Mechanical and Thermal Properties of Eucalyptus Fiber Composites Bonding by Blocked Polyurethane Adhesive

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ABSTRACT: In this work, composites from eucalyptus fiber (EF) and polyurethane emulsion (PU) were prepared. Ethyl cellosolve-blocked polyisocyanate (EC-bp) was used as a novel adhesive and the mechanical and water absorption properties of the prepared composites were analyzed. The results showed that the tensile, flexural, and water resistance properties of the composites modified by such adhesive were enhanced compared with those of unmodified ones. Effects of EC-bp on the thermal degradation and the morphology of the composites were also investigated and compared. The presence of modification on the surface of EC-bp treated EF/PU composites was identified by Fourier transform infrared spectroscopy (FTIR) from the appearance of CO bands absorbance and the reducing of relative intensity of OH. Thermo-gravimetric analysis (TGA) resulted that the thermal stability of the modified composites was improved. Environmental scanning electron microscopy (ESEM) was used to observe the morphology and evaluate the interfacial adhesion of the composites. The results showed that much better homogeneity morphology of the modified composites was achieved, which indicated that the prepared EC-bp as an adhesive could improve the interfacial adhesion. These findings appeared that the occurrence of strong bonds between the composite components in the presence of EC-bp, rather than the unique existence of Van der Waals interactions among the nonpolar structures or the hydrogen bonding interaction. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 984–991, 2012

Key words: composites; mechanical properties; thermal properties; morphology; blocked polyisocyanate

INTRODUCTION

In recent years, interest in the development of new composite materials derived from natural fibers has grown markedly in the composite science due to their degradable, renewable, and eco-friendly properties.[1–5] The growing commercial importance of these materials has expanded efforts to understand their structure-properties relations and for exploring new methodologies for their production.[6]

Natural fibers can be renewable and cheaper substitutes for synthetic fibers. They offer many advantages, such as low cost, low density, high toughness, and biodegradability.[7] In addition, from the environmental points of view, the development of biocomposites utilized the recycled natural materials is assuming greater importance since these biomaterial products can be reclaimed and recycled for the production of second-generation materials.[8] However, the low mechanical strength caused by its strong hydrophilic of natural fibers limits the application. This situation can be explained by the noneffective bonding between the natural materials.[9] Polyurethane emulsion has been used to modify eucalyptus fiber and hence to improve their morphological properties and to improve handle in this work. However, the improvement on mechanical properties was not evident, and the water resistance and thermal stability were not enhanced evidently.

Several methods of improving adhesion in natural fiber composites have been described in the literature. Some of them are based on fiber modification[10] and others are based on the addition of the coupling agent for interfacial adhesion improvement.[11–15] In addition, the chemical treatment of natural fibers with isocyanates, to be used as reinforcement in composites, has been also widely studied.[16–20] However, isocyanates are highly moisture sensitive, which lead to the difficulty in the practical application. Blocked isocyanates provide a solution for overcoming the drawbacks. It is therefore considered that introducing blocked polyisocyanate as an adhesive to produce chemical bonding between eucalyptus fibers and polyurethane in respect of all-round property improvement or improved property balance.

Blocked polyisocyanate are widely used for adhesives or crosslinkings, which could prevent the
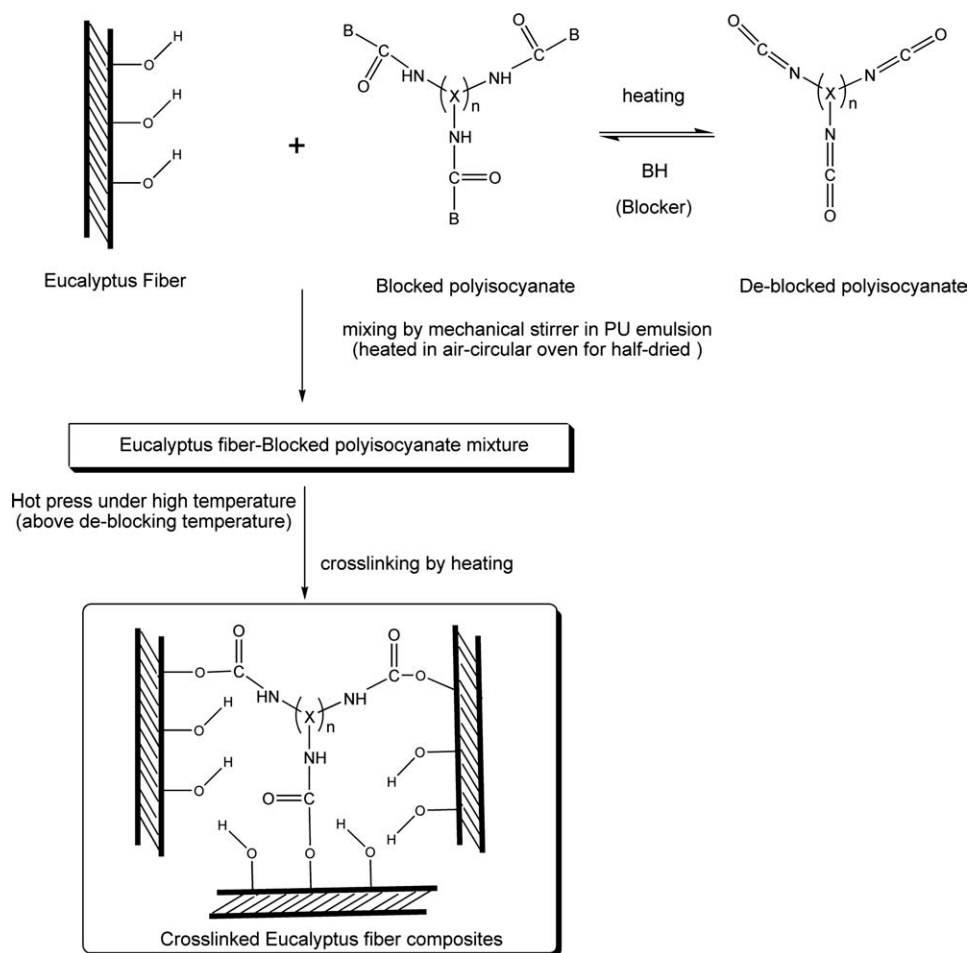
Scheme 1 The sketch map of EC-blocked polyisocyanate as an adhesive for eucalyptus fiber composites.

hydrolysis of the reagents and the crosslinking effect of the thermal released isocyanate groups would occurred directly in the manufactured process, avoiding the use of anhydrous organic solvents and consequently reducing the cost of the modification process. The efficiency of such adhesive in natural fiber composites is function to their electronic structure and to their reactivity. Therefore, the reactivity of aryl isocyanates toward natural fiber is much higher than that of alkyl isocyanates.[21]

In this study, EC-blocked polyisocyanate based on toluene 2, 4-diisocyanate (TDI) was introduced as a novel adhesive into the EF/PU composites. The sketch map of EC-blocked polyisocyanate as an adhesive for eucalyptus fiber composites was shown in Scheme 1. Under the de-blocking temperature, this blocked polyisocyanate could generate free isocyanate groups and further react with the plentiful hydroxyl groups of eucalyptus fibers. Polyurethane could also get crosslinking structure during the manufactured process. Effects of such adhesive on the mechanical, water resistance, and thermal stability properties of EF/PU composites were investigated and discussed.

EXPERIMENTAL

Materials

The eucalyptus fibers (EF) (50 ~ 80 mesh) used in this study were obtained from Shaoguan, China. The fibers were oven-dried at 100°C for about 48 h prior to use. EC-blocked polyisocyanate (EC-bp) and hydroxyl-terminated polyurethane emulsion (PU) were prepared in our lab. They were prepared according to the procedure reported in our previous work.[22] The maximum deblocking temperature was around 150°C. The synthetic route and the structure were presented in Schemes 2 and 3. All other chemicals were purchased from commercial sources.

Composites preparation

Eucalyptus fibers and polyurethane emulsion were firstly mixed in a Waring Blender for 10 min. Then, EC-blocked polyisocyanate as an adhesive was added in. The blender was used to blend the materials together thoroughly. In the next step, mixed samples were baked in the oven at 60°C until half-dried. Subsequently, the mixtures were placed in a rectangular
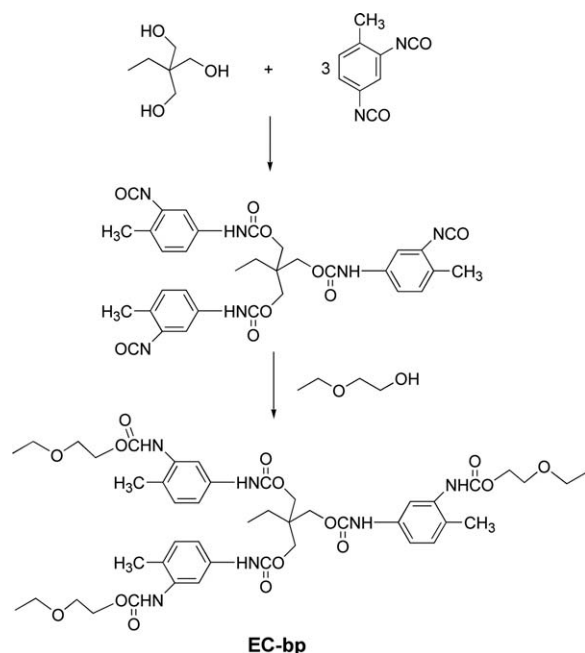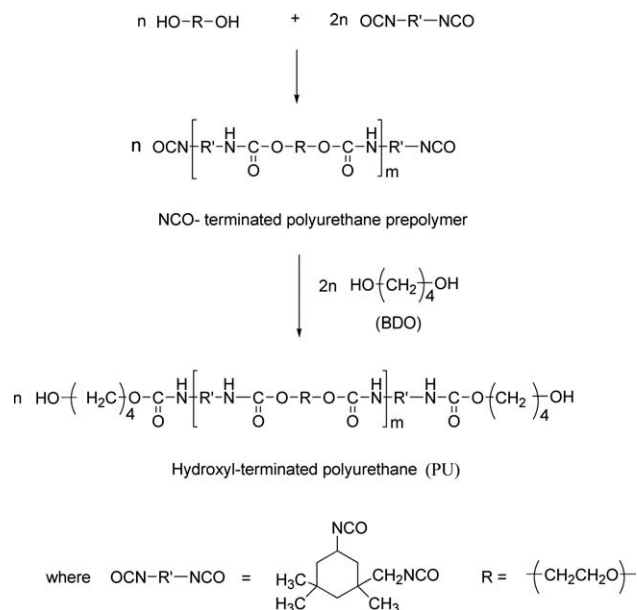
Scheme 2 Synthesis of EC-blocked polyisocyanate.

Scheme 3 Synthesis of hydroxyl-terminated polyurethane.

mold box with a size of 10 ×10 cm^2 and manually formed. A manually controlled, hot-press (Burkle L100) was used to press the panels at 180°C (above deblocking temperature) for 10 min and at a series of pressure of 5, 10, and 20 MPa, respectively. The panels were then cooled in the press for an additional 10 min until they reached a final approximately room temperature. Average target thickness of the panel was 3 mm. The compositions and the codes for panel production were listed in Table I.

FTIR analysis

Fourier transform infrared spectra (FTIR) of samples were recorded using an RFX-65A IR analyzer in the range 400–4000 cm^{-1} using KBr disks at room temperature.

Mechanical testing

All mechanical tests were performed according to ASTM D638 for tensile tests and ASTM D790 for flexural tests. Tensile and flexural properties of the produced composites were tested using an Instron 1122 universal testing machine. All results presented were the average values of five measurements.

Thermal stability

Thermo-gravimetric analysis (TGA) was carried out with a TA Instruments Model TGA Pyris1 thermogravimetric analyzer. The sample weight was 8–10 mg. The experimental run was performed from 30 to 800°C at a heating rate of 20°C min^{-1} in nitrogen atmosphere with a gas flow rate of 30 mL min^{-1}.

Water absorption

The water absorption of the composites was tested as follows: Preweighed dry slabs ($L \times W \times T = 50 \times 10 \times 3$ mm^3 in size) were immersed in deionized water for 24 h to study their water absorption at room temperature and 50°C. After immersing, the samples were blotted with a laboratory tissue and

TABLE I
Composites Prepared: Composition and Code

Composites	Composition (w/w)	Pressure (MPa)	Adhesive added	Adhesive amount (wt %)	Code
EF/PU	80/20	20	–	–	W1
EF/PU	70/30	20	–	–	W2
EF/PU	60/40	20	–	–	W3
EF/PU	70/30	5	EC-bp	10	W5-EC-10
EF/PU	70/30	10	EC-bp	10	W10-EC-10
EF/PU	70/30	20	EC-bp	3	W2-EC-3
EF/PU	70/30	20	EC-bp	5	W2-EC-5
EF/PU	70/30	20	EC-bp	10	W2-EC-10

weighed. The final water absorption was expressed as the weight percentage of water in the swollen sample:

$$\text{Water absorption } (\%) = (W_W - W_D)/W_D \times 100\%,$$

where W_D is weight of the dry sample and W_W is the weight of the water-swollen sample.

Environmental scanning electron microscopy

The fracture surfaces of specimens were analyzed using environmental scanning electron microscopy (ESEM) (Quanta 400 FEI) in order to evaluate the degree of interfacial adhesion, and for their morphological studies. The accelerating voltage applied was 20.0 kV. The fracture surfaces of samples for the ESEM were generated by tensile test.

RESULTS AND DISCUSSION

FTIR analysis of EF/PU composites

The presence of chemical modification on the surface of EC-bp modified EF/PU composites has been identified by FTIR spectroscopy, as shown in Figure 1.

The strong and broad absorption band around 3500 cm^{-1}, characteristic of hydrogen bonded OH stretching vibration is common to all the spectra in Figure 1. However, it was observed from Figure 1(a) that there was a gradual decrease in the intensity of the OH stretching band indicting a gradual increasing of the extent of EC-bp modification extent. In heating condition, thermal dissociation of EC-bp could happen and generated free isocyanate group, which could react with the hydroxyl groups of eucalyptus fibers and resulted in chemical modified products. In Figure 1(b), the lowering of intensities of the OH in-plane bending bands at 1375, 1355, and 1205 cm^{-1} in the spectra of the samples also indicated that EC-bp modified on EF fibers by reacting with its OH group. The corresponding FTIR absorption frequencies of the EC-bp modified EF/PU samples just confirmed the crosslinking reaction occurred by addition of EC-bp.

Mechanical properties

Results for the tensile strength (TS) and tensile modulus (EM) of both EC-bp modified and unmodified EF/PU composites were showed in Figure 2. It could be seen that the effect of EC-bp as an adhesive on the tensile properties of the composites was significant. In Figure 2(a), we found that both tensile strength and elastic modulus of EF/PU composites increased as the adhesive content increased. Com-
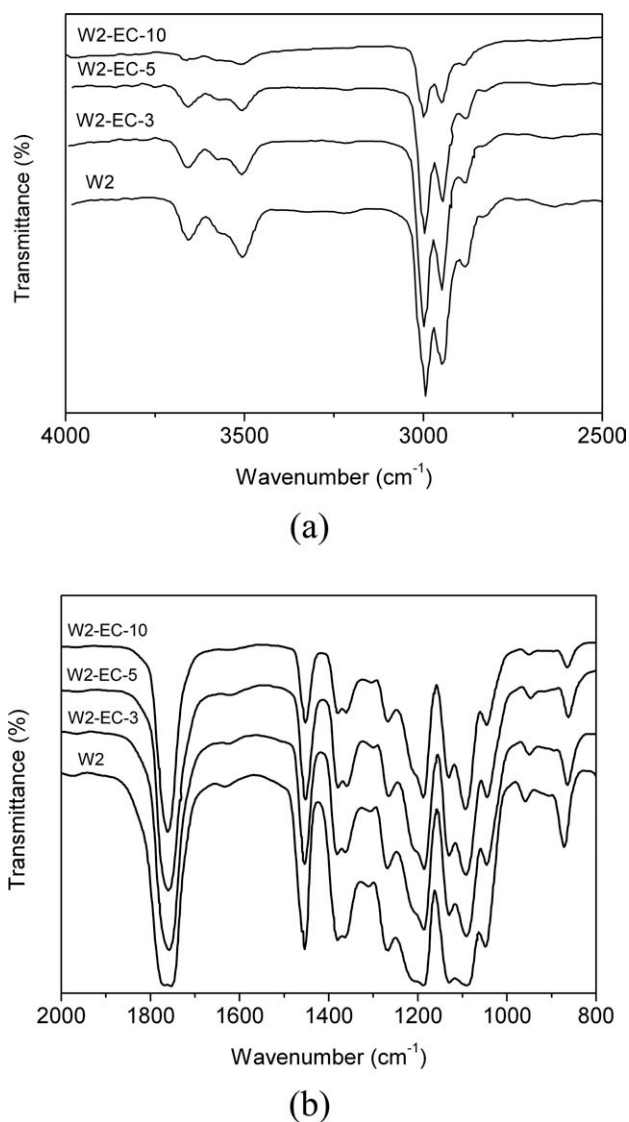

(a)

(b)

Figure 1 FTIR analysis for unmodified (W2) and EC-bp modified (W2-EC-3, W2-EC-5 and W2-EC-10) EF/PU composites: (a) in the region 4000-2500cm^{-1}, and (b) in the region 2000–800 cm^{-1}.

paring the tensile properties of the composite containing 10 wt % EC-bp (W2-EC-10) with pure one (W2), tensile strength value increased rapidly from about 11.56–18.21 MPa and elastic modulus increased from about 200–340 MPa. All above results suggested that tensile properties of the composites were improved by addition of EC-bp. This should be due to the strong crosslinking reaction of released NCO groups from EC-bp and OH groups of PU and EF fibers. In addition, the tensile strength and elastic modulus affected by manufactured pressure were also studied. In Figure 2(b), we observed that the tensile strength and elastic modulus of prepared composites both increased slightly when the pressure was enhanced.

Figure 3 illustrated the results of the flexural properties of the composites with and without adhesive
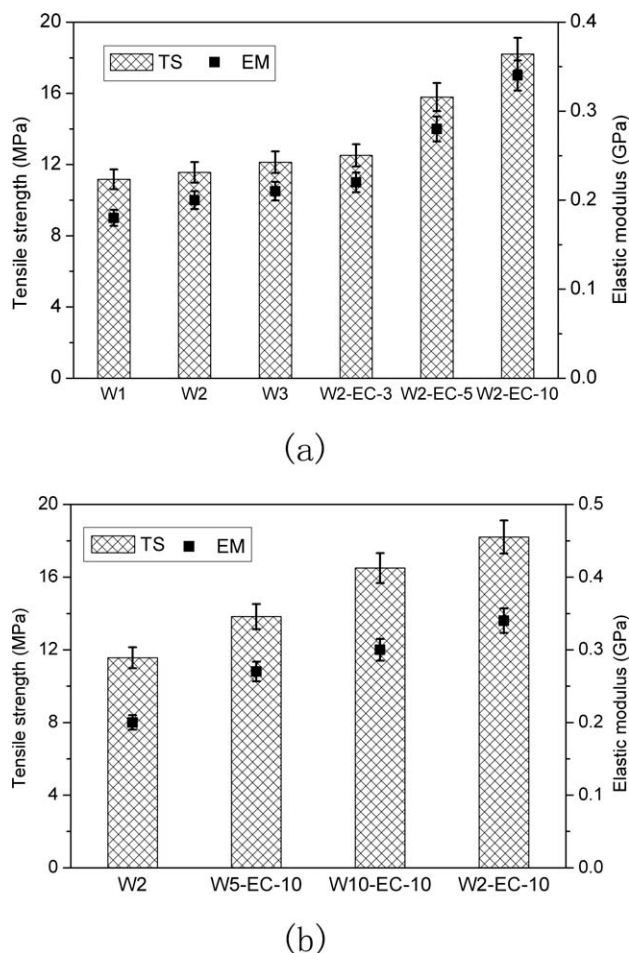
Figure 2 Tensile properties of EF/PU composites: (a) W1, W2, W3, W2-EC-3, W2-EC-5, W2-EC-10 and (b) W2, W5-EC-10, W10-EC-10, W2-EC-10.

treatment. As can be seen, the benefit of the EC-bp reinforced materials is readily apparent. In Figure 3(a), the modified composites showed better excellent flexural strength (FS) and flexural modulus (FM) in comparison with unmodified one. In the case of W2 composite, when it compounded with 10 wt % EC-bp, flexural strength increased from 17.38 to 28.28 MPa and flexural modulus increased sharply from 670 to 1840 MPa. These features suggested the improved interfacial adhesion by addition of EC-bp. The improvement on flexural properties may be attributed to enhanced interfacial adhesion between EF fibers and PU by crosslinking effect of EC-bp. In the meantime, we also observed from Figure 3(b) that the flexural properties of composites were also enhanced when the pressure increased.

Thermal stability

The thermal stability of the prepared composites was analyzed using TGA measurement. TGA and derivative thermograms (DTG) curves of the composites with and without EC-bp were depicted in Fig-

ure 4. It was observed that the incorporation of EC-bp had significantly affected the thermal stability of the composites. An important feature observed was the higher degradation temperature of the modified composites (371°C for W2-EC-5, 395°C for W2-EC-10) in comparison with the unmodified one (335°C for W2). In the composites, thermal degradation temperature was increased by increasing EC-bp content. It can be generally said that the compatibility and the interfacial bonding increased by crosslinking reaction between EF fibers and PU, or the crosslinking of the EF fibers matrix itself by addition of EC-bp. In addition, for the unmodified composites (W1, W2), it was verified that the maximum degradation rate was shifted to a slight higher temperature (around from 325 to335°C) as PU content increased. This may be due to the improved interfacial properties of the EF fibers matrix by increasing PU content.

Water absorption

Eucalyptus fibers are hydrophilic because it contains numerous hydroxyl groups available for interaction
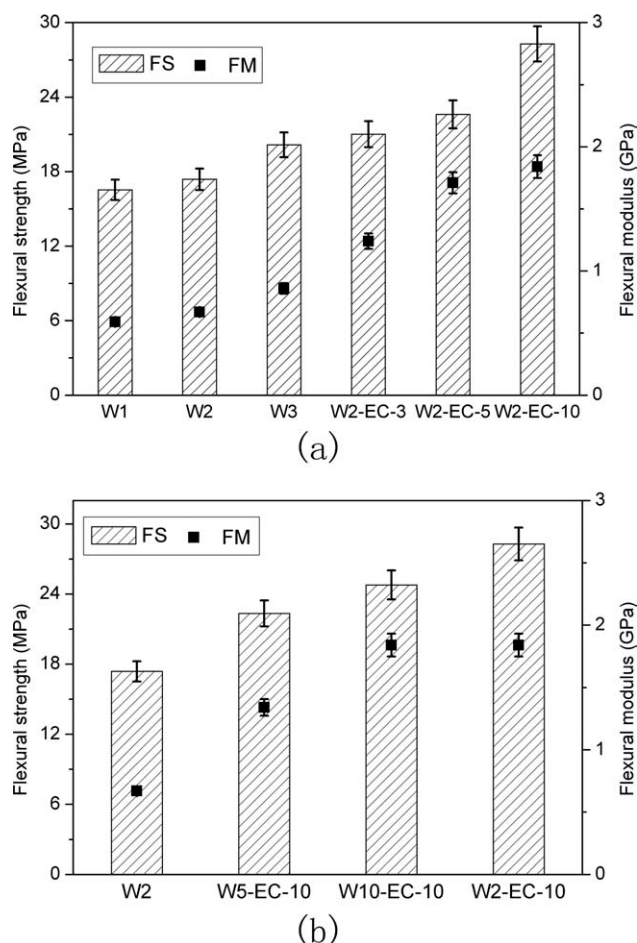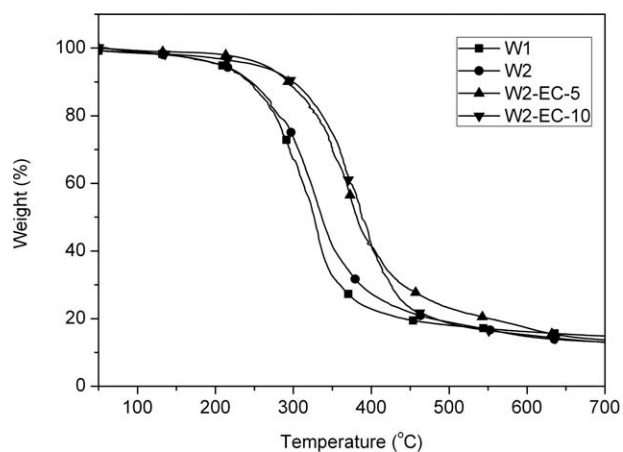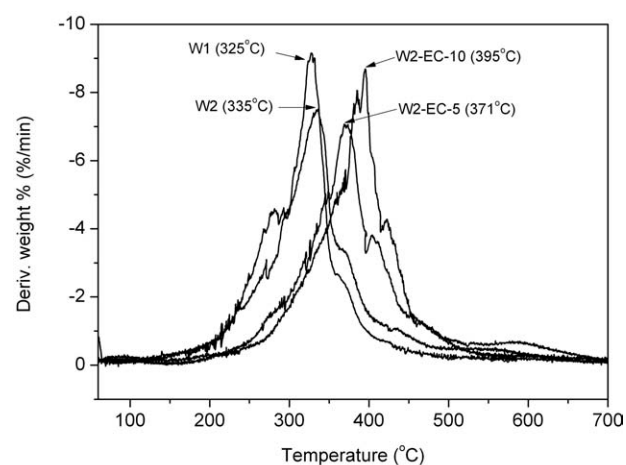

Figure 3 Flexural properties of EF/PU composites: (a) W1, W2, W3, W2-EC-3, W2-EC-5, W2-EC-10 and (b) W2, W5-EC-10, W10-EC-10, W2-EC-10.

(a)

(b)

Figure 4 (a) TGA and (b) DTG curves of unmodified EF/PU composites (W1, W2) and EC-bp modified composites (W2-EC-5, W2-EC-10).

with water molecules by hydrogen bonding, which generally leads to the reduction in mechanical properties.[23] The water absorption for all composites increased greatly during the first 20 h and then leveled-off. Therefore, the water absorption in different immersed time in 24 h for all the composites were studied and compared. Effects of the addition of EC-bp on the water absorption behavior of the composites in different time were shown in Figure 5. It was observed that all composites containing EC-bp showed lower degree of water absorption as compared to the unmodified one and the water absorption decreased as the adhesive content increased. This indicated that the addition of EC-bp improved the interfacial adhesion of the composites. Establishment of chemical bonds between hydroxyl groups on the fiber surface and released isocyanate groups from the EC-bp prevented bonding of eucalyptus fiber with water, thus limiting water absorption. This is a very important result, since water absorp-

tion usually affects the mechanical properties, dimensional stability, and other properties, limiting the applicability of these composites.

On the other hand, we also investigated that the effect of the temperature on the water absorption of the composites. Comparing water uptake of the composites in Figure 5(a) (under room temperature) with the ones in Figure 5(b) (at 50°C), we observed that the water absorption increased at a higher temperature. This should be due to the strong molecular movement, which caused the absorption rate to be quickened. However, it was also found that EC-bp as an adhesive enhanced the water resistance of the composites at a higher temperature (50°C).

Morphology analysis

Effects of the addition of EC-bp on the morphology of the composites were studied by ESEM. The ESEM micrographs were presented in Figure 6. In Figure
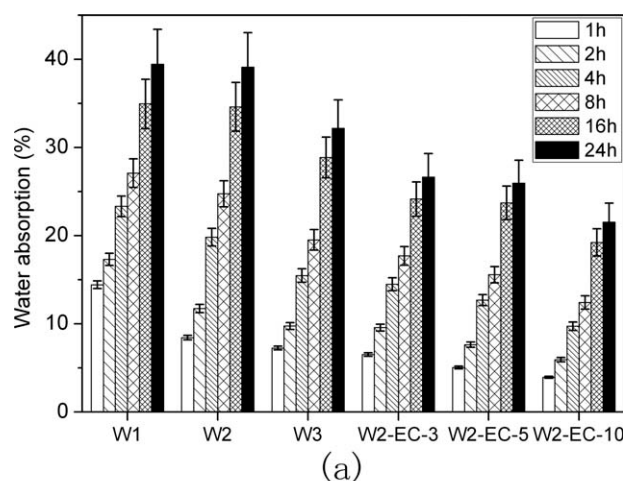
(a)
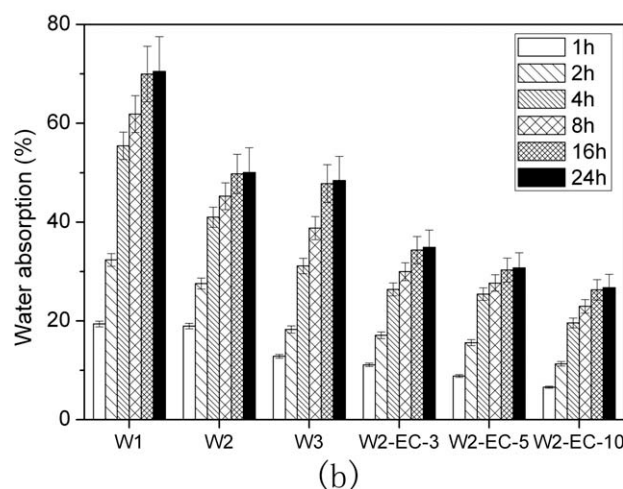
(b)

Figure 5 Water absorption of unmodified EF/PU composites (W1, W2, W3) and EC-bp modified composites (W2-EC-3, W2-EC-5, W2-EC-10) in different immersed time: (a) under room temperature, and (b) under 50°C.
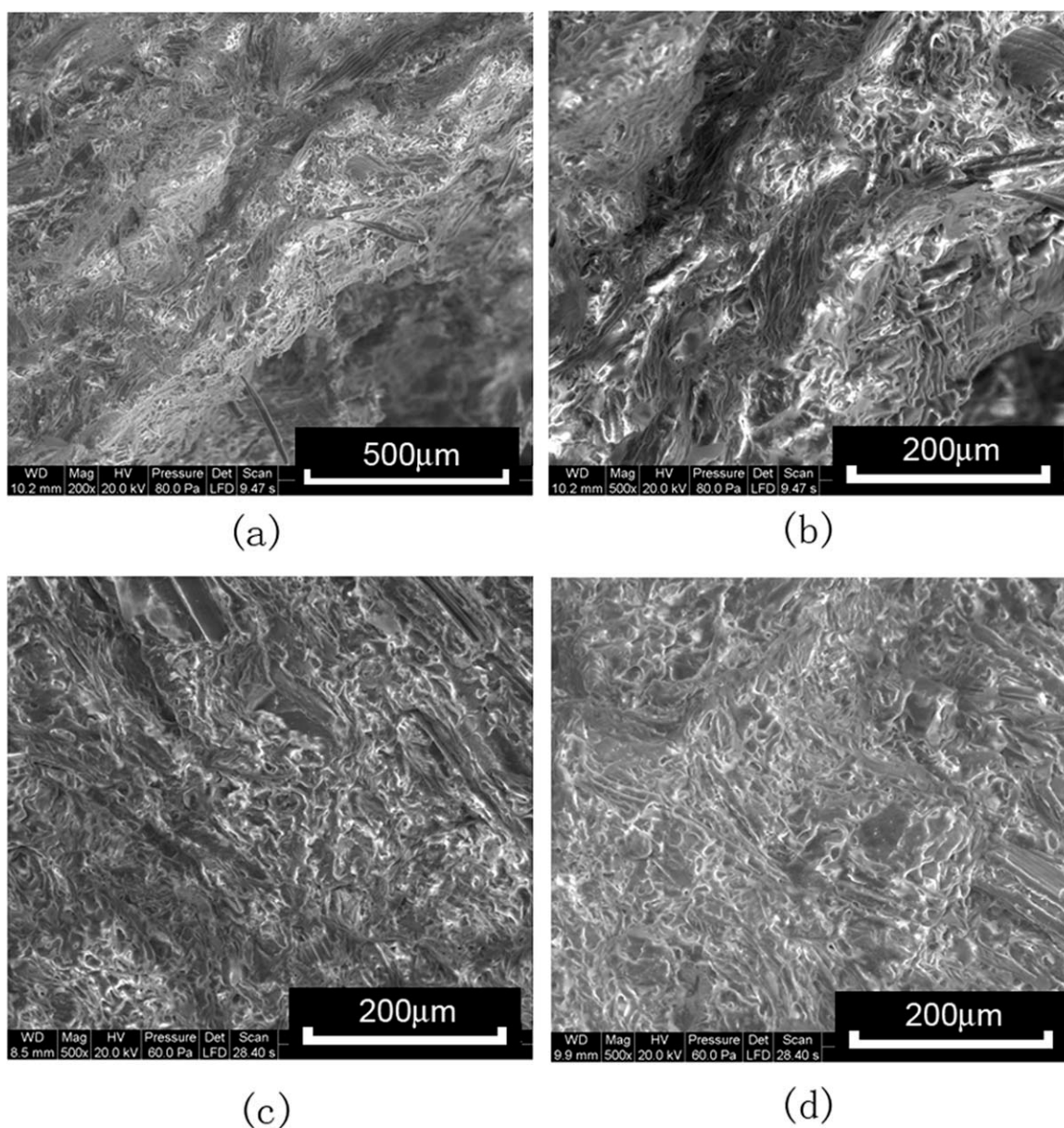
Figure 6 ESEM micrographs of EF/PU composites: (a) W2 (×200 magnification), (b) W2 (×500 magnification), (c) W2-EC-5 (×500 magnification), and (d) W2-EC-10 (×500 magnification).

6(a) (×200 magnification) and 6(b) (×500 magnification), the unmodified composite (W2) showed a rough morphology with the presence of many voids and cavities, which indicated weak interfacial adhesion, thus revealing the poor mechanical and water resistance behaviors. Figure 6(c,d) (×500 magnification) showed the morphology of modified composites (W2-EC-5 and W2-EC-10). It can be seen that the presence of the EC-bp changed the morphology of the composites. Addition of such adhesive to the composites produced a more homogeneous and smoother surface with less voids and cavities. By increasing EC-bp content, the morphology of the composite became smoother due to the crosslinking effect of EC-bp, which led to better interfacial adhe-

sion. In addition, the better mechanical, thermal stability and water resistance properties of the modified composites containing EC-bp can be explained by the enhanced interfacial adhesion due to the crosslinking effect among the composites.

CONCLUSIONS

In this study, EC-bp as a novel adhesive was firstly introduced into the EF/PU composites, which prepared using the hot press method. By this way, the composites could get crosslinking structure directly because the regenerated isocyanate groups reacted with the plentiful hydroxyl groups of the eucalyptus fibers under the manufactured temperature. FTIR

analysis demonstrated the crosslinking reaction. Mechanical testing results showed that the tensile and flexural properties of the composites were enhanced by addition of such adhesive. Comparing the tensile properties of the composite containing 10 wt% EC-bp (W2-EC-10) with pure one (W2), tensile strength value increased rapidly from about 11.56 to18.21 MPa and elastic modulus increased from about 200 to 340 MPa. In the case of flexural properties, the value increased from 17.38 to 28.28 MPa and flexural modulus increased sharply from 670 to 1840 MPa, respectively. In addition, effects of this adhesive on water absorption, thermal stability, and the morphology of the composites were also studied. The results demonstrated that improved water resistance, thermal stability, and interfacial adhesion of the composites were achieved, which indicated that EC-bp could be as an interesting adhesive for natural fiber composites.

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