Effect of Fiber Treatment on the Water Absorption and Mechanical Properties of Hemp Fiber/Polyethylene Composites

Haixia Fang,[1] Yaolin Zhang,[1] James Deng,[1] Denis Rodrigue[2]

[1]FPInnovations, 319 rue Franquet, Quebec, Quebec, Canada, G1P 4R4
[2]Department of Chemical Engineering, Laval University, Quebec, Canada, G1K 7P4

Correspondence to: J. Deng (E-mail: james.deng@fpinnovations.ca)

ABSTRACT: The hemp fiber/polyethylene (PE) composites were prepared by varying the fiber shape (hemp flour and hemp fiber from thermomechanical refining), coupling agent (maleic anhydride grafted and copolymerized onto PE), coupling agent loading method (during fiber treating process in the thermomechanical refiner and compositing process in twin screw extruder), and compositing method (twin screw extruding and batch mixing). The paper firstly measured the moisture absorption properties of the treated fibers. The introduction of coupling agent during fiber treating process decreased effectively the moisture uptake. Then, the water absorption and mechanical properties were investigated on the hemp/PE composites. The loading of coupling agent during fiber treating process decreased the water uptake but also decreased the flexural yield strength, consequently resulted in lower flexural yield strength after water exposure. The composites prepared by batch mixing method were better than by twin screw extruding for the water resistance and mechanical properties. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

The study on the wood fiber reinforced plastics has received considerable attention of researchers and manufacturers for their good mechanical properties and environmental benefits.[1] In the recent years, a wide variety of natural fibers, such as flax, jute, hemp, sisal, etc. have also been investigated for the reinforced plastics.[2] The natural fiber can be manufactured by thermomechanical refining or chemical pulping treatment. The treatment influences not only the physical morphology but also the chemical compositions of fibers.[3] During chemical pulping treatment of wheat straw, partial removal of lignin and hemicellulose resulted better mechanical and thermal properties of fibers. However, the mechanical properties of the result composites were less than that from mechanical treated fibers. The strong interaction between the hydrophilic hydroxyl groups of cellulose brought about the poor dispersion of fibers in polymer matrix.

Polyolefins (PO) are commonly used in wood/plastic or natural fiber/plastic composites because their processing temperatures are below the degradation temperature of lignocellulose materials. The typical commercial PO studied include polyethylene (PE), polypropylene.[4] When PO was used as matrices, the improvement of adhesion between the composites has been the aim of many researchers during the last decades. The most widely used compatibilizers for such composites are maleated PO. The introduction of maleated PO increases the interfacial adhesion between natural fiber and PO, as well decreases the agglomeration of natural fibers.

The application of natural fibers in composites is limited by their hydrophilic nature, low thermal stability, and poor dispersion in polymer melts. The effects of moisture absorption on the dimensional stability and mechanical properties of some natural fiber reinforced polymer composites have been reported in previous studies.[5–9] The absorption of moisture can reduce fiber-matrix interaction, lead to poor stress transfer efficiencies, and result in the reduction of mechanical and dimensional properties. For this reason, moisture absorption in natural fiber-plastic composites must be considered in those applications with long service needs in dynamic environments.

In this article, the hemp fiber was treated by thermomechanical refining process at different conditions. The objective of this article is to compare the moisture absorption properties of hemp fiber with different treatment conditions, the mechanical properties and water uptake of the treated hemp fiber/PE

Table I. Coupling Agents and Temperatures Used in Hemp Fiber Treatment

Fiber code	Treatment temperature (°C)	Coupling agent	Content (wt %)
150N	150	None	–
150C	150	Epolene C-26	3
150W	150	WPC-576D	3
180N	180	None	–
180C	180	Epolene C-26	3
180W	180	WPC-576D	3

composites, and the water absorption on the mechanical properties of composites. Second, this article will evaluate the types and loading methods of coupling agents for effectively improving the water absorption and mechanical properties. Then, the influence of compounding process (batch mixing and twin screw extruding) on the mechanical properties of hemp fiber/PE composites will be studied.

MATERIALS AND METHODS

Materials

The hemp fibers were kindly supplied by Stemergy (Ontario, Canada). The fibers were initially processed at Stemergy to remove the shives and other contaminants. The hemp fibers were refined in an Andritz pressurized refiner at the MDF Pilot Plant of FPInnovations (Quebec City, Canada) with steam temperature of 150 and 180°C. The coupling agents were mixed with natural hemp fiber and then underwent the refining. The treated fiber and corresponding sample code were listed in Table I. The matrix polymer applied for making composites was high density polyethylene (HDPE, Dow TM 12450N Health), purchased from PolyOne (Mississauga, Ontario), which has a density of 950 kg m^{-3} and a melt flow index of 12 g (10 min)$^{-1}$ (190°C, 2.16-kg load).

Two types of maleated polyethylenes were selected as coupling agents, Epolene C-26 (Harwick Standard Distribution Corporation), and DupontTM Fusabond WPC-576D. As the manufacturer claimed, WPC-576D is an ethylene-maleic anhydride (MAH) copolymer, in which MAH is covalently incorporated into polymer chain. This new technology results in a higher level of reactive sites for chemical links with cellulose fibers and hence in a better performance of WPC-576D at lower additive concentrations compared to traditional graft derivatives.

Composites Preparation

The mass ratio of the fibers to polymer was 40:60 (w:w) for all blends. The hemp and PE composites (Table II) were compounded in a Leistritz 27/40D co-rotating twin-screw extruder. The processing temperature profiles were: 165, 168, 170, 175, 175, 175, 175, 175, 175, and 185°C from the feed hopper to the die exit. The flow rate was 3.0 kg h^{-1}, and screw rotation speed was 95 rpm. The compounded materials were cooled in a water bath at room temperature at the die exit and the extruded strands were cut by a 6" Conair Pelletizer (Model 304) into small pellets. The pellets were then used to produce rectangular plates by compression molding. The hot press (Carver) was operated at 190°C using a constant force of 8000 lb with an aluminum mold. The composites were preheated for 25 min and pressed at 8000 lb for another 20 min. The Telfon sheets were used on both sides of the plates, and no releasing agent was used.

The coupling agents were introduced in the composites by two approaches: (a) The coupling agents were introduced during treatment process before compounding in the twin screw extruder; (b) The coupling agent were introduced during compounding in the twin screw extruder for the refined fibers without coupling agent.

It was recognized that the hemp fiber was severely damaged during the twin screw extruder. In this work, some composites were also melting blended in a Haake batch mixer. The fibers were loaded after the melting of HDPE and coupling agent at 160°C

Table II. Formulations of PE/Hemp Composites Produced

Composite code[a]	Refining Temperature (°C)	Coupling agent[b]	Coupling agent loading method
150C-C	150	Epolene C-26	Compounding
150W-C	150	WPC-576D	Compounding
150C-T	150	Epolene C-26	Refining
150W-T	150	WPC-576D	Refining
180C-C	180	Epolene C-26	Compounding
180W-C	180	WPC-576D	Compounding
180C-T	180	Epolene C-26	Refining
180W-T	180	WPC-576D	Refining
HFC-C	–	Epolene C-26	Compounding
150-M	150	None	None
150C-M	150	Epolene C-26	Compounding
150W-M	150	WPC-576D	Compounding

[a]150 and 180 refer to treatment temperature; The first letter (C and W) refer to the coupling agent Epolene C-26 or WPC-576D; The second letter (C and T) refer to the coupling agent being added during compounding in the twin-screw extruder or fiber treatment step; M refers to melt blending in the batch mixer, [b]3 wt % of coupling agent was based on the fiber weight.
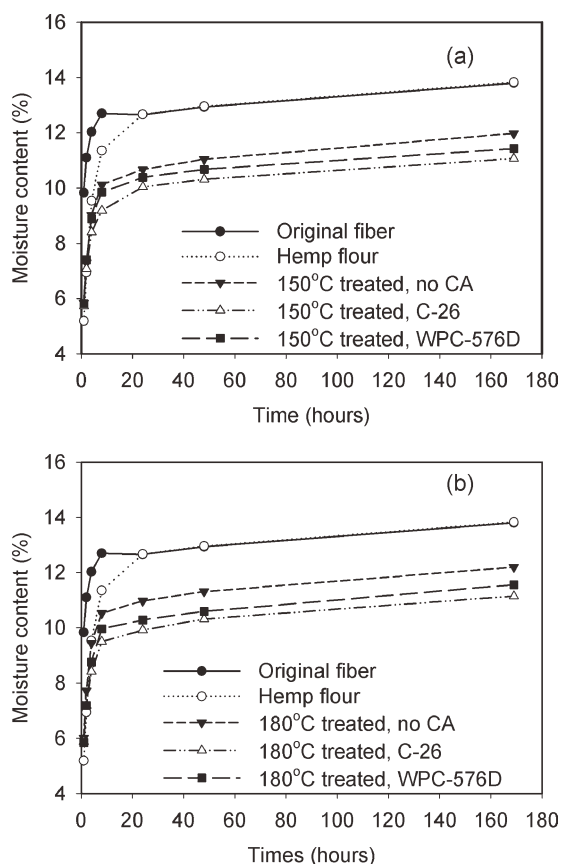
Figure 1. Moisture absorption properties of treated fibers (a: 150°C and b: 180°C), and comparison with original fiber and hemp flour.

and rotation speed of 30 rpm and then continued mixing for 6 min.

Measurement

Moisture Absorption of Treated Fibers. The original, treated hemp fibers, and hemp flour was oven dried at 105°C for 24 h and then cooled down to room temperature in a desiccator. The weights of the samples were taken before subjecting them to the humidity chamber (80% relative humidity and 20°C). The specimens were weighed regularly at 1, 2, 4, 8, 24, 48, and 169 h exposure. The moisture content of the sample at any given time (M_t) was calculated using the eq. (1):

$$M_t = \frac{W_t - W_0}{W_0} \quad (1)$$

Water Absorption of Composites. The water absorption test was carried out based on ASTM D-570. The samples were oven dried at 105°C for 24 h before immersing in distilled water at a temperature $20 \pm 1°C$. The specimens were removed from the water and the surface water was wiped off at certain periods of time and the equilibrium weight was determined. The content of water was calculated by the weight difference as eq. (1).

The bending tests were performed both on the dry and the water-soaked samples to determine the influence of the water content in the mechanical properties following the ASTM D-790 standard.

Scanning Electron Microscope. Scanning electron microscopy (SEM) (Jeol 840, Japan) was used to observe the fracture surface of the composites after bending test.

RESULTS AND DISCUSSION

Moisture Absorption of Original and Treated Fibers

The moisture absorption of the fibers and hemp flour were shown in Figure 1. Although the original hemp fiber absorbed much more moisture than hemp flour in the first 8 h, they reached the same moisture content after 24-h exposure. It can be concluded that the shape of the wood samples has influence on the initial moisture absorption rate but not on the long-term moisture absorption. The thermal mechanical refining on the fibers decreased the moisture absorption rate. The incorporation of coupling agent decreased the moisture absorption further. The coupling agent was supposed to distribute on the fiber surface and blocked the moisture permeation into the fiber. In addition, Epolene C-26 is more efficient to decrease the moisture absorption of treated fibers than WPC-576. The higher moisture of WPC-576 treated fibers may relate to the moisture absorption of copolymerized MAH function which was coated on the treated fiber. Between the treated fibers at two treatment temperatures, 150 and 180°C, the former one absorbed a little less water no matter with or without the coupling agent.

The cell wall of hemp fiber is composed of cellulose, hemicellulose and lignin. Their capacity to bind or store water was in an order of hemicellulose >cellulose > lignin.[10,11] The thermomechanical refining treatment can partially remove hemicellulose and lignin from hemp fiber and produce void on its surface. The treatment at 150°C eliminated partially the amorphous hemicellulose from the fiber surface and consequently decreased the moisture absorption content. However, the treatment at 180°C hydrolyzed more hemicellulose, leading to more free accessible hydroxyl groups and increased the moisture absorption comparing treatment at 150°C. The same effect of treatment on the surface characterise of fibers was reported by Wan et al.[12] The average pore diameter of Eucalyptu fiber decreased when the hemicellulose content decreased from 27.62 to 19.80% and then increased when the hemicellulose content decreased from 19.80 to 9.09%. The lower hemicellulose content promoted partially irreversible microfibril aggregation and leaded to more compact fibrillar structures and tensions in the microfibrils due to the finite dimensions of the cell wall. As a consequence, pores of the fiber cell wall were closed and average diameters of pores decreased. However, when the hemicellulose content decreased further, more micropores were produced and then connected to form large pores. More available hydroxyl function with removing of lignin and hemicellulose may also lead to higher moisture absorption of fibers.[13]

Mechanical Properties of Composites

Wood flour has a very low aspect ratio (ratio of length and diameter), less than 2.5. Sanschagrin et al.[14] reported the increasing mechanical properties of thermoplastic composites with the increasing aspect ratio of wood fibers from 5 to 25 and leveling off from 25 to 45% (column fraction of wood fiber 27%). Bledzki et al. found the increasing flexural modulus with fiber length from 5 to 40 mm (30 wt % fiber content).[15]
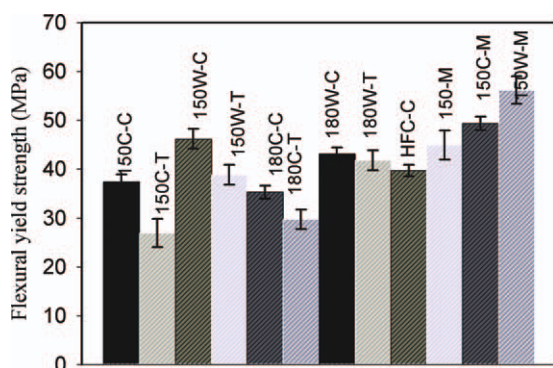
Figure 2. Flexural yield strength of the PE/hemp fiber composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Schirp and Stender reported the lower mechanical properties of treated wood fibers than wood flour (70% wood).[16] The fibers were shortened and uniformly dispersed in the matrix during twin screw extrusion. To obtain the improved mechanical properties with increasing fiber length, it needs good adhesion between wood fibers and the plastic matrix, uniform distribution of fibers in the matrix and adequate orientation of fibers.[17] Yam et al. pointed that dispersion of the fibers seems to be a dominating factor for the mechanical properties of wood fiber/HDPE composites.[18] The reduced mechanical strength occurs with both inadequate compounding causing poor dispersion and poor wetting of the fibers, and excessive compounding as well causing severe fiber damage. The other explanation is that the treatment removed partially the lignin and natural waxes, which can aid fiber dispersion in the nonpolar PE matrix.[18]

The average diameter for all the fibers was around 1mm, which was the gap distance between the blade discs. For the fiber lengths, there are two extremes: either the fibers are very small (less than 5 mm in length) or they are very long (more than 25 mm in length). The aspect ratio (L/D) was only influenced by the fiber length since the diameter is substantially constant to 1 mm. More than 80% of the fibers had the aspect ratio (L/D) higher than 35 and 15% of them had L/D of 5.[19]

The flexural stress and modulus of treated hemp fiber/PE composites were shown in Figures 2 and 3. Generally, the flexural strength and modulus was higher when coupling agent was loaded during extruding process than during fiber treating process. The flexural modulus of HFC-C was approximately similar to all the PE/hemp fiber composites except for 150C-C. The hemp flour/PE composites (HFC-C) had higher flexural yield strength than treated hemp fiber/PE composites (150C-C and 180C-C). The much lower flexural yield strength was found for composites with coupling agent introduced during fiber treating process (150C-T and 180C-T). WPC-576D was more efficient to improve the flexural yield stress and compatibilize the hemp/PE composites. The resulted composites were similar or higher than HFC-C.

Water Absorption of Composites
The moisture is predominantly absorbed by hemp fiber component in the composites, because PE matrix is water resistant.

The numerous free hydroxyl groups present in the hemp fiber cellulosic cell wall are responsible for forming hydrogen bonding with water molecules. The water absorption of the composites is dependent on the availability of free hydroxyl functions on the surface of the fiber. The study of Migneault et al.[20] presented the higher water absorption of extruded wood fiber/PE composites. The SEM analysis illustrated that the fibers at the surface of extruded WPC samples were randomly oriented, twisted, and damaged. The surface defects were clearly seen. The other two mechanism of water absorption into the composites include the diffusion of water molecules inside the microgap at the interface between the fiber and plastic phase due to incomplete wetability; the transport of water into the voids in the matrix formed during hot melt processing.

In most cases, water absorption processes of composites follow the prediction of Fick's law. First, the water uptake is linear to square root of time. Then it becomes slow gradually and reaches the equilibrium plateau at certain time. The water absorption values were fitted to eq. (2):

$$M_t/M_\infty = kt^n \tag{2}$$

where M_t and M_∞ are the moisture content at time t and that at the equilibrium. K and n are constants. The value of n is equal to 0.5 for Fickian diffusion. Referring to Table III, it is suggested that all composites followed the Fickian diffusion process as all showed n values closing to 0.5. The diffusion coefficient, D, can be determined from the linear regression analysis according to eq. (3):

$$M_t/M_\infty = (4/h)(D/\pi)^{1/2}t^{1/2} \tag{3}$$

where h is the sample thickness. The diffusion coefficients, D of the composites that reached equilibrium water content after 11 weeks water exposure were shown in Table III.

Effect of Hemp Fiber Shape. Figure 4 shows the water absorptions for the composites after 11 weeks of exposure, which varied upon the treatment temperature, coupling agent type and loading method. The composites containing hemp flour (HFC-C) absorbed the water the most slowly and did not reach the
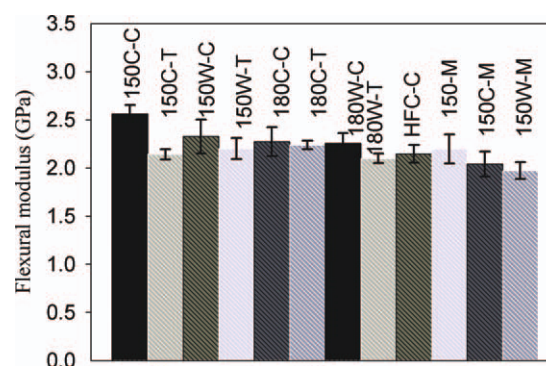

Figure 3. Flexural modulus of the PE/hemp fiber composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table III.** Equilibrium Water Uptake (M_∞), n and D for Some Composites

Composites	Equilibrium water uptake, (M_∞) (%)	n	Water diffusion coefficient $\times 10^{12}$, D ($m^2 s^{-1}$)
150C-C	8.96	0.55	1.05
150C-T	8.24	0.53	1.17
150W-C	8.58	0.59	0.54
150W-T	7.54	0.57	0.84
180C-C	7.97	0.58	0.78
180C-T	7.91	0.54	1.24
180W-C	7.96	0.58	0.62
180W-T	7.51	0.56	0.74

equilibrium until 11 weeks of exposure. It indicated that the better dispersion of hemp flour in PE matrix. The higher water absorption of composites manufactured from treated fibers can be explained: (a) the randomly orientation of fibers on the surface of samples; (b) incomplete encapsulation of the particles by the plastic matrix.

Effect of Loading Method of Coupling Agent. In general, the composites loaded with coupling agent during fiber treating
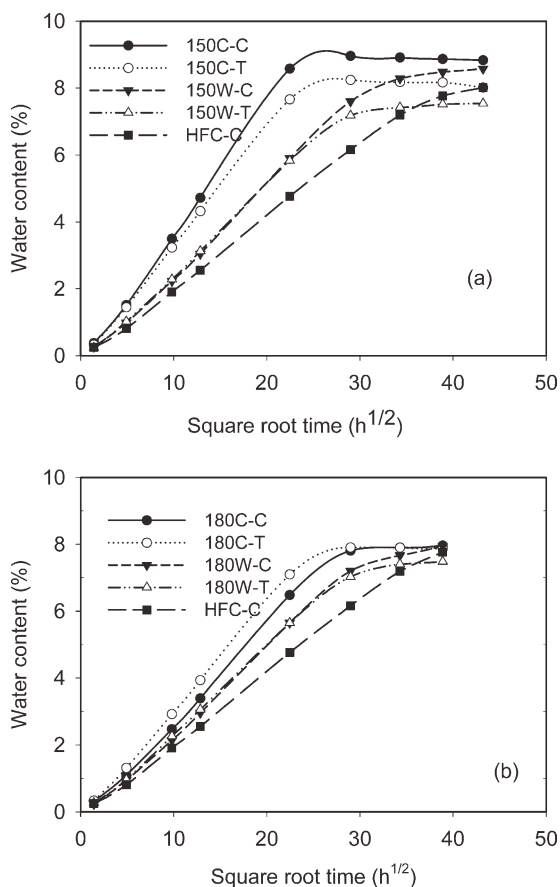
Figure 4. Water absorption of PE-hemp fiber composites: (a) 150°C and (b) 180°C treated fibers.
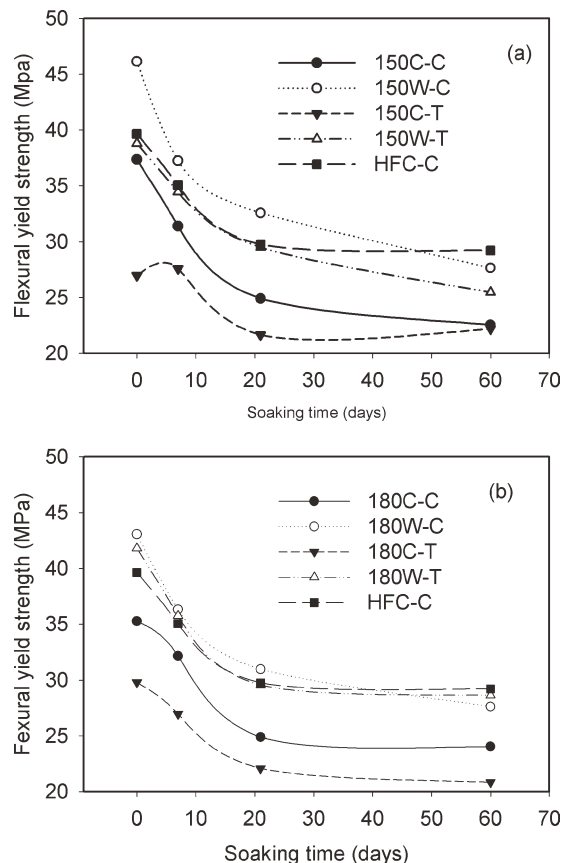

Figure 5. Flexural yield strength of PE/hemp fiber composites: (a) 150°C and (b) 180°C treated fibers.

process presented lower equilibrium water uptake (Figure 4). However, the initial water uptake rates were higher for most of the composites, with the excluding of 150C-C/150C-T. This explained the higher diffusion coefficient for those composites. The other explanation for this finding is that the water diffusion coefficient is reciprocal to the equilibrium water uptake.[21]

Effect of Coupling Agent. The coupling agent of WPC-576D is more effective than Epolene C-26 to lower the water absorption of composites, no matter it was loaded during treatment or compounding process. But they were still higher than HFC-C. It can be seen from Figure 1 that the moisture absorption of Epolene C-26 treated fibers was lower than WPC-576D treated one, but the corresponding plastic composites' water absorption was higher. The higher moisture absorption of WPC-576D treated fiber on account of the moisture absorption of MAH function exposure to the moisture. It confirmed the higher reactivity of coupling agent of WPC-576D with the hydroxyl function on hemp fibers.

Effect of Treatment Temperature. The fibers treated at 180°C absorbed a little more moisture than fibers treated at 150°C. However, the composites containing fibers treated at 180°C absorbed less water than fibers treated at 150°C. The higher hydroxyl function in the hemp fiber treated at 180°C
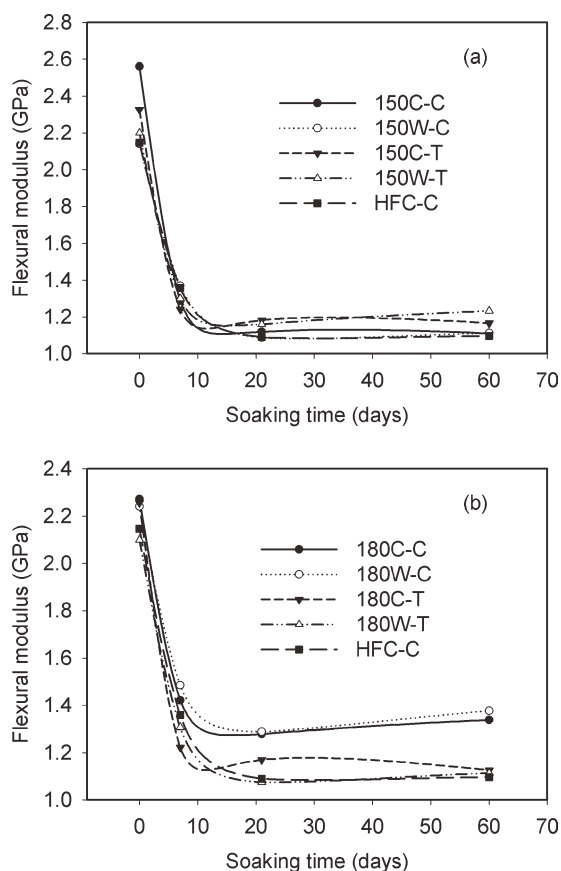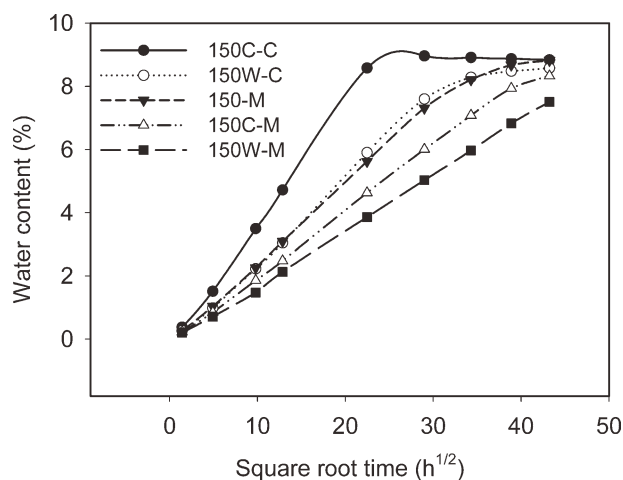
**Figure 6.** Lexural modulus of PE/hemp fiber composites: (a) 150°C and (b) 180°C treated fibers.

also resulted in the more bonding between fiber surface and PE matrix.

Effect of Water Absorption on the Mechanical Properties
Generally, the mechanical properties of natural fiber/polymer composites decrease considerably with the water absorption.
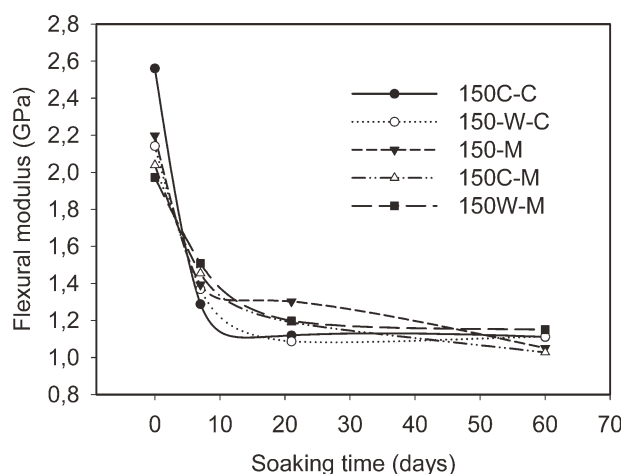

Figure 7. Water absorption of composites prepared by extruding/batch mixing and compression.
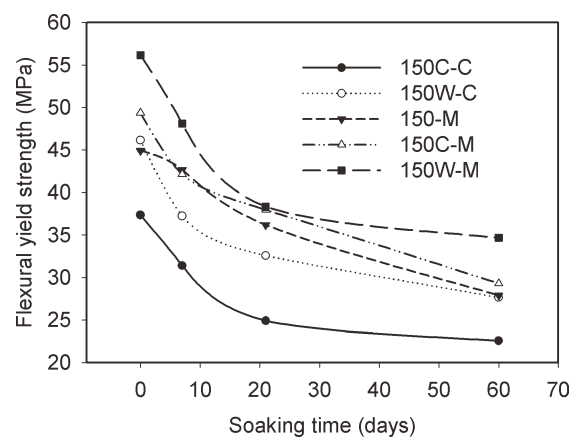

Figure 8. Flexural yield strength of composites prepared by extruding/batch mixing and compression.

Besides affecting the properties of the polymer matrix and the natural fibers themselves, water can seriously damage the fiber–matrix interface, leading to poor stress transfer efficiencies from matrix to reinforcement. The influence of water absorption on the bending properties of composites was shown in Figures 5 and 6.

From Figures 5 and 6, the flexural yield strength was higher for the composites with coupling agent loaded during compositing process in the extruder than during fiber treating process. Comparing with HFC-C, PE-hemp fiber composites (150C-C) had lower flexural yield strength before and after water exposure. However, PE-hemp fiber composites (150W-C) had higher flexural yield strength than HFC-C, although the latter absorbed less water. The flexural yield strength of 180W-C, 180W-T, and HFC-C were very close. HFC-C had the highest flexural yield strength after 60 days exposure in the water. The flexural modulus of all the composites decreased dramatically (33–50%) after 7 days exposure, and reached the low threshold after 21 days exposure.

Figure 9. Flexural modulus of composites prepared by extruding/batch mixing and compression.
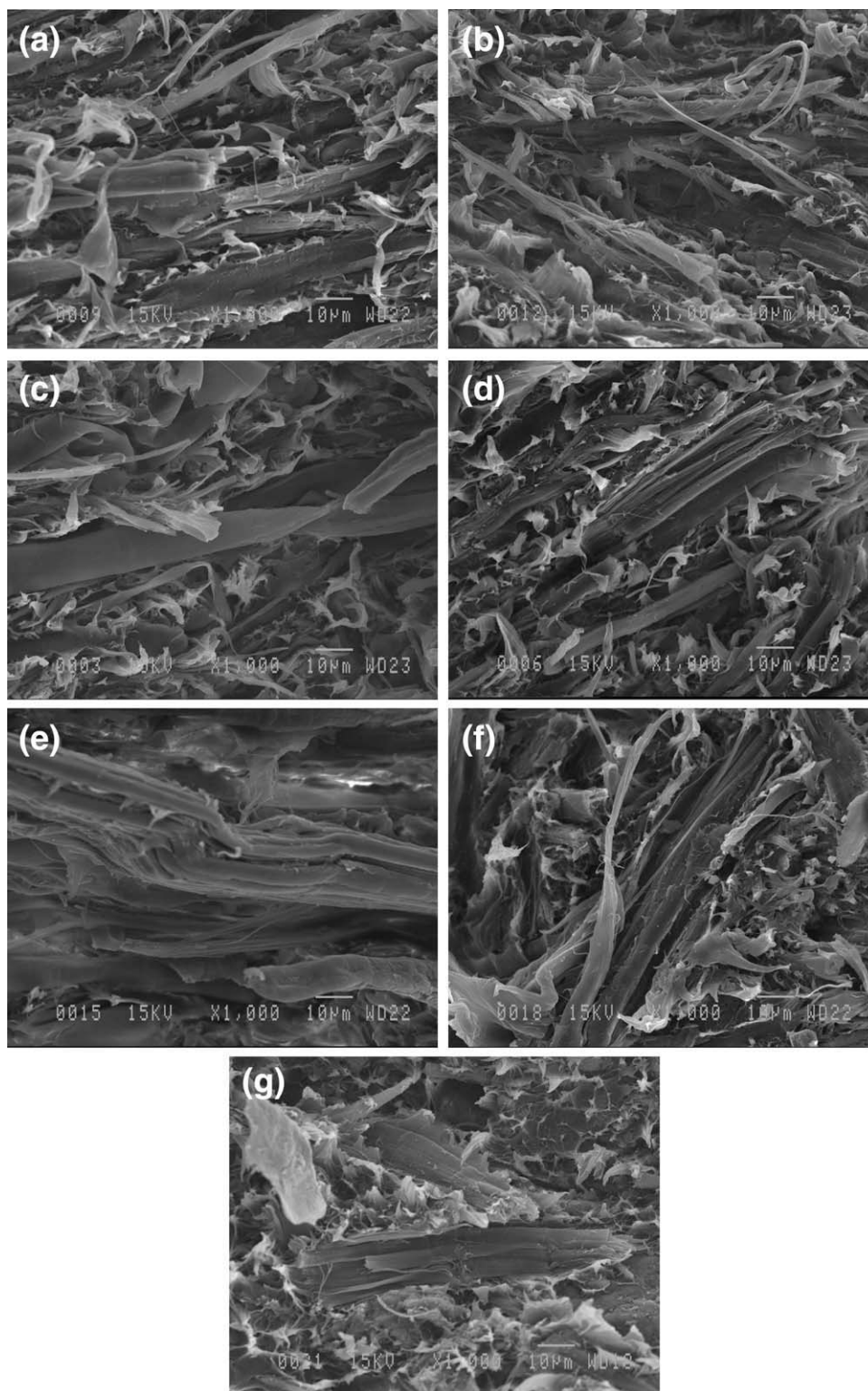
Figure 10. SEM micrograph of the fractured surface of composites. (a) 150C-T; (b) 150W-T; (c) 150C-C; (d)150W-C; (e) HFC-C; (f) 150C-M; and (g) 150W-M.

Effect of Compositing Method on the Mechanical and Water Absorption Properties

Figures 2 and 3 also showed the effect of compounding technique, extruding and batch mixing on the mechanical properties of treated fiber/PE composites. The batch mixed samples presented higher flexural yield strength due to the better dispersion and less damage of fibers. Similar behavior was also found by Schirp and Stender.[9] Figures 7–9 showed their difference of

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water uptake and the corresponding mechanical properties after water exposure. The batch mixed samples displayed lower water absorption rate and higher flexural yield strength.

SEM Microscopy

The SEM images of the fractured surfaces of the treated hemp fiber/PE composites are shown in Figure 10. It is clearly to see the gaps between the matrix and fiber for the composited compatibilized by coupling agent of Epolene C-26. The surface of hemp fiber was fairly clean. For the composites with coupling agent of WPC-576, the fibers were better covered by PE matrix and the gaps were reduced dramatically for both processing methods. These explained the better water resistance and mechanical properties of composites with WPC-576. With the same coupling agent (Epolene C-26), the hemp flour/PE composites (HFC-C) showed good adhesion between matrix and fiber.

CONCLUSIONS

1. The PE/hemp flour composites were superior to the large aspect ratio hemp fibers from thermomechanical refining. It indicated the importance of homogenous fiber dispersion in polymer matrix.
2. The coupling agent was more efficient to increase the flexural yield strength of composites when it was introduced during compositing process in the twin screw extruder than during fiber treatment process. The former composites had higher flexural yield strength after water exposure, although their water uptakes were higher.
3. The influence of compositing method on the mechanical and water absorption properties of the composites was investigated. The composites prepared in a batch mixer showed better properties than that from twin screw extruder.

ACKNOWLEDGMENTS

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