Effect of the Cross-Linking Modification on Corn Stalk Fiber Reinforced Polypropylene Composites

Shanshan Liu, Ke Li, 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 study, corn stalk fiber (CSF) was used as a reinforcement to prepare wood plastic composite (WPC). The primitive CSF was subjected to alkali treatment in a low alkali solution to expose the cellulose fiber. Alkali-treated CSF (AT-CSF) was cross-linking modified with chitosan and glutaraldehyde. Then, the untreated CSF (UT-CSF) and the cross-linked modified CSF (CL-CSF) were added to polypropylene (PP) with different contents (10 wt%, 20 wt%, 30 wt%, 40 wt%), respectively. The morphology, mechanical, thermal and water absorption behaviours of WPC were investigated in detail. The results indicated that the crosslinking modification is an efficient method to improve the mechanical properties of WPC. Compared with UT-CSF, the crystallinity index (CrI) of CL-CSF was increased from 33.8% to 39.5%. The cross-linking modification promoted an increase in flexural strength of 19.2% and an increase in flexural modulus of 8.3% compared to the composite reinforced by UT-CSF. The water absorption of the composite reinforced by CL-CSF was lower than the composite reinforced by UT-CSF.

1. Introduction

In recent years, natural fibers as reinforcements in wood plastic composites (WPC) have attracted the attention of many researchers. Low density, high specific tensile strength, high specific stiffness, and high aspect ratio are the main advantages of natural fibers [1], which make it possible for natural fibers to replace glass fiber [2].

Chitosan is the deacetylated form of chitin that is extracted from the shells of crustaceans. It has a unique advantage in some respects because of its biocompatibility, biodegradability, hydrophilicity, nontoxicity and nonantigenicity [3]. In addition, there is a tremendous potential for chitosan to develop as an excellent bio-coupling agent with its presence of rich hydroxyl and amino groups. Cross-linking modification of chitosan has wide application in the field of preparation of adsorbents and food packaging films [4].

Glutaraldehyde (GA) is a well-studied commercial adhesive, which has the efficient ability to react with the -NH₂ groups of chitosan [5]. Chitosan can be converted into a stable network structure with the help of crosslinking modification [6]. Hydrophilic amino groups are consumed resulting in the increase of hydrophobicity of the cross-linked product.

In this paper, the chemical crosslinking technique was supposed to increase the compatibility between the corn stalk fiber (CSF) and polypropylene (PP) matrix. CSF was modified via the crosslinking of chitosan with GA. The composite reinforced by the modified CSF was obtained by injection molding. The loading of CSF was increased from 0 to 40 wt%. Moreover, the mechanical properties and the water stability of the composite were investigated in detail.
2. Experiment

2.1. Treatment of CSF
Corn stalks were harvested on a local farm in Shan Dong Province, China. The stalks were crushed and screened using 80 mesh sieves to get powder. The dried powder was soaked in an alkali solution (3 wt%) at room temperature for 2 h. Then, washed several times with distilled water to pH = 7 and dried at 105°C for 24 h to get alkali-treated CSF (AT-CSF).

1 g chitosan was dissolved into 60 mL acetic acid solution (2 wt%) with stirring at room temperature for 30 min. 10 g AT-CSF were distributed in the chitosan solution with the help of mechanical stirring. Simultaneously, 60 mL liquid paraffin and 3 mL span 80 were added to the above system. The system was stirred at 40 °C for 30 min to get emulsion.

GA (5 wt%) was added into the above emulsion and the emulsion was adjusted to pH = 9-11. The system was stirred at 60 °C for 120 min and the obtained powder was washed with distilled water and absolute ethanol until the cleaner was transparent. The powder was dried to obtain cross-linked modified corn stalk fiber (CL-CSF).

2.2. Preparation of Composite
The formulations of the composite studied in this paper are given in table 1. The CSF used in this experiment was dried before mixing and the components were homogenized. The homogenized mixture was melt mixed by using a twin screw extruder (SJZS-10B with average screw diameter of 20 mm and average L/D ratio of 40). The hopper of the twin-screw extruder at a feed rate was 5 r/min and extrusion rate was 35 r/min. The temperatures of the four regions of twin-screw extruder were: 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. The composite combined CSF and PP was named as CSF-PP.

| Samples            | Fiber Content (wt%) | Samples           | Fiber Content (wt%) |
|--------------------|---------------------|-------------------|---------------------|
| 10UT*-CSF-PP       | 10                  | 10CL-CSF-PP       | 10                  |
| 20UT-CSF-PP        | 20                  | 20CL-CSF-PP       | 20                  |
| 30UT-CSF-PP        | 30                  | 30CL-CSF-PP       | 30                  |
| 40UT-CSF-PP        | 40                  | 40CL-CSF-PP       | 40                  |

*UT: untreated

2.3. Characterization
The Fourier transform infrared spectrophotometer (FTIR) spectra and the scanning electron microscope (SEM) were used to characterize fibers and composites. The flexural test of the WPC was carried out according to the ISO standards 527-1 using an advanced universal testing machine (Shanghai Shenli Testing Machine Company, China). The impact strength of all samples was measured on an impact type test machine (Chengde Jinjian Testing Machine Company, China) in accordance with ISO standards 179-1. The water absorption test was conducted in accordance with ASTM: D570-98 (2010).27.

The crystallinity of CSF was analysed with an X-ray diffractometer (D8 ADVANCE, Bruker, Germany). The crystallinity index (CrI) of CSF was calculated according to peak height method (equation (1)) [7].

\[
CrI (\%) = \frac{I_{002} - I_{am}}{I_{am}} \times 100 \%
\]
where $I_{002}$ is the peak intensity at a $2\theta$ angle close to 22° and $I_{am}$ is the amorphous counter reading at a $2\theta$ angle of around 18°.

3. Results and Discussion

![Figure 1](image)

**Figure 1.** SEM images of samples: (a) UT-CSF, (b) AT-CSF, (c) CL-CSF, (d) 20UT-CSF-PP, (e) 20CL-CSF-PP and (f) 40CL-CSF-PP

The different morphology of the CSF is shown in figure 1a-c. It is clear that the surface of UT-CSF contains impurities such as waxy and gummy materials. After the alkali treatment, the pectin, waxy and other impurities on the surface of CSF were removed and the cleaner and rougher surface can be observed in figure 1b. Besides, the alkali treatment made the structure of AT-CSF loosened, which is conductive for the crosslinking modification of CSF. Figure 1c shows that the surface of the CL-CSF is covered with transparent film, which is a product of the crosslinking of chitosan with glutaraldehyde. It can be clearly observed that the polymer film shows a wrinkled and distorted appearance on the surface of the CL-CSF, indicating that the polymer film has good toughness.

Figure 1d-e shows the fracture surface of the composites reinforced by UT-CSFs and CL-CSFs. Figure 1d shows the poor interfacial bonding of PP matrix to UT-CSF. Obviously, there are fiber pullouts and fiber breakage in the fracture surface, which indicates the poor interfacial adhesion between UT-CSF and PP matrix. The CL-CSF and PP matrix are in close contact with each other from the observation of figure 1e-f. The right hand twisted fibers can be observed, which are attributed to the stress transfer between the CSF and PP matrix. The excellent wetting of CL-CSF in PP matrix is presented in figure 1e-f. The cross-linking modification results in the better interfacial adhesion of the composite, which will facilitate mechanical properties and water resistance.
The FTIR spectra of chitosan, CL-CSF and AT-CSF are shown in figure 2a. The broad peaks of chitosan located around 3354 cm$^{-1}$ and 3280 cm$^{-1}$ correspond to the stretching vibrations of N-H and O-H respectively [8]. However, some changes have occurred in the FTIR of CL-CSF. The two independent peak of CL-CSF at 3354 cm$^{-1}$ and 3280 cm$^{-1}$ have been converted to single peak at 3289 cm$^{-1}$ could be attributed to the consumption of amino groups on the surface of chitosan [9]. Compared with chitosan, the FTIR of CL-CSF presents C=N stretching vibration at 1652 cm$^{-1}$, indicating that chemical reaction occurred during the cross-linking.

In figure 2b, XRD of three CSF shows two main peaks at 16$^\circ$ and 22$^\circ$, which are assigned to (1 0 0) and (0 0 2) reflection planes [7]. The peak at 20$^\circ$=16$^\circ$ refers to the amorphous phase of hemicellulose and lignin. The sharp peak with high intensity at 20$^\circ$=22$^\circ$, which is closely related to the crystalline cellulose phase of CSF. Fig. 2b clearly indicated that the alkali treatment and the crosslinking modification affect crystalline phase of CSF. The crystallinity index (CrI) is an important parameter for interpreting changes in the cellulose structure of plant fibers [8]. The CrI of AT-CSF increased to 40.7%, which was mainly related to the removal of amorphous material of CSF. Compared to AT-CSF, the CrI of CL-CSF is reduced to 39.5%. The decrease mainly caused by the crosslinking product attached to the surface of the fiber. Therefore, the cross-linked product covered by CSF surface is a network structure [9].

The flexural strength and modulus of composites reinforced by UT-CSF and CL-CSF have been presented in figure 3. It can be seen that both the flexural strength and the flexural modulus of the
composites increase as the content of CSF increases. The loading of CL-CSF (10 wt%, 20 wt%, 30 wt%, 40 wt%) promotes an increase in flexural strength of 4.2%, 4.0%, 14.5% and 19.2%, an increase in flexural modulus of 4.6%, 2.5%, 4.5% and 8.3% compared to those of UT-CSF composite.

![Figure 4. Impact strength of composites](image)

![Figure 5. Water absorption curves of composites](image)

The impact strength of the composites is shown in figure 4. The impact strength of the two composites increases first and then decreases with the increase of CSF content. When the CSF content is 20 wt%, the impact strength is the highest. Compared to UT-CSF-PP, the impact strength of CL-CSF-PP with different CSF content is increased 24.2%, 17.5%, 18.7%, and 34%, respectively. This is because the polymer film layer on the CL-CSF can improve the wettability between the CSF and the PP matrix.

Water absorption is of great significance for the application of WPC. The water absorption of composites over time is shown in figure 5. Obviously, CL-CSF-PP has lower water absorption than UT-CSF-PP. The water absorption of 40CL-CSF-PP (2.08 %) was lower than that of 40UT-CSF-PP (2.37 %) at 16 days. The lower water absorption implied that the cross-linking modification improved the interfacial compatibility between the CSF and PP.
4. Conclusion
In this study, the PP composites reinforced by UT-CSF and CL-CSF were fabricated by an injection molding machine. CL-CSF significantly enhanced the mechanical properties of the composite. Compared with UT-CSF, the CrI of CL-CSF was increased from 33.8% to 39.5%. The addition of CL-CSF promoted an increase in flexural strength of 4.2%, 4.0%, 14.5% and 19.2% and an increase in flexural modulus of 4.6%, 2.5%, 4.5% and 8.3% compared to UT-CSF composite. The water absorption of CL-CSF-PP was lower than that of UT-CSF-PP. The results indicate that the crosslinking modification is a promising method to improve the mechanical properties of WPC.

Acknowledgments
This work is supported by National Key R&D Program of China (Grant No.2016YFC0701005).

References
[1] Madsen B, Thygesen A and Lilholt H 2009 Compo. Sci. Technol. 69 1057
[2] Wambua P, Ivens J, and Verpoest I 2003 Compos. Sci. Technol. 63 1259
[3] Cheung H, Lau K, Lu T and Hui D 2007 Compos. B 38 291
[4] Kobayashi T and Furukawa I 1995 J. Antibact Antifung Agents 23 343
[5] Migneault I, Dartiguenave C, Bertrand M and Waldron K 2004 Biotechniques 37 790
[6] Ji X, Li B, Yuan B and Guo M 2017 Carbohydr. Polym. 176 273
[7] Motaung T E and Mtibe A 2015 Matei. Sci. & Appl. 6 1022-1032
[8] Li B, Shan C, Zhou Q, Fang Y, Wang Y, Xu F, Han L, Ibrahim M, Guo L, Xie G and Sun G 2013 Mar. Drugs 11 1534
[9] Kildeeva N, Perminov P, Vladimirov L Novikov W and Mikhailov S 2009 Russ. J. Bioorg. Chem. 35 360