MORPHOLOGY AND MECHANICAL PROPERTIES OF ALKALI-TREATED RICE STRAW FLOUR-POLYPROPYLENE COMPOSITES

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Effects of alkali treatment of rice straw flour on the mechanical properties of rice straw flour-polypropylene composites were investigated. Rice straw flour (40 mesh) was first treated with sodium hydroxide using two concentrations of sodium hydroxide, 5 and 10% (W/W), and two treatment times (45 and 90 min) for a total of four treatments. The composites were then made with the rice straw flour as a filler (30%), polypropylene (65%) as a matrix, and maleic anhydride (5%) as a coupling agent. The polypropylene/rice straw flour mixtures were blended in an internal Haake mixer and made into molds that were later used for mechanical testing. The results showed that the treatment of rice straw flour with 5% alkali (W/W) increased the tensile modulus and impact strength. Longer treatment time also resulted in a higher tensile modulus and impact strength. The fiber/matrix interaction was analyzed from the mechanical data and morphological (SEM) studies. Treatment of rice straw flour with 10% alkali (W/W), however, decreased these properties even under a longer treatment time. Increasing the alkali concentration and treatment time increased the flexural modulus, flexural strength, and tensile strength of the composites. The SEM results showed greater adhesion between the rice straw flour and the polypropylene matrix at higher alkali concentrations and longer treatment times.

Keywords: Alkali treatment; Flour rice straw; Polypropylene; Mechanical properties

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INTRODUCTION

In recent years, significant efforts have been made investigating the use of natural fibers as reinforcement in thermoplastic composites. Natural fiber-reinforced composites have many advantages such as being lightweight and renewable, having reasonable strength and stiffness, and being biodegradable. The composites therefore provide economical and ecological properties (Joshi et al. 2004; Vande and Kietkens 2001). The composites are widely used for building, packaging, and in automotive applications and are even extending their horizon to aerospace applications. Researchers have already exploited various types of lignocellulosic fibers, including wood flour, hemp, sisal, flax, and jute (Prasad and Sain 2003; Sain and Li 2003). The main group of plastics that is used in lignocellulosic-plastic composites is semicrystaline plastics such as polyethylene (PE) and polypropylene (pp). For cellulose fibers to be used in the reinforcement of nonpolar thermoplastics, the fibers must be modified. Effective wetting of fibers and strong interfacial adhesion are required in order to obtain composites with optimized mechanical properties. The main disadvantage of natural fiber/plastic composites is that the poor compatibility between the hydrophobic polymeric matrix and the hydrophilic fiber places limitation on its uses, as the natural fiber degradation point prohibits the use at high temperatures. This poor compatibility leads to the formation of a weak interface, which results in poor mechanical properties (Ishak et al. 2001); however, due to the increase in poor compatibility between hydrophobic thermoplastics and hydrophilic cellulosic fibers, several treatments have been reported to improve the fiber matrix interfacial bounding. Alkaline treatment or mercerization is the most popular chemical treatment of natural fibers used to reinforce thermoplastics and thermosets. The alkaline treatment is effective by disrupting hydrogen bonding in the network structure, thereby increasing the surface roughness. The treatment removes a certain amount of lignin, wax, and oils covering the external surface of the fiber cell wall, depolymerizes the cellulose, and exposes the short length crystallites (Mohanty et al. 2001). The addition of aqueous sodium hydroxide (NaOH) to natural fiber promotes the ionization of the hydroxyl group to the alkoxide (Agrawal et al. 2000).

$$Fiber - OH + NaOH \rightarrow Fiber - O - Na + H_2O \quad (1)$$

It is reported that alkaline treatment has two effects on fibers: (1) it increases the surface roughness and results in better mechanical interlocking; and (2) it increases the amount of cellulose exposed on the fiber surface, thus increasing the number of possible reaction sites (Valadez 1999).

EXPERIMENTAL

Materials

A polypropylene matrix with a melt flow index (MI) of 16 g/10min was supplied by Arak Petrochemical Company of Iran. Rice straw of different lengths were used as filler and obtained from the farms Royan of Iran. In this study, they were selected by a sieving process with 417× 10-6 (40 mesh) being the average particle size. Maleic anhydride with a melt index (MI) of 64 g/10min was used as a coupling agent and was supplied by Merk. Sodium hydroxide (NaOH) was used as fiber treatment and supplied by the Merk company.

Rice Straw Flour Treatment

Alkali treatment: the rice straw flour was introduced into a stainless steel vessel. Either a 5 wt% or a 10 wt% solution of NaOH was added into the vessel and stirred well. Two treatment times of 45 and 90 min were used for each alkali concentration. The fillers were then separated from the solution and washed with water to remove the NaOH. The rice straw flour was finally air-dried at 80ºC for 48 h.

Preparation of the Composite

Formulations of the composite mixes are shown in Table 1. Polymer/rice straw flour was blended in the Haake (internal mixer Haake HBI system 90) at 190ºC and 45 rpm for 11 minutes. After melting the polypropylene (65 wt%), the maleic anhydride (5 wt%) and rice straw flour (30%) were added to the Haake. The resulting hot, standard product samples were then pressed between cold plates and chipped in pilot Wieser chipper to produce granules. The samples were then placed into injection molds for later mechanical testing. A sample product ready for mechanical testing is shown in Fig. 1.

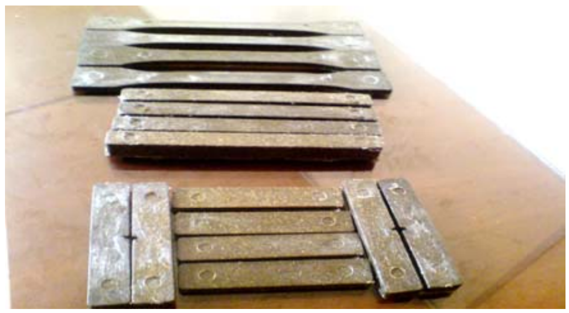

Fig. 1. Mechanical testing samples

Table 1. Formulation of Composites

MAPP (wt%)	pp (wt%)	Rice straw flour (wt%)	Treatment Times (min)	NaOH Concentration (wt%)	Code
5	65	30	-	-	UT
5	65	30	45	5	A11
5	65	30	90	5	A12
5	65	30	45	10	A21
5	65	30	90	10	A22

Mechanical Testing

The specimens were stored in a desicator before testing. For tensile and flexural testing, the standard specimens were placed in a computer-controlled electronic universal testing machine. The bending and tensile properties were evaluated according to ASTM D 790 and D 638 with a loading rate 5 mm/min, using an Instron (model 4489).

RESULTS AND DISCUSSION

Flexural Properties

Obtained results show that increasing the concentration and time of the alkali treatment of the rice straw flour increased the flexural modulus and flexural strength of the composites when compared to composites made with untreated rice straw flour (Figs. 2 and 3). The flexural modulus of the A11, A12, A21, and A22 composites increased by 12, 21, 25, and 32, respectively, compared to composites made without treated rice straw flour. The flexural strength of the treated rice straw composite increased by 10, 20, 30, and 33% compared with the composite of untreated rice straw.

The NaOH treatment increased the fiber surface roughness and number of possible reactive sites on the fiber surface, which increased the mechanical strength of the composite (Valadez 1999). The critical effect that the alkali treatment has on the lignocelluloses fiber is that it reduces the amount of hemicelluloses with no affect on the cellulose (Bledzki and Gassan 1999). As a result, the mechanical properties of the composite materials are mainly determined by the molecular structure of the cellulose, of which the alkali treatment plays an important role in reducing impurities, including hemicelluloses.

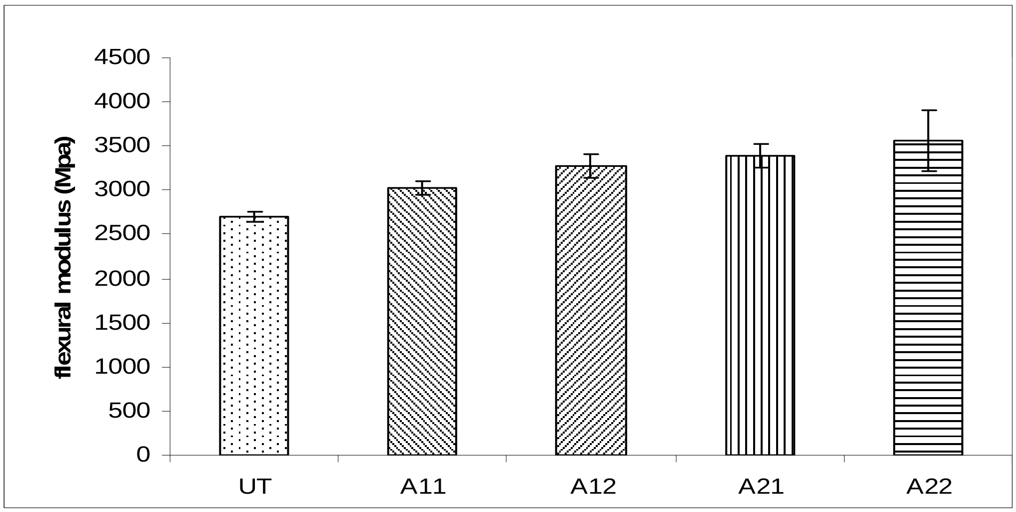

Fig. 2. Effect of the concentration and time of the alkali treatment on the flexural modulus of the composites

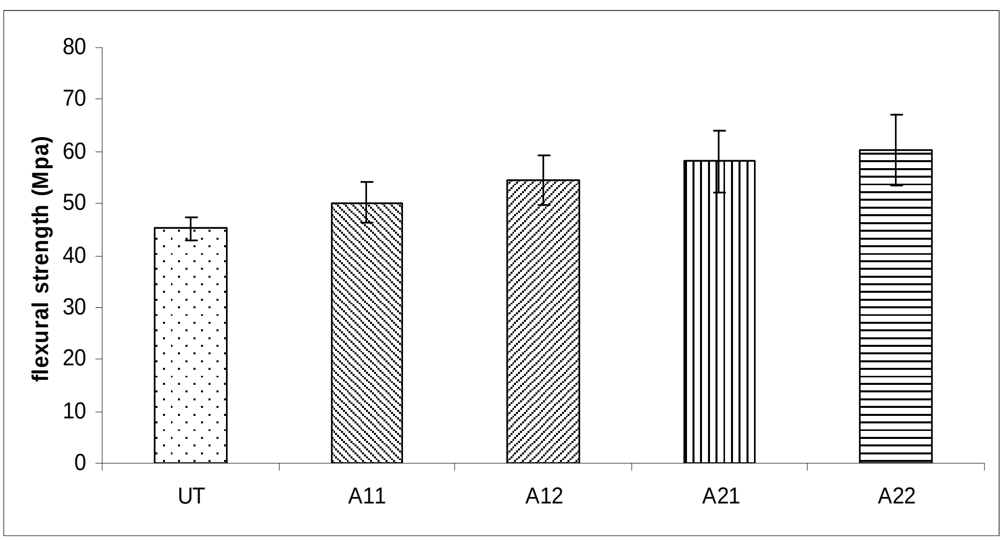

Fig. 3. Effect of the concentration and time of the alkali treatment on the flexural strengths of the composites

The alkali treatment with NaOH changes the crystal structure of the natural fiber from cellulose-I to cellulose-II. The original fiber crystal structure is cell-I, which is transformed into a different type of crystal structure, cell-II, typically at an NaOH concentration greater than 10 wt% (Borysiak and Garbarezyk 2003; Dinand et al. 2003; Prasad and Sain 2003); therefore, it might be explained that the mechanical strength of rice straw flour/polypropylene composite is more influenced by removing impurities than by changing the crystal structure with alkali treatment. Increasing the alkali concentration of the treatment (from 5 to 10%) and also the treatment time for each concentration (from 45 to 90 min) to the rice straw flour with removing impurities, thus increases the surface roughness of the rice straw flour, cause to increasing reaction and adhesion between rice straw flour and polypropylene.

Tensile Properties

Figures 4 and 5 show the effects that the various treatment concentrations and time of the rice straw flour alkali treatments have on the tensile modulus and tensile strength of the composite in comparison with the untreated rice straw composite. The treatment with sodium hydroxide at the different concentrations and times shows an increase in tensile strength.

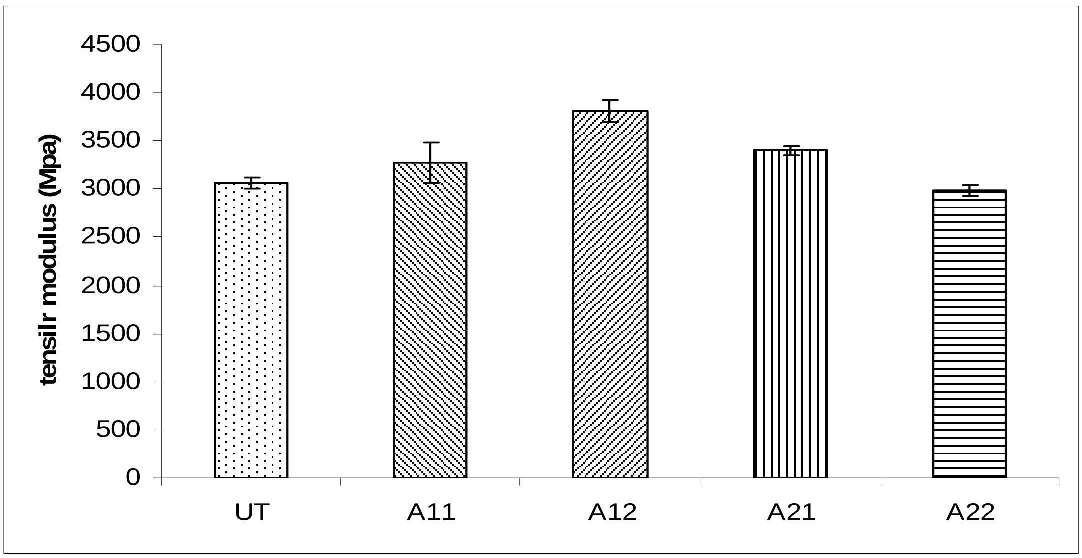

Fig. 4. Effect of the alkali concentration and treatment time on the tensile modulus of the composites

As shown in Fig. 5, the tensile strengths of the A11, A12, A21, and A22 composites were increased by 9, 19, 24, and 30, respectively, in comparison with the composite made without treated rice straw flour. Also, the tensile modulus of the A11, A12, and A21 composites increased by 7, 24, and 11%, respectively, when compared with the untreated composite. Treatment of the rice straw flour with an alkali concentration of 10%, however, slightly decreased this property, even with an increase in treatment time. This increase in tensile strength may be a result of the improved interfacial adhesion between the rice straw flour and polypropylene matrix. It is well known that the tensile strength of rice straw-polypropylene depends on the strength of both constituents and the adhesion between the rice straw flour and the matrix (Seki 2009).

The improved adhesion that is caused by the alkali-treated rice straw flour at the different alkali concentrations and treatment times more easily results in the stress being effectively transferred from the polypropylene matrix to the rice straw. Rice fiber consists of 43 to 49% cellulose, 23 to 28% hemicellulose, 12 to 16% lignin, and impurities (3 to 4% wax, 15 to 20% ash, and 9 to 14% silica) that conglutinate the fibers together in bundles. Thus, alkali solution is absolutely necessary in removing the pectin, hemicellulose, lignin, waxy substance, and natural oils covering the external surface of the fiber cell wall. Thereby, it results in a rough fiber surface and improves the fiber surface adhesion between the fiber and the matrix.

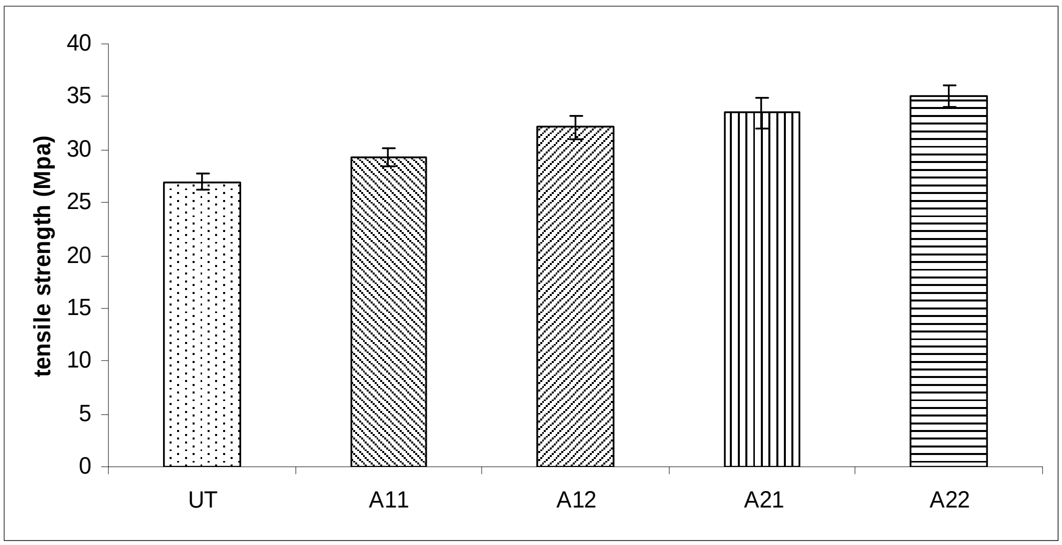

Fig. 5. Effect of the alkali concentration and treatment time on the tensile strengths of the composites

Figure 6 shows the SEM micrographs of the fracture surface of the different composites. The morphologies of the composites made with alkali-treated rice straw flour with 5 and 10% alkali concentration and 45 and 90 min of treatment can be observed in Fig. 6 (b), (c), (d), and (e). The morphology of the composite made without treatment is shown in Fig. 6 (a).

Although there is a large contact surface between the filler and matrix when the concentration and time of the alkali treatment increases, the rice straw flour/polypropylene adhesion remains good. Thus, the observed increase in mechanical properties of treated rice straw flour composites can be attributed to the fact that the alkali treatment removes natural and artificial products like hemicellulose, lignin, and waxes, producing a rough surface and causing fibrillation the cellulose fiber (Li et al. 2008).

Fibrillation increases the length/diameter ratio, thus enlarging the contact surface areas within the polymeric matrix, which produces better fiber-matrix adhesion and increases the composite's mechanical properties (Kuruvilla and Sabu 1996).

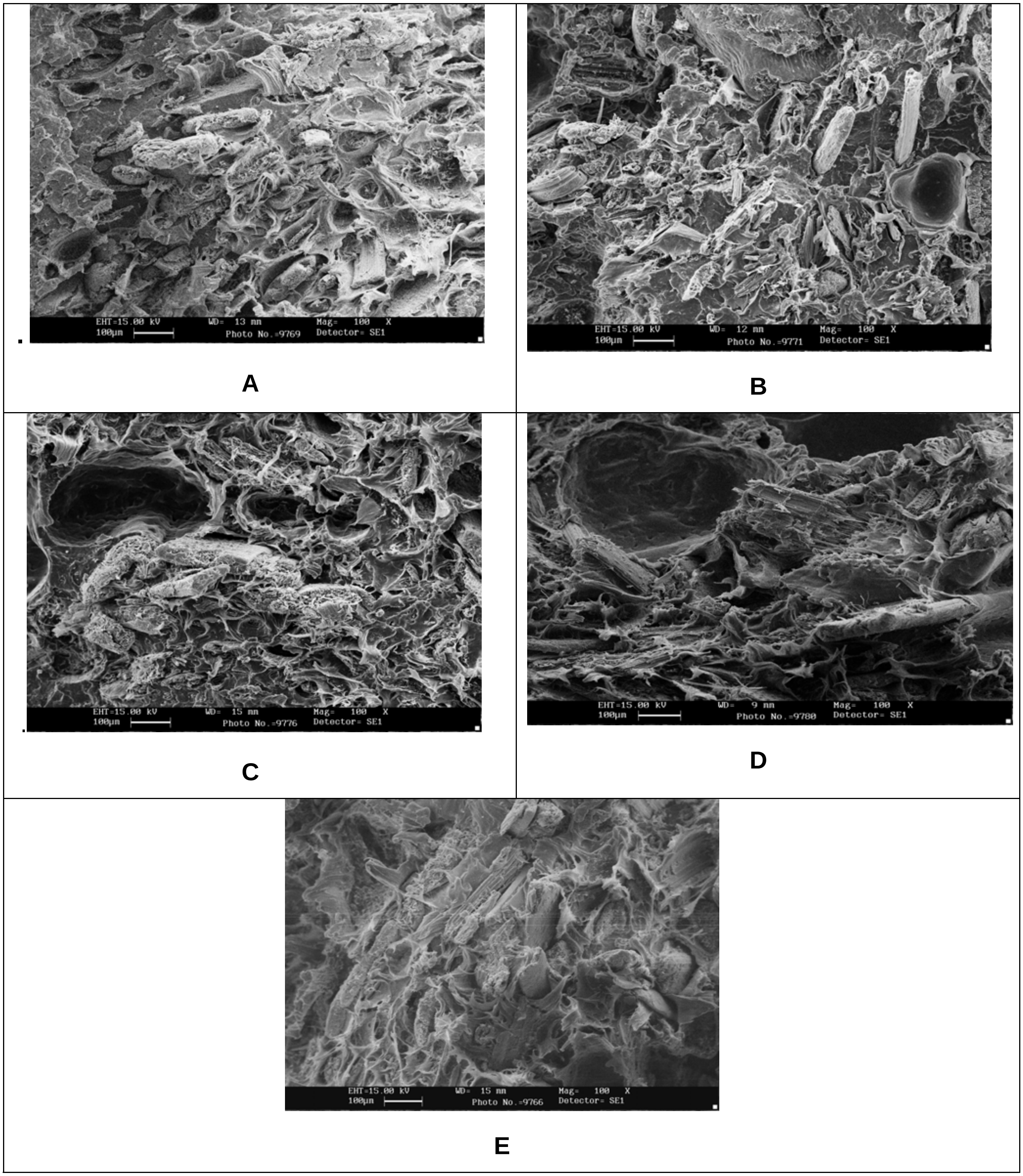

Fig. 6. SEM micrographs of the fracture surfaces of PP/rice straw flour composites made with different alkali concentrations and treatment times: UT (e), A11 (a), A12 (b), A21 (c), and A22 (d)

CONCLUSIONS

Mechanical properties such as tensile strength, tensile modulus, flexural strength, and flexural modulus of rice straw flour-reinforced polymer composites were investigated as a function of alkali treatment conditions of the rice straw flour. Based on the experimental results, the following conclusions were drawn:

1) Alkaline treatment releases the lignin and hemicellulose and creates fiber fibrillation. Fiber treatment by alkali results in an increase in interfacial adhesion between rice straw flour and polypropylene. At composition levels from 5 to 10% flour and time from 45 to 90 min, increasing mechanical properties were observed. Only tensile modulus showed decreases with increasing alkali concentration and time.
2) The results showed that increases in the alkali concentration and time of alkali treatment of the rice straw flour, as well as the use of functionalized polypropylene with maleic anhydride as a compatibilizer, improves the tensile and flexural properties of the composite.
3) The SEM micrographs of the fracture surface showed a larger contact surface between the rice straw flour and polypropylene at higher alkali concentrations and treatment times.

ACKNOWLEDGMENTS

The authors are grateful for the support of the Iran Polymer and Petrochemical Institute and Dr. Ghasmi.

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Article submitted: June 30, 2011; Peer review completed: August 22, 2011; Revised version received and accepted: Sept. 4, 2011, Published: Sept. 7, 2011.