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Biodegradable Composites from Rice Straw and Cornstarch Adhesives

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Abstract: The main goal of this study was to use Rice Straw (RS) in the production of environmentally sound composites using Cornstarch Adhesives (CA). Treatments of RS with NaOH, oxalic acid and hot-water were undertaken to evaluate the effect of such treatments on the characteristics of rice straw and the performance of produced composites. Results showed that all treatments were efficient in partially changing RS surface properties, as evidenced by FTIR and improving wettability of RS. The dependence of physical-mechanical properties of obtained composites on treatments performed on RS was studied. Hot-water treated straw composites displayed the best set of final mechanical properties. The composites exhibited poor waterproof performance, but considerable moisture resistance and environment-friendly properties.

Keywords: Biodegradable, physical-mechanical properties, rice straw/starch composites, wettability

INTRODUCTION

As the global demand for petroleum-based plastics continues to increase, environmental concerns and rising crude oil prices have triggered a search for replacements for these non-biodegradable plastics. The use of biorenewable resources for the production of biopolymers has gained a large amount of interest over the past decade because of their low cost and ready availability (Andjelkovic *et al*., 2005). Among them, agricultural residues are emerging as a source of raw materials which provide renewable and environmentally friendly alternative biomass resources for easing the high demand for woody materials (Sampathrajan *et al*., 1992). Besides their abundance and renewability, the utilization of agricultural residues has advantages for economy, environment and technology (Çöpür *et al*., 2007). Straw and starch are both rich in resources and their composites represented low density, renewable nature and biodegradable characteristic, which other composites cannot match (Reddy and Yang, 2007). Using straw and other agricultural residues for preparation of composites materials has become the focus of world. But discarded tires, formaldehyde resins, polymers are main matrix (Andrzej *et al*., 2010) and crushed materials (e.g., straw powder, rice husk powder, husk powder or extracted straw fiber) are main reinforcements for preparation of composite (Mingzhu *et al*., 2010). Such composites materials have lower water absorption and better acoustic insulation properties, higher internal bond strength and flexibility and flexural strength, bigger fracture coefficient. But smashing agricultural residues and extracting fiber from straw waste lots of energy and the matrix of such composites is difficult to degrade.

This study reported the preparation of cornstarch-based biodegradable composites using rice straw as a natural fiber filler by a compression molding process. Treatments of RS with NaOH, oxalic acid and hot-water were undertaken to evaluate the effect of such treatments on the characteristics of RS. Surface chemistry of RS was studied by FTIR. The effect of treatments on physical-mechanical properties: Modulus of Rupture (MOR), Modulus of Elasticity (MOE), Flexural Strength (FS), Impact Strength (IS), Tensile Strength (TS), Internal Bond (IB) and Moisture Absorption (MA), of the resulting composites were also investigated.

MATERIALS AND METHODS

The study is finished in Feb, 2012. Rice Straw (RS), was from Luhe, Nanjing (China), moisture content was 8.09%. After smash, RS was 1-30 mm length. Cornstarch (CS) was food grade and provided by Jincheng Food Co., Ltd (Shandong, China).

Methods: RS was extensively washed with distilled water in order to remove impurities (mainly dust). This operation was performed several times at room temperature and under vigorous stirring. After successive washings, RS was dried in an air-circulated oven at 103°C. This material was stored in hermetic plastic containers in order to prevent microbial attack (i.e., fungi) before using it in followed treatments. Washed RS without any further treatments was used as control and was labeled CRS.

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Some components of cellulose fibers represent a hydrophobic blockage for fiber wetting and they must be efficiently removed (Ndazi *et al*., 2007). RS is rich in silica and waxes, deteriorating the properties and making RS unsuitable for textile applications (Salam *et al*., 2007). In order to improve the RS wettability and performance, different treatments were applied. CRS was soaked in 2% NaOH solution, for 2 h at room temperature with occasional shaking followed by washing with distilled water for several times to leach out the absorbed NaOH until neutral was reached subsequently oven dried. The NaOH-treated CRS was labeled as NRS.

CRS was soaked in 2% oxalic acid solution, for 2 h at room temperature with occasional shaking. Afterward, the oxalic acid-treated RS was washed with abundant distilled water to leach out the absorbed oxalic acid until neutral was reached subsequently oven dried. The oxalic acid-treated CRS was labeled as ORS.

CRS was soaked in hot-water, for 2 h at 100°C followed by oven dried. The hot-water-treated CRS was labeled as HRS.

Cornstarch adhesives was prepared by the dispersion of the Cornstarch (CS) powder in distilled water at a CS-to-water ratio 1:10 under stirring at room temperature for 2 h with 1.2 wt% sodium thiosulfate ($Na_2S_2O_3.5H_2O$) on dry basis of CS for preventing deterioration. The resultant adhesives were then ready to be mixed with RS.

The composites were prepared using a hot compression molding process. Treated and untreated CRS were blended with the home-made CS-based adhesives (10 wt% solids) in an orbital paddle mixer for 10 min at room temperature. The equilibrated mixtures were subsequently hot-pressed into composites in a 10×10 cm steel mould equipped with stops to achieve the same thickness (0.45 cm). The press time, pressure and temperature were 30 min, 4 MPa and 120°C, respectively.

Analysis methods: A Nicolet iS-10 FTIR, Thermo Fisher Scientific, US was used to obtain spectra for the treated and untreated rice straw. FTIR spectra were recorded in a range of 4000-400 cm at a resolution of 4 cm with 32 scans.

The contact angle was measured to check the water repellent property of RS, using a jc2000D contact angle instrument (Jinchen, China). The temperature during measurements was 23±1°C and the relative humidity was 55±3%.

FS, MOE, IB, TS and MOR of the obtained composites were determined in a TMS-Pro test machine (FTC, US). IS was determined in a Charpy impact test machine, Jinjian XJJ-5 (Chengde, China). All samples were conditioned at 65% relative humidity at 20°C and for 7 days before testing. MA was also measured. The weight was measured immediately after soaking. The final values were the average of five measurements.

RESULTS AND DISCUSSION

RS had the same basic components as wood but in different proportions, depending on the rice variety. Therefore, it would be expected that RS should behave similarly to wood in composites production. RS had lower cellulose and lignin content than wood, but higher amounts of silica which reduced the interactions with adhesives such as cornstarch-based adhesives (Ndazi *et al*., 2007). Treatments on RS were undertaken in order to upgrade RS wettability and surface properties. The effectiveness of each treatment was evaluated by examining their influence on RS's relative FTIR, surface morphology and contact angle, as well as on the performance of the obtained composites.

Figure 1 showed the FTIR spectrum of CRS, HBS, NRS and ORS. Observation of the absorption bands showed that the changes between treated and untreated

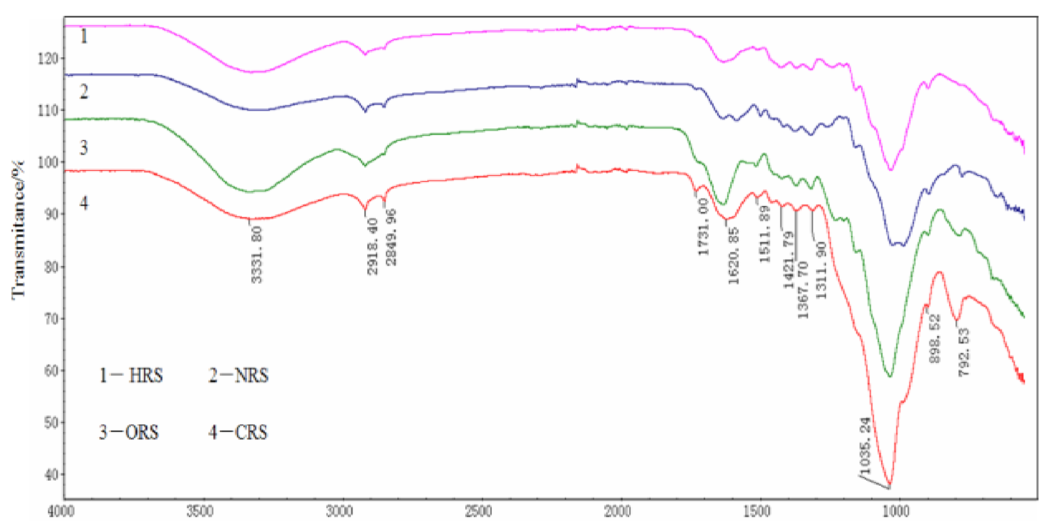

Fig. 1: FTIR of rice straw

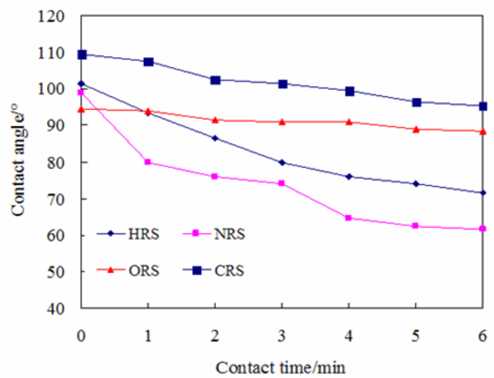

Fig. 2: Contact angles of rice straw

rice straw were mainly due to the formation of oxygen functionalities which were associated with 1800~700 cm range. The band centered at 1730 cm was usually ascribed to the stretching vibration of C = O in ketones, aldehydes, lactones and carboxyl groups (Anupama *et al*., 2010). The band around 1620 cm was attributed to COO-asymmetric stretching. The broad adsorption band in the 1300~1000 cm range could be assigned to various C-bonds, such as those in ethers, phenols and hydroxyl groups (Mascarenhas *et al*., 2000). These results indicated that all treatments gave rise to a large increase in carboxylic and lactone group C = O bonds.

The changes in the amount of hemicellulose could be seen by changes in the absorbance band approximately at 1640 cm which was associated with adsorbed water to this highly hydrophilic component that easily became hydrated after treatments. The treated RS had most likely absorbed moisture during storage as they were not kept in a moisture-free environment. This band showed a decrease after NaOH and hot-water treatments. The absorption band at approximately 1030 cm was characteristic for C-O stretching of an alcohol both in cellulose and hemicellulose; the spectra showed an unexpected decrease in absorption after NaOH and hot-water treatments. For lignin components the spectra showed an increase after NaOH and hot-water treatments.

Aromatic rings, characteristic for lignin, showed an increased absorption at the following bands: Aromatic skeletal vibrations (C-C stretch) assigned at 1600 and 1510 cm together with C-H out-of-plane bending vibrations assigned at 835 cm ; aliphatic C-H stretching assigned at 1370 cm. Lastly, an absorption band typical for guaiacyl rings were assigned at 1320 cm. Otherwise, the absorption bands typical for lignin compounds generally increased after NaOH and hot-water treatments which must related to the solubilisation of hemicellulose during treatments.

The final properties of composites depended on fiber properties and matrix properties as well as the adhesion between the reinforcing fiber and the matrix in composites. The wetting of the fiber was an integrated step in the adhesion process and played an important role. Figure 2 showed the contact angles of rice straw before and after treatments. Smaller contact angle indicated stronger infiltration, which indicated greater force with starch adhesives and higher interface bonding strength of the composites. Untreated rice straw had bigger surface contact angle and hot-water treatments, NaOH treatments and acid treatments could reduce the contact angle on rice straw surface in different levels. Hot-water treatments and NaOH treatments effected rice straw wettability greater. Although the contact angles decreased with contact time, the contact angle on untreated rice straw surface was still 24°, 34° and 7° higher than that on the hot-water-treated, NaOH-treated and acid-treated rice straw surface, respectively.

Figure 3 showed the mechanical properties results of obtained composites. The effect of RS treatments on mechanical properties would be the result of the competition between the increased adhesion due to the more exposed polar groups onto RS's surface and the damage (damnification, cracks, etc.) caused by the chemical agents used. The average values of modulus of rupture, modulus of elasticity, flexural strength, impact strength, tensile strength and internal bond (MOR, MOE, FS, IS, TS and IB, respectively) of composites produced with CRS, NRS, ORS and HRS and bonded with cornstarch adhesives, respectively. FS, MOE, IS, TS and MOR values showed that hot-water treatments on RS induced better performance on the obtained composites. NaOH treatments on RS improved IB and MOE values, but reduced FS, IS, TS and MOR values of the composites. In contrast, acid treatments on RS reduced IB, FS, MOE and IS of the composites significantly and only TS and MOR values were more than that of untreated rice straw composites. This could be attributed to the higher content of silica, which existed in the form of non-polar surface structure, resisting the adsorption of rice straw with cornstarch adhesives. Simultaneity, there was a smooth layer of wax on the surface of rice straw obviously, making less friction between rice straws and adhesives and cornstarch adhesives was difficult to enter through the surface of the rice straw inside and gluing process was difficult to form a "gel nails". Those had a negative impact on the producing of rice straw composites and reduced the strength of composites.

Hot-water treatments on RS removed the silica and wax on the surface partly, which reduced the contact angle on straw surface previously mentioned in Fig. 2 and increased infiltration with starch adhesives, making higher interface bonding strength between rice straw and adhesives. Rice straw also maintained better structure and the composites obtained from HRS had higher mechanical properties. NaOH treatments on RS, leading to greater physical and chemical changes and reducing the stiffness of rice straw, improved IB values

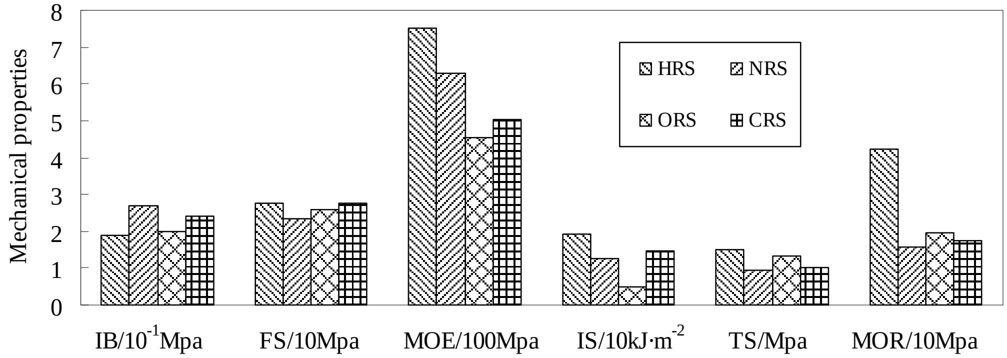

Fig. 3: Effect of treatments on mechanical properties of composites

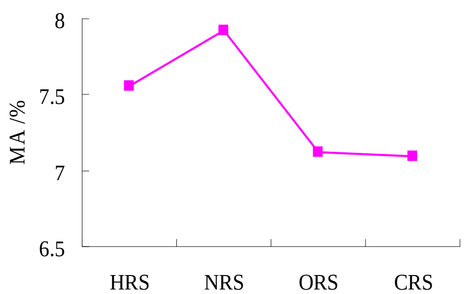

Fig. 4: Equilibrium moisture absorption of composites

only. On the other hand, IB proved to be more sensitive to NaOH treatments on RS. It is noteworthy that NaOH-treated RS produced an increment in the average IB values. These findings were mainly attributed to the exposed hydroxyl groups from the lignocellulosic substrate. NaOH can break internal structure of rice straw, which in turn unfolded and exposed many hydroxyl groups and able to bond with polar groups (hydroxyl and carboxyl side-chain groups) from the cornstarch adhesives. In addition, the unfolded fibers had increased contact area with cornstarch adhesives, which can also contribute to the increasing internal bond strength. Acid treatments on RS improved the wettability of the rice straw slightly, but because of cellulose degradation and structure destruction and deteriorated mechanical strength of the rice straw (Sahina and Youngb, 2008), so the composites obtained from NRS had lower IB, FS, MOE and IS.

RS-based composites can be used for indoor furniture and interior decoration. Due to its hydroxyl, such composites was susceptible to water and humidity. The weight, size and intensity of the composites would change. Therefore the water absorption and moisture absorption property of RS-based composites were important research topics.

The Equilibrium Moisture Absorption (EMA) for all composites was given in Fig. 4. From Fig. 4, EMA values of composites increased from 7.093 to 7.922%, respectively. NRS-based composites had maximum value and CRS-based composites had minimum value. This could be accounted for the better wettability of the NRS and better water resistant of CRS that had silica and wax, which can be served as a "raincoat" for RS. However, Compared with rice straw powder/PP composites, whose EMA values was 6.21% (Zhu, 2010) (rice straw powder loading contents of 80 wt %), rice straw/cornstarch adhesives biodegradable composites behaved lower moisture resistance slightly.

CONCLUSION

In this study, biodegradable composites had been prepared using Rice Straw (RS) as a natural fiber to reinforce a cornstarch-based adhesives being zero emissions of formaldehyde. Treatments on RS were undertaken in order to improve wettability of rice straw fiber and upgrade the adhesion with adhesives such as those derived from cornstarch. All treatments were efficient in partially changing RS surface properties, as evidenced by FTIR and improving RS wettability. Hot-water-treated straw composites displayed the best set of final mechanical properties. The composites exhibited considerable moisture resistance and environment-friendly properties. The biodegradable composites produced in this study should thus be good candidates for indoor applications for which the requirements for water resistance were not stringent.

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