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THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

FOREST INDUSTRIAL ENGINEERING

INVESTIGATION ON PROPERTIES OF WOOD PLASTIC COMPOSITES MADE OF TREATED WOOD FLOUR WITH TANALITH E AND POLY LACTIC ACID (PLA)

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DECLARATION

I Mohammed DALU hereby declare that this work, entitled “INVESTIGATION ON PROPERTIES OF WOOD PLASTIC COMPOSITE MADE OF TREATED WOOD FLOUR WITH TANALITH E AND POLY LACTIC ACID (PLA)” is the results of my own research, to the best of my knowledge, it contains no material perviosly published by another person nor material which has been acceptetedd for the award of any other degree of the University, except where due reference aknowledgement have been given in the text.

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SUMMARY

INVESTIGATION ON PROPERTIES OF WOOD PLASTIC COMPOSITE MADE OF TREATED WOOD FLOUR WITH TANALITH E AND POLY LACTIC ACID (PLA)

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The purpose of this study to investigate on the properties of Wood flour -PLA composites. Wood flour -PLA composites reinforced with 30, 40, and 50% of *Pinus sylvestris* L. wood flour were prepared by using twin-screw extruder. Part of the wood flour was treated with 3% of Tanalith E solution before being used for the composite preparation and the other was used without treatment. The density and void volume fraction composites were determined. The composite contains 30% of untreated wood flour absorbed the least amount of water and the least thickness swelling compared to all the other formulations. The highest value of tensile and flexure modulus at 50% of untreated wood flour content while tensile and flexure strength at 30% of untreated wood flour content in composites. Thermal properties of Wood flour -PLA composites were measured using the thermo gravimetric analysis and differential thermal analysis. Presence of WF in thermoplastic matrix reduced the degradation temperature of the composites while the increased weight loss. Results indicate that the mechanical properties of the chemically treated wood flour-PLA composites were found to be lower than those of the untreated. The water absorption test showed that composite prepared from the chemically treated wood flour absorbed higher amount of water compared to the untreated wood flour composite. This indicate the copper partly inhibit wood bonding and causes presence of high content of voids in the chemical treated wood flour compared to that of untreated. High voids in the chemically treated wood was also observed SEM studies. The results clearly show that the properties of WPCs depend on the wood flour content and also the treatment given to the wood.

KEY WORDS: Mechanical and Physical Properties, Polylactic acid, Tanalith E, Thermal stability

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ABBREVIATIONS

ACQ : Alkyl Copper Quat
CCA : Chromated Copper Arsenate
CuAz : copper azole
DMTA : dynamic mechanical thermal analysis
DSC : differential scanning calorimetry
FTIR : Fourier transform infrared spectroscopy
HDPE : high density polyethylene
LDPE : low density polyethylene
MAPE : maleated polypropylene
MAPP : maleated polyethylene
MC : moisture content
MFA : microfibril angle
M_w : molecular weight
PDLA : poly (D-lactic acid)
PE : polyethylene
PET : polyethylene terephthalate
PLA : poly (lactic acid)
PLLA : poly (L-lactic acid)
PP : polypropylene
PS : polystyrene
PVC : polyvinylchloride
RMT : reinforced matrix theory
S1 : outer layer
S2 : middle layerand
S3 : inner layer.
TGA : Thermo gravimetrical analysis
WPCs : wood-plastic composites
XPS : X-ray photoelectron spectroscopy

1. INTRODUCTION

1.1. Background and Justification

Biomaterial composites made from renewable resources, such as wood, are becoming more interesting. The main reason for this can be related to low materials cost, light weight, high specific modulus, global environmental challenges and the need for a sustainable development in society. There is a long tradition of using thermoplastic materials, such as polypropylene(PP), polyethylene(PE) and polyvinylchloride (PVC), and an even a longer tradition of using wood-based composites, such as oriented strand board, particleboards and fiberboards. A new material has emerged, which is a combination of a thermoplastic or thermoset component and a wood based component, known as wood-plastic composites (WPCs). The new and rapidly developing generation of WPCs exhibits superior mechanical properties, high dimensional stability and can be used to produce complex shapes. The term wood-plastic composites are historically a broad term that includes all wood containing composites in both a thermoset or a thermoplastic matrix. In this thesis, only wood-thermoplastic composites are considered, particularly bioplastic polymer which known as poly lactic acid (PLA) and the term WPCs will be used throughout this thesis for this type of material. Wood is a cheap and plentifully available material that possesses suitable characteristics for multiple applications, such as in the construction industry (Clemons 2008). Conversely, the combination of wood with the polymers, adhesives, and other substances provide unique properties that cannot be achieved with either wood or plastic products on their own. Thus, wood-plastic composites (WPCs) are recyclable, ecological good, and durable materials (Kim and Pal 2010). In WPCs, the wood fibers are surrounded by a continuous polymer matrix, and the compatibility between these two constituents is typically improved by adding coupling agents and other additives into the composite. WPCs have many advantages such as; easy to maintain and clean, environmentally friendly, no need to paint, can be shaped to almost any design, resistant to ultra violet light and its color does not fade easily, can replace wood in many outdoor applications, can replace neat plastics in applications where the increase in stiffness is required, low cost of raw materials .Wood plastic composites has many applications not only in decking, and fencing, but also in more sophisticated manufacturing, e.g., in the car-making industry (Klyosov 2007, Faruk et al. 2012). Even if the use of WPCs is becoming more and more common, at present, these materials cannot be used in applications where high mechanical strength is required. Despite the advantages of WPC over wood and plastic, the interaction between wood and plastic at fiber-matrix interface does not necessarily yield strong bonds. This is mainly due to the weak bonding between the hydrophilic wood fibers (the polar nature of the wood) and the hydrophobic polymer matrix (non-polar nature of polymers) (Gao et al. 2008, Yuan et al. 2008,). Besides, wood fibers contain a large amount of hydroxyl(OH) groups that can form hydrogen bonds with water molecules. For this reason, WPCs are susceptible to water absorption, thickness swelling and the creation of micro-cracks in the material (Li et al. 2014), which increases the risk of mold growth. To convert low-value to high-value wood plastic composite many researchers has been examined to eliminate, or at least reduce, these limitations in the present generation of WPCs. There are many ways to modify wood fibers, for instance, heat treatment (Ayrilmis et al. 2011), the extraction of hemicelluloses (Hosseinaei et al. 2012), chemical treatment (Segerholm et.al.2007, İbach and clemons,2006) and the treatment with coupling agents (Müller et al. 2012); these treatments can considerably increase the water resistance of the WPCs. In some instances, the mechanical properties of WPCs can be enhanced by using recycled polymers instead of virgin material (Adhikary et al. 2008a). Moreover, the mechanical durability of WPCs can be improved by incorporating additives, such as maleated polypropylene or polyethylene (MAPP or MAPE) (Pérez et al. 2012, Ndiaye et al. 2013), into the composite. Additives are materials that added in small amounts to enhance properties of materials. Current applications for WPCs are largely in finished products such as decking, cladding, window frames and furniture.

In the case of outdoor applications of WPCs, the problems are related to the requirements of durability and minimum maintenance material. Exposure to the outdoor environment implies moisture and temperature variations, the risk of attack by micro-organisms and degradation by UV radiation. The dimensional stability and biological durability of WPCs are highly dependent on content and types of reinforcement, matrix as well as additives and the processing of the material. If the wood component is allowed to sorb moisture, the risk of irreversible dimensional changes arises, i.e. wood polymer composites splitting into layers, and the risk of degradation by fungi and other micro-organisms also arises.

WPC producers often promote their products as maintenance-free and highly durable with a lack of cracking and splintering, often offering 10-year warranties (Clemons 2002).

However, the first generation of WPCs has shown to lack in long time durability and failures have led to class action law suits (Morris and Cooper 1998). The different studies on WPCs and moisture transport have shown that the initial moisture content (MC) is very low and the rate of sorption is very slow. However, the moisture in the composites is not uniformly distributed and the outermost part can reach very high moisture levels, high enough to support fungal degradation (Gnatowski 2009, Wang and Morrell ,2004). It is also important to stress that even if moisture uptake is slow in WPCs, even when immersed in water, the uptake may continue over a long period of time. The rate and extent of moisture sorption increase when the wood content greater than approximately 50% of the total weight of the composite (Clemons, 2012). Besides, a moist environment will swell the wood flour close to the surface, and the materials will shrink upon drying. This will cause stresses within the material and create micro-cracks, which will expose more particles deeper in the material. This swelling and shrinkage will also cause cracks at the interfaces between the wood flour and the matrix.

The focus of this thesis to minimize these problems, and moisture in WPCs with a high loading of the wood component is definitely one of the key reasons for their shortcoming in both mechanical durability and resistance to water absorptions.

1.2. Statement of Problems and Objectives

1.2.1. Statement of Problem

Today, the preservation and conservation of the environment in order to ensure sustainable development is much emphasized. In order to ensure preservation and conservation of the environment, the various waste generated have to be removed. The surest way to purify a waste is to recycle it into a useful product (Braunegg et al. 2004). Plastic waste can be recycled by forming a composite with lignocellulosic material residues. (Ashori & Nourbakhsh 2009b).

Using wood as natural reinforcement in a thermoplastic is a way to reduce both cost and environmental impacts of the material, inducing by the way some major changes in its properties. While most of the scientific research work on wood plastic composites has been done using petroleum based matrix, like polypropylene and polyethylene for their low cost, wide availability and good processability, there is a growing concern in developing composites based on a biodegradable matrix issued from renewable resources such as, PLA. The efforts put in the development of new environmentally friendly thermoplastics have brought to the market different bioplastics at reasonable price, and poly (lactic acid) (PLA) is one of them readily available. It has already been used as a matrix for WPCs, showing encouraging results regarding compatibility with wood and mechanical properties, while brittleness and low thermal stability are viewed as the main weaknesses (Drumright et al. 2000). PLA was chosen in this study as a reasonable solution to cope with the ecological expectation of a sustainable society.

Besides, it is now widely accepted that the use of a polymeric matrix can't prevent totally wood to be subjected to fluctuations in the surrounding climate. The combined actions of fungi and moisture result in a reduction of material properties at a rate depending on different characteristics of the composite (Segerholm 2007). As degradation of wood is a problem that has been investigated for decades, solutions already developed for massive wood can be readily used for the development of more resistant WPCs. It has been the purpose of a few studies using chemically modified wood as a raw material for WPCs, confirming the benefits of wood modification on biological and water absorption resistance and of the final composite (Segerholm 2007).

The hygroscopic behavior of wood and Its natural degradability micro-organisms are two major problems the wood production industry tries to overcome, developing different modification treatment to reduce or prevent the swelling of wood, or its decay, preferably both at once. Moreover, the use of arsenic based preservatives has been forbidden in most of developed countries and Some of copper based compounds are more and more generally considered harmful for environmental and health reasons, increasing the need for alternative treatments like tanalith E or copper azole arsenic free compound

1.2.2. Statement of Objectives

The objective of this thesis is to study some properties of wood plastic composites that incorporate Tanalith E treated or modified wood component in a polylactate (poly lactic acid) matrix to gain knowledge about the behavior of such materials with different ratio of wood to polymer. The emphasis has been to:

- Produce WPCs from yellow pine wood flour treated with and without 3% Tanalith E solution with PLA plastic as the matrix and MAPE as coupling agent by varying the percent composition of constituents.
- Determine morphological features of the WPCs and mechanical damage done to the wood component during processing
- Identify the compositional effect of wood flour as well as Tanalith E treatment of the wood on the physical and mechanical properties of WPC produced from PLA plastic and wood flour.
- Characterize and determine mechanical, physical, thermal of properties of the products formed.

1.3. Wood-plastic Composites

A composite material (also called a composition materials or shortened to composite), is a material made from two or more constituent materials with significantly different physical or chemical properties that, when combined, produce a material with characteristics different from the individual (Callister 2005). The two materials work together to give the composite unique properties. However, within the composite you can easily tell the different materials apart as they do not dissolve or blend into each other. Therefore, the individual components remain distinct within the finished material, and thus composites can possess properties that cannot be achieved with the individual constituent materials. Composites can be classified into particle-reinforced, fiber-reinforced, and structural composites.

In materials science, a fiber is commonly defined as a substance that has been drawn into a long and thin filament, i.e., the aspect ratio, which is defined as the ratio of fiber length to diameter, is at least 100 (Callister 2005). However, the term fiber may also refer to the spindle-shaped cells within the wood material (Clemons 2008), and in the case of natural fiber polymer composites, fiber can be defined as an object with an aspect ratio greater than one (Stokke et al. 2014). Thus, from the viewpoint of materials science, some WPCs can be classified as particle-reinforced composites although they are commonly referred to as fiber-reinforced composites. In this thesis, the definition of a fiber is adopted from the terminology used for natural fiber-polymer composites.

WPCs are fiber-reinforced composites produced by mixing wood components and polymers. In a WPC, a polymer forms a continuous matrix that surrounds the reinforcing wood components. The low price and high stiffness of wood makes it an attractive reinforcement for the commodity plastics. The way of processing of WPCs is similar to the plastic, there are several appropriate manufacturing technologies available for WPCs. In spite of the fact that, the majority of WPC products are extruded, injection and compression molding are other major technologies used in WPC production. (Godavarti 2005)

1.3.1. Raw Materials

The properties of WPCs are mainly determined by the properties of their two main constituents. Even though both are polymer-based materials, wood and plastic exhibit distinctive properties and have different origins (Clemons,2008). Matrix polymers are high-molecular-mass materials created by the polymerization of small repeating subunits, monomers. The individual building block of a polymer is termed a monomer. Polymers can be obtained from natural materials as well as synthetically processed and moreover, virgin material or recycled based on their origin (Adhikary et al. 2008a, Adhikary et al. 2008b). Many polymers are used as the matrix material in wood plastic composites manufacturing, for examples, polyethene (PE), polypropene (PP), polyvinyl chloride (PVC), polystyrene (PS), and polylactide (PLA). Due to the high molecular mass relative to the small molecule compounds, polymers possess unique physical properties, such as viscoelasticity and toughness.

Wood is a natural composite consisting primarily of three polymeric components: cellulose, hemicelluloses and lignin (Pettersen 1984). Cellulose constitutes 40–45%, hemicelluloses 25–35%, and lignin makes up much of the remaining 20–30% of wood. Wood is an attractive material to be incorporated in polymer composites not only because it is abundant but also due to its light weight in relation to its mechanical properties. In WPCs, the wood components are surrounded by the continuous polymer matrix.

In general, the development of high quality WPCs is limited by two physical factors (Godavarti 2005): the difference between the surface energy of the polymer matrix and wood components, and the upper temperature at which wood can be processed. There are several ways to offset or minimize these limitations and to improve the general performance of the WPC. The most common approach involves the incorporation of different types of additives. Examples of additives used in WPCs are coupling agents, lubricants, stabilizers, inorganic fillers, biocides, and flame retardants

1.3.1.1. Wood

Wood has unique and useful properties – it is a recyclable, biodegradable, renewable, bendable, and relatively stable material. In addition, wood has an important role in carbon sequestration; growing trees take up and store considerable amounts of atmospheric carbon dioxide (Hill 2006a).

The reinforced matrix theory (RMT) is a concept which can help to understand the cell wall structure of wood fibers, and ultimately the properties of wood. In short, the RMT describes the cell wall structure as follows: the cell wall of a plant consists of the thermoplastic matrix (lignin) reinforced by the high tensile strength fibers (cellulose) and the hygroscopic material (hemicellulose). (Stokke et al. 2014)

Wood can be anatomically divided into two classes: softwoods (gymnosperms) and hardwoods (angiosperms) (Wiedenhoeft 2010). Wood (xylem fiber) is composed of elongated cells; they are oriented in the longitudinal direction of the stem. When examined in the microscope, wood can be observed to be a composite of many cell types. It is a complex biological structure whose parts act together to fulfill the needs of a living plant: to conduct water from the roots to the leaves, to provide mechanical support for the plant's body, and to store and synthesize essential biochemical. Wood contains rays in horizontal direction. The central portion of the stem is called pith. As growth takes place, the heartwood gets deposited towards the center of the stem. The cambial zone is a thin layer consisting of live cells between the wood (xylem) and inner bark (phloem); the cell division and radial growth of the tree takes place in this region. Both softwoods and hardwoods consist mainly of tracheids – these are elongated and hollow cells arranged in parallel to each other along the trunk of the tree. In general, hardwoods have a complex structure than softwoods because softwoods have only two cell types and less variation in the structure within the cell types

(Pettersen ,1984, Godavarti ,2005, Wiedenhoeft ,2012). The major difference in the structure between hardwood and softwood is the presence of vessel elements in hardwoods; these elements are absent in softwoods. The wood substance in softwoods is comprised of two different types of cells: tracheids (90-95%) and ray cells (5-10%). Tracheids give softwood the mechanical strength and provide a water transport function, which occurs through the thin walled early wood tracheids and through the bordered pits. Generally, softwoods have longer (3–8 mm) wood fibers than hardwoods (0.2–1.2 mm), however, the length of wood fibers varies between wood species (Wiedenhoeft ,2010, Clemons, 2013).

The layered structure of wood fibers also explains the unique properties of wood. As shown in Figure .1, the cell wall of a wood fiber consists of two main parts: the primary and secondary wall. The secondary wall consists of three separate layers designated as outer layer(S1), middle layer(S2), and inner layer(S3).

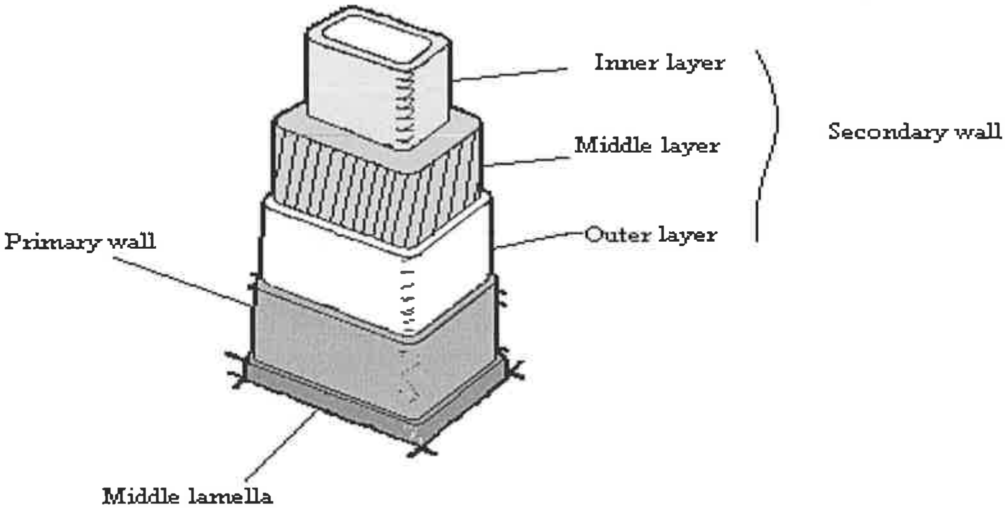


Figure 1. the layered structure of the cell walls of wood

The lines in the primary and secondary cell wall layers describe the orientation of microfibrils.). These layers differ from each other based on their chemical composition and their structure

The middle lamella is a lignin-rich region that binds the fibers together. The primary cell wall is made up of a loose and thin (0.1 µm) network of randomly oriented cellulose microfibrils. It also consists of hemicelluloses, proteins, and pectin. The first layer of the secondary cell wall, S1, is approximately 0.2 µm thick with a relatively high microfibril angle (MFA). The middle layer (S_2) forms a major portion of the cell wall. Its thickness in soft wood tracheids varies between 1-5µm and it may thus contain between 30 to more than 150 lamellae. and it primarily defines the mechanical properties of the fiber. S2 consists mainly of cellulose and hemicelluloses. S3 is a thin layer (0.1 μm) of cellulose microfibrils. (Pettersen 1984, Stokke et al. 2014)

1.3.1.1.1. Chemical Composition of Wood

The chemical composition of wood also varies from species to species. In general, dry wood has an elemental composition of approximately 50% carbon, 6% hydrogen, and 44% oxygen. In addition, wood contains trace amounts of other elements such as calcium, potassium, sodium, magnesium, iron, manganese, sulfur, and phosphorous. (Rowell et al. 2013)

The main constituents of wood are cellulose, hemicelluloses, lignin and extractives. The amount of each constituent in softwood and hardwood are presented in Table .1

Table 1. Chemical Composition of Wood

COMPONENT	SOFTWOOD	HARDWOOD
Cellulose	42 ± 2 %	45 ± 2 %
Hemicellulose	27 ± 2 %	30 ± 5 %
Lignin	28 ± 2 %	20 ±4 %
Extractives	3 ± 2 %	5 ± 3 %

Cellulose determines the character of fiber and as such the most important component in the wood. Cellulose is a homopolysacchride composed of repeating β-D-glucopyranosyl units, which are linked together by β (1-4) glycosidic bonds. Cellulose has a chemical formula ($C_6H_{10}O_5$) n where n is the number of repeating sugar units or the degree of polymerization, DP. The repeating unit consists of two glucose molecules (figure 2.). The DP varies depending on the cellulose source and the treatment it has received (Hietala, 2013). The properties of cellulose depend on the DP of cellulose molecules

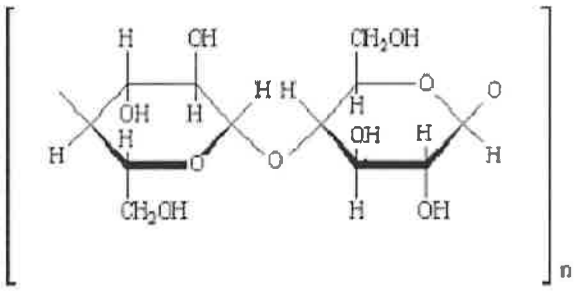


Figure 2. General Chemical Structure of Cellulose

Cellulose is a linear and highly crystalline polymer of D-glucopyranose units linked together by β -(14)-glucosidic bonds (Pettersen 1984, Li 2011). Bundles of cellulose molecules are thus aggregated together in the form of microfibrils in which the crystalline region alternates with the amorphous region. The repeating unit in cellulose is a two-sugar unit, cellobiose. When randomly oriented cellulose molecules form intra- and intermolecular hydrogen bonds, the packing density of cellulose increases, leading to the formation of crystalline regions. For example, wood-derived cellulose may contain as much as 65% of crystalline regions that confer the strength and structural stability to the wood. Hydroxyl groups on cellulose are largely responsible for its reactive nature. The absorption of water by cellulose depends on the number of hydroxyl groups that are not linked with other hydroxyl groups. As a result, water absorption is mainly concentrated in the amorphous region rather than in the crystalline region (Rowell et al. 2013, Stokke et al. 2014).

Hemicelluloses were originally believed to be intermediates in the biosynthesis of cellulose. Hemicelluloses are heteropolymers that include arabinoxylans, glucomannans, xyloglucans, glucuronoxylans and xylans (Rowell et al. 2013). Galactoglucomannans are the principal hemicellulose component in softwoods followed by arabino-4-*O* methylglucuronoxylan. Although there are variations among the hemicellulose obtained from hardwoods, it mostly comprised of *O*acetyl-4-*O*-methylglucuronoxylan. Besides, glucose, hemicelluloses can be made of other sugar monomers, such as xylose, mannose, and galactose. In contrast to the linear and crystalline structure of cellulose, hemicelluloses are branched and amorphous polymers with little strength. Whereas cellulose consists of approximately 10 000 glucose molecules per polymer, hemicelluloses have shorter chains of about 2 000 sugar units (Clemons ,2008).

Lignin is a polymer that is a 3-dimensional highly branched network. Lignin is relatively an inert material, which act as a bonding and stiffening agent within the wood cell wall and the middle lamella. Lignin is a complex, amorphous and cross-linked polymer, consisting of aromatic alcohols known as monolignols (Pettersen 1984, Li 2011, Stokke et al. 2014). There are three monolignol monomers incorporated into lignin during its biosynthesis in the form of phenylpropanoids: *p*aracoumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The reactivity and levels of the lignin precursors govern the final constitution of lignin. Lignin is covalently linked to hemicellulose molecules, increasing the mechanical strength of the cell wall. The chemical composition of lignin varies in the different wood species. Generally, softwoods have larger percentage of lignin than hardwoods, which accounts for 23-33% in softwoods and 16-25% in hard woods. For example, lignin in the softwoods consists almost entirely of guaiacyl moieties. In cell walls, lignin can be considered as a chemical adhesive that fills the gaps between hemicelluloses and cellulose. Lignin is a non-polar hydrophobic polymer whereas cellulose and hemicelluloses are hydrophilic (Thomas et al. 2011).

In addition to lignocellulose, wood contains small amounts (3–8%) of other organic components (Pettersen ,1984). Extractives from wood are comprised mainly of two forms that differ in their solubility in water or organic solvent. Extractives are considered non-structural wood constituents, mostly composed of extra cellular and low molecular weight compounds. Wood extractives include simple sugars, fats, waxes, resins, proteins, terpenes, and gums. The extractive compounds are crucial components of the prevention system of the tree, but they also services as energy reserves and support tree metabolism (Clemons 2008). And also, there are trace amounts (about 1%) of inorganic ash in wood (Rowell et al. 2013).

1.3.1.2. Polymers

Polymers are molecules made up of monomeric building block to form long chains and are typically of high molecular weight. The individual building block of a polymer is termed a monomer Polymers can be divided into two categories, either thermoplastics or thermosets. Thermoplastics are those that get soften when heated and can be reheated and reshaped. Thermoset on the other hand become hard when heated and cannot be reheated or remolded. Because thermoplastics can be reheated, it can be easily recycled without any difficulty. (Segerholm, 2012).

Thermoplastics have a unique property of repeated flow characteristics. Thermoplastics morphology can be subdivided into amorphous or crystalline, although polymers are rarely one or the other but a combination of the two. The amorphous region settles in a disorderly form when it cools while the crystalline region maintains an order. The molecular organization of these amorphous and crystalline parts plays a crucial role in the properties of the polymer (Segerholm 2012a). Polyolefin are of particular interest in the area of wood plastic composites. Polyolefin have a basic formula that represents its chemical composition consisting of carbon and hydrogen. A Polyolefin is any of a class of polymers produced from a simple olefin (also called an alkene with the general formula CnH2n) as a monomer.

Examples of thermoplastics are polypropylene (PP), polyethylene PE (high density, HDPE or low density LDPE), polyethylene terephthalate (PET), polyvinyl Chloride (PVC), and polystyrene (PS).

Other matrices that have gained increased interest in recent years are so-called bioderived plastics, e.g. cellulose esters and polylactates, which are made partly or fully from renewable resources.

The properties of a polymer are primarily defined by its molecular structure. Homopolymers contain only one type of monomer whereas copolymers or terpolymers consist of several kinds of monomers. The properties of polymers depend on its tacticity – the arrangement of monomers along the polymer backbone.

Polymer tacticity can be divided into three classes: an isotactic polymer has all of its substituents on the same side of the backbone, and polymers with alternating placements of substituents along the backbone are called syndiotactic. Atactic polymers lack any consistent arrangement in their substituents. (Clemons et al. 2013)

The branching of polymer chains has great effects on the polymer. For example, the highly branched low-density polyethylene (LDPE) is softer and has a lower density and poorer tensile strength than the more linear high-density polyethylene (HDPE). (Clemons et al. 2013)

The crystallinity of the polymer affects its optical, mechnical, thermal and physical properties because the crystalline regions inside the polymer structure increase the interactions between the polymer chains. PLA can be either amorphous or semi-crystalline depending on its stereochemistry and thermal history. The crystallinity of PLA is most commonly determined using the differential scanning calorimetry (DSC) technique. When the structure of the polymer is highly ordered, there are fewer possibilities for the polymer chains to move relative to one another. Therefore, more energy is required to transform the polymer into an unordered fluid state, meaning that polymers with high crystallinity have higher melting points in comparison with their more amorphous counterparts. (Beyler and Hirschler ,2002). High crystallinity also means that the polymer will be strong but brittle, which accounts for the high modulus and low impact resistance (Galeski ,2003). Semi-crystalline polymers have both crystalline and amorphous regions, i.e., these polymers combine the high strength of crystalline polymers with the flexibility of the amorphous types (Callister 2005). The tendency for PLA to crystallize upon reheat also depended on the heating rate. In composite materials, semi crystalline polymers are typically more efficiently reinforced by fibers than amorphous ones because the fibers act as nucleation sites for the crystallization process with the fiber becoming surrounded by a finely divided microcrystalline structure, which improves the modulus, especially the flexural modulus (Quan et al. 2005).

Thermoplastic matrices for the use in WPCs need to be processable at temperatures below 200 °C, since wood constituents start to thermally degrade at approximately 150 °C, and around 200 °C the degradation may be substantial for many wood species (Fengel and Wegener 1983). Thermal degradation is also dependent on the wood-plastic residence time at higher temperatures, i.e. if the processing cycle is kept short it is possible to use a higher peak temperature. Thermoplastic matrices currently used in commercial WPCs are mostly polyethylene (PE), polypropylene (PP). Other matrices that have gained increased interest in recent years are so-called bioderived plastics, e.g. cellulose esters and poly lactic acid (PLA), which are made partly or fully from renewable resources

1.3.1.2.1. Poly Lactic Acid (PLA)

Poly (lactic acid) (PLA) can be used as a substitute for some conventional petroleum-based plastics. PLA is a semi crystalline polymer with a glass transition temperature in the range of 65 – 70°C and a melting temperature around 160 - 170°C. (PLA) is a thermoplastic belongs to the family of aliphatic polyesters commonly made from a-hydroxy acids (2-hydroxy propionic acid), which include polyglycolic acid or polymandelic acid, and are considered biodegradable and compostable(Figure.2). Lactic acid could be manufactured by carbohydrate fermentation as well as by chemical synthesis while, the majority of lactic acid production is based on the fermentation route (Benninginga,1990). The fermentation manufacture of lactic acid allows for PLA to be made from 100% renewable resources, such as sour milk, corn, whey, molasses, and sugar beets(Haartmann,1998). PLA can decompose in the environment within two months. However, petroleum based plastics such as polystyrene (PS) and polyethylene (PE) takes from to 500 to 1000 years to decompose(Sinclair,1996). PLA decomposes into carbon dioxide, humus, and water which do not present any harm to the environment. PLA possesses the required mechanical and barrier properties desirable for a number of applications to compete with existing petroleum-based thermoplastics. Neat PLA has high tensile. strength and tensile modulus, but is brittle. PLA can be processed through extrusion, injection molding, film blowing, and fiber spinning and can be used to manufacture various products.

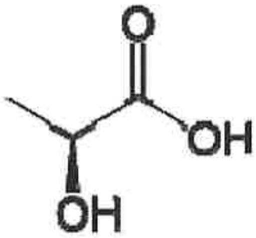


Figure 3. Lactic acid (2-hydroxy propionic acid

1.3.1.2.1.1. Synthesis of Poly (lactic acid)

Poly (lactic acid) (PLA) is lactic acid which, was first isolated in 1780 by Swedish chemist Scheele from sour milk and manufactured commercially in 1881(Hartmann ,1998) There are mainly two methods to synthesize PLA, direct condensation polymerization and ring opening polymerization. Direct condensation polymerization is the least expensive route, but in order to achieve high molecular weight ($M_w > 10^5$) PLA, the trace water in a reactor should be removed during the reaction process. It is still difficult to achieve high molecular weight PLA even by removing trace water using vacuum. There are also other factors, such as a viscous polymer melt, impurities, low concentration of reactive end-groups, and the formation of six-member lactide rings that can prevent the formation of high molecular weight PLA. The synthesis of PLA can follow two different route of polymerizations lactic acid is condensation polymerized to yield low molecular weight, brittle, which, for the most part, is unusable any applications unless external coupling agents are used to increase the molecular weight of polymers. Coupling agents or esterification-promoting additives are added in order to increase the molecular weight of the PLA condensation products, which also raises the cost and production complexity. Various esterification-promoting adjuvants and chain-extending agents have been employed (Buchholz,1994)

By and large, commercially available high molecular weight PLA are produced via the lactide ring-opening polymerization route. Usually the ring opening polymerization can be classified as cationic or anionic ring opening polymerization. During ring opening polymerization parameters such as reaction temperature, reaction time, pressure, catalyst type and concentration affect the molecular weight of the PLA. Among these parameters the catalyst type plays a very important role. Many researchers have reported various catalysts, such as tri fluoro methane sulfonic acid and methyltrifluoromethane sulfonic acid for cationic ring opening polymerization(Kricheldorf,1989), and primary alkoxides(Jedlinski,1991) for anionic lactide polymerization. In industrial manufacture the bulk melt polymerization is commonly used because it is less toxic, free of solvents, less racemization, less transesterification, and lower impurity levels. It has been found that the presence of tin, zinc, aluminum, and other heavy metal catalysts can readily initiate high molecular weight polymerizations.

Commercially available PLA grades are copolymers of poly (L-lactic acid) (PLLA) with meso-lactide or D-lactide. The amount of meso-lactide or D-lactide enantiomers affects properties, such as melting temperature and degree of crystallinity of the bulk PLA(Ray,2005).

1.3.1.2.1.2. Biodegradation and Thermal Degradation of Poly (lactic acid)

PLA is a biodegradable polymer which can completely decompose into carbon dioxide, water, and humus in the natural environment (Narayan,1993). PLA is compostable and derived from renewable sources, it has been considered as one of the solutions to reduce solid waste disposal problems and to lighten the dependence on petroleum-based plastics for packaging materials. The biodegradation combines two continuous steps (Drumright,2000). Initially, the humidity in the environment permeates into the polymer and cuts ester bonds through hydrolysis. PLA is degraded by simple hydrolysis of the ester bond and does not require the presence of enzymes to catalyze this hydrolysis. The cleavage of an ester bond yields one hydroxyl group and one carboxyl group. Based on autocatalytic degradation, the new carboxyl end groups have the capability to catalyze the hydrolysis of other ester bonds(Haffamn,1985). PLA degradation dependent on time, temperature, low-molecular-weight, impurities, and catalyst concentration. A decrease in molecular weight of the long chain polymer resulting in relatively small oligomers. Clearly, higher molecular weight PLA requires a longer time to degrade into oligomers, but small amounts D-lactide units enhanced the hydrolytic degradation of PLLA in the first 32 weeks due to decreased inter- and intersegmental interactions of the PLLA chains with D-lactide units(saha,2006). During this hydrolysis process microorganisms accumulate around the polymer. After the polymer is converted into small oligomers, microorganisms decompose them into carbon dioxide, water, and humus in a continuous fashion.

The heterogeneous hydrolytic degradation is associated with a reaction diffusion process. At first, the polymer is homogeneous. When placed in an aqueous environment, water molecules penetrate into the polymer and an initial hydrolytic reaction breaks the ester bonds and yields hydroxyl and carboxyl end groups. The new end groups in the interior of the sample are difficult to diffuse outward and they could accelerate the hydrolytic degradation. The end groups on the surface of the sample easily diffuse into the surroundings. This results in an increasing hydrolysis rate difference between the interior and the surface.

The physical, mechanical and barrier properties of PLA are dependent on the solid-state morphology and its crystallinity. Crystallinity also affects the biodegradation behavior of PLA. Compared to weeks for an amorphous sample, highly crystalline PLA takes a few months to decompose into lactic acid completely. This is mainly due to the impermeability of the crystalline regions(Krircheldorf).

Various fillers have different effects on the PLA hydrolytic degradation. These fillers include thermoplastic starch, short fiber-coir, maleic anhydride acting as coupling agent between polymer matrix and fillers, unmodified Montmorillonite-Na^+ (MMT-Na^+), and organo modified montmorillonite (OMMT). The thermoplastic starch enhanced PLA matrix degradation as did short fiber-coir due to its hydrophilicity. Maleic anhydride, however, delayed the degradation process as a result of improved interfacial adhesion, preventing water molecule penetration. (Iovino,2008)

Almost all biodegradation experiments use environment-like solvents, such as compost, phosphate buffer, Proteinase K, Lipase PS, and are performed at temperatures between 20°c- 60°c. PLA-based materials take several months to decompose completely in biotic environments and are suitable for landfill disposal after their use(Li,1999).

The main drawbacks of processing PLA in the molten state is its tendency to undergo thermal degradation, which is related both to the process temperature and the residence time in the extruder and hot runner. The mechanism of PLA thermal degradation is complicated. There are five different possible reaction pathways for the PLA thermal degradation based on experimental data at temperatures above 200°c and an element balance (Kopinke et al,1996). They are intra- and intermolecular ester exchange, *cis*-elimination, radical and concerted non radical reactions and selective Sn-catalyzed de-polymerization. Those degradation resulting in the formation of CO, CO_2, acetaldehyde and methylketene. The formation of acetaldehyde is expected to increase with increasing process temperature due to the increased rate of the degradation reactions. Thermal degradation results in a loss of mechanical properties of PLA. Developed a technique of in-line monitoring of the thermal degradation of PLA during melt extrusion by UV-vis spectroscopy has developed (Wang et al,2008). They proposed a relation which indicates that the molecular weight reduction of the extrudes resulted in the increased UV-vis absorption. They used this relationship to exploit the effects of various extrusion parameters such as heating zone temperatures, screw rotation speeds and filling rates on the PLA thermal degradation. They observed that low screw speed and filling rate, associated with longer residential times, increased the thermal degradation. The high heating zone temperature also caused increased thermal degradation. To improve the thermal stability of neat PLA, more purification is needed to reduce the catalyst content remaining in the bulk.

1.3.1.2.1.3. Mechanical and thermal properties of poly (lactic acid)

Neat PLA has excellent mechanical properties except for its brittleness compared to conventional thermoplastics such as PE and PP. Poly (lactic acid) PLA has higher tensile strength(53MPa) and tensile modulus than polyethylene (PE) and polypropylene (PP). PLA, PE and PP has tensile strength 53MPa ,10.3MPa and 35.5MPa respectively. And also PLA, PE and PP has tensile modulus 3450MPa ,800-1400MPa and 1380MPa respectively (Brandrup,1999). The flexural modulus, elongation, and notched izod results are worse than those of PE and PP. Annealed PLLA presents higher tensile moduli ranging from 4000 to 4200 MPa compared to 3550 - 3750 MPa for non-annealed PLLA. The highest flexural strength of crystalline PLLA is 119 MPa compared to 106 for amorphous PLLA. The mechanical properties are affected by the molecular weight and crystallization of the PLA and also vary with composition (L- and D- conformation). Generally, Poly (L-lactic acid) (PLLA) shows more interesting mechanical properties than poly (D, L-lactide) (PDLLA) for the same molecular weight. The mechanical properties improve with increasing molecular weight, to reach a plateau. For example, the plateau region of flexural strength appears around $M_v = 3.5 \times 10^4$ for PDLLA and amorphous PLLA and around 5.5×10^4 for crystalline PLLA (Perego,1996). Higher crystalline PLA possesses higher values of tensional and flexural modulus, Izod impact strength, and heat resistance. The compact resistance test showed the values of notched strength ranging from 19 to 26 J/m for amorphous PLLA and from 32 to 70 J/m for annealed PLLA. To reduce the brittleness of PLA, many researchers used various plasticizers. These plasticizers could be classified as high molecular weight plasticizers, such as polythermoplastic starch, poly (ethylene oxide), poly (ethylene glycol) (PEG), poly (ε-caprolactone), and poly (hydroxybutyrate), and monomeric plasticizers, such as oligomeric lactic acid, glycerol, and citrates. The brittleness results improved slightly, but other mechanical properties decreased (Nakafuku,2004).

Different researchers were used differential scanning calorimetry (DSC) and Thermo gravimetrical analysis(TGA) to investigate thermal properties of poly (lactic acid). Similar to many thermoplastic polymers, semicrystalline PLA exhibits T_g and T_m. Above T_g (~58 ∘C). The T_g of PLA is dependent on both the molecular weight and the optical purity of the polymer. Comparison of the experimental values of the specific heat increment at T_g with that predicted by Wunderlich's rule confirmed that after quenching, practically all the PLLA sample was in the amorphous state and underwent a glass transition. In the second scan, for quenched samples, cold crystallization exothermic peaks appeared before melting. The heat of fusion ΔH associated with the second run melting endotherm was lower than that obtained in the first scan (55 versus 71 J/g): this result indicated that at the heating rate employed (20 K/min) during cold crystallization, the sample cannot crystallize to the same extent as did the original PLLA powder(Witzke,1997). The T_g increases with molecular weight to maximum values at infinite molecular weight of 60.2, 56.4 and 54.6 ∘C for PLA consisting of 100, 80, and 50% l-stereoisomer contents, respectively. Furthermore, PLA with higher content of llactide has higher T_g values than the same polymer with the same amount of d-lactide (Dorgan,2005). The high molecular weight sample displayed a reduced ability to crystallize above T_g during a second repeated scan. The calorimetric T_g decreased with decreasing molecular weight. Amorphous PLLA samples, left at room temperature after quenching (following the melting) for six days before the test, showed an endothermic peak near the glass transition for all molecular weights examined. This could be attributed to enthalpy relaxation effects related to the thermal history of the samples. If a sample was annealed below T_g, it evolved towards the equilibrium state, and a hypothetical condition was attained only after an infinite long time.

1.3.1.3. Coupling Agent

Coupling agents belong to 1963 when Ford Motor Company invented a method to graft olefinic unsaturated monomers onto wood fiber using a catalyst system containing hydrogen peroxide and ferrous cations that enhances the compatibility between the wood fiber and the thermoplastic polymer (John,2000). The productions of wood-plastic composite require a good compatibility at the interface from polymeric matrix with the wood components (Catto et al. 2014a). The hydrophilic nature of the wood and the hydrophobic nature of the plastic results in the poor adhesion between the two phases (Rowell & Youngquist 1991).

Some categories of coupling agents have been used for the purpose of wood modification, these coupling agents includes organic, inorganic, and organic inorganic group. coupling agents increase the interfacial adhesion between the wood and the plastic matrix, and thereby improve the mechanical properties of the polymeric composite (Rowell & Youngquist 1991). An efficient approach to improve the interphase compatibility of the composite is the use of coupling agent (Lei et al. 2007).

A coupling agent is a chemical that function at the interface to create a chemical bridge between the wood component and the polymer matrix (Stark & Rowlands 2005). The primary aim of chemical modification of wood is to reduce the number of hydroxyl groups and to enhance the cross-linking with the polymer matrix. Which results in a hydrophobic interface The coupling agent chemically bonds with the OH groups in the wood flour and limits water absorption by the composites. As such, it is important to use coupling agents to improve the quality of adhesion between the plastic matrix and the wood filler. To reduce gaps in the interfacial region, and to block the hydrophilic groups, coupling agents must be used (Kord et al. 2011). The use of coupling agent also enhances the water resistance of WPCs by improving the polymer or fiber bonding (Kord ,2011b).

The good interfacial strength between polymer matrix and natural filler reinforcement have multiple effects on the properties of WPCs (Kord 2011b). The chemical bonds formed during process determine the stability of the composite. These bond interfere the properties of wood plastic composites. Coupling agents can increase physical and mechanical properties (the impact strength, flexural strength, hardness,) and also biological durability (natural durability and fungal resistance) of WPCs (Kord 2012). Poor adhesion between the matrix and the filler results in poor ability to transfer stress from the matrix to the filler thereby reducing the composite properties (Ghasemi & Farsi 2010b).

Over 40 different coupling agents have been assessed in various applications to improve the compatibility between different materials (Catto et al. 2014b). The most popular treatments have been to react the wood with, anhydrides, isocyanates or silanes or alternatively blend an anhydride modified copolymer with the matrix to aid coupling with wood at the interface. The two approaches usually used are to modify the wood fiber to make it more hydrophobic or to make the polymer it more hydrophilic.

To obtain a composite product based in non-polar thermoplastics with competitive final product, it is necessary to achieve a good compatibility between the filler and the matrix by the modification of the filler surface or by adding coupling agents (Bodirlau et al. 2009a). Coupling agents play a large role in helping to improve the compatibility between polar components (i.e., wood flour or fibers) and non-polar polymeric material.

Adhikary et al (2008) studied the effects of the fiber loading and addition of coupling agent on the mechanical properties of waste sawdust and post-consumer recycled HDPE. Maleic anhydride polyethylene-copolymers (MAPE) grafted to wood fibers can be tuned to manufacture of composites with improved adhesion, wettability and fiber dispersion. It has been noted that the moisture absorption and swelling of the composite is considerably reduced. This increase is attributed to the improved interfacial bonding between the HDPE matrix and the reinforcing wood flour due to the formation of ester bonds (Adhikary et al. 2010).

Lu et al. (2005a) studied issues concerning the use of coupling agent in an HDPE-wood composite. They concluded that for the modified composites, the improvement on the interfacial bonding strength, flexural modulus, and other mechanical properties was mainly related to the coupling agent type, function groups, molecular weight, concentration, and chain structure. The maximum value of interfacial adhesion was achieved at the 3 wt % concentration level for most maleated composites. MAPE coupling agents were more effective in improving interfacial adhesion in wood fiber–HDPE composites with compared to the other coupling agents used. MA grafted on synthetic polymers has been shown to form both covalent ester linkage and hydrogen bonding when reacted with hydroxyl groups in the wood surface. Maleic anhydride grafted PE, PP or HDPE are the most common coupling used in WPC.

From different seven coupling agents investigated by Semeralul (2009), the maleated polyethylene showed the best improvement in the interfacial bonding strength between HDPE and woods the most. The reason he gave was that the maleic anhydride groups of MAPE were easily hydrolyzed into double carboxylic groups. These double carboxylic groups were in turn more reactive for esterification under an initiator than the monocarboxylic groups of other coupling agents. It was observed that the tensile strength of the composite along with the stiffness increased due to the addition of a coupling agent (maleated polypropylene) (Semeralul 2009b).

Coupling agents usually account for about less than 5% of the total weight of a formulation of WPC. Generally, the effectiveness of the coupling agent will increase as concentration increases up to a certain surface saturation concentration (Cui et al. 2008). At this coupling agent saturated concentration, the mechanical properties will decrease due to inhibition to promote adhesion (George et al. 2001a). As a result, there is an optimal amount of coupling agent to be added to achieve superior properties. The properties that can be increased include flexural strength, and tensile strength, and impact strength (George et al. 2001b). Coupling agents have also been shown to influence crystallization morphology and nucleation behavior in semi-crystalline polymer matrices within WPCs. Consequently, due to this change, coupling agents have an impact on the mechanical properties of WPC (Ghasemi & Farsi 2010b).

1.3.2. Modification of Wood

Lignocellulosic materials are mostly utilized in wood fiber and thermoplastic composites (WPC) because of their low weight, relatively high strength and stiffness and processibility (Xue and Tao1 2005, Maldas and Kokta 1991, Rievld and Simon ,1992,).

The most important aspect with respect to optimal mechanical performance and the durability to be specific, of wood reinforced composites is the optimization of the interfacial bond between wood and polymer matrix (Bodirlau et al. 2009a). The quality of the wood-matrix interface is significant for the application of natural fibers as reinforcement for plastics. Since the fibers and matrices are chemically different, strong adhesion at their interfaces is needed for an effective transfer of stress and bond distribution throughout an interface (Caufield et al. 2007a). A good compatibility between cellulose fibers and nonpolar matrices is achieved from polymeric chains that will favor entanglements and interdiffusion with the matrix (Bakraji & Salman 2003).

Due to polarity mismatching of natural fibers and plastic, their interfacial boundaries are often weak and lead to undesirable mechanical properties (Ghasemi & Farsi 2010b). Many studies have been carried out to improve the adhesion between two phases including incorporation of coupling agent into the compound and modification of the fibers (Kord 2011a; Kord 2012; Kord et al. 2011). Different coupling agents have been used to modify the polymeric matrix and improve the interfacial strength and subsequently the mechanical properties of the products (Bodirlau et al. 2009a).

Another approach for enhancement of interfacial adhesion in WPC is fiber treatment before mixing with polymer. Some of these treatments have physical nature and some have chemical nature (Dányádi et al. 2010). Natural fibers have a good potential for chemical treatment due to presence of hydroxyl groups in lignin and cellulose. Reaction of hydroxyl groups can change the surface energy and the polarity of the natural fibers (Ghasemi & Farsi ,2010b).

Wood modification can change important properties of the wood such as biological durability, hardness, dimensional stability and UV stability by converting hydrophilic OH groups into a more hydrophobic groups (Bodirlau et al. 2009a).

Today, wood preservation plays an important role in our lives. Treated wood is used in foundations and decks of our homes, playgrounds, fences, utility poles, railroad ties, and a host of other applications (Zabel and Morrel 1992). The amount of treatment depends on the level of protection needed. Decay risk, length of service life, cost of treatment, and end-of-life disposal are all considered when determining which treatment method and chemicals to use. There are short-term and long-term levels of protection. Short-term protection, such as dipping in chemical, is used to minimize sap stain fungi on fresh cut lumber. Long-term protection is further divided into aboveground or ground contact levels of protection. Wood in contact with the ground requires more treatment because the decay risk is higher (Zabel and Morrel 1992). Copper based wood preservation is a common method for chemical treatment of natural fiber surfaces and long-lasting efficacy against wood destroyers.

1.3.2.1. Copper Based Wood Preservatives

Wood preservatives have long been used to limit wood decay. Preservatives extend wood service life by introducing toxic chemicals, making the wood resistant to fungal and insect attack. To be suitable for commercial use, wood preservatives should have broad, long-lasting efficacy against wood destroyers, produce no significant negative effects on wood strength, be harmless to wood and metal, have good penetration, uniform retention, be moisture repelling, have low toxicity to non-target organisms, be clean, odorless, and inexpensive. There are two main kinds of preservatives, based on the solvent used to introduce the chemicals into wood structure: oil borne and waterborne.

Oil borne preservatives include creosote, pentachlorophenol and copper naphthenate. These chemicals are mainly used to treat outdoor wood in industrial applications such as railroad ties, timbers, piles, and poles. These preservatives reduce surface checking and provide water repellency. Oil borne preservatives do not react with wood, but are relatively insoluble in water and have low volatility (Hunt and Garratt, 1967; Kollmann and Côté, 1968). Migration of whole oil can be a problem when the treating processes do not relieve internal pressure adequately, but the primary loss of chemical occurs as water contacts the wood surface, producing slow depletion.

Waterborne preservatives include both metal and organic based systems. Some of the metal systems react with wood, making them resistant to leaching. Organic systems are typically rendered water soluble by adding co-solvents. Once these systems dry, the chemical has low water solubility and resists leaching. Waterborne systems are often preferred because of the clean surface, paintability, lack of odor, low fire hazard and low cost of the solvent. The biggest market for waterborne systems is for residential applications.

The efficacy of waterborne metal preservatives is driven by fixation, where a series of reactions between preservative components and wood components results in the stabilization and insolubilization of toxic elements in wood (Cooper et. al., 1993). Salts formed by elements like copper, chromium, zinc, and arsenic that are contained in preservative solutions react to form insoluble preservative compounds (Hunt and Garratt, 1967).

Copper-based preservatives are the most commonly used waterborne preservatives due to their low cost and efficacy against insect and fungal attack. Copper is broadly toxic to fungi, causing membrane disruption and inhibiting many important enzymatic reactions. Low levels of copper are less effective against insect attack, although high copper levels are effective against most insects. The reaction sites for copper in wood are the carboxylic groups found in hemicelluloses (Thomason and Pasek, 1997), although, Xie et. al. (1995) and Cracium and Kamdem (1997) proposed that copper also complexed with hydroxyl groups from phenolic and carboxylic groups in lignin. Dahlgren (1972) postulated an ion exchange theory where weak acid groups in wood formed complexes with copper cation by exchanging H^+.

1.3.2.1.1. Chromated Copper Arsenate

The most commonly used waterborne preservative up until January of 2004 was Chromated Copper Arsenate (CCA). CCA was voluntarily withdrawn from residential uses because its arsenic and chromium (VI) components were viewed by the environmental community as unsafe to mammals. Although chromium (VI) is a known carcinogen, it reacts with wood and is reduced to a trivalent state, posing no threat to human health. According to the Best Management Practices for CCA (WWPI, 2006) 99.5% to 99.95% of hexavalent chromium is reduced after completion of wood treatment.

While the general public worries more about arsenic and chromium than about copper, copper is a more serious concern because of the high sensitivity of many aquatic organisms to this metal, especially larval stages of invertebrates. Although copper is a micronutrient at low levels, it can be extremely toxic to some aquatic organisms at concentrations above these levels (Brooks, 1996).

CCA was developed in India in the 1930's (Zabel and Morrell, 1992). At the time, copper was widely used, but most systems tended to leach. The chromium in CCA provided a mechanism for reducing these losses. This fixation markedly improved wood service life. Fixation is a process that reduces the leaching of a preservative component, and is defined by Cooper et. al. (1993) as "the state of chemical components of the preservative wood or other substrate when all chemical reactions are complete". CCA undergoes a series of reactions as hexavalent chromium is reduced to a trivalent state. This reduction simultaneously results in the insolubilization of both arsenic and copper components, providing leaching resistance. Copper is a broad spectrum fungicide, while arsenic contains insecticidal properties and also protects the wood from copper tolerant fungi. Chromium serves as a corrosion inhibitor and as a fixation agent.

The course of CCA fixation is divided into several phases (Dahlgren, 1975): a momentary initial reaction, a primary precipitation fixation, and a conversion reaction. Most conversion from hexavalent to trivalent chromium occurs during primary precipitation fixation. Four distinct regions have been identified during primary precipitation, each with different fixation rates. Chromium reduction occurs at a higher rate in the first region. During the first and second region, hexavalent chrome undergoes initial ion exchange and adsorption reactions with wood and is fixed as chrome chromate complexes in wood. The fundamental reaction that governs all other fixation reactions occurs in the third region with the fixation of chrome only in a trivalent form. Finally, the last stage consists of fixation of hexavalent chrome as basic chrome chromate. This period concludes when the pH of the wood and the CCA system reach a maximum. At the end of fixation, the final equilibrium fixation products fixed to the wood by ion exchange reaction include $CrAsO_4$, $Cu(OH)CuAsO_4$, an $Cr(OH)_3$. Anderson (1990) divided CCA fixation into macro-fixation and micro fixation modes. During macro-fixation, components react promptly in easy access fluid pathways, creating inorganic precipitates, while also reacting with extractives and readily available cell wall components. In micro-fixation, diffusion of preservative occurs through cell walls, resulting in a variety of inorganic and organic reaction products.

Most of the CCA reacts to form copper chromate or copper arsenate and these products are either complexed with lignin or physically precipitated into cellulose as inorganic salts. The remaining copper reacts with cellulose or lignin as Cu^{2+}, binding to cellulose and in lower amounts as chromate precipitates onto cellulose. The reduction of chromium occurs via reactions with cellulose, while insolubilization results from the reaction of hexavalent chromium with lignin (Pizzi, 1981).

Fixation can be affected by a variety of wood characteristics including pH, lignin content and extractive level. pH can affect the rates of hexavalent chromium reaction between lignin and cellulose. Wood with higher pH's take longer to complete fixation while those with low pH precipitate more hexavalent chrome early in the fixation process. Lignin content can affect fixation because chromium and copper form more stable complexes with guaiacyl units of lignin in softwoods than with syringyl units present in hardwoods. Polyflavanoid tannin extractives form complexes with metal ions and species with higher extractive levels may fix more rapidly. For example, CCA mixtures precipitate instantly in the presence of flavanoids and lignin at room temperature. The most stable complexes are formed with trivalent chromium and flavanoids. Bivalent copper fixation is nearly as stable as with chromium, while the arsenic fixation rate is much lower (Dahlgren, 1975).

While much has been made of the risks of hexavalent chromium and arsenic, a variety of studies on leachability of wood preservatives have shown that CCA has the greatest resistance to leaching of the various inorganic metallic based systems (Dubey et. al., 2005). Suttie et. al. (2002) stated that there is no alternative preservative that has shown better results in terms of cost or performance than CCA and that 1.5 times as much copper azole and 3 times as much Alkyl Copper Quat (ACQ) were needed to produce results equivalent to CCA. These higher levels result in much higher copper losses in the absence of a fixative agent such as chromium and it is this lack of strong copper fixation that has raised concerns about the potential environmental impacts of alternative copper systems.

1.3.2.1.2. Alkyl Copper Quat / Copper Azole

Despite its excellent performance, CCA was not widely used until the 1970's when the Koppers Company decided to sell CCA treated wood directly to home owners to meet the demand for durable wood for outdoor living (Connell and Nicholson, 1990). By 1997, CCA represented 97% of the waterborne preservative market (AWPI, 1997). The withdrawal of CCA from residential uses resulted in a shift to alternative wood preservatives like alkyl copper quat (ACQ) and copper azole (CuAz) (AWPI, 1997). Both ACQ and CuAz differ from acidic CCA in that they use alkaline compounds to solubilize copper.

A 2004 survey of US treating plants showed that ACQ accounted for 41% of waterborne preservatives used, followed by CCA with 35%, and CuAz with 18% (Vlosky, 2004). The fixation of copper in ACQ and CuAz differs markedly from that of CCA and larger amounts of copper must be used in order to attain the same efficacy. ACQ treatments need three times as much copper as CCA and CuAz needs twice as much copper in order to provide equivalent protection against decay and insect attack as CCA (AWPA, 2006d). The large quantity of copper in the alkaline systems, coupled with the limited number of available sites in wood that react with copper (mainly carboxylic groups in lignin and hemicellulose), results in excess mobile copper that remains available for leaching.

ACQ is composed of a copper oxide, a quaternary ammonium compound (quat) that functions as an organic co-biocide, and amines that can complex with and solubilize copper. Unlike CCA, where fixation occurs through an oxidation process forming insoluble copper, chromium and arsenic compounds copper in ACQ fixes by the reaction of amine complexing agents with wood components (Ruddick et. al., 2001), while the quaternary ammonium compounds promote fixation through ion exchange mechanisms (Archer and Lebow, 2006). The amine component (mono ethanolamine) forms donor or sigma bonds with copper (II) in the treatment solution, resulting in a solution with neutral and cationic species (depending on the pH). These copper species form highly stable *bis*-diamino copper(II) cations that will later complex with phenolic compounds (Ruddick et. al, 2001). Copper fixation begins by the neutralization of acidic groups in wood by the alkali amine system, culminating in the formation of a copper–amine-wood complex along with water insoluble copper complexes (Lucas and Ruddick, 2002). The amine component in the copper amine system forms stable copper ethanolamine complexes with wood (Ruddick et. al., 2001). Ethanolamine reacts with C=O groups in COOH groups of hemicellulose as well as with 1,3,4 substituted benzene ring groups in lignin (Humar and Petrie, 2000). This premise is supported by previous research showing that the reactive sites of copper amine fixation reactions are the carboxylic acid functional groups in hemicellulose and phenolic hydroxyl and ester groups in lignin (Thomason and Pasek, 1997; Zhang and Kamdem, 2000b). There is little evidence that copper reacts with cellulose (Lebow and Morrell, 1995), although hydrogen bonds can form between the hydroxyl groups in cellulose and the nitrogen in the amine, resulting in copper-amine-cellulose complexes (Cooper, 1991; Jin and Preston, 1991; Kamdem and Zhang, 2000; Rennie et. al., 1987).

Fixation of amine copper systems is a function of time, temperature, solution concentration (Tascioglu et. al., 2005), wood species and extractive content (Ung and Cooper, 2005). pH differences between the treatment solution and the wood (Habicht and Wittenzellner, 2003), and copper and amine chemistries (Zhang and Kamdem, 2000b) also affect copper complexation. The quantity and nature of copper-amine complexes with wood are affected by the pH of the solution (Druz et. al. 2001). Copper complexes increase at higher solution pH's because acidic wood functional groups are ionized, increasing the number of available reaction sites (Cooper, 1991; Jin and Preston, 1991). Copper fixation also increases as the wood temperature increases, but decreases with increased preservative retention. Preservative retention plays a very important role because cationic amines compete with copper for the same anionic sites in wood, thus higher concentrations of chemical decrease the sites available for selective copper adsorption (Jiang and Ruddick, 2004; Thomason and Pasek, 1997). Increased fixation requires low solution concentrations, but lower retentions will have lower efficacy. It has been estimated that 0.06 to 0.24 mmol of copper per gram of wood may be absorbed when treating wood (Cooper, 1991; Kamdem and Zhang, 2000; Rennie et. al., 1987; Smith and Tascioglu et. al., 2005).

Copper complexes with amine, in the form of mono ethanolamine (MEA), in treating solutions at a ratio of 1:4 (Kamdem and Zhang, 2000; Mazela et. al., 2003) but this ratio declines to 1:1 (Jiang and Ruddick, 2004) to 1:1.4 (Lucas and Ruddick, 2002) after leaching. This change occurs because free amine taken up by the cell wall structure in the wood is not strongly bound and is easily removed by leaching. Unfortunately, this excess amine competes with copper and copper-amine bonding to wood (Tascioglu et. al., 2005). Thus, the limited capacity of wood to bind copper at higher retentions (7.9 kg/m^3) results in excessive levels of unreacted copper (Waldron et. al., 2004). This ratio between unreacted amine and copper determines the subsequent leaching resistance of copper and amine complexes in wood (Lucas and Ruddick, 2002). Initial studies on didecyldimethyl ammonium chloride (DDAC) (Oertel, 1965), the quaternary ammonium compound most commonly used in ACQ, concluded that this compound fixes by an ion exchange mechanism, in which the ammonium cation replaces the proton on the hydroxyl groups present in cellulose chains. However, Preston et. al. (1987) and Tascioglu et. al. (2005) suggested that DDAC fixation to wood occurred through an ion exchange process where the carboxylic acids and phenolic hydroxyls in lignin were the potential reaction sites. Reactivity of DDAC with lignin is much higher than with any other wood component. The adsorption of quaternary compound with wood occurs as follows: lignin>hemicellulose>cellulose. Reactivity of hemicellulose with the quaternary compound is five times higher than with cellulosic materials (Jin and Preston, 1991).

Copper fixation associated with quats tends to increase with solution pH. The number of available reaction sites increases by the ionization of acidic wood functional groups at higher pH's (Tascioglu et. al, 2005; Jin and Preston, 1991; Cooper, 1991). Copper and ammonium compounds both fix through cationic exchange and ion pairing mechanisms, and the number of available reaction sites is limited. Thus, increasing the treatment solution concentration decreases the degree of fixation (Tascioglu et. al., 2005).

Copper Azole is a preservative formulation that relies on amine copper and an organic azole (tebuconazole) as a co-biocide. Tebuconazole is an insoluble, unleachable, light and heat stable compound that provides protection against copper-tolerant fungi (Grundlinger and Exner, 1990). CuAz functions by altering the structure of hemicellulose, mainly carboxylic groups, reducing the attractiveness of wood to invading organisms (Thomason et. al., 1997).

In general, leaching of components from preservative treated lumber is small, and primarily occurs immediately after the initial exposure of the treated member as unfixed components are removed from the wood surface (Bergholm, 1992; Evans, 1987). Fixed preservative components can also be leached when in continuous water contact, but this process is slow. Despite their overall low water solubility, components can gradually solubilize in water or the water may contain organic or inorganic components that can either react with fixed preservative material or can change the pH of wood to induce solubilization of fixed products. The result is a gradual release of chemical into the surrounding environment. This can have both environmental and efficacy effects.

Jiang and Ruddick (1999) and Zhang and Kamdem (2000b) suggested that around 9-12% of copper (as CuO) in ACQ treated blocks is lost after leaching with deionized water; however, others have reported losses of 15-22 % and 30 % after 336 hours (Humar et. al., 2003, 2005; Waldron et. al., 2003, 2005). Above ground depletion tests show that 10% of CuO is lost from ACQ treated samples and 9% CuO from CCA samples after 6 months of exposure. Deck tests show that 8-12% of copper leaches from formulations similar to those of CuAz after 20 months of exposure to rainfall, 8-10% copper is lost from ACQ-B decks and only 5% from CCA treated decks (Lebow, 1996). Copper leaching from ACQ on a mass basis has been shown to be two to twenty times higher than from CCA (Archer et. al., 1992; Solo-Gabriele et. al., 2000; Dickey, 2003), while copper losses from CuAz are 3.5 to 17.9 times greater than those of CCA (Dickey, 2003; Hickson Corporation, 1999).

Several models have been developed to predict the rates of metal losses from treated wood exposed in various environments (Brooks, 1998, 2000; Waldron, 2005; Ung et. al., 2005). Brooks' model shows that short-term copper losses from commodity sized ACQ treated wood was predicted to be 8 times higher than from wood treated with CCA and 5 times higher over long term periods (Brooks, 2000). Waldron (2005) predicted that leaching from the top surface of southern pine decking after one year of being continuously exposed to rainfall would result in loss of about 60% of available copper from ACQ and CuAz treated boards, while CCA leaching would be fairly low.

In addition to higher leaching rates, ACQ and CuAz treated wood accelerate corrosion of metal fasteners, thus only hot-dipped galvanized, copper or stainless steel fasteners and connectors can be used with treated wood

1.3.3. Manufacturing Technologies

There are several alternative methods for manufacturing WPCs. Compounding is a process in which filler and additives are added to the molten polymer. The compounded material can be formed into pellets or granules prior to future processing, or they can be immediately shaped into the final product (in-line processing) (Clemons et al. 2013). The processability of WPCs is similar to plastics, which is an advantage since WPCs are can typically be processed with the same machinery. Extruders are the most commonly used systems for WPC compounding. Hot cold mixers are also used but mainly for the processing of PVC based WPCs (Schwendemann ,2008).

The product manufacturing technologies for WPCs include sheet or profile extrusion, injection molding, and compression molding (Stokke et al. 2014). Profile extrusion is the most commonly used manufacturing method for a WPC, and it is used to produce composites with a continuous profile of the desired shape (Gonçalves et al. 2014). WPC panels can be produced by sheet extrusion. Injection and compression molding produce non-continuous pieces with a more complicated shape.

1.3.3.1. Extrusion

Extrusion produces continuous linear profiles by forcing a melted WPC through a die. Different types of extruders and processing strategies have been used to produce WPCs. For example, some processors manufacture WPCs in one step, using twin-screw extruders whereas some prefer to adopt several extruders in tandem to compound and finally form the desired profile of the WPC. (Clemons et al. 2013)

A typical screw extruder consists of feeders, modular barrels, screws, a gearbox, a heating, and cooling unit (Figure .4), and a centralized control unit to adjust the extrusion speed, feeding rate, temperature, and other process parameters (Schwendemann ,2008). The extruding screw system, consisting of screws and barrels, mixes, devolatilizes, and performs the reactions for multiple applications.

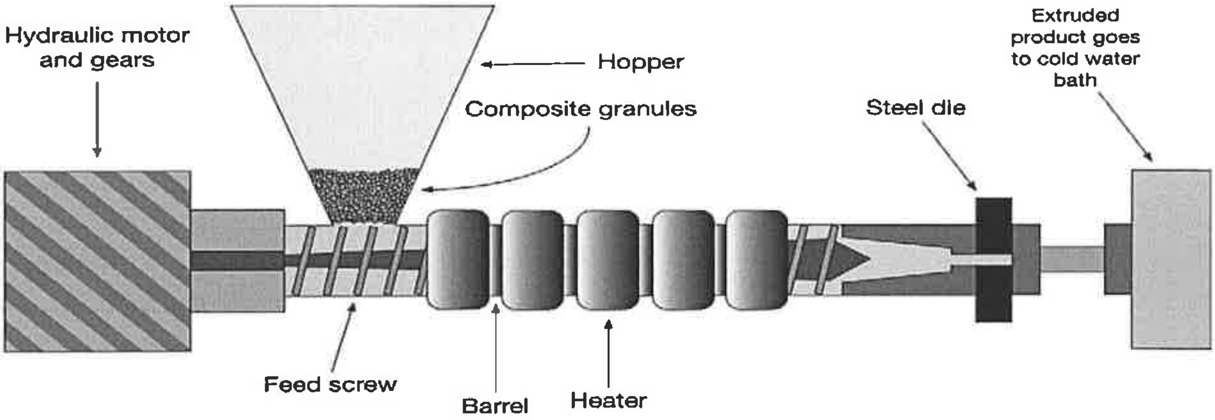


Figure 4. The Basic Structure of an Extruder.

The screws mix the components in order to produce a homogeneous blending fluid in the barrel. The screws are usually made up of three zones: the feeding, melting, and melt pumping zone. In the feeding zone, the raw materials for WPC are usually solid, but when they move to the melting zone, most polymers have melted while fillers and additives remain in a solid state. The melt pumping zone forms a continuous fiber polymer blend, which is finally pumped to the pelletizer after cooling or extruded through the die. (Stokke et al. 2014)

A typical barrel-length-to-diameter (L/D) ratio of a single screw extruder varies from 20 to 30. The screw builds up high pressure in the composite melt so that it can be extruded through the die. Even though the single-screw extruders are less expensive than those with twin-screw systems, they suffer from a limited mixing and self-cleaning ability as well as from the selective material intake. The twin-screw extruders, whether co-rotating or counter-rotating according to the screw rotation directions, are used for compounding, mixing or reactive polymer materials. L/D ratios for the twin-screw extruders vary from 39 to 48. The advantages of the twin-screw extruders include the self-cleaning and high mixing ability. However, unlike the single-screw extruders, these systems cannot develop up high pressure in the melt pumping zone. In addition, the twin-screw extruders are more expensive. (Schwendemann 2008, Stokke et al. 2014)

The barrels are divided into the sections heated with the individual control units (Stokke et al. 2014). The temperature of the barrel gradually increases from the rear to the front which allows the material to melt gradually and to prevent thermal degradation or overheating. Sometimes the friction and high pressure in the barrel provide the required heat for the system, and the heaters can be turned off.

Multi-layered WPC structures are produced by co-extrusion. This process utilizes multiple extruders (single or twin-screw) to melt and deliver different types of materials to a single extrusion die that will extrude the materials in the desired form (Stokke et al. 2014). In addition to the reduced material and production costs, co-extrusion makes the properties of final products highly controllable, which is a significant advantage over other production technologies.

1.3.3.2. Injection Molding

Injection molding is used for producing large quantities of WPC pieces with complex geometries (Migneault et al. 2009). The molding of WPCs begins by inserting the pelletized raw material into the hopper, which feeds the material into the heated barrel with a reciprocating screw (Figure .5). The majority of the injection molding machines are equipped with single screws. The increased thermal energy reduces the viscosity of the material, allowing the screw to push the material forward. The simultaneous mixing and homogenizing increase the friction and heat within the barrel. The material is collected at the front of the screw and then injected at high pressure and velocity into the mold. The volume of the material that is used to fill the mold is known as a shot (Stokke et al. 2014). The high packing pressure completes the mold filling and compensates for thermal shrinkage. Once the cavity entrance solidifies, no more material can enter the cavity. Consequently, the screw reciprocates and receives the new material for the next cycle. Meanwhile, the material inside the mold is cooled to the preset temperature and ejected from the mold. After the prepared piece is demolded by an array of pins, the mold closes and the process is repeated.

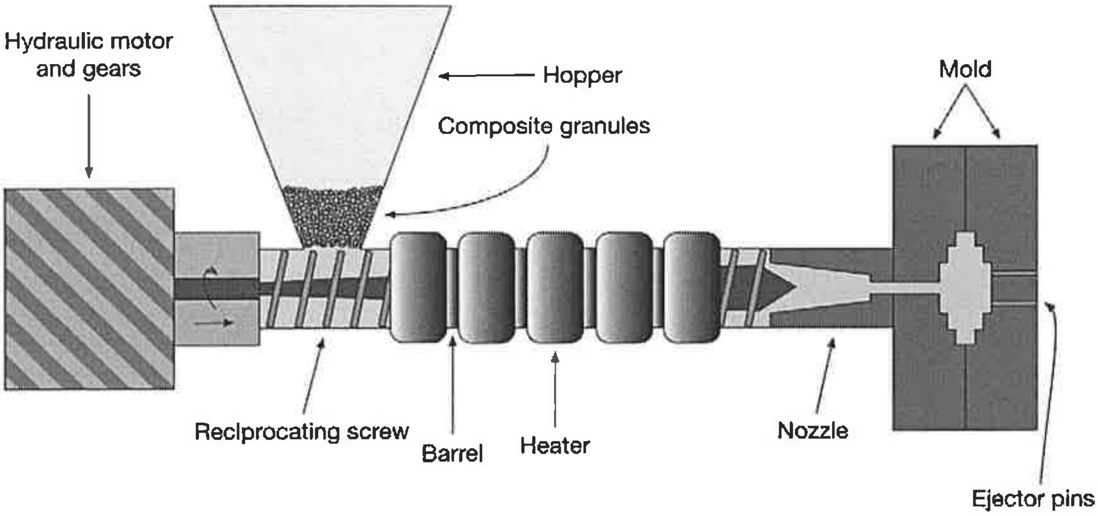


Figure 5. The Structure of an Injection Molding Apparatus

Most injection-molded WPCs are produced from pelletized raw materials. However, in-line compounding is also possible. It is a combination of a two-stage injection unit with a co-rotating twin screw. Once the raw materials are fed into the co-rotating twin screw, they are compounded and transferred to a shooting pot. The shooting pot pushes the material via the machine nozzle and hot runner into the mold. (Schwendemann, 2008)

1.3.3.3. Compression Molding

Compression molding of WPCs is utilized especially in the automotive industry due to its capability to produce large and complex parts. Moreover, it wastes relatively little raw material, and therefore, it is one of the least expensive molding methods. However, the product quality is not always consistent and it can be problematic to control for leakage between the two surfaces of the mold (flashing). (Clemons et al. 2013, Stokke et al. 2014)

The compression molding process (Figure 6.) starts by placing the WPC pellets or granules into the preheated mold (Stokke et al. 2014). To shorten the molding cycle time, the charge is also usually preheated. The material is softened by the heat and as the upper half of the mold moves downward, the charge is forced to conform to the shape of the mold. After the mold is opened, the part is removed by the ejector pin.

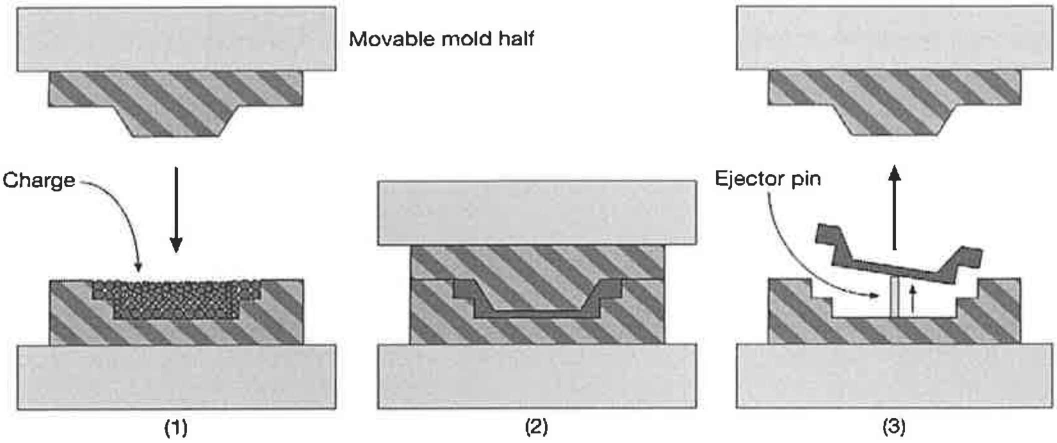


Figure 6.Aschematic Drawing of Compression Molding Process.

1.3.4. Properties of wood plastic composites

There are two common reasons to add wood to polymers: 1) to lower the price of the final product and 2) to reduce the dependency on mineral oil based products (Kim and Pal 2010). This, however, means a compromise as the properties of wood and plastics are altered, i.e., WPCs possess rather different characteristics. For example, WPCs absorb less water than wood but have higher tensile strength than plastics. WPCs have therefore found use in multiple applications. The low density and good processability of WPCs are favored in automobile industry, for instance. On the other hand, WPCs are widely used in building products, such as siding and decking because of their low water absorption and good creep performance. However, the properties of WPCs are highly dependent on the product formulation, manufacturing, and the quality of the raw materials.

1.3.4.1. Mechanical Properties

Wood fibers are added to polymers to increase their stiffness and strength (Wolcott and Englund 1999). The presence of wood fibers in the polymer matrix typically increases the strength and modulus of the composite (Bhaskar et al. 2012, Li et al. 2014). However, both the polymer matrix and the fiber reinforcement are responsible for the mechanical performance of the composite. Tensile strength is more sensitive to the properties of the polymer matrix whereas the modulus of elasticity of the composite is primarily dependent on the properties of the fiber. In order to increase tensile strength, a strong fiber-matrix interface, oriented fibers, and low stress concentration are required whereas the maximization of the tensile modulus requires fiber wetting in the matrix phase, a high fiber concentration and fibers with a high aspect ratio. (Saheb and Jog 1999)

The fiber must have a certain minimum length, i.e., the critical fiber length, in order to achieve the fully stressed properties to the fiber in the polymer matrix (Stark and Rowlands 2003, Sain and Pervaiz 2008). The critical length depends on the fiber characteristics and shear strength of the fiber-matrix bond. The fiber-matrix interface is likely to fail due to the de-bonding at lower stresses if the length of the fiber is less than its critical strength (Stark and Rowlands 2003, Bourmaud and Baley 2007). By contrast, exceeding the critical fiber length may reduce the strength of the composite because the effective stress transfer may be impaired due to fiber curling and fiber bending (Sreekumar et al. 2007).

Interphase and interface are two important concepts in fiber reinforced polymer composites. The interface is a two dimensional surface between the fiber and the matrix whereas the interphase is the three-dimensional intermediate between the matrix phase and the fiber phase (Pilato and Michno 1994, Oksman Niska and Sanadi 2008, Jesson and Watts 2012). The interface in any fiber-polymer composite system is responsible for transmitting stresses from the matrix to the fibers, and the contribution of surfaces to stress transfer depends on both the roughness and the surface chemistry of the constituents. The stress in WPCs is transferred not only by shear along the length of the fiber, but also by tension at the fiber-matrix interface. The stress transfer is limited by the fiber strength, the shear yield strength, and the tensile yield strength of the plastic matrix polymer. (Sretenovic et al. 2006, Sain and Pervaiz 2008) A composite failure can occur through several scenarios, and the uneven nature of the surfaces makes the process even more complex. However, in the simplest case, an adhesive failure can occur in the fiber-interphase interface or in the interphase matrix interface. A cohesive failure of the interphase is also possible. The typical techniques to evaluate interfacial interactions and adhesion between the main constituents include surface analysis methods, such as X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR), microscopy, single fiber-pullout and microbond tests, and dynamic mechanical thermal analysis (DMTA). (Sretenovic et al. 2006, Oksman Niska and Sanadi 2008)

The mechanical properties of WPCs have been extensively investigated. Changes in the amount of the wood component exert multiple effects on the characteristics of WPCs.

When the wood fiber content is increased, the tensile and flexural moduli tend to increase because wood, especially cellulose, is a highly crystalline material compared to PE, PP, and PVC (Bhaskar et al. 2012). However, the moduli of WPCs are highly dependent on the fiber type and source (Bouafif et al. 2009, Butylina et al. 2011, Ashori et al. 2011, Adhikari et al. 2012, Migneault et al. 2015). Although an increase in the wood fiber content may also lead to the higher hardness, it tends to reduce impact and tensile strength (Bledzki et al. 2002, La Mantia et al. 2005, Ndiaye et al. 2013). In addition, the tensile strain at break decreases considerably. Huang and Zhang (2009) and Ashori et al. (2011) concluded that higher loadings of wood flour in WPCs induced the agglomeration of wood particles, which may impair the mechanical durability of WPCs.

Interestingly, Bledzki et al. (2002) showed that WPCs consisting of hardwood fibers had a higher elongation at break and better impact strengths compared with WPCs containing softwood fibers. Their findings can be explained by the compositional differences between hardwoods and softwoods; hardwoods contain more cellulose and hemicelluloses than softwoods. On the other hand, the higher lignin content in softwoods could explain the better stiffness of those WPCs consisting of softwood fibers. (Sain and Pervaiz 2008, Lai 2012)

The durability of WPCs can be considerably modified by altering the characteristics of the wood fiber surface, which changes the compatibility between wood fibers and coupling agents. For example, if WPCs are manufactured with wood fibers from bark, then the esterification reactions between reinforcing fibers and the coupling agent are inadequate and these WPCs are mechanically weaker. Conversely, the manufacture of WPCs with pure cellulose fibers leads to stronger WPCs because cellulose fibers and polymer matrix can be more extensively coupled through coupling agents. The underlying reason for this phenomenon is the difference between the surfaces of fibers; the surface of pure cellulose fiber is more polar than the surface of bark because cellulose contains more polar hydroxyl groups. In contrast, bark consists mainly of lignin and extractives that are chemically non-polar. Furthermore, the coupling between wood fibers and polymers can be altered by treating wood fibers with coupling agents, acids or alkalis. (Bouafif et al. 2009, Müller et al. 2012, Zhang et al. 2013, Migneault et al. 2015)

Thermal treatment of wood fibers is another way to modify the properties of WPCs (Ayrilmis et al. 2011). In general, WPCs reinforced with thermally treated wood fibers are mechanically weaker than those reinforced with non-treated fibers. However, the thermal treatment of the wood fibers significantly increases the dimensional stability and water resistance of WPCs. The thermal degradation of hemicelluloses begins already at 120 °C. Hemicelluloses act as the connective bridges between cellulose fibers and lignin, leading to the stiffer wood material. The degradation of hemicelluloses, therefore, results in weakened mechanical properties.

Bouafif et al. (2009) demonstrated that wood fiber size also affected the mechanical properties of WPCs; increasing the fiber size improves the modulus of elasticity (MOE) and maximum strength in both flexural and tensile tests; the results have been confirmed by Kociszewski et al. (2012). Migneault et al. (2008) demonstrated that increasing fiber length and maintaining constant fiber diameter exerted beneficial effects on the tensile and flexural moduli and toughness of WPC.

There are other ways to optimize further the mechanical properties of WPCs, e.g., the incorporation of additives can help to overcome an incompatibility between the wood and the polymers. The use of MAPP or MAPE is a well-established approach to improve the durability of WPCs. Several studies have confirmed the effectiveness of MAPP and MAPE (Nourbakhsh and Ashori 2009, Pérez et al. 2012, Bhaskar et al. 2012, Ndiaye et al. 2013
To summarize, the mechanical properties of WPCs are highly dependent on the product formulation. The incorporation of additives, such as coupling agents, is usually required to produce WPCs with adequate mechanical properties.

1.3.4.2. Water Absorption

A well-known disadvantage resulting from the addition of wood fibers in plastics is the consequent susceptibility to water absorption (Adhikary et al. 2008b). Moisture penetrates into the composite materials by three different mechanisms. The first and the most common process is the diffusion of water molecules inside the microgaps between the polymer chains. The second mechanism is capillary transport into the gaps and flaws at the interfaces between the fibers and polymers. Moisture transport by microcracks formed during the processing is another mechanism. In general, water absorption on natural fiber reinforced composites follows the kinetics of a Fickian diffusion process. (Espert et al. 2004)

Wang et al. (2006) studied moisture absorption in natural fiber-plastic composites. They proposed that moisture absorption occurred via two mechanisms depending on the fiber content of the composite. At higher fiber loadings, when the accessible fiber ratio was high and the material more homogeneous, the diffusion process was the dominant mechanism. At low fiber loading, percolation is the dominant mechanism; the fiber loading threshold for percolation is about 50wt%. Percolation was applicable for nonhomogeneous materials and it takes into account the randomness of the composite structure.

As WPCs absorb water, not only do they become more vulnerable to the dimensional changes and microbial attack, but they also become mechanically weaker (Espert et al. 2004, Tamrakar and Lopez-Anido 2011). Several efforts have been made to improve the water resistance and dimensional stability of WPCs. Some manufacturers have attempted to reduce water absorption of WPCs by the addition of zinc borate, which also improves the fungal resistance. On the other hand, along with the improvements in mechanical properties, the addition of MAPP or MAPE also reduces moisture absorption (Adhikary et al. 2008a, Najafi et al. 2010).

An increase in wood fiber content or fiber size leads to a higher water absorption but like the mechanical durability, this property is also highly dependent on the fiber type and source (Yang et al. 2006, Migneault et al. 2008, Bouafif et al. 2009, Migneault et al. 2009, Ayrilmis et al. 2011, Butylina et al. 2011). In addition, the characteristics of the polymer matrix exert a considerable impact on water absorption (Adhikary et al. 2008a, Najafi et al. 2010, Sobczak et al. 2013); in general, water absorption of WPCs with PP as the polymer matrix is higher than of those with PE (Najafi et al. 2007). However, the water absorption of WPCs is also dependent on the temperature of the water, i.e., by increasing the temperature, then one also increases the amount of water absorbed (Najafi et al. 2007).

Water absorption of WPCs can be reduced by modifying the wood fibers. For instance, Dányádi et al. (2010) showed that the benzylation of wood fibers resulted in decreased water absorption. The wood modifications conducted by Müller et al. (2012) had similar effects. Wei et al. (2013) modified poplar wood fibers chemically by esterification and noted that the esterified fibers were more hydrophobic than the unmodified fibers. Consequently, the compatibility between wood fibers and the plastic matrix increased, leading to lower water absorption.

1.3.5. Applications of WPC

Ashori (2008) mentions the obvious fact that industries are always on the lookout for innovative materials and improved processes to produce better products to increase their profit margin and keep their technological edge. Therefore, it is not surprising to see WPC being used in large applications from aerospace to electronics (Ashori ,2008)

1.3.5.1. Building products

The building products are the largest market for WPCs which include decking, fencing, garden furniture, exterior windows and doors etc. As compared to solid wood, WPCs have advantages of lower maintenance, higher durability, and more resistance to warping and splintering. Since WPCs usually have lower mechanical properties than solid wood, it is not suitable for application where strength and stiffness are critical. Figure 7. shows some building products made from WPC.

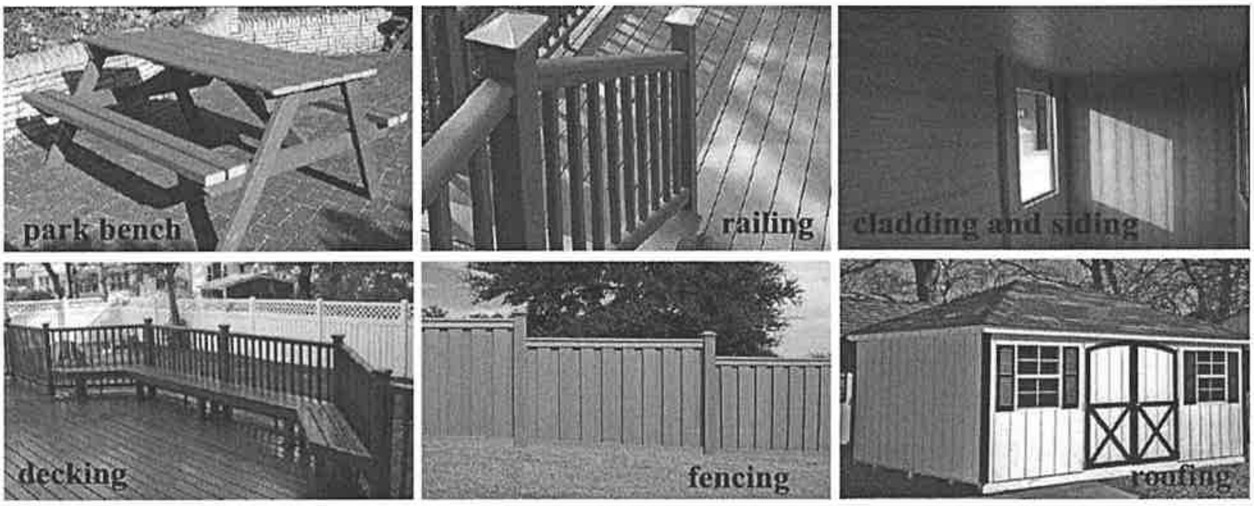


Figure 7.Applications of WPCs in building products.

1.3.5.2. Infrastructures

Marine use and railroad crossties are major applications of WPCs in infrastructure sector. As WPCs do not contain toxic preservatives that may leak into seawater and cause environmental problems, the WPCs can replace the preservative-treated lumber for marine use. This has great potential because high quality wood is becoming less and less available because of restriction on the logging of native species and tropical hardwood. Also the WPC use for railroad crossties appears to be suitable due to the stable and durable properties under tough conditions.

1.3.5.3. Transportation

Automotive and highway applications of the WPCs are also found in the transport sector where the WPCs are used as substrates for interior of door panels, roof headliners, seat backs, spare tone covers, and trunk-liners in automobiles (Youngquist et al. 1994b). Highway applications include the highway signs, noise barrier, guardrail posts, and fence posts.

1.3.5.4. Structural Applications of WPCs

All materials or products must be evaluated to ensure that they will perform adequately in their end-use application. For wood fiber thermoplastic composites, important characteristics requiring evaluation include ultraviolet light durability, engineering properties, creep, and thermal effects (English & Falk 1996). Testing, design, and evaluation standards are needed to measure and maintain the required performance.

Durability of WPCs can be enhanced by ultraviolet light stabilization of the polymer and a complete encapsulation of the wood component. Depending on the surface condition of the composite element, paints and other finishes may enhance durability as well. Properly manufactured, and properly specified, wood fiber-plastic composites should have excellent durability in exposed conditions (Caufield et al. 2007a).

1.3.5.5. Engineering properties

Performance requirements for structures and structural components are expressed in terms of designated design loads and displacements; therefore, characterization of structural performance must encompass these two aspects of product, component, or system behavior.

In designing any product, the first concern is the capacity to resist expected loads safely (English & Falk 1996).

The second concern is to ensure that the product performs within acceptable limits of serviceability (usually short- and/or long-term deflection) when subjected to loads not exceeding the design load. For example, to be used in building construction, wood-plastic composite products must be able to resist a design load with a low probability of causing member failure and a stiffness sufficiently high to meet acceptable limits.

The design load can be established through short-term engineering strength and stiffness testing as well as long-term creep and duration of load evaluation. One difficulty in determining design loads for wood-plastic composites is the tendency for the test specimens to deform excessively before failure.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Polymer Matrices

Thermoplastic matrixes for the use in WPCs need to be processable at temperatures below 200°C, since wood constituents start to thermally degrade at approximately 150 °C, and around 200 °C the degradation may be substantial for many wood species (Fengel and Wegener 1983). Thermal degradation is also dependent on the wood-plastic residence time at higher temperatures. For examples, if the processing cycle is kept short, it is possible to use a higher peak temperature. The PLA and MAPE was obtained from commercial sources. Poly lactic acid was used in this thesis (PLA, AK1500, OO-KUMA 3D printing materials, Turkey). It has a melting point at 210± 60°C (ASTM D3418) and a density of 1.24 g/cm^3. Its tensile strength (at yield) and Tensile modulus were 110 Mpa (ASTM 882) and 3309 Mpa (ASTM D882), respectively. Maleated polyethylene (MAPE) was used as the coupling agent (DuPont, Packaging and industrial Polymer Inc.). It's melt flow index and density were 8 g/10 min (2.16kg ,190°C) and 0.930g/cm^3, respectively.

2.1.2. Wood Materials and Treatment Processes

Sapwood of pine species (*Pinus sylestris* L.) with, specimens (30× 15× 5 mm) were vacuum pressure impregnated with aqueous solution of 3% Tanalith E, and the impregnation was conducted under vacuum (625 mm Hg) over the blocks were applied for 30 min. After vacuum, 600kpa pressure was applied for 30 min (Figure 8). Then the wood samples removed from the treatment solution, was wiped lightly to remove solution from the wood surface, and weighed to determine gross retentions for sample. Retention values were chosed according to the use class hazard 4 for ground contact. The retention for each treatment solution was calculated according to the following formula:

$$R = \frac{[\,(G\,XC)]}{V}\,X10kg/m^3, \qquad (1)$$

where

G are the grams of treating solution absorbed by the block,

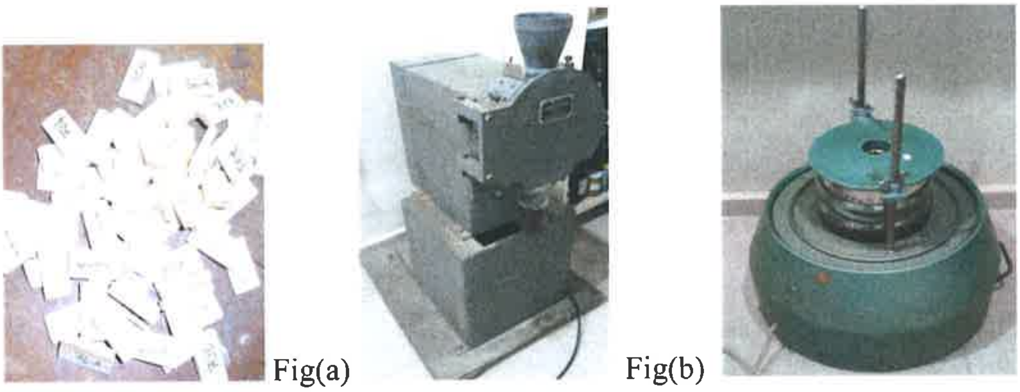
C are grams of preservative or preservative solution in 100 g of the treating solution,

V is volume of block in cubic centimeters.

After the treatment process, the samples treated with copper-based wood preservatives were kept at the room temperature for fixation for one week.

Figure 8. Wood Treatment Process.

The virgin Scotch pine sapwood (*Pinus sylvestris* L.) and treated wood with Tanalith E were first chipped with a planer. Then the chips were grounded to wood flour with a Wiley mill (figure 9b). The resulting particles were sifted with a vibration sieve and those that passed through a 40-mesh and 60-mesh screen were used (figure 9c).



Fig(a) Fig(b) Fig (c)

Figure 9. Wood components for WPCs preparations, (a) wood samples, (b) Thomas Milley for labratory for wood flour preparation, (c) vibration sieve

2.2. Methods

2.2.1. Wood Plastic Composite Preparation

The raw materials formulation for the composites in this study were polylactic acid(PLA) and Scotch pine (*Pinus sylverstris* L.) wood flour (30%,40%,50%) and, also maleic anhydride grafted by poly ethylene (MAPE) (3%).

The wood floor was dried for 24 h at 70 ± 2°C before composite preparation. Then it was mixed with the PLA and MAPE in a high-intensity laboratory mixer Figure 10(a). This mixture was compounded in a twin-screw laboratory extruder Figure (10 b). The seven-barrel temperature zones of the extruder were maintained at 170°C–175°C-180°C–185°C-190°C-- and 195°C (from feed zone to die zone) during the production. The temperature of the barrel gradually increased from the rear to the front which allows the material to melt gradually and to prevent thermal degradation or overheating, and the rotor speed was set at 100 rpm. Extruded samples were collected, cooled in cold water and pelletized with pelletizer. The hybrid pellets were dried at 70°C for 24 hours in oven dry to remove the absorbed moisture and cooled to room temperature.


(a)

(b)

Figure 10. high-intensity laboratory mixer(a) and twin-screw extruder(b)

The pellets were poured into a metal frame to form the experimental composite panels via compression molding (carver) in a hot press for 4 min at 195°C (Figure11c). Each WPC sample was produced in dimensions of 250 mm in length (L) X 250 mm in width (W) X 2 mm in thickness (T) Figure 11 (d and e). The compositions of the different wood plastic composites (WPCs) samples are summarized in the table 2.

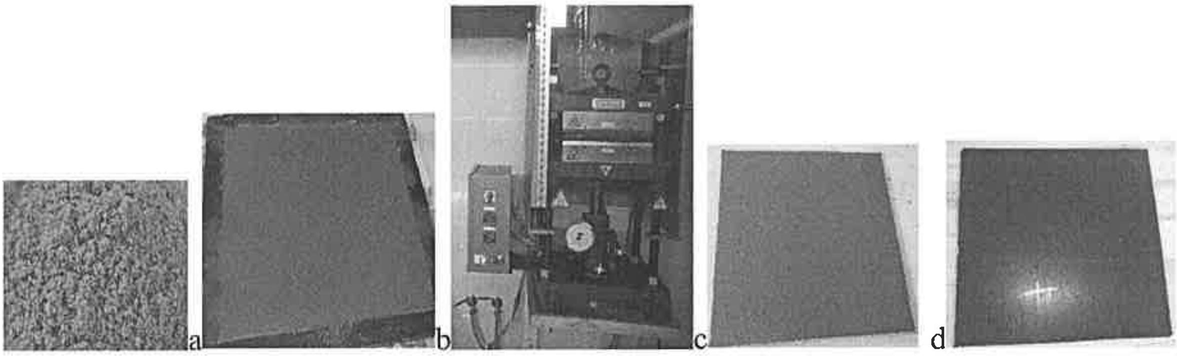


Figure 11. Mixture of Polylactic acid, Maleated polyethylene, and Woood flour(a), Metal frame used to form the experimental composite panels (b), compression molding press for laboratory application (carver) (c). and (d) wood plastic composite produced by dimension 250 mm x250 mm x 2 mm, but darker or black color (e) due to wood samples treated by chemical with Tanalith E

Table 2. The compositions of the different wood plastic composites

GROUP ID		MATERIALS			
No.	Group ID	Treated wood(%)	Untreated wood(%)	PLA(%)	MAPE(%)
1	TW30M3	30	-----	70	3
2	TW40M3	40	-----	60	3
3	TW50M3	50	-----	50	3
4	TW50M0	50	-----	50	0
5	UW30M3	-----	30	70	3
6	UW40M3	-----	40	60	3
7	UW50M3	-----	50	50	3
8	UW50M0	-----	50	50	0

TW30M3, TW40M3, TW50M3, and TW50M0, = Treated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively. UW30M3, UW40M3, UW50M3, UW50M0 = Untreated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively.

2.2.2. Physicical Properties of Wood Plastic Composites

2.2.2.1 Density of Wood Plastic Composites

2.2.2.2. Archimedes Density of WPCs

For the Archimedes density determination 25 (L) x 25 (W) x2 (T) mm^3 specimens were prepared according to density standards of ASTM D792. Five replicate specimens were tested for each formulation. To perform the density measurement using the Archimedes method the WPC specimen was wrapped and ends were intertwined (Figure 12). The balance was tarred and the specimen was placed on the weighing pan and weight of the specimen in air was recorded as M_{air}. The specimen was placed onto the weighing basket, the samples were submerged, and the weight was recorded as $M_{submerged}$.

Figure 12. Archimedes density of WPCs

The Archimedes density or experimental density of WPC is calculated using the following equation:

$$Density\ of\ solid = \left[\frac{(M_{air})}{M_{air} - M_{sebmerged}}\right] x\ density\ of\ water \tag{2}$$

In tests where a vacuum oven was used, after recording the specimen weight in air, the specimen was submerged in the immersion fluid, the suspension wire was removed and the beaker was placed in the vacuum oven. After the specified amount of time had elapsed, the container was removed from the vacuum oven and placed on the bridge over the weighing pan of the balance. Then suspension wire and weighing basket were put back in place, the balance was tarred again and a utensil was used to transfer the specimen from the bottom of the beaker to the weighing basket without any parts of the specimen being exposed to air; The submerged weight was recorded.

2.2.2.3.Void Volume Fraction of WPCs

Fiber and matrix materials were considered to determine the void content fraction of WPCs. The volume of the composite material is equal to the sum of the volume of the fibers and the volume of the matrix.

Therefore,

$$v_c = v_f + v_m \qquad (3)$$

where, v_c - volume of composite material

v_f - volume of fiber

v_m - volume of matrix

Let, the fiber volume fraction V_f (mm^3)and the matrix volume fraction V_m (mm^3) be defined as

$$V_f = \frac{v_f}{v_c} \qquad \text{and} \qquad (5)$$

$$v_m = \frac{Vm}{Vc} \qquad (6)$$

such that the sum of volume fractions is

$$V_f + V_m = 1 \qquad (7)$$

Assuming that the composite material consists of fibers and matrix material, the weight of the composite material is equal to the sum of the weight of the fibers and the weight of the matrix.

Therefore,

$$Wc = wf + wm \tag{8}$$

where, w_c - weight of composite material

w_f - weight of fiber (g)

w_m - weight of matrix (g)

The weight fractions (mass fractions) of the fiber (M_f) and the matrix (M_m) are defined as

$$M_f = \frac{w_f}{w_c} \quad \text{and} \tag{9}$$

$$Mm = \frac{w_m}{w_c} \tag{10}$$

such that the sum of weight fractions is

$$Mf + Mm = 1 \tag{11}$$

The density of composite material can be defined as the ratio of weight of the composite material to the volume of the composite material and is expressed as

$$\rho c = \frac{w_c}{v_c} \tag{12}$$

But, $vc = vf + vm$,and $v = w / \rho$, therefore the above equation can be rewritten as

$$\frac{wc}{\rho c} = \frac{wf}{\rho f} + \frac{wm}{\rho m} \tag{13}$$

$$\frac{1}{\rho c} = \frac{1}{\rho f}\left[\frac{wf}{wc}\right] + \frac{1}{\rho m}\left[\frac{wm}{wc}\right] \tag{14}$$

By writing in terms of weight fractions,

$$\frac{1}{\rho c} = \frac{Mf}{\rho f} + \frac{Mm}{\rho m} \tag{15}$$

The density of the composite material in terms of weight fractions can be written as,

$$\rho c = \frac{\rho f * \rho m}{\left[(Mfpf) + (Mm\rho m) \right]} \quad , \mathrm{g/cm^3} \tag{16}$$

During the incorporation of fibers into the matrix or during the manufacturing of composites, air or other volatiles may be trapped in the material. The trapped air or volatiles exist in the composites as micro voids, which may significantly affect some of its mechanical properties. A high void content (over 5% by volume) usually leads to lower fatigue resistance, greater susceptibility to water diffusion, and increased variation (scatter) in mechanical properties. The void content in a composite material can be estimated by comparing the theoretical density with its actual density

$$V_{void} = \left[\frac{(\rho_{ct} - \rho_{et})}{\rho_{ct}} \right] * 100 \tag{17}$$

where, ρ_{ct} - theoretical density of the composite material

ρ_{et} - experimental density of the composite material

2.2.2.4. Dimensional Stability

The water absorption of the composites was evaluated according to the ASTM D570. The specimens were oven dried at 70°C for 24 h, then cooled in desiccators and weighed (W_1) quickly. The dried specimens were soaked in distilled water at room temperature for 2h and 24 h interval for three weeks (Figure 13a). The specimens were removed from the distilled water and placed on a dry filter paper to blotted the excess water on the specimen surfaces, and then immediately weighed the wet weight (W_2) and thickness of wood plastic composite samples were determined by using wireless dimensional measurement instrument Figure 13(b). For the water absorption (WA) and thickness swelling (TS) tests 25 (L) x 25

(W) x 2 (T) mm^3 specimens were prepared. Five replicates were tested for each formulation. The WA and TS values were calculated using the following equations:

$$WA(\%) = \left[\frac{W_2 - W_1}{W_1}\right] * 100 \tag{18}$$

Where W_1 is the weight dry of specimen (in grams) and W_2 is the weight wet of specimen in (grams)

$$Ts(\%) = \left[\frac{T_2 - T_1}{T_1}\right] * 100 \tag{19}$$

Where T_1 is the thickness of dry specimen (in millimeter) and T_2 is the thickness of wet specimen (in millimeter)

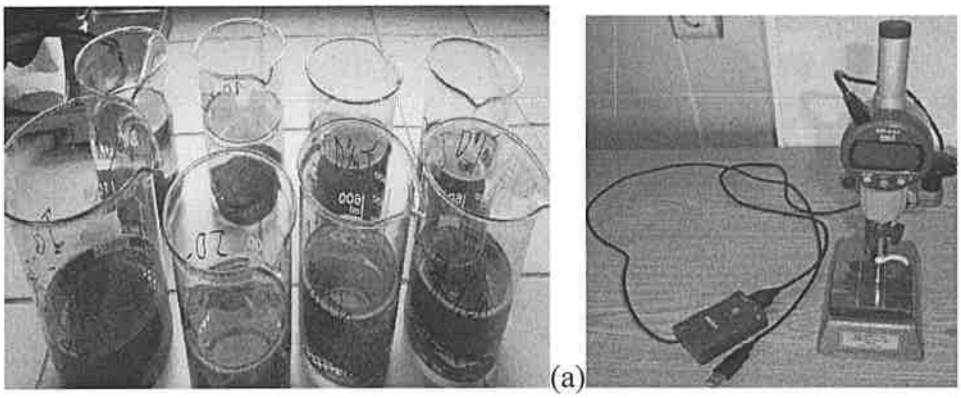

(a) (b)

Figure 13. WPC water absorption tests and thickness measurement instruments

2.2.3. Mechanical Properties of WPCs

The flexural and tensile properties of all samples were determined according to ASTM D790 and ASTM D683 standards, respectively, using a Zwick/Roell universal testing machine Z010 (Zwick Inc., Germany). The span length was determined as 16 times the thickness of the specimen (approximately 80 mm), as mentioned in the flexural properties standard. The Izod impact strengths was determined according to ASTM D256 standard using a HIT5.5P testing machine manufactured by Zwick Inc.

2.2.3.1. Tensile Properties

Tensile bar specimens with dimensions of 250 mm × 12,73mm × 2mm (thickness) were cut from the hot pressed composite panels. The tensile tests were performed in accordance with ASTM D638 using the universal testing machine Zwick/Roell Z010 at a crosshead speed of 5 mm/min. Figure 14

Elongation (strain) of the specimen was measured over a 25 mm gage length using an extensometer. Prior to the tensile test, the specimens were conditioned at 23±2°C and 50% RH for at least 40 h according to the ASTM D638. All measurements were performed at ambient conditions (23±2°C and 50% RH), and six replicates were tested for each composite formulation.

The tensile strength was calculated by dividing the maximum load in Newton by the original minimum cross sectional area of the specimen in square meters. The Young's modulus of elasticity (MOE) was calculated from the load-elongation curves by using the initial linear part. The MOE is equal to the stress increase over this linear period divided by the corresponding increase in the strain. The tensile stress was calculated as:

$$\sigma = \frac{F}{A} \tag{20}$$

Where, σ is the stress, F = Force (N), A = area. (mm^2)

Strain is express as the increase in length of specimen after stress is applied to it divided by the original length.

$$\varepsilon = \frac{L1 - Lo}{Lo} \tag{21}$$

$$E = \frac{\sigma}{\varepsilon} \tag{22}$$

Where ε = stress, E= modulus of elasticity, L1 = change in length and L_o is the original length of the specimen

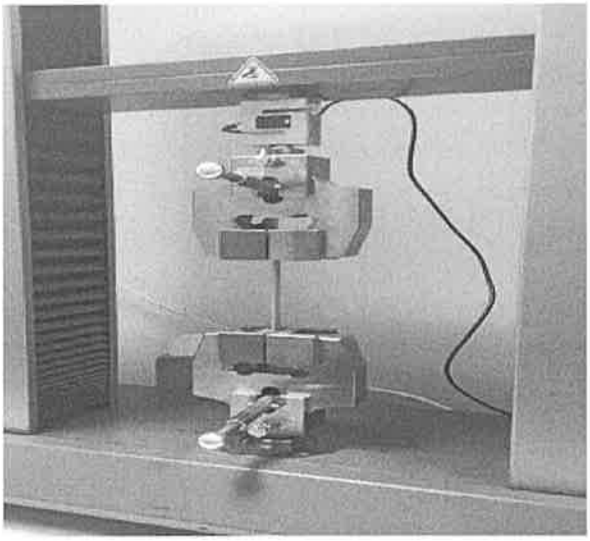


Figure 14. Experimental setup used for the tensile properties tests by using the universal testing machine Zwick/Roell Z010.

2.2.3.2. Flexural Properties

The flexural properties were measured in three-point bending tests using the universal testing machine Zwick/Roell Z010 at a crosshead speed of 2.8 mm/min in accordance with ASTM D790. The flexural test specimens were also cut from the composite panels with dimensions of 250mm × 12.73 mm × 2 mm (thickness). The bending measurements were also performed at the ambient conditions of 23±2°C and 50± 5% RH. Six replicates of each composite formulation were tested. The experimental setup used for the bending test is shown in Figure. 15. The flexural strength (MOR) is calculated for the load-deflection curve by using the following equation [24]:

$$\delta f = \frac{3PL}{2bd^2} \tag{23}$$

The flexural modulus of the elasticity (MOE) in the bending tests is calculated within the linear limit by using the following equation

$$EB = \frac{L^3 m}{4bd^3} \tag{24}$$

Where in equation (23) and (24)

δ_f = the stress in the outer layer at mid-length point of the specimens, MPa

E_B = the flexural modulus of elasticity of the specimens in bending tests, MPa

P = the load at the loading point (mid-length), N

L = the supporting span of the specimen, mm

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

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

m = the slope of the initial linear portion of the load deflection curve, N/mm

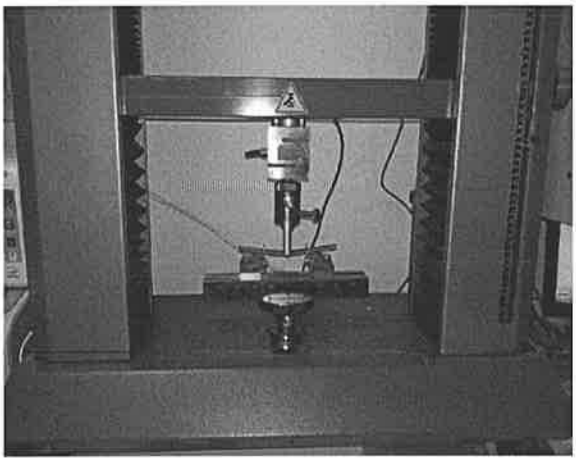


Figure 15. Experimental setup used for the flexural properties tests by

using the universal testing machine Zwick/Roell Z010.

2.2.3.3. The Izod Impact Strengths Properties

The Izod impact strengths were determined according to ASTM D256 standard using a HIT5.5P testing machine manufactured by Zwick Inc. The flexural test specimens were also cut from the composite panels with dimensions of 250mm × 12.73 mm × 2 mm (thickness). All samples were notched in the center according to the standard. Six replicate samples were tested for each group.

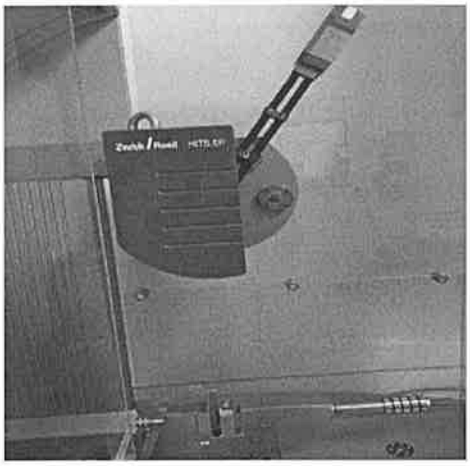


Figure 16. Experimental setup used for The Izod impact strengths properties tests by using the universal testing machine Zwick/Roell. HIT5.5P

2.2.4 Morphological Properties

First the specimens were dried at 50 ± 3°C for 48 h before SEM studies. Morphology of the fractured composites after tensile testing was observed using a scanning electron microscope (SEM) (ZEISS EVO LS10, Germany) with a field emission gun and an accelerating voltage of 5Kv Figure 17. A gold layer of a few nanometers in thickness was coated onto the fracture surfaces. The samples were scanned perpendicular to the fractured surface. SEM micrographs were taken at the magnification level of 250x.

Figure 17. Scanning electron microscopy

2.2.5 .Thermal properties of WPCs

The thermal decomposition behavior of the composites was measured with a SDT Q600 Thermo gravimetric analyzer (TA Instrument Inc., USA). Tests were done under nitrogen at a heating rate of 10°C/min over a temperature range of 30–600°C. A sample of 5–10mg was used for each run. The weight change was recorded as a function of heating temperature. Differential peak temperature (DT_p) was defined as the temperature of the maximum derivative of the weight change over time. DSC experiments were performed in a Q10 differential scanning calorimeter (TA Instrument Inc., USA). Each sample was heated and cooled at a heating rate of 10°C/min under nitrogen atmosphere. Each test sample of 5–10mg was placed in an aluminum pan and heated from 30 to 200°C and then cooled down to 30°C after keeping at 200°C for 3min. The glass transition temperature (T_g), melting temperature (T_m), melting enthalpy (ΔHm), and crystallinity (X_c) were determined from the first heating scan, while the crystallization temperature (T_c) and crystallization enthalpy (ΔHc) were obtained from the first cooling scan. T_m is defined as the maximum of the endothermic melting peak and T_g as the deflection of the baseline temperature from the first heating scan. The X_c was obtained by the following expression:

$$X_c(\%) = [\frac{\Delta Hm}{\Delta H_{m(crys)}}]X100 \tag{27}$$

where ΔHm is the enthalpy of the sample and $\Delta H_{m(crys)}$ is the enthalpy of 100% crystalline PLA taken as 93.7J/g (Raya,2003). The ΔHm, ΔHc, and X_c were converted by the mass fraction of the pure PLA in the composites.

2.2.6. Data Analyses

The mechanical and physical tests were evaluated with descriptive statistics. By using Statistical Package for the Social Sciences statistical program (SPSS Version 16, 2010).

3. RESULTS AND DISCUSSION

3.1. Physical Properties of WPCs

3.1.1. Density and Void Volume Fraction of WPCs

The average value ($\bar{x}$) and standard deviation (S) of density ,weight content of fiber (g) and void volume fraction for both treated and untreated wood flour –PLA comosites were shown inTable 3.

Table 3. Density (g/cm^3) and void volume fraction (%) of treated and untreated wood flour-PLA plastic composite

GROUP		**Archimedes density** (g/cm^3)		**Weight content of fiber (g)**		**Void volume (%)**	
No.	**CODE**	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
1	TW30M3	1.281	4.15	0.462	0.010	0.75	0.32
2	TW40M3	1.284	14.96	0.614	0.010	7.99	1.26
3	TW50M3	1.259	10.47	0.959	0.007	12.59	0.94
4	TW50M0	1.294	21.63	0.848	0.018	4.91	1.74
5	UW30M3	1.287	3.39	0.458	0.005	0.29	0.26
6	UW40M3	1.317	34.59	0.651	0.009	1.78	1.72
7	UW50M3	1.329	3.4	0.855	0.020	0.78	0.25
8	UW50M0	1.320	6.66	0.859	0.018	2.86	0.52

TW30M3, TW40M3, TW50M3, and TW50M0, = Treated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively. UW30M3, UW40M3, UW50M3, UW50M0 = Untreated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively.

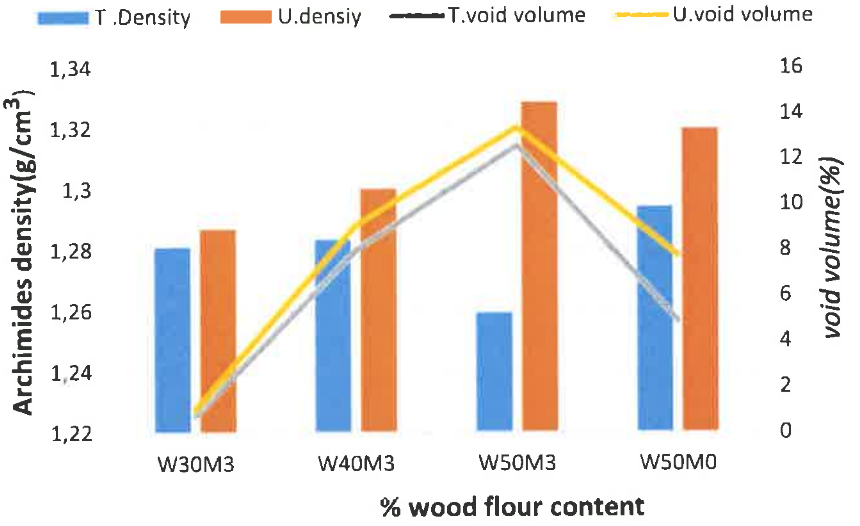


Figure 18. Density and void volume fraction of treated and untreated wood flour- PLA plastic composite

As can be seen from figure.18 that density of the composites from the treated and the untreated wood flour increased as the wood flour amount of loading increased. For example, Archimedes density of untreated wood flour contain composites in 30% to 50% of wood loading increased from 1.287g/cm^3 to 1.329 g/cm^3. Similar results were determined for treated wood flour contain composites except for 50% treated wood with MAPE. The untreated wood flour composite had higher densities compared to the treated ones of the same wood content and PLA amount of loading. For instance, wood flour -PLA composite at load levels 40%, the density for the untreated was 1.317g/cm^3 and that of the treated was 1.284g/cm^3. This indicated that there was present of high voids (12.59%) inside the 50% of chemical treated flour content composites. After the chemical treatment, bad interaction between the matrix and the fiber existed hence had resulted in void maximization in the composites. Comparing the densities of wood plastic composites with and without of MAPE, Composites containing untreated wood flour with MAPE had higher density than without MAPE. However, in case of treated wood flour-PLA composites had no significant effect on composites density. This might be due to the fact that the Tanalith E treated wood had more and high void found in side composites.

3.1.2. Dimensional Stability of WPCs

3.1.2.1. Water Absorption of WPCs

The average value ($\bar{x}$) and standard deviation (s) of water absorption tests done by three weeks immersion for both treated and untreated wood flour –PLA comosites are shown in Table 4.

Table 4. Water absorption tests (%) of treated and untreated wood flour – PLA composites

GROUP		2h		24h		48h		72h		96h		120h		144h	
No.	Group Id	$\bar{x}$	S	$\bar{x}$	S	$\bar{x}$	S	$\bar{x}$	S	$\bar{x}$	S	$\bar{x}$	S	$\bar{x}$	S
1	TW30M3	0.86	0.33	12.85	0.68	14.09	0.34	13.96	0.44	14.34	0.48	14.34	0.66	14.34	0.66
2	TW40M3	1.38	0.51	11.41	5.15	15.47	2.13	16.23	1.88	16.61	1.69	16.99	1.43	17.12	1.17
3	TW50M3	13.68	6.12	25.21	0.85	27.13	0.34	28.05	0.94	27.90	0.78	27.60	1.57	26.23	1.53
4	TW50M0	2.51	0.87	18.16	1.06	19.88	1.79	20.57	1.54	21.02	1.63	21.59	1.74	21.48	1.81
5	UW30M3	0.25	0.34	2.24	0.34	4.35	0.76	7.58	1.12	10.19	1.05	10.81	1.12	11.30	1.16
6	UW40M3	0.71	0.50	4.26	0.52	12.07	1.02	14.19	0.65	14.78	0.46	16.08	0.86	11.30	1.16
7	UW50M3	0.79	0.31	5.41	0.30	14.09	0.36	15.89	0.65	17.14	0.30	17.14	0.55	17.81	0.21
8	UW50M0	1.14	0.40	6.92	1.35	15.99	1.44	17.35	1.12	18.37	1.07	18.72	0.71	18.14	0.679

TW30M3, TW40M3, TW50M3, and TW50M0, = Treated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively. UW30M3, UW40M3, UW50M3, UW50M0 = Untreated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively.

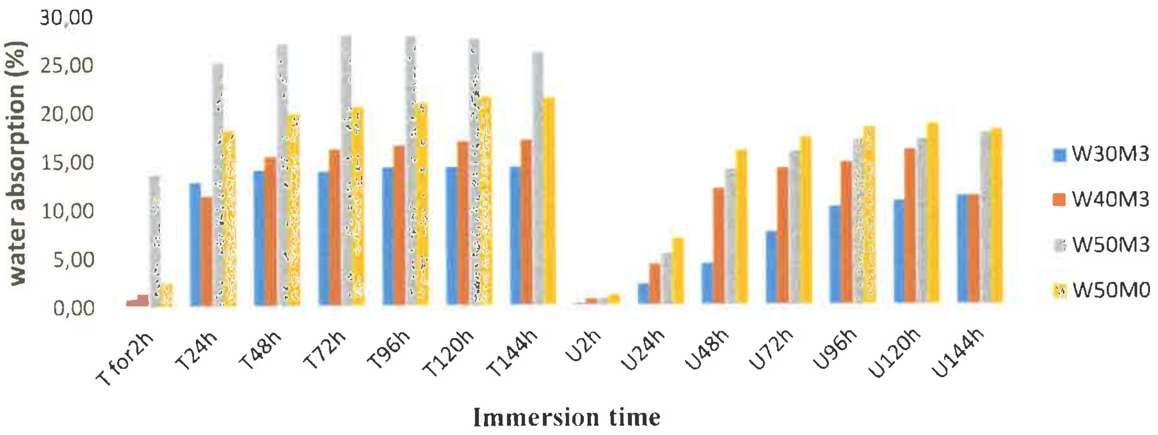


Figure 19. Water absorption (%) for both treated and untreated wood flour – PLA composite

Water absorption behaviors of the composites at room temperature against wood flour contains loading are shown in Figure 19. It is evident in the figure. 19 that water absorption (%) increased with an increase in wood content in composite and duration of immersion in water. For examples, the water absorption with 30wt% wood flour content is 0.25% after 2h immersion and 4.26% after 24h, and the corresponding values for the composites with 40% wood flour are 0.71 and 5.41%, respectively. This supports the research done by (Abdul et al. 2011c) and (Adhikary et al. 2008a).

Treated wood flour with Tanalith E content composites absorbed more water than untreated wood flour content composites (Figure 19). For instances, during 48h immersion in water the composite made from 30% treated wood flour absorbed 14.09 % water whereas the same amount of treated sawdust absorbed 4.35%. The highest water absorption occurred during the 72hours of immersion in water by 50% treated wood flour –PLA composite (28. 05%).The results showed that treated wood flour-PLA composites had absorbed more water than that of untreated wood-PLA composites. This can be attributed weak bonding of treated wood with PLA due to copper inhibition effect. Researchers reported that wood material containing copper interfered negatively bonding of wood (Kamdem et al. 2004).

The composites made of MAPE have lower water absorption compared to those made of without MAPE for the same wood content for untreated wood flour contain composites. The MAPE provided better bonding with wood flour and PLA for untreated wood flour content in in composites. However, higher water absorption in case of treated wood flour –PLA. This might be due to effects of copper treatment on the bonding of wood flour with polymer matrix. The impact of wood to plastics ratio on the water absorption can be explained by the differences in water absorption between wood and plastics. The moisture absorption in composites is mainly due to the presence of lumens, fine pores and hydrogen bonding sites in the wood fiber, the gaps and flaws at the interfaces, and the microcracks in the matrix formed during the compression moulding press process. Similar finding with (English and Falk 1996) reported that water absorption is due to individual fibers, microgaps in the interface between fibers and plastic, voids due to water vapor generation during hot melt process. These might be the reason why the water absorption increased as the wood flour contains loading increased.

3.1.2.2. Thickness Swelling of WPCs

The average value ($\bar{x}$) and standard deviation (s) of thickness swelling tests done by three weeks immersion for both treated and untreated wood flour –PLA comosites are shown in Table 5.

Table 5: Thickness swelling (%) of treated and untreated wood flour – PLA composites

GROUP		2h		24h		48h		72h		96h		120h		144h	
No.	Group ID	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
1	TW30M3	2.26	0.65	12.89	5.11	13.64	5.07	14.40	4.77	14.03	4.59	13.54	5.08	13.9	6.13
2	TW40M3	2.76	1.23	14.00	6.88	18.51	6.74	19.58	6.64	19.40	7.04	19.19	6.82	19.38	6.67
3	TW50M3	19.69	6.10	30.50	6.96	31.40	6.75	29.94	6.75	29.16	6.60	29.27	6.25	28.26	5.56
4	TW50M0	5.40	2.04	32.38	8.63	32.63	8.01	35.19	9.22	34.75	8.99	35.01	8.70	35.28	8.63
5	UW30M3	1.32	0.39	3.49	1.67	7.63	5.60	9.15	5.08	10.57	3.56	11.80	4.26	11.80	3.87
6	UW40M3	2.66	0.35	6.61	1.09	19.54	11.18	20.67	12.20	21.31	12.23	22.72	13.99	21.95	12.6
7	UW50M3	2.88	0.73	8.26	1.13	18.42	5.05	17.34	3.69	17.97	4.37	17.5	4.18	18.59	4.17
8	UW50M0	3.30	1.3	10.73	4.45	21.91	3.35	20.84	4.10	21.44	4.58	21.92	3.50	23.60	3.98

TW30M3, TW40M3, TW50M3, and TW50M0, = Treated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively. UW30M3, UW40M3, UW50M3, UW50M0 = Untreated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively.

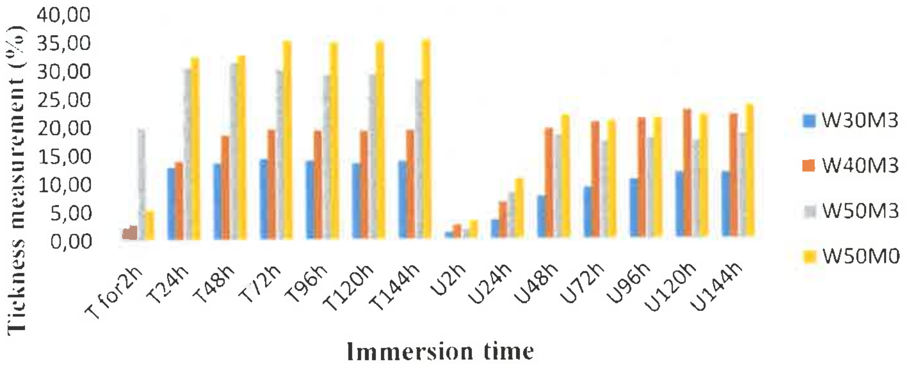


Figure 20: Thickness swelling for both treated and untreated wood flour – PLA composite

Thickness swelling rates of the composites at room temperature against wood contents

are shown in Figure 20. Like water absorption, it is evident in the figure that thickness swelling (%) increased with an increased wood content in composites. For example, the 30% treated wood flour content is 2.26% after 2h immersion and 12.89 % after 24h, and the corresponding values for the composites with 40% treated wood flour are 2.76% and 14.00%, respectively. The highest thickness swelling occurred during the 144hours immersion in water by 50% treated wood flour –PLA composite without MAPE (35. 28%).

The results obviously showed that treated wood flour-PLA composites had higher thickness swelling than that of untreated wood-PLA composites. This can be attributed weak bonding of treated wood with PLA due to copper inhibition effect. Researchers reported that wood material containing copper interfered negatively bonding of wood (Kamdem et al. 2004).

The composites with MAPE have lower thickness swelling compared to those made of without MAPE sample for the same wood content due to providing better bonding with hydrophilic (wood) and hydrophobic (plastic) materials. For examples, the 50% treated wood flour content with MAPE for 24-hour immersion is 30.50% and for 24hours immersion for treated wood flour without MAPE is 32.63%, and the corresponding values for the composites with 50% untreated wood flour are 8.26% and 10.73%, respectively. Dányádi et al. (2010) reported that wood can absorb large amounts of moisture; even when wood embedded into the polymer absorbs a considerable amount of water, which may change the dimensions of large products and cause problems in certain applications

3.2. Mechanical Properties of WPCs

3.2.1. Tensile Strength and Modulus of WPCs

3.2.1.1. Tensile Modulus of WPCs

The average value ($\bar{x}$) and standard deviation (s) of tensile strength and modulus made of both treated and untreated wood flour –PLA composites are shown in Table 6.

Table 6. Tensile strength and modulus of treated and untreated wood flour-PLA plastic composite

GROUP		Tensile modulus (MPa)		Tensile strength(MPa)	
No.	Group ID	$\bar{x}$	S	$\bar{x}$	S
1	TW30M3	1248.90	116.4	11.29	1.6
2	TW40M3	1414.17	138.7	14.01	2.4
3	TW50M3	912.23	221.4	5.09	1.8
4	TW50M0	1114.18	153.4	5.87	1.5
5	UW30M3	1489.44	117.1	26.32	1.17
6	UW40M3	1568.32	99.01	19.01	3.1
7	UW50M3	1874.25	74.9	25.03	2.7
8	UW50M0	1714.41	36.1	16.70	0.4

TW30M3, TW40M3, TW50M3, and TW50M0, – Treated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively. UW30M3, UW40M3, UW50M3, UW50M0 = Untreated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively.

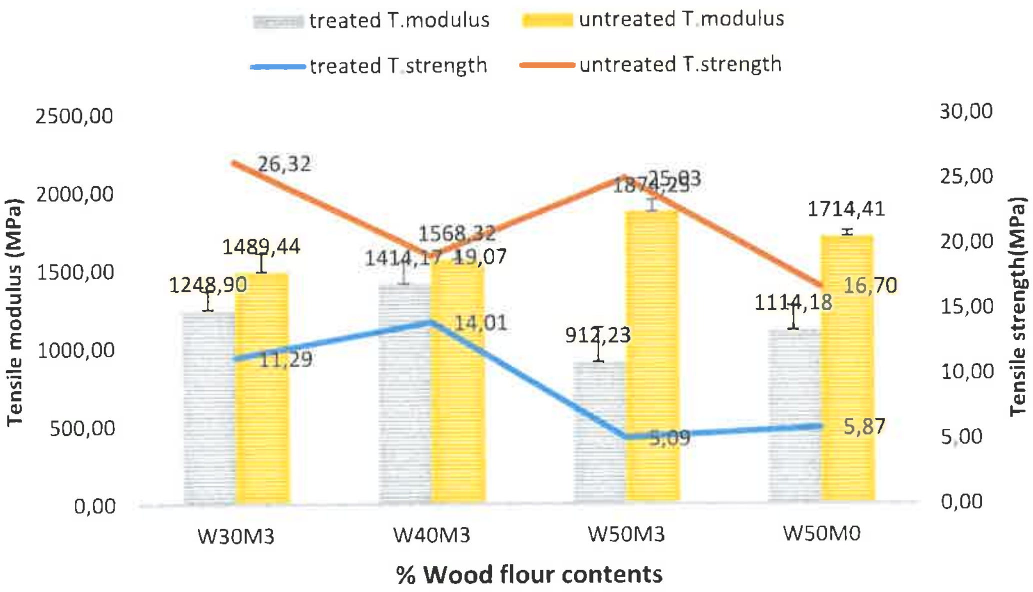


Figure 21. Tensile strength and modulus of treated and untreated wood flour – PLA composite

Results showed that the tensile modulus increases with increasing loading of wood flour except for treated wood flour containing 50% wood. As seen in the figure 21, the tensile modulus increased from 1489.44MPa to1874.25 MPa when the amount loading of untreated wood flour increased from 30% to 50%. Similar trends were observed for treated wood flour increases from 30%to 40 % loading. However, tensile modulus at 50% loading of treated wood was less than others. This might be due to chemically treated wood flour –PLA composites interfered negatively bonding of wood and had more and high void volume.

Comparing the treated and the untreated wood flour- PLA composites, it was observed from figure.21 that the untreated wood flour -PLA composites have higher tensile modulus than that of the treated sawdust composites. For example, at 40% loading, the tensile modulus of the untreated wood flour –PLA was 1568.32MPa and that of the treated formulation was 1414.17MPa. All the other formulations gave high values for the untreated compared to the treated. This might be as explained above due to the copper partly inhibit wood bonding and causes presence of high content of voids in the chemical treated wood flour compared to that of untreated. High voids in the chemically treated wood was also observed by SEM studies

The addition of wood flour into composites increased the modulus of composites that results from the inclusion of rigid filler particles into the thermoplastics except for the 50% treated wood flour content composites. It is evident from the Figure (21) that increase in both untreated and treated wood flour content in the matrix results in an increase in the modulus of the composites. This finding similar to the research done by Afrifah (2010).

3.2.1.2. Tensile Strength

Figure 21, shows the tensile strength of the composite formulated from the untreated and chemical treated with Tanalith E with PLA. The tensile strength has highest value at 30% of untreated wood flour loading was 26,32 MPa and lowest at 50% loading (16.70 MPa), and treated wood flour achieved highest value at 40% loading (13,3MPa) and lowest at 50% (4,8MPa) loading of the wood flour. As the amount of loading wood flour increased, the weak interfacial area between the filler and the matrix increased, which consequently decreased the tensile strength Ashori & Nourbakhsh (2009a) also observed this. An increase in the wood content increases the micro spaces between the filler and the matrix, which weaken the filler–matrix interfacial adhesion. As a result, the values of tensile strength show a decreasing trend with increasing filler content in the composite.

Comparing the tensile strength of the untreated wood flour and the treated wood flour composites, it can be seen that the tensile strength of all the untreated wood flour-PLA composites were higher than that of the treated filler formulations. For example, at 30% wood flour loading, from figure (21), the tensile strength of the untreated wood flour was 26.32MPa while that of the treated one was 11.29MPa.

The low density of treated wood four composite might also be a factor for the low tensile strength. Treated wood flour has a lower density compared to untreated and this might result in high void content in the treated wood flour than the untreated. High voids content reduced the tensile strength of the composite since voids do not transmit stresses and can cause stress concentration. The presence of void content is a significant factor affecting the performance of WPCs and the expected to failure (Gacitua & Wolcott 2009).

3.2.2. Flexural Strength and Modulus

3.2.2.1. Flexural Modulus

The average value ($\bar{x}$) and standard deviation (s) of flexural strength and modulus made of both treated and untreated wood flour –PLA comosites were shown in Table 7.

Table 7. flexure strength and modulus of treated and untreated wood flour-PLA plastic composite

GROUP		Flexural modulus (MPa)		Flexural strength (MPa)	
No.	Group ID	$\bar{x}$	S	$\bar{x}$	S
1	TW30M3	4228.70	208.77	21.97	1.64
2	TW40M3	4440.01	238.01	28.66	4.96
3	TW50M3	3466.32	322.45	13.12	1.95
4	TW50M0	4374.09	484.81	19.52	4.88
5	UW30M3	3946.81	233.51	52.31	2.07
6	UW40M3	4799.11	130.65	36.50	4.60
7	UW50M3	5426.89	237.65	48.17	6.31
8	UW50M0	5338.20	293.96	37.00	2.58

TW30M3, TW40M3, TW50M3, and TW50M0, = Treated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively. UW30M3, UW40M3, UW50M3, UW50M0 = Untreated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively

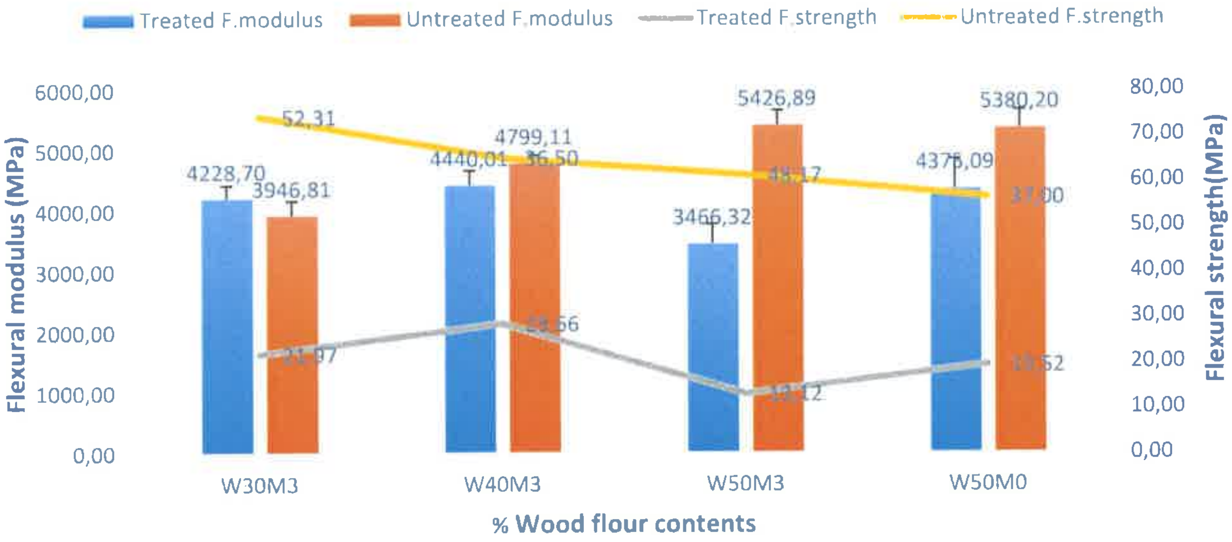


Figure 22: Flexural Modulus and Strength of both treated and untreated wood flour – PLA composite.

The flexural modulus increased with increased loading of wood flour except for 50% of treated wood loading. As seen in the figure.22, the flexural modulus increased from 3946.81MPa to 5426.89MPa by 37.5% when the % loading of untreated wood flour increased from 30% to 50%. And the same is true for treated wood flour increases from 30% to 40% loading, flexure modulus increases from 4228.70MPa to 4440.01MPa by 4.99%. But flexure modulus of treated wood flour at 50% loading is less than others. The reason may be compatibility issue of poor interphase adhesion caused by copper treatment between wood and plastic matrix. Comparing the treated and the untreated Wood flour-PLA composites, it was observed that the untreated wood flour -PLA composites have higher flexure modulus than that of the untreated wood flour contain composites. For example, at 40% loading, the flexure modulus of the untreated wood flour –PLA was 4798.5MPa and that of the treated formulation was 4439.5MPa. increased by 8%. All the other formulations gave high values for the untreated compared to the treated ones. This might be due to the presence of high content of voids in the chemical treated wood flour compared to that of untreated ones.

3.2.2.2. Flexural Strength

Figure 22 shows the tensile strength of the composite made of from the untreated and chemical treated with Tanalith E with PLA. Unlike the flexure modulus, flexure strength had highest value at 30% of untreated wood flour loading was 52.31MPa and lowest at 40% loading (MPa), and treated wood flour achieved highest value at 40% loading (26.60MPa) and lowest at 50% (13,2MPa) loading of the wood flour.

The highest values of flexure strength for untreated wood flour and treated were achieved with wood content of 30 % and 40% respectively. A similar finding was also reported by Ndiaye et al. (2013), Bhaskar et al. (2012) and Yuan et al. (2008). The decrease in flexural and tensile strength was probably due to the limited bonding between the cellulose fibers and the PLA matrix. On the other hand, Huang and Zhang (2009) also suggested that when the fiber content exceeded 40 %, WPCs became more susceptible to the formation of fiber agglomeration that decrease the mechanical strength of the composites.

3.2.3. Impact Strength

The average value ($\bar{x}$) and standard deviation (s) of impact made of both treated and untreated wood flour –PLA comosites were shown in Table.8

Table 8. Impact Strength of treated and untreated wood flour-PLA plastic composite

GROUP		Impact strength	
No.	Group ID	$\bar{x}$	S
1	TW30M3%	1.33	0.20
2	TW40M3%	1.93	0.63
3	TW50M3%	1.03	0.17
4	TW50M0%	1.42	0.41
5	UW30M3%	2.67	0.27
6	UW40M3%,	2.13	0.30
7	UW50M3%,	2.42	0.41
8	UW40M0%,	2.28	0.50

TW30M3, TW40M3, TW50M3, and TW50M0, = Treated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively. UW30M3, UW40M3, UW50M3, UW50M0 = Untreated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively

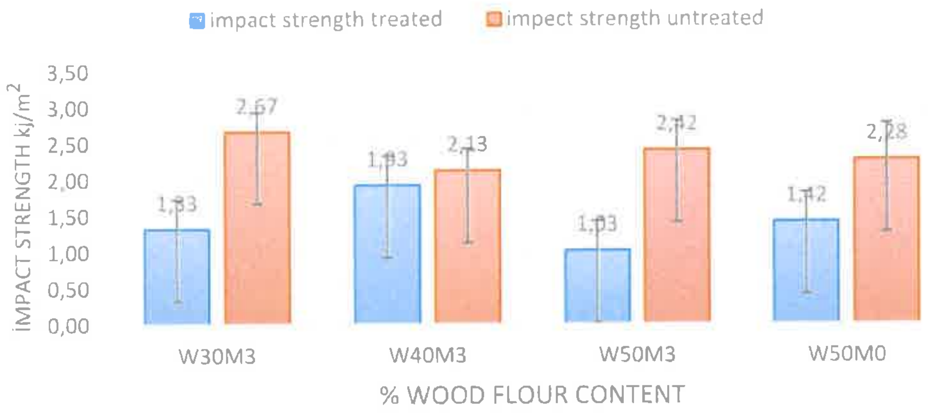


Figure 23. Impact strength of treated and untreated wood flour – PLA composites

The impact strength has highest value at 40% of treated wood flour loading was 1.93 k.j/m^2 and lowest at 50% loading (1.03 kj/m^2), and untreated wood flour achieved highest value at 30% loading (2.67 k.j/m^2) and lowest at 40%(2.13 k.j/m^2) loading of the wood flour. Comparing the treated and the untreated WF formulations, it was observed that the treated wood flour -PLA composites have lower impact strength than that of the untreated sawdust composites. For example, at 30% loading, the impact strength of the treated wood flour – PLA was 1.33 k.j/m^2 and that of the untreated formulation was 2.67 k.j/m^2 increased by 50.18% . All the other formulations gave high values for the untreated compared to the treated. This mean all chemically treated wood flour-PLA composite reduced by 10.36% to 134.95%. The great variation at 50 % of wood flour content composites . This might be due to the presence of high content of voids in the chemical treated wood flour, caused by poor interphase adhesion compared to that of untreated.

3.3. Morphological Properties

The fracture surfaces of the wood plastic composites used in tensile tests were observed by SEM. Figure.24 shows the morphology of a fracture surface of composites with wood flour contents (30%,40%,50%), PLA (70%,60%,50%), and without and with 3% of MAPE at 250x magnification scales.

Figure .24 confirms that in chemical treated wood flour contain composites more and larger voids appear when the wood content loading increases to 50%. Furthermore, chemically modified wood flour with Tanalith E had less the interfacial adhesion between the WF and the PLA matrix than untreated with Tanalith E.

The wood plastic composites without MAPE showed that a poor compatibility between the wood flour and PLA except for 50% of treated wood flour contents of wood-PLA composite. The surface of wood flour particle was believed to be pull off from the PLA matrix, and micro-size voids were formed during tensile testing.

The use of MAPE significantly improved the compatibility, leading to increases wood flour –PLA matrix bounding. The WPCs contain 70% PLA/30 % wood four with MAPE, when compare to other exhibits good interfacial adhesion among the other group as shown in Figure 24(a, b)

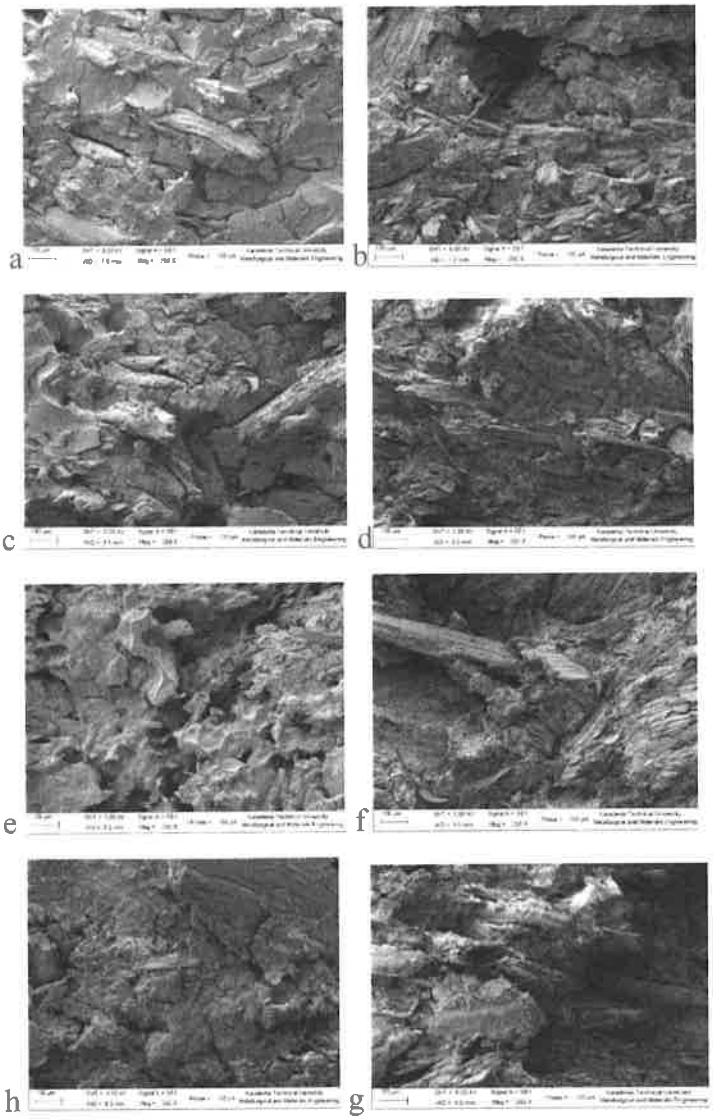


Figure 24: SEM images of wood flour-PLA composite with and without MAPE % at 250x

(a) TW30M3, (c) TW40M3, (e) TW50M3, and (h) TW50M0 and (b) UW30M3, (d) UW40M3, (f) UW50M3, (h) UW50M0

3.4. Thermal Properties of WPCs

3.4.1. Thermo Gravimetrical Analysis (TGA)

The Weight loss (%) and residual ratio (%) for both treated and untreated wood flour –PLA composites by Thermograph analysis are shown in Table 9.

Table 9.Weight loss percentage at different temperature and residual ratio at 785°C for both treated and untreated wood flour-PLA plastic composites

Group ID	Weight loss(%)							At 785°C
	5%	10%	20%	40%	60%	80%	85%	Residue(%)
TW30M3	288°C	309°C	32°C	339°C	350°C	374°C	437°C	8.20
TW40M3	278°C	305°C	323°C	339°C	352°C	385°C	451°C	9.18
TW50M3	245°C	280°C	304°C	330°C	351°C	429°C	482°C	12.12
TW50M0	264°C	295°C	315°C	335°C	351°C	383°C	453°C	10.62
UW30M3	303°C	320°C	331°C	341°C	351°C	364°C	381°C	6.47
UW40M3	289°C	315°C	32°C	343°C	354°C	379°C	440°C	9.11
UW50M3	279°C	308°C	327°C	342°C	355°C	392°C	458°C	10.29
UW50M0	277°C	308°C	326°C	342°C	354°C	379°C	436°C	9.92

TW30M3, TW40M3, TW50M3, and TW50M0, = Treated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively. UW30M3, UW40M3, UW50M3, UW50M0 = Untreated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively

Thermo gravimetric analysis involves measurement of the weight loss of composites as a function of time and temperature. In Figure 25, showed that the percentage of weight loss and residual ratio increased with increases in both the wood flour content and the temperature. Higher values of weight loss percentage indicate lower thermal stability of the composites (Syed,2011). WPCs, containing treated wood flour showed higher weight losses at low temperature(°C) than untreated wood flour –PLA composites. For example, Wood flour-PLA composites with 30% of both treated and untreated wood flour contents were loss 5% weight at 288°C and 303°C respectively. Similar tends for all other wood flour-PLA composites.

The highest weight loss and residual ratio were in wood flour-PLA composite containing 50% of treated wood flour with Tanalith E and 3% of MAPE (TW50M3%).This result was probably due to more degradation of wood flour than PLA occurring, and the poor interfacial adhesion between the wood flour and the polymer matrix(PLA). Moreover, Tanalith E was one of copper based compounds and it reduces the bonding between wood flour and polymer matrix.

The lowest weight loss and residual ratio were in wood flour-PLA composite containing 30% of untreated wood flour with and 3% of MAPE (UW30M3%). An increase in interfacial adhesion between the fibres and the matrix increased the thermal stability and decreased the percentage of weight loss. This result indicates a significant effect on the thermal stability of the composites after incorporating wood four content. (Mohanty,2006)

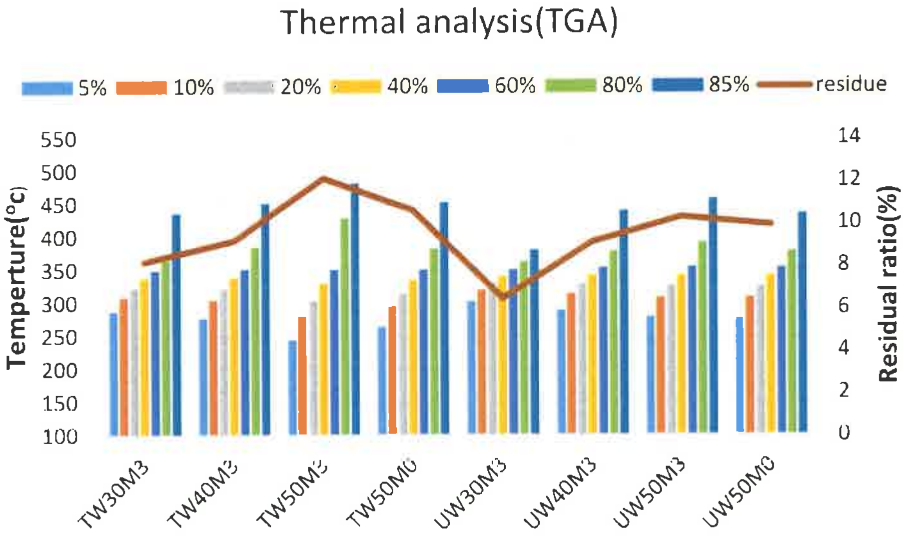


Figure 25: Weight loss (%) of wood flour-PLA for both treated and untreated wood flour at different temperatures

The derivative thermo gravimetric (DTG) curves of wood flour-PLA composites containing 30%, 40 %, and 50 % of wood flour is shown in Fig.26. The thermal stability was markedly reduced with increasing wood flour content. Fig.26 shows that the decomposition profiles of the wood flour - PLA composites are characterized by two peaks. The first one, which corresponded to the degradation of wood components (e.g., hemicelluloses, cellulose, lignin), for treated wood flour –PLA at 346, 350, and 345°C and untreated wood flour-PLA composites at 348,350, and 353 °C for the composites with 30 %, 40 %, and 50 % of wood content, respectively. The cellulose, hemicelluloses component of the natural filler in the composites degraded in the temperature range 274–459°C. (Enayati et al. 2009; Clemons 2002).) The next degradation peak was due to the degradation of the polymer matrix (PLA) in the composites at 468,469, and 470°C for both treated and untreated wood four containing 30 %, 40 %, and 50 % of content, respectively.

For the treated wood –PLA composites, it was verified that the maximum degradation rate was at lower temperature than untreated wood flour content composites. From all over, the lowest thermal stability at treated wood flour –PLA composite with 50% wood content with MAPE. This is indicated that the present of the high amount of wood flour treated with Tanalith E lowered the thermal stability of the composites. Moreover, the copper based (Tanalith E) treated wood flour lower bonding between wood flour and matrix. And also the addition of coupling agent lowered the degradation temperature of the composites. It was concluded that maleic anhydride, in the presence of moisture from wood, could convert to maleic acid which stimulated to degradation of the composites (Maged, 2003). However, the highest thermal stability for wood –PLA composite was for 30% content of untreated wood flour in composites,

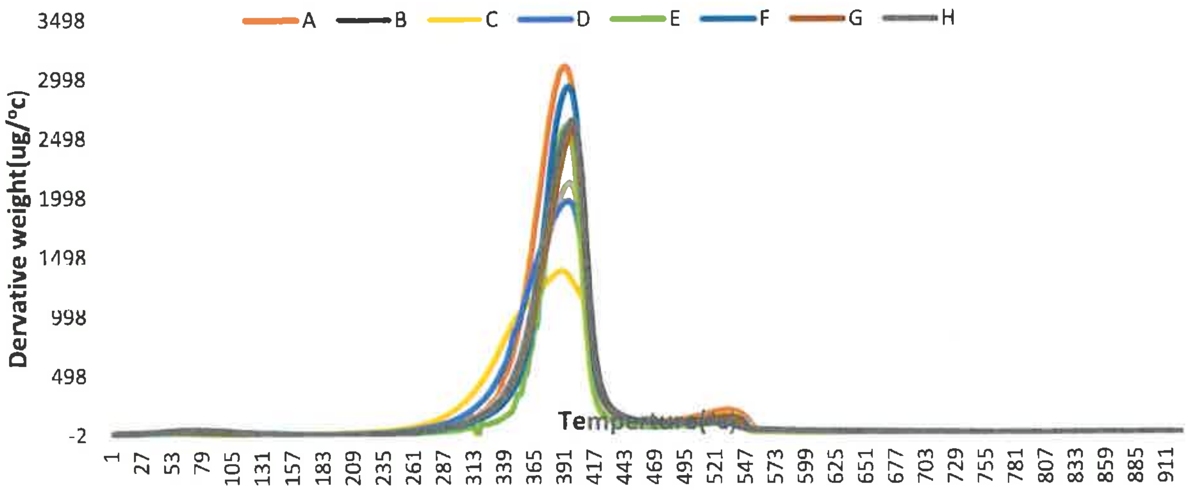


Figure 26. DTG curves of Wood flour -PLA composites for both treated and untreated wood flour

The Letter A-H represent legend on graph 26 as follow. A, B, C, and D=Treated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively. And E, F, G, and H = Untreated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively.

3.4.2. Differential Thermal Analysis (DTA)

Differential Thermal Analysis (DTA) is a technique to measure the enthalpy of an endothermal or exothermal change as a result of temperature difference of a material. Figure 27 shows thermal analysis and melting enthalpy of composites formulations indicate that the untreated wood flour-PLA composites reveal higher melting enthalpy compared with the all treated wood flour containing composites with the same contents of materials. The melting enthalpy (ΔH_m) decreased with increasing the wood flour content in all composites except for 50% treated wood flour with MAPE composite which increased. This is due to the poor bonding between the treated wood flour with Tanalith E and PLA.

The melting temperature is increased with increasing the wood content in all composite formulations except for 50% treated wood flour with MAPE composite which decreased. This is due to the poor bonding between the treated wood flour with Tanalith E and PLA. The addition of coupling agent (MAPE) had significant effect on melting temperature which lower. For instance, wood flour-PLA composites with 50% of untreated wood flour with MAPE and without MAPE were melt at 349.18°C and 350.72°C, respectively. Similar trends for untreated wood flour –PLA composites. (Maged,2003)

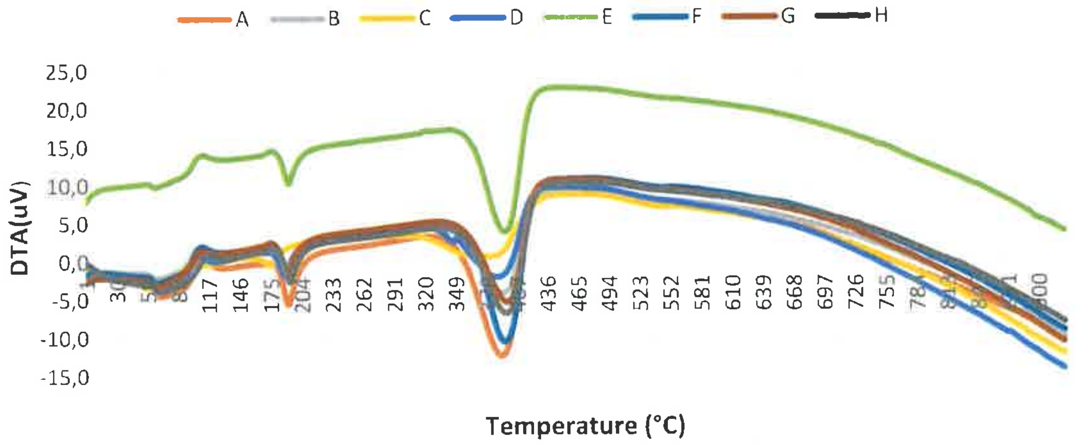


Figure 27. DTA curves of Wood flour -PLA composites for both treated and untreated wood flour containing 30, 40, and 50 % of wood contents.

The letter A-H represent legend on graph 26 as follow. A, B, C, and D=Treated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively. And E, F, G, and H = Untreated wood flour contents with 30%,40%,50% with 3% of MAPE and 50% without MAPE respectively.

4. CONCLUSION AND RECCOMENDATION

4.1. Conclusion

In this study, properties of wood plastic composites made of chemically treated wood flour with Tanalith E and poly lactic acid was determined. The WPCs were manufactured from pine species (*Pinus sylestris* L.) wood flour as filler, Poly lactic acid (PLA) as the matrix and Maleated polyethylene (MAPE). The woods were used chemically treated with copper based preservative (Tanalith E) and untreated wood flour also used as control.

The conclusions made from the investigations were as follows;

The general trend was that density increases as wood flour content increased except for 50% treated wood flour content which lowest from all over group the group. The untreated wood flour-PLA composite had the highest density of 1.329g/cm^3 at 50% wood flour content. Treated wood flour –PLA composite had highest void volume content of 12.59% at 50% wood flour content while untreated wood flour –PLA composite had lowest void volume of 0.29% at 30% wood flour content.

The amount of water absorbed depends on the wood flour content of the composite. In all the wood flour –PLA composites, the amount of water absorbed increased as the wood flour content increased. Comparing all the formulations, the WPCs with 30% untreated wood flour content absorbed the least amount of water of 0.25% while 50% treated absorbed the highest amount of water of 28.05%.

Thickness swelling properties of wood flour–PLA composite was improved with addition of 3% MAPE.

The wood flour-PLA composite with MAPE lower thickness swelling than without MAPE. Tensile, flexural and impact tests indicated that various wood flour loadings affect the mechanical properties of wood flour-PLA composites. The tensile modulus increased from 1489.44MPa to 1874 .5MPa when the amount of loading of untreated wood flour increased from 30% to 50%. And similar trends for treated wood flour increased as wood flour loading increased except 50% treated wood flour content which the lowest among the group. Among all the composite formulations, the untreated wood flour- PLA composite gave the highest tensile modulus of 1874.5 MPa at 50 % wood flour content. However, the tensile strength had highest value at 30% wood flour content. The flexural modulus and strength follow a similar trend as the tensile properties. The flexure modulus increased from 3946.81MPa to 5426.89MPa for untreated wood flour content and also increased for treated wood flour increased as wood flour loading increased 30% to 40% from 4228.70MPa to 4440.01MPa while decreased to 3465.6MPa at 50% treated wood flour content. The highest flexural modulus was 5426.89 MPa at 50 % wood flour content. However, the highest flexure strength was 52.31 MPA at 30% wood flour content. The highest impact strength was 2.67 kj/m^2 at 30% untreated wood flour content composite. However, the lowest impact strength was 1.03 kj/m^2 at 50% treated wood flour content in composite. The Tanalith E have an adverse effect on the interfacial adhesion between the wood flour and the PLA matrix. SEM images confirm that the Tanalith E treated wood flour in the WPCs cause to high and more voids that weaken the mechanical properties.

The TGA and DTG data showed that the decomposition of the composites occurred at two peaks, corresponding to the temperatures at which the wood flour and PLA degraded, and thermal stability was observed to decrease with a higher proportion of wood flour content in the composites. The percentage of weight loss and residual ratio increased with increases in both the wood flour content and the temperature. The highest weight and residual ratio at 50% treated wood flour content WPCs. Higher values of weight loss percentage indicate lower thermal stability of the composites. The result observed by Differential thermal analysis (DTA) show that the melting temperature is increased with increased the wood content in all composite formulations except for 50% treated wood flour with MAPE composite which decreased. This is due to the poor bonding between the treated wood flour with Tanalith E and PLA. The addition of coupling agent (MAPE) had significant effect on melting temperature which lower the melting temperature of wood flour composite when compared to uncoupled with MAPE composites.

4.2. Recommendation

Future work on chemical modified wood flour-PLA composites should focus on the following points in order to further improve the composite properties.

- The appropriate modification of wood flour with chemical prior to compounding with PLA should be investigated. Alkaline based Chemical, such as NaOH can modify the surface properties of wood flour so that better interfacial adhesion with the PLA matrix can be expected.

- Other types of wood flour modification should be considered to improve the better composite properties

- Coupling agent, such as maleic anhydride grafted poly lactic acid (MAPLA) better interfacial adhesion with the PLA matrix can be expected. MAPLA should also improve wood flour dispersion within the PLA matrix

5. REFERENCES

Abdul, M., Idrus., M., Hamdan, S., Rahman, and Muhammad., R., 2011b. Treated Tropical Wood Sawdust-Polypropylene Polymer Composite: the mechanical and morphological study. Journal of biomaterial and Nano biotechnology .435-444

Adhikari, R., Bhandari, L., Le, H., Henning, S., Radusch. H., Michler,H., Garda, M. and Saiter,,M.,2012.Thermal,mechanical and morphological behavior of poly(propylene)/wood flour composites. Micromole Symp.315,1, 24-29.

Adhikary, B., Pang, S. and Staiger, P.2008a. Dimensional stability and mechanical behaviour of wood–plastic composites based on recycled and virgin high-density polyethylene (HDPE). Composites Part B: Engineering, 39,5, 807–815.

Adhikary, B., Pang,S. and Staiger, P. 2008b. Long-term moisture absorption and thickness swelling behaviour of recycled thermoplastics reinforced with Pinus radiate sawdust. Chem Eng J.142,2, 190-198.

Adhikary, B., Rizvi, M., Park, B., Islam, R. 2010. Effects of Lubricant Content on Extrusion Processing and Mechanical Properties of Wood Flour-High Density Polyethylene Composites. Journal of Thermoplastic Composite Materials, 24,2, 155–171.

Adhikary,B., Pang, S.and Staiger, P.2008c. Dimensional stability and mechanical behaviour of wood–plastic composites based on recycled and virgin high-density polyethylene (HDPE). Compos Part B - Eng.39,5, 807-815.

American Wood Preservers' Association (AWPA). 2006. "Standard P5-04: Standard for waterborne preservatives." AWPA Book of Standards (Selma, Alabama): 203-208.

American Wood Preservers Institute (AWPI). (1997). The 1996 wood preserving industry production statistical report: Available from American Wood Preservers Institute (Fairfax, VA): 12,22031-4312.

Archer, K., Jin,L., Preston,F., Richardson, F., Thies, D.and Zahora, A. 1992. ACQ: Proposal to the American Wood Preserver's Association Treatment Committee to include ammoniacal copper quat, ADCQ type B, in AWPA standards under the jurisdiction of the Treatment Committee. Charlotte, NC, Chemical Specialties, Inc.

Ashori, A and Nourbakhsh, A. 2009. Characteristics of wood – fiber plastic composites made of recycled materials. Waste Management, 29,4, 1291–1295.

Ashori, A. 2008. Wood – plastic composites as promising green-composites for automotive industries, Bio resource Technology, 99, 4661–4667

Ashori, A., Kiani, H. and Mozaffari,A. (2011). Mechanical properties of reinforced polyvinyl chloride composites: Effect of filler form and content. Journal of Applications of Polymer Science, 120,3, 1788-1793.

ASTM D256,2010. Standard Test Method for Determining the Izod Impact Resistance of Notched Specimens for Plastics, American Society of for Testing and materials West Conshohocken,USA, 20 p.

ASTM D570,2010. Standard Test Method for Water Absorption of Plastics. American Society of for Testing and materials West Conshohocken,USA, 15 p.

ASTM D638,2010. Standard Test Method for Tensile Properties of Plastics. American Society of for Testing and materials West Conshohocken,USA, 17 p.

ASTM D790. Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials. American Society of for Testing and materials West Conshohocken,USA, 17 p.

ASTM D792. Standard Test Method for density and specific gravity of Plastics by displacement. American Society of for Testing and materials West Conshohocken,USA, 6 p.

Ayrilmis, N., Jarusombuti, S., Fueangvivat,V.and Bauchongkol, P. 2011.Effect of thermal-treatment of wood fibres on properties of flat-pressed wood plastic composites. Polym Degrad Stab. 96,5,818-822.

Benninga, H. 1990. A History of Lactic Acid Making, Kluwer Academic Publishing, Boston.

Beyler, C. L.; Hirschler, M. 2002. Thermal Decomposition of Polymers. In SFPE Handbook of Fire Protection Engineering, 3rd ed; DiNenno, P. J., Ed; National Fire Protection Association: Quincy, MA, 2002; Section 1, Chapter 7, 110-131.

Bhaskar, J., Haq.S. and Yadaw.S. 2012.Evaluation and testing of mechanical properties of wood plastic composite. Journal of Thermoplastic Composite Materials. 25(4), .391-401.

Bledzki, K., Faruk,O.and Huque, M. 2002.Physico-mechanical studies of wood fiber reinforced composites. *Polymer Plastic Technology Engineering*. 41 ,435-451.

Bodirlau, R., Teaca, A. and Spiridon, I. 2009. Preparation and Charcterization of Composite Comprising Modified Hardwood and Wood Polymers/Poly (Vinly Chlorides). Journal of Bio Resources Composites, 4,1285,1285–1304.

Bouafif, H., Koubaa, A., Perré, P. and Cloutier, A. 2009.Effects of fiber characteristics on the physical and mechanical properties of wood plastic composites. Composite Part A-Application of Science. 40 ,121975-1981.

Bourmaud, A and Baley,C. 2007.Investigations on the recycling of hemp and sisal fibre reinforced polypropylene composites. Polymer Degradation Stability .92,6 1034-1045.

Brandrup, J., Immergut, E. H. and Grulke, E. A. 1999. Polymer Handbook, John Wiley & Sons, INC., New York.

Braunegg, G., Bona, R., Schellauf, F., Wallner, E, 2004.Solid Waste Management and Plastic Recycling in Austria and Europe. Polymer-Plastics Technology and Engineering, 43,6, 1755–1767.

Brooks, M. 1996. Evaluating the environmental risks associated with the use of chromated copper arsenate-treated wood products in aquatic environments. Estuaries Vol. 19,2, 296-305.

Butylina, S., Martikka, O. and Kärki,T. (2011).Properties of wood fibre polypropylene composites: Effect of wood fibre source. Application of Composite Materials, 18,2,101-111.

Callister, W.,2005. Fundamentals of Materials Science and Engineering: An Integrated Approach. John Wiley & Sons, Hoboken, NJ, US.

Catto, L., Stefani, V., Ribeiro,V and Santana, R. ,2014. Influence of Coupling Agent in Compatibility of Post-consumer HDPE in Thermoplastic Composites Reinforced with Eucalyptus Fiber. Materials Research. 1-7

Caufield, F., Clemons, C. and Rowell, M.,2007. Wood Thermoplastic Composite. In Wood Handbook. 141–159.

Clemons, C. ,2002. Wood–plastic composites in the United States: the interfacing of two industries. Forest Product Journal .52,10–18

Clemons, C. ,2008. Raw materials for wood-polymer composites. In: Oksman Niska K and Sain M (Eds.). Wood-Polymer Composites. Cambridge, CRC Press.

Cooper.A., Alexander,D. and Ung. T. (1993). "What is chemical fixation?" Chromium-Containing Waterborne Wood Preservatives: Fixation and Environmental Issues. Forest Products Society (Madison, WI) .7-13

Cui, Yihua., Lee, Stephen., Noruziaan, Bahman., Cheung, Moe.,Tao, Jie., 2008. Fabrication and interfacial modification of wood / recycled plastic composite materials. Composites Part A: Applied Science and Manufacturing, 39, 655– 661.

Dahlgren, E. (1972). The course of fixation of Cu-Cr-As wood preservatives. Rec. Ann. Brit. Wood Preservers' Assoc. 109-128

Dányádi, L, Móczó, J, and Pukánszky, B. 2010. Effect of various surface modifications of wood flour on the properties of PP/wood composites. Composite Part A-Application Science .412, 199-206.

Drumright, E., Gruber, R. and Henton, E. ,2000. Polylactic acid technology, Advanced Materials (Weinheim, Germany), 12, 1841-1846.

Dubey, B., Townsend, T. and Bitton, G. ,2005. Comparison of temporal changes in metal leaching and aquatic toxicity from wood treated with CCA and alternative preservatives." International Research Group on Wood Protection (Stockholm, Sweden). Doc. No. IRG/WP 05-50236,15

Eaton, A. and Hale, M. ,1993. Wood: Decay, Pests and Prevention. London, New York: Chapman & Hall.

Enayati. AA, Hosseinaei O, Wang S, Mirshokraie SA, Tajvidi M ,2009. Thermal Properties of wood–plastic composites prepared from hemicellulose-extracted wood flour. Iranian. Journal Polymer Science Technology. 3,171–181

English, W. and Falk, H. ,1996. Factors that Affect the Application of Wood Fiber Plastic Composites. Wood Fiber-Plastic Composites, 7293, 189-194.

Espert,A., Vilaplana, F.and Karlsson, S. ,2004 .Comparison of water absorption in natural cellulosic fibres from wood and one-year crops in polypropylene composites and its influence on their mechanical properties . Composite Part A-Application Science 35,11, 1267-1276.

Farsi, M.,2000. Thermoplastic Matrix Reinforced with Natural Fibers: A Study on Interfacial Behavior. In Some Critical Issues for Injection Molding. 225–247.

Faruk., O, Bledzki., K, and Nicolais L.,2012. Wood plastic composite: Present and future. Wiley Encyclopedia of Composites, 1-20.

Galeski, A. ,2003. Strength and toughness of crystalline polymer systems. Journal of Polymer Science.28,12, 1643-1699.

Gallagher, L.W., 2006. The effect of Utilizing Micrometer Sized Wood Fiber Wood Plastic Composites. University of Idaho, pp. 1-57

George, J., Sreekala, M.S. and Thomas, S., 2001. A Review on Interface Modification and Characterization of Natural Fiber Reinforced Plastic Composites. Polymer Engineering and Science, 41,9, 1471–1484.

Ghasemi, I. & Farsi, M., 2010a. Interfacial Behaviour of Wood Plastic Composite: Effect of Chemical Treatment on Wood Fibres. Iranian Polymer Journal, 19,10, 811–818.

Godavarti, S. ,2005. Thermoplastic wood fiber composites. In: Mohanty A, Misra M, and Drzal L (Eds.). Natural Fibers, Biopolymers, and Bio composites. CRC Press, FL, US, 348-386.

Gonçalves, N.,Teixeira, P., Ferrás,L., Afonso, A., Nóbrega, J. and Carneiro, O. ,2014.Design and optimization of an extrusion die for the production of wood–plastic composite profiles. Polymer Engineering Science.55,8, 1849-1855.

Hietala, M. ,2013. Extrusion Processing of Wood-Based Biocomposites. University of Oulu, 1-56

Highley, L., Clausen, A., Croan, C., Green, F., Illman, L. and Micales, A. 1994. Research on biodeterioration of wood, 1987-1992. I. Decay mechanisms and biocontrol. Research Paper - Forest Products Laboratory, USDA Forest Service, Madison WI, No. FPL-RP-529, 20

Hill, S., 2006.The use of timber in the twenty-first century. In: Hill CAS (Ed.). Wood Modification: Chemical, Thermal and Other Processes. John Wiley & Sons, Chichester, UK. 1-18.

Hosseinaei, O., Wang S., Enayati, A., and Rials, G.,2012. Effects of hemicellulose extraction on properties of wood flour and wood– plastic composites. Compos Part A-Appl ication Science ,43,4, 686-694.

Huffman, R. and Casey, J.,1985. Effect of carboxyl end groups on hydrolysis of polyglycolic acid, Journal of Polymer Science, Polymer Chemistry Edition, 23, 1939-1954.

Hunt, M. and Garratt. G.,1967. Wood Preservation. San Francisco, McGraw-Hill, Inc.

Iovino, R., Zullo, R., Rao, M. A., Cassar, L. and Gianfreda, L. ,2008. Biodegradation of poly (lactic acid)/starch/coir biocomposites under controlled composting conditions, Polymer Degradation and Stability, 93, 147-157.

Kamdem, D.P 2004 . Properties of wood plastic composite made of recycled HDPE and wood flour from CCA-treated removed from services. Applied science and Manufacturing, 35,347-355

Kim, J and Pal, K. 2010. Overview of wood-plastic composites and uses. In: Kim J and Pal K (Eds.). Recent Advances in the Processing of Wood-Plastic Composites. Springer, Berlin, Germany, 1-22.

Kociszewski.M., Gozdecki,C., Wilczyski, A., Zajchowski,S., and Mirowski,J. (2012). Effect of industrial wood particle size on mechanical properties of wood-polyvinyl chloride composites. Eur Journal of Wood Production.70,1-3, 113-118.

Kollmann, F. and Côté,W.(1968). Principles of Wood Science and Technology I: Solid Wood. New York, Springer-Verlag Inc.

Kopinke, D., Remmler, M., Mackenzie, K., Moder, M. and Wachsen, O. (1996). Thermal decomposition of biodegradable polyesters-II. Poly (lactic acid), *Polymer Degradation and Stability*, 53, pp.329-342.

Kord, B. (2011a). Influence of Maleic Anhydride on the Flexural, Tensile and Impact Characteristics of Sawdust Flour Reinforced Polypropylene Composite. *World Applied Science,* 12(7), pp.1014–1016.

Kord, B.(2011b). Evaluation on the effect of wood flour and coupling agent content on the Hygroscopic. *bioresources.com*, 6, pp.3055–3065.

Kord, B., (2011c). Investigation of Reinforced Filler Loading on the Mechanical Properties of Wood Plastic Composites. *World Applied Science*, 13(1), pp.171–174.

Kord, B., (2012). The Influence of Coupling Treatment on Fungal Resistance of Wood Flour / Polypropylene Composites. , *World Applied Science Journal,* 17(1), pp.75–79.

Kricheldorf, R., Kreiser-Saunders, I., Jurgens, C. and Wolter, D. (1996). *Macromolecular Symposia*, 103, pp.85-102

Lei, Yong., Wu, Qinglin., Yao, Fei., Xu, Yanjun., 2007. Preparation and properties of recycled HDPE/natural fiber composites. Composites Part A: *Applied Science and Manufacturing*, 38(7), pp.1664–1674.

Li ,X., Lei,B., Lin, Z., Huang, L., Tan, S, and Cai, X. (2014).The utilization of bamboo charcoal enhances wood plastic composites with excellent mechanical and thermal properties. Mater Des. 53, pp. 419-424.

Li, Y. (2011). Wood-polymer composites. In: Tesinova P (Ed.). Advances in Composite Materials - Analysis of Natural and Man-made Materials. *In Tech, pp.* 229-284.

Lu, Z., Wu, Q and Negulescu, I. (2005). Wood-Fiber / High-Density-Polyethylene Composites: Coupling Agent Performance. *Journal of Applied Polymer Science*, 96, pp.93–102

Lucas, N., and Ruddick, N. 2002. Determination of the amine to copper ratio remaining in wood after water leaching. International Research Group on Wood Protection (Stockholm, Sweden). Doc. No. IRG/WP 02-30285: 12p

Maged, B., Equistar Chemicals. 2003. Development of new generation coupling agents for wood plastic composites. In: InterTech Conference the Global Outlook for Natural and Wood Fiber Composites. New Orleans, December 3-5.

Migneault, S., Koubaa, A., Perré, P. and Riedl, B. ,2015. Effects of wood fiber surface chemistry on strength of wood–plastic composites. Application Surface Science.343, 11-18.

Migneault, S., Koubaa, A., Erchiqui, F., Chaala, A., Englund, K.and Wolcott,P. 2009. Effects of processing method and fiber size on the structure and properties of wood–plastic composites. Compos Part A-Application Science. 40,1, 80-85

Mohanty.S., Verma SK, Nayak SK ,2006. Dynamic mechanical and thermal properties of MAPE treated jute/HDPE composites. Composite Sci Tech 66,538-547.

Müller, M., Gellerich, A., Militz., H and Krause, K. ,2013. Resistance of modified polyvinyl chloride/wood flour composites to basidiomycetes. European journal of wood and wood products.71, 2,199-204.

Müller,M., Radovanovic. I., Grüneberg.T, Militz, H. and Krause, A. ,2012. Influence of various wood modifications on the properties of polyvinyl chloride/wood flour composites. Journal of Application Polymer Science. 125 ,1, 308-312.

Najafi, K., Mostafazadeh-Marznaki, M and Chaharmahali, M. ,2010. Effect of thermo-mechanical degradation of polypropylene on hygroscopic characteristics of wood flour-polypropylene composites. Journal Polymer Environ.18,4, 720-726.

Nakafuku, C. and Takehisa, S. Y. 2004. Glass transition and mechanical properties of PLLA and PDLLA-PGA copolymer blends, Journal of Applied Polymer Science, 93, 2164-2173.

Narayan, R., Degradation of Polymeric Materials, Oardc, 1993.

Ndiaye D, Matuana LM.,2011). Thermal and mechanical properties of polypropylene/wood-flour composites. Applied polymer Science, 119,3321-8

Nourbakhsh, A. and Ashori, A.,2009. Preparation and properties of wood plastic composites made of recycled high-density polyethylene. Journal of Composite Materials.43,8 ,877-883.

Oksman,K and Sanadi, A. ,2008.Interactions between wood and synthetic polymers. In: Oksman Niska K and Sain M (Eds.). Wood Polymer Composites. CRC Press, Cambridge, UK, 41-71.

Perego, G., Cella, G. D. and Bastioli, C.1996. Effect of molecular weight and crystallinity on poly (lactic acid) mechanical properties, Journal of Applied Polymer Science, 59, 37-43.

Pérez, E., Famá, L., Pardo, S., Abad, M. and Bernal, C. ,2012. Tensile and fracture behaviour of PP/wood flour composites. Composite Part B - Eng. ,43 7,2795-2800.

Pettersen,C. ,1984.The chemical composition of wood. In: Rowell R (Ed.). The Chemistry of Solid Wood. American Chemical Society, Washington, DC, US, 57-126.

Pizzi, A. 1981. The chemistry and kinetic behavior of Cu-Cr-As/B wood preservatives. I. Fixation of chromium on wood. Journal of Polymer Science Polymer Chemistry. 19,12,3093-3121.

PlaBenninga, H. ,1990). A History of Lactic Acid Making, Kluwer Academic Publishing, Boston.

Quan, H., Li,Z., Yang, M and Huang, R. ,2005.On transcrystallinity in semicrystalline polymer composites. Composites Science Technology, 65 ,7,999-1021.

Rowell, M. &Youngquist, A.,1991. Composites from Recycled Materials., pp.301– 314.

Rowell, M., Pettersen, R.and Tshabalala. A. 2013.Cell wall chemistry. In: Rowell RM (Ed.). Handbook of Wood Chemistry and Wood Composites. CRC Press, Boca Raton, FL, US, pp. 33-72, 2013.

Ruddick, R., Xie,C., and Herring, F. 2001. "Fixation of amine copper preservatives. Part 1: Reaction of vanillin, a lignin model compound with monoethanolamine copper sulphate solution." Holzforschung 55,585-589.

Saha, K. and Tsuji, H., 2006.Effects of molecular weight and small amounts of Dlactide units on hydrolytic degradation of poly (L-lactic acid), Polymer Degradation and Stability, 91,1665-1673.

Saheb,N and Jog, J. ,1999 .Natural fiber polymer composites: A review. Advantage Polymer Technology.18,4,351-363.

Sain,M and Pervaiz,M. ,2008 .Mechanical properties of wood-polymer composites. In: Oksman Niska K and Sain M (Eds.). Wood Polymer Composites. CRC Press, Cambridge, UK, 101-117

Schmidt, L. ,1993. A review of biological agents on aspen composites and needs for future research. In Proceedings: International Union of Forestry Research Organization (IUFRO) Symposium on the Protection of Wood-Based Composite Products pp. 23-25

Schwendemann,D. ,2008.Manufacturing technologies for wood-polymer composites. In: Oksman Niska K and Sain M (Eds.). Wood Polymer Composites. CRC Press, Cambridge, UK, 72-100.

Semeralul, O. ,2009. Advancing the Technology Development for Better Quality Wood Plastic Composites: Process ability Study,1-92

Selçuk .A. ,2015. Investigation on evaluation of opportunities of impregnated products containing creosote that completed the service life in Wood plastic composites (WPCs)

Sretenovic,A., Müller, U., and Gindl,W. ,2006.Mechanism of stress transfer in a single wood fibre-LDPE composite by means of electronic laser speckle interferometry. Composite Part A-Appl S.37,9,1406-1412.

Stark, M., Service, F. & Rowlands, E.,2005. Effect of Wood Fiber Characteristics on Mechanical Properties of Wood/Polypropylene Composites Wood and Fiber Science, 35,2, 167–174.

Stark,M and Rowlands, E. ,2003.Effects of wood fiber characteristics on mechanical properties of wood/polypropylene composites. Wood Fiber Science,35,2, 167-174.

Stokke, D,, Wu, Q. and Han, G. 2014. Introduction to Wood and Natural Fiber Composites. John Wiley & Sons, West Sussex, UK.

Suttie, D., Bravery, A and Dearling. T.2002. "Alternatives to CCA for ground contact protection of timber: a perspective for UK on performance and service life expectations." International Research Group on Wood Protection (Stockholm, Sweden). Doc. No. IRG/WP 02-30289, 21.

Tamrakar, S and Lopez-Anido, A. ,2011. Water absorption of wood polypropylene composite sheet piles and its influence on mechanical properties. Construction Building Materials. 25 ,10, 3977-3988.

Thomason, S. and E. Pasek. ,1997. Amine copper reaction with wood components: acidity versus copper adsorption. International Research Group on Wood Protection (Stockholm, Sweden). Doc. No. IRG/WP 97-30161, 18.

Vlosky, P. ,2006). Statistical overview of the U.S. wood preserving industry: 2004. Louisiana State University Agricultural Center. Baton Rouge, LA. 65.

Wang, Y. M., Steinhoff, B., Brinkmann, C. and Alig, I.,2008. In-line monitoring of the thermal degradation of poly L-lactic acid during melt extrusion by UV-vis spectroscopy, Polymer, 49, 1257-1265.

Wang,W., Sain, M., and Cooper, P. 2006 .Study of moisture absorption in natural fiber plastic composites. Composites Science Technology. 66 ,3, 379-386.

Wei, L., McDonald,G., Freitag,C. and Morrell, J. Effects of wood fiber esterification on properties, weatherability and biodurability of wood plastic composites. Polymer Degradation Stability. 98 ,7, 1348-1361.

Wiedenhoeft, C. ,2010. Structure and function of wood. In: Ross RJ (Ed.). Wood Handbook: Wood as an Engineering Material. Forest Products Laboratory, Madison, WI, US, 2010

Wiedenhoeft, C. ,2012. Structure and function of wood. In: Rowell RM (Ed.). Handbook of Wood Chemistry and Wood Composites.CRC Press, Boca Raton, FL, US, 9-32.

Wolcott, P and Englund, K.,1999. A technology review of wood-plastic composites. In: 33rd International Particleboard/Composite Materials Symposium Proceedings. Pullman, WA, US, April 13-15, 103-111.

Xie, C., Ruddick, J., Rettig, S. and Herring, F.,1995). "Fixation of ammoniacal copper preservatives: reaction of vanillin, a lignin model compound with ammoniacal copper sulphate solution." Holzforschung 49: 483490.

Yeh, S and Gupta,K. ,2008.Improved wood–plastic composites through better processing. Compos Part A-Appl S. 39 ,11, 1694-1699.

Youngquist, A., Myers, E., Muehl, H., Krzysik, M., Clemens, M., Brown, Lisa., 1994. Composites from Recycled Wood and Plastics,1-20

Yuan.Q., Wu, D., Gotama, J and Bateman, S. ,2008. Wood fiber reinforced polyethylene and polypropylene composites with high modulus and impact strength. Journal Thermoplastic Composite Materials ,21,3,195-208,

Zabel, A., & Morrell, J. ,1992. Wood Microbiology: Decay and Its Prevention. San Diego, CA: Academic Press, Inc.

Zhang, H., Cui,Y., and Zhang, Z. ,2013.Chemical treatment of wood fiber and its reinforced unsaturated polyester composites. Journal Vinyl Additive Techn.19,1, 18-24

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