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Thermoplastic Matrix Reinforced with Natural Fibers: A Study on Interfacial Behavior

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1. Introduction

The composites and their constituent components and structures have to meet increasingly development during recent decades. Some important concerns such as increasing price of petroleum and the impending depletion of fossil fuels and the interest in reducing the environmental impact of polymers is leading to the development of newer materials that can reduce stress on environment. Current developments and likely future trends are covered across key areas of the natural fibers reinforced polymer industry, together with existing and potential opportunities for the innovative use of plastic and bio-based fibers products. The challenges facing the world, such as environmental requirements and the need for recycling of plastic materials, are also included. Hence, the attention is increasingly being given to the use of natural fibers as reinforcement filler in low melting thermoplastic matrix manufactured by conventional plastic process such as extrusion and injection molding process. Injection molding is one of the most widely used processes for manufacturing molded parts from reinforced thermoplastic materials. Short natural fiber reinforced composites can be processed into complex shaped components using standard thermoplastic injection molding equipment.

Although the use of bio-based fillers is not as popular as the use of mineral or inorganic fillers, natural fiber-derived fillers have several advantages over traditional fillers and reinforcing materials such as low density, flexibility during the processing with no harm to the equipment, acceptable specific strength properties and low cost per volume basis.

The worldwide markets show the increased demands for natural and bio-based fibers. In 1967, the USA demand for fillers by the plastic industry was 525,000 tons; filler use had grown to 1,925,000 tons by 1998 (Eckert, 1999) and the projected use of fillers by the USA plastic industry in 2010 is to 8.5 billion pounds, of which 0.7 billion pounds (8%) was estimated to be bio-based fibers. It has been also summarized major markets for natural fibers in plastic composites as fig. 1a, on a weight basis (Eckert, 2000). Based on Fig. 1a, the main application areas of bio-based fibers filled composites are the building products in which they are used in structural applications as fencing, decking, roofing, railing, cladding and siding, park benches and etc. as shown in Fig. 2.

Most bio-fiber plastic additives are derived from wood that incorporated in Wood-plastic composites (WPCs). WPCs contain wood (fiber or flour) and polymer as matrix. The
Fig. 1. Application areas and countries share for wood- and natural fiber-thermoplastic composites.

Fig. 2. Applications of natural fiber reinforced plastics in building products.

The elasticity of wood fiber is approximately forty times greater than that of neat polyethylene and the overall strength is about twenty times higher (Oksman and Selin, 2004). However, other natural fibers, such as flax or wheat straw are finding their way into the fiber/plastic industry. WPCs represent one of the rapidly growing markets within the plastics industry. More than 1.5 million tons of WPCs are produced worldwide, with the bulk of composites manufactured in the U.S., as shown in Fig. 1b.

Based on Freedonia Group report on 2010, Demand for WPC and plastic lumber is projected to advance 9.2 per cent per year to US$5.3 billion in 2013, creating a market for 3.3 billion pounds of plastic. WPC lumber will post more rapid gains than plastic lumber, advancing 10.5 per cent annually to US$2.4 billion in 2013. Growth in demand for plastic lumber is forecast to rise 8.2 per cent per year to US$2.9 billion in 2013. Demand for WPC and plastic lumber to reach $5.3 billion in 2013 (Centre Magazine, 2010).

In the USA, the wood- and natural fiber-plastic composites market has been dominated by rail and decking products, while in Europe more emphasis has been placed on automotive applications. Applications for these composites include interior panels, headliners, dashboard; car roofs, seat panels, parcel shelves, and acoustic panels (Fig. 3,4).
Thermoplastic Matrix Reinforced with Natural Fibers: A Study on Interfacial Behavior

The WPCs global market for automotive applications is estimated at 0.3 million metric tons in 2011 and is expected to increase at 17.1% compound annual growth rate to reach nearly 0.8 million metric tons in 2016 (BCC Research Report, 2011).

In China and other parts of Asia, wood and natural fiber reinforced plastics are beginning to experience considerable growth along with a wider variety of product offerings including pallets, doors, and architectural moldings. While other countries are manufacturing these products, international trade is still limited, in part due to the weight of the finished products. Despite all the advantages there are also serious concerns. For explanation of these, must be said that:

1. the density of WPCs is almost twice that of solid lumber (Li and Matuana, 2003). The concept of creating cellular foamed structures has been shown to greatly reduce the weight of WPCs.
2. Exposure to ultraviolet (UV) radiation during outdoor use is of particular concern for WPCs.
3. the main disadvantages of using natural fibers as fillers is their high water absorption or desorption when subjected to changes in the relative humidity of the environment.

Fig. 3. Some applications of natural fibers in the automotive field.

Fig. 4. Interior automotive parts made of wood and natural fiber reinforced plastics.
4. Thermoplastics typically perform poorly in long-term loading because linear polymer molecules exhibit a strong time and temperature dependent response. Addition of wood filler to the polymer matrix decreases creep response during loading (Bengtsson et al., 2005), but it is still a problem.

5. The processing temperature of the cellulose fibres in thermoplastics is limited due to the potential fibre degradation at higher temperatures. This limits their application with plastics of low melting temperatures.

6. Low impact strength is another disadvantage of WPCs, due to the presence of natural fibers in the polymeric matrix provides points of stress concentrations, thus providing sites for crack initiation and potential composite failure.

But there is more important drawback in natural fiber-thermoplastic composites that limit its applications. The highly hydrophilic nature of natural fibers causes compatibility problems with the hydrophobic thermoplastics in composites. The mechanical properties of composites depend strongly on the interfacial adhesion between components. This can be maximized by improving the interaction and adhesion between the two phases in final composites. There are two approaches to improve the interfacial adhesion: polymeric matrix and lignocelluloses fiber modification. Different coupling agents have been used to modify the polymeric matrix and improve the interfacial strength and subsequently the mechanical properties of the products. Maleic anhydride grafted styrene-ethylene-butylene-styrene (SEBS-\(\gamma\)-MA)( Oksman et al., 1998) and maleic anhydride grafted polyolefin such as HDPE-\(\gamma\)-MA (Polec et al., 2010), PP-\(\gamma\)-MA (Farsi, 2010), and LDPE-\(\gamma\)-MA (Tasdemir et al., 2009) are the most common examples of reported works in the literature.

Another approach for enhancement of interfacial adhesion in natural fiber reinforced thermoplastic matrix is fiber treatment before mixing with polymer. Some of these treatments have physical nature and some of them are of chemical nature. Plasma and corona treatments of the fibers as physical methods have been reported in some papers (Gassan & Gutowski, 2000; Yuan et al., 2004). Their results show enhanced polymer-matrix adhesion.

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. Many studies have been undertaken to modify the performance of natural fibers. Different surface treatment methods such as alkali treatment (Chang et al., 2009), isocyanate treatment (Maiti et al., 2004,) acrylation (Huda et al., 2008), benzoylation (Mohnty et al., 2001), latex coating (Sreekala, 2000), permanganate treatment (Joseph, 2000), acetylation (Larsson-Brelid et al., 2008), silane (Bouza et al., 2008) and peroxide treatment (Sapieha et al., 1990) have been applied on the fiber to improve its strength, size and its shape and the fiber-matrix adhesion. The aforementioned methods have their own merits and demerits, e.g., alkali treatment improves the fiber-polymer adhesion due to the removal of natural and artificial impurities and changes in chemical composition of the fiber by removing the cementing substances like lignin and hemicelluloses. Generally, mechanism of the performance of these methods is different and is depended on the chemical structure of the reagent.

There are also several other challenges presented by natural fibers filled polymer composites such as large variability of mechanical properties (Sydenstricker et al., 2003) lower ultimate strength, lower elongation, problems with nozzle flow in injection molding machines,
bubbles in the product (Toriz et al., 2002), and poor resistance to weathering (Pavithran, 1981).

In this chapter, we focus on structure and composition of natural fiber and review some research on optimization of interfacial adhesion between natural fibers and thermoplastic matrix which published during the past decades and then report the effect of various chemical modifications of wood fiber and contemporaneous effect of PP-g-MA coupling agent on the interfacial strength of wood polypropylene injection molded composites. The effects of chemical treatments and PP-g-MA coupling agent on the interfacial behavior were evaluated by mechanical properties and dynamic mechanical analysis and so determined tensile strength, adhesion factor, storage modulus and loss factor.

2. Natural fibers

2.1 Characteristics of natural fibers

Natural fibers are subdivided based on their origins, coming from plants, animals or minerals. All plant fibers are composed of cellulose while animal fibers consist of proteins (hair, silk and wool). Natural fibres can be classified according to which part of the plant they are obtained from, as shown in Fig. 5.

![Fig. 5. Classification of natural fibres.](image)

The strength characteristics of fiber depend on the properties of the individual constituents, the fibrillar structure and the lamellae matrix (Joseph et al., 2000).

Natural fibers exhibit considerable variation in diameter along with the length of individual filaments. Quality and other properties of fibers depend on factors such as size, maturity and processing methods adopted for the extraction of fiber (Mohanty et al., 2001). Properties such as density, electrical resistivity, ultimate tensile strength and initial modulus are related to the internal structure and chemical composition of fibers (Mohanty et al., 2001).

The structure, microfibrillar angle, cell dimensions, defects, and the chemical composition of fibres are the most important variables that determine the overall properties of the fibres.
Long term supply of resources is an important point about natural fibers that can influence on natural fiber–thermoplastic composites production. The world consumption of natural fibers as illustrated in Table 1. The data presented in Table 1 suggests that wood with 68.5% of the total world consumption, will continue to be a major source of bio-based fibers.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Quantity(*10^3 tons)</th>
<th>% of the total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood fiber</td>
<td>1,750,000</td>
<td>68.5</td>
</tr>
<tr>
<td>Rice straw</td>
<td>700,000</td>
<td>27.4</td>
</tr>
<tr>
<td>Rice husks</td>
<td>70,000</td>
<td>2.8</td>
</tr>
<tr>
<td>Cotton</td>
<td>18,645</td>
<td>0.75</td>
</tr>
<tr>
<td>Bamboo</td>
<td>10,000</td>
<td>0.39</td>
</tr>
<tr>
<td>Jute</td>
<td>3,630</td>
<td>0.14</td>
</tr>
<tr>
<td>Kenaf</td>
<td>970</td>
<td>0.04</td>
</tr>
<tr>
<td>Flax</td>
<td>830</td>
<td>0.03</td>
</tr>
<tr>
<td>Sisal</td>
<td>380</td>
<td>0.01</td>
</tr>
<tr>
<td>Hemp</td>
<td>220</td>
<td>0.009</td>
</tr>
<tr>
<td>Ramie</td>
<td>110</td>
<td>0.004</td>
</tr>
<tr>
<td>Coir</td>
<td>100</td>
<td>0.0039</td>
</tr>
</tbody>
</table>

Table 1. Annual world production of natural fibers (Kandachar, 2000; Bolton, 1995).

### 2.2 Structure of natural fibers

The cell wall in a fiber is not a homogenous membrane. Each fibril has a complex, layered structure consisting of a thin primary wall that is the first layer deposited during cell growth encircling a secondary wall (Fig. 6).

Fig. 6. Positioning of the cellulose fibrils in wood fibres. M) Middle lamella; P) Primary wall; S) Secondary wall; S1) Secondary wall I; S2) Secondary wall II; S3) Secondary wall III.

The secondary wall is made up of three layers and the thick middle layer determines the mechanical properties of the fiber. The middle layer consists of a series of helically wound cellular microfibrils formed from long chain cellulose molecules: the angle between the fiber axis and the microfibrils is called the microfibrillar angle. The characteristic value for this parameter varies from one fiber to another. The outer secondary cell wall (S1) is comparable...
in thickness to the primary wall and consists of four to six lamellae which spiral in opposite
directions around the longitudinal axis of the tracheid. The main bulk of the secondary wall
is contained in the middle secondary cell wall (S2), and may be as little as 1 pm thick in early
woods and up to 5 pm in summer wood. The microfibrils of this part of the wall spiral
steeply about the axial direction at an angle of around 10 to 20°. The inner secondary wall
(S3), sometimes also known as the tertiary wall, is not always well developed, and is of no
great technological importance. The orientation of the microfibrils within the S2 layer has an
important bearing on mechanical properties of the fibre such as its modulus of elasticity.

Mechanical properties are determined by the cellulose content and microfibril angle. A high
cellulose content and low microfibril angle are desirable properties of a fiber to be used as
reinforcement in polymer composites (Williams & Wool, 2000).

Selective removal of non-cellulosic compounds constitutes the main objective of fiber
chemical treatment. Both the hemicellulosic and pectic materials play important roles in
fiber bundle integration, fiber bundle strength and individual fiber strength as well as water
absorbency, swelling, elasticity and wet strength. The production of individual fibers
without the generation of kink bands will generate fibers with much higher intrinsic fiber
strength which is very useful for composite application (Mooney et al., 2001).

2.3 Composition of natural fibers

2.3.1 Cellulose

The reinforcing efficiency of natural fiber is related to the nature of cellulose and its
crystallinity. Cellulose is a natural linear homopolymer (polysaccharide), in which
D-glucopyranose rings are connected to each other with β- (1-4)-glycosidic linkages. The
structure of cellulose units is shown in Fig. 7.

![Molecular structure of cellulose](https://www.intechopen.com)

Fig. 7. Molecular structure of cellulose (Raven et al., 1999).

It is thus a 1, 4-β-D-glucan. The cellobiose polymer chains are ordered in three-dimensional
levels, which give the supramolecular structure of cellulose. The linear polymeric chains
(one dimension) form sheets that are held together with hydrogen bonds (second
dimension). Then, these sheets are connected by Van der Waals bonds generating microfibril crystalline structures (third dimension). The crystal nature (monoclinic sphenodic) of naturally occurring cellulose is known as cellulose I. Cellulose is resistant to strong alkali (17.5 wt%) but is easily hydrolyzed by acid to water-soluble sugars. Cellulose is relatively resistant to oxidizing agents. Native cellulose (cellulose I) has two crystalline allomorphs, Iα and Iβ. The main difference between the two crystalline phases is the relative position of the chains to each other. These hydroxyl groups and their ability to hydrogen bond play a major role in directing the crystalline packing and also govern the physical properties of cellulose. Solid cellulose forms a microcrystalline structure with regions of high order, i.e. crystalline regions, and regions of low order, i.e. amorphous regions. Although the chemical structure of cellulose from different natural fibers is the same, the degree of polymerization (DP) varies. Its degree of polymerisation is typically between 10000 and 15000 glucose residues depending upon source and it is never found in a completely crystalline form, but occurs as a partly crystalline.

2.3.2 Hemicellulose

Hemicelluloses are another component of plant fibers. Hemicelluloses are polysaccharides and differ from cellulose in that they consist of several sugar moieties, are mostly branched, and have lower molecular mass with a degree of polymerization (DP) of 50 – 200. They are not, as the name seems to imply, biosynthetic precursors of cellulose. The two main types of hemicelluloses are xylans and glucomannans. Fig. 8 shows partial structure of hemicelluloses with a combination of 5-ring carbon ring sugars.

![Fig. 8. Structure of softwood galacto-glucomannan (Bledzki & Gassan, 1999).](image)

Hemicellulose differs from cellulose in three aspects. Firstly, they contain several different sugar units whereas cellulose contains only 1,4-b-D-glucopyranose units. Secondly, they exhibit a considerable degree of chain branching containing pendant side groups giving rise to its noncrystalline nature, whereas cellulose is a linear polymer. Thirdly, DP of hemicellulose is around 50–300, whereas that of native cellulose is 10–100 times higher than that of hemicellulose.

2.3.3 Lignin

After cellulose, lignin is the most abundant natural organic polymer. Its content is higher in softwoods (27–33 %) than in hardwoods (18–25 %) and grasses (17–24 %). Lignin is totally amorphous and hydrophobic in nature. It is the compound that gives rigidity to the plants. It is thought to be a complex, three-dimensional copolymer of aliphatic and aromatic constituents with very high molecular weight. Lignin is a randomly branched polyphenol,
made up of phenyl propane (C9) units and it is the most complex polymer among naturally occurring high-molecular-weight materials. Due to its lipophilic character, lignin decreases the permeation of water across the cell walls, which consist of cellulose fibres and amorphous hemicelluloses, thus enabling the transport of aqueous solutions of nutrients and metabolites in the conducting xylem tissue. Secondly, lignin imparts rigidity to the cell walls and, in woody parts, together with hemicelluloses, functions as a binder between the cells generating a composite structure with outstanding strength and elasticity. Finally, lignified materials effectively resist attacks by microorganisms by impeding penetration of destructive enzymes into the cell walls. When incorporated in a plastic, lignin, due to its phenolic base structure, could improve the mechanical properties (Thielemans et al., 2002).

Fig. 9 shows building blocks of lignin. There is a wide variation of structure within different plant species (Alder, 1977). Lignin is considered to be a thermoplastic polymer exhibiting a glass transition temperature of around 90°C and melting temperature of around 170°C (Olesen & Plackett, 1999). It is not hydrolyzed by acids, but soluble in hot alkali, readily oxidized, and easily condensable with phenol.

Fig. 9. Partial structure of a spruce lignin fragment (Alder, 1977).

3. Natural fiber for use in injection molded composite

Injection molding is a widely used technique for mass producing articles with a high degree of geometrical complexity. Injection molding has many advantages, such as short product cycle, excellent surface of the product and easily molded complicated shapes. The characteristics of the product are easily affected by the flow type of the melt, the heat transfer effect, the material properties and the specific geometry of the mold. Thus, different injection molding conditions will induce different fiber orientation. The degree of fiber orientation depends on the fiber characteristics, the variation of the cross-sectional area for flow, and the injection molding conditions. Composite materials for use in injection molding applications must be capable of fluid-like flow during processing and thus usually consist of
short fibers with a relatively low fiber fraction. Natural fiber compounds offer numerous advantages over other injection molding compounds, for instance, low wear of manufacturing tools, often reduced cycle time, and ease of recycling. The final properties of natural fiber thermoplastic composites manufactured by injection molding depend not only on the properties of raw materials used and their compositions, but also on processing methods. Injection molding is a very suitable procedure to process natural fiber reinforced polymers into sophisticated 3-dimensional parts. In this case, the use of granular material, which already includes natural fibers and coupling agent, proves a success. But the incorporation of natural fibers to thermoplastics leads to flow limitation, which are increased by the incompatibility of natural fibers and thermoplastics. A lot of methods have been used to solve this incompatibility problem, and natural fiber chemical modification and coupling agent have a better result that is explained below.

4. Natural fiber surface modification: Case study outline

Natural fibers are amenable to modification as they bear hydroxyl groups from cellulose and lignin. The hydroxyl groups may be involved in the hydrogen bonding within the cellulose molecules thereby reducing the activity towards the matrix. Chemical modifications may activate these groups or can introduce new moieties that can effectively interlock with the matrix. Interfaces play an important role in the physical and mechanical properties of composites (Joseph et al., 2000). Simple chemical treatments can be applied to the fibers with the aim of changing surface tension and polarity of fiber surface.

4.1 Most important surface modification

The different surface chemical modifications of natural fibers have achieved various levels of success in improving fiber strength, fiber fitness and fiber-matrix adhesion in natural fiber composites. Brief descriptions of some important fiber chemical modifications which applied in this research are summarized in the following sub-sections.

4.1.1 Alkaline treatment

The important modification done by alkaline treatment is the disruption of hydrogen bonding in the network structure, thereby increasing surface roughness. This treatment removes a certain amount of lignin, wax and oils covering the external surface of the fiber cell wall, depolymerizes cellulose and exposes the short length crystallites (Li et al., 2000). Addition of aqueous sodium hydroxide (NaOH) to natural fiber promotes the ionization of the hydroxyl group to the alkoxide (Agrawal et al., 2000). Thus, alkaline processing directly influences the cellulose fibril, the degree of polymerization and the extraction of lignin and hemicellulosic compounds (Jahn et al., 2002). Alkali treatment increases surface roughness resulting in better mechanical interlocking and the amount of cellulose exposed on the fiber surface. This increases the number of possible reaction sites and allows better fiber wetting. The following reaction, takes place as a result of alkali treatment.

\[
\text{Fibre} \quad \rightarrow \quad \text{OH} + \text{NaOH} \quad \rightarrow \quad \text{Fibre} \quad \rightarrow \quad \text{O}^{\text{Na}^+} + \text{H}_2\text{O}
\]

Fig. 10. Alkaline treatment reaction (Pothan et al., 2006).
Many attempts have been done by researchers to increase mechanical properties of biocomposites by alkaline treatments. For example, the effect of alkali treatment on properties of hybrid fiber biocomposite was reported by John et al., (2008). It has been reported that alkali treatment leads to fiber fibrillation i.e. breaking down of fiber bundles into smaller fibers which increases the effective surface area available for contact with the matrix.

Partial removal of lignin and hemicellulose on the alkali modification of cellulose fibers was reported by Sreekala et al., (1997). Mukherjee et al., (1993) reported that the removal of hemicellulose produces less dense and less rigid interfibrillar region. Kokot et al., (1995) also noted that as lignin is removed, the middle lamella joining the ultimate cells is expected to be more plastic as well as homogeneous, due to the gradual elimination of microvoids. Alkaline treatment increases the amount of crystalline cellulose and removes natural and artificial impurities, producing a rough surface topography.

### 4.1.2 Silane treatment

Silane is a chemical compound with chemical formula SiH4. Silanes are used as coupling agents to let glass fibers adhere to a polymer matrix, stabilizing the composite material. Silane coupling agents may reduce the number of cellulose hydroxyl groups in the natural fiber-matrix interface. Silanes undergo hydrolysis, condensation and the bond formation stage. The reaction scheme is given as follows:

![Reaction Scheme](image)

**Fig. 11. Hydrolysis of silane and hypothetical reaction of fibers and silane (Sreekala et al., 2000).**

Bledzki et al., (1996) concluded that in the process of interaction between natural fibers and silanes, alkoxy silanes are able to form bonds with hydroxyl groups. In presence of moisture hydrolyzable alkoxy group of silans leads to the formation of silanols. Silanols can form polysiloxane structures by reaction with hydroxyl group of the fibers.

John et al., (2008) and Mathew et al., (2004) investigated the effect of silane treatment on the mechanical properties of biocomposites. They observed a marked improvement in the properties after chemical modification. Sreekala et al., (1997) also suggested that the silane treated cellulose fiber composite showed an increase in nucleation density compared the untreated fiber composite. The increased nucleation yielded smaller crystals that result in a transcrystalline interphase region, with improved bonding between the fiber and the matrix (Agrawal et al., 2000).
4.1.3 Benzoylation treatment

Benzoylation is an important transformation in organic synthesis (Paul et al., 2003). Benzoyl chloride is most often used in fiber treatment. The Benzoyl chloride forms an ester linkage to the natural fibers, reducing its hydrophilicity and making it more compatible with matrix. The reaction between the cellulosic-OH group of natural fiber and benzoyl chloride is shown as follows:

\[
\text{Fibre} \quad \text{OH} + \text{NaOH} \rightarrow \text{Fibre} \quad \text{O}^+\text{Na}^+ + \text{H}_2\text{O}
\]

\[
\text{Fibre} \quad \text{O}^+\text{Na}^+ + \text{Cl}^- \rightarrow \text{Fibre} \quad \text{O} \quad + \text{Cl}^- + \text{Na}^+\text{Cl}^{-}
\]

Fig. 12. Reaction between cellulosic-OH groups and benzoyl chloride (Joseph et al., 2000).

Abu bakar & Baharulrazi (2008) also indicated that the benzoylated oil palm empty fruit bunch was able to improve the tensile properties, impact strength and the increase of water resistance, and the reduction of glass transition temperature of composites when compared to the untreated fiber.

4.1.4 Acrylation treatment

Acrylation reaction is initiated by free radicals of the cellulose molecule. Cellulose can be treated with high energy radiation to generate radicals together with chain scission (Bledzki & Gassan, 1999). The reaction was accomplished between OH groups and acrylic acid as follows:

\[
\text{Fiber} \quad \text{OH} + \text{CH}_2 = \text{CH} \quad \text{COOH} \rightarrow \text{Fiber} \quad \text{O} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{COOH}
\]

Fig. 13. Reaction between cellulosic-OH groups and acrylic acid (Mohanty et al., 2001).

Sreekala et al., (2000, 2002) used acrylic acid in natural fiber surface modification. acrylation led to strong covalent bond formation and thereby, the tensile strength and Young’s modulus of treated fibers were improved marginally.

4.1.5 Polyolefin-g-MA coupling agents

Coupling agents such as PP grafted with maleic anhydride (PP-g-MA) and PP grafted with acrylic acid (PP-g-AA) are usually employed to improve interfacial properties. Esterification reaction and H-bond interactions may take place at the interface of the cellulosic filler and the PP-g-MA as suggested in Fig. 14. The PP chain permits maleic anhydride to be cohesive and produce maleic anhydride grafted polypropylene (PP-g-MA). Then the treatment of cellulose fibers with hot PP-g-MA copolymers provides covalent bonds across the interface. After this treatment, the surface energy of cellulose fibers is increased to a level much closer to the surface energy of the matrix. This results in better wettability and higher interfacial adhesion of the fiber.
Many of maleic anhydride grafted polyolefin such as HDPE-$\gamma$-MA, PP-$\gamma$-MA, and LDPE-$\gamma$-MA studied by Polec et al., (2010), Farsi, (2010) and Tasdemir et al., (2009) respectively. They observed strong interfacial strength by incorporation of the coupling agents.

4.2 Role of chemical treatment on thermo-mechanical behavior

One of the most important methods for studying the effect of natural fiber chemical surface treatment on the interfacial strength of the composites is dynamic mechanical thermal analysis (DMTA). The effect of wood chemical surface modification on the interfacial strength was tracked using adhesion factor. This parameter is obtained from DMTA data. Effect of PP-$\gamma$-MA as coupling agent on the interface adhesion of WPC investigated by Correa et al., (2007). They mentioned a method based on a simplified single rule of mixtures aiming to compare differences in interface adhesion in the presence of PP-$\gamma$-MA is proposed in terms of relaxation spectra of polypropylene–wood composites obtained by DMTA. DMTA has been widely used to investigate the structures and viscoelastic behaviors of composite materials as determined by their storage modulus ($E'$), loss modulus ($E''$) and loss factor ($\tan \delta$). This analysis technique can provide information on the stiffness of the composites (Kim et al., 2005). Relaxation peaks ($\alpha$, $\beta$ and $\gamma$) are observed for the $\tan \delta$ curves, which are caused by the onset of the various motions of the chain molecules. The dominant $\beta$ peak represents the glass-to-rubber transition of the amorphous portion in composites and is assigned to the glass transition temperature.

For determination of adhesion factor as interfacial interaction criterion, Correa et al., (2007) has been used equation originated from Kubat et al., (1990) work, about high density polyethylene filled with 20 Vol. % glass fibers. They assumed that the mechanical loss factor ($\tan \delta_c$) of the composite can be written:

$$\tan \delta_c = \Phi_f \tan \delta_f + \Phi_i \tan \delta_i + \Phi_p \tan \delta_p$$

Where the subscript $f$, $i$ and $p$ denotes filler, interphase, and matrix respectively and $\Phi$ is the corresponding volume fraction. By considering $\delta_i = 0$ and since the volume fraction of the interphase is rather small, above equation can be rearranged as follows:

$$\tan \delta_c = \Phi_f \tan \delta_f + \Phi_p \tan \delta_p$$
\[
\frac{\tan \delta_c}{\tan \delta_p} = (1 + \Phi_f)(1 + A)
\] (2)

\[
A = \left[ \frac{\Phi_f}{(1 + \Phi_f)} \right] \frac{\tan \delta_c}{\tan \delta_p}
\] (3)

Where Equation (3) can be rewritten as:

\[
A = \left[ \left( \frac{1}{1 + \Phi_f} \right) \left( \frac{\tan \delta_c}{\tan \delta_p} \right) \right] - 1
\] (4)

With calculating A factor from DMAT data, one can interpret the interaction in the interphase, where there is strong interaction between wood fiber and polymer matrix due to reduction of macromolecular mobility in the vicinity of the filler surface, A factor decreases. In other words, a low value of A factor is an indication of good adhesion or high degree of interaction between two phases. This factor presents a macroscopic quantitative measure of interfacial adhesion during dynamic loading.

5. Experimental

5.1 Materials

Polypropylene of Arak Petrochemical Company in Iran (Trade Name of V30S) with a density of 0.9 g/cm³, and the melt flow index (MFI) of 16 g/10 min was used in this study as matrix. 60-mesh virgin wood flour was used as filler. The characteristics of the natural fibres are shown in Fig. 15.

![Chemical Components (%)](image)

Cellulose: 41, Hemicellulose: 30, Lignin: 25 and Others: 4

Fig. 15. Characteristics of the wood flour.
The chemical structure of natural fibres was measured according to TAPPI standard and aspect ratio was obtained using optical microscopy. Triethoxy vinyl silane, acrylic acid; benzoyl chloride and sodium hydroxide were from Merck Co, Germany.

5.2 Preparation of natural fibers

5.2.1 Modification with sodium hydroxide
The Wood flour was introduced in a stainless steel vessel and 2 wt.% solution of NaOH was added into the vessel and stirred well. Wood flour was immersed for half an hour. Once this time was over, the fillers were separated from the solution and washed with distilled water containing a few percent of acetic acid to remove residual of alkali. The washed fiber was then dried in the oven at 80° C for 24 hours.

5.2.2 Modification with benzoyl chloride
Wood flour was dipped in solution of 5% of NaOH and benzoyl chloride for 15 minutes. Ethanol solution was used to remove extra benzoyl chloride for one hour. Finally the fiber was washed with distilled water and dried in oven at 80° C for 24 hours.

5.2.3 Modification with acrylic acid
Wood flour (which was treated with NaOH) was immersed to acrylic acid solution at 50° C for half an hour and was then washed and dried similar to previous steps.

5.2.4 Modification with silane
The silane used was Triethoxy vinyl silane. 1% of the respective silane was prepared by mixing with an ethanol/water mixture in the ratio 60/40 and was allowed to stand for 1 h. The pH of the solution was maintained between 3.5- 4 with the addition of acetic acid. Wood flour dipped in this solution and was allowed to stand for 1.5 h. The ethanol/water mixture was drained out and the washing and drying steps were repeated as mentioned in previous treatments.

5.3 Processing of the composites
The modified and unmodified wood flour was dried at 103±2 °C to constant weight before mixing process. PP and the modified and unmodified wood flour were blended in a batch mixer (Haake Buchler) at 190°C and 60 rpm for 8 min. In all cases, the weight ratio of fiber and polymer was 40:60 (Table 2). From the compounds which had been granulated, specimens were injection molded into ASTM standard by an injection molder at a molding temperature of 190°C and injection pressure was 3 Mpa.

5.4 Measurements

5.4.1 Thermo-mechanical test
Dynamic mechanical thermal analysis (DMTA) was carried out by using Triton instrument, Model Tritic 2000 made by UK in triple-point bending mode. The dimension of each sample...
was 5×1×2 cm. The range of testing temperature was from -50 to 150°C and the experiments were performed at 1 Hz frequency and heating rate of 2°C/min. During testing DMTA parameters of storage modulus and loss factor were recorded as function of temperature. Then based on equation (4) data analyzed for determining A factor.

<table>
<thead>
<tr>
<th>Code*</th>
<th>Polypropylene content (Wt. %)</th>
<th>Wood flour content (Wt. %)</th>
<th>PP-g-MA (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>UW-P</td>
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<td>40</td>
<td>0</td>
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<tr>
<td>SW-P-M</td>
<td>60</td>
<td>40</td>
<td>3</td>
</tr>
</tbody>
</table>


Table 2. Composition of the Studied WPCs.

5.4.2 Mechanical test

Tensile strength tests of the specimens were carried out according to ASTM D-638 by Instron 6025 model from UK at crosshead speed of 5 mm/min. For each test and type of the composite, five specimens were tested and the average values are reported.

5.4.3 Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectra of raw and treated wood flour were recorded on a Bomem, 150-MB series model Spectrophotometer to characterize the chemical change upon treatment of the wood flour with chemical components.

5.4.4 Scanning Electron Microscopy (SEM)

The morphology of the wood modified-PP composites and interfacial bonding between the filler and the PP matrix was examined using a scanning electron microscope (JXA-840) supplied by JEOL Company Limited, Japan. The samples were viewed perpendicular to the fractured surfaces.

6. Results and discussion

6.1 FTIR

FTIR Spectrum in Fig. 16 shows a spectrum of modified and unmodified wood flour samples. As can be seen, the intensity of the peak around 3400 cm\(^{-1}\), which is evidence of OH band, is decreased after treatment of fibers. The intensity of the band around 1730 cm\(^{-1}\)
increased due to formation of ester band from the reaction between OH group and bezoyl chloride. The intensity peak for aromatic ring at 1508.2 cm$^{-1}$ is decreased after surface modification due to removal of lignin. A strong peak at 1730 cm$^{-1}$ in the FTIR spectrum indicates the presence of acetyl group in the fiber. The intensity peak at 1037.6 cm$^{-1}$ is increased after silane absorbance, which is an overlap of si-o-si band and c-o stretching of fiber (Lu & Drazel, 2010). In the presence of moisture, hydrolysable alkoxy group leads to the formation of silanols. The silanol then reacts with the hydroxyl group of the fiber, forming stable covalent bonds to the cell wall that are chemisorbed onto the fiber surface (Agrawal et al., 2000).

### 6.2 Adhesion factor

Results for the adhesion factor as an evaluation parameter for fillers-polymer interactions versus temperature is presented in Fig. 17 for different chemical modification.

Fig. 16. FTIR spectra of the chemical treated wood flour.

Fig. 17. Adhesion factor versus temperature for the treated WPCs.
Adhesion factor presents a macroscopic quantitative measure of interfacial adhesion during dynamic loading and at high levels of interface adhesion, the molecular mobility surrounding the filler is reduced, and consequently low values of the adhesion factor suggest improved interactions at the matrix-filler interface (Kubat et al., 1990). As can be seen, below of glass transition temperature, the maximum amount of adhesion factors are related to untreated samples which means the weakest interface has been formed for samples containing untreated wood flour. It seems the chemical modification facilitates the interaction between fillers polymer and decreases the adhesion factor. It is important to note that adhesion factor seems to be very sensitive to glass transition temperature of samples. Around this temperature (around 22°C), slope of curves changes and the adhesion factor passes through a maximum due to more polymer chains mobility. According to Kubat et al., (1990) by increasing the temperature there was a release of the thermal stresses at the filler surface and reduced filler–matrix friction and should be related to a more cohesive matrix–filler interface (lower A). In other words, a strong interfacial adhesion i.e. samples which are treated with silane, restricts the chain mobility at the filler matrix interface, therefore the adhesion factor decreases and its maximum shifts to higher temperature. At the higher end of the temperature range, the most curves converge.

6.3 Storage modulus

The variation of the storage modulus (E’) value of the composites as a function of temperature is shown in Fig. 18 for different chemical treatment. E’ Value determines relevant stiffness of WPCs (Kim et al., 2005).

![Fig. 18. Storage modulus versus temperature for the treated WPCs.](image)

The stiffness of the composites is greater than that of the neat PP in the whole temperature range, and this trend is more significant in the higher temperature range. Fillers play an important role in increasing the storage modulus of polymeric materials. As can be seen, a general decrease trend was also observed over the entire range of temperature and with incorporation of wood flour to PP, significant increase in the E’ values of composites is clearly seen. This is probably due to increase in the stiffness of the matrix with the reinforcing effect
Thermoplastic Matrix Reinforced with Natural Fibers: A Study on Interfacial Behavior

imparted by the fiber, which allowed a greater degree of stress transfer at the interface (Jain et al., 1992). As the temperature is increased, relaxation process of the molecular matrix is initiated. Also, thermal expansion occurs which decreases the intermolecular forces (George et al., 1999). An appreciable improvement in the storage modulus was observed for the treated composite, due to the increase in the interfacial stiffness brought about by the more intense filler-matrix interaction. The composite modified by silane improves the interfacial adhesion more than other composites and this more lessens the molecular mobility in the interfacial region. In Storage modulus plots, around temperature 22°C, slope of most curves change that can be considerable as β transition. At the higher end of the temperature range, the curves of PP and unmodified composites converge.

6.4 Tan δ

Fig. 19 shows the loss factor (tan δ) versus temperature for wood-PP composites and their corresponding different chemical treatment. The tan δ peak was shifted to higher temperature for filled samples in comparison to neat polypropylene. Relaxation peaks for treated and untreated samples are present for the tan δ curves in the vicinity of -40°C (γ), 22°C (β) and 100°C (α) which are caused by the onset of the various motions of the chain molecules. The dominant β-peak represents the glass-to-rubber transition of the amorphous portion in PP and is assigned to the glass transition temperature.

![Graph showing Tan δ versus temperature for the treated WPC.](image)

Table 3 depicts the shift in glass transition temperature of the sample which is taken from tan δ curves. Depending on the nature of lignocelluloses filler and filler/matrix interaction, glass transition of the composites shifts to higher temperature. In other words, during stress transfer at the interface the strong bonding causes the fiber constraint and the poor bonding leads to dissipation energy. Among composites, those containing unmodified samples have the lowest values, whereas those containing acrylic acid treated samples have the highest tan δ values compared with the other samples. The difference between various chemical modifications becomes more pronounced at higher temperatures.

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Table 3. Shift in glass transition temperature of the treated WPC.

The effects of PP-g-Ma coupling agent on the storage modulus and tan δ of the silane treated wood flour /PP composites are shown in Fig. 20. As can be seen, the addition of PP-g-MA improved E’ of the composites, that was because PP-g-MA could lead to the creation of a thin and irregular polymer layer, which could assist formation of plastic deformation zone around the fiber (Hristov et al., 2004). Further, incorporation of compatibilizer to composites containing silane treated wood flour decreased tan δ due to the more intense filler-matrix interaction. This results indicated that, simultaneous use of silane and coupling agent on storage modulus and tan delta had synergic effect.

Fig. 20. Simultaneous effect of compatibilizer and silane on storage modulus and loss factor of the wood flour/PP composite.

6.5 Tensile properties

Results for the tensile strength and modulus of composites as function of chemical modification are presented in Fig. 21. Incorporation of wood flour in PP matrix significantly increased strength and modulus of composites. The increase in tensile strength or modulus is primarily attributed to the presence of fiber, which allowed a uniform stress distribution from continuous PP matrix to dispersed fiber phase (Coutinho et al., 1997).

Benzoylation treatment of fiber enhancement the tensile modulus of composites, but all other modulus has no significant variation together. Wood flour after modification are
somewhat leached, leading to dissolution of hemicellulose, lignin and pectin. The removal of surface impurities can make the fiber cleaner and rougher than before (Liu et al., 2009). Wood flour reinforced plastic composites often showed enhancement in tensile strength upon different modification owing to the increased fiber-matrix adhesion. Optimum strength is observed for alkali treated composite.

Fig. 21. Tensile strength and modulus of neat PP and the ones reinforced with modified and unmodified fiber composites.

Fig. 22 illustrated the result of tensile strength conducted on the modified specimens with and without PP-g-MA. The tensile strength of the composites increased with using coupling agent; because of improve the bonding strength between wood flour and PP matrix. So, the tensile strength of composites increased with conjunction of use both modified fiber and coupling agent.

Fig. 22. Tensile strength of modified and unmodified fiber composites with and without coupling agent.
6.6 Surface morphology

It is also clear from the SEM images in Fig. 23a that the wood fibers in unmodified sample are pulled out easily and some holes are noticed around the fibers which imply that there are weak interactions between the filler and polymer. As it can be seen in Fig. 23e, there is a better polymer-filler adhesion with the silane treatment than in the composite prepared with untreated wood flour, which implies an increase in the thickness of the interface between the particles and polymers. In samples undergone alkali treatment (Fig. 23b), fibers removed from pp matrix and broken, but not the isolated fibrils were observed, which means that the interactions between the phases are not strong enough. Similar trend is also observed for samples containing acrylic acid (Fig. 23c) and benzoyl (Fig. 23d) treated fibers. As in the case of adhesion factor, the best encapsulation of wood fibers with polymer matrix can be seen in samples with silane treatment. This explanation is similar to that of adhesion factor results.

Fig. 23. SEM Micrographs of modified wood polymer composites with: (b) alkali, (c) acrylic acid, (d) benzoyl chloride, (e) silane, and (a) unmodified samples.

7. Conclusion

Due to the growing competition in producing cost-effective products, in addition to the excreted environmental limitations, natural fibers have recently become attractive to researchers because of their advantages over conventional mineral fillers. However, several limitations must be overcome in order to exploit the full potential of natural fibres. The incompatibility between natural fiber and polymer matrix is a major problem for interfacial adhesion between these two component materials, which is of critical importance for the mechanical properties of the composite. In the present chapter, we focused on the natural fiber-thermoplastic composites and its worldwide application markets, reviewed some influence factors on the injection molding process to produce the natural fibers thermoplastic compound and introduced some research on interfacial adhesion strength between natural fibers and thermoplastic matrix and then reported the effect of various chemical modifications of wood fiber on the interfacial strength of wood polypropylene injection molded composites. The results showed that, at first, chemical modification of natural fiber is necessary and respectively silane and alkaline treatment of wood flour improved interfacial adhesion and so increased the mechanical performance of these composites. Secondly, simultaneous use of chemical modification and coupling agent on the properties had synergic effect. Thirdly, however, adhesion factor is a good way for understanding interfacial behavior of WPCs, further evidences of improved matrix-filler interactions is observed by SEM. Finally, future areas of interest should be focused on developing new coupling agents and new class of natural fiber modification such as enzymatic treatment.
8. References


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This book is composed of different chapters which are related to the subject of injection molding and written by leading international academic experts in the field. It contains introduction on polymer PVT measurements and two main application areas of polymer PVT data in injection molding, optimization for injection molding process, Powder Injection Molding which comprises Ceramic Injection Molding and Metal Injection Molding, ans some special techniques or applications in injection molding. It provides some clear presentation of injection molding process and equipment to direct people in plastics manufacturing to solve problems and avoid costly errors. With useful, fundamental information for knowing and optimizing the injection molding operation, the readers could gain some working knowledge of the injection molding.

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