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Glutaraldehyde/Polyvinyl Alcohol Crosslinked Nanosphere Modified Corn Stalk Reinforced Polypropylene Composite

Shanshan Liu, Heyi Ge, Yu Zou and Juan Chen*

School of Materials Science and Engineering, University of Jinan, Jinan 250022, People's Republic of China

*corresponding author: mse_chenj@ujn.edu.cn

Abstract. In this paper, polypropylene (PP) based wood-plastic composite (WPC) was prepared from corn straw fiber (CSF), and a new green way was found for the treatment of agricultural waste. In order to improve the interfacial compatibility between CSF and PP matrix, the glutaraldehyde (GA) and polyvinyl alcohol (PVA) crosslinked modified CSF was used. GA and PVA were crosslinked to form polymer particles on the surface of CSF. The WPC was characterized by SEM, FTIR, XRD and electronic universal testing machine. When the loading of modified CSF was 30 wt%, the flexural strength of WPC was up to 62 MPa, which was 12.3% higher than that of WPC reinforced by untreated CSF. Meanwhile, the composite reinforced by modified CSF had lower water absorption compared with that of the untreated CSF composite.

1. Introduction

Wood-plastic composite (WPC) is a green, high-performance material processed by different molding processes using wood powder and thermoplastic resin. The waste corn stalk is an ideal reinforce of WPC, which has good tensile strength, tensile modulus, hardness, flexural strength and flexural modulus. Compared with wood fiber, corn stalk fiber has better dimensional stability, processing properties, good environmental performance and low cost [1].

Interfacial compatibility between natural fibers and plastics is an important topic for scholars. Plant fibers contain a large number of polar groups, while plastic surface has non-polar groups. As a result, the compatibility between the two materials is poor, influencing the mechanical properties of the composites. Some methods have been adopted to improve the interfacial compatibility between plant fibers and plastics, including physical methods and chemical methods [2].

Polyvinyl alcohol (PVA) is a hydrolysis product of polyvinyl acetate, a polymer obtained by polymerization of a monomer without polymerization of a monomer [3]. It has excellent solvent resistance, biocompatibility, non-toxicity and good film-forming properties, and can form a smooth, strong tear-resistant film [4]. Glutaraldehyde (GA, $C_5H_8O_2$), is a transparent oily liquid with a pungent odor. It is soluble in hot water and can be used as a processing aid for food industry, wood preservatives, pharmaceuticals and synthetic raw materials for polymers. Chiellini et al. confirmed that PVA could cross-link with GA and GA could react with the hydroxyl functional group of PVA polymer chain to form an acetal bond [5].

Researchers have conducted a lot of research on the poor combination between natural fibers and thermoplastic substrates. However, the method for improve the interface compatibility by modifying CSF using GA and PVA has not been reported so far. In this paper, GA and PVA were modified on the CSF by a crosslinking reaction and the modified CSF was extruded with PP. The modified CSF and the composite were named as GA/PVA-CSF and GA/PVA-CSF-PP, respectively. GA/PVA-CSF



had better compatibility with PP matrix than the untreated CSF (UT-CSF). GA/PVA-CSF-PP had higher interface bonding strength and mechanical properties such as flexural strength and flexural modulus.

2. Experiment

2.1. Materials

Corn stalks were collected directly from farmland. PP was supplied by Lanyu Plastic Raw Materials Co., Ltd., Dongguan. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, PVA, GA and liquid were purchased from Aladdin Reagent Company, Shanghai. All chemical reagents were analytical reagent (AR).

2.2. Preparation of GA/PVA-CSF

After corn stalks were dried at 105 °C for 12 h, the inner core was stripped out and the skin was crushed by two steps of coarse grinding and fine grinding. The standard test sieve was used to sieve the CSF. The particle size was about 80-100 mesh. 295 g deionized water, 5 g PVA and 50 mL liquid paraffin were added to the three-neck flask, and the system was stirred at 95 °C for 1 h. 5 g CSF was added into the flask and stirred for 1 h. 3 mL GA and 4.5 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were added in the system and stirred at 95 °C for another 3 h. The product was filtered, washed with absolute ethanol and deionized water until the washing solution was clear and dried at 85 °C for 24 h to get GA/PVA-CSF.

2.3. Preparation of Composites

CSF and PP coupling agent were uniformly mixed (the mass ratio of CSF to PP was given in Table1), which were slowly added to the hopper of the twin-screw extruder at a feed rate of 5 r/min and an extrusion rate of 35 r/min. The temperature of the set twin-screw extruder was 160°C, 165°C, 170°C and 175°C. The hopper temperature of the micro injection molding machine was 205°C. The mold temperature was 40°C and the injection pressure was 5 MPa.

Table 1. Constituents of composites and abbreviations for respective samples

Samples	GA/PVA-CSF Content (wt%)	Samples	UT-CSF Content (wt%)
10GA/PVA-CSF-PP	10	10UT-CSF-PP	10
20GA/PVA-CSF-PP	20	20UT-CSF-PP	20
30GA/PVA-CSF-PP	30	30UT-CSF-PP	30
40GA/PVA-CSF-PP	40	40UT-CSF-PP	40

3. Results and Discussion

Figure 1a is a view of the surface morphology of the UT-CSF. The UT-CSF has a smooth surface. After modified with GA/PVA, as can be seen from Figure 1b, many white polymer particles are formed on the surface of the CSF, which are the product of the cross-linking. It can be seen from Figure 1c that the spherical particles have a diameter of about 100 nm.

Figure 1d is the image of 40UT-CSF-PP section. It can be seen that the CSF is not tightly bonded to the PP matrix, and there is a gap between them. This is because the UT-CSF has a smooth surface, and it is difficult to be compatible with PP. It can be seen from Figure 1e,f that the GA/PVA-CSF is closely combined with PP, and there is no void between the two parts. The reason is that the surface of CSF has produced a lot of polymer particles after cross-linking modification, which increases the roughness of the CSF surface. Therefore, the modification of CSF can strengthen the physical bond between CSF and PP matrix.

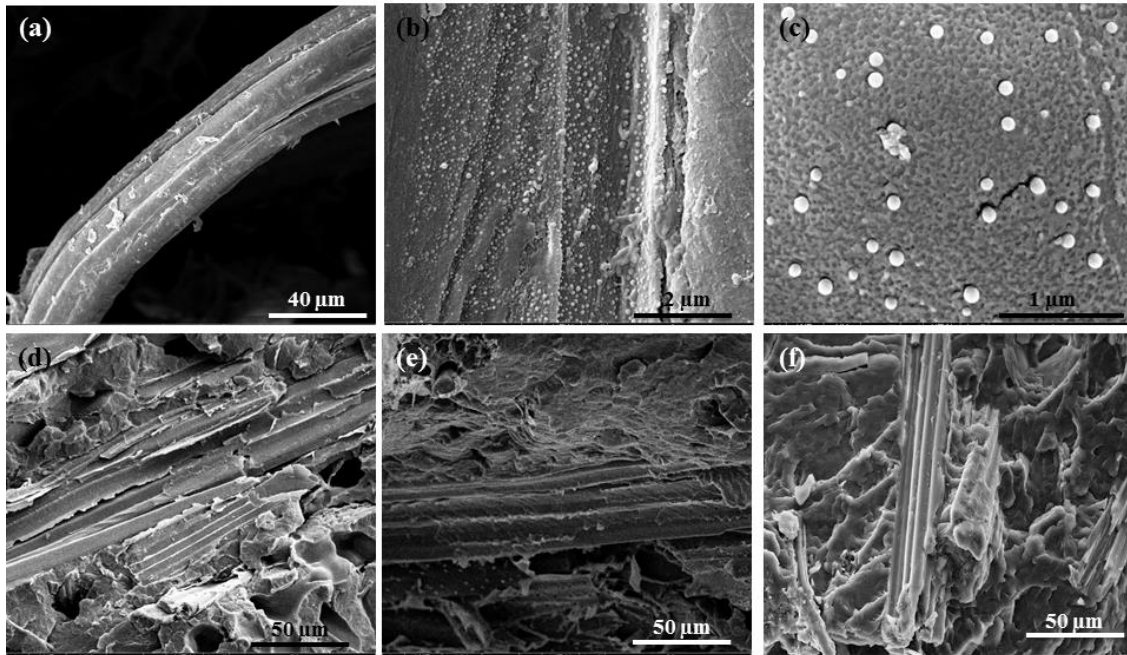


Figure 1. SEM of the samples: (a) UT-CSF, (b) GA/PVA-CSF, (c) magnified GA/PVA-CSF, (d) 40UT-CSF-PP, (e) 40GA/PVA-CSF-PP and (f) 30GA/PVA-CSF-PP.

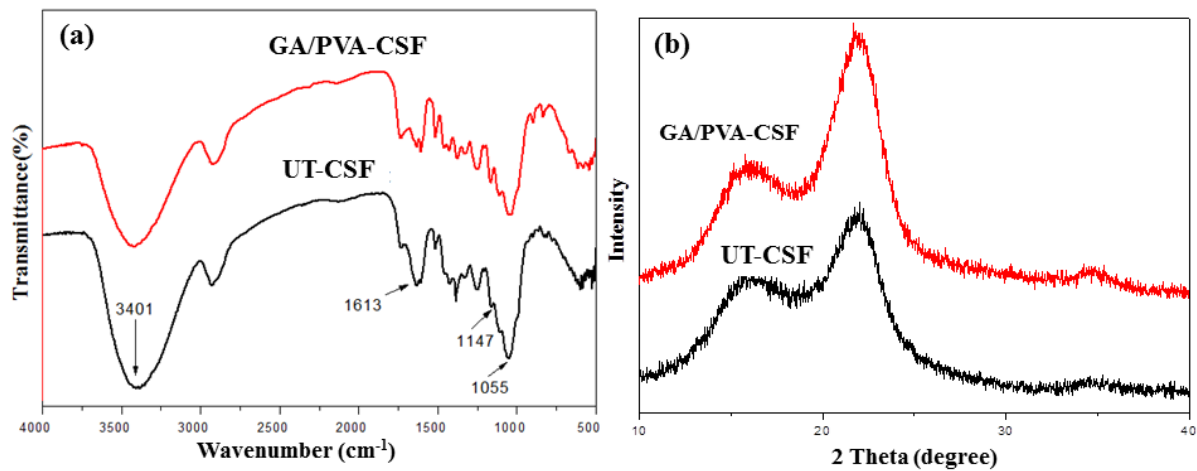


Figure 2. FTIR of CSF (a) and XRD of CSF (b)

The FTIR of the two kinds of CSF is shown in Figure 2a. The band at $3500\sim 3300\text{ cm}^{-1}$ is correspond to the stretching vibration of cellulose hydroxyl group ($-\text{OH}$), and the band at $1600\sim 1900\text{ cm}^{-1}$ is the stretching vibration peak of $\text{C}=\text{O}$ bond in cellulose. The band at $1100\sim 1300\text{ cm}^{-1}$ is the stretching vibration peak of $\text{C}-\text{O}$ [6-8]. It can be seen from Figure 2a that the single peak at 1631 cm^{-1} has been splitted into two independent peaks around 1600 cm^{-1} , and the peak at 1147 cm^{-1} is increased on the FTIR spectrum of GA/PVA-CSF compared to UT-CSF, indicating that the polymer particles have formed by the cross-linking reaction of GA and PVA on the surface of CSF.

The XRD spectrum of the two kinds of CSF is shown in Figure 2b. Obviously, there are two main peaks at 16° and 22° , reflecting the (100) and (002) planes of hemicellulose and lignin. The peak at 16° represents the amorphous phase of hemicellulose and lignin, and the peak at 22° is closely related to the crystalline cellulose phase of CSF. The crystallinity index (CrI) calculated from equation (1) is a parameter used to measure the content of crystalline cellulose in cellulosic materials [9].

$$CrI (\%) = \frac{I_{002} - I_{am}}{I_{am}} \times 100 \% \quad (1)$$

where I_{002} is the peak intensity at a 2θ angle close to 22° and I_{am} is the amorphous counter reading at a 2θ angle of around 18° . Compared with UT-CSF, the CrI of GA/PVA-CSF increases from 33.6% to 35%, which is mainly due to the damage the amorphous substance at high temperature and the formation of polymer particles on the surface of CSF.

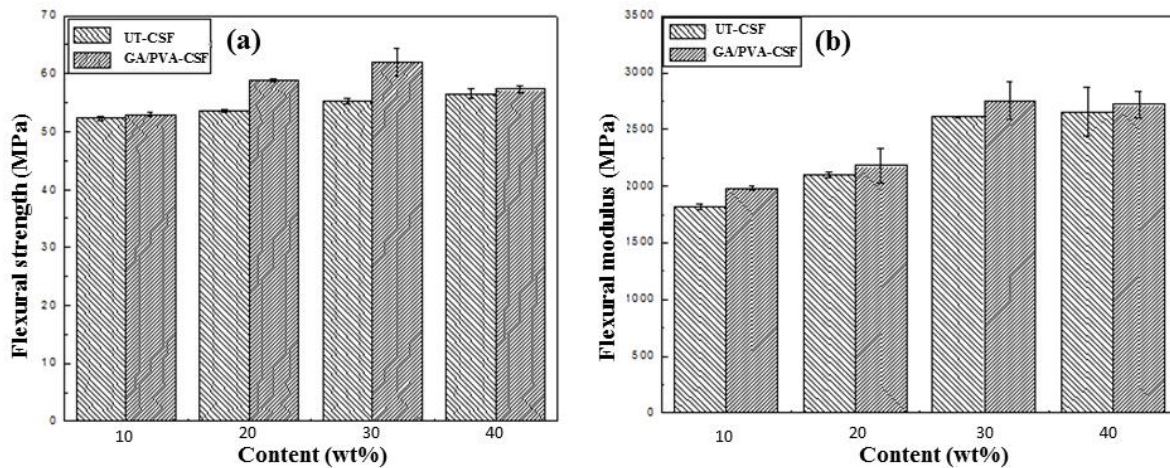


Figure 3. Flexural strength (a) and flexural modulus (b) of the composites.

Figure 3 is a graph of flexural strength and flexural modulus of WPC. For the two kinds of CSF, both the flexural strength and the flexural modulus increase when the CSF loading is less than 30 wt%. It can be seen from Figure 3a that the flexural strength of GA/PVA-CSF-PP is higher than that of UT-CSF-PP because the surface of the modified CSF generates polymer particles, which makes the surface of CSF rougher. The contact area between the CSF and the PP becomes larger, and the interface bonding strength is increased, so that the flexural strength is enhanced. The 30GA/PVA-CSF-PP has the highest flexural strength of 62 MPa. When the loading of GA/PVA-CSF is more than 30 wt%, the flexural strength of the composite is reduced. Meanwhile, it can be seen from Figure 3b that the flexural modulus of GA/PVA-CSF-PP is higher than that of UT-CSF-PP, indicating that the ability of GA/PVA-CSF-PP to resist flexural deformation within the elastic limit is further improved. It is verified that the interfacial bonding strength between the modified CSF and the PP matrix is enhanced.

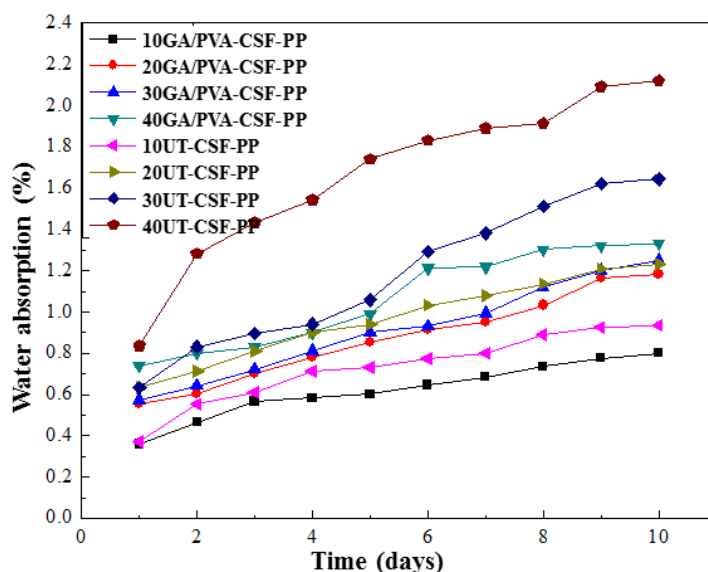


Figure 4. Water absorption rate of the prepared composites.

The interface compatibility of WPC is important factor affecting the water absorption of WPC. If the water absorption rate is too high, the defects such as damage of interface, fracture deformation, and mildew will occur. Therefore, it is of great significance to reduce the water absorption of WPC.

Figure 4 shows the water absorption of the prepared WPCs. It can be seen that after 10 days, the water absorption rate of 10GA/PVA-CSF-PP is the lowest; the highest water absorption of 40UT-CSF-PP is 2.12%. The water absorption of GA/PVA-CSF-PP is lower than that of UT-CSF-PP because the PP matrix is more tightly bound to CSF in GA/PVA-CSF-PP. The more the percentage of CSF is added, the higher the water absorption rate. This is because there is a large amount of hydroxyl groups in the cellulose, which makes CSF polar, and CSF has the same polarity as water, so the water absorption increases.

4. Conclusion

This study provides a new method to modify CSF to improve the interface compatibility of WPC. The microstructures of GA/PVA-CSF and GA/PVA-CSF-PP were characterized. The flexural properties and the water absorption of WPC were studied. Through the cross-linking reaction, a large number of nanoparticles were formed on the surface of the CSF. The presence of these particles could increase the roughness of the surface of the CSF, thereby increasing the occlusal force area between CSF and PP. The interfacial compatibility of the composite was improved. Moreover, it was found by flexural performance test that the flexural strength and the flexural modulus of GA/PVA-CSF-PP were higher than those of UT-CSF-PP. The water absorption performance test results showed that the water absorption of GA/PVA-CSF-PP was less than that of UT-CSF-PP. Therefore, GA/PVA modified CSF can effectively improve the compatibility and the strength of CSF-PP composite. This study provides an effective solution to the interface compatibility problem of WPC.

Acknowledgments

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