Kenaf Fiber/Soy Protein Based Biocomposites Modified with Poly(carboxylic acid) Resin

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ABSTRACT: In this research, three different types of biocomposites were made from kenaf fiber/soy protein, kenaf fiber/DS 3530, and kenaf fiber/soy protein/DS 3530. Fourier transform infrared spectra of the biocomposites showed that there were chemical reactions among the kenaf fiber, soy flour, and BASF Acrodur resin. The hot-pressing time had a significant effect on the flexural properties and density of both the kenaf fiber/soy flour composites and kenaf fiber/BASF Acrodur resin composites. However, the effect was opposite for the composites from 10 to 20 min of hot pressing. As the hot-pressing time increased, the flexural properties and density increased for the kenaf fiber/soy flour composites and decreased for the other two composites with BASF Acrodur resin. BASF Acrodur resin reduced the hot-pressing time of the biocomposites. With 28 wt % BASF Acrodur resin (on the basis of 100% solid content) as a binder and with the biocomposites hot-pressed for 10 min, the swelling thickness and water absorption of the composites were reduced by 55 and 64%, and the flexural strength and modulus were improved by 72 and 188%, respectively. More simultaneous failures of the fiber and adhesive were observed at the fracture surface of the kenaf fiber/soy flour/BASF Acrodur resin composite. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

The shortage of petroleum and increasing environmental concerns have resulted in great interest in the use of renewable bioproducts to replace petroleum-based products. Natural fibers can be viewed as natural biocomposites that are naturally formed and mainly composed of cellulosic fibers embedded in a lignin and pectin matrix. The cellulosic fibers present attractive properties, such as a high specific strength, elastic modulus, and low density. They can be good reinforcement candidates because of their excellent mechanical properties.[1–3] Natural fibers are lignocellulosic materials. They can be obtained from pulping processes, such as mechanical pulping or chemical pulping. Kenaf is a warm-season annually grown fiber crop. It grows in large amounts every year in the United States. Currently, there are around 4300 acres of kenaf cultivated in the United States and 2000 acres grown in Mississippi.[4] It is a relatively underused biomass in Mississippi. Kenaf bast fiber is attractive also because of its high cellulose content and good mechanical properties. The cellulose content of kenaf bast fiber is about 46–57%.[5] The tensile strength and modulus of a single kenaf fiber can be as high as 11.9 and 60.0 GPa, respectively.[6,7] Thus, kenaf bast fiber is an excellent cellulose resource for fiber-based products. It is also a good reinforcement candidate for natural-fiber-reinforced composites applications in cars by some automobile manufactures.[7–13]

Soybean oil is an edible oil and is also used to make biodiesel; it accounts for about 90% of the fuel stock in the United States.[14] Hence, defatted soy flour is available in large quantities and at low cost. The composition of defatted soy flour includes soy protein, soy carbohydrate, and soy whey. Soybean protein consists mainly of acidic amino acids (aspartic and glutamic acids) and their amides, nonpolar amino acids (alanine, valine, and leucine), basic amino acids (lysine and arginine), and an uncharged polar amino acid (glycine). Hence, soy protein contains carboxyl ($-COOH$), amine ($-NH_2$), or hydroxyl ($-OH$) chemical groups. These reactive chemical groups of soybean protein can interact and/or react with cellulose fibers.[15] Medium-density particleboard from rice husks and soy protein concentrate bases have been fabricated.[16,17] The method of making particleboard with soy-based, formaldehyde-free adhesives consists of soy flour and a curing agent.[18] Completely biodegradable soy protein/jute biocomposites have been developed

and have shown better mechanical properties than polypropylene/jute composites.[19] Kenaf-fiber-reinforced soy-based biocomposites were fabricated with extrusion/injection molding and compression molding.[20] The compression-molded samples showed higher thermal and mechanical properties, and the modulus, impact strength, and heat deflection temperature values of the biocomposites increased as the fiber length, fiber content, and fiber orientation increased.

Polymeric carboxylic acids have been used as environmentally friendly wet-strength agents of paper. Bleached kraft hand sheets treated with 1,2,3,4-butane tetracarboxylic acids (BTCA) showed significant wet-strength improvement.[21] Paper has been treated with BTCA, tricarballylic acid, and succinic acid, and BTCA has been found to be the most effective crosslinking agent for wood pulp cellulose.[22,23] Poly(carboxylic acid) resin was accessed for its ability to reduce the moisture swelling of densified wood; the water absorption and swelling thickness of flakes decreased with increasing loading of poly(carboxylic acid).[24] Poly(carboxylic acid) has also been used as a formaldehyde-free binder for wood fibers and bast fibers, such as flax, sisal, and kenaf.[25,26]

In this study, biocomposites were prepared from kenaf fiber and defatted soybean flour. BASF Acrodur DS 3530 resin, an aqueous solution of a modified poly(carboxylic acid) with a poly(hydric alcohol) as crosslinking component, was used as a binder to improve the physical and mechanical properties of the biocomposites.

EXPERIMENTAL

Materials
Kenaf bast fiber was provided by Kengro Corp. (Charleston, MS, USA), and defatted soy flour was purchased from Ware Milling (Houston, MS, USA). Acrodur DS 3530 resin was provided by BASF. Table I shows the physical and chemical properties of the BASF Acrodur DS 3530 resin.

Sample Preparation
Kenaf Fiber/Soy Protein Composites. Kenaf fiber ground to 5 mm in length and defatted soybean flour were mixed well in a 1 : 1 weight ratio. The previous mixture (25 g) was put into a 3 × 5-in. mold and pressed at 5 MPa for 1 min to form a mat. Water (40 wt %) was sprayed onto the mat. The wetted mat was put into oven at 80°C until the moisture content of the mat was less than 15 wt %. Then, the mat was hot-pressed under a pressure of 5 MPa and at a temperature of 150°C. Three pressing times were used: 10, 15, and 20 min.

Kenaf Fiber/DS 3530 Composites. Acrodur DS 3530 (20 g) was sprayed onto a 15-g kenaf fiber mat. The same drying and curing protocols described previously were used.

Kenaf Fiber/Soy Protein/DS 3530 Composites. Acrodur DS 3530 (20 g) was sprayed onto a 25-g kenaf fiber and defatted soybean flour mat. The same drying and curing protocols described previously were used.

Composite Characterization
Fourier Transform Infrared (FTIR) Spectroscopy. The sample was placed in an oven at 120 ± 2°C until a constant weight was obtained. We recorded the FTIR spectra of the samples with a

Table I. Physical and Chemical Properties of the BASF Acrodur Resin[a]

Property	Typical value
Solid content (ISO 3251, 2 h at 120°C)	50%
pH (ISO 976, 10% in distilled water)	2.5–4.0
Viscosity at 23°C (ISO 2555)	150–300 mPa S
Density at 20°C (ISO 2811)	1.20 g/cm^3
Miscibility with water	Miscible in all proportions

[a]An aqueous solution of a modified poly(carboxylic acid) with a poly(hydric alcohol) as a crosslinking component.

Thermo Nicolet 6700 FTIR instrument (Vernon Hills, IL) over the range 400–4000 cm^{-1} at room temperature with a 4-cm^{-1} spectral resolution by averaging 128 scans. The cured samples were tested in sheet form, and the transmitted IR was used.

Swelling Thickness. The specimens were dried in an oven for 24 h at 102°C. The thicknesses of the dried specimens were measured to a precision of 0.001 mm by a caliper. The specimens were then placed in distilled water and kept at room temperature for 24 h. Then, the specimens were removed from the water, and the surface water was wiped off by a paper towel, and the thicknesses of the specimens were measured. Five replicates were measured and averaged. The 24-h swelling thickness (T_{ab}) was calculated with eq. (1):

$$T_{ab}(\%) = \frac{T_a - T_b}{T_b} \times 100 \quad (1)$$

where T_a is the specimen thickness after the water absorption and T_b is the specimen thickness before the water absorption.

Water Absorption. The 24-h water absorption of the specimens was measured in accordance with the procedure described in ISO 62. The specimens were immersed entirely in distilled water at room temperature for 24 h. Then, the specimens were taken out and weighed after the surface water was removed by a paper towel. Three replicates were measured and averaged. The 24-h water absorption (W_{ab}) was calculated with eq. (2):

$$W_{ab}(\%) = \frac{W_a - W_b}{W_b} \times 100 \quad (2)$$

where W_a is the specimen weight after the water absorption and W_b is the specimen weight before the water absorption.

Density. We determined the density of the composites by averaging the mass-to-volume measurements of six specimens in accordance with the procedure described in ASTM D 1622-03.

Mechanical Property Testing. The flexural strength and modulus of the biocomposites were tested on the basis of six replicates with an Instron universal testing machine (model 5869, Canton, MA) in accordance with the procedure described in ASTM D 790. The specimen dimensions were 80 × 25 × 3.2 mm^3 (Length × Width × Thickness). A three-point bending setup was used, with a span of 50 mm and a crosshead speed of
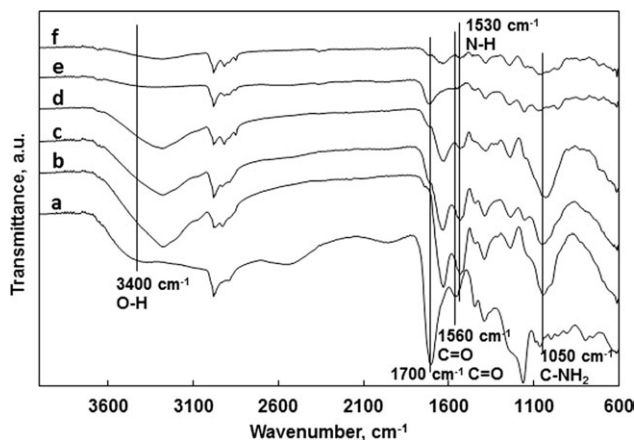
Figure 1. FTIR spectra of the (a) BASF Acrodur resin, (b) soy flour, (c) soy flour/BASF Acrodur resin composite, (d) kenaf fiber/soy flour composite, (e) kenaf fiber/BASF Acrodur resin composite, and (f) kenaf fiber/soy flour/BASF Acrodur resin composite.

1.3 mm/min. The flexural strength and flexural modulus were determined.

Scanning Electron Microscopy (SEM). A JSM-6500F field emission scanning electron microscope (JEOL USA, Inc., Peabody, MA) with accelerating voltages of 0.5–30 kV, and magnifications ranging from 10 to 500,000× were used to examine the fracture morphology of the specimen and study the effects of the incorporation of poly(carboxylic acid) on the morphology of the biocomposites. The specimens were platinum-coated before scanning to obtain an electrically conductive surface.

RESULTS AND DISCUSSION

FTIR Spectroscopy

Figure 1 shows the FTIR spectra of the BASF Acrodur resin, soy flour, soy flour/BASF Acrodur resin composite, kenaf fiber/soy flour composite, kenaf fiber/BASF Acrodur resin composite, and kenaf fiber/soy flour/BASF Acrodur resin composite. The spectrum of the BASF Acrodur resin also showed a broad band at 1560 cm^{-1}; this band was ascribed to the asymmetric carboxylate stretching vibrations of a carboxylate [v_{as}(COO—)].[27] These two bands disappeared, and a new band appeared at 1720 cm^{-1} in the spectra of the soy flour/BASF Acrodur resin composite, kenaf fiber/BASF Acrodur resin composite, and kenaf fiber/soy flour/BASF Acrodur resin composite. The new band was attributed to the stretching vibrations of the ester carbonyl bond. This band indicated that the formation of the ester linkage between the carboxyl group of the BASF Acrodur resin and the hydroxyl groups of the cellulosic fiber and soy flour was predominant.[28]

The soy flour sample had characteristic absorption bands arising from N—H and O—H groups in the region around 3280 cm^{-1}. The characteristic C—H asymmetric and symmetric stretching of the CH$_2$ and CH$_3$ groups was observed in the range 3000–2850 cm^{-1}. There were characteristic peaks of amides I, II, and III at 1650, 1539, and 1235 cm^{-1}, respectively.[29] The bands at 1398 and 1050 cm^{-1} were attributed to COO— and C—NH$_2$ bending. The peaks attributed to COO— bending (1398 cm^{-1})

and C—NH$_2$ bending (1050 cm^{-1}) of the cured soy flour/BASF Acrodur resin composite, kenaf fiber/soy flour composite, and kenaf fiber/soy flour/BASF Acrodur resin composite were both narrower and less intense than those of the corresponding peaks for the neat soy flour; this implied that some chemical reactions occurred in the composites during hot pressing.

Swelling Thickness and Water Absorption

The swelling thickness and water absorption of the composites were affected by the nature of the substrate and adhesive and the interactions between the substrate and the adhesive. Figure 2 shows the 24-h swelling thickness and water absorption of the kenaf fiber/soy flour composites at 10, 15, and 20 min of hot pressing. In the kenaf fiber/soy flour composites, the swelling thickness and water absorption of the composites decreased as the pressing time increased. Kenaf fiber is a carbohydrate and mainly contains cellulose, hemicelluloses, and lignin. Soy flour contains both soy protein and soy carbohydrate. The presence of carbohydrates in the kenaf fiber and soy flour favored water uptake because of the hydrophilic nature of carbohydrates. Water could penetrate and diffuse into the composites through the amorphous regions of cellulose. There were some chemical reactions and hydrogen bonding between the cellulosic fiber and soy flour. The polar groups, such as carboxyl (—COOH), amine (—NH$_2$), and hydroxyl (—OH) groups, of the amino acids in the soy flour reacted and hydrogen-bonded with the —OH groups of the cellulosic fiber.[15] The longer the hot-pressing time was, the greater the number of chemical reactions were going on and the fewer —OH groups of carbohydrates were available to absorb water. Hence, the water absorption of the kenaf fiber/soy flour composites was reduced as the hot-pressing time increased. This was also evidenced by the swelling thickness of the composites, which depended on the hot-pressing time. The longer the hot-pressing time was, the greater number of chemical reactions were going on and the stronger the bonding between the fiber and soy flour was. Strong interactions between the fiber and soy flour reduced the water absorption and, hence, reduced the swelling thickness.

The 24-h swelling thickness and water absorption of the kenaf fiber/BASF Acrodur resin composites at 10, 15, and 20 min of hot pressing are shown in Figure 3. When the BASF Acrodur resin was used as an adhesive, the longer pressing time did not
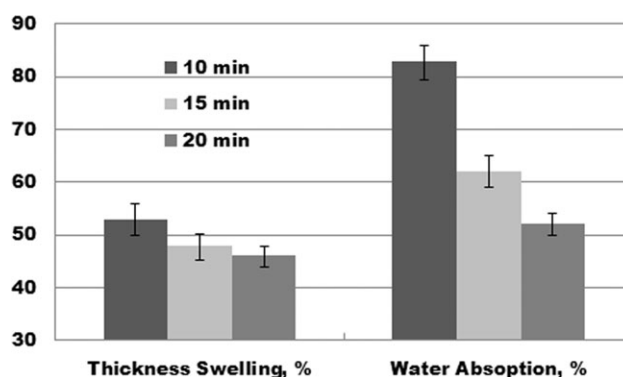

Figure 2. Twenty-four-hour swelling thickness and water absorption of the kenaf fiber/soy flour composites at 10, 15, and 20 min of hot pressing.
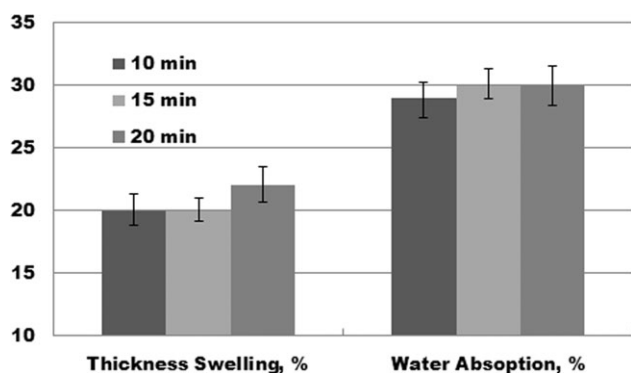
Figure 3. Twenty-four-hour swelling thickness and water absorption of the kenaf fiber/BASF Acrodur resin composites at 10, 15, and 20 min of hot pressing.

Figure 5. Flexural strength (MOR), flexural modulus (MOE) and density of the kenaf fiber/soy flour composites at 10, 15, and 20 min of hot pressing. MOR, modulus of rupture; MOE, modulus of elasticity.

help to reduce the hygroscopic performance of the composites. Instead, the swelling thickness and water absorption of the kenaf fiber/BASF Acrodur resin composites increased. This might have been due to irreversible acid-catalyzed depolymerization and the reversible crosslinking of cellulose molecules.[30] The longer the hot-pressing time was, the higher the depolymerization extent was and the lower the crosslinking density was inside the composite. The composites were more vulnerable to water as the crosslinking density decreased. Hence, the swelling thickness and water absorption of the composites increased as the pressing time increased. However, the use of the BASF Acrodur resin as a bonding agent substantially reduced the swelling thickness and water absorption of the composites, regardless of the hot-pressing time, at 10, 15, and 20 min.

Figure 4 shows the 24-h swelling thickness and water absorption of the kenaf fiber/soy flour/BASF Acrodur resin composites at 10, 15, and 20 min of hot pressing. The swelling thickness and water absorption of the kenaf fiber/soy flour/BASF Acrodur resin composites were affected by several factors, such as the chemical reactions among the kenaf fiber, soy flour, and BASF Acrodur resin; the irreversible acid-catalyzed depolymerization; and the reversible crosslinking of cellulose molecules. The effect of the irreversible acid-catalyzed depolymerization was predominant and resulted in increases in the swelling thickness and water absorption of the composites as the pressing time
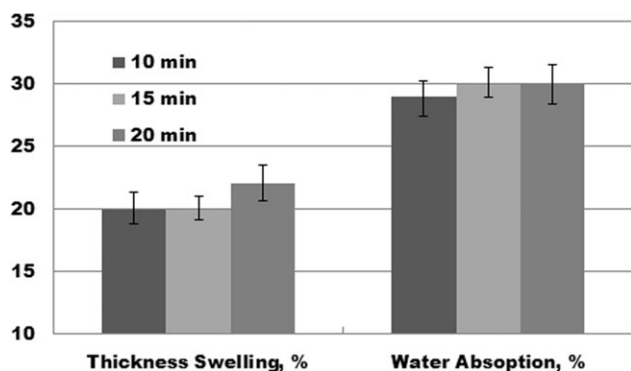
increased. Meanwhile, the use of the BASF Acrodur resin as a bonding agent substantially reduced the swelling thickness and water absorption of the composites, regardless of the hot-pressing time, at 10, 15, and 20 min. The BASF Acrodur resin reduced the swelling thickness and water absorption of the kenaf fiber/soy flour composites by 55 and 64%, respectively, at 10 min of hot pressing.

Mechanical Properties and Density

The mechanical properties and density of the composites were also affected by the substrate and adhesive nature, and the interactions between the substrate and adhesive. Figure 5 shows the flexural properties and density of the kenaf fiber/soy flour composites at 10, 15, and 20 min of hot pressing. The hot-pressing time had significant effects on the properties of the composites. A long pressing time promoted interaction between the protein and fiber surface and led to a higher mechanical strength.[31] A longer hot-pressing time allowed the water residues to evaporate from the composites and improved the flexural strength and modulus of the composites. Water vapor might not have completely evaporated to the surface of the composites and resulted in a reduction in the mechanical properties at short pressing times. The flexural strength and modulus and density of the kenaf fiber/soy flour composites increased as the hot-pressing time increased.

Figure 4. Twenty-four-hour swelling thickness and water absorption of the kenaf fiber/soy flour/BASF Acrodur resin composites at 10, 15, and 20 min of hot pressing.
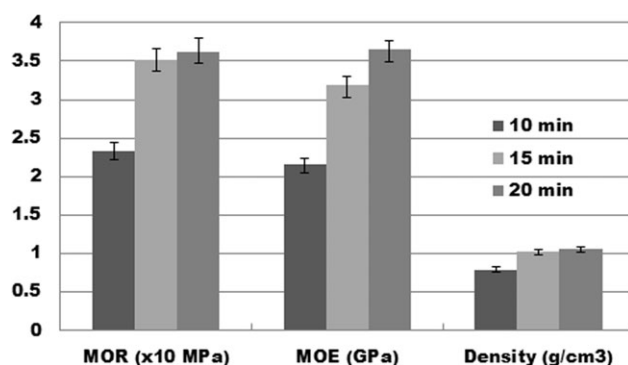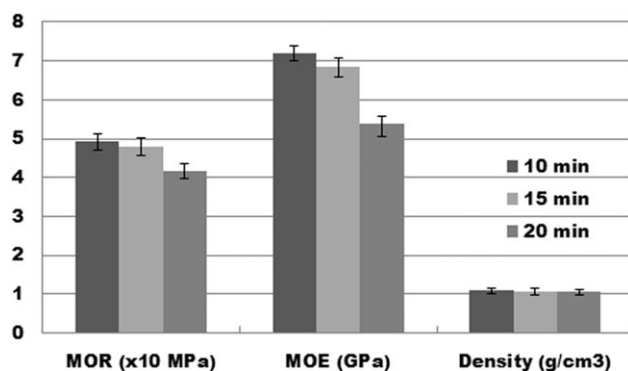

Figure 6. Flexural strength (MOR), flexural modulus (MOE) and density of the kenaf fiber/BASF Acrodur resin composites at 10, 15, and 20 min of hot pressing. MOR, modulus of rupture; MOE, modulus of elasticity.
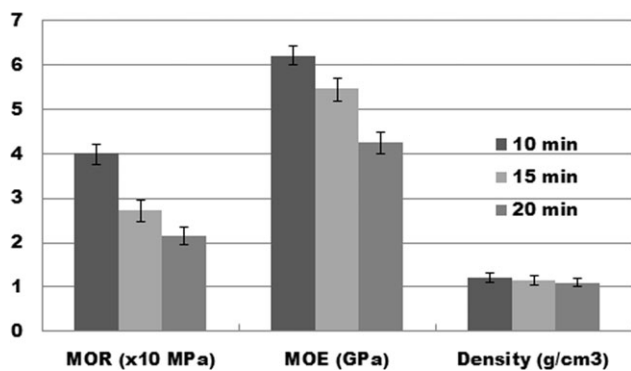
Figure 7. Flexural strength (MOR), flexural modulus (MOE) and density of the kenaf fiber/soy flour/BASF Acrodur resin composites at 10, 15, and 20 min of hot pressing. MOR, modulus of rupture; MOE, modulus of elasticity.

The flexural properties and density of the kenaf fiber/BASF Acrodur resin composites at 10, 15, and 20 min of hot pressing are shown in Figure 6. The flexural strength and modulus and density of the kenaf fiber/soy flour composites decreased as the hot-pressing time increased. As mentioned earlier, a longer hot-pressing time caused a higher depolymerization extent of the cellulosic fiber and a lower crosslinking density inside the composite. A higher depolymerization rate of the cellulosic fiber and a lower crosslinking density inside the composite resulted in lower mechanical properties and lower density in the composites.

Figure 7 shows the flexural properties and density of the kenaf fiber/soy flour/BASF Acrodur resin composites at 10, 15, and 20 min of hot pressing. As with the swelling thickness and water absorption, the longer hot-pressing time was detrimental to the bending properties of the composites when the BASF Acrodur resin was added. Still, the use of 28 wt % Acrodur resin (on the basis of 100% solid content) as a binder improved the flexural strength and modulus of the kenaf fiber/soy flour composites by 72 and 188%, respectively, at the 10 min of hot pressing.

SEM

Figure 8 shows the fracture surface SEM micrographs of the kenaf fiber/soy flour composite, kenaf fiber/BASF Acrodur resin composite, and kenaf fiber/soy flour/BASF Acrodur resin composite at 10 min of hot pressing, respectively. Fiber pullout was one of the failure mechanisms in the fiber-reinforced composites. There was a lot of fiber pullout at the fracture surface of
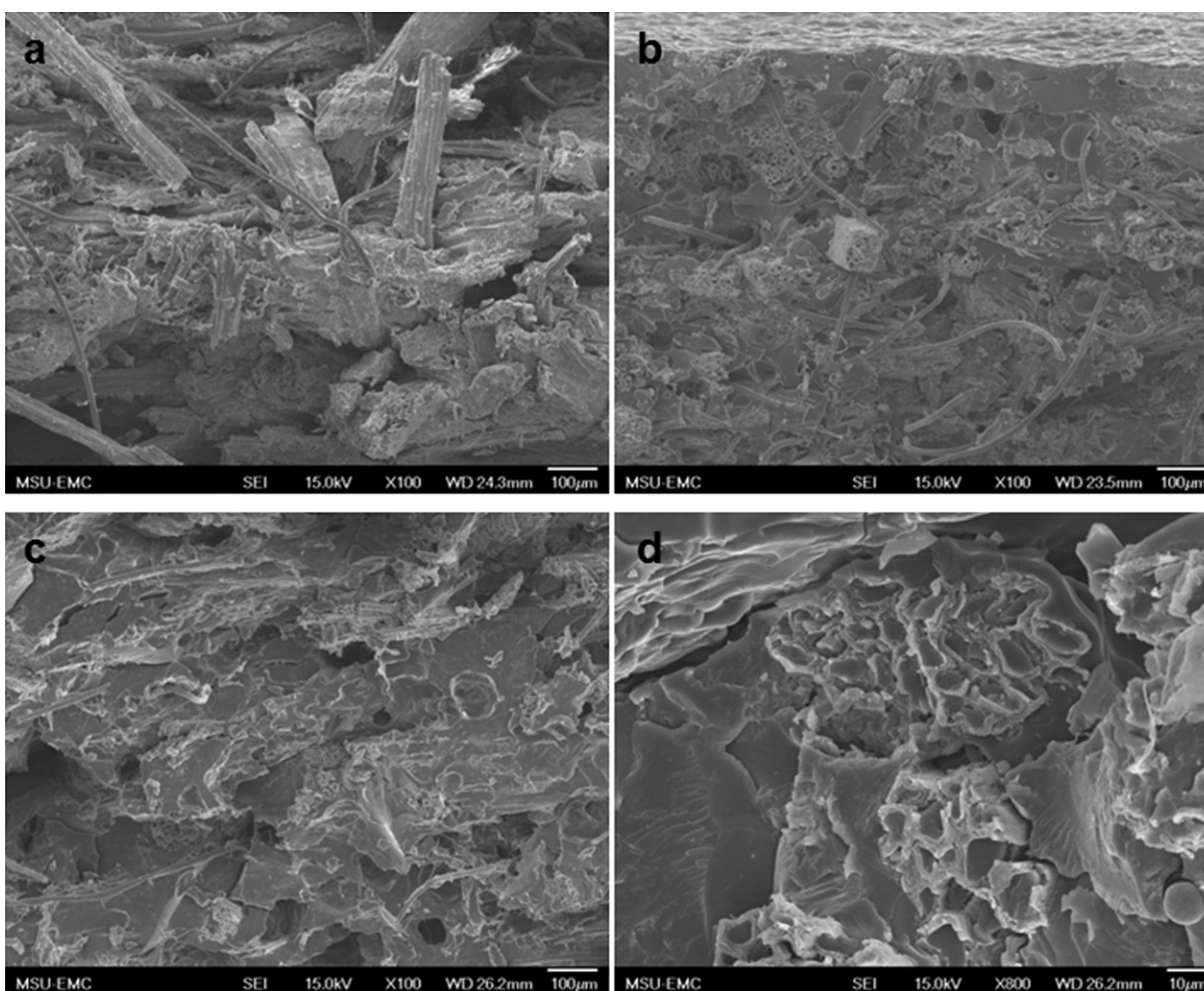

Figure 8. Fracture surface SEM micrographs of the (a) kenaf fiber/soy flour composite, (b) kenaf fiber/BASF Acrodur resin composite, and (c, d) kenaf fiber/soy flour/BASF Acrodur resin composite.

the kenaf/soy resin composites. The pullout fiber showed not much soy plastic matrix adhering to the fiber surface; this was indicative of bad adhesion with the matrix. The fiber pullout at the fracture surface of the kenaf fiber/BASF Acrodur resin composite was much less than that of the kenaf/soy resin composites. With the BASF Acrodur resin as a binder, more simultaneous failures of the fiber and adhesive were observed for the kenaf fiber/soy flour/BASF Acrodur resin composites. This evidence indicated good adhesion within the composites because the bonding strength resulting from the BASF Acrodur resin with soy flour adhesive was stronger that of soy flour alone.

CONCLUSIONS

FTIR spectra of the biocomposites showed the formation of ester linkages between the carboxyl groups of the BASF Acrodur resin and the hydroxyl groups of the cellulosic fiber and soy flour during hot pressing.

The hot-pressing time had a significant effect on the flexural properties and density of both the kenaf fiber/soy flour composites and the kenaf fiber/BASF Acrodur resin composites. However, the effect was the opposite for the composites from 10 to 20 min of hot pressing. As the hot-pressing time increased, the flexural properties and density increased for the kenaf fiber/soy flour composites and decreased for the kenaf fiber/BASF Acrodur resin and the kenaf fiber/soy flour/BASF Acrodur resin composites.

The BASF Acrodur resin reduce the hot-pressing time of the biocomposites. With 28 wt % BASF Acrodur resin (on the basis of 100% solid content) as a binder and with the biocomposites hot-pressed for 10 min, the swelling thickness and water absorption of the composites were reduced by 55 and 64%, respectively, and the flexural strength and modulus were improved by 72 and 188%, respectively. More simultaneous failures of the fiber and adhesive were observed at the fracture surface of the kenaf fiber/soy flour/BASF Acrodur resin composite.

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