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EFFECT OF SURFACE FREE ENERGY OF WOOD-FLOUR AND ITS POLAR COMPONENT ON THE MECHANICAL AND PHYSICAL PROPERTIES OF WOOD-THERMOPLASTIC COMPOSITES

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Abstract. The primary objectives of this study were to investigate the relationship between surface free energy of wood-flour (WF) and the mechanical and physical properties of wood-high density polyethylene (HDPE) composites (WPCs). The contact angles of different liquids against unmodified and modified poplar WF with 4% n-stearylacrylate were measured with capillary rise methods, the surface free energy and the correspondent dispersive and polar components were calculated based on Washburn equation and the methodology suggested by Owens-Wendt-Kaelble. The results showed that the surface free energy of WF increased from 23.43 mJ/m^2 to 46.88 mJ/m^2, which was higher than the surface free energy of HDPE (31.2 mJ/m^2), and its correspondent polar component decreased from 18.79 mJ/m^2 to 1.21 mJ/m^2 and the dispersive component increased from 4.64 mJ/m^2 to 45.67 mJ/m^2 after the modification with 4% n-stearylacrylate, which make it ready for the spreading of HDPE on the surface of WF. The tensile strength and flexural strength of WPC samples made with modified WF were obviously improved due to the modification. The water absorption and thickness swelling of WPC samples prepared with the modified WF were lower than those with the unmodified WF which could be attributed to the poor adhesion between the unmodified WF and polymer matrix. The improved compatibility between WF and HDPE was well confirmed by SEM.

1. INTRODUCTION

Wood plastic composites (WPCs) have received considerable attention from industry in recent years because of the increasing environmental awareness and the worldwide shortage of trees in many areas. The term WPC refers to any composite that contains wood fibers and thermosets or thermoplastics. Thermosets are plastics that, once cured, cannot be melted by repeating. Thermoplastics are plastics that can be repeatedly melted. This property allows other materials, such as wood fibers, to be mixed with the plastic to form a composite product. Polypropylene (PP), polyethylene (PE), and polyvinyl chloride (PVC) are the widely used thermoplastics for WPCs, and currently they are very common in building, construction, furniture and automotive products [1]. The interfacial adhesion between wood fibers and the thermoplastic matrix plays an important role in determining the performance of polymer-wood composites. Strong interactions result in good adhesion and efficient stress transfer from the matrix to the filler, leading to good mechanical properties and water-resistance [2,3]. High-density-polyethylene (HDPE) is commonly used as a matrix in WPCs. The problem is that the combination the wood-flour with a HDPE matrix often leads to the composites having poor

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mechanical properties and strong water absorption. This can be attributed to poor compatibility between the polar hydrophilic wood-flour and the non-polar hydrophobic HDPE matrix, and also to the poor dispersion of wood-flour in HDPE matrix due to the strong interactions between wood particles resulting from hydrogen bonding [4,5].

To improve the compatibility, the fiber surface or the matrix surface has to be modified. A number of studies showed that the fiber-matrix bonding can be enhanced by the use of coupling agents [2,6-12]. However, there are not many reports related to the effect of fiber modification using n-stearylacrylate. In this work an attempt was made to analyze the suitability of using n-stearylacrylate as coupling agent for wood fiber/HDPE composites and evaluate the characteristics of wood fibers by surface free energy and its components, and the effect of surface free energy of wood-flour and its polar component on the mechanical and physical properties were also investigated.

2. EXPERIMENTAL

2.1. Materials

High-density-polyethylene (HDPE) was obtained from PetroChina Company Ltd. under the trade name T60-800 with a density of 0.963 g/cm3, and a melt index 6-8 g/10min at 190 °C.

The poplar wood fibers used in this study were collected from a local sawmill and subsequently, were manually screened on a sieve and 40-60 mesh particles were collected, and then were dried in an oven at 105 °C for 24 h to a moisture content ~3%.

Methanol, formamide were provided by Beijing Chemical Plant, n-stearylacrylate and distilled water were prepared in the laboratory by ourselves.

2.2. Surface treatment of wood-flour and analysis

2.2.1. Surface treatment

The poplar wood fibers were treated using 4% n-stearylacrylate in an SHR-50A high-speed mixer at 120 °C for 5 min and stored in a sealed bag for evaluating the characteristics and preparing samples.

2.2.2. Contact angle measurements

According to Washburn equation [13,14]

$$h^2 = \frac{\gamma_L R t \cos\theta}{2\eta}, \quad (1)$$

where h is the height of liquid penetration into the capillary at time t; γL is the surface free energy of liquid; η is the viscosity of liquid; θ is the contact angle of the liquid against a solid; R is the average effective radius of capillary.

If make

$$K = \frac{\gamma_L R \cos\theta}{2\eta}. \quad (2)$$

Eq. (1) will be transformed into

$$h^2 = Kt. \quad (3)$$

K can be obtained from the coefficient of the equation of h^2-t based on the experiment.

Then

$$R = \frac{2K\eta}{\gamma_L \cos\theta} \quad (4)$$

and

$$\cos\theta = \frac{2K\eta}{\gamma_L R}. \quad (5)$$

The contact angles of different liquids against a solid can be determined by the equation of h^2-t. The WF system can be considered as a capillary system, and the average effective radius of capillary can be considered as a constant when the filled conditions (the filled speed, height and weight) of WF in the glass tube are identical, it can be calculated as per the liquid whose contact angle against WF is zero. Then the contact angles of other liquids against WF can be obtained according to Eq. (5).

The poplar WF was filled in the glass tube under the same condition (the same speed, height and weight), then the filled glass tubes were fixed upon the liquid for 2 h to reach adsorption balance of liquid molecules on the surface of WF. After that, the height of glass tube was adjusted to make sure the glass tube was in the liquid for 2 mm. When the liquid rose to the 2 mm scale line, the stopwatch began to work, and the height (h) of liquid in the glass tube and the time (t) of rising were recorded at a certain interval. Six replicates were tested for a certain liquid and the mean was used.

2.2.3. Calculation of surface free energy and its polar component

The principle of calculating the surface free energy of a solid and its polar component through the

contact angles of liquids against the solid is the equation of Young [15-17]:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta, \quad (6)$$

where γ_{SV} is the surface free energy of a solid which is equilibrated with the steam of liquid; γ_{SL} is the free energy of liquid-solid interface; γ_{LV} is the surface free energy of a liquid; θ is the contact angle of a liquid against the solid.

According to the viewpoint of Owens-Wendt-Kaelble [18,19], the surface free energy of a solid can be divided into dispersive and polar components and the summation of the components is approximately equal to the surface free energy of the solid ($\gamma_S^0 = \gamma_S^d + \gamma_S^p$). if there exist interactions of dispersion and polar forces between a solid and a liquid, the free energy of the interface between the liquid and the solid can be determined by the following equation:

$$\gamma_{SL} = \gamma_{LV} + \gamma_S^0 - 2\left(\gamma_S^d \times \gamma_{LV}^d\right)^{1/2} - 2\left(\gamma_S^p \times \gamma_{LV}^p\right)^{1/2}, \quad (7)$$

where γ_{SL} is the free energy of the interface between a liquid and a solid; γ_{LV} is the surface free energy of the liquid; γ_S^0 is the surface free energy of the solid; γ_S^d is the dispersive component of the surface free energy of the solid; γ_S^p is the polar component of the surface free energy of the solid; γ_{LV}^d is the dispersive component of the surface free energy of the liquid; γ_{LV}^p is the polar component of the surface free energy of the liquid.

Then combine Eq. (7) with Eq. (6) and the difference between γ_S^p and γ_{LV} was ignored [24], the following equation can be obtained:

$$\gamma_{LV}\left(1+\cos\theta\right) = 2\left(\gamma_S^d \times \gamma_{LV}^d\right)^{1/2} + 2\left(\gamma_S^p \times \gamma_{LV}^p\right)^{1/2}. \quad (8)$$

In Eq. (8), only γ_S^d and γ_S^p are unknown. if we can find two liquids whose γ_{LV}^d and γ_{LV}^p are known, γ_S^d and γ_S^p can be calculated through the contact angles of the two liquids against the solid.

Here methanol was chosen as the liquid whose contact angle against the poplar WF is zero because of its low surface free energy. Therefore, the average effective radius of capillary *R* can be calculated as per the Eq. (4). Then the contact angles of methanol and formamide against the poplar WF can be obtained from Eq. (5). The γ_S^d and γ_S^p of poplar WF can be calculated by Eq. (8).

The dispersive and polar components of the surface free energies and viscosities of the liquids in the experiment were given in Table 1.

2.3. Composite fabrication

The raw and treated poplar wood fibers were compounded with HDPE at the ratio 70:30 (wt/wt) in the SHR-50A high-speed mixer at room temperature, respectively. The mixture was processed with a Giant SHJ-30 twin-screw extruder to make composite pellets. The temperatures of the first to the last chambers were 130, 135, 140, 140, 130 °C, respectively. The rotational speed was 20 rpm. Then the composite pellets were extruded in an XSS-300 single-screw extruder with a die. The temperatures of the first to the last chambers were 150, 157, 162 °C and the die was 150 °C. The screw rotational rate was 10 rpm.

2.4. Mechanical properties test

The mechanical behavior of the composites was characterized via tensile and flexural tests in accordance with ASTM Standards D 638 and D 790, respectively. Strength measurements of samples were conducted using an Instron testing machine (Model 1186). The crosshead speed of tension testing was 10 mm/min. Six specimens were tested in each experiment to obtain a reliable average value. Prior to testing, all specimens were conditioned at 23±2 °C, 50±5% RH for at least 40 h according to ASTM D 618 to eliminate residual stresses due to processing.

Table1. The surface free energies, corresponding components [25] and viscosities of probe liquids.

Liquids	Items				
	γ_{LV} [mJ/m^2]	γ_{LV}^d [mJ/m^2]	γ_{LV}^p [mJ/m^2]	η* [mN·s/m^2]	η** [mN·s/m^2]
Distilled water	72.8	21.8	51	1.272	1.181
Formamide	57.9	34.4	23.5	4.934	4.222
Methanol	22.5	22.5	0	0.688	0.664

η* and η** were the viscosities of the liquids at the ambient temperature which were measured by Ubbelohde viscometer, respectively.

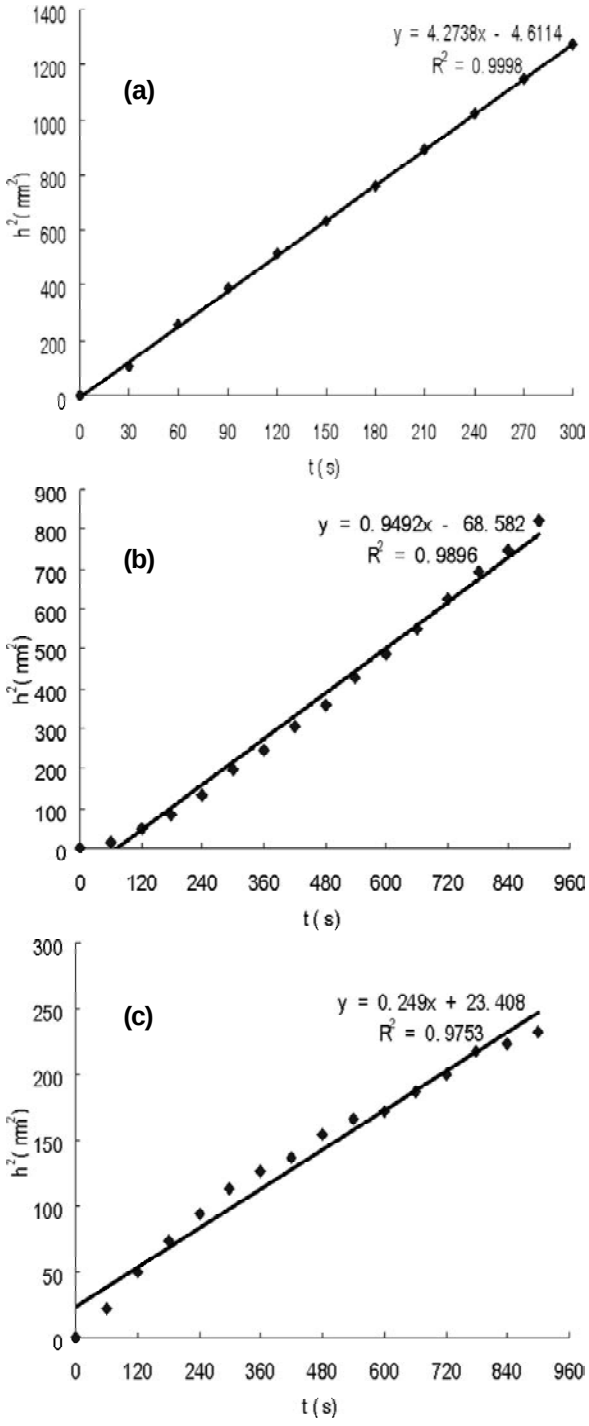

Fig. 1. The curves of h^2-t of three liquids against the raw WF. (a) The curve of h^2-t of methanol against the raw WF; (b) The curve of h^2-t of distilled water against the raw WF; (c) The curve of h^2-t of formamide against the raw WF.

2.5. Fracture surface analysis

The fractured surfaces of the flexural test specimens were sputter coated with gold and characterized with a HITACHI S-3000N SEM at an accelerating voltage of 5 kV and emission current of 95 μA.

2.6. Water absorption and thickness swelling

Water absorption and thickness swelling tests were conducted in accordance with ASTM D570-98, in which five specimens of each formulation were selected and dried in an oven for 24 h at 105 °C. The weight and thickness of the dried specimens were measured to a precision of 0.001 g and 0.001 mm, respectively. The specimens were then placed in distilled water and kept at a temperature 23±1 °C. For each measurement, specimens were removed from the water, and the surface water was wiped off with blotting paper. The weights and thicknesses of the specimens were measured at different time intervals during the long period of immersion. The measurements were terminated after the equilibrium states of the specimens were reached. Equilibrium moisture content (EMC) of the specimen is the moisture content when the daily weight change of the sample was less than 0.01% and thus the equilibrium state was assumed to be reached. The values of the water absorption as percentages were calculated with the following equation:

$$WA(t) = \frac{W_t - W_0}{W_0} \times 100, \quad (9)$$

where $WA(t)$ is the water absorption (%) at time t, W_0 is the oven-dried weight, and W_t is the weight of the specimen at a given immersion time t.

Also, the values of the thickness swelling as percentages were calculated with Eq. (10):

$$TS(t) = \frac{T_t - T_0}{T_0} \times 100, \quad (10)$$

where $TS(t)$ is the thickness swelling (%) at time t, T_0 is the initial thickness of the specimen, and T_t is the thickness at time t.

3. RESULTS AND DISCUSSION

3.1. The contact angles of three liquids against the untreated and treated WF

Fig. 1 and Fig. 2 show the curves of h^2-t of three liquids against the raw and treated WF. The values of K and cosine of contact angles of the liquids

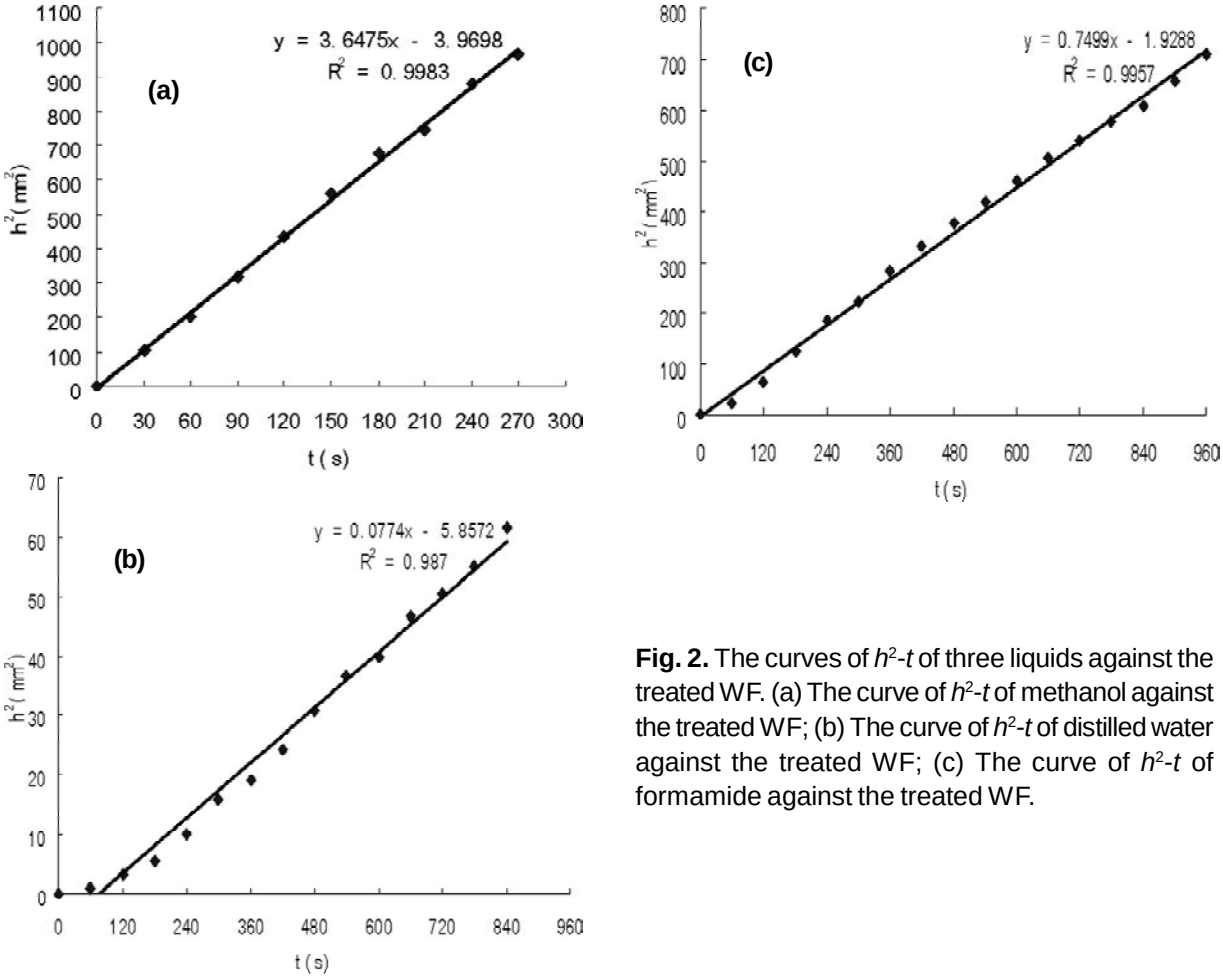

Fig. 2. The curves of h^2-t of three liquids against the treated WF. (a) The curve of h^2-t of methanol against the treated WF; (b) The curve of h^2-t of distilled water against the treated WF; (c) The curve of h^2-t of formamide against the treated WF.

against the raw and treated WF were listed in Table 2.

3.2. The surface free energies and its components of the raw and treated WF

The surface free energies and its components of the raw and treated *WF* were derived from putting the values of cosθ, γ_{LV}^d and γ_{LV}^p of distilled water and formamide in Eq. (8) and were listed in Table 3. From Table 3, we can see that the surface free energy of the raw poplar WF is 23.43 mJ/m^2 and the corresponding dispersive and polar components are 4.64 mJ/m^2 and 18.79 mJ/m^2, respectively. After treated using 4% n-stearylacrylate, the surface free energy of the treated poplar WF is 46.88 mJ/m^2 and the corresponding dispersive and polar components are 45.67 mJ/m^2 and 1.21 mJ/m^2, respectively. According to the standpoint of Zisman [21-24], only when the surface tension of a liquid is below the critical surface tension (γ_c) of a solid, the liquid can spread on the surface of the solid. HDPE is in liquid form at the processing temperature and its surface free energy is 31.2 mJ/m^2 [25], it is below the surface free energy of the treated poplar WF, so HDPE can spread on the surface of the treated poplar WF and it is possible for forming a good interfacial adhesion between HDPE and the treated poplar WF.

Table 2. The values of *K* and cosine of contact angles of three liquids against the untreated and treated WF.

Liquids	Types			
	Untreated WF		Treated WF	
	K	cosθ	*K*	cosθ
Methanol	4.2738	1.0000	3.6475	1.0000
Distilled water	0.9492	0.1269	0.0774	0.01167
Formamide	0.2490	0.1623	0.7499	0.50796

Table 3. The surface free energies and its components of the untreated and treated WF.

Types	Items γ_S [mJ/m^2]	γ_S^d [mJ/m^2]	γ_S^p [mJ/m^2]
Untreated WF	23.43	4.64	18.79
Treated WF	48.31	47.91	0.4

3.3. Mechanical properties

The tensile strength and flexural strength of WPCs with raw and treated poplar WF are shown in Fig. 3. The tensile strength of the composites with the poplar WF treated by 4% n-stearylacrylate increased by about 60% and the flexural strength increased by about 40%. N-stearylacrylate has a positive on the mechanical properties of the composites, because it strengths the interfacial bonding between the wood fiber and the matrix polymer, which resulted in good stress propagation and improved the mechanical performance.

3.4. Water absorption and thickness swelling

Water absorption curves for WPCs with raw and treated WF are illustrated in Fig. 4, in which the percentage of water absorbed is plotted against the time for the test specimens. As can be clearly seen, water absorption generally increased with the immersion time, reaching a certain value at which

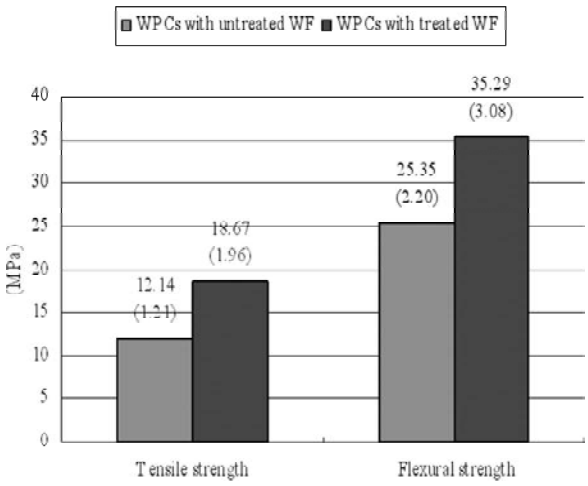

Fig. 3. Mechanical properties of WPCs with raw and treated WF (values in parentheses are standard deviations).

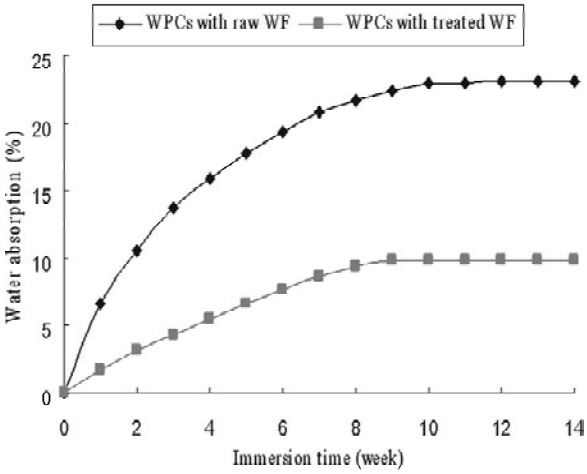

Fig. 4. Water absorption curves for WPCs with raw and treated WF.

no more water could be absorbed and the water content in the composites remained constant.

Fig. 4 also shows that the composites with treated WF exhibited lower water absorption than those made with raw WF. Adding n-stearylacrylate reduced the maximum water absorption by about 15%. The water absorption in the composites is mainly due to the presence of lumens, fine pores and hydrogen bonding sites in the WF, the gaps and flaws at the interfaces, and the microcracks in the matrix formed during the compounding process [26]. The presence of hydroxyl and other polar groups in various constituents of the WF resulted in poor compatibility between the hydrophilic WF and the hydrophobic plastics, which increases the water absorption. Water absorption by cellulose and hemicelluloses depends on the number of free hydroxyl groups thus the amorphous regions are accessible by water. On the other hand, plastics are water repellent and have much lower water sorption capability than wood. With the addition of n-stearylacrylate, the compatibility between WF and HDPE is improved because the ester groups entered into an esterification reaction with the surface hydroxyl groups of WF.

Thickness swelling curves for WPCs with raw and treated WF are illustrated in Fig. 5, in which the percentage of thickness swelling is plotted against the time for the test specimens. The thickness swelling of the composites increases with the water absorption and thus has a similar trend to the water absorption regarding the impact of coupling agent. WPCs with treated WF show that the maximum thickness swelling is reduced by about 5% compared to WPCs with raw WF.

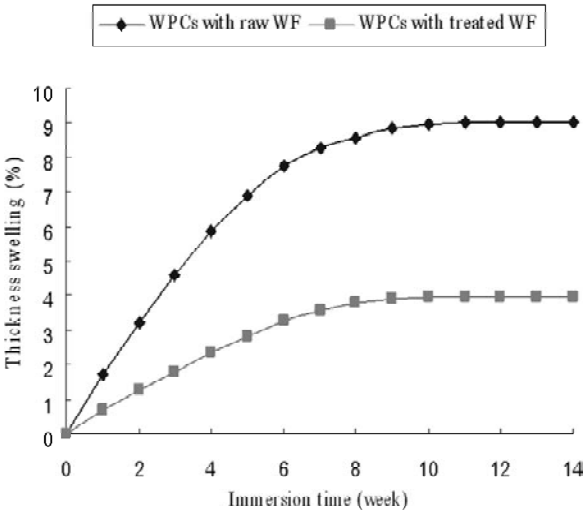

Fig. 5. Thickness swelling curves for WPCs with raw and treated WF.

3.5. Fracture surface observation

As reported in the literature, the morphology of polymer composites is a very important characteristic because it determines the physico-mechanical properties [27]. In this study, the state of the matrix/filler interface of with and without n-stearylacrylate as coupling agent was investigated by SEM.

Fig. 6 shows the SEM micrographs of the fracture surfaces of WPC samples with raw and treated poplar WF. As shown in Figs. 6a and 6b, the surfaces of the wood fibers are quite smooth and cavities can be seen between WF and the matrix polymer, these clearly indicate the poor interfacial adhesion between WF and the matrix polymer. This result contributes to the poor stress transfer from matrix polymer to WF leading to poor mechanical properties. Fig. 6c and shows the SEM micrographs taken from the fracture surface of the WPC samples with treated poplar WF. It can be observed better polymer/filler interfacial adhesion than in the WPC samples with raw poplar WF resulting in a reduction of the interfacial tension between WF and the matrix polymer. This would be expected to increase the mechanical properties and decrease the water absorption and thickness swelling of the composites. This conclusion can be supported by the mechanical properties values of WPCs shown in Fig. 3, water absorption values shown in Fig. 4 and thickness swelling values shown in Fig. 5.

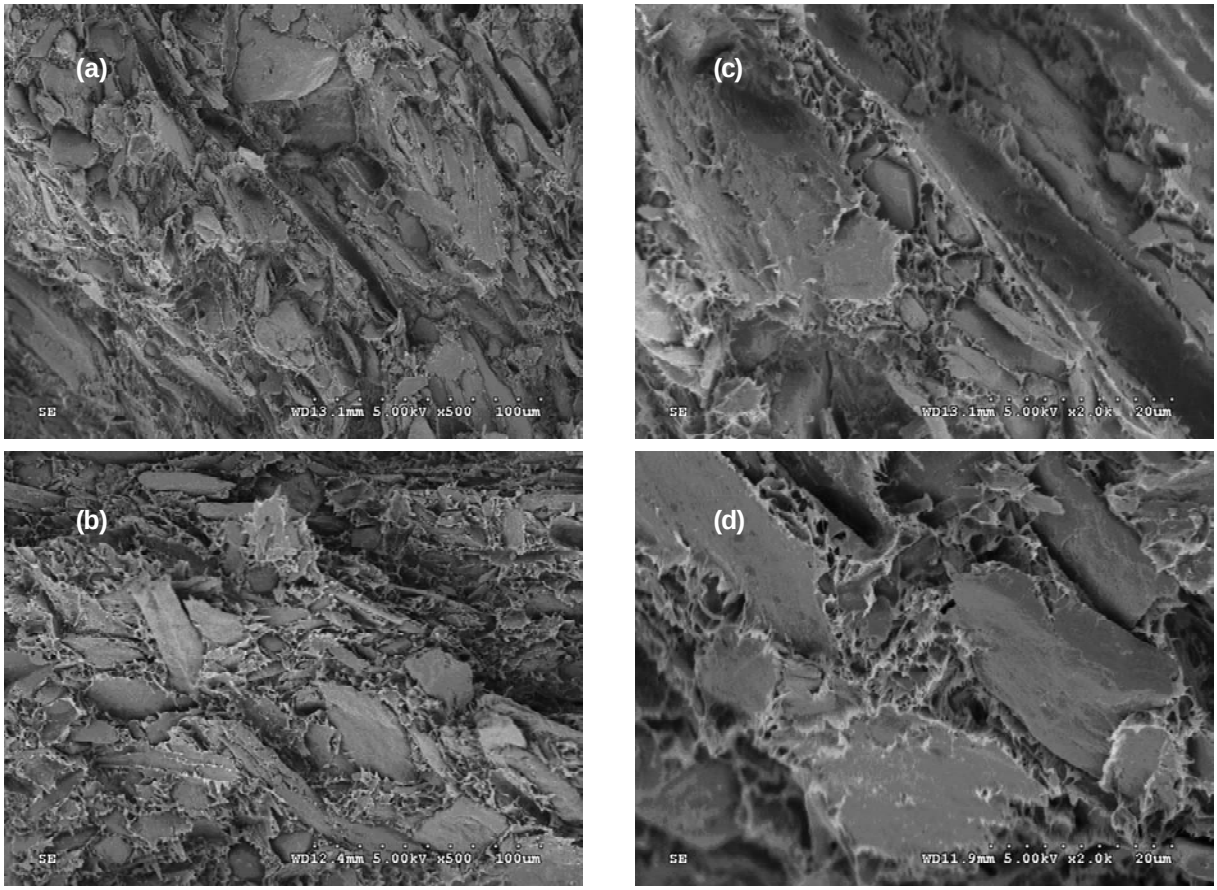

Fig. 6. Flexural fracture surfaces of WPCs with raw and treated WF. (a) WPCs with Raw WF; (b) WPCs with Raw WF; (c) WPCs with treated WF; (d) WPCs with treated WF.

4. CONCLUSIONS

The study shows that after the modification with 4% n-stearylacrylate, the surface free energy of the poplar WF increased from 23.43 to 46.88 mJ/m^2, which was higher than the surface free energy of HDPE (31.2 mJ/m^2), and its correspondent polar component decreased from 18.79 to 1.21 mJ/m^2 and the dispersive component increased from 4.64 to 45.67 mJ/m^2, So it was possible for the spreading of HDPE on the surface of the treated poplar WF and forming a good interfacial adhesion between the treated poplar WF and the matrix polymer. The tensile strength of the composites with the treated poplar WF increased by about 60% and the flexural strength increased by about 40%. The maximum water absorption of the WPCs with the treated poplar WF was reduced by about 15% and the maximum thickness swelling was reduced by about 5%. N-stearylacrylate is an effective coupling agent. The improved compatibility between WF and HDPE was well proved by SEM micrographs.

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