



Effect of Fiber Surface Modification on the Thermo-Mechanical Behaviour of Wood-Polymer Composite

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The effects of fiber surface modification on the thermo-mechanical behaviour of wood polypropylene composites have been studied. The filler was treated with different chemical components including: alkaline, silane, acrylic acid and benzoyl chloride. The samples were fabricated by melt compounding in an internal mixer and then injection molding. The structure of the treated sample was studied by FTIR spectroscopy and scanning electron microscopy. Dynamic mechanical thermal analysis was performed in the range of -50 to +150 °C and adhesion factor, storage modulus and mechanical loss factor ($\tan \delta$) were recorded over the selected temperature range. The results showed that surface modification of wood flour decreased OH group intensity occurs on 3400 cm^{-1} band. It is found that with incorporation of wood to polypropylene the glass transition of the composites shifts to a higher temperature. The polypropylene composites made of silane treated wood showed the highest E' and $\tan \delta$ and lowest adhesion factor than the untreated ones. However, good correlations of chemical treatment and adhesion factor have been found for wood plastic composites, Further evidences of improved matrix-filler interactions is observed by scanning electron microscopy.

Key Words: Composite, Wood fiber, Chemical treatment, Storage modulus, Adhesion factor.

INTRODUCTION

The highly hydrophilic nature of some natural reinforcing materials, such as wood fibers, causes compatibility problems with the hydrophobic polymers in composites. The mechanical properties of the 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 composites¹. There are two approaches to improve the interfacial adhesion *i.e.*, polymeric matrix and lignocelluloses fiber modification. Different coupling agents have been used to modify the polymeric matrix and improve the interfacial strength and subsequently mechanical properties of wood plastic composites (WPCs)²⁻⁴. Another approach for enhancement of interfacial adhesion in wood plastic composite is fiber chemical surface modification before mixing with polymer⁵⁻⁷. Mechanism of the performance of these methods is different and is depended on the chemical structure of the reagent. For example, Kokot *et al.*⁸ reported alkaline treatment increases the amount of crystalline cellulose and removes natural and artificial impurities, producing a rough surface topography. Li *et al.*⁹ reported benzoylation makes the fibers more reactive due to their attachment to the benzoyl ($\text{C}_6\text{H}_5\text{C}=\text{O}$) and thus forms chemical links with the active sites on the matrix. Effect of some chemical

treatments of natural fiber such as silane and acrylic acid on the mechanical properties of wood plastic composite reported by farsi¹⁰. He observed silane and acrylation treatment onto the wood fibre improves interfacial adhesion with polypropylene matrix, which increases the mechanical strength of the composite. Morphological studies of chemical treated wood plastic composites by Ichazo *et al.*¹¹ showed that the silane improved wood fibre-polymer adhesion and the dispersion of particles, while the alkaline treatment only improves the dispersion. Effect of PP-MAH as coupling agent on the interface adhesion of wood plastic composite investigated by Correa *et al.*¹². They mentioned a method based on a simplified single rule of mixtures aiming to compare differences in interface adhesion in the presence of PP-MAH is proposed in terms of relaxation spectra of polypropylene-wood composites obtained by dynamic-mechanical thermal analysis (DMTA). Dynamic mechanical thermal analysis has been widely used to investigate the structures and viscoelastic behaviours 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^{13,14}. Relaxation peaks (α , β and γ) are observed for the $\tan \delta$ curves, 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 composites and is assigned to the glass transition temperature.

The effect of wood chemical surface modification on the interfacial strength was tracked using adhesion factor. This parameter is obtained from dynamic mechanical thermal data and has been originated from Kubat *et al.*¹⁵ 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:

$$\tan \delta_c = \Phi_f \tan \delta_f + \Phi_i \tan \delta_i + \Phi_p \tan \delta_p \quad (1)$$

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

$$\frac{\tan \delta_c}{\tan \delta_p} \cong (1 - \Phi_f)(1 + A) \quad (2)$$

$$A = \left[\frac{\Phi_i}{(1 - \Phi_f)} \right] \left(\frac{\tan \delta_i}{\tan \delta_p} \right) \quad (3)$$

where eqn. 3 can be rewritten as:

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

with calculating A factor from dynamic mechanical thermal 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.

In this paper, we report the effect of various chemical modifications of wood fiber on the interfacial strength of wood plastic composite. The effects of chemical surface treatments on the interfacial behaviour were evaluated by dynamic mechanical analysis and determined adhesion factor, storage modulus and loss factor. The structural and chemical changes occurred to the fiber upon treatments were characterized by scanning electron microscopy and FTIR spectroscopy.

EXPERIMENTAL

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 chemical composition of the wood flour was measured according to TAPPI standard is shown in Table-1. Triethoxy vinyl silane, acrylic acid, benzoyl chloride and sodium hydroxide were from Merck Co, Germany.

Fiber chemical modification: Wood flour was treated with mercerization, acetylation, benzoylation, acrylation and silane. The surface modifications were detailed in the previous

TABLE-1
CHEMICAL COMPOSITION OF WOOD FLOUR

Sample	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Others (%)
Wood flour	41	30	25	4

work¹⁰. For mercerization and benzoylation, the concentration of aqueous solution of sodium hydroxide and benzoyl chloride was 2 and 5 %, respectively. Finally the fiber was washed with distilled water and dried in oven at 80 °C for 24 h. For acetylation, the treatment time was 0.5 h and the wood fiber was then washed and dried similar to previous steps. For silane treatment, the NaOH treated fiber was immersed to 1 % triethoxy vinyl silane in solution of ethanol/water (60/40 ratio) for 2 h.

Processing of the composites: The untreated and treated wood flour was dried at 103 ± 2 °C to constant weight before mixing process. Polypropylene and the untreated and treated 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.

TABLE-2
COMPOSITION OF THE STUDIED COMPOSITES

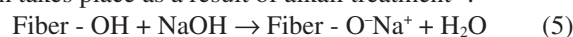
Code*	Polypropylene content (wt. %)	Wood flour content (wt. %)
PP	100	0
UW-P	60	40
AW-P	60	40
BW-P	60	40
CW-P	60	40
SW-P	60	40

*PP: Polypropylene, W: Wood Flour, U: Unmodified, A: Alkaline, B: Benzoylation, C: Acrylation, S: Silane

Dynamic mechanical thermal analysis was performed by Triton, Model Tritic 2000, UK. Dimension of samples were 5 cm × 1 cm × 2 cm. The range of testing temperature was from -50 to +150 °C and the experiments were carried out at 1 Hz frequency. The experiment was performed in the triple points bending mode for evaluation of storage modulus and loss factor. Then based on eqn. 4 data analyzed for determining A factor, storage modulus and loss factor. A scanning electron microscope (SEM, Jeol jxa-840, Japan) was used to study the microstructure of composites. FTIR Spectroscopy was carried out by Bomem, 150-MB series model machine.

RESULTS AND DISCUSSION

FTIR spectrum (Fig. 1) 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 following reaction takes place as a result of alkali treatment¹⁶:



The intensity of the band *ca.* 1730 cm⁻¹ increased due to formation of ester band from the reaction between OH group and bezoyl chloride. The reactions in this treatment can be illustrated as follows¹⁷:

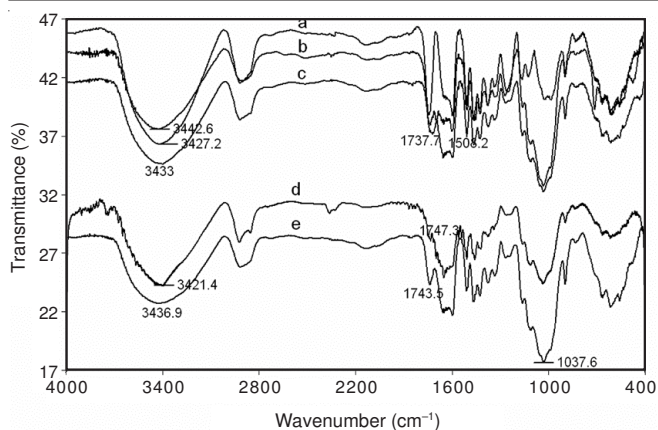
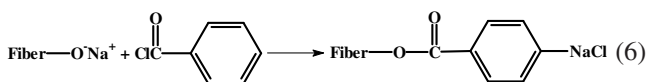
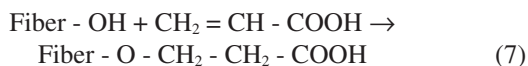


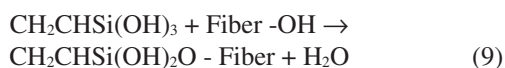
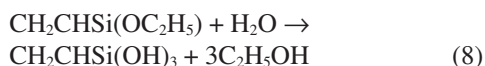
Fig. 1. FTIR spectra of the chemical treated wood flour (a) unmodified (b) benzoyl chloride (c) acrylic acid (d) alkali (e) silane



The intensity peak for aromatic ring at 1508 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 reaction was accomplished between OH groups and acrylic acid as follows¹⁸:



The intensity peak at 1037 cm^{-1} is increased after silane absorbance, which is an overlap of Si-O-Si band and C-O stretching of fiber¹⁹. In the presence of moisture, hydrolyzable 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 surface²⁰. The reaction schemes are given as follows:



Adhesion factor: Results for the adhesion factor as an evaluation parameter for fillers-polymer interactions *versus* temperature is presented in Fig. 2 for different chemical surface modification. The significant increase in the degree of interfacial adhesion on polypropylene-wood composites with applying different chemical modification of wood fiber was also confirmed by dynamic-mechanical thermal analysis, using an adhesion factor 'A' as evaluation parameter for filler-matrix interactions. This 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 interface¹⁵. 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.

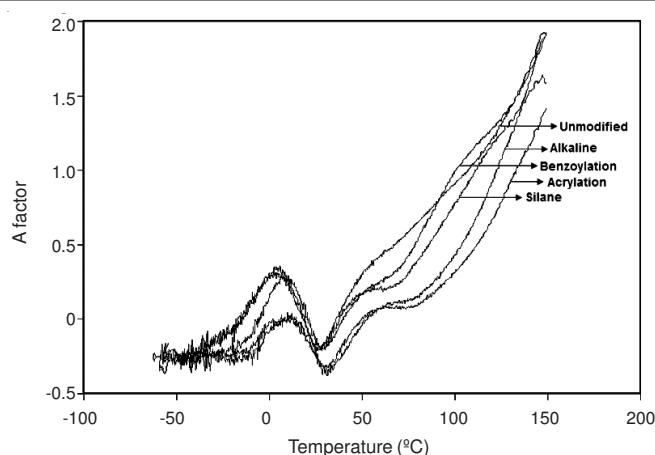


Fig. 2. Adhesion factor *versus* temperature for the treated wood plastic composite

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 (*ca.* $22 \text{ }^\circ\text{C}$), slope of curves changes and the adhesion factor passes through a maximum due to more polymer chains mobility. According to Kubat *et al.*¹⁵ and Chua²¹ 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.

Storage modulus: The variation of the storage modulus (E') value of the composites as a function of temperature in the range from -50 to $+150 \text{ }^\circ\text{C}$ is shown in Fig. 3 for different chemical treatment. Storage modulus (E') value determines relevant stiffness of wood plastic composites¹³. The stiffness of the composites is greater than that of the neat polypropylene 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 polypropylene, significant increase in the storage modulus values of composites is clearly seen. This is probably due to increase in the stiffness of the matrix with the reinforcing effect imparted by the fiber, which allowed a greater degree of stress transfer at the interface²². As the temperature is increased, relaxation process of the molecular matrix is initiated. Also, the thermal expansion occurs which decreases the intermolecular forces²³. 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 at $22 \text{ }^\circ\text{C}$, slope

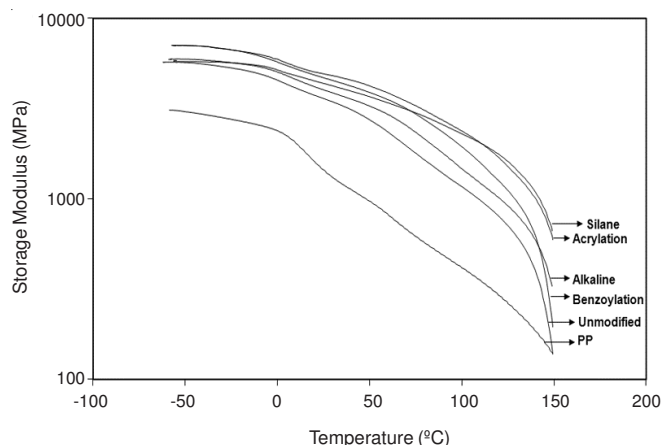


Fig. 3. Storage modulus *versus* temperature for the treated wood plastic composite

of most curves change that can be considerable as β -transition. At the higher end of the temperature range, the curves of polypropylene and unmodified composites converge.

Mechanical loss factor (Tan δ): Fig. 4 shows the mechanical loss factor ($\tan \delta$) *versus* temperature for wood-polypropylene composites and their corresponding different chemical treatment. The $\tan \delta$ 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 $\tan \delta$ 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 polypropylene and is assigned to the glass transition temperature. Table-3 depicts the shift in glass transition temperature of the sample which is taken from $\tan \delta$ 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 $\tan \delta$ values compared with the other samples. The difference between various chemical modifications becomes more pronounced at higher temperatures.

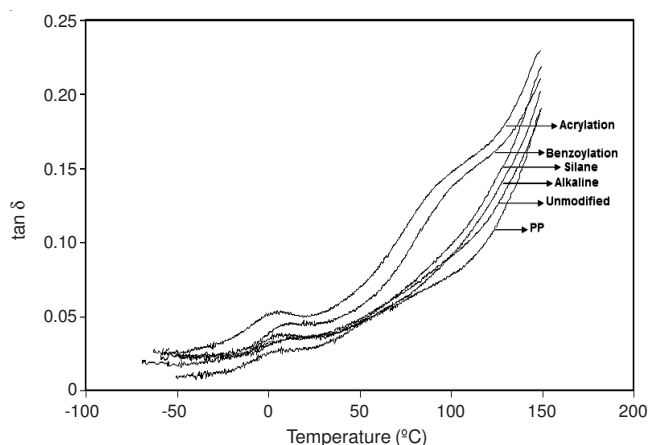


Fig. 4. $\tan \delta$ *versus* temperature for the treated wood plastic composite

TABLE-3
SHIFT IN GLASS TRANSITION TEMPERATURE OF
THE TREATED WOOD PLASTIC COMPOSITE

Sample	Shift in T_g ($^\circ\text{C}$)
Polypropylene	–
Unmodified	2
Acrylation	7
Benzoylation	8
Alkaline	6
Silane	13

Surface morphology: It is also clear from the SEM images in Fig. 5a 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. 5e, 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. 5b), fibers removed from polypropylene 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. 5c) and benzoyl (Fig. 5d) 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 treat-

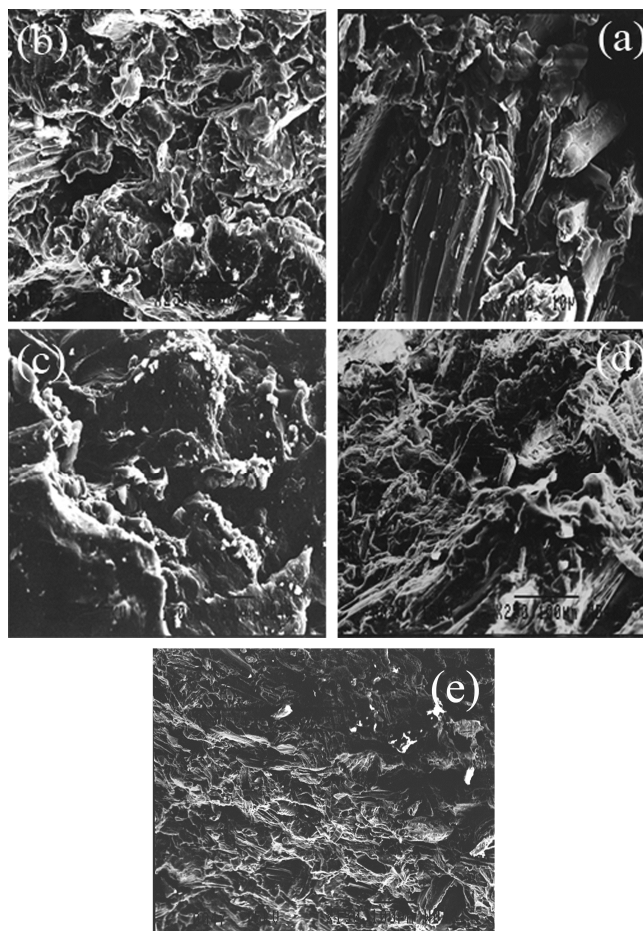


Fig. 5. SEM micrographs of modified wood polymer composites with: (b) alkali, (c) acrylic acid, (d) benzoyl chloride, (e) silane and (a) unmodified samples

ment. This explanation is similar to that of adhesion factor results. But, further evidences of adhesion are observed by scanning electron microscopy.

Conclusion

The present work showed the analysis of the interfacial behaviour of wood/polypropylene composites which treated by four chemical components including silane, sodium hydroxide, benzoyl chloride and acrylic acid. The following conclusions were drawn:

(1) FTIR spectra of treated wood fiber showed that the bonds at 3400, 1740, 1730 and 1037 cm^{-1} were highlighted due to reaction of OH groups, formation of ester, presence of acetyl and Si-O-Si group in samples, respectively.

(2) The maximum amount of adhesion factors are related to untreated samples which means the weakest interface has been formed for samples containing untreated lignocellulosic fillers. Chemical treatment facilitated the interaction between fillers-polymer and decreased the adhesion factor and best interfacial adhesion was demonstrated in composite containing silane.

(3) The maximum shift in peak of $\tan \delta$ was observed for δ sample containing silane treated wood fiber due to the highest interaction between fiber and matrix.

(4) SEM micrographs showed that the best encapsulation of wood flour by polymer matrix *i.e.* the best interaction between polymer and wood flour is observed in samples containing of silane.

(5) However, adhesion factor is a way for understanding interfacial behaviour of wood plastic composites, further evidences of improved matrix-filler interactions is observed by scanning electron microscopy.

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