

STUDIES OF THE PHYSICO-MECHANICAL PROPERTIES OF CHEMICALLY
TREATED WOOD FIBER-REINFORCED POLYPROPYLENE COMPOSITES

BY

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SESSION: APRIL 2008

A DISSERTATION SUBMITTED

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF PHILOSOPHY (M. PHIL.) IN CHEMISTRY



POLYMER RESEARCH LABORATORY

DEPARTMENT OF CHEMISTRY

FACULTY OF ENGINEERING

BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY

DHAKA-1000, BANGLADESH

MARCH 2013

BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY

DHAKA-1000, BANGLADESH

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THESIS APPROVAL

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MY BELOVED PARENTS, LATE UNCLE AND FAMILY MEMBERS

ACKNOWLEDGEMENT

I express my deepest sense of gratitude and indebtedness to my thesis supervisor Professor **Dr. Md. Monimul Huque**, Department of Chemistry, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh for his invaluable guidance, thoughtful suggestions, constant encouragement and infinite patience throughout my research work.

I am very grateful to Prof. Dr. Shakila Rahman, Head, Department of Chemistry, BUE for her kind cooperation and sympathy during this whole period of work.

I like to acknowledge Jagannath University authority, specially, Prof. Dr. Md. Sirazul Islam Khan, former Vice-Chancellor of Jagannath University, Dhaka, Bangladesh for his kind permission to peruse the M. Phil. degree in the Department of Chemistry, BUET as a part-time student beside a full time faculty member in Department of Chemistry, Jagannath University, Dhaka, Bangladesh.

I shall be ever grateful, deeply indebted and extremely pleased to expressing my deepest thanks with respect to my respected teachers Prof. Dr. Md. Manwarul Islam, Prof. Dr. Md. Rafiq Ullah, Prof. Dr. Al Nakib Chowdhury and Assoc. Prof. Dr. Md. Nazrul Islam, Department of Chemistry, BUET, Dhaka, Bangladesh for their teaching in theoretical courses, continuous inspiration, occasional help, valuable advice and keen interest through the preparation of this thesis.

I am also grateful to Prof. Dr. Md. Wahab Khan, Department of Chemistry, BUET for his cordial cooperation in recording FT-IR spectra and allowing me to use his laboratory facilities.

I am most indebted to Prof. A. I. Mostafa, Chairman, BCSIR, Dhaka, Bangladesh for his kind permission to use the laboratory facilities.

My sincere thanks to Dr. Md. Abdul Gafur, SSO and PD in PP & PDC, BCSIR, Dhaka, Bangladesh for his cordial and constant help during sample analysis in his Laboratory.

Thanks to Dr. Most. Hosney Ara Begum, Senior Engineer, PP & PDC, BCSIR, Dhaka, Bangladesh for her help during thermal analysis of samples. I also thank Mr. Rakib, SO, PP & PDC, BCSIR, Dhaka, Bangladesh for various cooperation during my work in the laboratory.

My pleasant thanks to Md. Hakim, Abu Bakar Patwary, Md. Kabir, Md. Soakat, Md. Mamun or Rashid, Rasul, Alamgir Hossain and all other staffs of Department of Chemistry, BUET for helping me at various stages.

I am thankful to my colleagues and co-workers for their help, inspiration and constructive suggestion to complete this work successfully.

I can't forget my father, mother, brothers, sisters and other family members for their constant love, sacrifice and support in my research work. Thanks to my relatives specially my father in law, mother in law and sister in laws for their encouragement regarding higher studies.

My friends and well-wishers inspired me a lot during the study period which helped me to reach to the final stage of M. Phil. study.

I am grateful to my wife who gave me the moral support always and extended her hands all the times regarding this research. She accompanied me many times even in the laboratory at night when needed and I was alone. Finally, I greatly dedicate this work to my beloved parents and late uncle for their constant love and inspiration and sacrificed in my whole life that helped me to reach at this stage of life.

Author

ABBREVIATIONS

PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl Chloride
KPa	Kilo Pascal
MPa	Mega Pascal
GPa	Giga Pascal
PSI	Per Square Inch
WPC	Wood Plastic Composite
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
TG	Thermo Gravimetry
TGA	Thermo Gravimetric Analysis
DTA	Differential Thermal Analysis
DTG	Derivative Thermo Gravimetry
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infra-Red
ASTM	American Society for Testing and Materials
e. g.	example gratia
<i>et al</i>	and others

ABSTRACT

Wood plastic composites (WPCs) have been popular day by day in Bangladesh as well as in the whole world and have characteristics similar or close to commercial wood. In this research work, different types of soft wood reinforced polypropylene (PP) composites were prepared by injection moulding technique. To prepared improved sawdust-PP composites by chemical treatment, 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. The effects of treatments on the physico-mechanical properties of composites were studied. Untreated raw sawdust was modified by sodium hydroxide and the effect of alkali treated sawdust reinforced PP composites was studied comparing with the raw sawdust-PP composites. FT-IR spectroscopic analyses were done for chemical treatment and results showed the evidence of positive reactions. The effects of fiber content on the physico-mechanical properties of composites were studied by preparing the composites with different percentage of fiber loading (from 20 wt.% to 35 wt.%) for each type of composites. Mechanical properties; tensile strength, tensile modulus, elongation at break, flexural strength, flexural modulus and hardness were measured for both alkali treated sawdust-PP composites and raw sawdust-PP composites. Improved mechanical properties were obtained for most of the treated sawdust-PP composites over untreated raw sawdust-PP composites.

Thermal analysis was done with the fractured part of the composite specimens and increased thermal stability was found for alkali treated sawdust-PP composites compared to that of raw sawdust-PP composites.

Scanning Electron Microscopy (SEM) and water absorption test were done to study the physical properties of both types of composites. SEM was taken to investigate the interfacial adhesion and bonding between the sawdust and PP matrix from various chemical treatments. Improved interfacial interactions were found for treated composites than untreated composites.

Water absorption tests were carried out of all composites to investigate the effect of chemical treatment on the moisture absorption characteristics of hydrophilic sawdust in sawdust-PP composites which has direct effect on the dimensional stability of the composites. Reduced water absorption was found for alkali treated sawdust-PP composites. All the findings are reported in details in this thesis.

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CHAPTER 01

INTRODUCTION

1.1 Introduction

Wood plastic composites (WPCs) were prepared in this research by using polypropylene (PP) and sawdust as reinforcing material. The term composite means a substance, which is made up by mixing two or more distinct different substances. The use of natural fibers, more precisely wood as sawdust, thanks to their fibrous structure, as reinforcement of polymer materials is becoming more and more interesting. A technique commonly employed to improve the mechanical properties of polymers is to add short or long reinforcing fibers. In this way stresses on the composite materials are transmitted via the fiber-polymer matrix interface to the reinforcing fibers which enhance the stiffness and strength of the materials. Polymer composites consist of one or more discontinuous phases embedded in a continuous-phase polymer matrix. The discontinuous phase is usually harder and stronger than the continuous phase, and is called reinforcement. The matrix can be classified as thermoplastic (capable of being separately hardened and softened by the decrease and increase of temperature respectively) or as thermoset (changing into a substantially infusible and insoluble material when cured by the application of heat or through chemical means).¹ Over the last few years, a good number of reports have appeared in the literature on thermoplastic polymer composites reinforced with natural fiber.²⁻⁹ Natural fiber reinforced polymer composites have attract much attention as they are cheap, light weight, environment friendly and non-abrasive in nature.¹⁰ The advantage of using lignocellulosic materials also include high specific stiffness and mechanical strength.¹¹ WPCs are emerging as one of the dynamic growth materials in the building industry.

Synthetic fibers such as glass, graphite (carbon), boron, organic, metallic and ceramics are commonly used in reinforcements for

plastics. These materials are heavy, expensive and harmful to the environment. Lignocellulosic fibers offer many advantages over these most commonly used synthetic fibers as filler reinforcement in thermoplastic matrix. The replacement of inorganic fillers with comparable lignocellulosic fibers provides less weight and decreases the cost without reducing the mechanical properties of the composites.¹² Any substance that contains both cellulose and lignin is a lignocellulosic material which includes wood as sawdust, agricultural crops like jute, kenaf, sisal etc.; agricultural residues such as bagasse, corn stalks, rice husk etc. and also other plant materials. Generally, what is true for sawdust is also true for lignocellulosic materials even though they may differ in chemical composition and matrix morphology.¹³

The processing temperature of the lignocellulosic fibers in thermoplastics is limited due to fiber degradation at higher temperatures. Thus the plastics that can be used with it are limited to those with low melting temperatures. In general, no deterioration of properties due to fiber degradation occurs when processing temperatures are maintained below 200°C for short periods.¹⁰ These thermoplastics include polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), low-density polyethylene (LDPE) and high-density polyethylene (HDPE). The most common polyolefin used to prepare composites is PP, a commodity polymer.¹⁴ PP provides most of the advantages with regards to economic (price), ecological (recycling behavior) and technical requirements (higher thermal stability like HDPE).¹⁵ PP is a semicrystalline polymer and its property and classification depends on its percentage of crystallinity. The melting temperature of commercial PP lies in the range 160-170°C, with purified polymer reaching 176°C.¹⁶ Commercial isotactic PP was used in this research and its melting

point was found 160°C. Isotactic structure of this PP was confirmed by FT-IR spectroscopy.

WPC was manufactured by dispersing sawdust into PP mesh 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 sawdust that was used for Roll-Rayce gearshift knob in 1916, and it was reborn as a modern concept in Italy in 1970s and popularized in North America in early 1990s.¹⁷ 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 PP and sawdust.¹⁸

Since then production and market demand for the WPCs have been growing rapidly worldwide. The share in North America 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.¹⁹ It is expected to increase about 500 million pounds over the next ten years in UK and other European markets.²⁰

Currently WPCs are mainly used as building products like decking, fencing, siding, garden furniture, exterior windows and doors^{19,20}, although other applications can also be found in marine structures, railroad crossties, automobile parts and highway structures as such as high way sign, guardrail posts and fence posts.²¹ WPCs possess many advantages over the raw materials of polymers and wood filler. WPCs had better dimensional stability and durability against

bio-deterioration as compared to wood. In addition, WPCs also reduce the machine wear and tear of processing equipment, and lowers the product cost significantly against inorganic fillers when waste streams such as sawdust are used.²⁰ Compared to the polymers, WPCs had higher mechanical properties, thermal stability and more resistance to the ultraviolet light and degradation.²⁰

In Bangladesh, situated in South Asia, we have 18% forest of total land area, a lot of timber houses are spreading all over the country. A lot of sawdust generated from this timber houses but these are 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 sawdust, fibers or pulp are suitable as filler for polyolefin's matrix composites.^{22,23} Wood fibers possess physical and mechanical properties suitable for reinforcement in plastics.²⁴ Hence, increased usage of the sawdust as reinforcing material with plastic for WPCs offer the prospect of lessening of environment pollution and lowering production cost. Virgin thermoplastics such as HDPE, LDPE, PVC, PS and PP are widely used for the production of WPCs, and significantly numbers of papers have appeared in the literature regarding mechanical properties, dimensional stability, inter adhesion and durability.²⁵⁻³¹ However, published reports on PP and sawdust/wood based WPCs are rather limited.³²⁻³⁶ Increased moisture content in the composites reduces mechanical properties, dimensional stability and tends to biodegradation.³⁸

The main disadvantages of using lignocelulosic fibers as fillers in thermoplastics is their affinity to absorb moisture (which can be as

high as 3-13%) and consequent deformation of finished products.³⁸ Another problem of using natural fiber in thermoplastic composite is the poor interfacial adhesion between the filler and the polymer matrix.³⁹ 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 hydrophilic polymer matrix.^{26,40-42} Several studies were conducted to examine the effect of moisture content on mechanical properties and stability of the natural fiber and thermoplastic composites.^{37,43,44} In recent research in our laboratory it has been shown that interfacial adhesion can be significantly improved by suitable chemical treatment of fiber.^{45,46}

However, this study was conducted only for virgin PP composites where sawdust of 'Cadamb' (*Anthocephalus Cadamba*) variety was used as filler; briefly it is called wood plastic composites (WPCs). As dimensional stability is of the WPCs is the important property in exterior applications, understanding and quantification of the moisture absorption and dimensional change of WPC is focused in the present work. Due to the uncertainties regarding WPCs 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 been shown that changes in ambient humidity and temperature may have an adverse effect on physical and mechanical properties of the WPCs.⁴⁷⁻⁵⁰

The processing method can also affect the moisture absorption and extruded WPCs trend to absorb greater moisture than compression or injection moulded products.⁵¹ In addition to stability, durability is

an important property of WPC for the exterior applications and this is gaining more attention recently. Durability of the WPCs made from virgin thermoplastics with organic fillers (such as wood, other natural fibers and rice hull) exposed to biological organism^{52,53} and ultraviolet radiation UV) have been investigated.⁵⁴⁻⁵⁷ There are limited reports available for the WPCs made from virgin or recycled thermoplastic and wood and natural fibers.⁵⁸⁻⁶⁰ If WPCs are to be used in different environmental conditions, it is essential to investigate the physico-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 formation and processing. WPCs performance can be optimized by investigating wide range of composite formulations and processing technique. Considering the potentials for applications and resource availability PP was chosen as the matrix material to produce the WPCs with sawdust through the injection moulding technique. Subsequently, dimensional stability, durability, mechanical and thermal properties need to be investigated.

In this work all chemical modification of sawdust by pre treatment were carried out in aqueous solution instead of using any inert or toxic solvents. Chemical modifications were characterized by FT-IR spectroscopic analyses. Water absorption behaviors of all composites were carried out and reported in this thesis.

1.2 Aim of the present investigation

In the literature lot of work has been found on natural fiber-polypropylene composites. Some of the works have been reported on pretreatment on natural fibers. The aim and objective of the present research is to find out a cost effective technology of using sawdust as a reinforcing material in thermoplastic composites. Another aim of the present study is to improve the mechanical properties of sawdust-plastic composites. The specific aim and objective of this research work are as follows:

1. To use sawdust as cheap, available and environmentally friendly reinforcing materials.
2. To modify sawdust by chemical treatment.
3. To prepare better quality sawdust-PP composites.
4. To develop better resistance to water absorption, high mechanical properties of composites by chemical treatment of sawdust.
5. To characterize the interfacial bonding between plastic and sawdust in the composite by morphological analysis.
6. To prevent environmental pollution and ecological imbalance by preparing biodegradable (at least partially) composites with sawdust and plastic materials.
7. To compare the properties of sawdust-PP composite with that of other composites.

CHAPTER 02

REVIEW OF LITERATURE

This chapter covers a brief review on the literature related to the concept of lignocellulosic fiber, structure and composition of sawdust, structure and properties of PP, chemical modification of sawdust, concept of polymer composite materials and preparation of sawdust-PP composites. The details of chemical treatments of other natural fibers and their effects on the properties of composite materials are also discussed.

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 another as filler or reinforcements. Normally, the matrix is the materials that holds the reinforcements together and has lower strength than the reinforcement. In the plastic based composites, the polymers, thermoplastics or thermoset, act as a matrix and fibers of wood or other natural fibers as fillers. The reinforcing fillers are the main load carrying components 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 fibers and the matrix is the key to transfer the stress from the matrix into fillers across the interface. The interface adhesion between the polymer matrix and wood fillers can be improved using coupling agents. The coupling agent will form a bond between the fibers and the matrix through improved compatibility (wettability) and developing a mechanical or chemical bonding. To achieve the required properties of the composites, properties of both fibers and matrix are important although the extent of influence of the fibers and matrix may vary depending on the required properties of the composite. The tensile strength of short fiber composite is more strongly dependent on the fiber properties.⁶¹ As WPC contained low density

plastic (PP) matrix reinforced with stiff wood and wood fibers due to lower modulus than the fibers. Therefore, stiffness of the matrix has impact on 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.

At first a short description will be given about lignocellulosic fibers.

2.2 Lignocellulosic fibers

Lignocellulosic fibers refer to those agro based substances which contain cellulose, hemicelluloses, and lignin as their structural molecules. Lignocellulosics include wood, agricultural residue, water plants, grasses, and other plant substances.⁶² To better understand the properties of lignocellulosic fiber-reinforced composite materials, it is necessary to know the physical and chemical properties of lignocellulosic fibers. Fibers are classified as^{63,64}

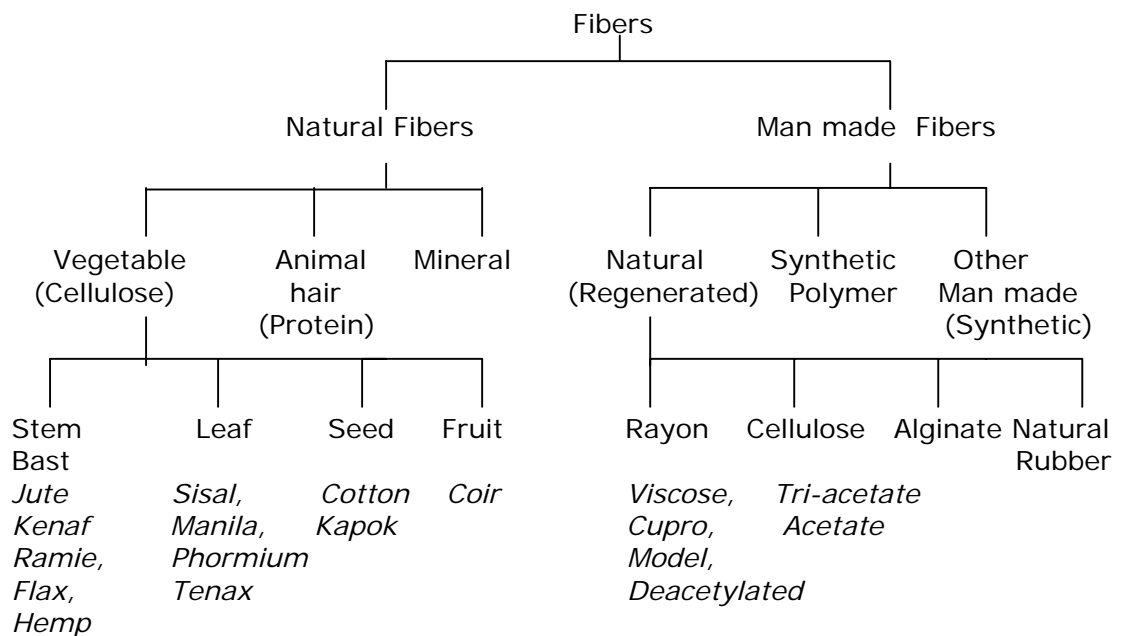


Figure 2.1: Classifications of fibers⁶⁴

Agro-based lignocellulosic fibers are also classified on the basis of part of the plant where they stored in.⁶⁵ Five different classes of

fiber are: (1) bast or stem fibers, which are the fibrous bundles in the inner bark of the plant stem running the length of the stem; (2) leaf fibers, which run the length of leaves; (3) seed-hair fibers; (4) core, pith or stick fibers, which form the low density, spongy inner part of the stem of certain plants; and (5) all other plant fibers not included above.⁶⁵ Examples of bast or stem fibers include jute, flax, hemp, kenaf, ramie, roselle, and urena. Leaf fibers include banana, sisal, henequen, abaca, pineapple, cantala, caroa, mauritius, and phormium. Seed-hair fibers include coir, cotton, kapok, and milkweed floss. Core fibers represent the center or pith fibers of such plants as kenaf and jute and can represent over 85 percent of the dry weight of these plants. The remaining fibers include roots, leaf segments, flower heads, seed hulls and short stem fiber. While individual single fibers in all of these classes are quite short (except for flax, hemp, ramie, cotton, and kapok). However, the fibers obtained from inner bark of the plant are quite long. For example, hemp, jute, and kenaf can have fiber bundles as long as 400 cm and abaca, mauritius, and phormium are about half this length. Considering all types plant fiber, there is a vast array of potential long and short fibers for composite production.⁶⁵ Table 2.3 shows a comparison of properties of natural lignocellulosic fibers and conventional man-made fibers. Jute, ramie, flax, and sisal are the most commonly used fibers for polymer composites.

2.3 Concept of composite materials and classification

The composite materials contain 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 which are used as filler content. Composites materials are broadly classified by Kundu.⁶⁶ Classification is discussed below.

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

- a. Mineral fibers
- b. Animal fibers
- c. Plant fibers

Then Among the three types of fibers, plant fibers (soft wood fiber) in particular are described in this chapter. Concerning vegetable fibers, these are classified depending on the place of plant (stem, leaves, seeds, grass etc) from they are extracted. Figure 2.2 shows the classification of plant fibers according to their origin.

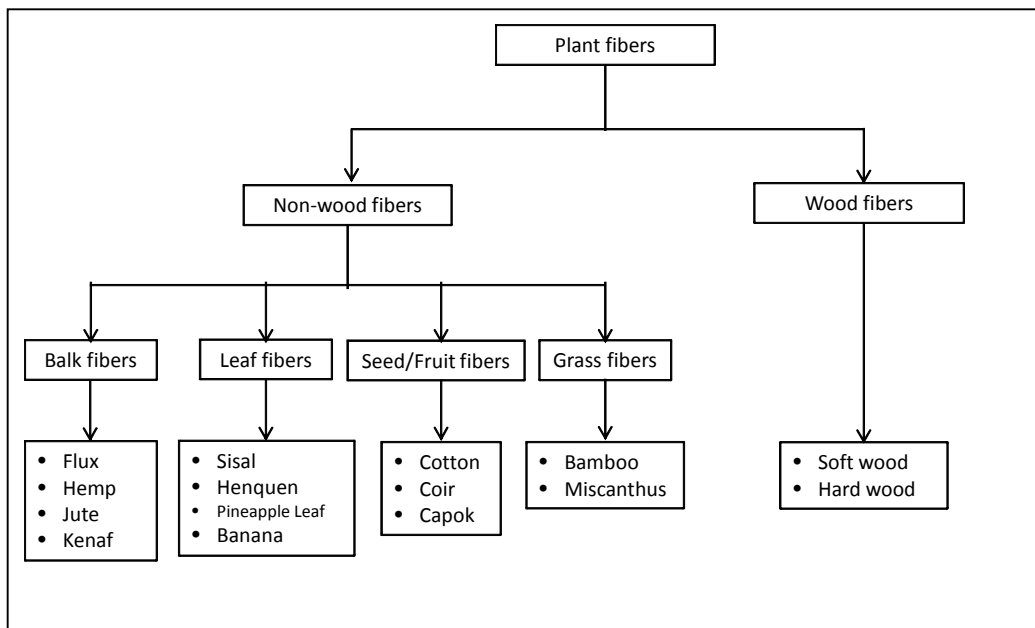


Figure 2.2: Classification of plant fibers according to their origin.⁶⁷

Table 2.1: Properties of natural & synthetic fibers⁶⁸

	Fibers	Density	Tensile strength MPa	Tensile Modulus GPa	Elongation at break, %	Decomposition Temperature, °C	Price in Euros/kg
Natural	Jute	1.3-1.5	187-540	3-55	1.4-3.1	270	0.7
	Ramie		585-900	33	2.0-3.5	260	
	Hemp fibers	1.4-1.5	580-1110	3-90	1.3-4.7	258	
	Bamboo			1.7-29	3.2		
	Flax	1.4	250-1000	12-100	1.3-40	280	0.15-0.76
	Sisal	1.4	507-855	24	2.9	270	0.7-1.02
	Cotton	1.5-1.6	350	11	2-10		0.35
	Banana fibers	1.3	791	30	2.10		0.7-0.9
	Kenaf	1.4	930	53		270	
	Coconut		544	14			0.36-0.45
	Wood fibers	0.6		12	2.90		0.31-0.35
	Cellulose fibers	1.2		2.1			
	Wood flour	0.6		10			
Synthetic	E-glass fibers	2.5	1625-3400	72	2-5	756	1.6-2.0
	C-glass fibers	2.5	2800	69		756	9.3-16
	S-glass fibers	2.5	4600	87		946	8.3-20
	A-glass fibers	2.5	2400	68		696	2.5
	Aramid (Kevlar)	1.4	2380-3100	124		496	16-67
	Carbon fibers	1.8-1.9	2090-5200	525		3647	33-166
	Zirconia fibers	5.6	700	100		2497	41.7
	Alumina fibers	2.8	1000	100		1997	

2.4 Sawdust filler in WPCs

Wood has been used as reinforcing filler in thermoset polymer for decades; however, its use in thermoplastics is 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 processing equipment as compared inorganic fillers (e.g. glass fiber 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 microstructural properties of wood species depends on the type of species such as for softwood and hardwood. Hence selection of wood species for the use of WPCs could have significant influence on the microstructure and properties of WPCs. The wood may have the forms of sawmill chips, sawdust, wood fiber, wood powder or pulps are available for WPCs production.⁶⁹

However, for the plastic based composites, the wood should be grounded to fine flour or refined to fibers. When sawdust is used, the sawdust reinforcement to the plastic is not through individual fibers but through particulates consisting of broken fiber bundles of wood. Tajvidi et al⁷⁰ 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 al⁷¹ had reported the composites made from sawdust-PP with various sizes of wood particles (35, 70, 120 and 235 mesh) showed that aspect ratio, not the particle size, had the great effect on strength and stiffness. However, in case of wood fiber, the tensile strength 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 sawdust used as fillers in thermoplastics are less than 0.425mm (40 mesh size), which has the aspect ratio of 3.4.⁷² Very fine sawdust can cost more and increase melt viscosity more than coarser sawdust, 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.

2.5 Chemical composition of soft wood

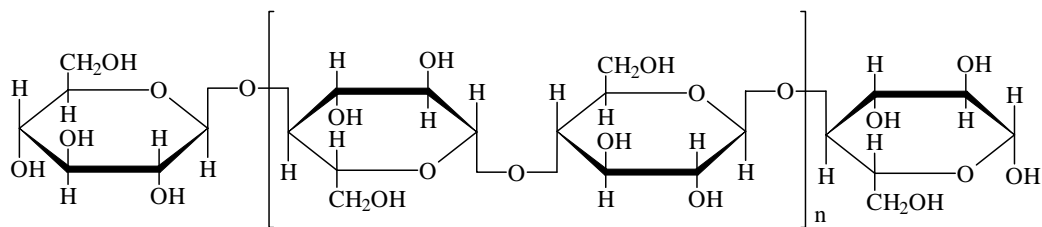
Wood is classified as a lignocellulosic material and made up of three major chemical constituents (cellulose: 45-50%, hemi-cellulose: 20-25% and lignin: 20- 30%) and other minor constituents (ash: 0-0.5%, and extractives: 1-10%).^{73,74} The chemical composition of wood varies between wood species. The major constituents 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 originated into anhydrous glucopyranose linked via N1 4 glycosidic bonds (Figure 2.3). It is a high 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 group. A high portion of cellulose is crystalline, held together by intermolecular hydrogen

bonding. The hydroxyl group 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 active nature. The cellulose is hygroscopic because it consists of polar molecules and easily undergoes hydrogen bonding.⁷³ 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

Figure 2.3: Segment of a cellulose molecule showing linear and non branched structure.⁷⁵

As early as 1920, Herzog and Janeke⁷⁶ recognized that cellulose from such widely different sources as cotton, ramie, wood, jute, and flax gave identical X-ray diagram and concluded that 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.

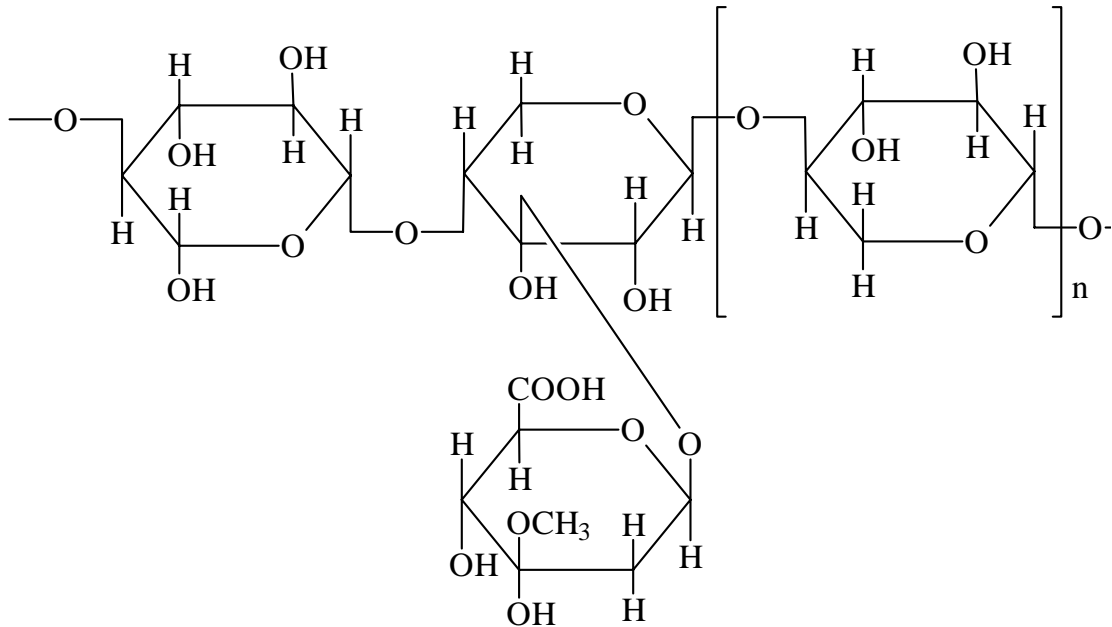


Figure 2.4: Structure of hemicelluloses

❖ *Lignin*

Lignin is an insoluble, resin like substance of phenolic character. It is built up to large content, of phenyl propane building stones, often having a hydroxyl group/groups in meta position/positions to the side chain.⁷⁷⁻⁷⁹ 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 hemicelluloses, serving the function of a cross-linking agent. Postulated monomer in lignin⁸⁰ as shown in the figure 2.5.

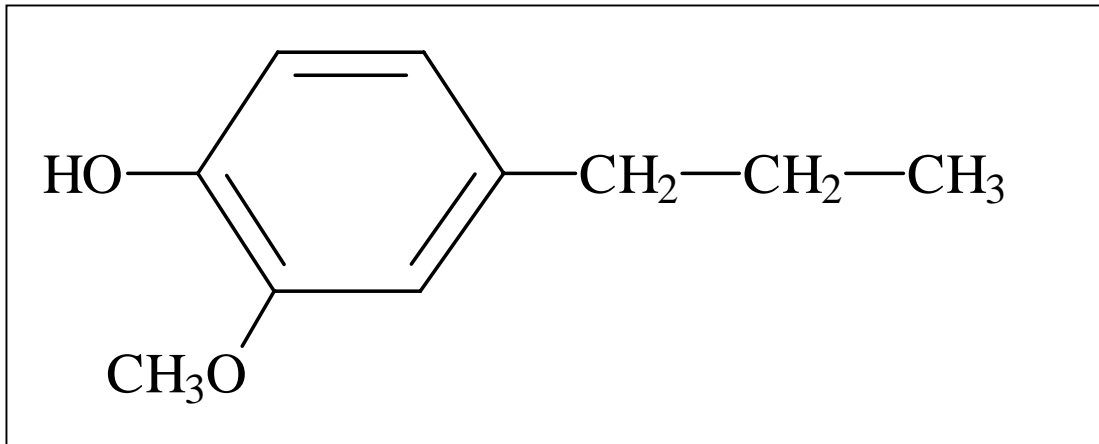


Figure 2.5: Structural unit of lignin molecule

Lignin is a binding agent that holds cellulose fiber 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.

Most plant tissues contain, in addition to carbohydrate and extractives, an amorphous polymeric gummy material is called lignin.^{78,79} The nature of lignin and its relationship to cellulose and other constituents of fiber are still uncertain. Unlike cellulose and hemicelluloses, lignin gives a series of color reaction⁸¹ that indicates the presence of compounds for which these reactions are typical. Isolated lignin is generally an amorphous material having average high molecular weight.

2.6 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 wood for energy. About 10,38,996 m³ round wood equivalents of wood chip residuals (wood off-cuts, slab wood, planner savings and sawdust) was produced by New Zealand forest industry in 2002, which are mostly from radiate pine forest.⁸² The use of waste wood in WPCs helps to offset the disposal costs. The waste wood in the form sawdust, fibers or pulp are suitable filler for polyolefin's matrix composites.^{22,23} The Pinus radiata fiber possesses physical and mechanical properties suited to the reinforcement of plastics.²⁴ According to Lightsey et al⁸³ there was little difference in tensile modulus of composites made from either sawdust 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 1200°C, most common thermoplastics (PE, PP, PS and PVC) are easily processed with wood below this thermal decomposition temperature.²¹

2.7 Introduction and classification of composite materials

The term composite material is used to describe macroscopic combinations of two or more materials. The fundamental goal in the production and application of composite materials is to achieve a performance from the composite that is not available from the separate constituents or from other materials. The concept of improved performance is broad and includes increased strength or reinforcement of one material by the addition of another material.¹⁴ The modern interest in composite materials can be traced in the development of Bakelite or phenolic resin, which was synthesized by Backeland a Belgium scientist, in 1906.¹⁴ Bakelite was a hard, brittle material that had a very few mechanical applications of its own. However, the addition of a filler, (the earliest applications used

short cellulose fibers) yielded Bakelite molding compounds that were very strong and tough and found several applications in mass-produced automobile components. The wood flour additives improved Bakelite's processibility, physical, chemical, and electrical properties, as well as reducing its cost.¹⁴

Polymer composites are now an important class of engineering materials. The properties of composites are largely influenced by the properties of their constituents and the distribution and interactions among them. The constituents usually interact in a synergistic way, providing properties that are not accounted for by a simple volume-fraction sum of the components. Along with the volume fraction and the distribution of discrete units in the discontinuous phase, the interfacial area plays an important role in determining the extent of interaction between the reinforcement and the matrix and, in this way, the final properties of the composite. The fabrication technology of composites, as well as some of their physical properties, is dominated by the chemistry and rheology of the matrix resin and by the type and physical form of the reinforcement.¹

The use of reinforcing agents makes it possible for any thermoset- or thermoplastic-matrix property to be improved or changed to meet varying requirements. Thus most polymer composites have been developed or fabricated to improve mechanical properties such as strength, stiffness, or toughness. The strengthening efficiency of the discontinuous phase plays the most important role in these products, and the strengthening mechanism depends strongly on the geometry of the reinforcements. Therefore, polymer composites can be classified according to geometry of reinforcement materials. The three major classes of polymer composites are fibrous, laminar,

and particulate. The commonly accepted classification scheme for polymer composites is presented in Figure 2.6.¹

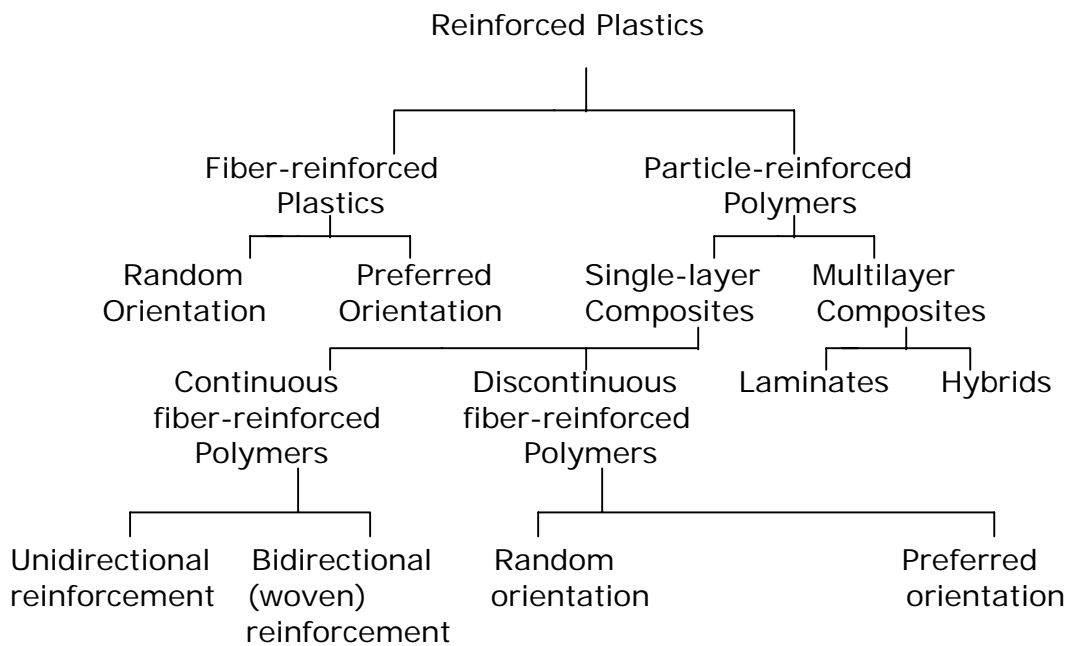


Figure 2.6: Classification of polymer composites.

2.8 Matrix materials

The mechanical properties of composites based on the fibers depend not only on the characteristics of the fibers but also on the matrix itself as well as on the fiber-matrix interface. The matrix in a polymer composite serves both to maintain the position and orientation of the fibers and to protect them from potentially degrading environments. Polymer matrices may be thermosets or thermoplastics. Thermosetting polymers are rigid, cross-linked materials that degrade rather than melt at high temperatures. Thermoplastic polymers are linear or branched molecules that

soften upon heating. Thermoset-based composites are somewhat less expensive than thermoplastic-based composites, but have lower heat distortion temperatures and poorer toughness when tested in an interlaminar mode. Thermosetting polymers, includes unsaturated polyesters, epoxies, and phenolic resins. Whereas thermoplastic polymers are polyamides, polyolefin's, polycarbonates and saturated polyesters.¹⁴

Many of the thermoplastic-based composites offer excellent resistance to impact loading and are thereby suitable for use in high performance engineering applications. Other interesting aspects of these composites include the possibility of thermoforming and shaping at elevated temperature and the potential for thermal joining and repair, as well as recycling.¹⁴

2.9 Thermoplastic polymer

Thermoplastic resins have received considerable attention in the past few years as the matrix material in organic resin-based composites.¹⁴ Whereas, thermosetting materials date back 5000 years, when Egyptians used a straw-reinforcing agent in a clay matrix to form bricks. So, thermoplastic composites are relatively new development. Although their use in advanced composites is not widespread, thermoplastic composites are used extensively in commercial applications ranging from automobiles to durable goods.¹⁴

Thermoplastic polymers are usually linear molecules with no chemical linkage between the chains of the molecules. The molecules are held together by weak secondary forces, such as van der Waals or hydrogen bonding. These are readily deformed by the application of heat or pressure. Thermoplastic resins can be amorphous, that is, structure less, or semi crystalline, in which

some of the molecules form an ordered array. A material is usually considered semi crystalline if as little as 5% of the polymer is in the crystalline form. Semi crystalline resins exhibit higher modulus, but amorphous materials are tougher. Amorphous materials are usually more solvent sensitive and can be processed at lower temperature. One of the most important advantages of thermoplastic resins is their toughness that is, high impact strength and fracture resistance, which, unfortunately, is not linearly transmitted into properties of the composite. Other advantages of thermoplastic polymers include long life at room temperature; post formability, that is, thermal reforming; ease to repair by thermal welding or solvents; and ease of handling, that is, they are not tacky.¹⁴ One of the principal advantages of true thermoplastic polymer is their ability to consolidate or flow at elevated temperature; however, this quality also limits their use at higher temperature. Amorphous materials begin to flow or creep above the glass-transition temperature, T_g , whereas crystalline resins must be heated above the melting point, T_m . As a rule of thumb, T_g is approximately $2/3 T_m$ (Kelvin temperature). So crystalline polymers may begin to degrade at the temperature required for processing. Even a relatively low temperature material such as polypropylene, which melts between 168°C and 175°C , must be heated to approximately $180\text{-}190^{\circ}\text{C}$ to process the composite. In many instances the processing window is quite narrow owing to a lower temperature limit set by the melting point and an upper temperature limit set the rate of thermal degradation.¹⁴

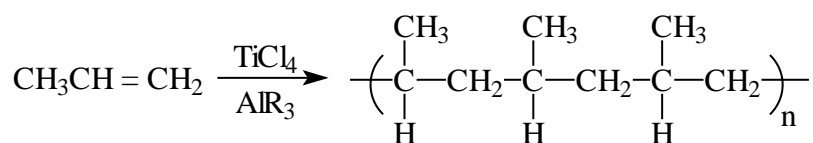
2.10 Polymers in WPCs

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 molecule 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 is reversible. It can go through a number of melting-freezing cycles without appreciable chemical changes, which makes it suitable for recycling.⁸⁴ On the other hand, thermosets are network polymers formed by cross-linking reactions and cannot be remelted. Thermoset resins are such as phenolics and epoxies are generally used in structures that require higher mechanical properties or integrity at higher temperatures. Polypropylene (PP) is one of the thermoplastic polymers consisting of long chains of monomer propylene ($\text{CH}_3\text{-CH}_2\text{-CH}_3$), and is produced through polymerization of propylene, and contains small proportion of additives.

2.10.1 Polypropylene (PP)

The most common polyolefin used to prepare composites is polypropylene, a commodity polymer that has been in commercial production for the last 40 years following its controlled polymerization by Natta in 1954.¹⁴ Natta used a Ziegler catalyst consisting of titanium tetrachloride and an aluminum alkyl to produce isotactic polypropylene directly from propylene:



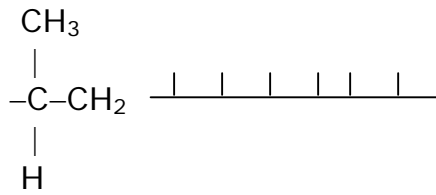
Stereoregular

Polypropylene is available with many different reinforcing agents or fillers, such as talc, mica, or calcium carbonate; chopped or continuous strand fiber. Glass is the most common reinforcing agent used for composites. Many additives have been developed to

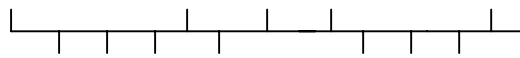
enhance the thermal stability of polypropylene to minimize degradation during processing. One of the most important requirements of the polypropylene used in the manufacture of composites is that, it should be relatively pure and free of residual catalyst. Recent developments to form copolymers of polypropylene and polyethylene have great promise for relatively inexpensive, tough, thermoplastic composite applications.¹⁴

2.10.2 Molecular structure of PP

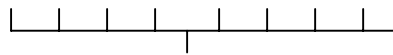
In 1955, Natta¹⁵ first determined the molecular structures of the various types of PP and introduced the descriptive nomenclature universally being used today. Commercial interest lies primarily in highly crystalline PP, together with its further modifications through copolymerization. In isotactic PP, each monomer unit in the chain is arranged in a regular head-to-tail assembly without any branching. Furthermore, the configuration of each methyl group is the same (Figure 2.7 A). This is caused by the template type constraints of the stereospecific catalytic site. Such a regular structure is the hallmark of a good catalyst. Occasionally, some imperfect monomer insertion gives the type of fault shown in Figure 2.7 C, amounting to about 0.3-1.5 per hundred monomer units in the salable polymer. An extreme example of defects is atactic PP (Figure 2.7 B), with complete loss of steric control. In syndiotactic configuration, methyl groups are alternatively on either side of the carbon chain. Syndiotactic polymer is of theoretical, but not commercial importance.⁸⁵



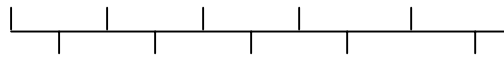
(A) Isotactic polypropylene; mp 176^oC



(B) Atactic polypropylene rubber



(C) Chain imperfection; mp < 176^oC



(D) Syndiotactic polypropylene; mp ca. 130^oC

Figure 2.7: PP chain structure

2.10.3 Crystallization of PP

PP is semi-crystalline, which means it always has two phases, an amorphous and a crystalline one. The useful properties of PP stem from its ability to crystallize and form rigid and tough articles. Highly isotactic polymer, with its regular structure, forms a helical coil having three monomer units per turn. These coils stack together into thin lamellar crystallites which force the chains to fold several times as they emerge and reenter lamellae.⁸⁵ Three crystalline forms are known (Table 2.2) of which the α -form is the most stable. The more stable α -form is favored at higher temperatures and

slower cooling rates. Rapid quenching yields the β -form with a lower density and melting point of 150°C. Polymers of lower stereoregularity and random copolymers usually contain low-melting γ -crystallites in addition to the α -form.

Formation of crystallites from a viscous melt is hindered by chain entanglements and by the need for helices to fold as they close pack into lamellae. This, and the formation of nuclei might contribute to the low degree of crystallization even in highly stereoregular polymers. Commercial articles vary from 30% crystallinity in rapidly quenched films to 50-60% in moldings. Even purified and annealed samples of very stereoregular polymer rarely achieve more than 70% crystallinity. It is to be pointed out that high helical contents are not synonymous with high crystallinities, which require three-dimensional long-range order. PP is properly regarded as a semicrystalline polymer for these reasons.⁸⁵ Crystalline properties of PP are given in Table 2.2. The most predominant and stable crystal form being the form, having a monoclinic structure. The more stable form is favored at higher temperatures and slower cooling rates.

Table 2.2: Crystalline properties of PP⁸⁷

Crystal form	System	Crystal density (20°C), g/cm ³	Chains per unit cell	MP, °C
Iso α	Monoclinic	0.932-0.943	4	171
Iso β	pseudo Hexagonal	0.922	9	150
Iso γ	Triclinic	0.939	1	131
Amorphous	-	0.85	-	-
Syndio	orthorhombic	0.93	2 (4/1 helix)	138

2.10.4 Properties of PP

Polypropylene is a linear hydrocarbon polymer containing little or no unsaturation. It is therefore not surprising that polypropylene and polyethylene have many similarities in their properties.⁸⁶ Basic mechanical properties are largely influenced by molecular mass and molecular mass distribution (MMD), chain stereoregularity, and processing conditions, which introduce orientation, structural strain, etc. Various additive packages must be tailored to the application to achieve good and durable performance. Some typical properties of PP are given in Table 2.3. The final melting point of commercial PP lies in the range 160⁰-170⁰C, with purified polymer reaching 176⁰C. Within the range of commercial polymers, the greater the amount of isotactic material the greater the crystallinity and hence, greater the softening point, stiffness, tensile strength, modulus and hardness.⁸⁵ The crystalline and nonpolar nature of PP confers good resistance to a wide range of aqueous and polar media, including emulsifier solutions with their strong stress cracking abilities. Powerful oxidizing agents, highly aromatic and chlorinated solvents are too aggressive for safe storage in PP containers.⁸⁵ One disadvantage of PP is the susceptibility of its methyl groups to thermo oxidative degradation.⁸⁷

Table 2.3: Properties of PP^{86,87}

Parameters	Standard Used	Values
Specific gravity	ASTM D792	0.90-0.91
Crystallinity, %	-	82
Melting temperature, °C	-	165-171
Tensile strength, MPa	ASTM D638	31-41
Tensile modulus, GPa	ASTM D638	1.10-1.55
Elongation-to-break, %	ASTM D638	100-600
Impact strength, notched Izod, J m ⁻¹	ASTM D256	21-53
Rockwell hardness (R-scale)	ASTM D785	90-95
Heat-deflection temperature, °C, at 455 kPa (66psi)	ASTM D648	225-250

2.11 Matrix materials

The mechanical properties of composites based on the fibers depend not only on the characteristics of the fibers but also on the matrix itself as well as on the fiber-matrix interface. The matrix in a polymer composite serves both to maintain the position and orientation of the fibers and to protect them from potentially degrading environments. Polymer matrices may be thermosets or thermoplastics. Thermosetting polymers are rigid, cross-linked materials that degrade rather than melt at high temperatures. Thermoplastic polymers are linear or branched molecules that soften upon heating. Thermoset-based composites are somewhat less expensive than thermoplastic-based composites, but have lower heat distortion temperatures and poorer toughness when tested in an interlaminar mode. Thermosetting polymers, includes unsaturated polyesters, epoxies, and phenolic resins. Whereas thermoplastic polymers are polyamides, polyolefin's, polycarbonates and saturated polyesters.¹⁴

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long life at room temperature; post formability, that is, thermal reforming; ease to repair by thermal welding or solvents; and ease of handling, that is, they are not tacky.¹⁴ One of the principal advantages of true thermoplastic polymer is their ability to consolidate or flow at elevated temperature; however, this quality also limits their use at higher temperature. Amorphous materials begin to flow or creep above the glass-transition temperature, T_g , whereas crystalline resins must be heated above the melting point, T_m . As a rule of thumb, T_g is approximately $2/3 T_m$ (Kelvin temperature). So crystalline polymers may begin to degrade at the temperatures required for processing. Even a relatively low temperature material such as polypropylene, which melts between 168°C and 175°C , must be heated to approximately $180\text{-}190^{\circ}\text{C}$ to process the composite. In many instances the processing window is quite narrow owing to a lower temperature limit set by the melting point and an upper temperature limit set by the rate of thermal degradation.¹⁴

2.13 Lignocellulosic fiber reinforced thermoplastic composites

There is a long story of the use of lignocellulosic materials with thermosetting polymeric materials, like phenol or urea formaldehyde in the production of composites. The use of lignocellulosics with thermoplastics, however, is a more recent innovation. Lignocellulosic fibers have been incorporated in a wide variety of thermoplastic materials such as polypropylene, polyethylene, polystyrene, poly-vinyl chloride, polyamides. Thermoplastic materials selected for use with lignocellulosic materials must melt at or below the degradation point of the lignocellulosic component, normally $200\text{-}220^{\circ}\text{C}$.⁶²

2.13.1 Lignocellulosics in combination with other materials

Combining of lignocellulosic materials with thermoplastic materials can be done in several ways.⁸⁸ In one case, thermoplastic materials are simply mixed with biobased powder or fiber (nut shell powder or wood fiber are presently used) and the mixture are heated. The plastic melts, but the wood fiber and plastic components remain as distinct separate phases. One example of this technology is reinforced thermoplastic composites, which are light weight, have improved acoustical, and heat reformability properties, and cost less than comparable products made from plastic alone. These advantages make possible the exploration of new processing techniques, new applications, and new markets in such areas as packaging, furniture, housing and automobiles.

A second way to combine wood fiber and plastics is to use a compatibilizer to make the hydrophobe (plastic) mix better with the hydrophil (wood). The two components remain as separate phases, but if delamination and/ or void formation can be avoided, properties can be improved over those of either separate phase. These types of materials are usually referred to as wood fiber/ plastic blends.⁸⁸

A final combination of wood fiber and thermoplastics is in products that can best be described as wood-plastic alloys. In this case the wood and plastic have become one material and it is not possible to separate them. The formation of wood-plastic alloys is possible through fiber modification and grafting research. This can be done if we consider that biobased fibers consist of a thermoset polymer (cellulose) in a thermoplastic matrix (lignin and the hemicelluloses). The glass transition temperature (GTT), however, of the thermoplastic matrix is higher than the decomposition temperature

of the fiber. If the GTT were lowered through chemical modification, it should be possible to thermoplasticize the lignin and the hemicelluloses at temperatures below decomposition. If a reactive thermoplastic is used it is then reacted with the modified biobased fiber, it should be possible to form biobased fiber/ thermoplastic alloys.⁸⁸ Rowell et al⁸⁹ reported that only the hemicelluloses and lignin have been modified in thermoplasticization using maleic and succinic anhydrides. Matsuda et al⁹⁰ also extensively investigated the esterification of wood in order to make a totally thermoplastic material. They esterified wood without a solvent by simply heating wood powder with succinic anhydride in a mixer for 3 h at temperatures higher than 60°C.

2.13.2 Properties of lignocellulosic fiber-thermoplastic composites

Before 1980, the concepts of blends and alloys were essentially unknown in the plastics industry. Blends and alloys have revolutionized the plastics industry, as they offer new materials with properties that were not achieved before. These materials can be tailored for specific end uses. Sawmills and jute industries have the same opportunity to follow this trend and greatly expand markets for new materials based on blends and alloys with other resources. Newer materials and composites that have both economic and environmental benefits are being considered for applications in the automotive, building, furniture, and packaging industries. Mineral fillers and fibers are used frequently in the plastics industry to achieve desired properties or to reduce the cost of the finished article. For example, glass fiber is used to improve the stiffness and strength of plastics, although there are several disadvantages associated with its use. Glass-fiber production requires a great deal of energy processing temperatures can exceed 1200°C. They tend

to abrade processing equipment and increase the density of the plastic system. The use of lignocellulosic fibers in thermoplastics has received a lot of interest due to their low densities, low cost, and non-abrasive nature. The inherent polar and hydrophilic nature of the wood and jute fibers and the nonpolar characteristics of the polyolefins lead to difficulties in compounding and result in inefficient composites.¹⁰ The high moisture absorption of the lignocellulosic fibers and their low microbial resistance are disadvantages (Table 2.8) that need to be considered, particularly during shipment and long-term storage as well as during processing of the composites.¹⁵ Proper selection of additives is necessary to improve the interaction and adhesion between the fiber and matrix phases. Recent research on the use of jute and kenaf fiber suggests that these fibers have the potential for being used as reinforcing fillers in thermoplastics.¹⁰ The low cost and densities and the nonabrasive nature of the fibers allow high filling levels and thereby result in significant cost savings. The primary advantages of using these fibers as additives in plastics are: low densities, low cost, nonabrasive, high filling levels, low energy consumption, high specific properties, renewability, wide distribution, biodegradability, and improvement of the rural/agricultural-based economy.¹⁰

Table 2.4: Main advantages and disadvantages of lignocellulosic fibers¹⁵

Advantages	Disadvantages
Low cost	High moisture adsorption
Renewable	Poor microbial resistance
Low density	Low thermal resistance
Nonabrasive	Local and seasonal quality variations
Low energy consumption	Demand and supply cycles limited
High specific properties	
High strength and elasticity modulus	
No skin irritations	
No residues when incinerated	
Fast water absorption/desorption	
Good thermal conductivity	
Biodegradability	

Wood and other lignocellulosic materials change dimensions with changing moisture content because the cell wall polymers contain hydroxyl and other oxygen-containing groups that attract moisture through hydrogen bonding.⁹¹ This hydrophilic behavior affects the properties of the fibers themselves as well as the properties of their composites. The hydrophilic character of fibers is usually incompatible with hydrophobic matrix material unless a compatibilizer or coupling agent is used. This leads to poor interfacial adhesion between the fiber and matrix as well as poor fiber dispersion.

In general, cellulosic fillers or fibers have a higher Young's modulus as compared to commodity thermoplastics, thereby contributing to the higher stiffness of the composites. The increase in the Young's modulus with the addition of cellulosic materials depends on many

factors such as amount of fibers used, orientation of the fibers, interaction and adhesion between the fiber and matrix.⁹⁴ In general, dispersing agents and/or coupling agents, are necessary for the property enhancement, when fibers are incorporated into thermoplastics. Dispersing agent facilitates the fiber dispersion and improves the interfacial adhesion between the fibers and the polymer matrix⁹². Grafting of chemical species on to the fiber surface has also been reported to improve the interaction between the fibers and matrix. Although grafting can improve the properties of the composite to a significant extent, this process increases the material cost of system. The use of dispersing agents and/or coupling agents is a cheaper route to improve properties and makes more practical sense for high volume, low cost composite systems.⁹²

In a natural fiber-thermoplastic composite the lignocellulosic phase is present in a wide range of diameters and lengths, some in the form of short filaments and others in the form that seem closer to the individual fiber. The high shearing energy of blending the filaments and the polymer in a mixer results in fiber attrition but can also axially separate the filaments into discrete individual fibers. Cellulosic fillers/fibers can be classified under three categories depending on their performance when incorporated to a plastic matrix. Wood flour and other low cost agricultural based flour can be considered as particulate fillers that enhance the tensile and flexural moduli of the composite with little effect on the composite strength. Wood fibers and recycled newspaper fibers have higher aspect ratios and contribute to an increase in the moduli of composite and can also improve the strength of the composite when suitable additives are used to improve stress transfer between the matrix and the fibers. The improvement in modulus is not

significantly different than the cellulosic particulate fillers. The most efficient cellulosic additives are some natural fibers such as kenaf, jute, flax, etc. The specific Young's modulus, specific flexural modulus, the ratio of the composite modulus to the composite specific gravity of composites with natural fibers such as kenaf are significantly higher than those with wood fibers. The specific moduli (the ratio of the composite modulus to the composite specific gravity) of high fiber volume fraction of bast fibers-PP composites are high and in the range of glass fibers-PP composites. The most efficient natural fibers are those that have a high cellulose content coupled with a low micro fibril angle resulting in high filament mechanical properties.⁹² A list of mechanical properties of PP composites reinforced by different natural fiber and inorganic substances is given in Table 2.8.^{10,93-94}

2.14 Effect of reinforcement on the composite properties

The reinforcing effect of fillers depends on their chemistry, shape (fibers, flakes, spheres), and size (fiber length, particle size). The most important reinforcement effects are:⁹⁵

1. Increased strength, ultimate elongation, rigidity (modulus of elasticity), and in some cases impact strength
2. Improved heat distortion temperature and dimensional stability, reduced shrinkage, and improved stability of mechanical values at high temperatures and over extended times (fatigue)
3. Modification of density (usually increased)
4. Improved chemical resistance and lower water absorption
5. Better surface quality and surface hardness

Special fillers are used to obtain compounds with the following properties:

1. Low flammability
2. Electrical conductivity and electromagnetic shielding
3. Radiation and UV shielding
4. Biodegradability
5. Noise suppression

2.15 Improvement of interfacial bonding between sawdust and PP

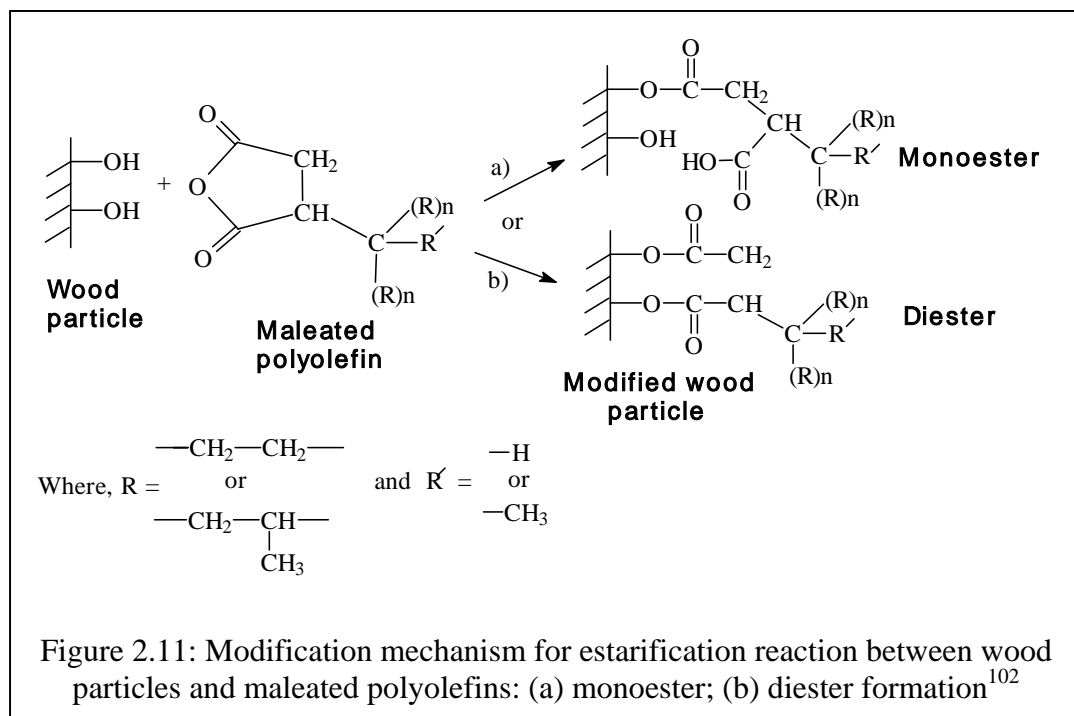
The processing and desired properties of sawdust can be improved by using additives such as lubricants, coupling agents, antioxidants, UV-absorbers and antimicrobial agents among others.⁴² Properties of sawdust depend on many factors including the species and forms of the wood filler, types and forms 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.⁹⁶ 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.^{42,97} Functionalized polyolefins coupling agents with maleic anhydride grafted polymer (LLDPgMA, HDPEgMA, HDPEgAA and PPgMA) has been used in WPCs to improve the compatibility and bonding between hydrophilic wood filler and hydrophobic polymer matrix.⁴¹ The maleated polypropylene (MAPP) and maleated polypropylene (MAPE) are

more commonly used in WPCs and highly regarded as the effective coupling agents.^{41,96,98,99} These coupling agents improved the overall performance of the WPCs through the approved 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 loading is lowered when coupling agents used in the processing. Furthermore, wood dispersion and wettability in plastic matrix can be improved by the wetting agents (lubricant) such as metallic stearates, fatty acids and paraffins wax.¹⁰⁰ 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 sawdust through the esterification mechanism.^{75,101} 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 sawdust (Figure 2.11).

The MAPP coupling agent improves the dispersion and adhesion of the wood filler in the polymer matrix and enhances the stiffness the

flexural strength for a wide range of wood contents, with 2-5 wt.% providing the best result.⁹⁶ Succinic acids is the byproduct through the hydrogenation of maleic anhydride. It is believed that succinic anhydride reduces in MAPP serve as a wood-bonding domain with the polymer matrix and polymer (PP or HDPP) chains co-crystallize or form entanglements with the polymer.



2.16 Fabrication of sawdust reinforced polymeric composites

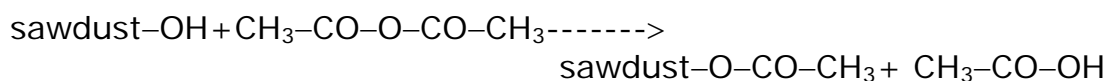
The manufacturing of the thermoplastic based composites is usually through a two-step process: (1) compounding of the wood filler and the plastic with coupling agent or other additives, and (2) extrusion moulding, injection moulding or compress moulding of the compounded mixture to produce a panel type product.¹⁰³ 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, and the compounding process directly affects the properties of resultant composites.^{104,105}

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 molding 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 in specially designed equipment such as Gelimate mixture, single or twin screw extruder. Mixing of wood filler and plastic can be done in different way depending on the type of equipments, such as pre-drying of the wood and pre-mixing with polymer / or additives, or predrying and split feeding the material into an extruder.⁷⁴ 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 moulding 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 press closing, lateral confinement and final cooling under pressure.¹⁰⁶ The previous studies show that the hot platen press system is suitable for producing flat and curved composite panels using thermoplastic and wood filler.

2.17 Some chemical modification for property enhancement of lignocellulosic fiber reinforced thermoplastic composites

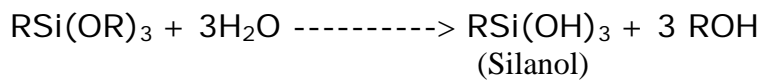
The properties of lignocellulosic materials result from the chemistry of the cell wall components. The basic properties of a fiber can be changed by modifying the basic chemistry of the cell wall polymers. Many chemical reaction systems have been reported for the modification of agro-fiber. These chemicals include anhydrides (such as phthalic, succinic, maleic, propionic and butyric anhydride etc.), acid chlorides, ketene carboxylic acids, different types of isocyanates, formaldehyde, acetaldehyde, disfunctional aldehydes, chloral, phthaldehydic acid, dimethyl sulfate, alkyl chlorides, beta-propiolactone, acrylonitrile, epoxides (such as, ethylene, propylene, butylene) and some difunctional epoxides.¹⁰⁷ By far, the most research has been done on the reaction of acetic anhydride with cell wall polymer hydroxyl groups to give an acetylated fiber. Many different types of lignocellulosic fibers including wood,¹⁰⁰⁻¹⁰¹ bamboo, bagasse, jute⁵, kenaf etc. have been acetylated using a variety of procedures. Although acetylation is not the only chemical modification procedure that has been shown to improve properties of lignocellulosic materials even then it has been the most studied and are used in many cases.¹⁰⁷ Some researchers¹¹⁰⁻¹¹³ have reported that acetylation of the lignocellulosic fibers have reduced the hydrophilicity and water absorption behavior of lignocellulosic fibers. The scheme of the reaction of lignocellulosic fiber with acetic anhydride is given below:



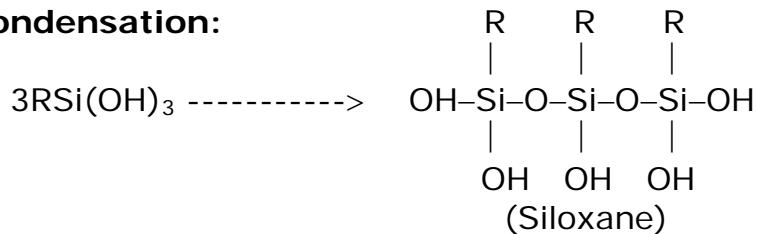
Scheme 2.1: Reaction of acetic anhydride with natural fiber¹¹³

Modification of fiber surface by reacting with silane were investigated and reported by some researchers.^{114,115} Silane treatment of fibers led to increase mechanical properties of the composites. The reaction steps in the silane grafting of biofibers are shown below:

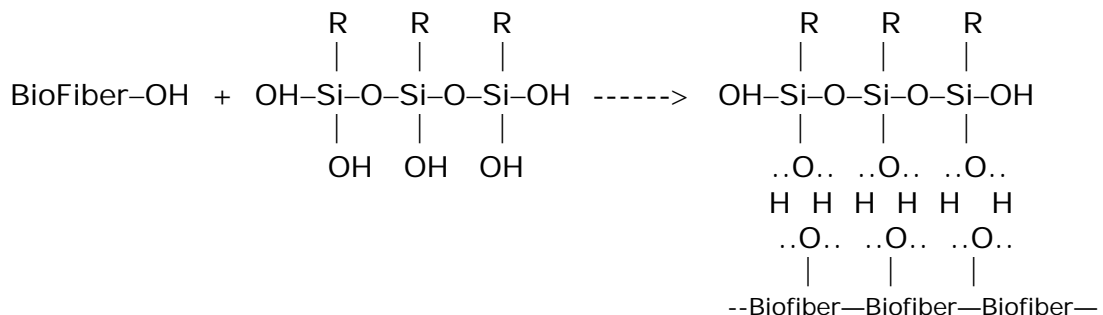
Hydrolysis:



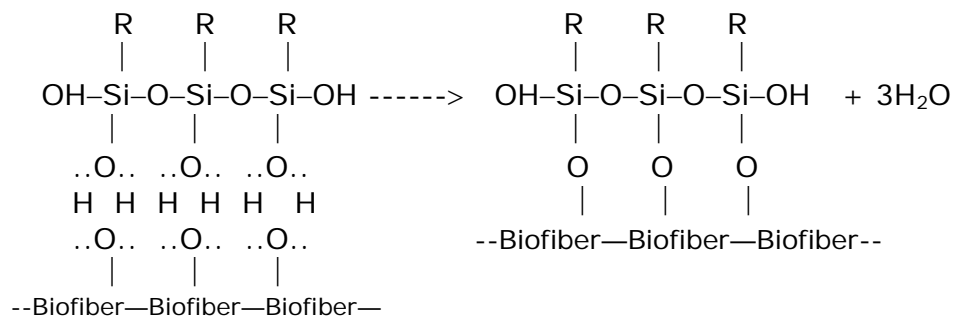
Condensation:



Hydrogen Bonding:

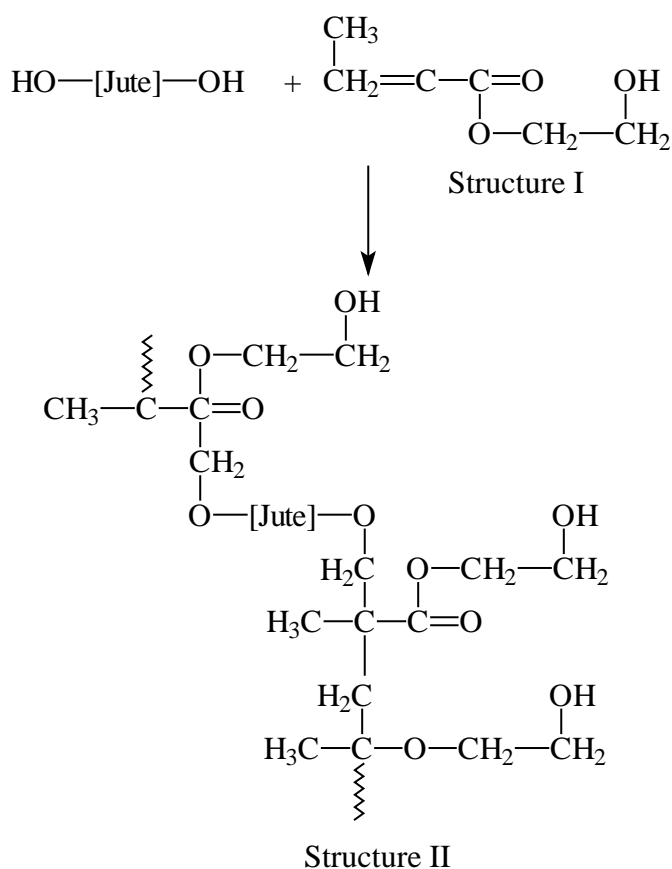


Surface Grafting:



Scheme 2.2: Reaction steps in the silane grafting of biofibers¹¹⁴

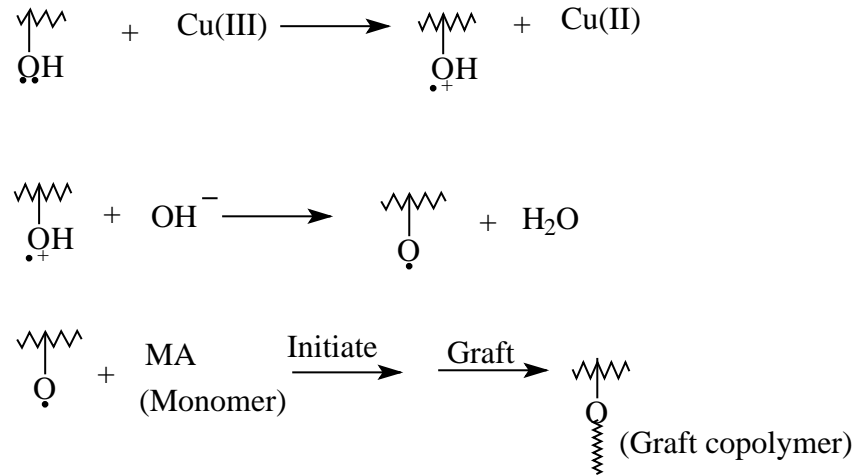
Modification of jute fiber with HEMA and the effect of HEMA on the mechanical and thermal properties of jute-polycarbonate composite were investigated and reported.¹¹⁸ It has been reported that HEMA deposited on hessian cloth might have quite extensively reacted with the cellulosic backbone of cellulose through graft-copolymerization reaction (Scheme 2.3).



Scheme 2.3: Proposed graft-copolymerization reaction of jute fiber with HEMA¹¹⁶

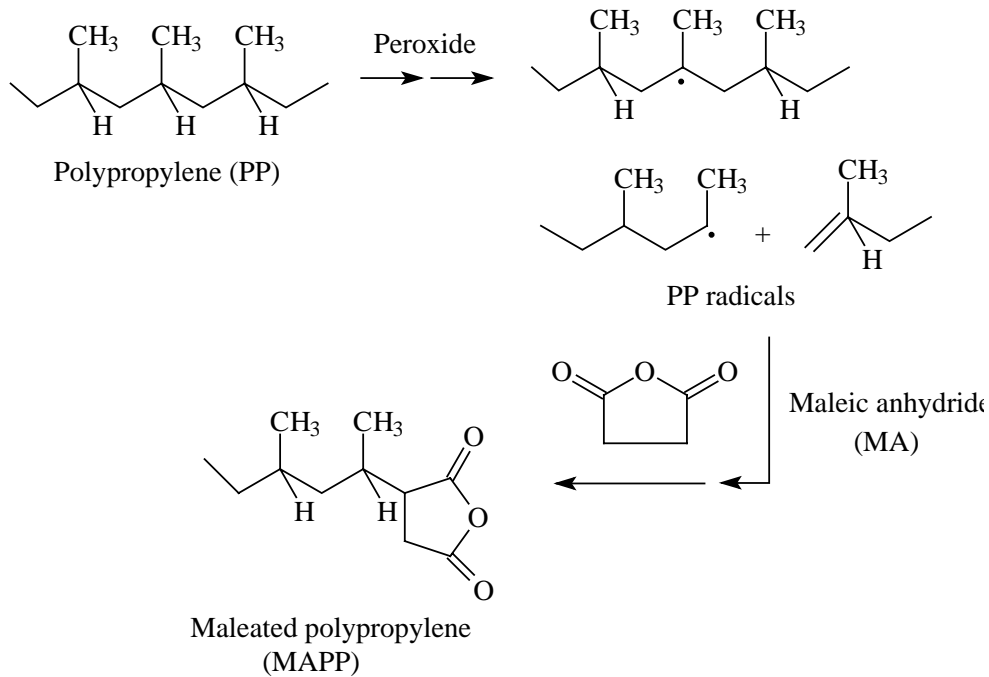
Grafting of polymethyl acrylate (PA) onto pure cellulose by potassium dperiodatocuprate (III) initiating system was carried out

by L. Yinghai et al¹¹⁷ and reported that the thermal stability of grafted product has been improved greatly. The initiation mechanism of grafting reaction is shown below:



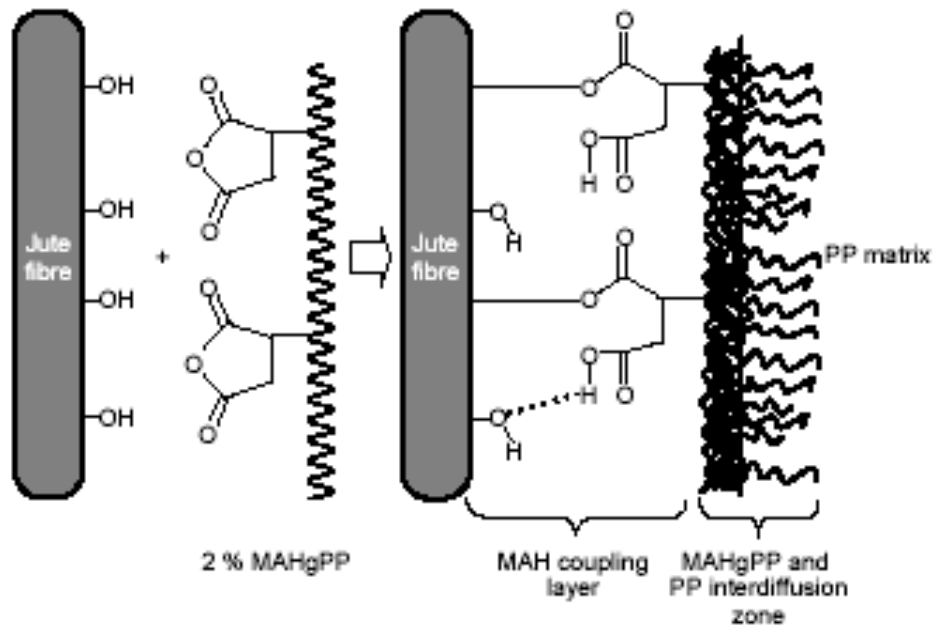
Scheme 2.4: Proposed graft-copolymerization of MA onto cellulose¹¹⁷

A considerable amount of research has been done on the use of MA as a coupling agent to improve the compatibility and adhesion between the fibers and matrix using a variety of procedures. A proposed method of grafting MA on PP chain is shown in Scheme 2.5.¹⁰



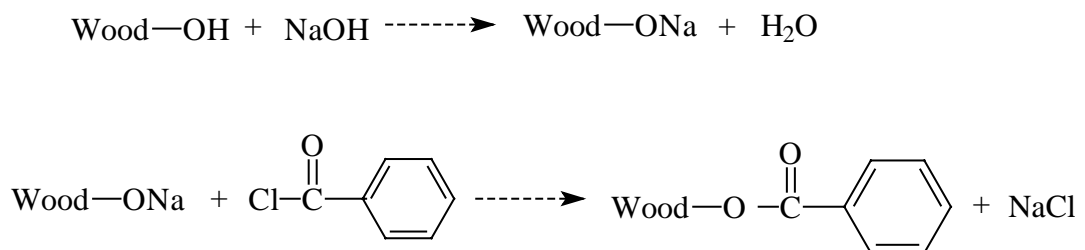
Scheme 2.5: Proposed reaction mechanism of MA on PP chain¹¹⁴

It is now evident from the literature that the addition of 0.5-2 wt-% maleic anhydride grafted polypropylene (MAHgPP) to PP matrices significantly improved the adhesion strength of jute fibers and in turn the mechanical properties of composites.¹¹⁰ A hypothetical structure of coupling of MAHgPP with jute fiber is given below:



Scheme 2.6: Hypothetical structure of MAHgPP coupling with jute fiber at the interface¹¹⁸

L. K. Poh et al¹¹⁹ carried out the esterification of palm oil empty fruit bunch (EFB) fibers using benzoyl chloride and reported that benzoylation treatment has improved the thermal stability and changed the suprastructure of the EFB fibers which may improve the interfacial bonding of the lignocellulosic material and thermoplastic materials. The chemical reactions involved are shown below:



Scheme 2.7: Chemical reactions between EFB fibers and benzoyl chloride¹¹⁹

Many other researches on chemical modifications have been reported to modify wood, kenaf, sisal, flax, banana, rice husk powder etc. lignocellulosic fibers using various additives (i.e. alkali, silane, potassium permanganate, sodium chlorite, and acrylic acid treatments) by various procedures.¹²⁰⁻¹³³ Some of these works are briefly presented here.

2.18 Some recent work in this field

A good number of published article in this field have been reviewed. These have been reported in the previous part of this section. Some other recent works have been presented below in brief:

B. V. Kokta¹³⁴ reported the effect of compounding, molding and fiber length on the properties of wood fiber reinforced thermoplastic composites. He reported that when critical fiber length was achieved the increase of fiber length did not improve composite properties. He also reported that there was practically no difference in resulting properties due to different way of compounding.

X. Li et al¹³⁵ reported on biodegradable composites prepared by poly(propylene carbonate) (PPC) reinforced with short *Hildegardia populifolia* natural fibers. They observed the effect of alkali treated fibers comparing with untreated fibers on the composites and reported that better bonding and approximately similar mechanical properties were obtained for both alkali-treated and untreated *Hildegardia populifolia* fiber reinforced PPC composites. They also reported that tensile strength and tensile modulus of the composites increased dramatically with increasing fiber content but elongation at break decreased sharply with increasing fiber content.

S. Das et al⁹¹ reported on a new process development to improve the dimensional stability of jute composite. They said that steam pretreatment process can minimize the irreversible swelling of jute fibers without any chemical modification of jute fibers.

K. Takemura¹³⁶ reported on the effect of water absorption on static and creep properties for jute fiber reinforced composite (JFRC). He mentioned that the static strength and stiffness for JFRC decreases with increased water absorption. He also mentioned that the effect of water absorption is greater at the secondary creep stage than that of the other creep stages.

M. J. Saad et al¹³⁷ reported on the empty fruit bunch (EFB) fiber reinforced polypropylene (PP) composites. They modified the EFB fibers with maleic anhydride (MAH) before preparing the composites. They observed that MAH-treated fiber reinforced PP composites produce higher tensile and better dimensional stability properties.

G. S. Tay et al¹³⁸ investigated on the effect of chemical (epichlorohydrin) loading on the epichlorohydrin modified oil palm empty fruit bunch (EFB) fiber reinforced polyurethane composites (PU). They reported that composites made with EFB modified with EPH to 8% weight percent gain (WPG) produced higher tensile properties than the others. They expressed that higher degree of modification could cause disruption of crystalline region to the EFB.

K. Oksman and C. Clemons¹³⁹ studied and reported on the mechanical properties and morphology of polypropylene(PP)-wood flour(WF) composites with different impact modifiers and maleated polypropylene (MAPP) as a compatibilizer. They used three types of

elastomers as impact modifiers and observed improved impact strength for PP-WF composites. Addition of maleated elastomers gave the greatest improvements in impact strength of the composites. MAPP didn't affect the impact properties of the composites but showed better tensile strength.

CHAPTER 03

EXPERIMENTAL METHODS AND APPARATUS

3.1 Materials

3.1.1 Polypropylene

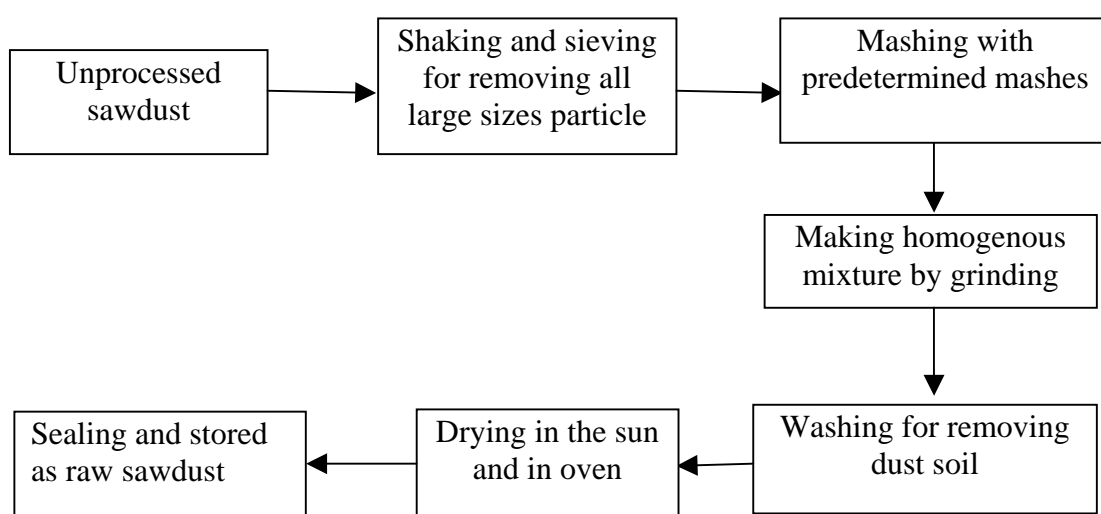
A commercial grade polypropylene (PP) was used in this study. It was manufactured by The Polyolefin Company, Pvt., Ltd., Singapore; and its commercial name is Cosmoplene. Melting point of this PP was measured and found to be 160°C. Melting point and FT-IR spectroscopic observations indicated that the used PP was an isotactic polypropylene and commercial grade. In the literature it is mentioned that the melting point of commercial grade PP lies in the range 160-170°C but Pure PP melts at 176°C.⁸⁵

3.1.2 Sawdust

3.1.2.1 Collection and Processing of Sawdust

The sawdust was collected (20 kg) from local timber house (Sawmill) named Barasha Match Factory, Postagola, Sampur, Dhaka, Bangladesh. The supplied sawdust were of "Cadamba" variety (*Anthocephalus Cadamba*) which is used to made match stick. The sawdust is very soft and available. Sawdust was used because it is recyclable. Collected sawdust was processed by using several physical methods like shaking, sieving, meshing and washing. Initially the sawdust sample was shaken on a large particle such as stone, concrete, bark etc then sieving for removing all undesirable particles and confirmed these are 100% sawdust. This 100% sawdust exist many particle sizes. In this experiment the specific meshes are used. The used meshes in this experiments are mesh70+, mesh100+, mesh140+ and mesh120+. The predetermined particle size sawdust is taken which as above mentioned then these are mixed thoroughly and make it homogenous by using a grinding machine. Previous investigation in our Laboratory reported that the large particle sized sawdust

reinforced composites badly affect the physic-mechanical properties of composites. So no large sizes sawdust and bark is expected in the processed sawdust. After that the pure sawdust washed with distilled water for separating soil and mud in dust from then dried at open atmosphere in sunny place. Finally dried in sun then in oven at 105C and air tight packed and stored. The following diagrams will insight overall processing of sawdust.



Scheme 3.1: Schematic flow diagram of raw sawdust processing

3.1.2.2 Chemicals

The alkali agent sodium hydroxide (reagent grade) was used. The coupling agents used in this study were reagent grade urotropine and adipic acid. The list of chemicals used in this study and their suppliers name are given below:

Chemicals/ Reagents used	Name of Suppliers
Sodium hydroxide (NaOH)	Merck, India
Sulphuric acid (H ₂ SO ₄)	Merck, India

3.2 Surface modification of sawdust by chemical treatment

The chemical modifications of sawdust were conducted by pre-treatment reaction with 10% NaOH solution. The chemical reaction between sawdust and above mentioned chemical was accomplished in our polymer research laboratory, Department of Chemistry, BUET, Dhaka, Bangladesh. The overall process and chemical modification is explained by the following representation.

3.2.1 Chemical modification of sawdust by alkali (NaOH)

Previously cleaned, washed, oven dried and air tight packed required amount sawdust were taken and heated again at 105⁰C for two hours till to get constant weight. Sodium hydroxide solution (10%) was prepared in distilled water in large volume of glass or plastic vessel. Dried sawdust was immersed in 10% sodium hydroxide solution. Sawdust to liquor ratio was 1:20 (w/v). Alkali treatment was carried out for 50 minutes. The reaction between sawdust and NaOH was carried out with occasional stirring by glass rod and carried out at atmospheric condition and no external heat was applied. At the end of the experiment, the color of sawdust transferred golden into blood red as well the solution becomes deep blood red color. After completion of the treatment, the mixture was cooled and filtered to isolate the lignin free cellulose containing sawdust. The alkali treated sawdust were thoroughly washed in tap water and finally washed with distilled water. The pH of the washed sawdust was found neutral by washing again and again with water. The washed alkali treated sawdust were first air-dried and then dried in oven at 105⁰C for 6 hours to get constant weight. The chemical modification basically separated lignin molecule from sawdust as a result finally sawdust becomes softer and raw. In this chemical treatment, NaOH reacts with OH radical at 2, 6 position of

cellulose unit and reduced its affinity to react with moisture content. This alkali treated sawdust was used for fabrication for manufacturing composites specimen with PP. The basic chemical reaction between sawdust and NaOH is given in Scheme 4.1.

3.2.2 FT-IR analysis of raw and chemically treated sawdust

3.2.2.1 Principle

Light from the source is split into two beams. One of the beams is passed through the sample 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.¹²⁰ The absorption of the sample at a particular frequency can be calculated as¹²¹

$$\text{Absorbance, } A = \log (I_0 / I) \quad \dots\dots\dots (3.1)$$

$$\text{Transmittance, } T = I / I_0 \quad \dots\dots\dots (3.2)$$

$$\text{Or, } A = \log (1/T) \quad \dots\dots\dots (3.3)$$

3.2.2.2 FT-IR spectrophotometer

The infrared spectra of raw and alkali treated sawdust were recorded on a Shimazu FT-IR-8101 spectrophotometer. The sample pellets FT-IR spectroscopy was prepared as follows. Approximately 0.5mg of powdered sawdust samples were mixed thoroughly with approximately 100mg 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.

3.2.3 Sampling techniques

Various techniques can be employed for placing the sample in the path of 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 solid and least in case of gases.

Thus the sample of the same substance shows shifts in the frequencies of absorption as we pass beam 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 mention the state of the sample on the spectrum which is scanned for its correct interpretation.¹²¹ Solid for the infra red spectrum may be explained 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.

3.3 Composite fabrication

Sawdust-polypropylene composites were prepared using raw and alkali treated sawdust following the procedure described below:

The raw and alkali treated sawdust were further dried in an oven at 105°C for 6 hours to remove the moisture gained during handling and preservation to maintain the moisture content of about 2-3%. PP polymers were dried in oven for 3 hours at 105°C. Sawdust were mixed thoroughly with polypropylene to prepare composites. PP matrix and sawdust were taken in different weight fractions (Table 3.1).

Table 3.1: Relative amounts of reinforcing materials and polymer matrix by weight fraction (%)

Reinforcing material (%)	Polymer Matrix (%)	Composites
None	PP: 100	100 (wt.%)PP
Raw sawdust: 20	PP: 80	20:80 (wt.%) Raw sawdust-PP
Raw sawdust: 25	PP: 75	25:75 (wt.%) Raw sawdust-PP
Raw sawdust: 30	PP: 70	30:70 (wt.%) Raw sawdust-PP
Raw sawdust: 35	PP: 65	35:65 (wt.%) Raw sawdust-PP
Alkali treated sawdust: 20	PP: 80	20:80 (wt.%) Alkali treated sawdust-PP
Alkali treated sawdust: 25	PP: 75	25:75 (wt.%) Alkali treated sawdust-PP
Alkali treated sawdust: 30	PP: 70	30:70 (wt.%) Alkali treated sawdust-PP
Alkali treated sawdust: 35	PP: 65	35:65 (wt.%) Alkali treated sawdust-PP

Composites were prepared by passing mixtures through a single screw extruder machine (Figure 3.1). The processing temperature of extrusion was controlled at $120^{\circ}\text{C}\pm 5^{\circ}\text{C}$ and pressure was uniform. The sawdust-PP mixtures prepared by extruder machine were continuously fed into the extruder. The composites were delivered through a die of rod shape at a uniform rate. Then the extruded were cut into small pieces of 2-3 cm length by the scissors. The small pieces were then crashed into small granules using a grinding mill (Model FFC-23, Speed 5800 rpm, Machinery Co. Ltd., China). The granulated products were dried in an oven at 105°C for 6 hours and then used in injection moulding.

The extruder used in manufacturing composites was designed and made in our laboratory taking the help of local experts. The photograph of extruder machine is shown below:



Figure 3.1: Extruder machine

3.4 Preparation of composites by injection moulding

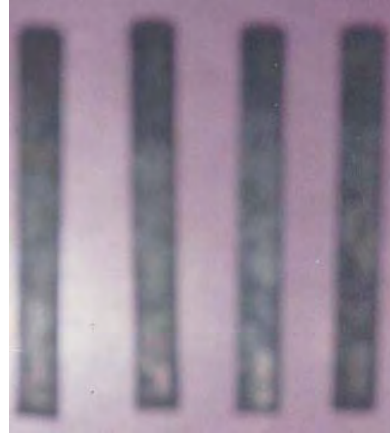
The dried granulated products were moulded as per ASTM standard specimens (tensile and flexural test bars) by an injection-moulding machine (Figure 3.2) at a molding temperature of 120⁰C. The pressure, temperature and heating time of the samples were controlled at the same rate to prepare all composites. The used injection-moulding machine is vertical and operated manually. The sample was heated to melt in the heating chamber, then pumped into closed mould die

applied by the use of a plunger or ram into the heated cylinder. Load (approx. 900 N) was applied for few minutes and then the mould was opened to remove the finished sample. By this way, all the tensile and flexural test specimens were prepared by injection moulding technique. Single moulds were used to prepare tensile and flexural test bars. Injection moulded tensile and flexural test

specimens are shown in Figure 3.2. The photograph of injection moulding machine is shown in Figure 3.3 below:



(a)



(b)

Figure 3.2: Tensile test specimens (a) and flexural test specimens (b)



Figure 3.3: Injection-moulding machine

3.5 Characterization of composites

The composite materials i. e., the fabricated specimens were characterized by the following physico-mechanical properties. These are listed below. FT-IR Spectroscopy, Scanning Electron Microscopy and Thermo gravimetric analysis as stated below:

3.5.1 FT-IR Spectroscopy

The infrared spectra of the PP polymer, raw sawdust, alkali treated sawdust and 30 wt.% raw sawdust reinforced PP composites and 30 wt.% alkali treated sawdust reinforced PP were recorded on a Shimadzu FTIR-8101 spectrophotometer. The samples pellets for FT-IR spectroscopy were prepared according to previous description. IR spectra with all information about absorbance were obtained in the printed form. IR spectra obtained this study are presented in the result and discussion section.

3.5.2 Methods for the Determination of Physical Properties

3.5.2.1 Scanning electron microscopy (SEM) analysis

The fractured surfaces of the tensile test specimens were used to examine by a scanning electron microscope (S-3400 N, Hitachi Co. Ltd., Japan). A computer is integrated with the machine with relevant software. Scanning electron micrographs of the samples is obtained from computer. The photographs and their nature are presented in the result and discussion section.



Figure 3.4: Scanning Electron Microscope

3.5.2.2 Thermal analysis

Thermal analysis includes a group of techniques where some physical property of the sample is monitored under controlled conditions with variation of temperature at a programmed rate. When the mass change is monitored, which indicate chemical reactions, are called Thermogravimetry (TG). When heat absorption is monitored, the result indicate crystallization, phase change etc. as well as reactions. This is called Differential Thermal Analysis (DTA). Together, they represent a powerful method of analysis. DTG stands for Differential Thermo Gravimetry. If not the weight

itself rather the first derivative of the sample weight with respect to time at constant temperature or with respect to temperature at constant value of heating is determined then this procedure is termed as DTG. The fractured surfaces of the tensile test specimens were used to TG/DTA analysis. The thermal test of the fractured composite specimen was taken computer controlled TG/DTA 6300 system controlled to an EXTAR 6000 STATION, Seiko Instrument, Inc. Japan. The TG/DTA module uses a horizontal system balance mechanism. The graphs are presented in the result and discussion section.



Figure 3.5: TGA/DTA/DTG Analyzer

3.5.2.3 Water absorption test of composites

In order to measure the water absorption of the composites, flexural tested rectangular specimens were cut from each sample having dimensions of 39 mm x 10mm 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 for about 24 h at room temperature and in boiling water for 2 hours as described in ASTM D570-99.¹⁴⁰ Excess water on the surface of the samples was removed by using a 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:¹⁴⁰

$$\text{Increase in weight, \%} = \frac{(\text{wet wt} - \text{conditioned wt})}{(\text{conditioned wt})} \times 100$$

3.6 Methods for the testing of mechanical properties

In order to investigate the mechanical properties of the prepared composites the following tests were carried out; (a) tensile (b) three point flexural and (c) hardness. For these tests the appropriate ASTM methods / Universal Testing Methods were followed. Specification and picture of the used machines, set-up of the tests, operating conditions and dimension of the test specimens are described below.

3.6.1 Tensile strength test

The static tensile test of the composites were carried out in an universal tensile testing machine, model: HOUNSFIELD, H 10KS capacity: 10 KN, HOUNSFIELD Co. Ltd., Japan (Fig. 3.5) at a cross head speed of 10mm/min. Tensile tests were conducted following ASTM D 638-01¹⁴¹ and each test was performed until tensile failure

occurred except 100% PP composite. Dumbbell-shaped injection moulded composites were used as test specimen without having any kind of machining. Dimension of tensile test specimen is shown in Fig. 3.4 and its width and thickness were 10mm and 4mm respectively. Eight to ten specimens of each composition were tested and the average values were reported by calculating of maximum five values. The load vs elongation curves were obtained by the electronic chart recorder of the instrument. The maximum (peak) load values were also recorded by the instrument, which can be recalled after the completion of the test. The highest load in the tensile test gives the tensile or ultimate strength.

Tensile stress and strain values were calculated from the load vs elongation curves. Then the tensile stress vs strain curves were drawn and tensile modulus were automatically obtained from graph by computer. To determine the tensile strength, programmable computer runned machine was calibrated by setting the following data:

Load: 1000, Extension: 100/50, Gauge: 60, Speed: 10, Approach: 5, Preload: 0

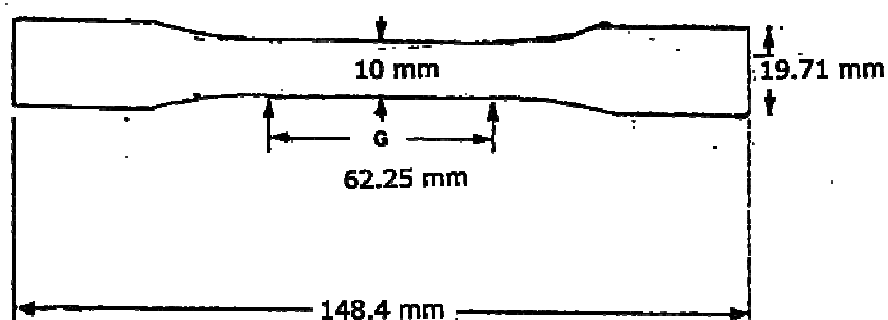


Figure 3.6: Dimension of tensile test specimen



Figure 3.7: Tensile test machine

3.6.2 Three point flexural test

The static flexural tests of the composites were carried out by same machine that was used for tensile test only by changing the attachment. Set-up of the three point flexural test and dimension of the specimen are shown in Fig.3.6. Dimension of flexural test specimen is 66mm length, 10mm width and 4mm thickness. Flexural tests were conducted following Universal Testing Method /ASTM D 790-00¹⁴² at a cross head speed of 2mm/min. Injection moulded test specimens (Fig. 3.6) were used directly to perform the flexural testing operation and the operating conditions were Load

range: 10000, displacement range: 20, preload: 0 and auto run: off. Five specimens of each composition were tested and the average values were reported. The load displacement curves were obtained from the electronic chart recorder and the maximum (peak) load values were also recorded by the instrument, which can be recalled after the completion of the test. The flexural strength (σ_{fM}) and modulus of elasticity (E_B) were calculated by the computer program.

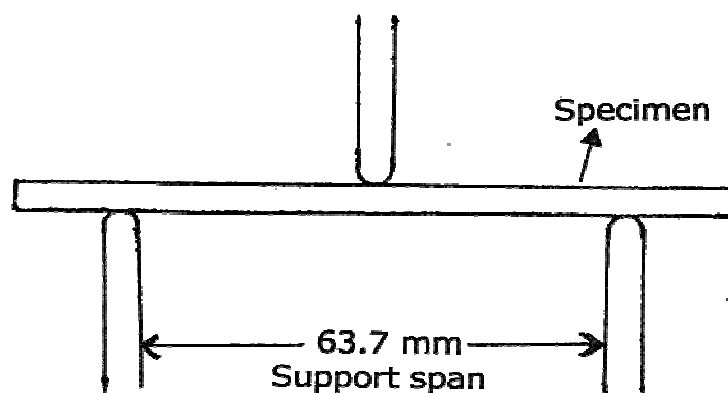


Figure 3.8: Set-up of three point flexural test and dimension of specimen

3.6.3 Hardness test

Rebound hardness of composites were carried out following ASTM D 785-98.¹⁴³ A Rebound 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.¹⁴³ Specimen samples used in flexural test were used to conduct this experiment. Procedure A was followed using C scale with a 6.35 mm diameter indenter and 490 N major load. Rebound hardness testing instrument is shown in Figure 3.9. Five measurements were taken for each specimen and the results were

averaged of ten specimen. The results are presented in the results and discussion chapter.



Figure 3.9: Rebound hardness testing instrument

CHAPTER 04

RESULTS AND DISCUSSION

Physico-mechanical properties of sawdust reinforced polypropylene composites have been studied in present research work. Two types of composites have been prepared, viz. raw sawdust-PP composites and alkali treated sawdust-PP composites. Sawdust have been chemically modified by alkali. Sodium hydroxide was used as alkali agent. The structural change of sawdust due to alkali treatment was confirmed by IR-spectra (shown in Figure 4.3). Raw and alkali treated sawdust were used separately to prepare sawdust-PP composites by using a single screw extruder. Sample specimens of specific size and shape have been prepared by using an injection moulding machine for the study of mechanical properties. Tensile strength, tensile modulus, elongation at break, flexural strength, strain at break, strain at maximum and flexural modulus of the prepared composites were measured by using universal testing machine. The results are presented in the following sections.

4.1 FT-IR spectroscopic analysis of raw sawdust, alkali treated sawdust and polypropylene

FT-IR spectra of raw sawdust, alkali treated sawdust and chemically treated sawdust were taken in the Infra-red Spectrophotometer (Shimadzu FTIR-8101). The spectra and their brief descriptions are presented in the following sections.

4.1.1 FT-IR spectroscopic analysis of raw sawdust

The FT-IR spectrum of raw sawdust is shown in Figure 4.1. The peak assignments of the absorption bands corresponding to various groups are summarized in Table 4.1 which are quite similar to the literature values.^{144-147,135} The FT-IR spectrum of raw sawdust shows a band in the region near 1636cm^{-1} , which is probably due to

the CO group of acylester in hemicellulose or aldehyde group in lignin.¹¹³ On the other hand, absorption bands of raw sawdust give clear peak of cellulose, lignin, hemicelluloses. It was found that the existence of aromatic ring with desired functional group spectrum.

Table 4.1: FT-IR spectral data of untreated raw sawdust

Position/ cm^{-1}	Assignment
~ 3600-3200	$\nu(\text{OH})$ broad, strong band from the cellulose, hemicellulose and lignin of sawdust
~ 3000-2900	$\nu(\text{C-H})$ in aromatic ring and alkanes
~ 1750-1710	$\nu(\text{C=O})$ most probably from the lignin and hemicelluloses
~1650-1630	possibly aromatic ring
~ 1635	adsorbed water
~ 1608	$\nu(\text{C=C})$ aromatic in-plane
~ 1508.2	$\nu(\text{C=C})$ aromatic skeletal ring vibration due to lignin
~ 1455	$\delta(\text{C-H})$; $\delta(\text{C-OH})$ 1° & 2° alcohol
~ 1419.5	$\delta(\text{C-H})$
~ 1365	$\delta(\text{C-H})$
~ 1315	$\delta(\text{C-H})$
~ 1280	$\delta(\text{CH}_2)$ twisting
~ 1255.6	$\delta(\text{C-OH})$ out-of-plane
~ 1200	$\delta(\text{C-OH})$; $\delta(\text{C-CH})$
~ 1155	$\nu(\text{C-C})$ ring breathing, asymmetric
~ 1105	$\nu(\text{C-O-C})$ glycosidic
~ 1050	$\nu(\text{C-OH})$ 2° alcohol
~ 1033.8	$\nu(\text{C-OH})$ 1° alcohol
~ 1005	$\rho(-\text{CH}-)$
~ 985	$\rho(-\text{CH}-)$
~ 895	$\nu(\text{C-O-C})$ in plane, symmetric

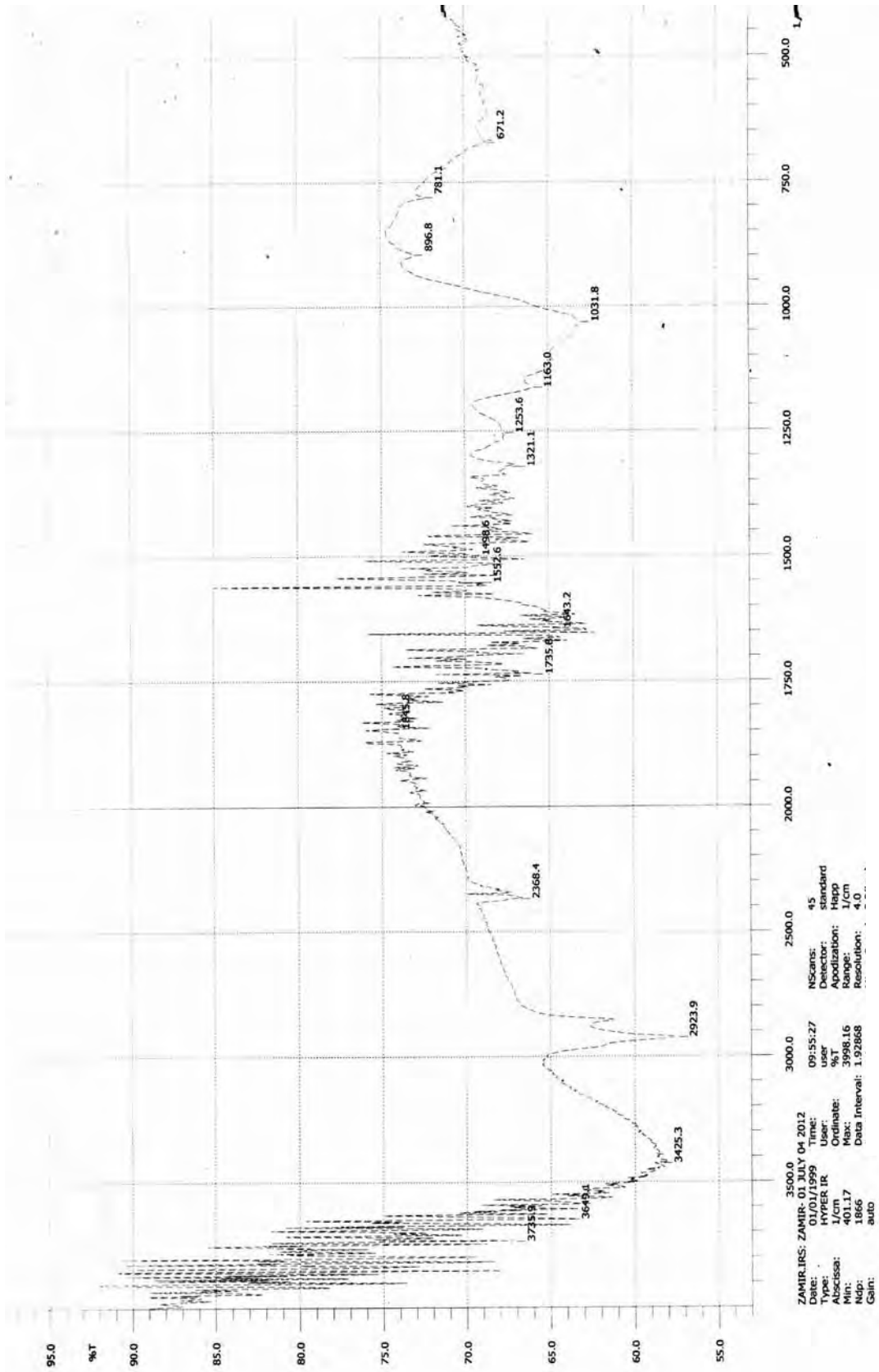


Figure 4.1: Infrared spectrum of raw sawdust

4.1.2 FT-IR spectroscopic analysis of polypropylene

Polypropylene is a semicrystalline polymer. For a semicrystalline polymer, its crystallinity 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 PP, an IR spectrum was taken which has been presented in Figure 4.2. FT-IR spectroscopic observation was used to identify the crystalline and amorphous domains in the PP structure. Absorptions at 1167.1, 997.3, 898.9, 842 and 808.3 cm^{-1} positions are due to the crystalline phase of PP and absorptions at 974.2 cm^{-1} positions is due to the amorphous or irregular phase of PP. The peak assignments of the absorption bands of PP are summarized in Table 4.2 which are quite similar to the literature values.^{95,147-149} The main peaks, their associated vibrational modes, associated microstructures, and dipole moment orientation angles with respect to the main chain are listed below:

Table 4.2: FT-IR spectral data of polypropylene

Wave Number (cm^{-1})	Possible Assignment
~ 2900—2880	Doublet due to C—H vibration of $-(\text{CH}_3)$ group
~ 1458.4	Methyl asymmetric deformation vibration
~ 1377.3	Methyl symmetric deformation vibration
~ 1167.1	C—C stretching, CH_3 wagging
~ 997.3	C—C stretching, CH_2 rocking, CH_3 rocking Absorptions are due to the crystalline phase of PP
~ 974.2	C—C stretching, CH_2 rocking, CH_3 rocking Absorption due to the amorphous or irregular phase of PP
~ 898.9	C—C stretching, Coupled C—H deformation
~ 841.1	C—C stretching, CH_2 rocking
~ 808.3	C—C stretching, Coupled C—H deformation

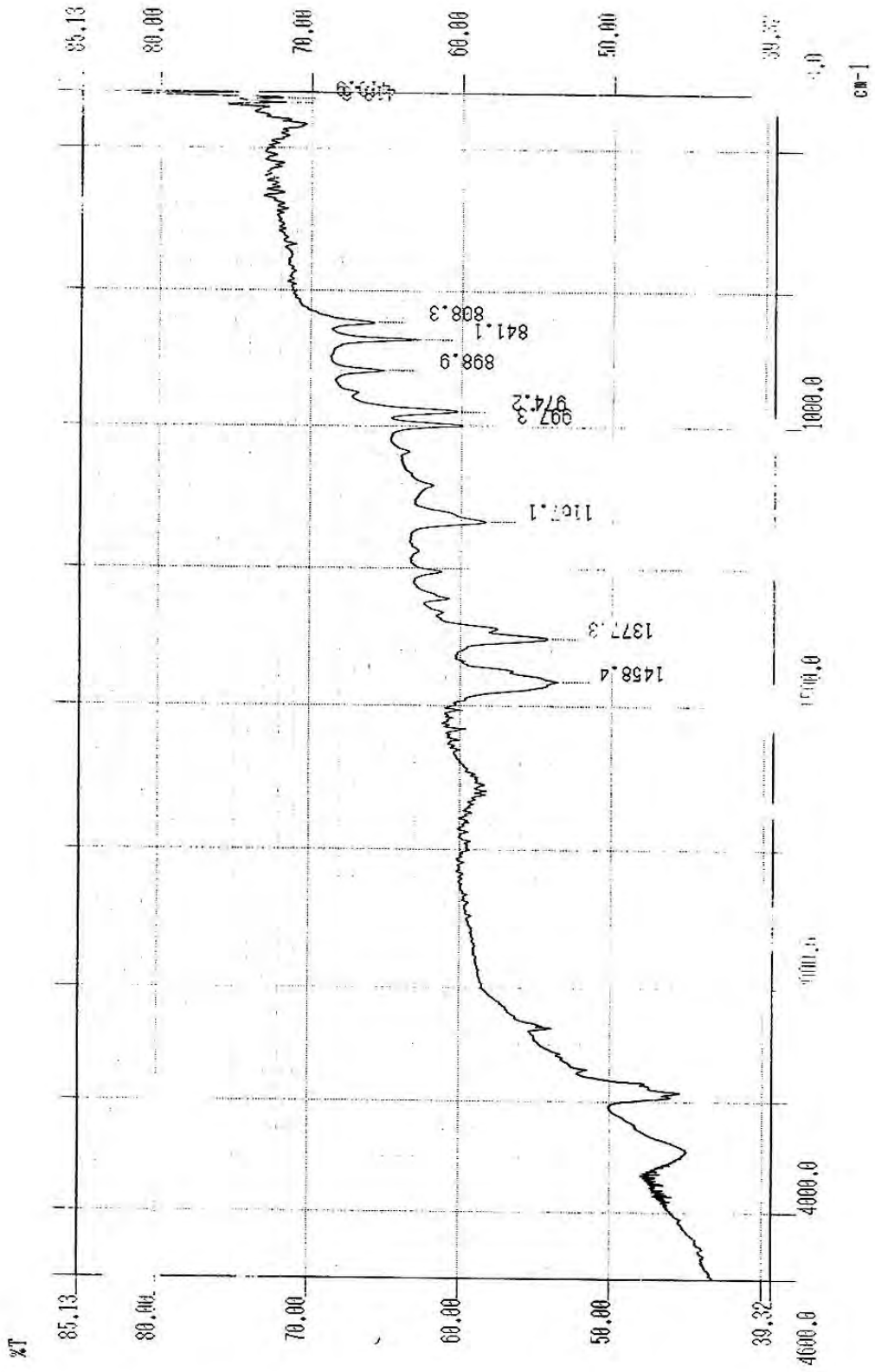
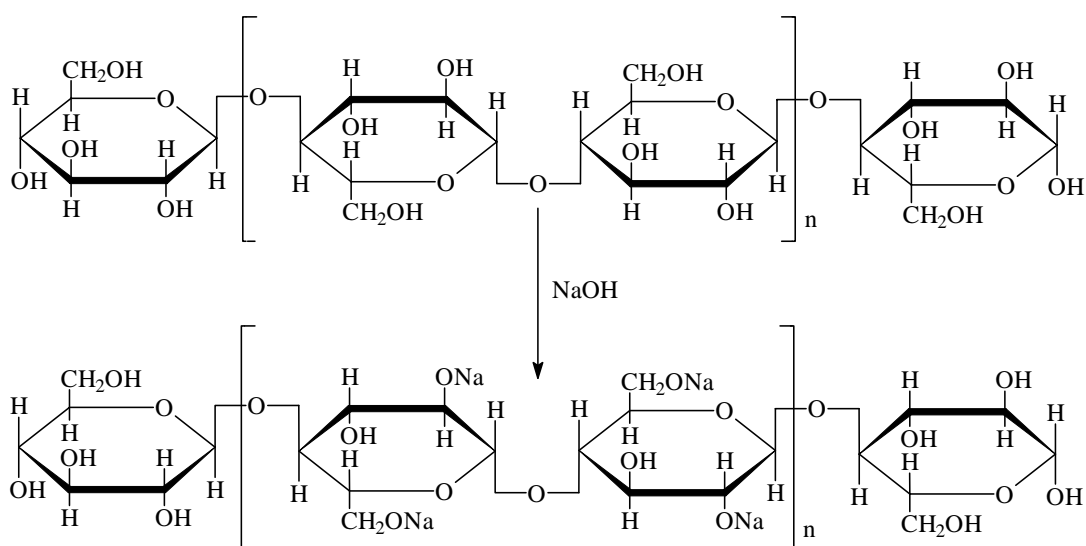


Figure 4.2: Infrared spectrum of polypropylene

4.2 Chemical modification of sawdust by alkali treatment

Sodium hydroxide treatment was done to remove the lignin from cellulose of raw sawdust. Upon chemical treatment of sawdust by alkali, NaOH breaks the OH groups at C₂ and C₆ positions of the cellulose of sawdust, producing 2, 6-disodium cellulose¹³⁹ as shown in the Scheme 4.1. May be due to steric effect, the hydroxyl group at C₃ does not undergo chemical reaction with the Na⁺ ion of alkali NaOH. In this chemical treatment NaOH react with radical in 2, 6 position of cellulose unit and reduced its affinity to react with moisture content.



Scheme 4.1: Chemical reaction of sawdust with alkali

4.2.2 FT-IR spectroscopic characterization of alkali treated sawdust

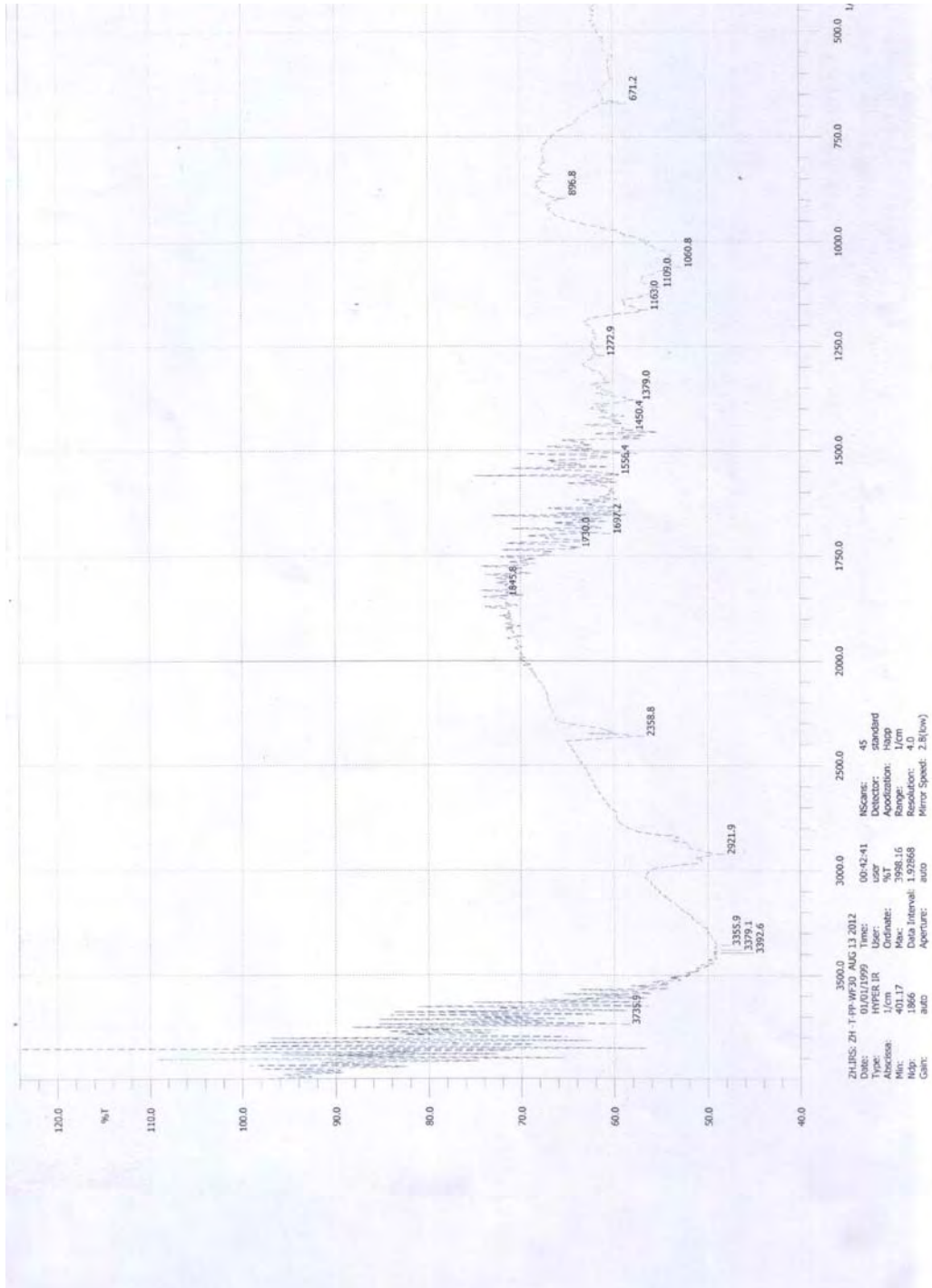


Figure 4.3: Infrared spectrum of alkali treated sawdust

4.2.4 FT-IR spectroscopic characterization of chemically treated sawdust

The chemically treated product 2, 6-disodium cellulose has been characterized by infrared spectroscopic analysis. The IR spectrum of chemically treated sawdust is presented in Figure 4.3. The IR spectrum shows characteristic bands of nitro group at the region of 1374.3 cm^{-1} and 896.91 cm^{-1} which may be due to the stretching frequency of nitro group present in the urotropine. There is another absorption band at 896.91 cm^{-1} was found which proved the presence C-H stretching and at the region of near 1716 cm^{-1} due to carbonyl stretching. Untreated sawdust show the absorption band near 1716 cm^{-1} due to the carbonyl group of acetyl ester in hemicellulose and carbonyl aldehyde in lignin.¹⁵⁰ But in the chemically treated sawdust, there is an increased absorption band near 1716 cm^{-1} as compared to the untreated sawdust which is due to the carbonyl aldehyde of dialdehyde cellulose.

4.3 Raw and alkali treated sardust reinforced polypropylene composites

As mentioned earlier sawdust reinforced polypropylene composites were prepared both by using raw and alkali treated sawdust. The composites were characterized by IR-spectroscopic method. The results are presented in the following section.

4.3.1 FT-IR spectroscopic characterization of raw and alkali treated sawdust reinforced polypropylene composites

The FT-IR spectra of 30% (w/w) sawdust-polypropylene composites is shown in Figure 4.4. The peak assignments of the absorption bands corresponding to various groups of sawdust and PP are summarized in Table 4.3.

Table 4.3: FT-IR spectral data of 30 % (w/w) raw sawdust reinforced polypropylene composite

Position/ cm^{-1}	Assignment
~ 3600-3200	$\nu(\text{OH})$ broad, strong band from the cellulose, hemicellulose and lignin of sawdust
~ 3000-2800	$\nu(\text{C-H})$ due to C—H vibration of $-(\text{CH}_2)_n$ group of PP and sawdust
~ 1750-1710	$\nu(\text{C=O})$ most probably from the lignin and hemicellulose of sawdust
~1650-1630	possibly aromatic ring of sawdust
~ 1635	adsorbed water of sawdust
~ 1608	$\nu(\text{C=C})$ aromatic in-plane of sawdust
~ 1508.2	$\nu(\text{C=C})$ aromatic skeletal ring vibration due to lignin of sawdust
~ 1458.4	Methyl asymmetric deformation vibration of PP
~ 1455	$\delta(\text{C-H})$; $\delta(\text{C-OH})$ 1° & 2° alcohol of sawdust
~ 1419.5	$\delta(\text{C-H})$ of sawdust
~ 1377.3	Methyl symmetric deformation vibration
~ 1365	$\delta(\text{C-H})$ of sawdust
~ 1315	$\delta(\text{C-H})$ of sawdust
~ 1280	$\delta(\text{CH}_2)$ twisting of sawdust
~ 1255.6	$\delta(\text{C-OH})$ out-of-plane
~ 1167.1	C—C stretching, CH_3 wagging of PP
~ 1105	$\nu(\text{C-O-C})$ glycosidic of sawdust
~ 1050	$\nu(\text{C-OH})$ 2° alcohol of sawdust
~ 1033.8	$\nu(\text{C-OH})$ 1° alcohol of sawdust
~ 997.3	C—C stretching, CH_2 rocking, CH_3 rocking absorptions are due to the crystalline phase of PP
~ 974.2	C—C stretching, CH_2 rocking, CH_3 rocking absorption due to the amorphous or irregular phase of PP
~ 898.9	C—C stretching, Coupled C—H deformation of PP
~ 841.1	C—C stretching, CH_2 rocking of PP
~ 808.3	C—C stretching, Coupled C—H deformation of PP

FT-IR spectra of 30 % (w/w) alkali treated sawdust reinforced PP composites are shown in Figure 4.5. The characteristic aldehyde band of alkali treated sawdust (Figure 4.3) and C–H vibration of methyl group for PP (Figure 4.2) are merged at the same region. The presence of 70% (w/w) PP in the FT-IR spectrum shows the absorption bands intensity more in PP than the absorption bands intensity in wood fibers. Injection moulded fractured tensile test specimens were used to take FT-IR spectrum of the composites. It is observed that peak or absorption band numbers of wood (both untreated and treated) in sawdust-PP composites show less number than the FT-IR spectra of pure untreated sawdust and treated sawdust. It may be due to the degradation of some ingredients of untreated and treated sawdust through injection moulding process at a high temperature of about 120⁰C.

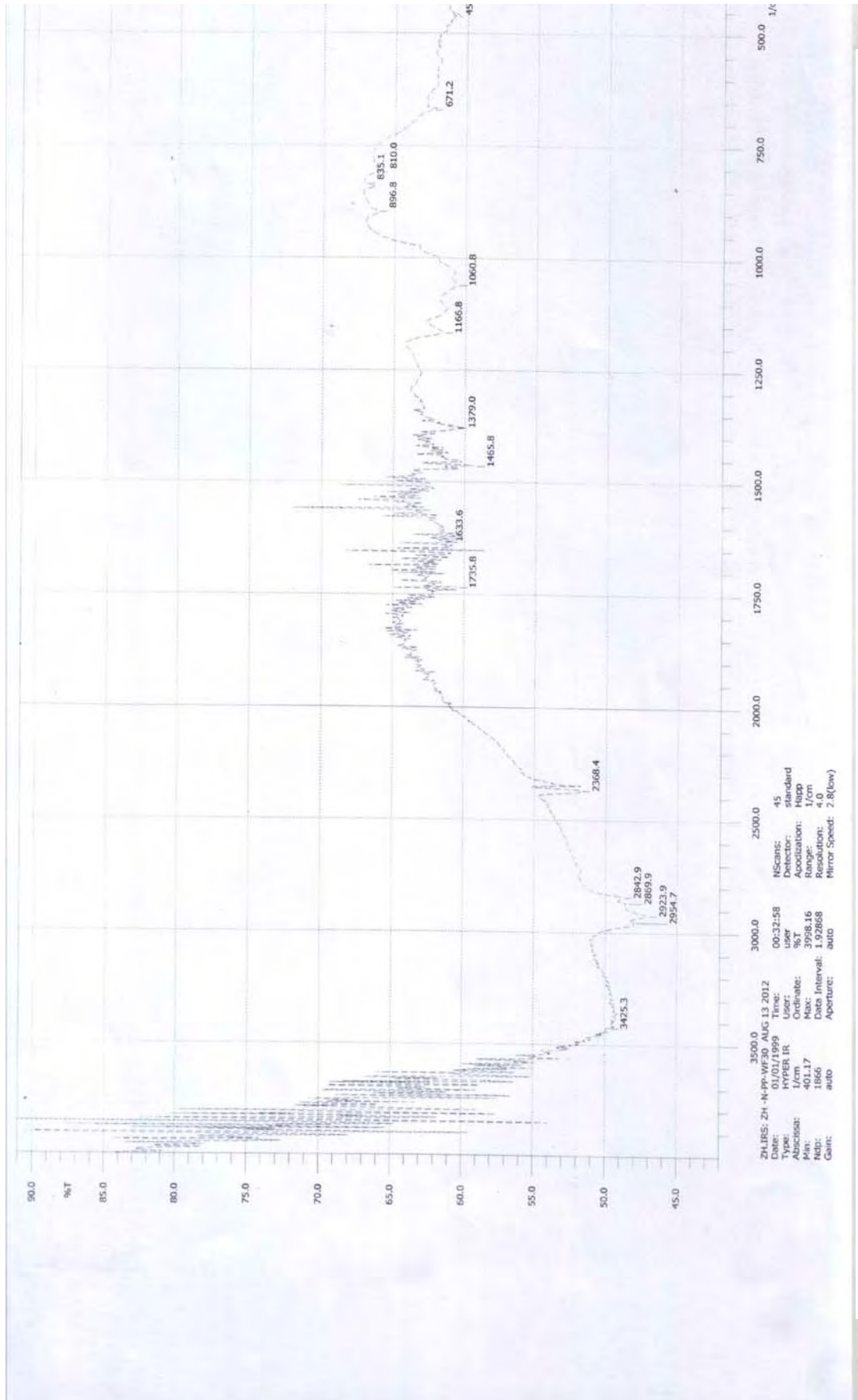


Figure 4.4: Infrared spectrum of 30 % (w/w) raw sawdust reinforced polypropylene composites

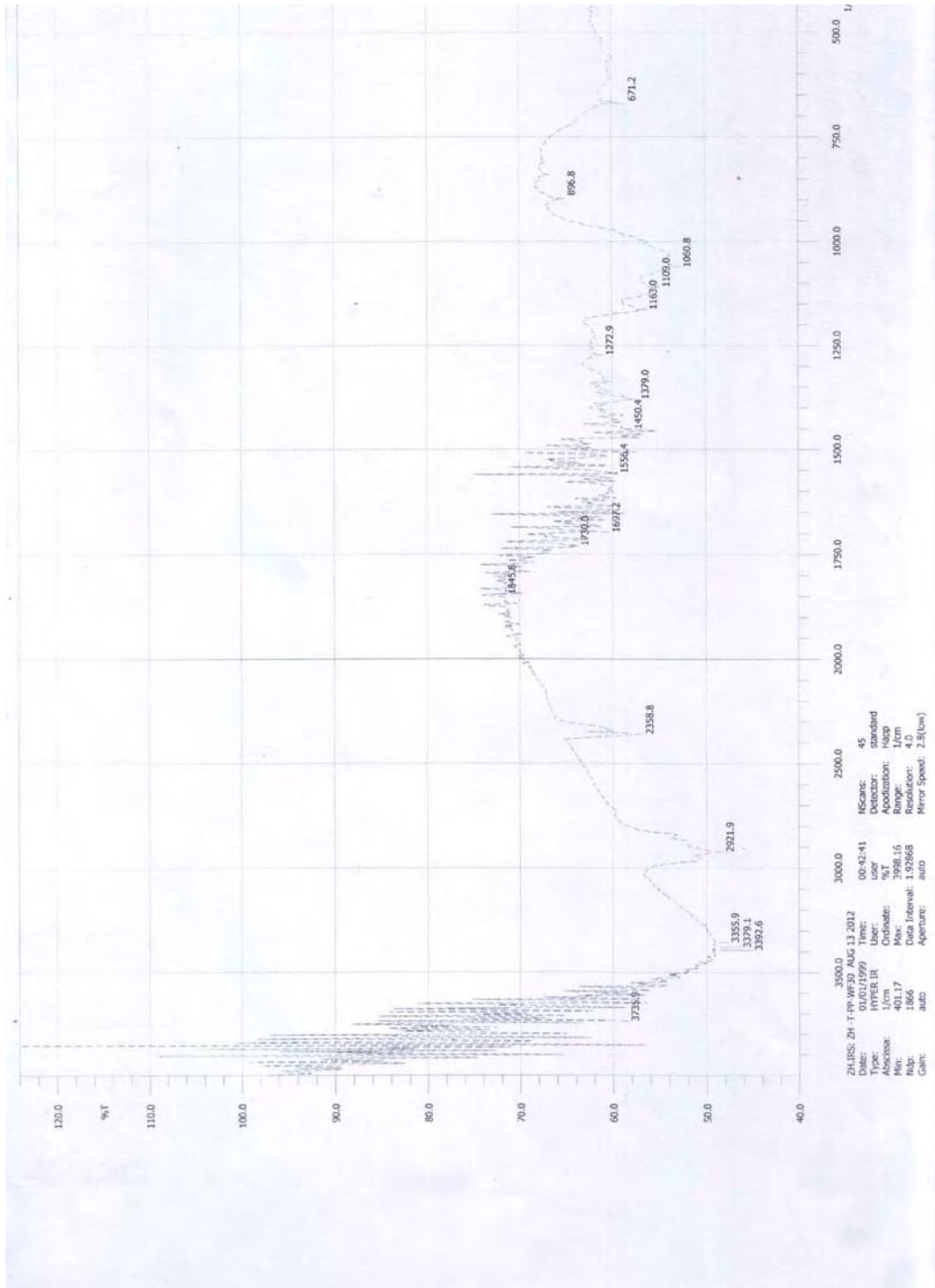


Figure 4.5: Infrared spectrum of 30 % (w/w) alkali treated sawdust reinforced polypropylene composites

4.3.2 Mechanical properties of raw and alkali treated sawdust reinforced polypropylene composites

Tensile strength, tensile modulus, elongation at break, flexural strength, flexural modulus, strain at break and strain at maximum and hardness of the raw and alkali treated sawdust reinforced polypropylene composites have been determined following ASTM and Universal Testing method described in the experimental sections. The results obtained in this study are presented below.

4.3.2.1 Tensile strength, modulus and elongation at break

The tensile strengths of the raw sawdust reinforced PP composites decrease with increasing sawdust loading by weight fraction from 20% (w/w) to 30% (w/w) (Figure 4.6). This may be due to the lack of stress transfer from the PP matrix to fibers. However, the tensile strength of composites starts to increase at 35% (w/w) sawdust loading. Approximately similar results were found for kenaf-PP composites¹³⁷ and empty fruit bunch (EFB) fibers-PP composites¹⁰¹ in the literature. The Tensile modulus increases with increasing sawdust loading (Fig. 4.7) as compared to 100 wt.% PP. Elongation at break decreases with increasing sawdust loading (Fig. 4.8). Stress versus strain curves of the raw sawdust-PP composites are shown in Figure 4.9, where a decrease in failure strain was observed with an increase in sawdust content.

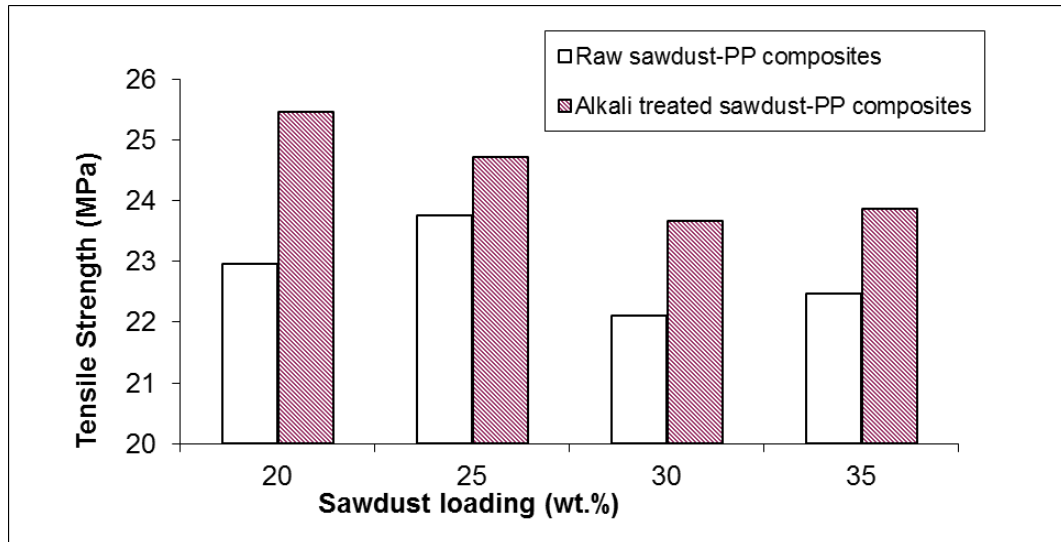


Figure 4.6: Tensile strength vs fiber content (wt.%) curve for raw and alkali treated sawdust-PP composites

From the Figure 4.6 it is observed that the tensile strengths of the alkali treated sawdust reinforced PP composites are 1.5 to 4% more than that of raw sawdust-PP composites. But tensile strength of the alkali treated sawdust-PP composites fluctuates with increasing fiber loading by weight fraction from 20 wt.% to 35 wt.% unlike raw sawdust-PP composites. It is also observed from the figure that the tensile strength starts to increase at 35 wt.% sawdust loading. Figure 4.7 and Figure 4.8 shows that with the increase of sawdust loading to the polymer composites the tensile modulus increases and elongation at break decreases from 25% to 35% sawdust loading. It is also found that elongation at break of alkali treated sawdust-PP composites is slightly higher than that of untreated sawdust-PP composites. Increasing of the elongation at break of the composites increases the toughness or ductility of the composites. Stress versus strain curves of untreated and alkali treated sawdust-PP composites are shown in Figure 4.9 with comparing to 100 wt.% matrix polymer PP. It is observed that the initial tensile modulus or

stiffness of the composites significantly increases with increasing sawdust loading as compared to 100 wt.% PP matrix.

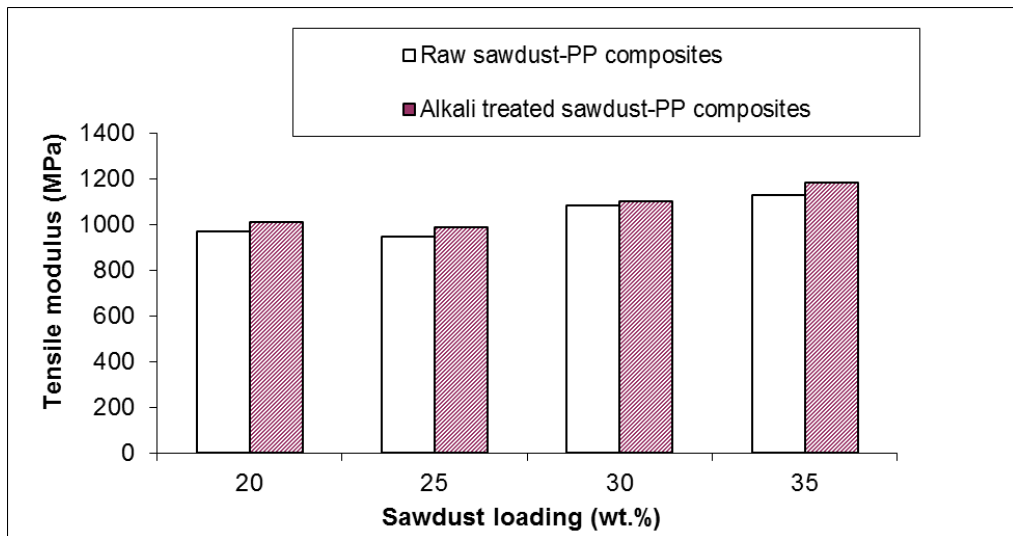


Figure 4.7: Tensile modulus vs sawdust loading (wt.%) curves for raw and alkali treated sawdust-PP composites

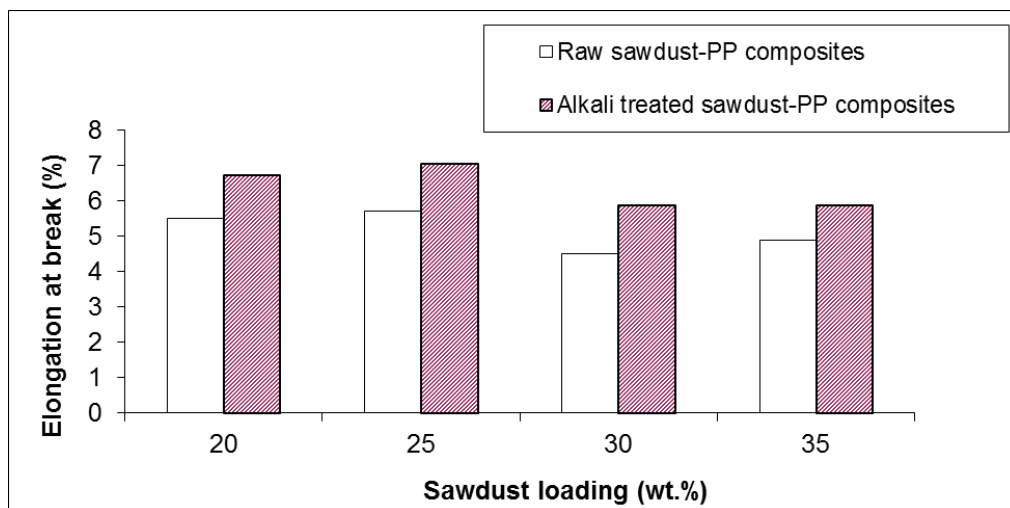


Figure 4.8: Elongation at break vs fiber loading (wt.%) curves for raw and alkali treated sawdust-PP composites

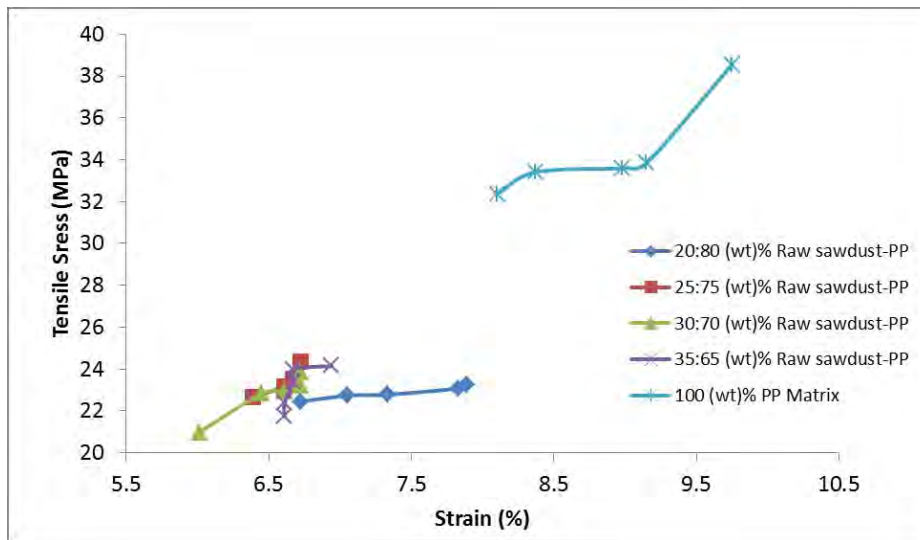


Figure 4.9: Tensile stress vs strain (%) curves for raw sawdust-PP composites

4.3.2.2 Flexural strength and modulus

Results on flexural strength of the raw and alkali treated sawdust-PP composites have been presented in Figure 4.10 against the percentage (wt.) of sawdust loading. It is observed from the figure that the values of flexural strength for both the composites increase with increasing sawdust loading up to 30 wt.%, then it starts to decrease at 35 wt.% sawdust loading as compared to 100 wt.% PP matrix. The experimental values of flexural modulus at different sawdust loading have been presented in Figure 4.11. It is observed from the figure that flexural modulus for both raw and alkali treated sawdust-PP composites increases significantly with increasing sawdust loading. It is also seen from the figure that the flexural strength and modulus of alkali treated sawdust-PP composites have

similar sawdust content effects like raw sawdust-PP composites. However, higher values of flexural strength and flexural modulus observed in the case of alkali treated sawdust-PP composites than

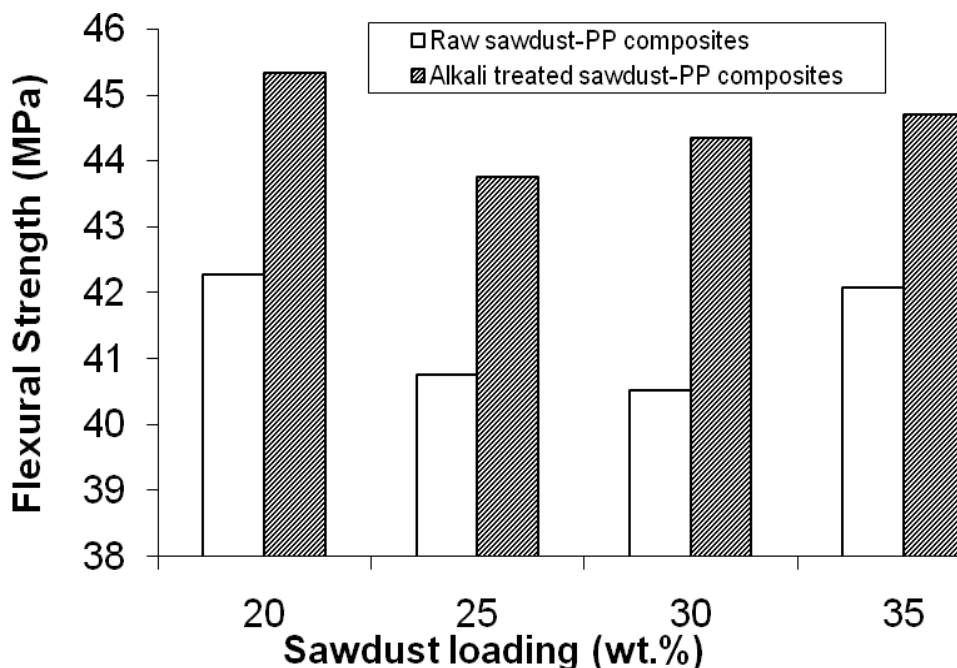


Figure 4.10: Flexural strength vs sawdust loading (wt.%) curves for raw and alkali treated sawdust-PP composites

that of raw sawdust-PP composites. This may be due to the better compatibility of alkali treated sawdust for the formation of sawdust-PP composites than that of raw sawdust. The better compatibility may arise from the opening of glucoside ring of cellulose molecules (Scheme 4.1). It is quite logical to expect that better entanglement is possible from the open chain large molecule than the cyclic molecule.

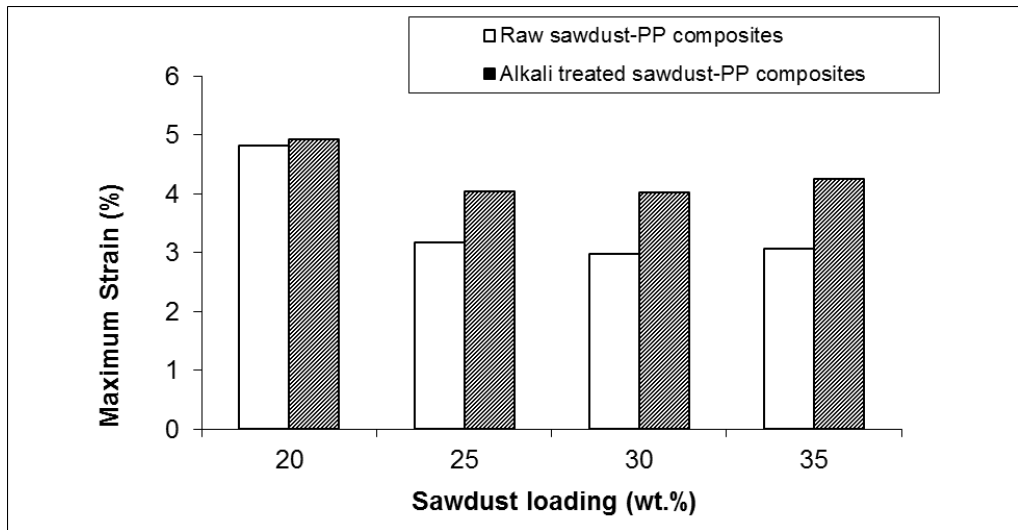


Figure 4.11: Maximum strain vs fiber loading (wt.%) curves for raw and alkali treated sawdust-PP composites

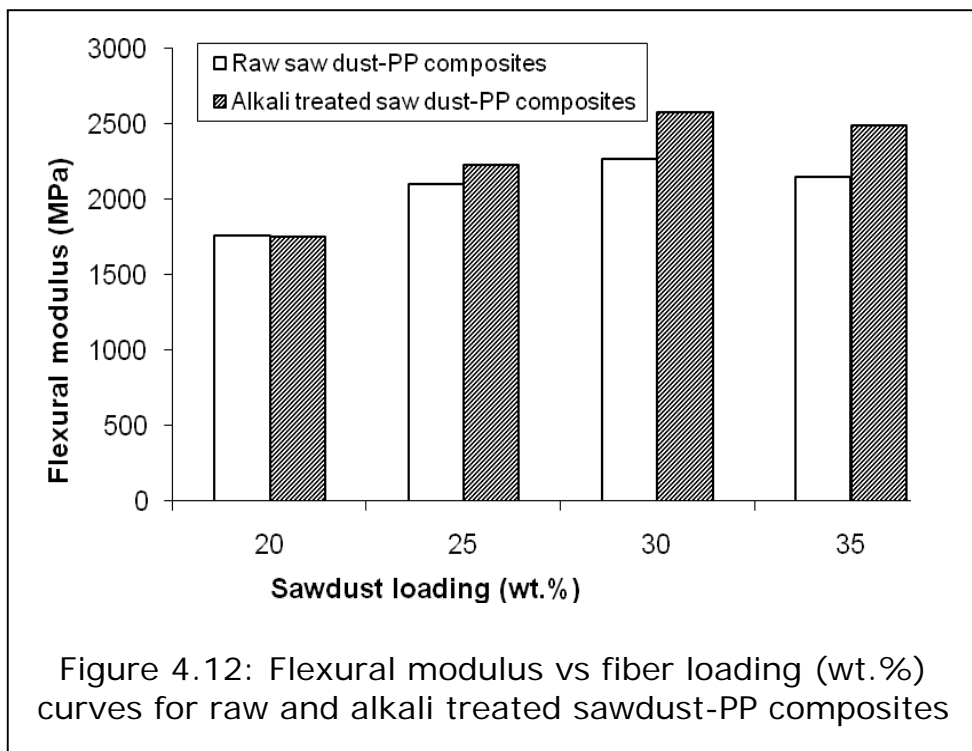
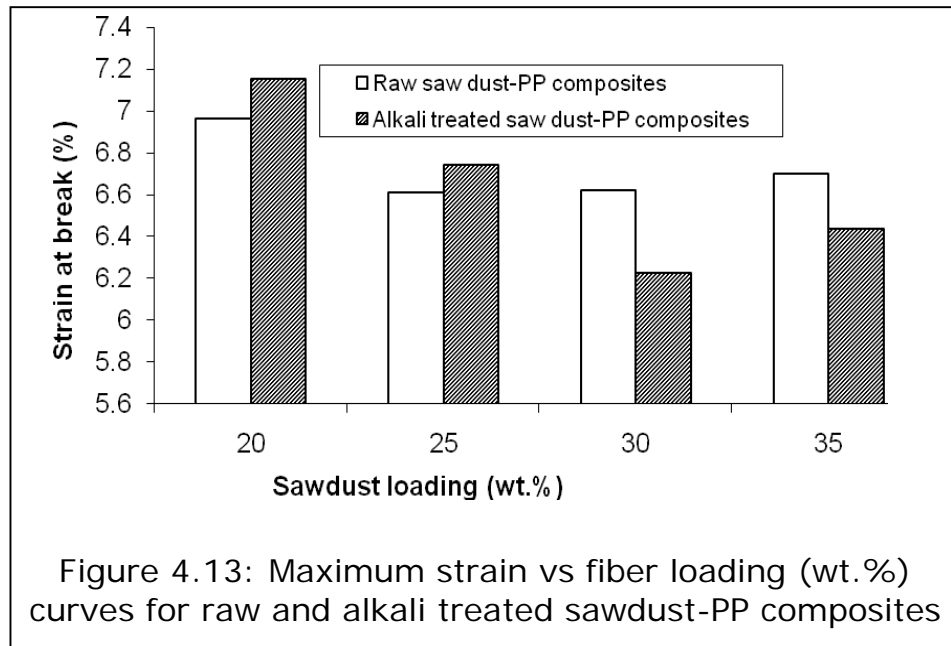


Figure 4.12: Flexural modulus vs fiber loading (wt.%) curves for raw and alkali treated sawdust-PP composites



4.3.2.3 Hardness

Rockwell and Rebound hardness of the samples were measured by using Hardness Tester. Surface of the samples were treated with glycerin before measuring the rebound hardness. A Rockwell hardness number is directly related to the indentation hardness of a plastic material, with the higher the reading, the harder the material.¹⁴³ Rockwell and Rebound hardness of the composites are shown in Table 4.4. It is found that Rockwell hardness of the alkali treated sawdust-PP composites is higher than raw sawdust-PP composites. It is also found that Rockwell hardness of the composites is higher than PP polymer matrix and it increases with increasing fiber loading.

4.3.3 Effect of alkali treatment of sawdust on the mechanical properties of alkali treated sawdust reinforced PP composites

All the mechanical properties according to series of formulation based on the raw sawdust-PP and alkali treated sawdust-PP composites are summarized in the Table 4.4. Most of the results are significantly more for alkali treated sawdust-PP composites than raw sawdust-PP composites. The reasons of these enhancement results may be explained on the basis of hydrophilic nature of sawdust and hydrophobic nature of PP matrix. There is very poor wettability and adhesion between hydrophilic sawdust and hydrophobic PP matrix. Chemical treatment of sawdust decreases its hydrophilic nature as compared to raw sawdust. Cellulosic hydroxyl group of sawdust forms intermolecular hydrogen bonding and so weakly dispersed in the raw sawdust-PP composite. But chemically treated sawdust contains disodium cellulose and disodium groups are not capable of forming intermolecular hydrogen bonds since disodium groups contain hydrogen bonded only to carbon⁹⁷. Polarity of disodium group is less than hydroxyl group and there is no intermolecular hydrogen bonding in the disodium cellulose. So it increases the wettability and adhesion of chemically treated sawdust to PP matrix. The improved interfacial bonding between chemically treated sawdust and PP matrix in the treated sawdust-PP composites increases their mechanical properties as compared to raw sawdust-PP composites. M. Kazayawoko et al also investigated and reported that presence of strong intermolecular hydrogen bonding in the hydrophilic bleached kraft pulp (BKP) fibers decreases the tensile strength properties of BKP reinforced PP composites.

Table 4.4: Results of mechanical tests of raw and alkali treated sawdust reinforced PP composites.

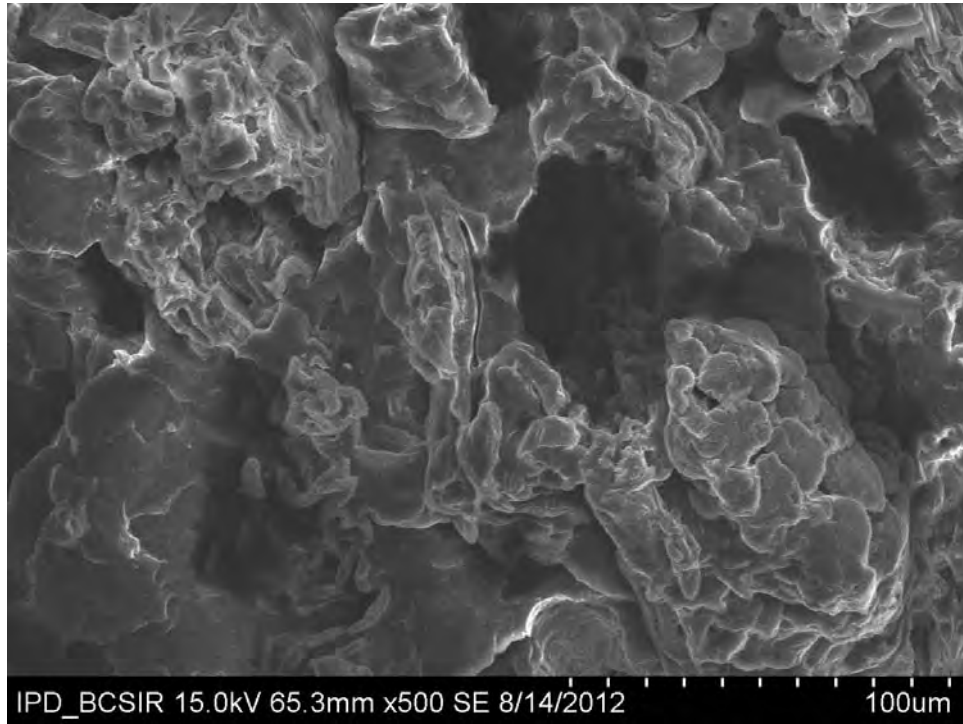
Material	Tensile			Flexural		Hardness	
	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation at break (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Rebound (L Scale)	Rockwell
PP only	26.282	537	46.5	34.354	954.8	602	35.50
PP-Raw sawdust 20 % (wt)	22.968	972.8	5.502	42.284	1757	644.4	40.17
PP-Raw sawdust 25 % (wt)	23.756	948.7	5.706	40.764	2099	637.7	39.72
PP-Raw sawdust 30 % (wt)	22.108	1086	4.4979	40.526	2261.4	635.4	38.79
PP-Raw sawdust 35% (wt)	22.484	1128.8	4.898	42.074	2142.2	654.1	41.23
PP-alkali treated sawdust 20% (wt)	25.45	1014	6.74	45.33	1749	660.9	42.31
PP-alkali treated sawdust 25 % (wt)	24.716	991	7.062	43.758	2221	664.5	42.84
PP-alkali treated sawdust 30% (wt)	23.658	1102	5.888	44.34	2575	661.5	42.65
PP-alkali treated sawdust 35% (wt)	23.866	1183	5.892	44.705	2483.6	661.9	42.61

4.3.4 Morphological (SEM) characterization of raw and alkali treated sawdust reinforced polypropylene composites

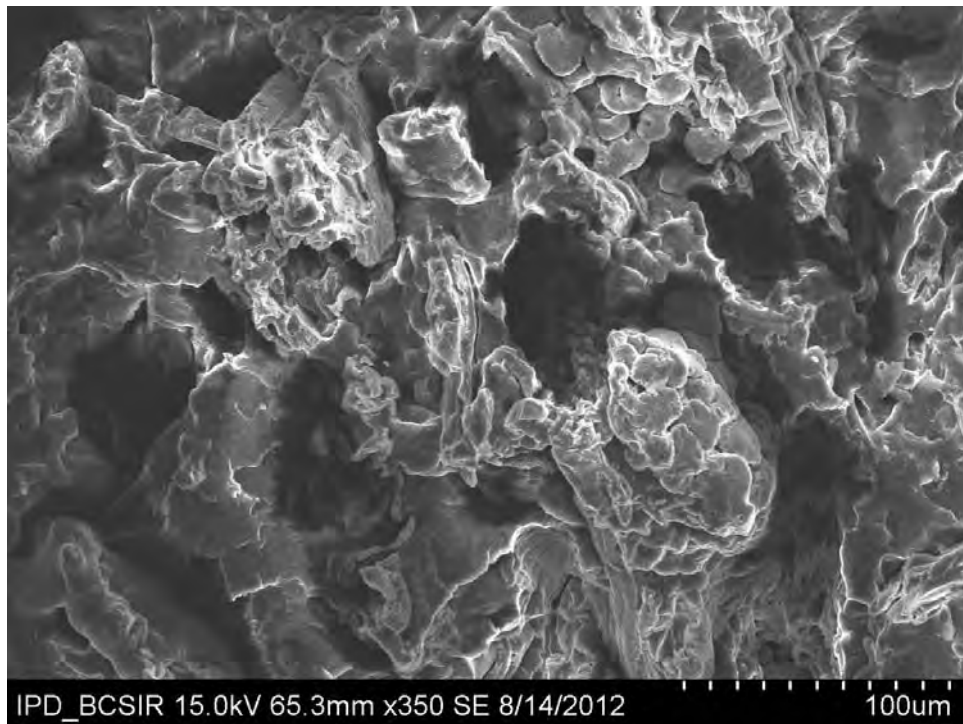
To study the surface morphology of the prepared composites scanning electron micrograph (SEM) were taken using 30 wt.% raw and alkali treated sawdust loading PP composites. Scratched pieces from fractured surfaces of tensile test specimens were used to take SEM and are shown in Figures 4.11 and 4.12. SEM of raw sawdust-PP composite indicates that there is a lack of interfacial interaction that gives the insufficient adhesion between the raw sawdust and PP matrix. Due to intermolecular hydrogen bond formation between sawdust and hydrophobic nature of PP matrix, hydrophilic sawdust

tends to agglomerate into bundles and become unevenly distributed throughout the matrix.

SEM observation of the alkali treated sawdust-PP composite (Fig. 4.13) indicates the better interfacial adhesion between alkali treated sawdust and PP matrix in the alkali treated sawdust-PP composite as compared to raw sawdust-PP composite (Fig. 4.11). Raw sawdust weakly dispersed in the raw sawdust-PP composite due to intermolecular hydrogen bonding and agglomeration. But alkali treated sawdust contains aldehyde group which are not capable of forming intermolecular hydrogen bonds since aldehyde groups contain hydrogen bonded only to carbon⁹⁷. So, alkali treated sawdust dispersed uniformly in the alkali treated sawdust-PP composites. The improved interfacial bonding of alkali treated sawdust-PP composite is clearly seen in the Figure 4.15 than that of raw sawdust-PP composite (Figure 4.14).

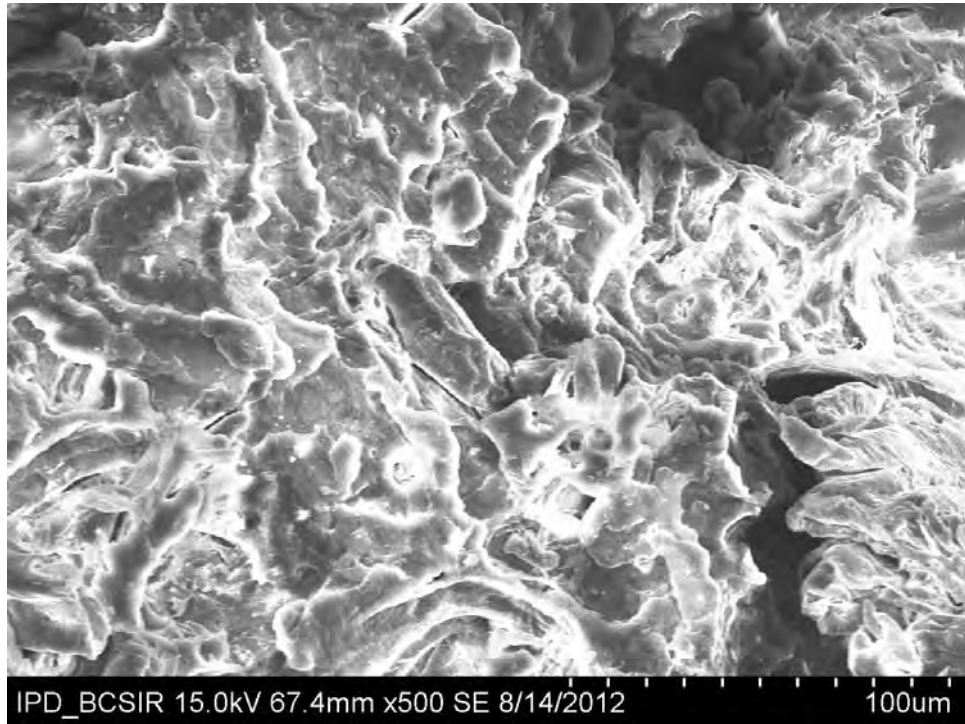


(a)

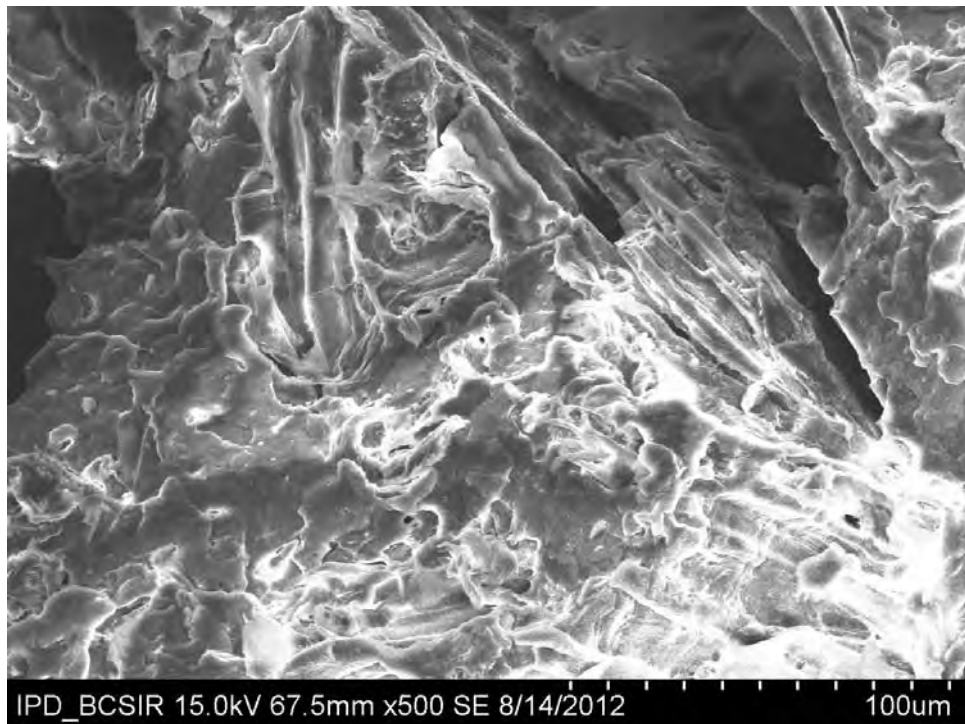


(b)

Figure 4.14: SEM micrograph of 30 wt.% raw sawdust-PP composite



(a)



(b)

Figure 4.15: SEM micrograph of 30 wt.% alkali treated sawdust-PP composite

4.3.5 Thermal Analysis (TGA/ DTA/DTG)

Thermogravimetric analysis (TGA), Differential thermal analysis (DTA) and Derived thermogravimetry (DTG) were performed using a TG/DTA 6300 system controlled by an EXTAR 6000 controller (Seiko Instrument Inc., Japan) with mass of 5-40 mg for different samples . These analyses were run under a stream of nitrogen (20 ml/min) at heating rate of 20⁰C/min within temperature range 20-600⁰C. Thermal properties of PP, raw sawdust (20 wt.% to 35 wt.%)-PP composites and alkali treated sawdust (20 wt.% to 35 wt.%)-PP composites were carried out from different spectra like TG (upper line), DTA (middle line) and DTG (lower line) from graph. Thermal analysis describes on a microscopic scale the removal of all water molecules present in the structure and stepwise loss of less stable part of the composites. Therefore, the weight loss could be attributed to dehydration of molecules absorbed around exchangeable cations, absorbed to internal and external part or condensed in pore space.

The matrix PP was moulded with sawdust of various compositions. The incorporation of sawdust had a significant effect on the thermal stability of composites. The thermal stability of the composites was enhanced due to sawdust incorporation. Following figures depict the TGA/DTA/DTG analysis of the sawdust-PP composites of various ratios.

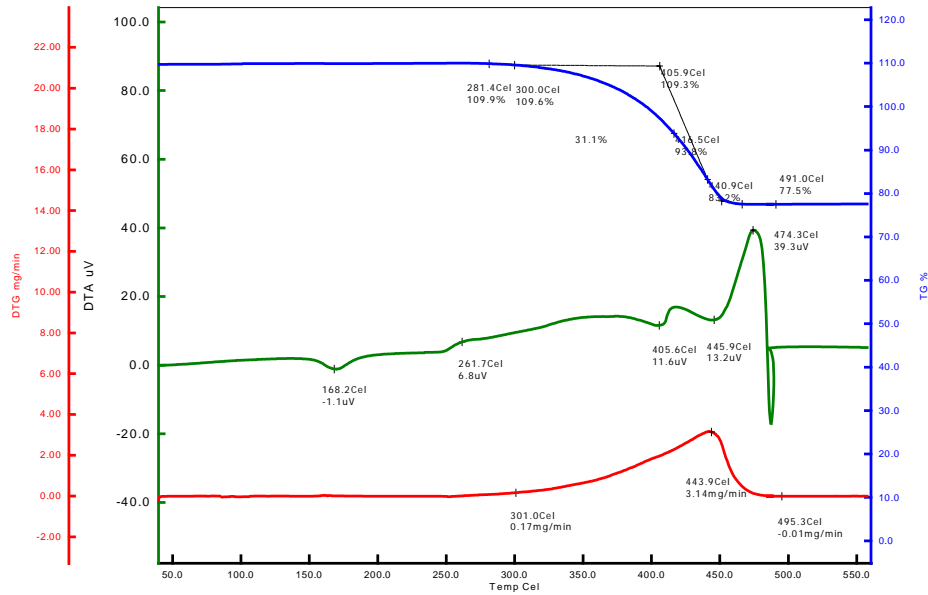


Figure 4.16: TGA/DTA/DTG curves of 100 (wt.%) PP composite

Above Figure 4.16 depicts the TGA/DTA/DTG curves of 100 (wt.%) PP composite. The upper line (Blue line) indicates TG, the middle line (Green line) indicates DTA and lower line (Red line) indicates DTG of PP. From the graph, it is seen that melting of PP starts at 168.2°C. It is also seen that at 600°C, 78% residue filler of PP was found. Three more weight loss happened at 261.7°C, 405.6°C and 445.9°C which was found from DTA line.

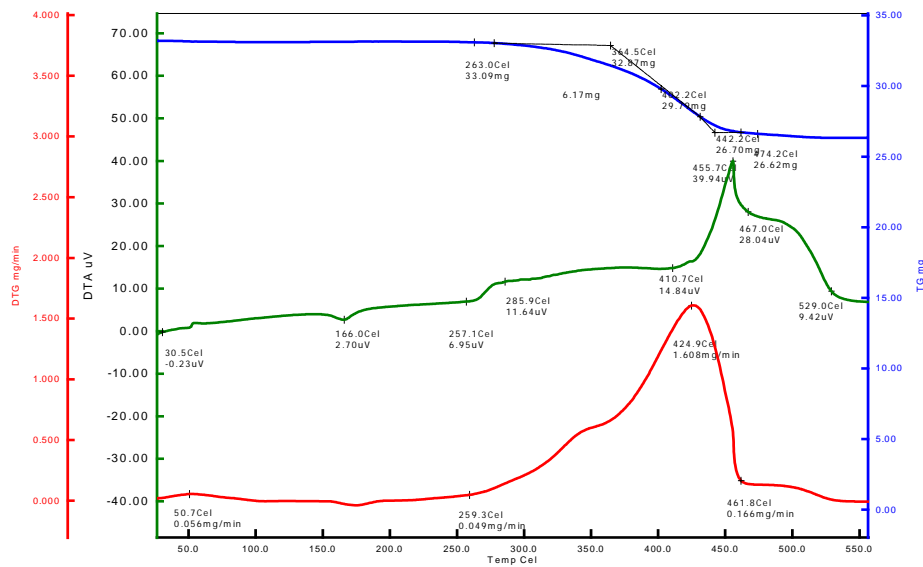


Figure 4.17: TGA/DTA/DTG curves of 20 (wt.%) raw sawdust-PP composites

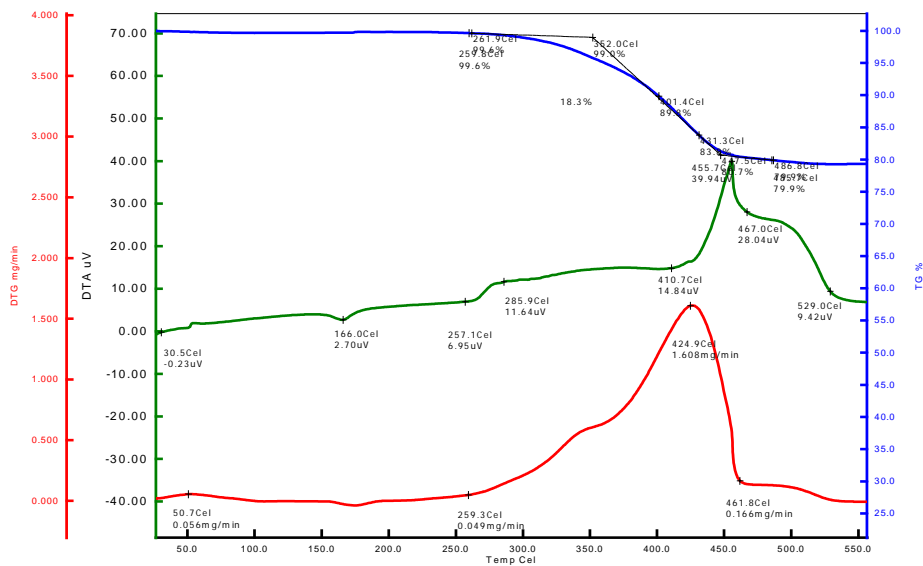


Figure 4.18: TGA/DTA/DTG curves of 20 (wt.%) alkali treated sawdust-PP composites

It is observed from the DTG lines (lower lines) of Figure 4.17 and 4.18 that major reactions occurred i. e.; major weight loss occurred at 424.9°C for both 20 (wt.%) raw sawdust-PP composites and 20 (wt.%) alkali treated sawdust-PP composites.

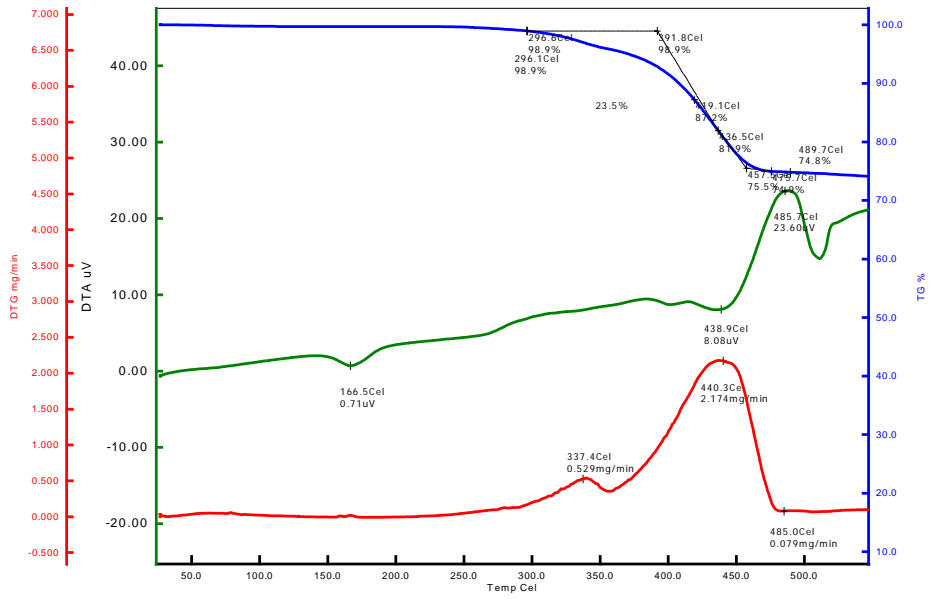


Figure 4.19: TGA/DTA/DTG curves of 25 (wt.%) raw sawdust-PP composites

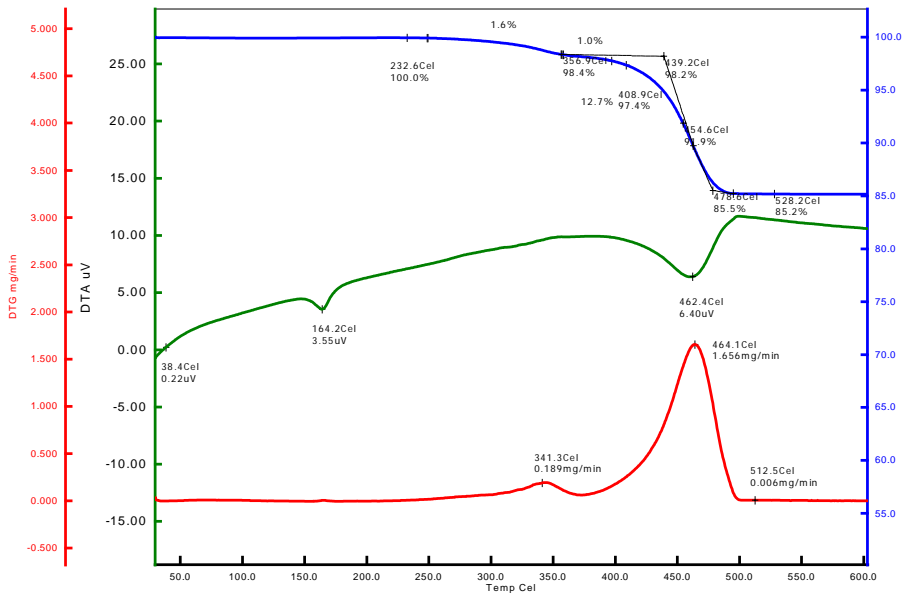


Figure 4.20: TGA/DTA/DTG curves of 25 (wt.%) alkali treated sawdust-PP composites

From the TG lines (Blue lines) of Figure 4.19 and Figure 4.20, it is observed that the residue was 75% of primary weight for 25 (wt.)% raw sawdust-PP composites whereas that was 85% for 25 (wt.)% alkali treated sawdust-PP composites. Again, from the lower line of the graph 4.19, it is observed that the major weight loss was at 440.3⁰C in case of 25 (wt.)% raw sawdust-PP composites. Whereas it was at 464.1⁰C for 25 (wt.)% alkali treated sawdust-PP composites. These values indicate that 25 (wt.)% alkali treated sawdust-PP composites was thermally more stable compared to 25 (wt.)% raw sawdust-PP composites.

Again, from Figure 4.21 and Figure 4.22, it is observed that major weight loss was at 431.3⁰C in case of 30 (wt.)% raw sawdust-PP composites whereas it was at 335.2⁰C in case of 30 (wt.)% alkali treated sawdust-PP composites. These values also indicate the comparative stability of alkali treated sawdust-PP composites.

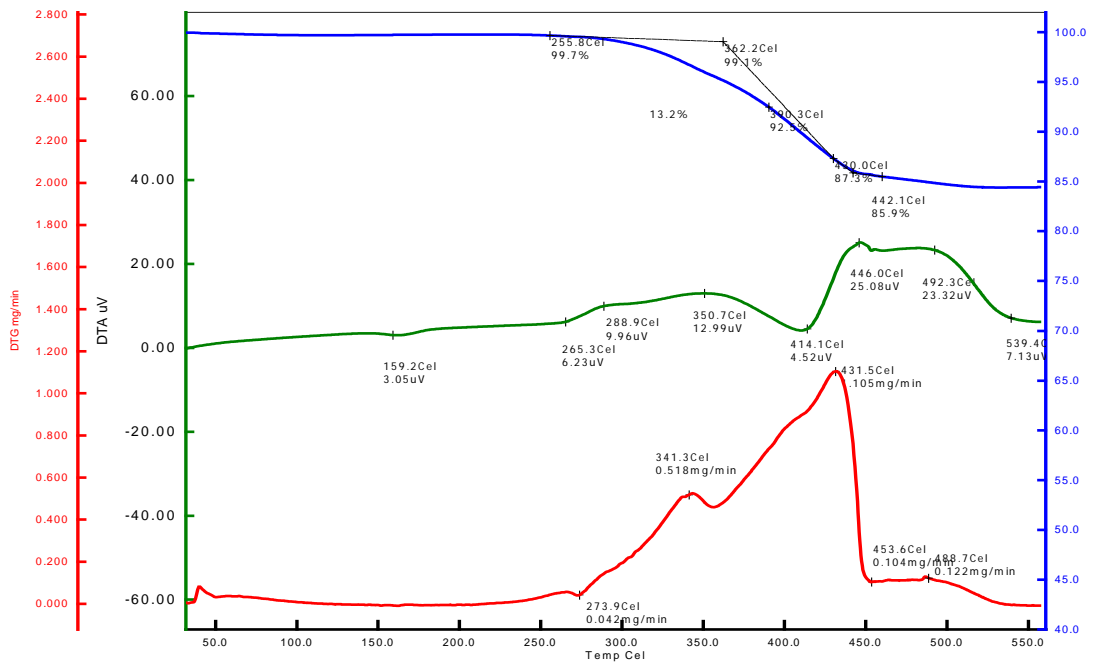


Figure 4.21: TGA/DTA/DTG curves of 30 (wt.%) raw sawdust-PP composites

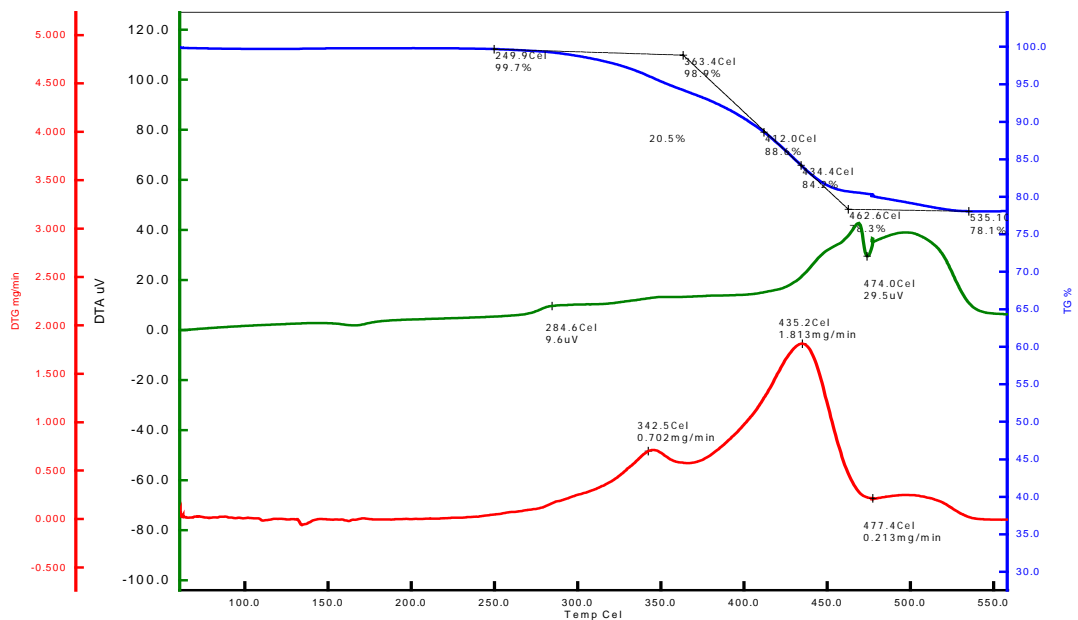


Figure 4.22: TGA/DTA/DTG curves of 30 (wt.%) alkali treated sawdust-PP composites

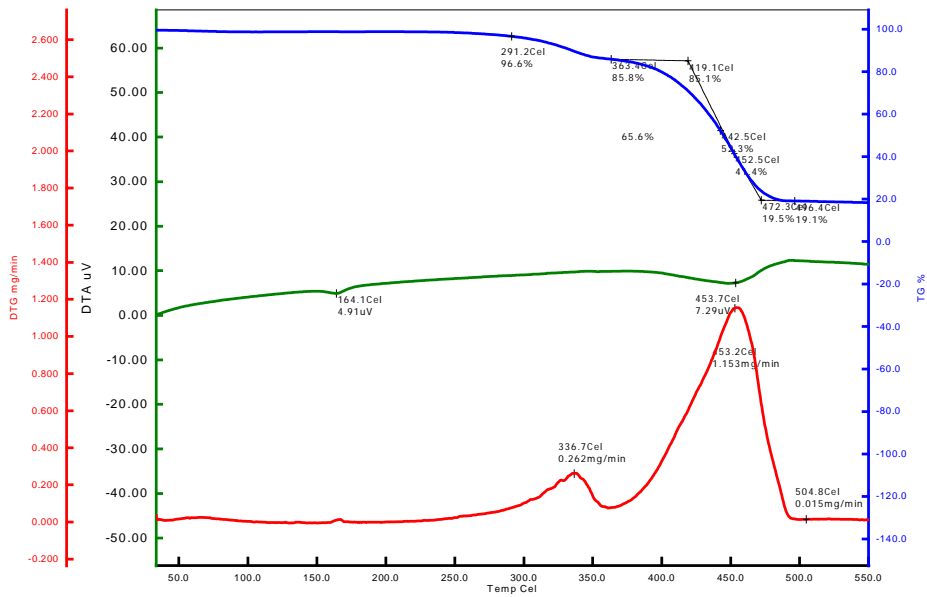


Figure 4.23: TGA/DTA/DTG curves of 35 (wt.) % raw sawdust-PP composites

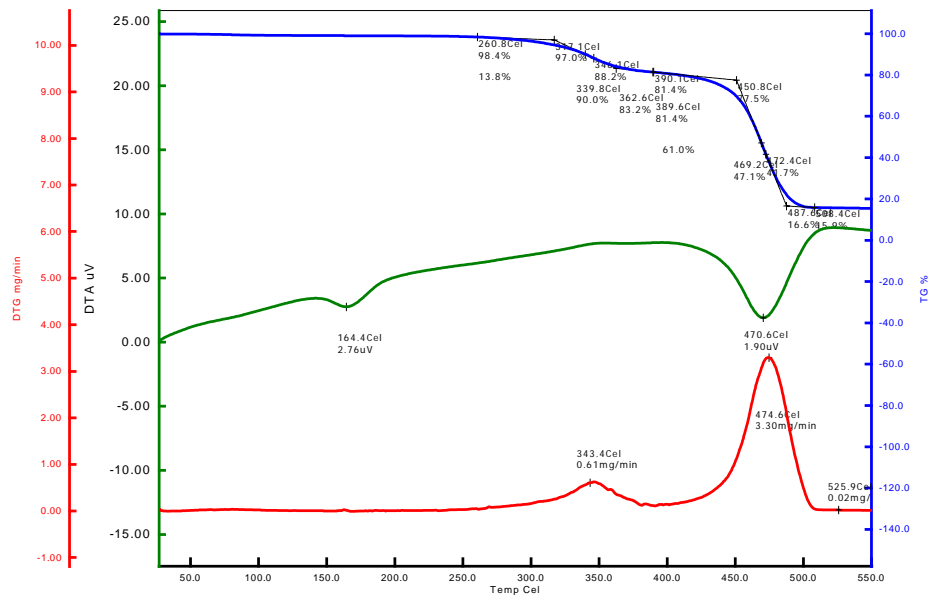


Figure 4.24: TGA/DTA/DTG curves of 35 (wt.)% alkali treated sawdust-PP composites

Lower lines of Figure 4.23 and Figure 4.24 show the thermal stability of 35 (wt.) % raw sawdust-PP composites and 35 (wt.)% alkali treated sawdust-PP composites. It is seen from the graphs that the first weight loss occurred for 35 (wt.) % raw sawdust-PP composites and 35 (wt.)% alkali treated sawdust-PP composites at 336.7⁰C and 343.4⁰C respectively. Similarly, major weight loss occurred for 35 (wt.) % raw sawdust-PP composites and 35 (wt.)% alkali treated sawdust-PP composites at 453.2⁰C and 474.6⁰C respectively. Here, both the starting and major weight loss temperature indicate thermal stability of alkali treated sawdust-PP composites over raw sawdust-PP composites.

From the above discussion it can be summarized that most of the alkali treated sawdust-PP composites are thermally stable compared to raw sawdust-PP composites.

4.3.5.1 Water absorption

Water absorption and specific gravity of lignocellulosic sawdust composites are important characteristics that determine end use applications of these materials.⁵² Water absorption could lead to a decrease in some of the properties and needs to be considered when selected for applications. It is difficult to eliminate entirely the absorption of moisture from the composites without using expensive surface barriers on the composite surface. Water absorption in lignocellulosic based composites can lead to build up of moisture in the fiber cell wall and also in the fiber-matrix interphase region. Moisture build up in the cell wall could result in fiber swelling and concerns on the dimension stability cannot be ignored.⁹² So chemical modification is needed to reduce the moisture absorption of the fibers.

Results of water absorption obtained in our study are shown in Table 4.5. It is observed from the Figure 4.25 that water absorption of the raw sawdust-PP composites increases in boiling water with increasing fiber loading except 30wt.% sawdust loading. But water absorption of the alkali treated sawdust-PP composites are less than that of raw sawdust-PP composites except 30 wt. % sawdust loading. Cellulose, hemicellulose and lignin of sawdust contains hydroxyl group. Hydroxyl group forms hydrogen bond with water molecule. Water absorption of untreated sawdust-PP composites are higher than that of treated sawdust-PP composites with an exception at 30 wt% sawdust loading. It may be due to presence of lignin in untreated sawdust which have hydroxyl group to bound with water molecule.

Table 4.5: Water absorption of the raw and alkali treated sawdust-PP composites

Material	2 h in boiling water (%)	24 h in cold water (%)
PP only	0.09	0.02
PP-Raw sawdust (20wt.%)	0.31	0.33
PP-Raw sawdust (25wt.%)	0.40	0.47
PP-Raw sawdust (30wt.%)	0.48	0.97
PP-Raw sawdust (35wt.%)	0.52	1.4
PP-alkali treated sawdust (20wt.%)	0.18	0.29
PP- alkali treated sawdust (25wt.%)	0.37	0.21
PP- alkali treated sawdust (30wt.%)	0.38	0.10
PP- alkali treated sawdust (35wt.%)	0.48	0.07

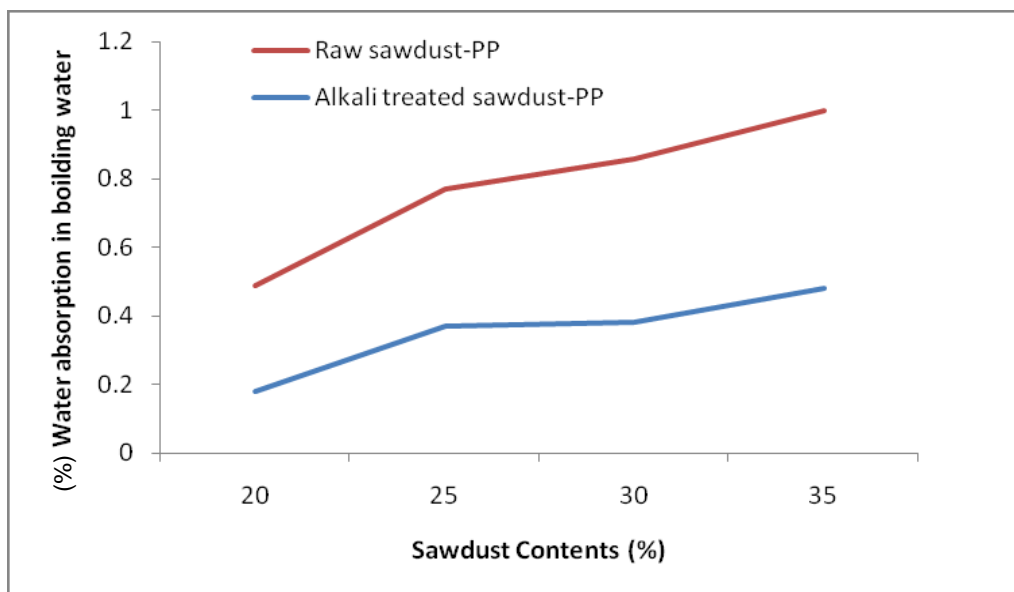


Figure 4.25: Water absorption vs sawdust content (wt.%) curves for raw sawdust-PP composites and alkali treated sawdust-PP composites in boiling water

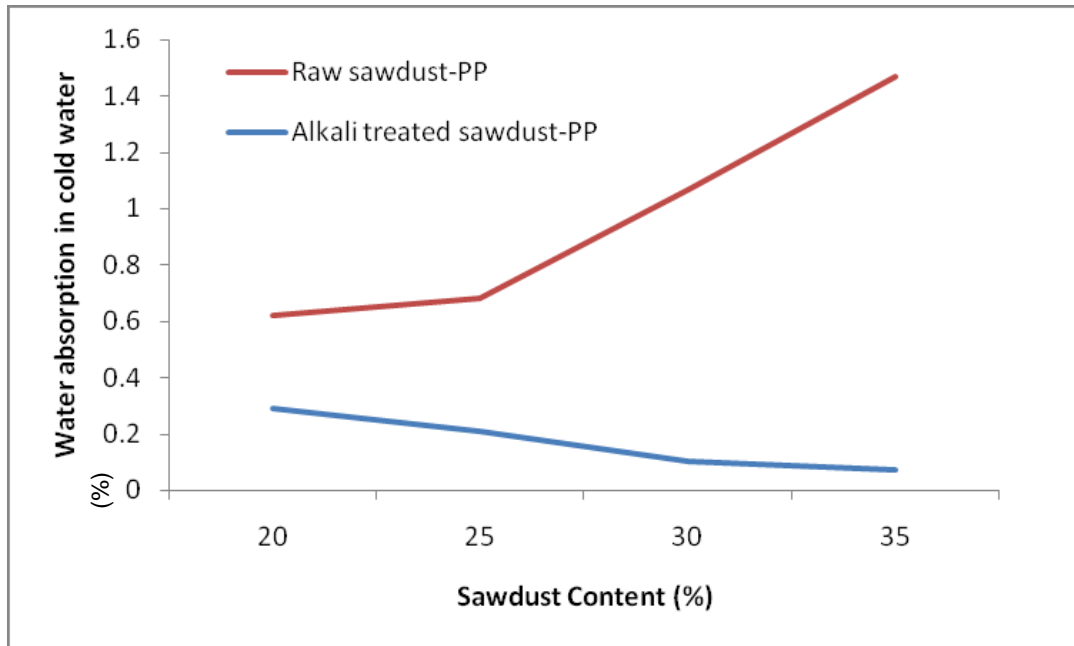


Figure 4.26: Water absorption vs fiber content (wt.%) curves for raw and alkali treated sawdust-PP composites in cold water

It is seen from the Figure 4.26 that the water absorption in cold water decreases for alkali treated sawdust-PP composites compared to raw sawdust-PP composites.

CHAPTER 05

SUMMARY AND CONCLUSION

In this chapter the overall performance of fabricated composites were discussed in a condensed form. The physico-mechanical properties of PP composites reinforced with raw and alkali treated sawdust were studied in this hypothesis. The filler-matrix adhesion was improved in most cases due to the surface treatment using NaOH. 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 the properties of composites

In order to characterize the physico-mechanical properties of sawdust-PP composites, various ASTM standards method were followed. For each series of tests five to ten specimens were tested and the average values were presented. Each specimen was labeled based on the percentage of sawdust, type of surface modification and specimen number that one is explained in chapter 5 elaborately. Table 5.1 indicates the test standard, sizes and number of the 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 D570-99	10	39×10×4mm ³
Hardness Test	ASTM D785-98	10	39×10×4mm ³
Tensile Strength	ASTM D 638-01	10	39×10×4mm ³
Tensile Modulus	ASTM D 638-01	10	39×10×4mm ³
Flexural Strength	ASTM D 790-00	5	39×10×4mm ³
Flexural Modulus	ASTM D 790-07	5	39×10×4mm ³
Thermal Analysis	ASTM D 785-98	1	Several (5-40) mg
Scanning Electron Microscopy	ASTM D 785-98	2	Several mg
FT-IR		1	0.5mg

The major aim of the present research was to prepare WPCs from PP reinforced sawdust and develop chemical modification techniques for improving physic-mechanical properties of WPCs. To justify the better application of sawdust, which may help to develop the economy of Bangladesh was another aim of this study. To do so, the experimental determination and theoretical interpretation of a series of works on “Study of the physico-mechanical properties of chemically treated wood fiber reinforced composites” was done. The total work of this study is summarized below:

WPCs were fabricated by using PP reinforced with sawdust as filler. The used filler sawdust was treated with sodium hydroxide. WPC panels were prepared through extruder and injection moulding machine at different percentage filler loading with PP.

Reaction takes place at C₂ and C₆ position of cellulose unit in raw sawdust to form disodium cellulose by sodium hydroxide. The disodium derivative of cellulose in sawdust is found to be less active to the moisture content.

Most of the mechanical properties of the alkali treated sawdust-PP composites are higher than those of raw sawdust-PP composites. Tensile strength, Tensile modulus, flexural strength, flexural modulus and hardness of the raw and alkali treated sawdust-PP composites are significantly higher than polypropylene (PP). Flexural strength of the both type of composites increases from 20 wt.% to 35 wt.% fiber loading than unfilled PP matrix. Tensile strength of the alkali treated sawdust-PP composites decreases with increasing sawdust loading whereas tensile modulus increases gradually. Elongation at break had higher values for alkali treated sawdust-PP composites compared to raw sawdust-PP composites with fluctuations from 20 wt.% to 30wt.% sawdust loading. Tensile modulus, flexural modulus and hardness of these fibers loaded composites increases with increasing sawdust loading with few exceptions.

Morphological studies of these composites show better interfacial bonding between sawdust fiber and matrix for alkali treated sawdust-PP composites than raw sawdust-PP composites. Water absorption properties of the composites also show better result for alkali treated sawdust-PP composites than raw sawdust-PP composites, which will improve the dimensional stability of the composites.

From these observations, it can be concluded that modification of sawdust by sodium hydroxide enhances the physico-mechanical

properties of the sawdust reinforced composites. The absence of intermolecular hydrogen bonding of disodium cellulose in treated sawdust improves the adhesion between sawdust and PP matrix in the composites interface. As a result treated sawdust dispersed more uniformly in the composites than raw sawdust.

Tensile modulus, flexural modulus and hardness significantly increase with increasing sawdust loading. With increase of sawdust content at percentage (above 30 wt.%) the mechanical properties are found to be decreased. This may be due to nonformation of chemical bonds between PP and treated sawdust. Better mechanical properties of the composite may be obtained by converting the hydrophobic PP into hydrophilic PP or by maleating the PP with maleic anhydride.

From this observation it can be recommended that moisture-protecting coating is needed for the use of utropine and adipic acid treated composites. For this purpose nitrogen containing less hydrophilic larger molecule might give better positive coupling reaction with alkali treated sawdust thereby would enhance the dimensional stability of composite materials.

SEM observation and water absorption test gives better result for alkali treated sawdust-PP composites. Alkali treated raw sawdust-PP composites reduce the hydrophilic nature of the composites, which enhances the dimensional stability of the composites.

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, alkali treated sawdust-PP

composites showed higher hardness than raw sawdust-PP composites.

Finally, it can be concluded that positive results are obtained by the alkali treatment of sawdust of composites. Improved injection moulded sawdust-PP composites have been prepared. So, it can be said that chemical modification of wood by various ways may improve the quality of sawdust-PP composites which might have bright future in Bangladesh.

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