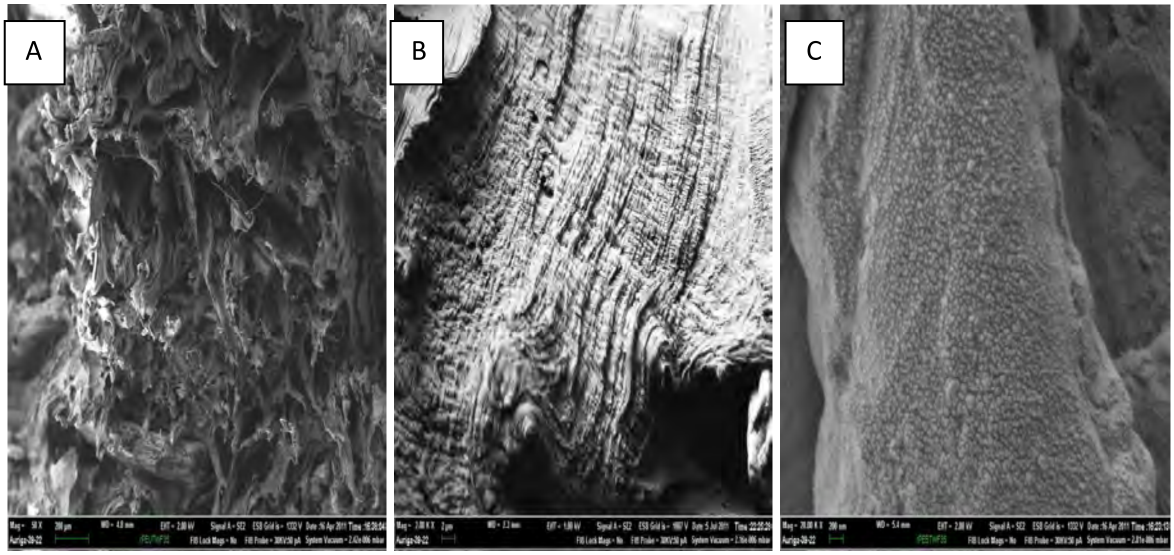

Figure 4.23: FESEM images of RPE composites reinforced with 35% untreated, alkali treated and benzoyl chloride treated saw-dust.

Alkali treated composites shows relatively lower fiber agglomeration and fiber pullout traces than untreated (image B). In figure 4.23 numerous cavities and pulled-out traces and fiber can be seen. The presence of these cavities and pulled-out fibers confirms that the interfacial bonding between the filler and the matrix polymer was poor and weak. In addition, localised bunch of fibers and patches of HDPE matrix are seen, which indicates the poor dispersion of fillers within the RPE matrix.

On the other hand, chemically treated SD-RPE composites show almost uniform dispersion of the filler into the matrix, which results in better interfacial adhesion between the filler and the matrix with improved mechanical properties (image C). This is also implies that hydroxyl groups are being reduced by NaOH and converted into –ONa, which upon coupled with benzoyl chloride has reduced the hydrophilic nature of sawdust, providing favorable interaction with the RPE straight chain with improved mechanical properties (images C). It is evident from image C that fiber pullout traces and fiber agglomeration as well as the micro-voids in the composites have significantly reduced in the composite upon treatment of sawdust with benzoyl chloride and surfactant. This result suggests that interfacial bonding between the filler and the matrix has become much more favorable for treated SD and the matrix compared to that of the untreated one.

In the image C, no clear gaps can be seen between the wood fibers and the RPE matrix, indicating good interface bonding. However, a crack is seen running through the wood fiber, and this could be an indication of stress-transfer from the weaker matrix to the stronger sawdust fiber. In this case, the fracture occurred at the filler itself. This means that the stress was well propagated between the filler and the matrix polymer, resulting in enhanced flexural strength and modulus in response to stress. In addition, the fracture surface shows a very limited amount of torn matrix, suggesting that the composite is more brittle. The figures also shows very smooth and polish surface which means that part of the wood lumen was filled with plastic that could increase the strength of the composites because of mechanical interlocking.

4.1.6 Miscellaneous Result and Discussion

4.1.6.1 Molecular weight determination of untreated and treated SD

The physico-chemical properties of macromolecules depend on and vary with molecular weight. Mechanical properties increase and reach a limiting value with molecular weight. From figure 4.24, the intrinsic viscosity of UTSD, ATSD and BTSD were found 2.4, 2.3, and 2.2 respectively.

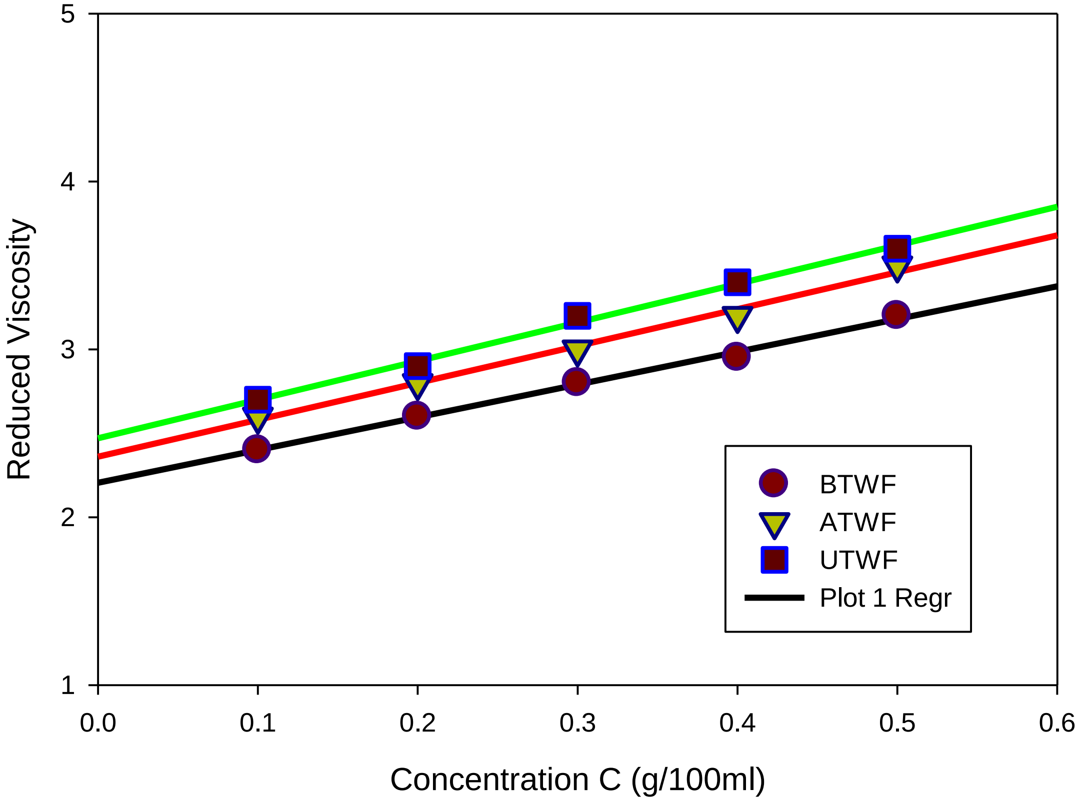

Figure 4.24: Plots of reduced viscosity verses concentration for the intrinsic viscosity of untreated, alkali treated and benzoyl chloride treated SD.

The respective molecular weights were found 1.34×10^5, 1.29×10^5 and 1.23×10^5 by using the equation 3.13 where as the value of a is 1.00 and K is 1.78×10^5. It was seen that the molecular weight of raw SD is higher than alkali treated and benzoyl chloride treated SD. This is due to the chemical modification of NaOH and benzoyl chloride SD constituents. During chemical modification, lignin is removed and the cellulosic chains are broken-down by oxidation. So, molecular weight decreases with the decrease of cell length of the wood fiber. Also, a-cellulose is obtained in pure state after removing all other constituents. Thus, cell length becomes smaller, and molecular weight is reduced in proportion [166].

4.1.6.2 Biodegradability Test

The experimental data of biodegradation test for UT, AT, BT types of composites and plastic resin are given in the figure 4.25. From this figure it was found that UT type of composite showed high rate of biodegradation. This figure, shows the biodegradation result for the untreated composites specimens RPEUTSD35, RPEATSD35 and RPEBTSD35. These three untreated composites are fabricated with 35% with untreated, alkali treated and benzoyl chloride treated sawdust. During the observation of biodegradation test, high sawdust containing composites showed high biodegradation. The trends of biodegradation of these three untreated composites specimens followed the order i.e. RPEUTSD35> RPEATSD35> RPEBTSD35>RPE>VPE. These observations were in agreement with the findings reported in the open literature works [167, 168].

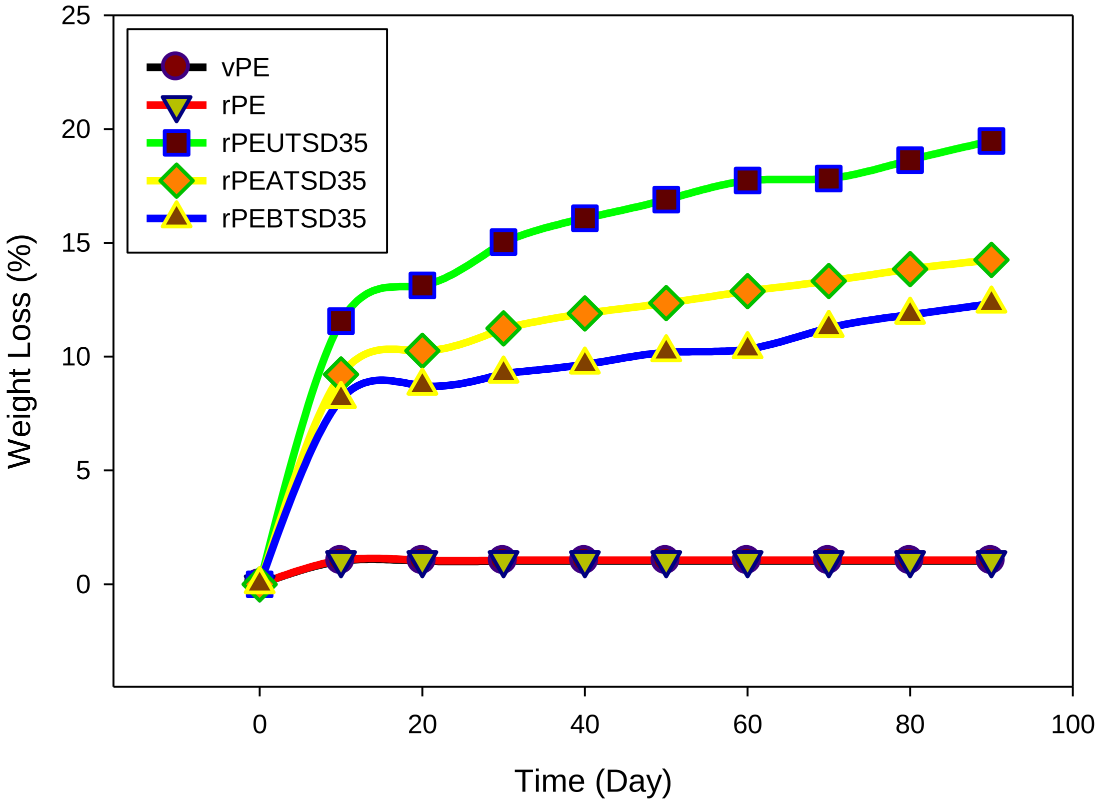

Figure 4.25: Variation of biodegradability of rPEUT35, rPEAT35, rPEBT35 composites with VPE and RPE for 90 days.

4.1.6.3 Melt Flow Index Analysis

The molecular weight of experimental resin RPE and VPE were not determined by viscosity method because these two plastics are insoluable in normal solvent but we have conduct MFI test to get its molecular weight. This analysis does not give us direct molecular weight of polymer and thermoplastics. We have a generic concept about the molecular weight of polymer from melt flow rate. In the open literature the molecular weight of RPE and VPE were found like the data given in the Table-4.8.

Table 4.8: Molecular weight of RPE and VPE

Si. No.	Resin/Matrix	Molecular Wet. (M_v)
01	Recycled Polyethylene (RPE)	1,45,182.00
02	Virgin Polyethylene (VPE)	1,28,165.00

The melt flow index of RPE and VPE was determined in this hypothesis and it was found that RPE had a lower MFI (0.136/10 min., 2.16kg/190°C) compared to VPE (0.302g/10 min., 2.16kg/190°C) (table-4.21) and thus RPE had higher molecular weight, which helped for better dispersion and bonding. In generally higher molecular weight compounds have high viscosity and low melt flow rate on the other hand lower molecular weight compounds showed the opposite result. This obtained result is identical with the open literature value which given in the table 4.9.

Table 4.9: Melt flow index data for RPE and VPE

Si. No.	Resin/Matrix	Melt Flow Rate (g/10 min)
1	Recycled Polyethylene (RPE)	0.136
2	Virgin Polyethylene (VPE)	0.302

4.2 Performance of Untreated, Alkali Treated and Surfactant Treated Saw-Dust Reinforced Recycled Polyethylene Composites

In this part of this chapter thermal, mechanical, physical properties and the microstructure of three different classes of wood-plastic composites (WPCs), which were made through injection moulding machine using recycled PE with saw-dust as filler. The three different classes of composites are UT, AT and ST. The recycled PE (RPE) was collected from a local plastics recycling plant and pine SD was obtained from a local sawmill. The composite made from RPE and chemically treated SD exhibited excellent physico-mechanical property as compared to those made from raw SD and RPE. Several chemical treatments were conducted for SD but surfactant treated composite formulation significantly improved both physical and mechanical properties compared to untreated (UT) and alkali treated (AT) composites. Microstructure analysis of the fractured surfaces of the raw and treated SD composites confirmed that chemical modification of SD improved interfacial bonding between filler and matrix. Water absorption and strength properties of the composites can be improved by increasing the plastic content or by the chemical modification of SD filler. The final result were found to follow this trends ST>AT>UT by considering all conducted test.

4.2.1 Chemical Modification

This part of this chapter is mainly discussing the following tests and the chemical reaction occurred between SD with NaOH and surfactant. FT-IR analysis confirmed the occurred chemical reaction with SD by giving right peak of relevant functional groups.

4.2.1.1 Chemical Modification of Saw-dust (SD) by Sodium Hydroxide and Surfactant:

Chemical modification of SD by NaOH and cetyl trimethyl ammonium bromide (CTAB) shown in the following chemical reaction Figure 4.26. At the end of this treatment alkali treated dried SD transferred brick color to dark brick color then separated by filtration and dried at sunlight first, then finally in the oven at 105˚C. The occurred chemical reaction between SD and surfactant is given below. In this chemical reaction cationic part of the CTAB reacts with alkali treated cellulose unit. It was assumed that surfactant molecule having long chain end which inhibited side reaction with water by the formation of bonding at 2 and 6 position of cellulose unit. On the other hand methyl and cetyl group of surfactant molecule act as a pendent or bulky radical these are capable to protect any further reaction of cellulose. Surfactant modified dried SD was taken for the fabrication of the composites specimen with virgin polyethylene and recycled polyethylene and finally measured various engineering properties.

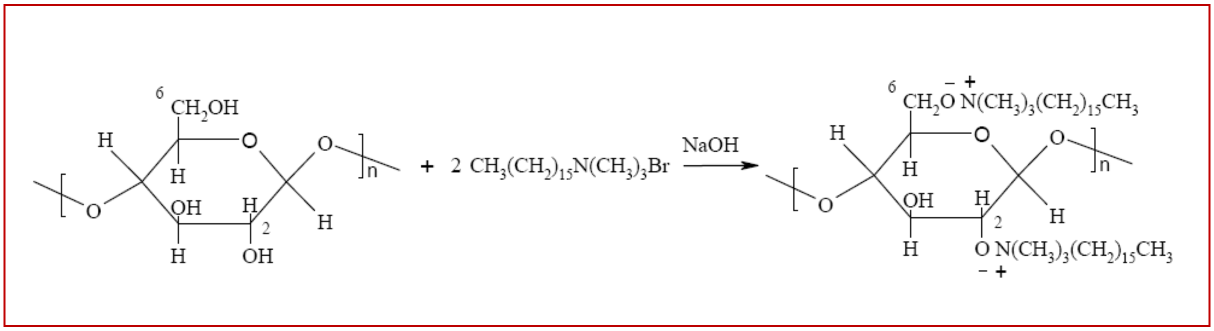

Figure 4.26: Double pretreatment coupling reaction of SD by alkali and benzoyl chloride.

4.2.1.2 FT-IR Spectrum of Alkali and Surfactant Treated SD

Figure 4.27 shows the FT-IR spectra of surfactant treated SD. It is clear in the spectrum that untreated SD shows presence of absorption band near 1734 cm^{-1}, which is assigned to CO group of acyl ester of hemicellulose and aldehyde group in lignin [115]. On the other hand, chemically treated SD shows the absorption band in the regions 1700–1600 cm^1 and 1250-1000 cm^{-1} for N–O and C–N stretching, respectively. Some additional absorption bands were also obtained for C-H, -OH, and CH_2 functional groups present in cellulose, hemicellulose and lignin unit of sawdust. These results suggest that chemical modification of SD has occurred upon treatment with alkali and surfactant.

Table 4.10: FT-IR spectral data of alkali and surfactant treated SD

Peak	Intensity	Position/cm^{-1}	Assignment
1053.15	91.09	~1000-1250	C-N
1165.02	90.733	~1000-1260	OH, -O-, COOR, COOH
1374.3	90.583	~1260-1390	NO_2 (Symmetrical)
1460.14	89.928	~1350-1470	C-H (Alkanes)
1509.32	90.254	~1500-1560	NO_2 (asymmetrical)or Aromatic ring
s1556.88	89.985	~1500-1560	NO_2 (asymmetrical)or Aromatic ring
2333.91	83.396	~2100-2360	Si-H Silane
2869.16	85.845	~2850-3000	Alkanes: CH_3, CH_2, CH
2925.1	84.646	~3000-2900	v(C-H) in aromatic ring and alkanes
3457.46	81.244	~3600-3200	v(OH) broad, strong band from the cellulose, hemicellulose and lignin of SD

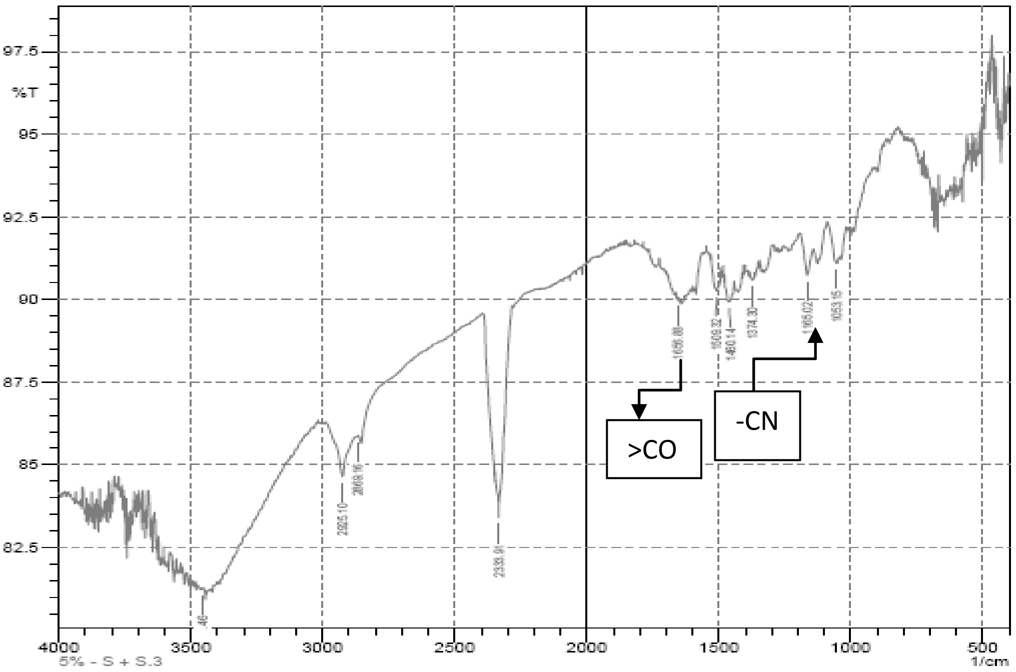

Figure 4.27: FT-IR spectrum of alkali and surfactant treated SD

4.2.2 Physical Properties of Fabricated Composites

The physical properties of fabricated composites are briefly explaining the following test analysis according to the standard ASTM methods.

4.2.2.1 Water Absorption Test

Water absorption test gives us the preconception about the stability and engineering properties of any composites. High water absorption means higher swelling, lower stability and poorer engineering properties. By considering all sides water absorption test was conducted in hot and cool water. In both cases water absorption of untreated sample is greater than chemically treated sample. On the other hand water absorption of all WPC in hot water is greater than cool water. This absorption is also increased with time but decreased with surface modification of SD. These results are consistent with previous studies with chemically modified filler reinforced composites which showed higher water absorption resistance with lower porosity and thus had better interfacial strength as compared to the composites without chemical modification [150-154].

4.2.2.1.1 Cold water absorption test

Cool water absorption tests are classified into two types i.e. **short term** cool water absorption for 24hr and **long term** cool water absorption for 72hr these are mentioned in the following figures. The short term cool water absorption behaviors of composites were shown in the following figure 4.28. From the figure, it is clear that absorption behavior follow the order UT>AT>ST in case of short and long term water absorption test.

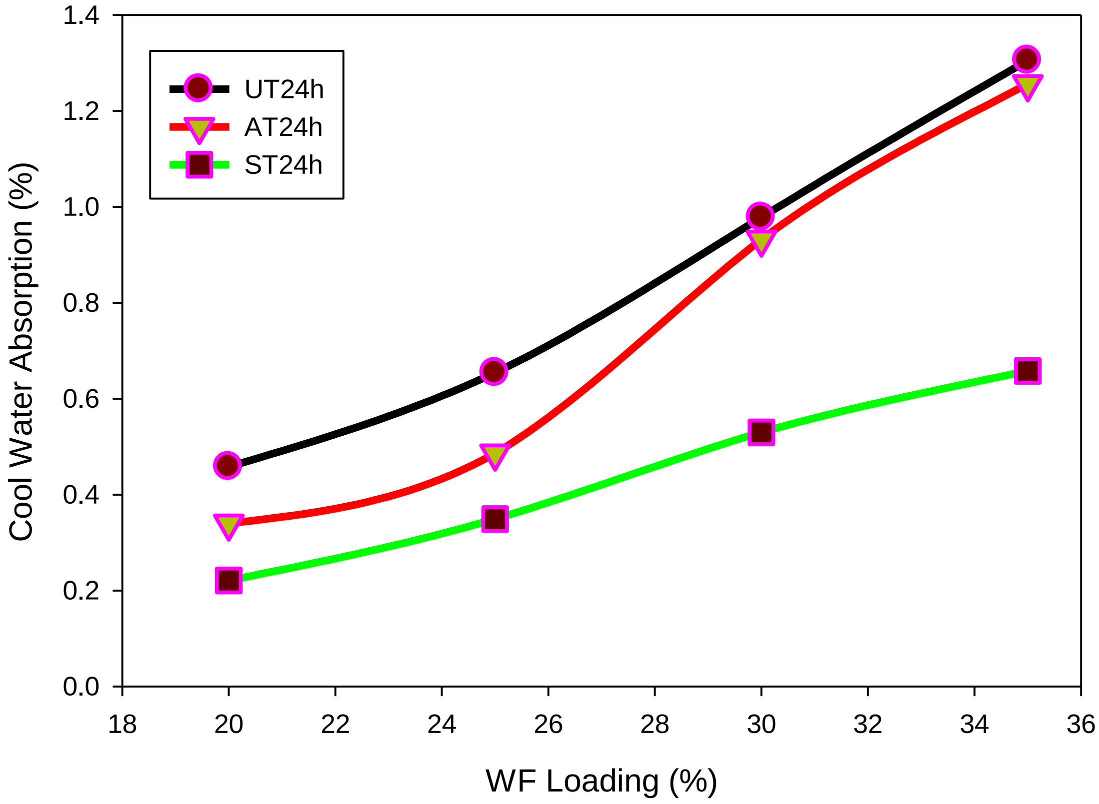

Fig. 4.28: Variation of cold water absorption of RPE composites reinforced with untreated (UT), alkali treated (AT) and surfactant treated (ST) SD for 24h.

Figure 4.29 highlighted the absorption behavior of composites for 72 h. Here it can be considered the above mentioned order UT>AT>ST. In this figure the composites RPEATSD20 showed greater absorption than RPEUTSD20 which is disproportionate with figure 4.28. To overcome this difficulty the composites were immersed into the hot water and continued these absorption experiments for 24h to 72h. Therefore, from the cold water absorption test it was concluded that upon surfactant with which is contains non-polar chain shows lower attraction to water.

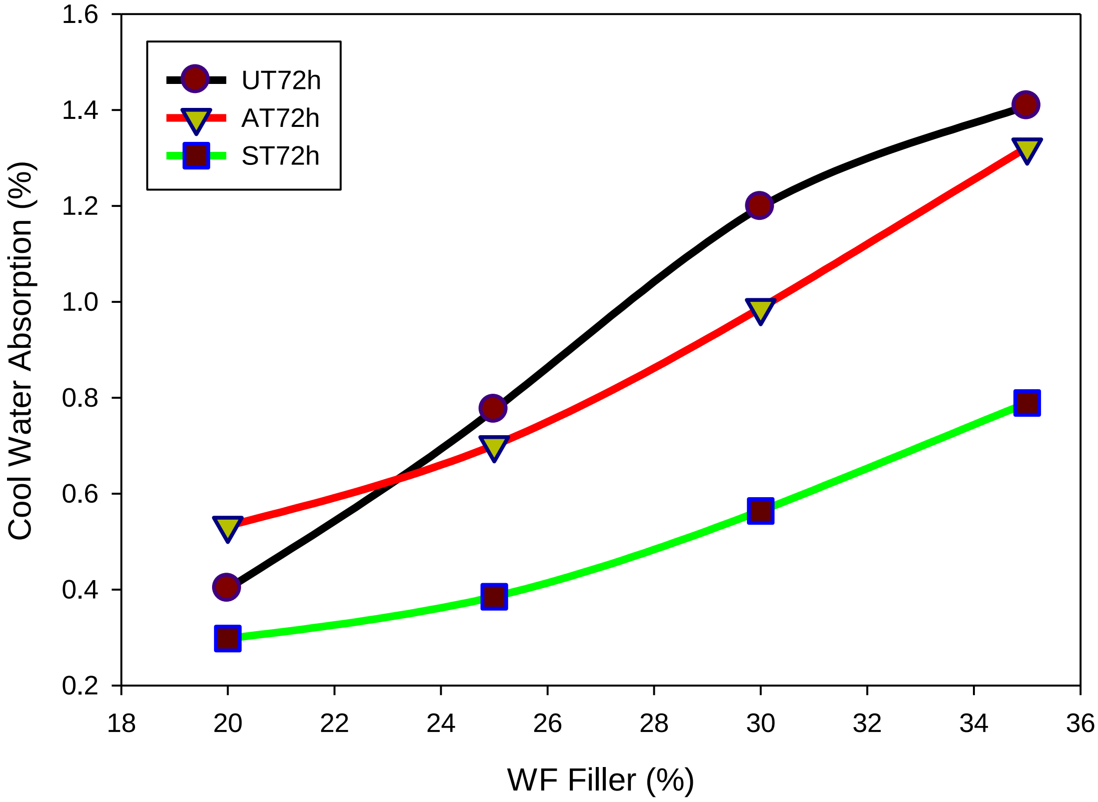

Fig. 4.29: Variation of cool water absorption of RPE composites reinforced with untreated (UT), alkali treated (AT) and surfactant treated (ST) SD for 72h.

4.2.2.1.2 Hot Water Absorption Test

Hot water absorption test are also conducted for short term duration and long term duration. Hot water absorption is greater than cool water absorption it follows the same trends like cold water. In the figure 4.30 the composites RPESTSD20, RPESTSD25, RPESTSD30 and RPESTSD35 shown lower absorption and found to be more stable. The composite RPEATSD20 showed greater absorption than other composites such as RPEUTSD20 and RPESTSD20 but is showed lower absorption in case of 25%, 30% and 35% SD content. In hot water all chemical is not same in behavior that's why affected by experimental condition. During the water absorption test the different experimental condition should be emphasized to get better composites properties. In the both figures 5.30 and 5.31 the same absorption trends were found for these three types of composites i.e. UT>AT>ST.

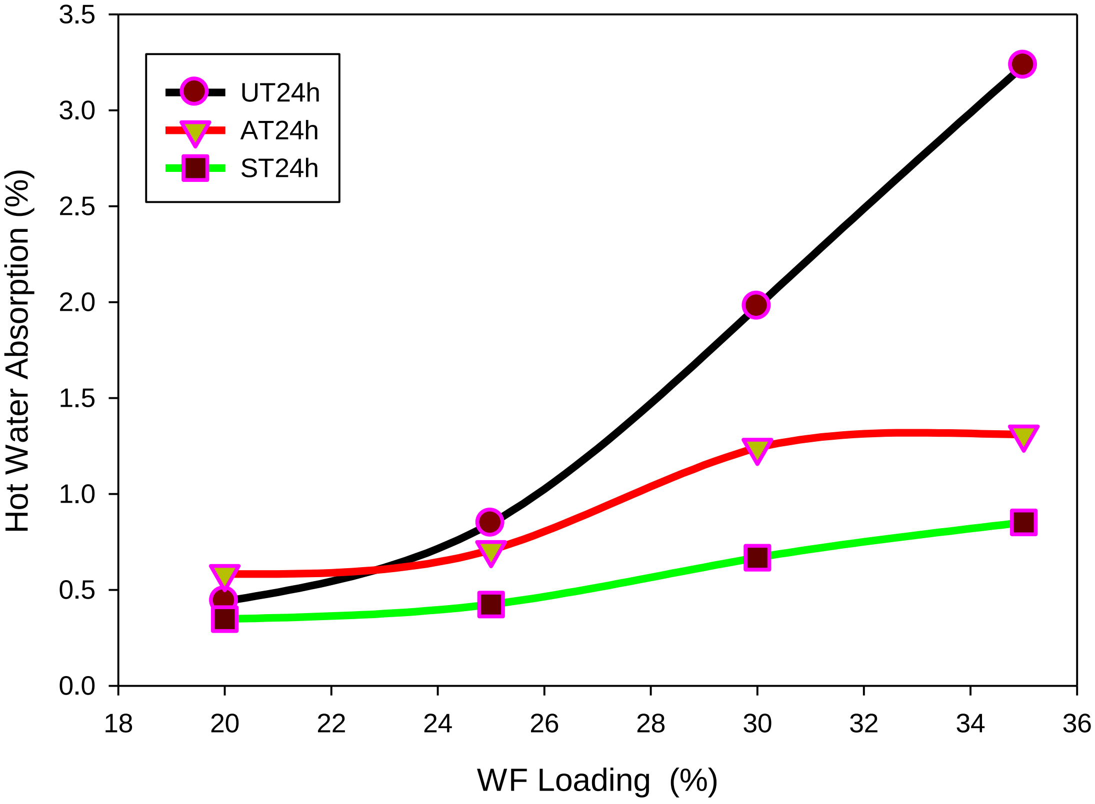

Fig. 4.30: Variation of hot water absorption of RPE composites reinforced with untreated (UT), alkali treated (AT) and surfactant treated (ST) SD for 24 h.

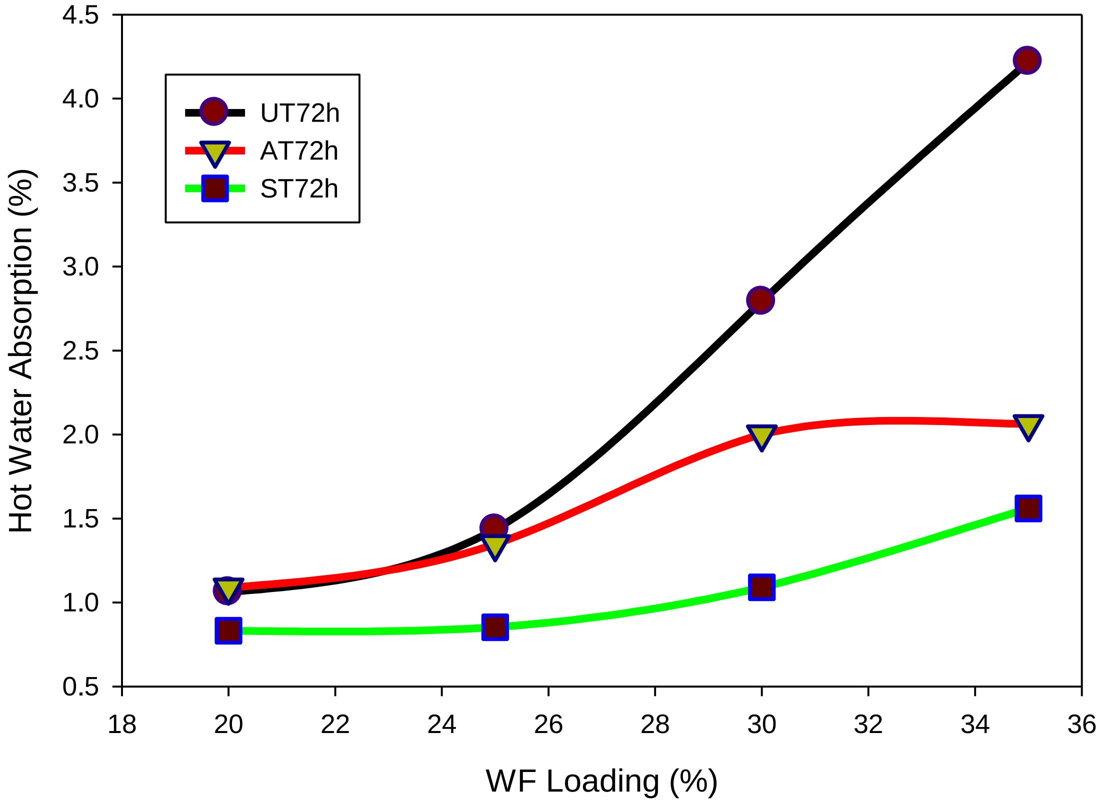

Fig. 4.31: Variation of hot water absorption behavior of RPE composites reinforced with untreated (UT), alkali treated (AT) and surfactant treated (ST) SD for 72 h.

Additionally the water absorption behavior of the entirely VPE and RPE were also conducted. RPE showed slightly greater absorption than VPE because its constituents are not pure, some dust or foreign elements added during recycling. This is the reason for discriminating of water absorption of RPE and VPE.

Water absorption in composites is mainly due to the presence of lumens, fine pores and hydrogen bonding sites in the saw-dust, the gaps and flaws at the interfaces, percentage of wood-plastics contents and the micro-cracks in the matrix formed during the compounding process [63]. These are explained in the 4.1.3 section of this chapter. The recycled PE and treated SD based composites absorbed less water compared with RPE and untreated SD based composites for the same sawdust content. The possible reason could be the enhanced interfacial bonding due to the chemical treatment and different molecular differences between SD and recycled plastics. The interfacial bonding of surfactant treated sawdust reinforced composites was found to be stronger than other two. The sequence of interfacial bonding of WPCs followed the trends i.e. ST>AT>UT.

4.2.2.2 *Thickness Swelling Test (TST)*

Thickness swelling of the sawdust-RPE composites increased with the water absorption and thus had similar trend to the water absorption regarding the impacts of sawdust to RPE ratio and chemical treatment. In general, the composite made of virgin and recycled plastics had similar dimensional stability properties without adding the coupling agent which is consistent with previous findings by Chen et al. [140]. Thickness swelling behavior of UT, AT and ST composites were showed in the figure 4.32 where as their swelling order is UT>AT>ST. Among these three types of composites ST composites showed lower thickness swelling i.e. 0.43663% in case of 25% filler loading. The swelling behavior of CTAB surfactant treated composites is increases very slightly with filler loading. On the other hand in case of untreated and alkali treated composites this behavior increased very highly. Here also found that the dimensional stability of surfactant treated composites is much higher than UT and AT composites. So the order of the dimensional stability of composites can be written as ST>AT>UT.

The thickness swelling had the linear relationship with the water absorption and changes attributed due to the similar mechanism as that of water absorption. Now the possible reasons of lowering and increasing the thickness swelling behavior of composites can be said that the surface modification of filler by CTAB significantly decreased up to 8O%. The molecular weight of resin, degree of crystallinity (Xc) of sawdust upon treatment.

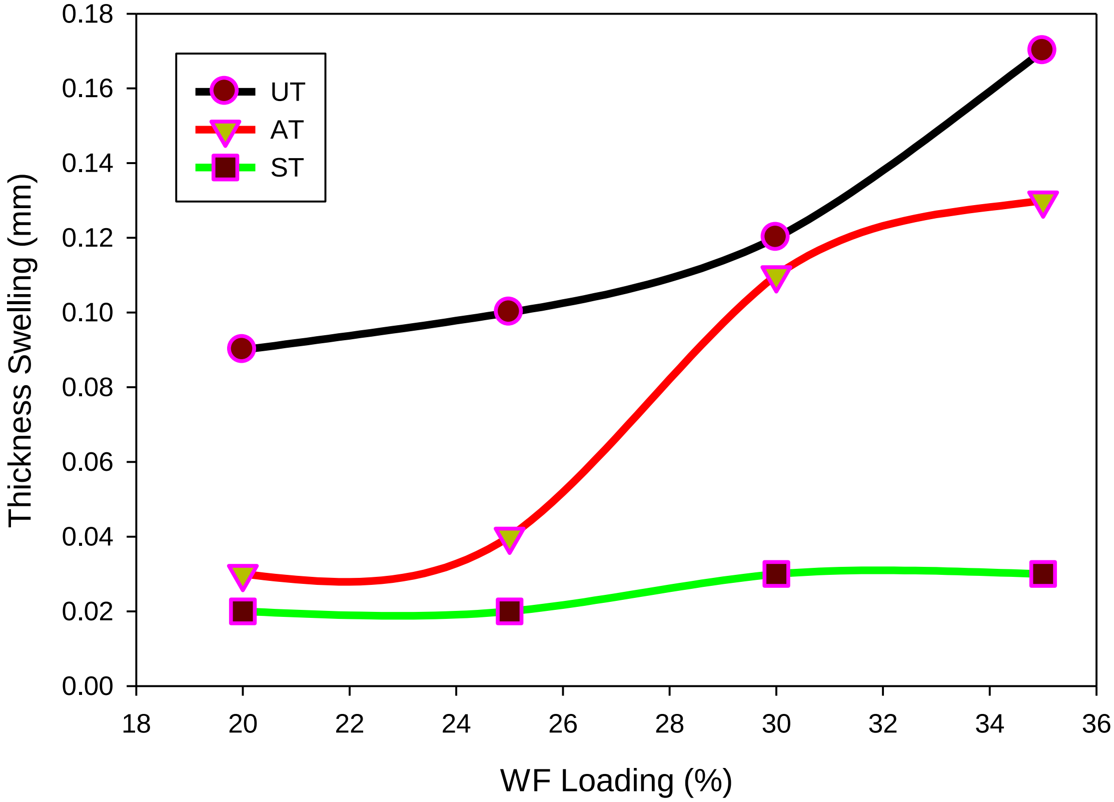

Fig. 4.32: Variation of thickness swelling of RPE composites reinforced with untreated (UT), alkali treated (AT) and surfactant treated (ST) SD filler.

4.2.3 Mechanical Properties

The result and discussion of tensile properties, flexural properties, hardness and impact strength and impact energy are briefly explaining the following listed analysis for composites specimen. The standard ASTM methods were followed to test replicate, the details of ASTM described in the fifth chapter. The results obtained are presented below.

4.2.3.1 Tensile Properties

The tensile strength increases with molecular weight due to the effect of better entanglement. Furthermore, composites based on RPE and modified SD exhibited higher tensile strength than those prepared from RPE and untreated SD for the same plastic to wood ratio. In addition, the tensile strength of the composites increased with decreasing wood content in the resin or matrix.

Tensile strength values of both UT, AT and ST types of composites at different filler loading (20%-35%) are shown in Figure 4.33. For raw and treated filler reinforced composites, the tensile strength decreased with an increase in fiber loading [151-153, 155]. As the filler load increased, the weak interfacial area between the filler and the matrix increased, which in turn decreased the tensile strength.

The figure 4.33 showed better tensile strength properties of surfactant treated composites than alkali and untreated composites. Untreated composites RPEUTSD20, RPEUTSD25, RPEUTSD30 and RPEUTSD35 showed lower tensile strength than alkali and surfactant treated sample. The tensile strength of composites in the figure 4.33 followed the order ST>AT>UT. All composites showed similar sequence i.e. with increase in filler loading tensile strength is decreased. From the figure 4.33 it can be concluded that tensile strength increased significantly by the chemical modification and surfactant treated is the highest in properties.

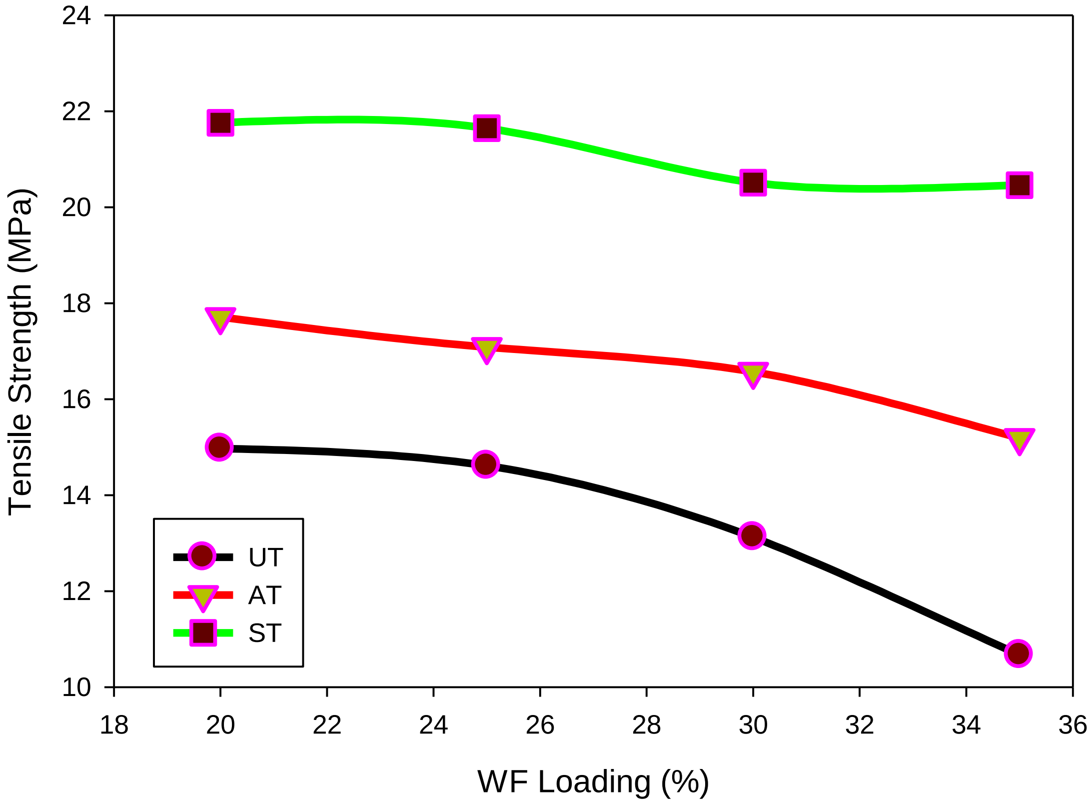

Fig. 4.33: Variation of tensile strength of RPE composites reinforced with untreated (UT), alkali treated (AT) and surfactant treated (ST) SD filler.

This figure 4.34 shows the variation of the Young's modulus at different filler loading. The Young's modulus increased with an increase in filler loading [151, 152, 156-160]. During tensile loading, partially separated micro-spaces are created, which obstructs stress propagation between the filler and the matrix [161]. As the fiber loading increases, the degree of obstruction increases, which in turns increases the stiffness. Again there is a slight increase in stiffness in treated SD reinforced composites compared to the untreated ones.

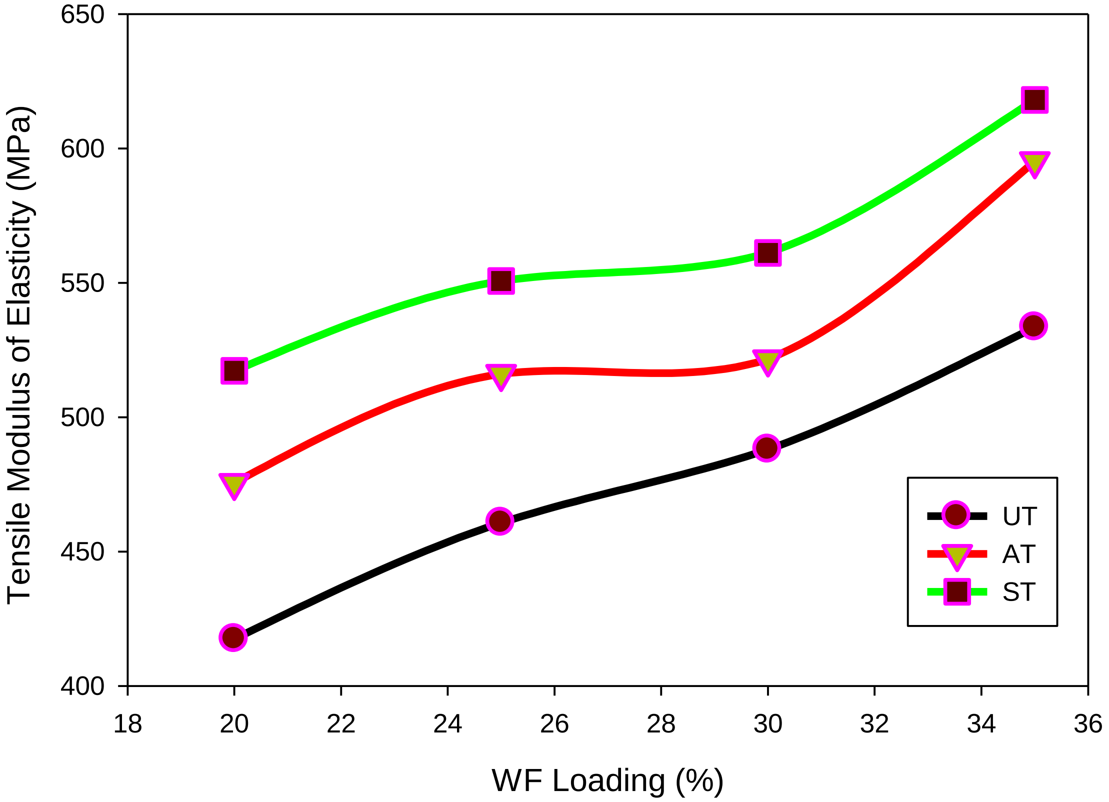

Fig. 4.34: Variation of MOE of RPE composites reinforced with untreated (UT), alkali treated (AT) and surfactant treated (ST) sawdust filler.

The elongation decreased with an increase in filler loading due to the increase in stiffness of the corresponding composites. Again CTAB surfactant treated SD reinforced composites had slight greater elongation compared to the raw ones due to the same reason but here also due to the filler loading elongation properties decrease for increasing stiffness.

Figure 4.35 represented the variation of elongation properties of surfactant treated composites (RPESTSD20, RPESTSD25, RPESTSD30 and RPESTSD35) with untreated and alkali treated composites. Surfactant treated composites showed slightly greater elongation than untreated and alkali treated composites. In between these three composites the variation of elongation properties were found in figure 4.35 is like this order ST>AT>UT.

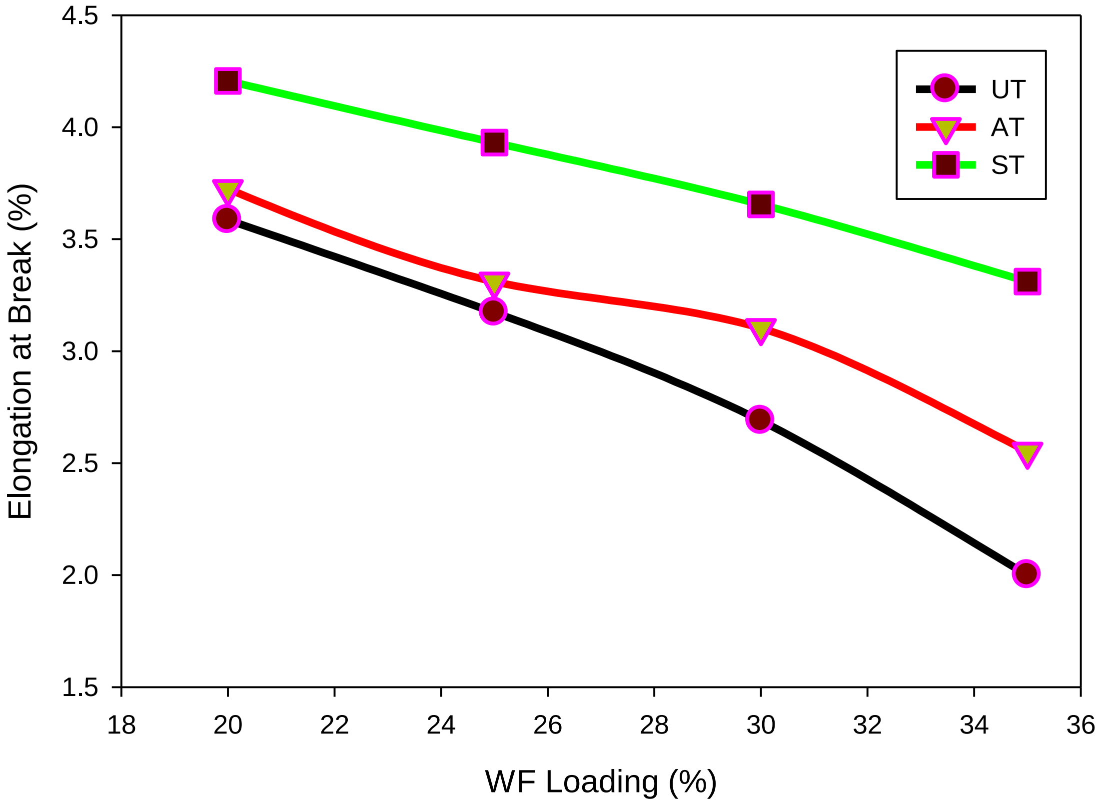

Fig. 4.35: Variation of EAB of RPE composites reinforced with untreated (UT), alkali treated (AT) and surfactant treated (ST) SD filler.

The elongation properties of composites can be explained in such a way that in the case of untreated composites the interfacial bonding between fiber and matrix is poor than treated sample, hence lower elongation properties. Chemically treated SD reinforced composites showed much greater elongation properties for good interfacial bonding between filler and matrix.

Tensile properties closely related with ductility, stiffness, chemical modification of sawdust, interfacial bonding between fiber and matrix, filler-matrix adhesion properties etc. The other related properties are MFI of matrix, fiber dispersion and Xc of fiber upon treatment. These properties are explained in the section 4.1 of this chapter. The observed increase in the tensile strength and stiffness is attributed to the improved interfacial bonding between the saw-dust and the matrix as well as the modification of individual components [2, 138].

The results presented here are in line with the observation of the studies [71, 115, 152, 153] that showed 2,4-DNPH, diazonium salt and anhydride moieties of functionalized polyolefin coupling agents entered into the reaction with the surface hydroxyl groups of saw-dust. These changes created interfacial wetting between the saw-dust and the RPE matrix and thereby improved the compatibility between the saw-dust and RPE matrix, which in turn, enhanced the mechanical properties.

4.2.3.2 Flexural Properties

The flexural strength and modulus of the RPE-Modified SD filler based composites were higher than those of RPE-Untreated SD based composites at the same plastic to sawdust ratio. It was also observed that flexural strength increased with increasing wood content up to 35 wet. %. Results of flexural strength of UT, AT and ST types of composites at different filler loading (20%-35%) are shown in Figure 4.36. The order of the flexural strength of these three types of composites was found to follow the order ST>AT>UT. In this figure three different composites had same ratio SD to RPE ratio. The maximum flexural strength were found for 35 wet. % of SD reinforced composites and 20 wet. % SD loaded composites had lowest flexeral strength. The following figure gives clear concept about the variation of flexural strength with different filler loading i.e. 20 % to 35%. The obtained results were found in this work which is similar with the result available in the open literature reported by other researchers [151-153, 157-160].

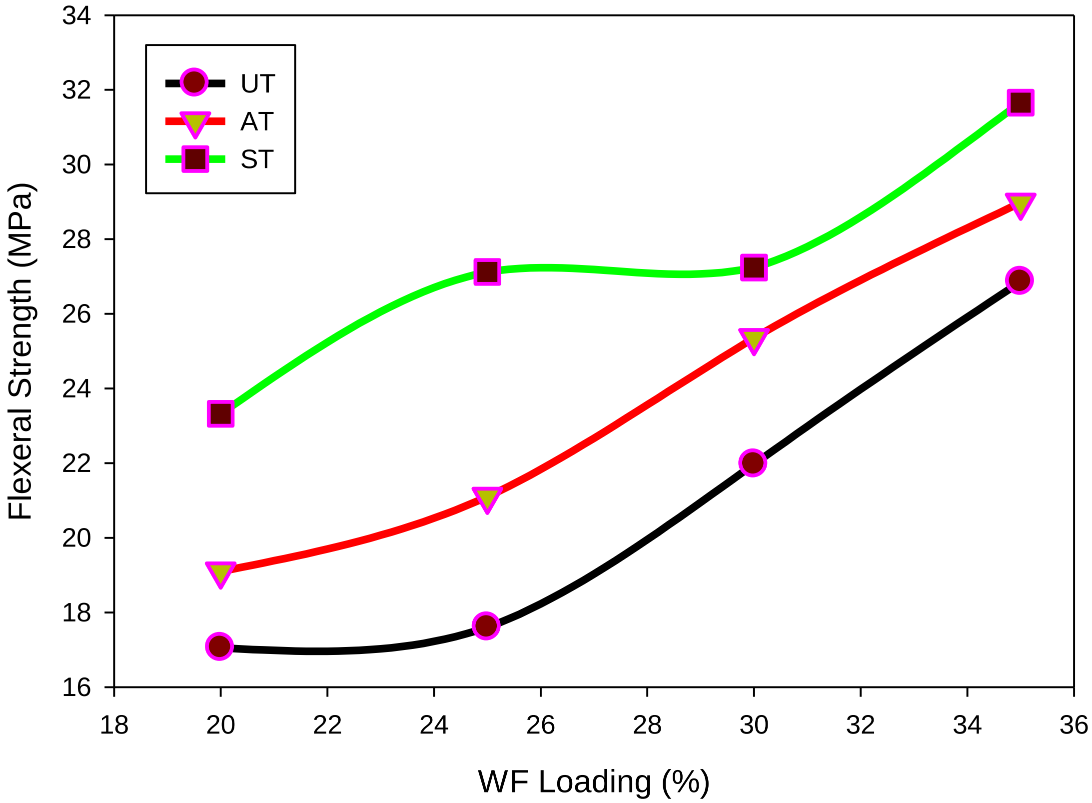

Fig. 4.36: Variation of flexural strength of RPE composites reinforced with untreated (UT), alkali treated (AT) and surfactant treated (ST) SD filler.

Figure 4.37 presented flexural modulus of ST, AT and UT composites each of these had same trends i.e. MOE increased with filler loading and their found order is ST>AT>UT. From this result it was observed that ST and AT composites had greater MOE than UT one. Fiber dispersion, interfacial bonding between filler and matrix, cross linking of polymer etc. of ST and AT composites is better than UT composites. Modified composites exhibited higher MOE than UT composites. Similar results were also reported in the literature by many researchers [151-153, 157-160].

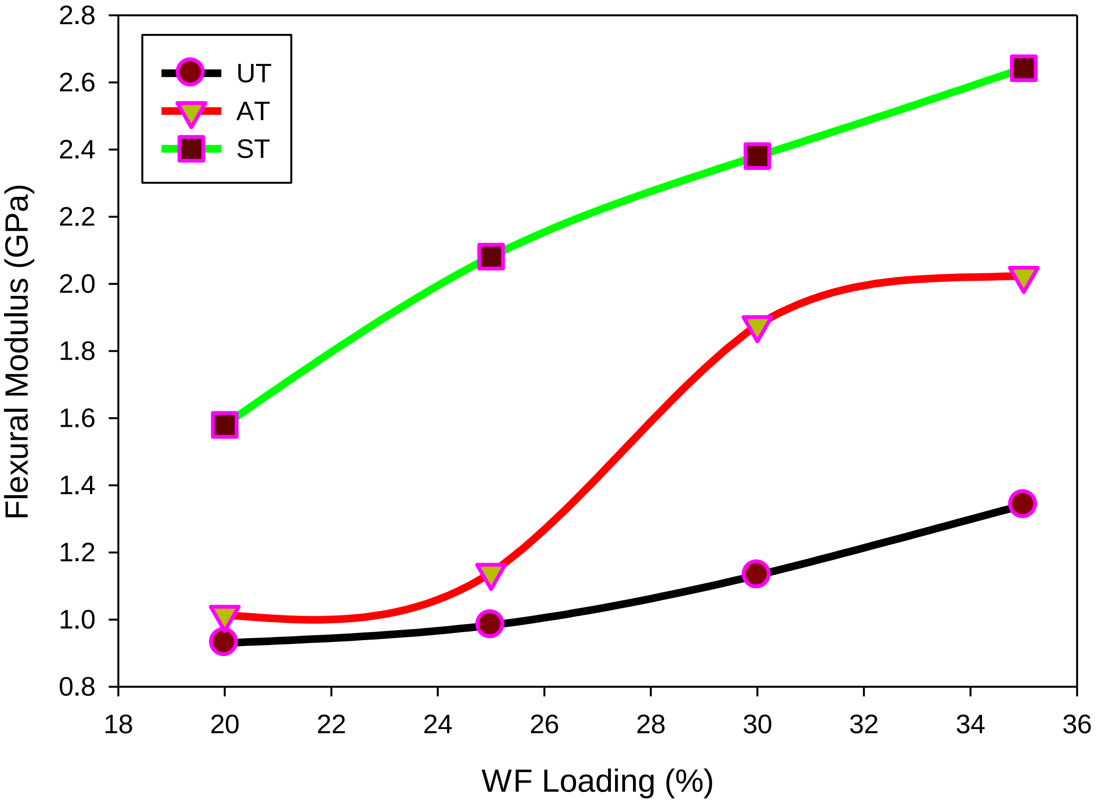

Fig. 4.37: Variation of flexural modulus of RPE composites reinforced with untreated (UT), alkali treated (AT) and surfactant treated (ST) SD filler.

From the experimental results presented, it was found that effect of wood was notable in material properties of the composites. Wood is a lignocellulosic material made up of three major constituents (cellulose: 42-44%, hemicelluloses: 27-28%, and lignin: 24-28%) with some minor constituents (extractives: 3-4%) [62, 63]. The major portion of wood is crystalline cellulose. The aligned fibril structure of cellulose along with strong hydrogen bond has high stiffness thus addition of the saw-dust can increase the stiffness of the polymer based composites.

Lignin as an amorphous polymer does not greatly contribute to the mechanical properties of saw-dust but plays an important role in binding the cellulose fibrils that allows efficient stress transfer to the cellulose molecules. Hence, wood filler increased the stiffness of RPE without excessively increasing the density. Furthermore, these composites have potential to take up water under humid conditions due to the presence of numerous hydroxyl groups available for interaction with water molecules via hydrogen bonding. The surface modification of SD improved the compatibility between the wood filler and RPE through esterification and thus reduced the water absorption and improved the stability and mechanical properties.

4.2.3.3 Izode Notched Impact Energy and Strength

Impact strength is a measure of the tolerability, when the composite is subjected to a sudden impact that results in crack propagation through the material. For fiber-reinforced polymeric composites, it depends on a number of factors, such as the nature of the fiber, polymer matrix, and the polymer-matrix interfacial bonding [162]. Sanadi et al. reported that high fiber content increases the possibility of fiber agglomeration, which results in regions of stress concentration that require less energy for crack propagation and that an increase in the resistance of crack propagation occurs if fiber bridges the crack in the composites [163].

As shown in Figure 4.38, impact strengths of both treated and untreated RPE-SD composites show a slight increasing trend with an increase in the filler loading, indicating that the filler is capable of absorbing energy because of strong filler-matrix interfacial adhesion. It has been reported that improved interfacial bonding provides an effective resistance to crack propagation during impact tests [162, 164]. Thus, higher impact strengths of the treated SD-RPE composites suggest a better interfacial bonding compared to those of untreated ones. This could be due to better kneading of the matrix-filler system during the preparation of composites, their grinding and then specimen fabrication in injection molding method. Slightly higher impact strength for AT and ST types of composites is probably due to the favorable interaction between the treated SD and the hydrophobic RPE chain of the matrix. So-called fiber pullout and fiber agglomeration could be responsible for lower impact strengths of untreated SD composites.

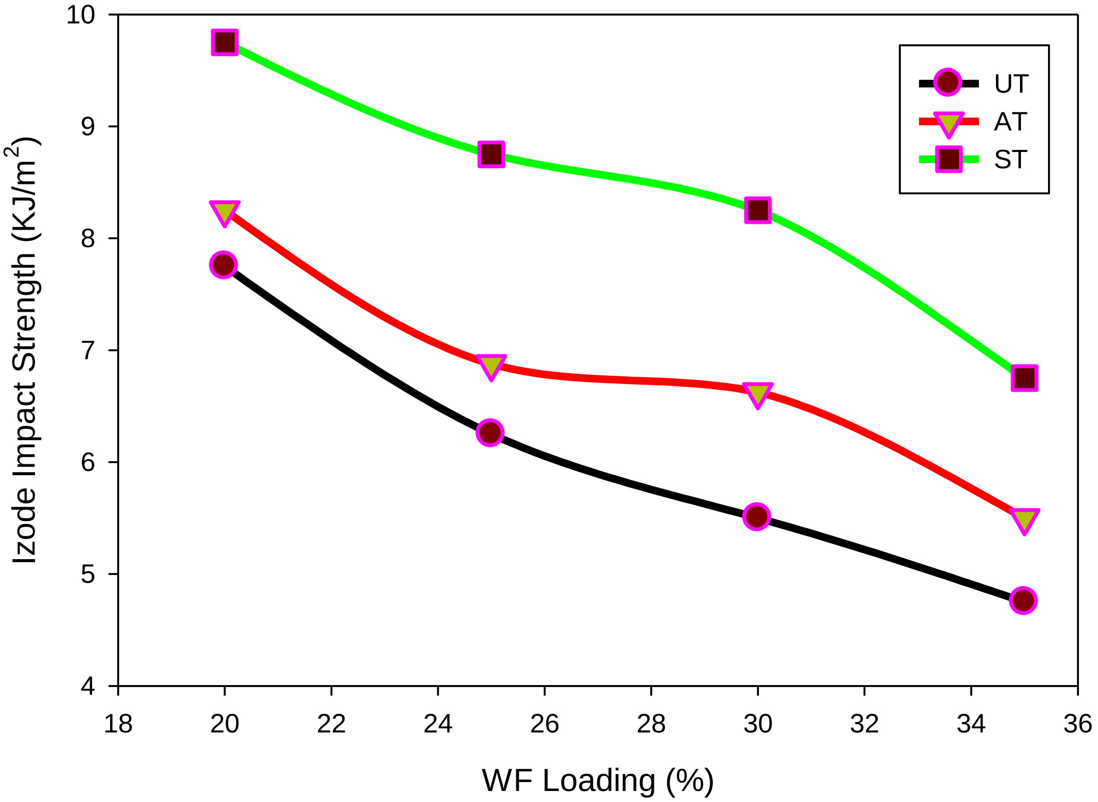

Fig. 4.38: Variation of izode notched impact strength of RPE composites reinforced with untreated (UT), alkali treated (AT) and surfactant treated (ST) SD filler.

Figure 4.39 shows the variation of impact energy of SD reinforced RPE composites at the same filler loading which also followed the same trends like impact strength. The possible reason for the variation of result is the filler-matrix ratio in fabricated composites, chemical treatment of filler, interfacial bonding between filler and resin and filler dispersion into the resin. Saw dust or SD is a notable fibril that can be properly homogenate into the matrix than any other fiber as a result fabricated composites showed greater hardness than RPE matrix. Raw and chemically treated filler reinforced composites in this hypothesis showed relatively lower impact energy than 100% RPE matrix and VPE but treated composites showed higher impact energy than untreated one. Finally order of impact energy were found ST>AT>UT which as follows.

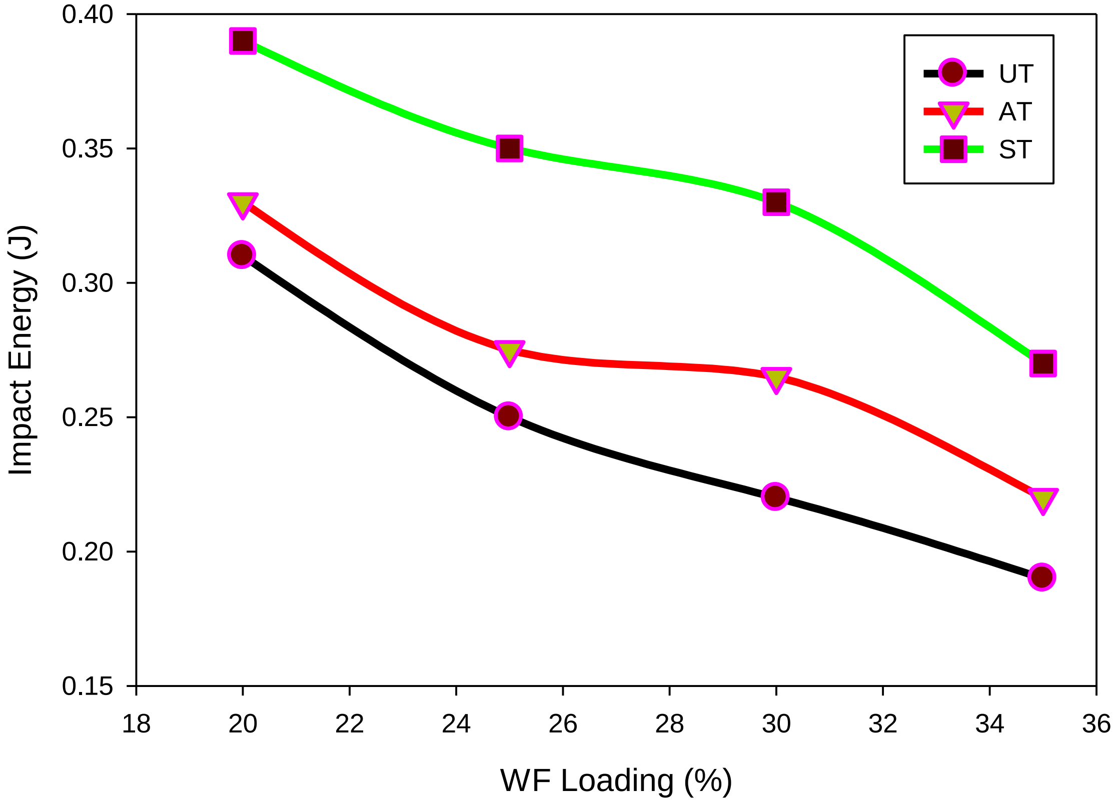

Fig. 4.39: Variation of izode notched impact energy of RPE composites reinforced with untreated (UT), alkali treated (AT) and surfactant treated (ST) SD filler.

4.2.3.4 Hardness

Hardness of a composite material refers to its resistance to shape changes when force is applied on it. For composites, it depends on the distribution of the filler into the matrix [162]. Usually the presence of a more flexible matrix causes the resultant composites to exhibit lower hardness [165]. As shown in Figure 4.40, incorporation of both treated and untreated SD into the RPE matrix has reduced the flexibility of the matrix, resulting in more rigid composites.

The hardness of both treated and untreated composites is found to increase with an increase in the filler loading. The incorporation of filler particles into the RPE matrix has reduced the mobility of the polymer chain in the rigid composites. The treated saw-dust or SD composites seem to have better hardness compared to untreated ones. This could be attributed to both better dispersion of the fiber into the matrix with minimization of internal voids and stronger interfacial adhesion between the matrix and the filler.

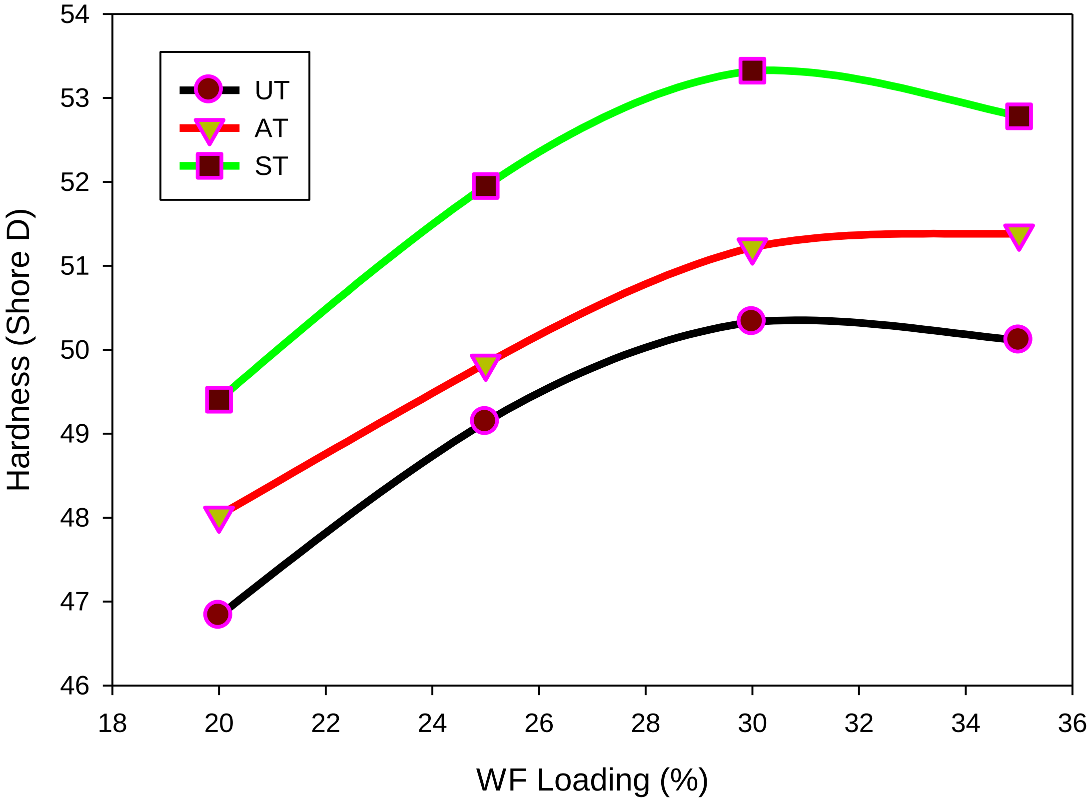

Fig. 4.40: Variation of hardness of RPE composites reinforced with untreated (UT), alkali treated (AT) and surfactant treated (ST) SD filler.

4.2.4 Characterization of Surface Morphology

The tensile fractured surface morphologies of untreated and treated SD-RPE composites prepared with 35 wt. % SD are shown in the following figures. The FESEM image of the untreated SD reinforced RPE composite (figure 4.41) shows a number of fiber agglomerations and fiber pullout traces in the composites (image A). On the other hand, chemically treated SD-RPE composites show almost uniform dispersion of the filler into the matrix, which results in better interfacial adhesion between the filler and the matrix with improved mechanical properties (image B, C).

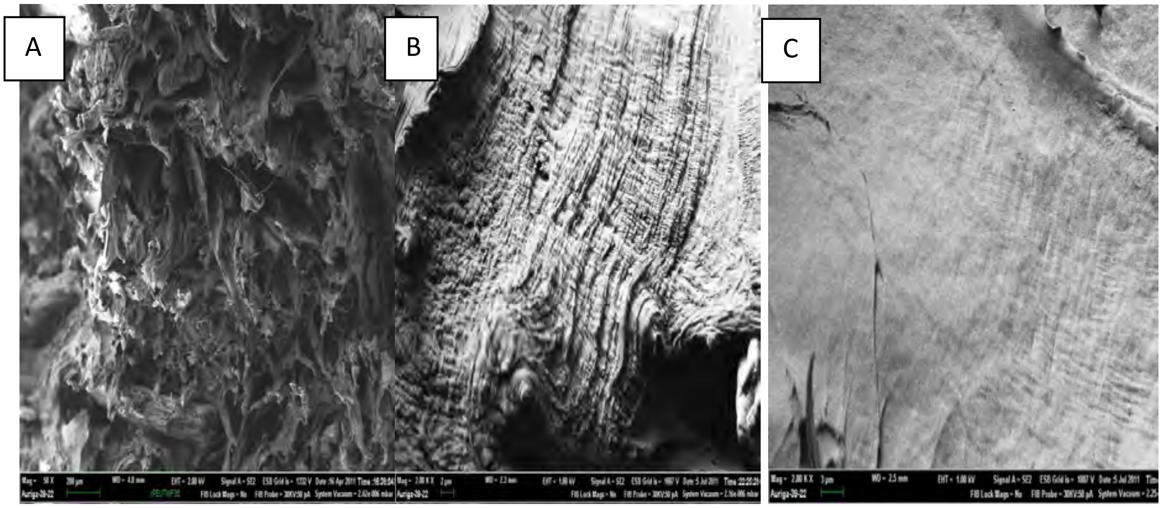

Figure 4.41: FESEM images of RPE composites reinforced with 35% untreated, alkali treated and surfactant treated sawdust (image A, B, C).

It is evident from image C that fiber pullout traces and fiber agglomeration as well as the micro voids in the composites have significantly reduced in the composite upon treatment of SD with surfactant. This result suggests that interfacial bonding between the filler and the matrix has become much more favorable for surfactant treated SD and the matrix compared to that of the untreated one.

4.2.5 Miscellaneous Result and Discussion

4.2.5.1 Molecular weight determination of untreated and treated SD

From Figure 4.42, the intrinsic viscosity of UTSD, ATSD and STSD were found 2.9, 2.3, and 2.2 respectively where as the value of a is 1.00 and K is 1.78×10^5. The respective molecular weight of UTSD, ATSD and STSD were found to be 1.34×10^5, 1.29×10^5 and 1.23×10^5. It was seen that the molecular weight of raw SD is higher than alkali treated and surfactant treated SD. This is due to the chemical modification of NaOH and cetyl triomethyl ammonium bromide (CTAB) and SD constituents. During chemical modification, lignin is removed and the cellulosic chains are broken-down by oxidation. So, molecular weight decreases with the decrease of cell length of the wood fiber. Also, *a*-cellulose is obtained in pure state after removing all other constituents. Thus, cell length becomes smaller, and molecular weight is reduced in proportion [166].

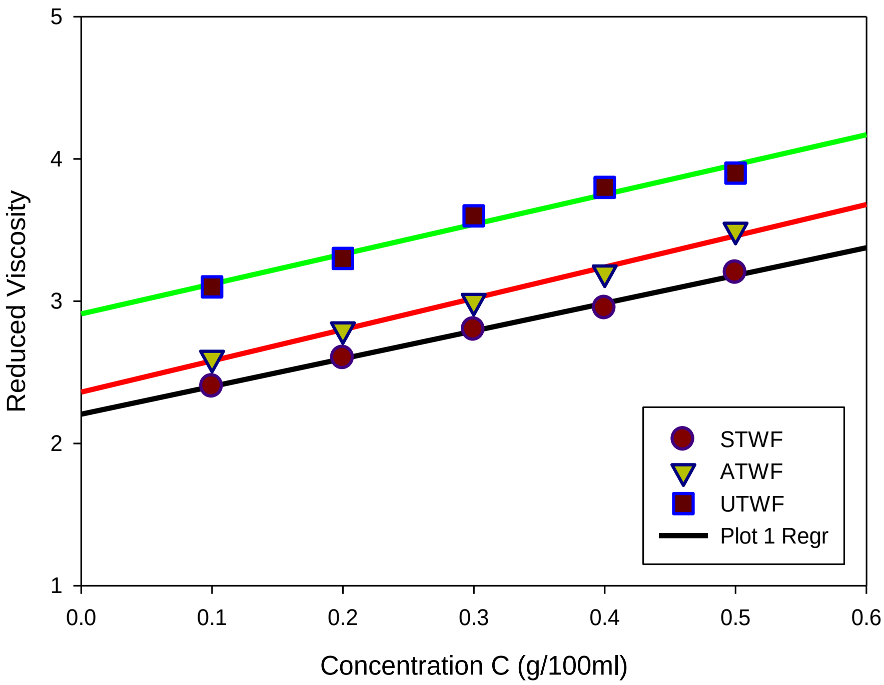

Figure 4.42: Plots of reduced viscosity verses concentration for the intrinsic viscosity of untreated, alkali treated and benzoyl chloride treated SD.

4.2.5.2 Biodegradability Test

Figure 4.43 shows the biodegradation result for the untreated, alkali treated and surfactant treated composites specimens of 35% filler content. The trends of the biodegradation was found to follow this order UT>AT>ST>RPE>VPE. Biodegradation depends on the filler contents of composites materials. During the observation period of biodegradation test, high SD containing composites showed high biodegradation. These observations were in agreement with the findings reported in the open literature works [167, 168].

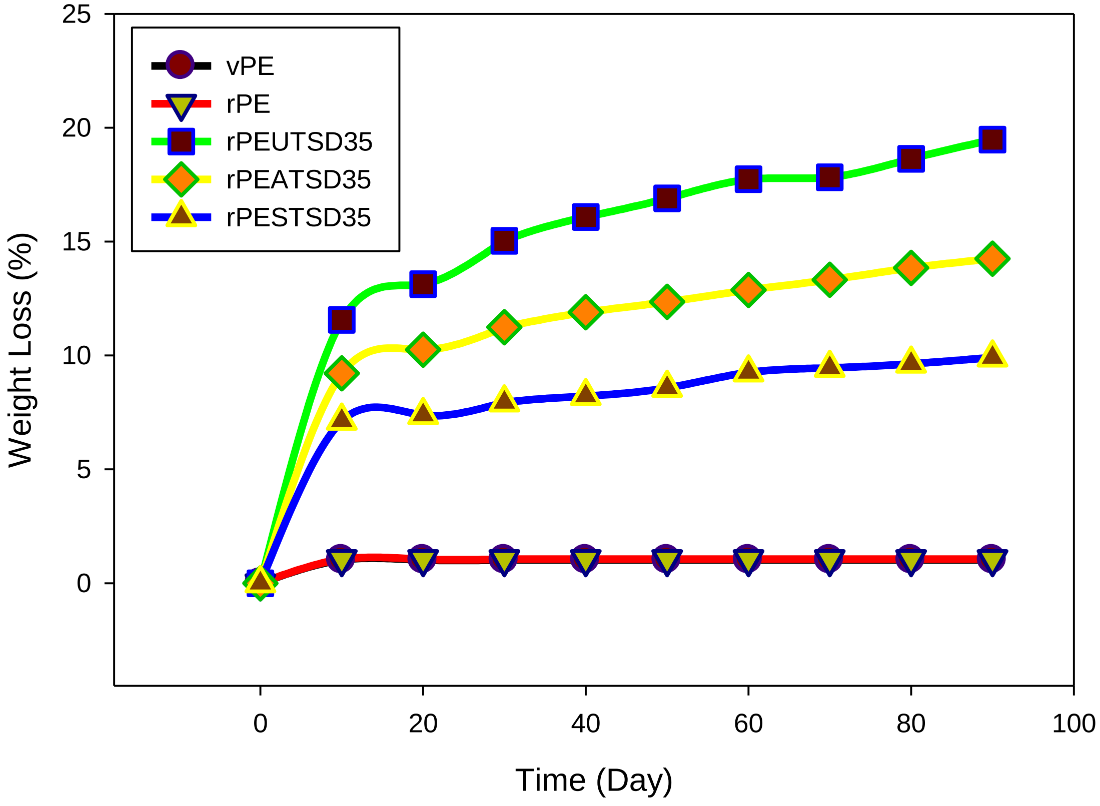

Figure 4.43: Variation of biodegradability of UT, AT, ST composites with 100% RPE and VPE for 90 days.

CHAPTER 05

SUMMERY OF RESULTS AND DISCUSSION

In this chapter the overall performance of fabricated composites were discussed in a condensed form. The mechanical properties of recycled polyethylene (RPE) composites reinforced with raw and treated sawdust were studied in this hypothesis. Fiber-matrix adhesion was significantly improved due to the surface treatment using NaOH, benzoyl chloride and CTAB. The use of the treated filler improved the interfacial adhesion between the fiber and the matrix. However, it was found that the resulting strength, stiffness and overall engineering properties of the composite materials depended on the surface modification and the composition of the sawdust.

5.1 Details of the test standards and specimens dimension for Composites Properties

In order to characterize the physico-mechanical properties of RPE-sawdust composites various ASTM standards methods were followed. For each series of tests minimum five specimens were tested and the average values were presented. Each specimen was labeled based on the percentage of sawdust, types of surface modification, and specimen number that one is explained in the chapter 5 elaborately. Table 5.1 indicates the test standard, sizes and number of specimens evaluated in this study.

Table 5.1: List of standard ASTM methods for the experimental hypothesis

Test Name	Test Standard	No. of Replicates Tested	Dimension of Specimen /Amount of Sample
Water Absorption	ASTM D570-98	5	39×10×4 mm^3
Izode Impact Strength	ASTM D256	5	68×10×4 mm^3
Izode Impact Energy	ASTM D256	5	68×10×4 mm^3
Hardness Test	ASTM E18-08 ASTM D2240	5 5	145×10×4 mm^3
Tensile Strength	ASTM D638-08	5	145×10×4 mm^3
Tensile Modulus	ASTM D638-08	5	145×10×4 mm^3
Flexural Strength	ASTM D790-07	5	145×10×4 mm^3
Flexural Modulus	ASTM D790-07	5	145×10×4 mm^3
Estimation of SD Composition	TAPPI Std. Method	--	--
Molecular Weight Determination	Viscosity Method	--	0.1, 0.2, 0.3, 0.4, 0.5 (g/100 ml)
Melt Flow Index	ASTM D1238-94a	--	g/10 Min; 2.1Kg/190 $^{\circ}$C

Thickness Swelling	ASTM D570-98	3	$39\times10\times4$ mm^3
Biodegradability	ASTM D6003-96	3	$39\times10\times4$ mm^3

5.2 Surface Modification of Sawdust

The surface modification of sawdust was carried out in this hypothesis by sodium hydroxide, benzoyl chloride and cetyltrimethylammonium bromide (CTAB). Upon chemical treatment of sawdust by NaOH breaks the OH groups at C_2 and C_6 positions of the cellulose in the sawdust, producing 2,6-disodium cellulose [141] as shown in Scheme 1 (Fig. 4.1), chapter 04. Maybe due to the steric effect, the hydroxyl group at C_3 does not undergo chemical reaction with the Na^+ ion of alkali NaOH. On the other hand benzoyl chloride produced benzoylcellulose and hexadecyl trimethylammoniumcellulose produced by surfactant. During the treatment of sawdust by CTAB Br^- ion react with alkali treated cellulose unit and separated Na^+ ion by the formation of NaBr. It was assumed that surfactant molecule having long chain end which inhibited side reaction with water by the formation of bonding at 2 and 6 position of cellulose unit.

5.3 Water Absorption Behavior of RPE-SD Composites

5.3.1 Cold water absorption test

Figure 5.1 and 5.2 shows the cold water absorption separately for short and long term duration. From these two graph same trends of absorption were obtained i.e. UT>AT>BT>ST. For long term absorption process high water absorption was observed.

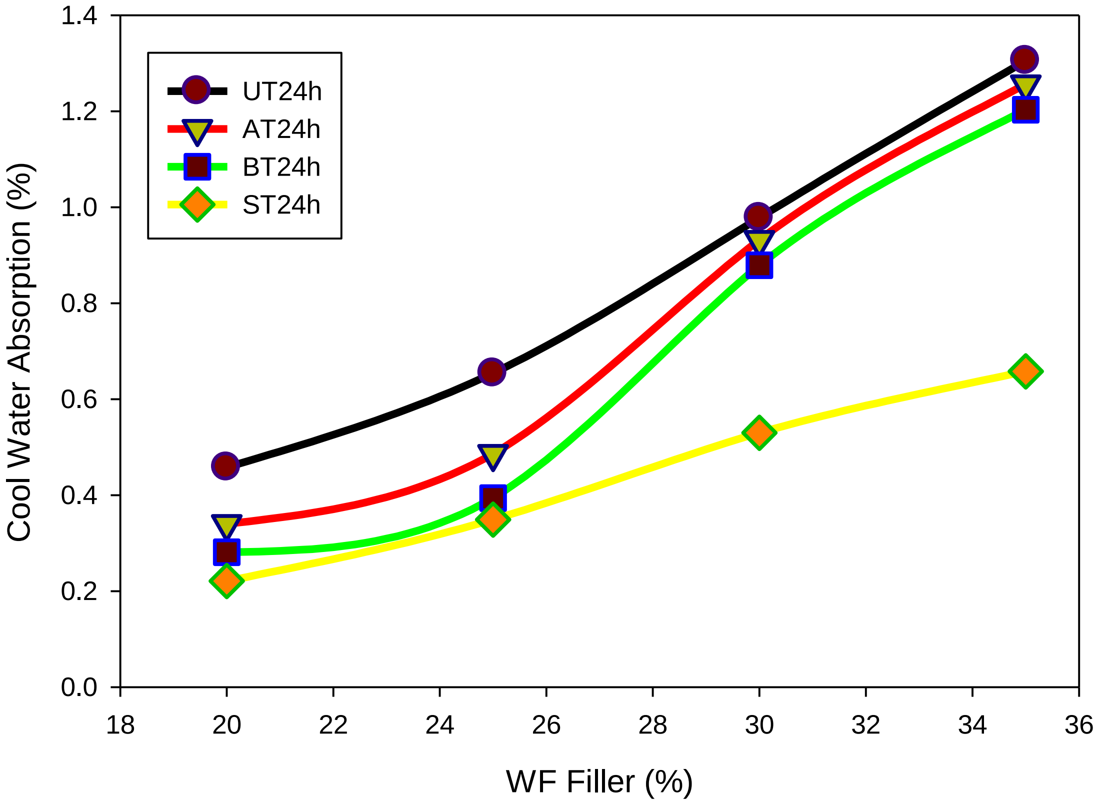

Fig. 5.1: Variation of short term cold water absorption of recycled PE composites reinforced with untreated (UT), alkali treated (AT), benzoyl chloride treated (BT) and surfactant treated (ST) saw-dust (SD) for 24h.

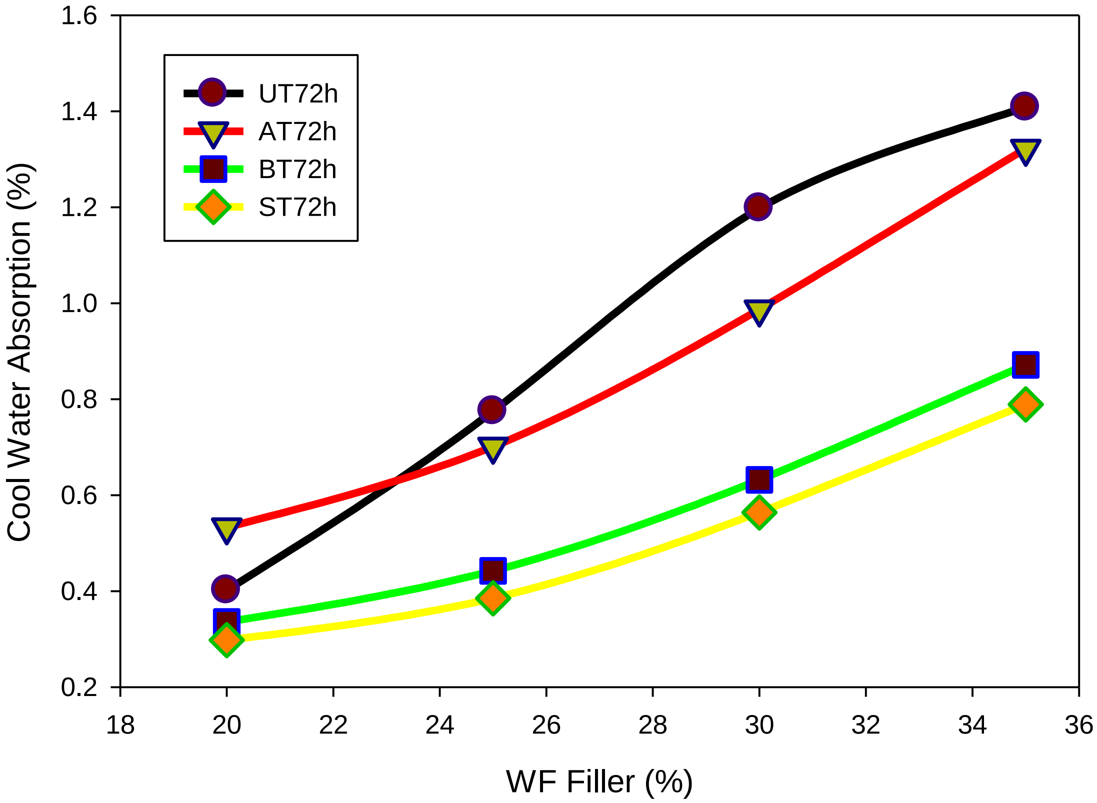

Fig. 5.2: Variation of long term cold water absorption of recycled PE composites reinforced with untreated (UT), alkali treated (AT), benzoyl chloride treated (BT) and surfactant treated (ST) saw-dust (SD) for 72h.

5.3.2 Hot Water Absorption

Hot water absorption test observations were conducted for the same duration and the absorption trends were found similar to the cold water absorption test. The main difference between cold water and hot water absorption test is that in hot water absorption test water absorption rate is higher than that of cold water. So the trends of the hot water absorption were found in both figures 5.3 and 5.4 is that UT>AT>BT>ST.

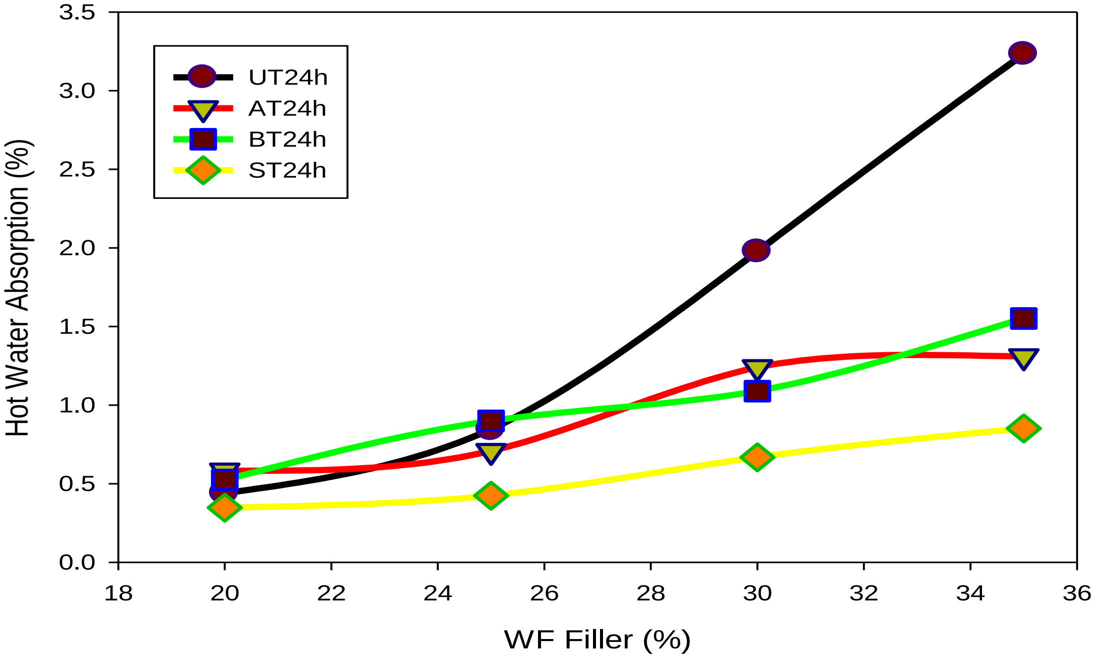

Fig. 5.3: Variation of short term hot water absorption of recycled PE composites reinforced with untreated (UT), alkali treated (AT), benzoyl chloride treated (BT) and surfactant treated (ST) saw-dust (SD) for 24 hours.

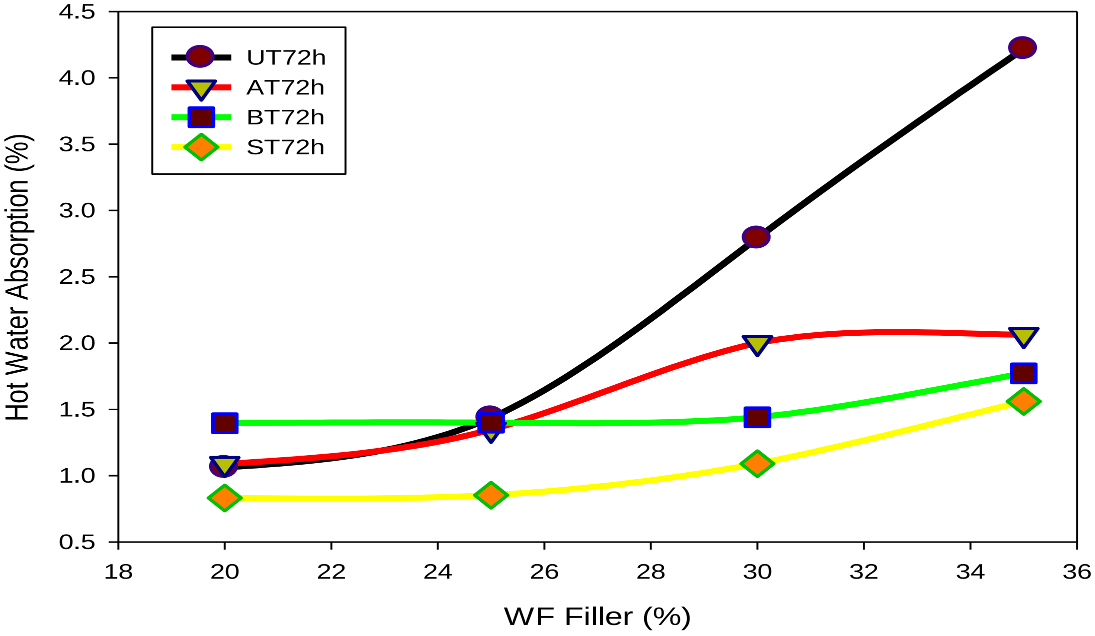

Fig. 5.4: Variation of long term hot water absorption of recycled PE composites reinforced with untreated (UT), Alkali treated (AT), benzoyl chloride treated (BT) and surfactant treated (ST) saw-dust (SD) for 72hours.

5.4 Mechanical Properties

5.4.1 Hardness

As shown in Fig. 5.5, the incorporation of both treated (AT, BT, ST) and untreated (UT) sawdust reinforced composites increased their hardness up to 30% filler loading and then showed only a slight decreasing trend upon further increases in filler content. This indicates a decrease in flexibility and an increase in stiffness of the composites with increasing filler content. The treated sawdust reinforced composites are found to show better hardness compared to those of the untreated ones. The final hardness results for the various composites were found to follow the order: ST>BT>AT>UT. This could be due to both better filler–matrix interfacial wetting and surface crystallization upon chemical treatment of the fiber [169].

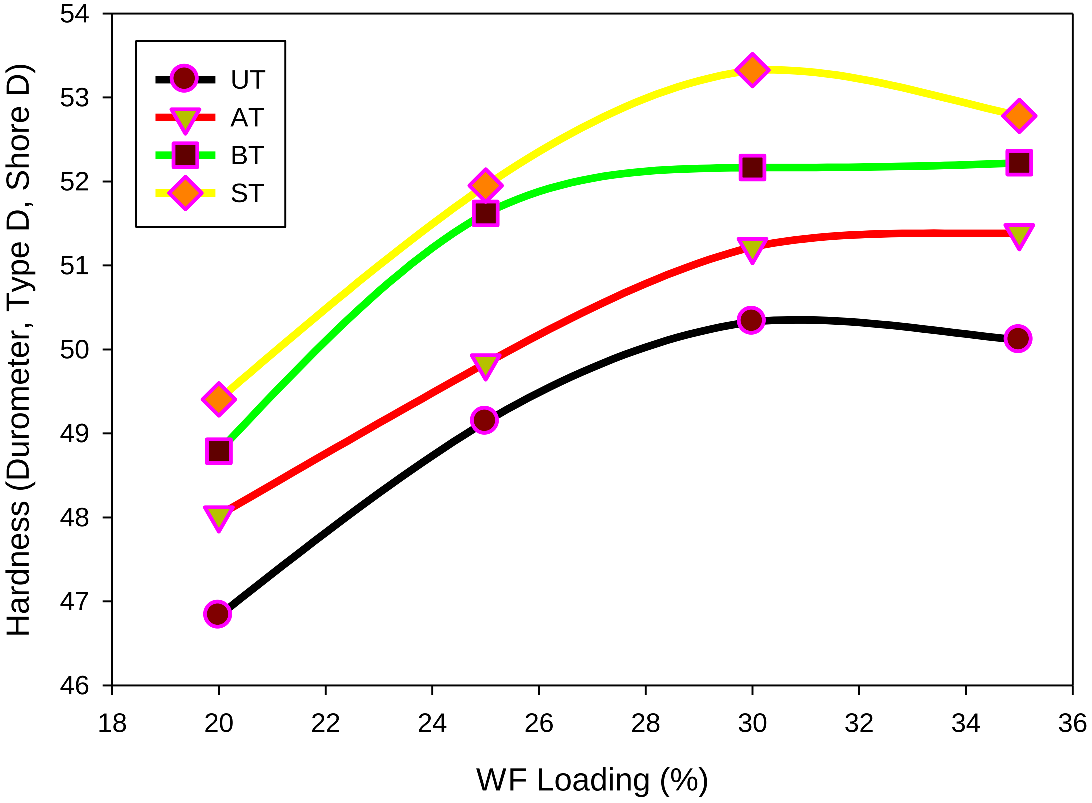

Fig. 5.5: Variation of hardness of recycled PE composites reinforced with untreated (UT), alkali treated (AT), benzoyl chloride treated (BT) and surfactant treated (ST) saw-dust (SD).

5.4.2 Izode Notched Impact Strength and Energy

Fig. 5.6 and 5.7 shows the variation of izode notched impact energy and strength of both treated and untreated SD-RPE composites as a function of filler content. It is evident in the both Figures that impact strength and energy are decreases with filler loading up to 35%. But the variation of energy and strength follows the order ST>BT>AT>UT. Higher values of impact strength and energy for treated SD reinforced composites (AT, BT, ST) could be due to more favorable interaction between the chemically modified filler and the matrix.

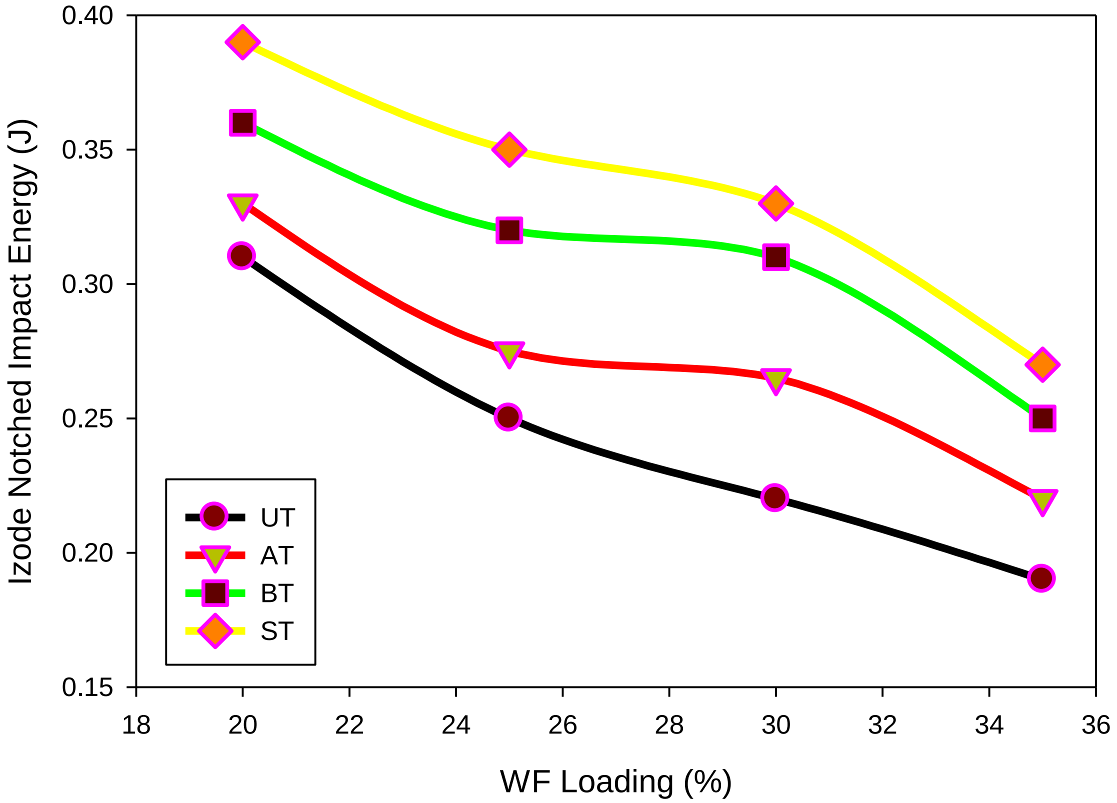

Fig. 5.6: Variation of izode notched impact energy of recycled PE composites reinforced with untreated (UT), alkali treated (AT), benzoyl chloride treated (BT) and surfactant treated (ST) saw-dust (SD).

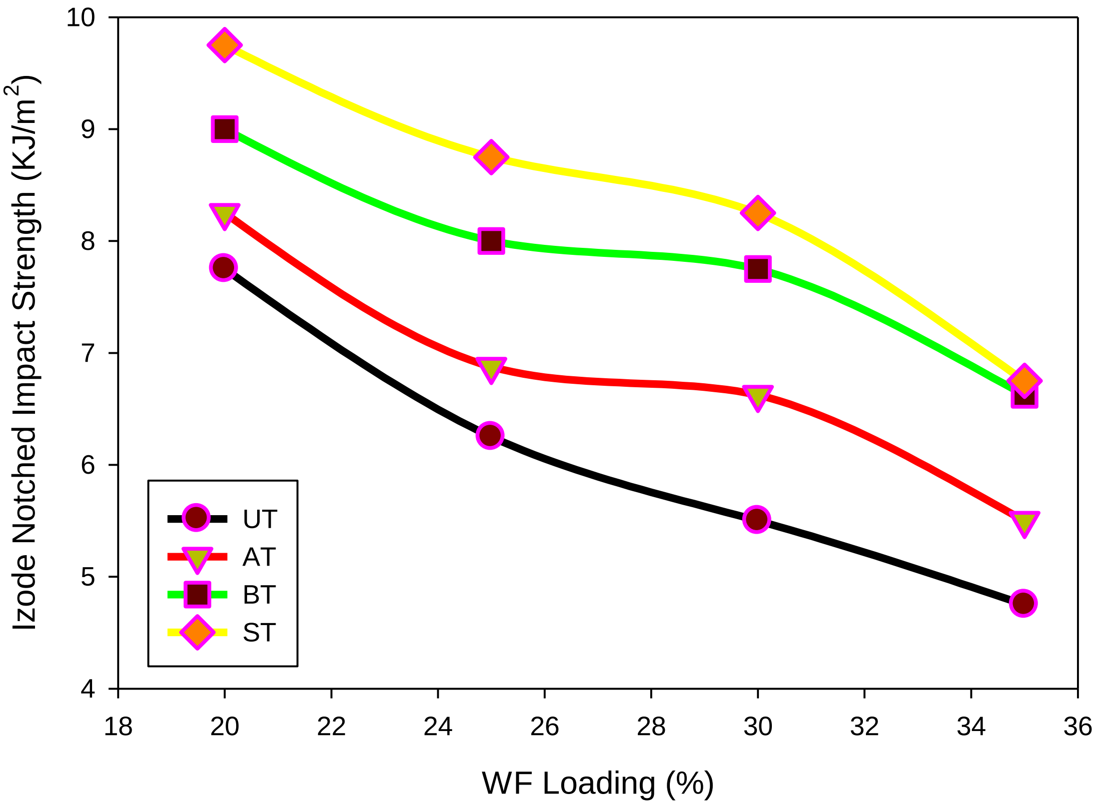

Fig. 5.7: Variation of izode notched impact strength of recycled PE composites reinforced with untreated (UT), alkali treated (AT), benzoyl chloride treated (BT) and surfactant treated (ST) saw-dust (SD).

5.4.3 Thickness Swelling Test

Thickness swelling behavior of UT, AT, BT and ST composites were showed in the Figure 5.8, where as their swelling order is found as UT>AT>BT>ST. Among these four types of composites ST composites showed lower thickness swelling i.e. 0.43663% in case of 25% filler loading. The thickness swelling behavior of ST composites increased very slightly with filler loading. On the other hand in the case of untreated and alkali treated composites this behavior increased slightly. It has also been found that the dimensional stability of CTAB treated composites is much higher than UT, AT and BT composites. The order of the dimensional stability of composites follow the order: ST>BT>AT>UT.

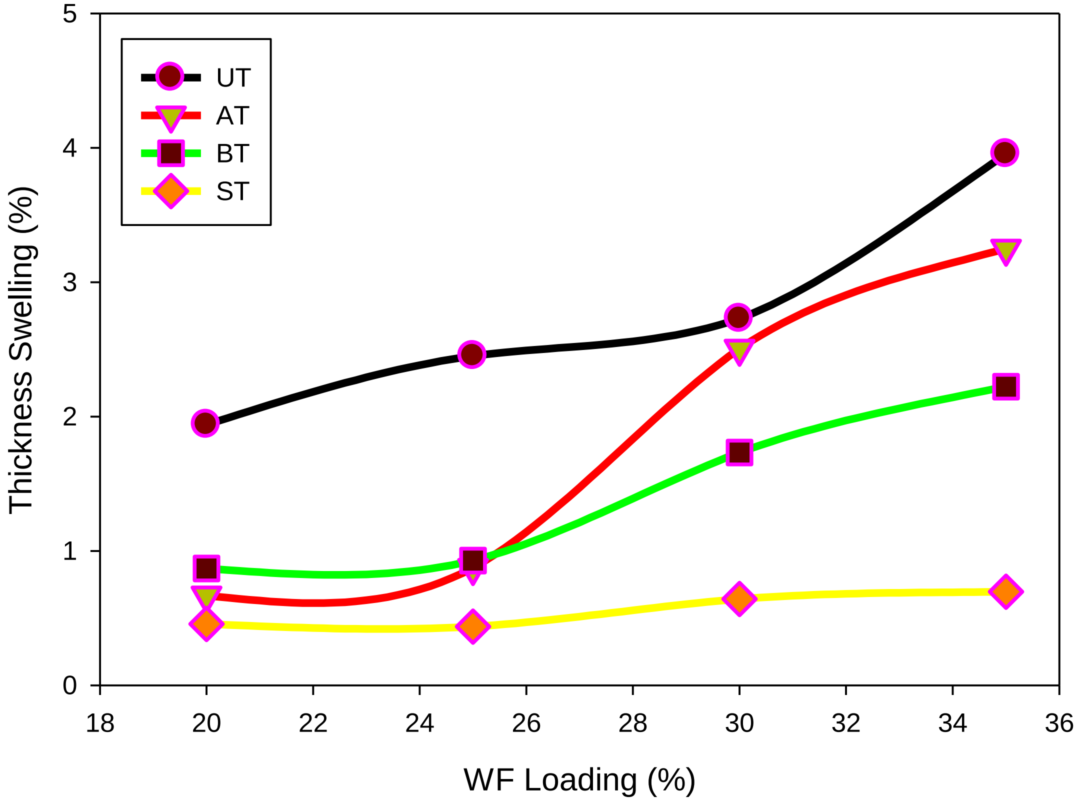

Fig. 5.8: Variation of thickness swelling of RPE composites reinforced with untreated (UT), alkali treated (AT) and benzoyl chloride treated (BT) SD filler.

5.4.4 Tensile Properties of WPCs

It is evident from the Figure 5.9 that the tensile strengths of both raw and chemically treated sawdust-RPE composites decreased gradually with an increase in filler loading. Increases in filler content increase the interfacial area and weaken the filler–matrix interaction, resulting in a decreasing trend of the tensile strength [53, 153, 157, 159]. The final results of tensile strength were found to follow this order: ST>BT>AT>UT.

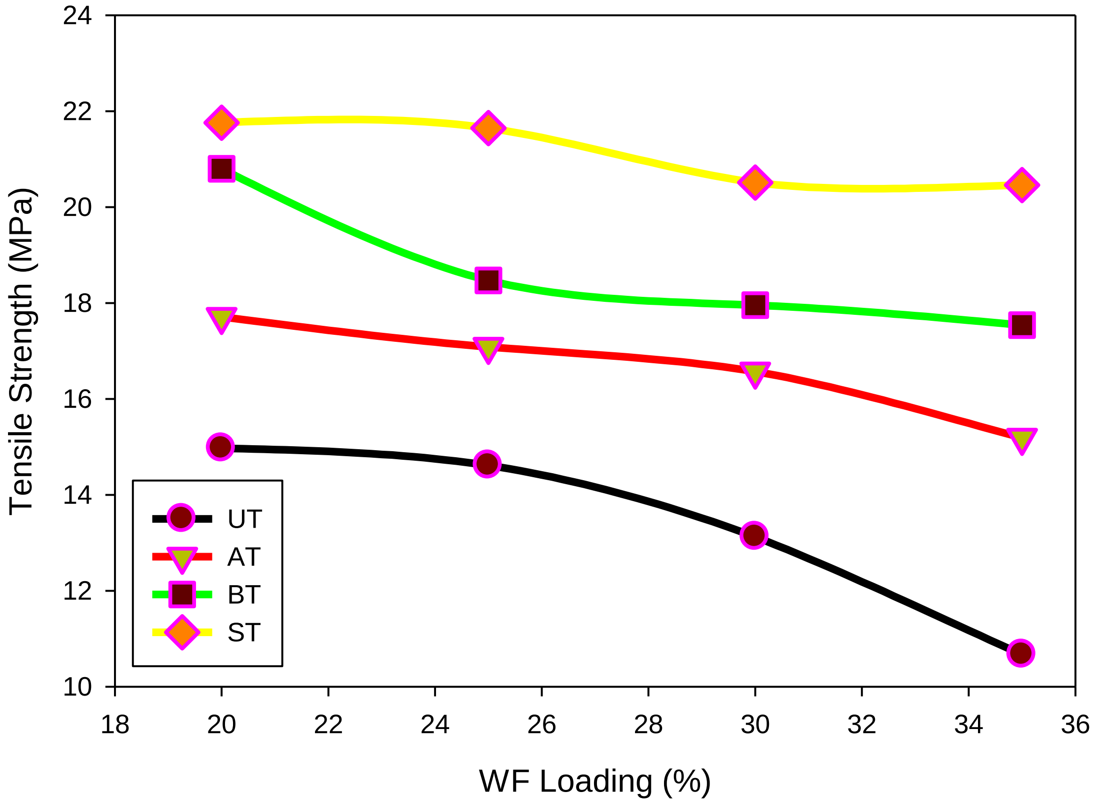

Fig. 5.9: Variation of tensile strength of recycled PE composites reinforced with untreated (UT), alkali treated (AT), benzoyl chloride treated (BT) and surfactant treated (ST) saw-dust (SD).

Fig. 5.10 shows the Young's modulus of the composites of raw and treated SD at different filler loading. It is clear in the figure that incorporation of fiber has significantly increased the modulus with increasing filler loading, as modulus is considered to be a linear function of filler concentration. The values of Young's modulus were found to follow this order: ST>BT>AT>UT.

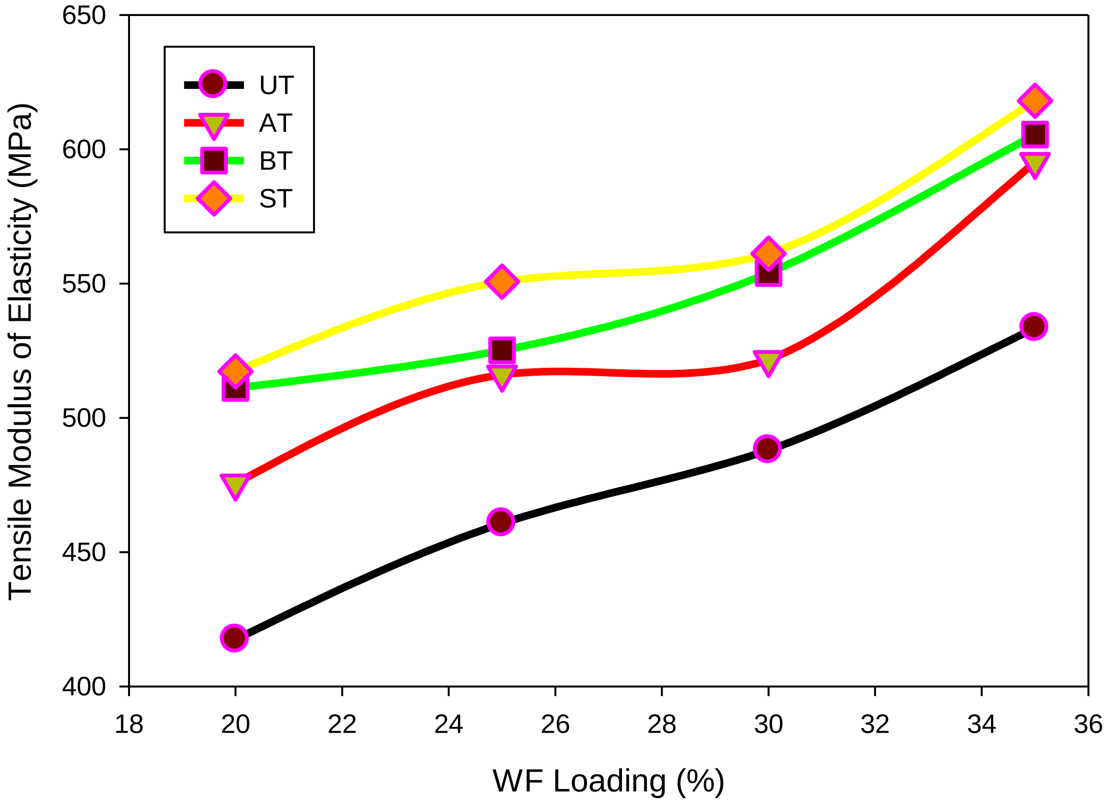

Fig. 5.10: Variation of tensile modulus of elasticity of recycled PE composites reinforced with untreated (UT), alkali treated (AT), benzoyl chloride treated (BT) and surfactant treated (ST) saw-dust (SD).

Figure 5.11 showed the elongation properties of raw and treated composites. The final result were found to follow this order ST>BT>AT>UT. This result follows the same trends like tensile strength. Elongation properties decreased with an increase in filler content.

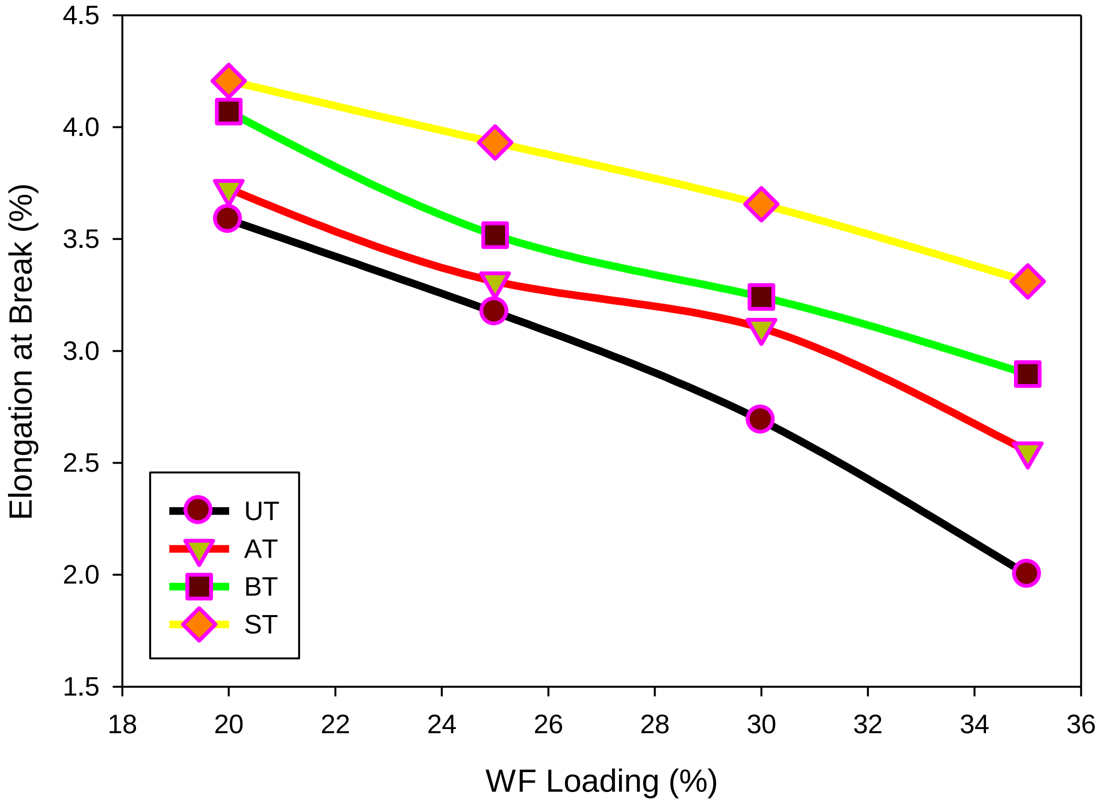

Fig. 5.11: Variation of elongation properties of recycled PE composites reinforced with untreated (UT), alkali treated (AT), benzoyl chloride treated (BT) and surfactant treated (ST) sawdust (SD).

5.4.5 Flexural Properties of WPCs

Flexural strength and flexural modulus of the composites of both raw and chemically treated SD reinforced RPE composites are shown in Fig. 5.12 and Fig. 5.13, respectively. In both cases, addition of fiber has increased the flexural strength and flexural modulus of the composites compared to neat RPE and VPE.

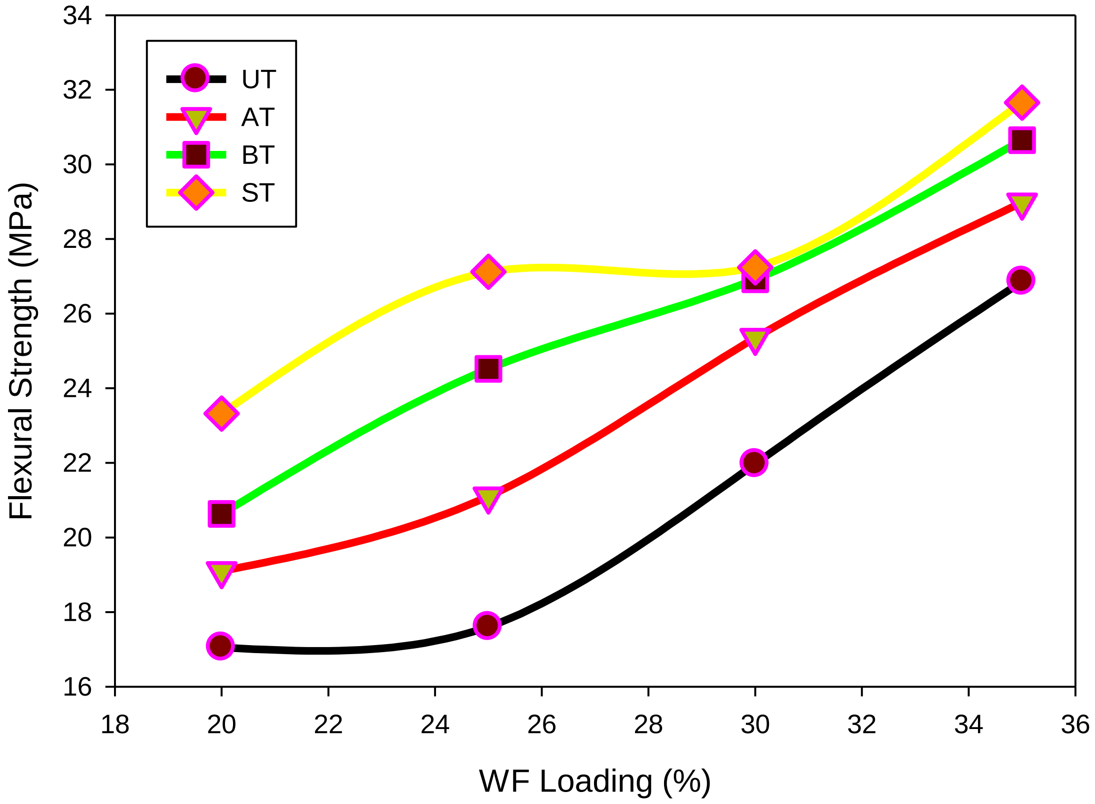

Fig. 5.12: Variation of flexural strength of RPE composites reinforced with untreated (UT), alkali treated (AT), benzoyl chloride treated (BT) and surfactant treated (ST) sawdust filler.

From the presented experimental results, it was found that effect of wood was notable in material properties of the composites. The addition of filler contents up to 35% increased both flexural strength and modulus for untreated and treated composites and their followed order is ST>BT>AT>UT.

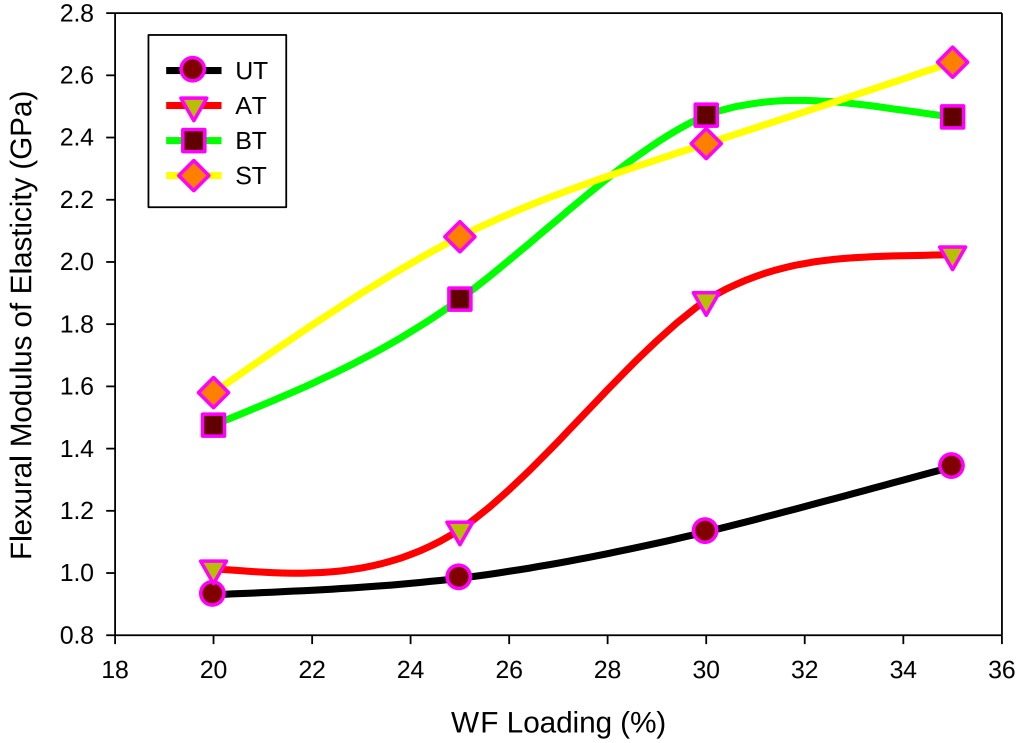

Fig. 5.13: Variation of flexural modulus of RPE composites reinforced with untreated (UT), alkali treated (AT), benzoyl chloride (BT) and surfactant treated (ST) sawdust filler.

5.5 Micro Structural Analysis of Fabricated Composites

The morphological features of tensile fractured surfaces of 35% sawdust reinforced RPE composites investigated by FESEM are shown in Fig. 5.14. It can be easily traced out that there are a number of agglomerations, resulting from strong fiber–fiber interaction and fiber pullout marks in the FESEM images of the untreated sawdust-RPE composite. This implies that there is poor interfacial bonding between the matrix and the untreated filler (image A). Alkali treated composites shows relatively lower fiber agglomeration and fiber pullout traces than untreated one (image B). These features suggest fiber-fiber interaction as well as interfacial bonding between the hydrophilic filler and the hydrophobic matrix is better than untreated one. Numerous cavities and pulled-out fibers can be seen extensively in the image A and relatively lower in B. The presence of these cavities and pulled-out fibers confirms that the interfacial bonding between the filler and the matrix polymer was poor and weak. In addition, localized bunch of fibers and patches of RPE matrix are seen, which indicates the poor dispersion of fillers within the RPE matrix.

It is evident from the both images C and D that fiber pullout traces and fiber agglomeration as well as the microvoids in the composites have significantly reduced in the composite upon treatment of sawdust with benzoyl chloride and CTAB. This result suggests that interfacial bonding between the filler and the matrix has become much stronger for treated sawdust and the matrix compared to that of the untreated one.

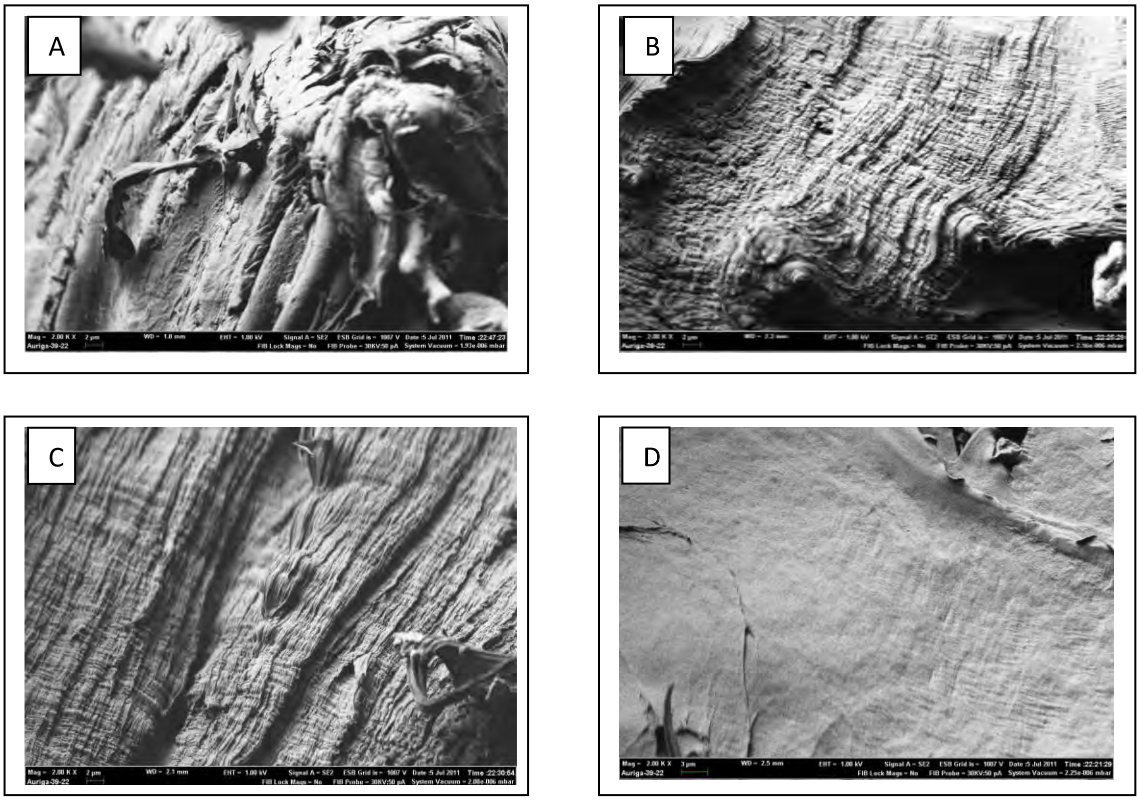

Figure 5.14: Field emission scanning electron microscopy (FESEM) images of RPE composites reinforced with 35% untreated (UT, A), alkali treatred (AT, B), benzoyl chloride treated (BT, C) and surfactant treated (ST, D) saw-dust.

5.6 Biodegradability Test

The biodegradability of the biocomposites was measured during natural soil burial test for three months. Figure 5.15 shows that the biodegradability of fabricated composites increased with filler loading and the untreated one showed greater degradation than treated one. The degradation behavior was found to follow this order: UT>AT>BT>ST. Among the chemically treated composites CTAB treated composites shows greater resistance to biodegradation by comparing with alkali and bezoyl chloride treated composites. In this work a comparative investigation of biodegradability between fabricated composites, 100% recycled PE and 100% virgin PE were conducted and it was found that RPE and VPE show no biodegradability under this experimental condition.

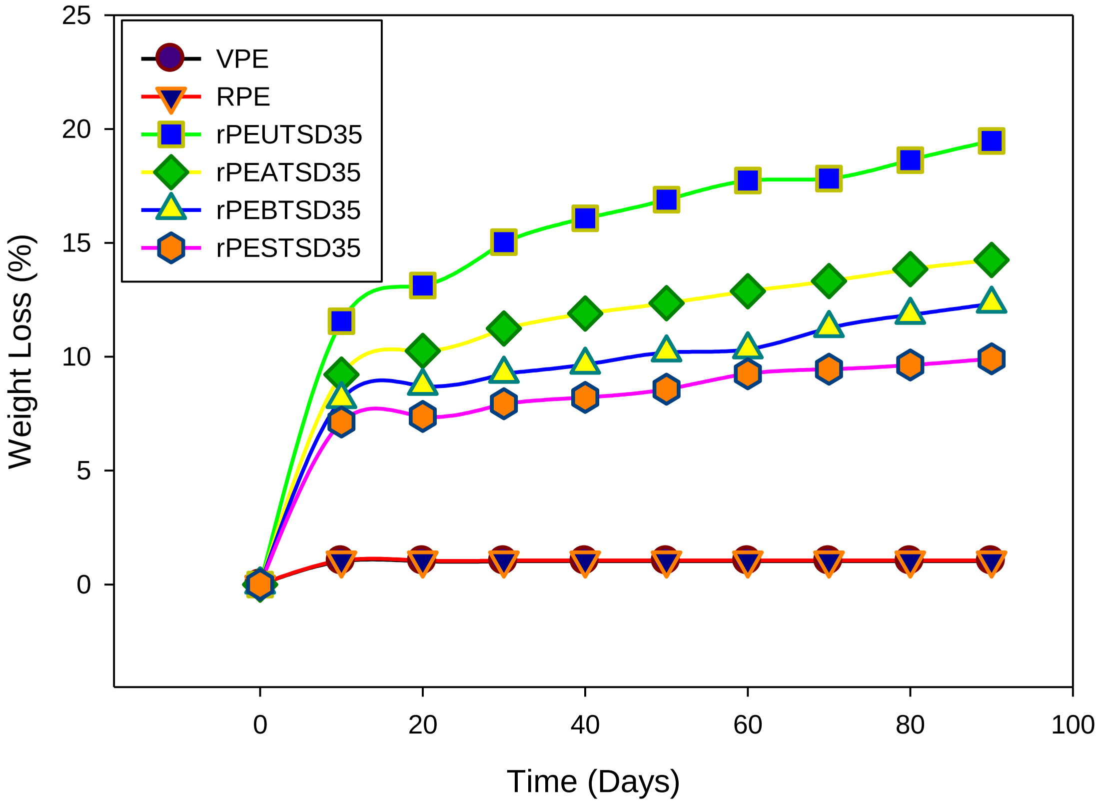

Fig. 5.15: Variation of biodegradability of RPE composites reinforced with untreated (UT), alkali treated (AT), benzoyl chloride treated (BT) and surfactant treated (ST) SD filler.

CHAPTER 06

CONCLUSIONS

Conclusions:

The aim of this study was to fabricate WPCs from RPE reinforced with biodegradable sawdust and develop chemical modification techniques improving mechanical properties of WPCs. Another aim of this study was to look for better application of SD which may help to develop the rural economy of Bangladesh. The third aim is to reduce the environmental pollution by using RPE as matrix of WPCs. The experimental determination and theoretical interpretation of a series of works on “Physico-Mechanical Properties of Recycled Polyethylene Composites Reinforced with Chemically Treated Saw-Dust” was conducted in this work.

Wood plastic composites (WPCs) were fabricated by using recycled polyethylene (RPE) reinforced with mixture of five different trees saw-dust (Pinus radiate) as filler. Post-consumer plastics and waste SD were used as raw materials. 100% pure PE specimens and 100% recycled PE specimens were also prepared for comparative studies. WPCs panels were made through extruder and injection moulding machine at different filler loading with recycled PE. Long and short term water absorption, thickness swelling, biodegradability, surface morphology (FESEM), mechanical and physical properties were examined. The used filler sawdust was treated at constant pH with sodium hydroxide, benzoyl chloride and CTAB to investigate the effect of chemical treatment on the physico-mechanical properties of fabricated composites.

The major findings drawn from these studies are explained in subsequent sections. It has been found that the RPE possesses slightly different properties than the virgin PE. From this study, it was found that sawdust can be successfully reinforced in RPE to produce stable and strong WPCs, which have properties similar or comparable to that made from virgin PE. Dimensional stability and strength properties of the composites can be improved by chemical modification of filler and increasing the polymer content. The experimental results further showed that the dimensional stability and the mechanical properties of the sawdust reinforced RPE composites could be optimized with an appropriate chemical treatment of the filler. In this study CTAB was found to be the best surface modifier among the three chemicals used. Therefore, WPCs with improved stability and mechanical properties have great potential to use as various engineering materials. The findings of this study are summarized below:

- **Tensile Properties:**

I. Tensile Strength: The Tensile strength values of CTAB treated sawdust reinforced RPE composites were found to be highest followed by benzoyl chloride treated, alkali treated and untreated sawdust reinforced RPE composites. The tensile strength of the composites decreased with an increase in sawdust content up to 35% in the case of raw and treated condition but the chemically treated sawdust reinforced RPE showed better physico-mechanical properties. However, the trend of tensile strength of the four types of WPCs follows the order: ST>BT>AT>UT compared to the RPE or VPE alone.

II. Young's Modulus: The Young's modulus of the composites followed the opposite trends with tensile strength which increased with an increase in filler loading. The trends of the Young's modulus were found to follow this order ST>BT>AT>UT.

III. Elongation at Break (EAB): Elongation properties of the fabricated composites were found to follow the same trends with tensile strength. This property decreased with an increase in filler loading but the chemically treated WPCs showed higher value than that of the untreated one. The order of these properties was found: ST>BT>AT>UT.

- **Flexural Properties:** Flexural strength and flexural modulus increased with an increase in filler loading. However the 35% filler loaded composites showed higher flexural strength and modulus values compared to that prepared from 20% sawdust. The trend of the flexural properties of the four types of fabricated composites was found to follow this order: ST>BT>AT>UT.

- **Izode Notched Impact Strength and Energy:** Izode notched impact strength and energy decreased with an increase in filler loading up to 35%. The lowest filler loaded WPC composites showed highest impact strength and impact energy. Here also chemically treated WPCs showed greater values than that of the untreated one. The followed order is found to be ST>BT>AT>UT.
- **Water Absorption Test:** The water absorption increased with the filler loading, whereas the surfactant treated SD-RPE composites absorbed lowest amount water compared to the untreated, alkalitreated and benzoylchloride treated composites. The trend of the water absorption test was found to follow the order: UT>AT>BT>ST.
- **Thickness Swelling Test:** It was observed that the chemically treated composites showed lowest thickness swelling than the untreated one. But the swelling behavior increased with an increase in filler loading in the case of both untreated and treated composites. Among the four types of composites CTAB treated composites showed better dimensional stability i.e. lowest thickness swelling compared to raw, alkali and benzoyl chloride treated composites. The final results of thickness swelling were found to follow the order: ST>BT>AT>UT.
- **Hardness Test:** Hardness of WPCs increased with an increase in filler loading up to 30% and decreased at 35% filler loaded composites. Among the four types of fabricated composites CTAB treated composites showed highest hardness than another three one. The final results of hardness were found to follow this order: ST>BT>AT>UT.

- **Biodegradability Test:** Biodegradability test of WPCs was conducted for three months. It was found that all the composites significantly degraded but the untreated one showed faster degradation within the time span of the experiment compared to those prepared from chemically treated sawdust. It was also found that the fabricated composites degraded significantly but virgin PE and RPE remained almost unchanged under the same experimental condition. So the fabricated composites can be considered to be environmentally friendly. The biodegradation behavior of the composites was found to follow the order: UT>AT>BT>ST.
- **Surface Morphology Analysis:** Surface morphology of fabricated composites was evaluated by field emission scanning electron microscopy (FESEM). It was found that untreated composites showed very rough surface, more cracked, defect, bunch and pullout symbols than treated one. Among the four types of composites, CTAB treated composites showed better surface smoothness than alkali treated; benzoyl chloride treated and untreated composites. The surface smoothness and fiber dispersion in the RPE matrix was found to follow order: ST>BT>AT>UT.

Plastic materials play an important role in our daily life in the form of a wide variety of household articles. As a result, in municipal solid waste all over the world plastics account for a significant amount made up of mostly polyethylene and polypropylene. Unregulated dumping, open burning and uncontrolled land filling are their common disposal methods particularly in developing countries. The present study reveals that both polyethylene-based polymeric waste and low-cost agricultural residues such as sawdust can be successfully used for the production of composites for engineering applications.

Table- 6.1: Comparative Study of Mechanical Properties of Chemically Treated Sawdust Reinforced Recycled Polyethylene Composites.

Type of Composites	UT C				ATC				BTC				STC			
SD Contents (%)	20	25	30	35	20	25	30	35	20	25	30	35	20	25	30	35
CWAT (24h)	0.458	0.654	0.978	1.305	0.458	0.654	0.978	1.305	0.281	0.394	0.879	1.203	0.221	0.349	0.530	0.658
CWAT (72h)	0.402	0.775	1.198	1.408	0.533	0.701	0.987	1.322	0.335	0.442	0.631	0.871	0.298	0.385	0.564	0.789
HWAT (24)	0.440	0.846	1.977	3.233	0.583	0.708	1.241	1.310	0.524	0.901	1.089	1.551	0.348	0.424	0.668	0.852
HWAT (72)	1.062	1.435	2.791	4.219	1.089	1.347	2.00	2.062	1.396	1.40	1.440	1.772	0.832	0.853	1.090	1.560
Hardness	46.83	49.14	50.33	50.11	48.02	49.83	51.22	51.38	48.78	51.61	52.16	52.22	49.40	51.95	53.32	52.78
Izode Impact Strength	7.75	6.25	5.50	4.75	8.25	6.875	6.625	5.5	9.0	8.0	7.75	6.625	9.75	8.75	8.25	6.75
Izode Impact Energy	0.310	0.250	0.220	0.190	0.330	0.275	0.265	0.220	0.360	0.320	0.310	0.250	0.390	0.350	0.330	0.270
Thickness Swelling	1.939	2.450	2.727	3.953	0.668	0.873	2.505	3.25	0.869	0.928	1.732	2.222	0.456	0.436	0.642	0.696
Tensile Strength	14.97	14.61	13.12	10.66	17.70	17.08	16.57	15.18	20.79	18.46	17.95	17.53	21.75	21.64	20.50	20.45
Tensile Modulus	417.4	460.7	487.9	533.4	475.5	516.0	521.5	595.2	511.1	525.0	553.8	605.4	517.2	550.6	561.0	618.0
Elongation at Break	3.586	3.172	2.689	2.000	3.724	3.310	3.103	2.551	4.068	3.517	3.241	2.896	4.206	3.931	3.655	3.310
Flexural Strength	17.05	17.60	21.97	26.86	19.10	21.10	25.35	28.98	20.63	24.52	26.92	30.65	23.32	27.12	27.24	31.66
Flexural Modulus	0.93	0.983	1.132	1.341	1.014	1.139	1.877	2.024	1.475	1.880	2.472	2.466	1.580	2.081	2.380	2.642

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APPENDIX

APPENDIX A: LIST OF CHEMICALS USED IN THIS WORK

List of using chemicals for the surface modification of SD

Chemicals	Mol. Formula	Mol. Wet.	Company	CAS No.	Assay (%)
Sodium Hydroxide	$NaOH$	40.00	Mercks	1310-73-2	>99.00
Distilled Water	H_2O	18.00	Self Produced	--	--
Benzoyl Chloride	C_6H_5COCl	140.57	Mercks	98-88-4	99.00
Hexadecyl trimethyl ammonium bromide	$CH_3(CH_2)_{15}$-$N(Br)(CH_3)_3$	364.45	Sigma Aldrich	57-09-0	99.99
Potassium hydroxide	KOH	56.11	Sigma-Aldrich	1310-58-3	85.00
Benzene	C_6H_6	78.11	Sigma -Aldrich	71-43-2	99.80
Ethanol	C_2H_5OH	46.07	Sigma-Aldrich	64-17-5	99.50
Ammonium oxalate	$C_2O_4(NH4)_2$	142.11	Sigma-Aldrich	6009-70-7	99.00
Sulphuric acid	H_2SO_4	98.08	Sigma-Aldrich	7664-93-9	95-98
Hydrochloric acid	HCl	36.46	Sigma-Aldrich	7647-01-0	37.00
Sodium chlorite	$NaClO_2$	90.44	Sigma-Aldrich	7758-19-2	80.00
Acetic acid	CH_3COOH	60.05	Sigma-Aldrich	64-19-7	>99.70
Sodium acetate	CH_3COONa	82.03	Sigma-Aldrich	127-09-3	99.00
Sodium metabisulfite	$Na_2S_2O_5$	190.11	Sigma-Aldrich	7681-57-4	97.00
Liquid soap	--	--	--	--	--
Detergent powder	--	--	Sigma-Aldrich	--	--
Bleaching powder	$Ca(OCl)Cl$	--	--	--	--
Calcium hypochlorite	$Ca(OCl)_2$	142.98	Sigma-Aldrich	7778-54-3	65.00
O-amino phenol	$H_2NC_6H_4OH$	109.13	Fluka	95-55-6	>99.00
P-aminophenol	$H_2NC_6H_4OH$	109.13	Aldrich	123-30-8	>98.00
M-aminophenol	$H_2NC_6H_4OH$	109.13	Aldrich	591-27-5	98.00
2,4-DNPH	$(O_2N)_2C_6H_3NHNH_2$	198.14	Sigma-Aldrich	119-26-3	97.00
Sodium nitrite	$NaNO_2$	69.00	Sigma-Aldrich	7632-00-0	97.00

APPENDIX B: MOLECULAR WEIGHT DETERMINATION

Molecular weight determination of untreated wood flour

Sample [g/100ml]	Time (t)second	Relative viscosity η/η_0=t/to	Specific viscosity $\eta/\eta_0-1=\eta_{sp}$	Reduced viscosity η_{sp}/C	Intrinsic viscosity $[\eta]$	Molecular weight
H_3PO_4	386.56	……	……	……	2.9	1,62,929.60
0.1	506.39	1.31	0.31	3.1		
0.2	641.68	1.66	0.66	3.3		
0.3	804.04	2.08	1.08	3.6		
0.4	974.13	2.52	1.52	3.8		
0.5	1140.35	2.95	1.95	3.9		

Calculation:

$[\eta] = KM^a$ ……………………………………………………3.13

$$\therefore M = \text{Antilog}\left[\log\frac{[\eta]}{K} \div a\right] \text{ ………………………………………3.20}$$

Here, K=1.78×10^5; a = 1.0; $[\eta]$=2.9, by using the equation 4.20 the molecular weight of UTSD was found to be 1,62,929.60

Molecular weight determination of alkali treated wood flour

Sample [g/100ml]	Time (t)second	Relative viscosity η/η_0=t/to	Specific viscosity $\eta/\eta_0-1=\eta_{sp}$	Reduced viscosity η_{sp}/C	Intrinsic viscosity $[\eta]$	Molecular weight
H_3PO_4	386.56	……	……	……	2.4	1,34,803.13
0.1	490.93	1.27	0.27	2.7		
0.2	610.76	1.58	0.58	2.9		
0.3	757.65	1.96	0.96	3.2		
0.4	912.28	2.36	1.36	3.4		
0.5	1082.36	2.80	1.80	3.6		

Molecular weight determination of benzoyl chloride treated wood flour

Sample [g/100ml]	Time (t)second	Relative viscosity η/η_0=t/to	Specific viscosity $\eta/\eta_0 -1= \eta_{sp}$	Reduced viscosity η_{sp}/C	Intrinsic viscosity $[\eta]$	Molecular weight
H_3PO_4	386.56	……	……	……	2.3	1,29,211.15
0.1	487.06	1.26	0.26	2.6		
0.2	603.03	1.56	0.56	2.8		
0.3	734.46	1.90	0.90	3.0		
0.4	881.35	2.28	1.28	3.2		
0.5	1063.04	2.75	1.75	3.5		

APPENDIX C: PHYSICAL PROPERTIES

Cool water absorption test (CWAT) of the wood flour-rPE composites

Sample Code	Type of Composites	Filler (g)	Resin(g)	CWAT (%), 24 hr	CWAT (%), 72hr
vPE100	n/a	0.00	100.00	0.060	0.090
rPE100	n/a	0.00	100.00	0.070	0.130
rPEUTWF20	UT	20.00	80.00	0.458	0.402
rPEUTWF25	UT	25.00	75.00	0.654	0.775
rPEUTWF30	UT	30.00	70.00	0.978	1.198
rPEUTWF35	UT	35.00	65.00	1.305	1.408
rPEATWF20	AT	20.00	80.00	0.4580	0.533
rPEATWF25	AT	25.00	75.00	0.6540	0.701
rPEATWF30	AT	30.00	70.00	0.9780	0.9870
rPEATWF35	AT	35.00	65.00	1.3050	1.3220
rPEBTWF20	BT	20.00	80.00	0.281	0.3357
rPEBTWF25	BT	25.00	75.00	0.394	0.4423
rPEBTWF30	BT	30.00	70.00	0.879	0.6318
rPEBTWF35	BT	35.00	65.00	1.203	0.8714
rPESTWF20	ST	20.00	80.00	0.221	0.2980
rPESTWF25	ST	25.00	75.00	0.349	0.3850
rPESTWF30	ST	30.00	70.00	0.530	0.5640
rPESTWF35	ST	35.00	65.00	0.658	0.7890

Hot water absorption test (HWAT) of the wood flour-rPE composites.

Sample Code	Type of Composites	Filler (g)	Resin(g)	HWAT (%), 24 hr	HWAT (%), 72hr
vPE100	n/a	0.00	100.00	0.070	0.101
rPE100	n/a	0.00	100.00	0.080	0.160
rPEUTWF20	UT	20.00	80.00	0.440	1.062
rPEUTWF25	UT	25.00	75.00	0.846	1.435
rPEUTWF30	UT	30.00	70.00	1.977	2.791

rPEUTWF35	UT	35.00	65.00	3.233	4.219
rPEATWF20	AT	20.00	80.00	0.583	1.089
rPEATWF25	AT	25.00	75.00	0.708	1.347
rPEATWF30	AT	30.00	70.00	1.241	2.001
rPEATWF35	AT	35.00	65.00	1.310	2.062
rPEBTWF20	BT	20.00	80.00	0.524	1.396
rPEBTWF25	BT	25.00	75.00	0.901	1.400
rPEBTWF30	BT	30.00	70.00	1.089	1.440
rPEBTWF35	BT	35.00	65.00	1.551	1.772
rPESTWF20	ST	20.00	80.00	0.348	0.832
rPESTWF25	ST	25.00	75.00	0.424	0.853
rPESTWF30	ST	30.00	70.00	0.668	1.090
rPESTWF35	ST	35.00	65.00	0.852	1.560

Thickness swelling of the wood flour-rPE composites

Sample Code	Type of Composites	Filler (g)	Resin (g)	T_i	T_f	$T_f - T_i$	Th. Swelling (%)
vPE100	n/a	0.00	100.00	4.00	4.01	0.00	0.00
rPE100	n/a	0.00	100.00	4.02	4.03	0.01	0.24875
rPEUTWF20	UT	20.00	80.00	4.64	4.73	0.09	1.93965
rPEUTWF25	UT	25.00	75.00	4.08	4.18	0.10	2.45098
rPEUTWF30	UT	30.00	70.00	4.40	4.52	0.12	2.72727
rPEUTWF35	UT	35.00	65.00	4.30	4.47	0.17	3.95348
rPEATWF20	AT	20.00	80.00	4.49	4.52	0.03	0.66815
rPEATWF25	AT	25.00	75.00	4.58	4.62	0.04	0.87336
rPEATWF30	AT	30.00	70.00	4.39	4.50	0.11	2.50569
rPEATWF35	AT	35.00	65.00	4.00	4.13	0.13	3.25000
rPEBTWF20	BT	20.00	80.00	4.60	4.64	0.04	0.86956
rPEBTWF25	BT	25.00	75.00	4.31	4.35	0.04	0.92807

rPEBTWF30	BT	30.00	70.00	4.04	4.11	0.07	1.73267
rPEBTWF35	BT	35.00	65.00	4.50	4.60	0.10	2.22222
rPESTWF20	ST	20.00	80.00	4.38	4.40	0.02	0.45662
rPESTWF25	ST	25.00	75.00	4.58	4.60	0.02	0.43668
rPESTWF30	ST	30.00	70.00	4.67	4.70	0.03	0.64239
rPESTWF35	ST	35.00	65.00	4.31	4.34	0.03	0.69605

Note: T_i = Thickness of the specimen before absorption, T_f= Thickness of the specimen after absorption

Sample Code	**Type of Composites**	**W_i**	**Percentage of weight loss per ten days intervals (W_L/10)**								
			10	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**
vPE100	n/a	1.0208	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
rPE100	n/a	1.0547	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
rPEUTWF20	UT	1.1890	09.6315	10.0526	10.4122	10.5701	11.0087	11.3859	11.4210	11.4561	11.5526
rPEUTWF25	UT	1.1705	09.2268	09.5856	10.0982	11.7642	12.1315	12.6612	12.9004	13.3618	13.6010
rPEUTWF30	UT	1.1400	08.9907	10.5634	11.2531	12.0941	12.4137	12.6576	13.8772	14.8444	15.1219
rPEUTWF35	UT	1.2760	11.5595	13.1269	15.0313	16.0815	16.8965	17.7351	17.8213	18.6363	19.4749
rPEATWF20	AT	1.1425	07.1213	07.8041	07.9562	08.1542	08.2741	08.4527	08.5647	08.6748	8.75460
rPEATWF25	AT	1.1935	08.1761	08.6125	08.9521	09.2156	09.5621	09.8754	10.6548	10.9745	11.2564
rPEATWF30	AT	1.2249	08.4245	09.2145	09.8513	10.2135	10.6523	10.9014	11.6745	11.9852	12.3543
rPEATWF35	AT	1.2215	09.2147	10.2541	11.2364	11.8975	12.3514	12.8745	13.3214	13.8459	14.2513
rPEBTWF20	BT	1.1250	06.1325	06.4125	06.9514	07.1123	07.3458	07.6012	07.7548	07.8741	7.94680
rPEBTWF25	BT	1.1688	07.2213	07.4180	07.2159	07.9847	08.2154	08.7584	08.9754	09.4195	9.74560
rPEBTWF30	BT	1.2470	07.5784	07.9124	08.2465	08.5874	08.8475	09.2145	09.2653	09.6451	10.2354
rPEBTWF35	BT	1.2500	08.1425	08.7231	09.2549	09.6514	10.1874	10.3214	11.2589	11.8387	12.3256
rPESTWF20	ST	1.1358	04.2513	04.6043	05.2314	06.3834	06.5834	06.7514	06.9521	07.0251	7.22190
rPESTWF25	ST	1.1800	05.1322	05.4384	05.6249	05.9704	06.9352	07.1450	07.5547	08.0214	8.39870
rPESTWF30	ST	1.2623	06.5874	06.9603	07.2301	07.6750	08.0024	08.2314	08.7904	09.2010	9.36540
rPESTWF35	ST	1.2646	07.1327	07.3807	07.9368	08.2153	08.5742	09.2549	09.4521	09.6351	9.91020

APPENDIX D: MECHANICAL PROPERTIES

Tensile strength, Elongation at Break (EAB) and Young's modulus (MOE) of WF-rPE composites

Composites Details				Tensile properties		
Sample Code	Type of Composites	Filler (g)	Resin (g)	Strength (MPa)	MOE (GPa)	EAB (%)
vPE100	n/a	0.00	100.00	10.575	0.55396	10.900
rPE100	n/a	0.00	100.00	12.425	0.57948	11.500
rPEUTWF20	UT	20.00	80.00	14.9719	417.4885	3.5862
rPEUTWF25	UT	25.00	75.00	14.6157	460.7217	3.1724
rPEUTWF30	UT	30.00	70.00	13.1250	487.9800	2.6896
rPEUTWF35	UT	35.00	65.00	10.6690	533.4500	2.000
rPEATWF20	AT	20.00	80.00	17.7094	475.5190	3.7241
rPEATWF25	AT	25.00	75.00	17.0844	516.0790	3.3103
rPEATWF30	AT	30.00	70.00	16.5720	521.5680	3.1034
rPEATWF35	AT	35.00	65.00	15.1890	595.2440	2.5517
rPEBTWF20	BT	20.00	80.00	20.7969	511.1120	4.0689
rPEBTWF25	BT	25.00	75.00	18.4688	525.0990	3.5172
rPEBTWF30	BT	30.00	70.00	17.9530	553.8690	3.2413
rPEBTWF35	BT	35.00	65.00	17.5367	605.4350	2.8965
rPESTWF20	ST	20.00	80.00	21.7594	517.2220	4.2068
rPESTWF25	ST	25.00	75.00	21.6470	550.6690	3.9310
rPESTWF30	ST	30.00	70.00	20.5090	561.0950	3.6551
rPESTWF35	ST	35.00	65.00	20.4590	618.0320	3.3103

Calculation:

$$\sigma_T = \frac{F}{A} \tag{3.23}$$

$$E_M = \frac{FL}{A\Delta L} \tag{3.24}$$

In the above two equations 3.23 and 3.24

σ_T = Tensile strength; F = Maximum load; A = Area (width × thickness); E_M = Modulus of elasticity; L = Original length of specimen sample

ΔL = Stroke or length of the object changes

In case of VPE: $\sigma_T = \frac{F}{A} = \frac{0.480}{10 \times 4} = 0.012$ GPa and $E_M = \frac{0.480 \times 145.00}{40 \times 5.7} = 0.305$ GPa

Variation of flexural strength and flexural MOE of wood flour reinforced rPE composites at different chemical treatment with untreated one.

Composites Details				**Flexural Properties**	
Sample Code	Type of Composites	Filler (g)	Resin (g)	Strength (MPa)	MOE (GPa)
vPE100	n/a	0.00	100.00	14.1703	0.8020
rPE100	n/a	0.00	100.00	16.9218	0.8190
rPEUTWF20	UT	20.00	80.00	17.05	0.9300
rPEUTWF25	UT	25.00	75.00	17.60	0.9830
rPEUTWF30	UT	30.00	70.00	21.97	1.1320
rPEUTWF35	UT	35.00	65.00	26.86	1.3410
rPEATWF20	AT	20.00	80.00	19.10	1.0140
rPEATWF25	AT	25.00	75.00	21.10	1.1390
rPEATWF30	AT	30.00	70.00	25.35	1.8770
rPEATWF35	AT	35.00	65.00	28.98	2.0240
rPEBTWF20	BT	20.00	80.00	20.63	1.4754
rPEBTWF25	BT	25.00	75.00	24.52	1.8801
rPEBTWF30	BT	30.00	70.00	26.92	2.4720
rPEBTWF35	BT	35.00	65.00	30.65	2.4661
rPESTWF20	ST	20.00	80.00	23.32	1.5800
rPESTWF25	ST	25.00	75.00	27.12	2.0810
rPESTWF30	ST	30.00	70.00	27.24	2.3801
rPESTWF35	ST	35.00	65.00	31.66	2.6420

Calculation:

$$\sigma_f = \frac{3PL}{2bd^2} \quad \text{(3.25)}$$

$$E_B = \frac{L^3 m}{4bd^3} \quad \text{(3.26)}$$

In Equations (3.25) and (3.26),

σ_f is the flexeral Strength or the stress in the outer layer at mid-length point of the specimens

E_B is the flexural modulus of elasticity of the specimens in bending tests

P is the load at the loading point (mid-length)

L is the supporting span of the specimen, mm

b is the width of the specimens in perpendicular to the loading direction, mm

d is the depth of specimens tested in parallel to the loading direction, mm

m is the slope of the initial linear portion of the load deflection curve

In the case of VPE the value of FS and FM are shown in the following calculation:

$$\sigma_f = \frac{3PL}{2bd^2} = \frac{3 \times 0.03023 \times 50}{2 \times 10 \times 4 \times 4} = 0.0141 \text{ GPa}$$

$$E_B = \frac{L^3 m}{4bd^2} = \frac{50 \times 50 \times 50 \times 0.0041}{4 \times 10 \times 4 \times 4} = 0.802 \text{ GPa}$$

Variation of impact behavior of wood flour reinforced rPE composites at different chemical treatment with untreated one.

Composites Details				**Izode Impact Strength and Energy**	
Sample Code	Type of Composites	Filler (g)	Resin (g)	Strength (KJ/m^2)	Energy (J)
vPE100	n/a	0.00	100.00	17.90	0.716
rPE100	n/a	0.00	100.00	21.40	0.856
rPEUTWF20	UT	20.00	80.00	7.750	0.310
rPEUTWF25	UT	25.00	75.00	6.250	0.250
rPEUTWF30	UT	30.00	70.00	5.500	0.220
rPEUTWF35	UT	35.00	65.00	4.750	0.190
rPEATWF20	AT	20.00	80.00	8.250	0.330
rPEATWF25	AT	25.00	75.00	6.875	0.275
rPEATWF30	AT	30.00	70.00	6.625	0.265
rPEATWF35	AT	35.00	65.00	5.500	0.220
rPEBTWF20	BT	20.00	80.00	9.000	0.360
rPEBTWF25	BT	25.00	75.00	8.000	0.320
rPEBTWF30	BT	30.00	70.00	7.750	0.310

rPEBTWF35	BT	35.00	65.00	6.625	0.250
rPESTWF20	ST	20.00	80.00	9.750	0.390
rPESTWF25	ST	25.00	75.00	8.750	0.350
rPESTWF30	ST	30.00	70.00	8.25	0.330
rPESTWF35	ST	35.00	65.00	6.75	0.270

Variation of hardness behavior of wood flour reinforced rPE composites at different chemical treatment with untreated one.

Sample Code	**Type of Composites**	**Filler (g)**	**Resin(g)**	**Hardness (Shore D)**
vPE100	n/a	0.00	100.00	45.0000
rPE100	n/a	0.00	100.00	45.9320
rPEUTWF20	UT	20.00	80.00	46.8300
rPEUTWF25	UT	25.00	75.00	49.1400
rPEUTWF30	UT	30.00	70.00	50.3300
rPEUTWF35	UT	35.00	65.00	50.1100
rPEATWF20	AT	20.00	80.00	48.0251
rPEATWF25	AT	25.00	75.00	49.8350
rPEATWF30	AT	30.00	70.00	51.2200
rPEATWF35	AT	35.00	65.00	51.3829
rPEBTWF20	BT	20.00	80.00	48.7863
rPEBTWF25	BT	25.00	75.00	51.6183
rPEBTWF30	BT	30.00	70.00	52.1660
rPEBTWF35	BT	35.00	65.00	52.2220
rPESTWF20	ST	20.00	80.00	49.4057
rPESTWF25	ST	25.00	75.00	51.9520
rPESTWF30	ST	30.00	70.00	53.3240
rPESTWF35	ST	35.00	65.00	52.7810

APPENDIX E: MISCELLANEOUS PROPERTIES

Density of fabricated composites and polyethylene (recycled and virgin)

Sample Code	Type of Composites	Filler (g)	Resin(g)	Wet. of specimen ($39\times10\times4$ mm^3)	Density (g/cc)
vPE100	n/a	0.00	100.00	1.0206	0.654230
rPE100	n/a	0.00	100.00	1.0647	0.682500
rPEUTWF20	UT	20.00	80.00	1.1973	0.767500
rPEUTWF25	UT	25.00	75.00	1.1779	0.755064
rPEUTWF30	UT	30.00	70.00	1.1491	0.736602
rPEUTWF35	UT	35.00	65.00	1.2907	0.827371
rPEATWF20	AT	20.00	80.00	1.1425	0.732371
rPEATWF25	AT	25.00	75.00	1.1935	0.765064
rPEATWF30	AT	30.00	70.00	1.2249	0.785192
rPEATWF35	AT	35.00	65.00	1.2215	0.783012
rPEBTWF20	BT	20.00	80.00	1.2004	0.769487
rPEBTWF25	BT	25.00	75.00	1.2082	0.774487
rPEBTWF30	BT	30.00	70.00	1.2203	0.782243
rPEBTWF35	BT	35.00	65.00	1.2691	0.813525
rPESTWF20	ST	20.00	80.00	1.1358	0.728076
rPESTWF25	ST	25.00	75.00	1.1800	0.756410
rPESTWF30	ST	30.00	70.00	1.2623	0.809166
rPESTWF35	ST	35.00	65.00	1.2646	0.810641

Melt flow index data for rPE and vPE

Si. No.	Resin/Matrix	Melt Flow Rate (g/10 min)
1	Recycled Polyethylene (rPE)	0.136
2	Virgin Polyethylene (vPE)	0.302

APPENDIX F: AUTHOR VITA

Mr. Md. Sakinul Islam was born on 18 August, 1979 in Village- Nando, P.O- Walia, P.S-Lalpur, Natore, Bangladesh to Festus Mr. Md. Year uddin and Mrs. Sahera Begum. He graduated with a Bachelor of Science and Masters of Science degrees from the Department of Applied Chemistry and Chemical Technology, Islamic University, Kushtia 7003, Bangladesh in 2003 and 2005 respectively. After a year of teaching service, he entered as an M. Phil researcher in the department of Chemistry, under the faculty of Engineering at BUET, Dhaka, Bangladesh.

This thesis was typed by the author and the university is fully concern about this hypothesis which entitled as "Physico-Mechanical Properties of Recycled Polyethylene Composites Reinforced with Chemically Treated Saw-Dust".

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APPENDIX G: LIST OF PUBLICATIONS

Research article

Md. Nazrul Islam and Md. Sakinul Islam, Mechanical properties of Chemically Treated SD-Reinforced Recycled Polyethylene Composites, *Industrial and Engineering Chemistry research*, Published by ACS, In Press,)

Haque, Mominul[1]; Islam, Nazrul[2]; Huque, Monimul[2]; Hasan, Mahbub[3]; Islam, Saiful[2]; **Islam, Sakinul[2]**; Coir Fiber Reinforced Polypropylene Composites: Physical and Mechanical Properties; Advanced composites materials; Vol. 19, No. 1, pp. 91-106 (16), 2010.

Md. Mominul Haque[1], Md. Saiful Islam[1], Md. Sakinul Islam[1], Md. Nazrul Islam[1], Md. Monimul Huque[1] and Mahbub Hasan, PhD[2*], Physico-Mechanical Properties of Chemically Treated Palm Fiber Reinforced Polypropylene Composites, Journal of reinforced plastics and composites, vol. 29, No. 11, 1734-1742, 2010.

Conferences Presentation

Md. Sakinul Islam[a*], Md. Mominul Haque[b], Md. Monimul Huque[c], Md. Nazrul Islam[d] & Ahmed Sharif[e]., Effect of particle size and chemical treatment on wood flour reinforced polypropylene (PP) composites, Bangladesh chemical congress-2008, pp-94.

Md. Mominul Haque[*a], **Md. Sakinul Islam[b],** Md. Nazrul Islam[c], Md. Monimul Huque[d] & Mahbub Hasan[e], Mechanical properties of chemically treated coir fiber reinforced polypropylene composites, Bangladesh chemical congress-2008, pp-94.