INVESTIGATION OF HUMIDITY AGEING MECHANISM OF HEMP FIBER REINFORCED POLYPROPYLENE COMPOSITES

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Abstract

In this paper, the humidity ageing mechanism of hemp fiber reinforced polypropylene (PP) composites was studied. Four composites with different interfacial adhesion states were firstly prepared, which were performed by adding maleic anhydride grafted polypropylene (PP-g-MAH) and the treatment of hemp fiber by water/alkali. Then accelerated humidity ageing experiments for 8 weeks and tensile tests of these composites were performed. The water uptake and dimensional stability of composites were also determined. The results showed that the water absorbed in composites leads to the fiber swelling, results the increase of interface pressure and the enhancement of composites mechanical properties in initial ageing periods. With the process of ageing, the absorbed water degrades the fiber/matrix interface and fiber, results the composites mechanical properties decrease.

1. Introduction

Agro-composite attracts lots of investigation in reinforced composite for their environmental advantages and numerous potential applications [1]. The natural hydrophilicity of hemp fiber, due to the rich hydroxyl groups, results poor interfacial adhesion in reinforcement of hydrophobic thermoplastic polymers [2]. It also leads to agro-composites being sensitive to environmental humidity [3]. Moreover, the water absorption behavior affects the dimensional stability and decrease the mechanical properties of composites, which limits their applications like exposing to atmosphere or contact with aqueous media, for example, windows frames, decking and construction materials[4].

The humidity ageing of planted fiber reinforced PP composite is normally believed occurring in the interface of fiber/matrix and fiber itself caused by water absorption. PP-g-MAH is one of the most popular coupling agents used in planted fiber reinforced thermoplastic polymers. In addition, hemp fiber is usually treated with alkali or silane agent to decrease their hydrophilicity and improve the interfacial adhesion strength with nonpolar thermoplastics such as polyethylene (PE) and polypropylene (PP) [5]. Compared with alkali treatment, water treatment cleans the fiber surface by effectively removing the water-soluble polysaccharides while ensures minimum degradation of elementary fiber structure [6].

The objective of this paper is to investigate the humidity ageing mechanism of hemp fiber reinforced PP composites. Four composites with different interfacial adhesion strength were firstly prepared, which was carried out by adding MAH-g-PP and using water/alkali to treat hemp fiber. Then accelerated humidity ageing experiments for 8 weeks and tensile tests of these composites were performed to study the effects of humidity ageing on composites mechanical properties. The water uptake and the cross-section swelling of composites were also determined to evaluate the composites water uptake behavior and dimensional stability.

2. Experiments and analysis

2.1 Materials

Hemp fibers were kindly supplied by Fiber Research Development FRD®. The fiber arrived in a form of bundles and was cut into short fiber of 2.5 mm. PP was purchased from Dow, France, with density of 0.91 $g{\cdot}cm^{-3}$ and melt index of 8.1 $g{\cdot}$ $(10\ min)^{-1}$ (190 °C, 2.16 kg). MAH-g-PP with density of 0.91 $g{\cdot}cm^{-3}$ was supplied by DOW, France. Sodium hydroxide (Analysis pure) was obtained from Sigma-Aldrich.

2.2 Preparation of composites

Untreated fiber was washed with tap water for 3 times, 10 minutes each time. The ratio of fiber/water was 1: 50 (by weight). To obtain the alkali treated fiber, the water washed fiber were immersed in 5 wt.% sodium hydroxide solution at ambient temperature for 1 hour, followed by washing with tap water to remove the residual sodium hydroxide in the fiber until pH achieved 7. Finally, the water and alkali treated fiber was dried in an oven at 60 °C for 48 hours.

Hemp fiber, PP and MAH-g-PP were mixed in an extruder Brabender KE 19 at 170-185 °C. Tensile testing specimens (according to the standard ISO 527-2) were fabricated by injection moulding Engel spex victory 50 at 170-180 °C, 158 MPa. The formulation of composites is presented in Table 1.

Specimens	PP (phr)	MAH-g-PP (phr)	Fiber (phr)	Notations
Comp.1	100	0	42.86	untreated fiber
Comp.2	100	7.14	42.86	untreated fiber
Comp.3	100	7.14	42.86	water treated fiber
Comp.4	100	7.14	42.86	water, alkali treated fiber

Table 1. Formulation of composites

2.3 Analysis methods

Humidity accelerated ageing was performed in Atlas suntest XXL for 8 weeks. The ageing condition was: relative humidity 80±5 %, chamber temperature 20±2 °C, 102 minutes dry and 18 minutes water spray. SEM Hitachi S3500 was employed to observe the fracture surface of composites after tensile tests. To determine water uptake of composites, the specimens was dried firstly in an ovens at 80 °C for 24 hours to evaporate the residual water in composites and note the composite weight as M_0. These dried specimens were then completely put in

distilled water. For each 5-7 days, specimens' weight was measured after wiping the water on specimens' surface, noted as M_t. The weight increase of specimens should equal to the weight of absorbed water M_{H_2O}. The water uptake of composites $W_t(\%)$ can be calculated by the following formula:

$$W_t(\%) = \frac{M_t - M_0}{M_0} \times 100\% = \frac{M_{H_2O}}{M_0} \times 100\% \quad (1)$$

The tensile tests were carried out in a static tension machine Instron 4484 at room temperature with an imposed displacement rate of 2 mm·min^{-1}. An extensometer with a 12.5 mm initial opening length was placed at the center of specimens to measure the deformation.

2.4 Composites swelling

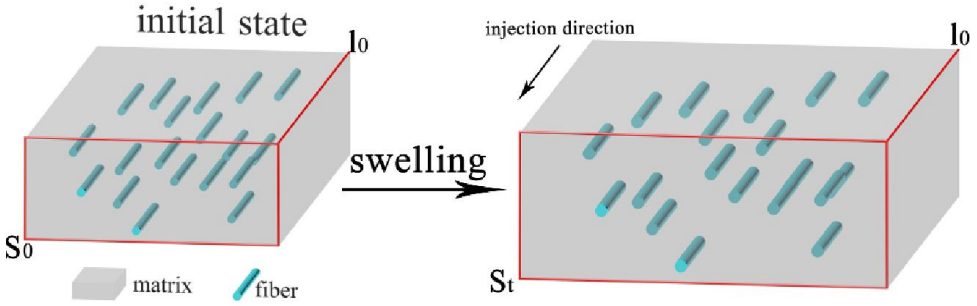

Figure 1. Schematic illustration of composites specimens subjects swelling. The present study assumed that the fiber oriented along the injection direction and swollen only in the fiber radial direction. Thus, the composites swollen in specimens cross-section with S_t (%) = [(S_t - S_0)/ S_0] × 100%, no swollen in fiber oriented direction (l_0).

The schematic illustration of composites specimens subject to swelling is displayed in figure 1. The volume of composites specimens before and after swollen is V_0 and V_t, respectively. So,

$$V_0 = S_0 \times l_0 \quad (2)$$

$$V_t = S_t \times l_0 \quad (3)$$

S_0, S_t is the cross-section area of specimens initial and after swollen, respectively. l_0 is the length of specimen along the fiber orientation. The cross-section area increasing of specimen was obtained by measuring the width and thickness of specimen. Moreover, it could be calculated from the specimen weight gains. Supposing the composites specimen has no voids, the swelling volume of V_t - V_0 should equal to the volume of absorbed water V_{H_2O}. So that the swelling rate of composites $V_t(\%)$ can be written as:

$$V_t(\%) = \frac{V_t - V_0}{V_0} \times 100\% = \frac{V_{H_2O}}{V_0} \times 100\% \quad (4)$$

Based on previous studies, the fibers generally distribute along the injection direction [7] and mainly swell along fiber radial direction [8]. Thus, if there are no swollen along the fiber axial

direction, the increase of specimens' cross-section area $S_t(\%)$ should equal to the volume increase:

$$S_t(\%) = V_t(\%) = \frac{V_{H_2O}}{V_0} \times 100\% \tag{5}$$

Combining Eqn. (5) with Eqn. (1), the relationship between composites specimens' weight gains and area cross-section increase can be conducted:

$$S_t(\%) = W_t(\%) \times \frac{1}{\rho_{H_2O}} \times \frac{M_0}{V_0} \tag{6}$$

where ρ_{H_2O} is the absorbed water density 1.0 g·cm^{-3}, M_0 is the initial mass of specimens; V_0 is the initial volume of specimens. M_0 and V_0 can be obtained by the following equations:

$$M_0 = m_m + m_f \tag{7}$$

$$V_0 = \frac{m_m}{\rho_m} + \frac{m_f}{\rho_f} \tag{8}$$

Where m_m, m_f is the mass of polymer matrix and fiber; ρ_m and ρ_f is the density of matrix and hemp fiber. The density of hemp fiber is 1.07 g·cm^{-3}[9].

3. Results and discussions

3.1. Tensile tests results

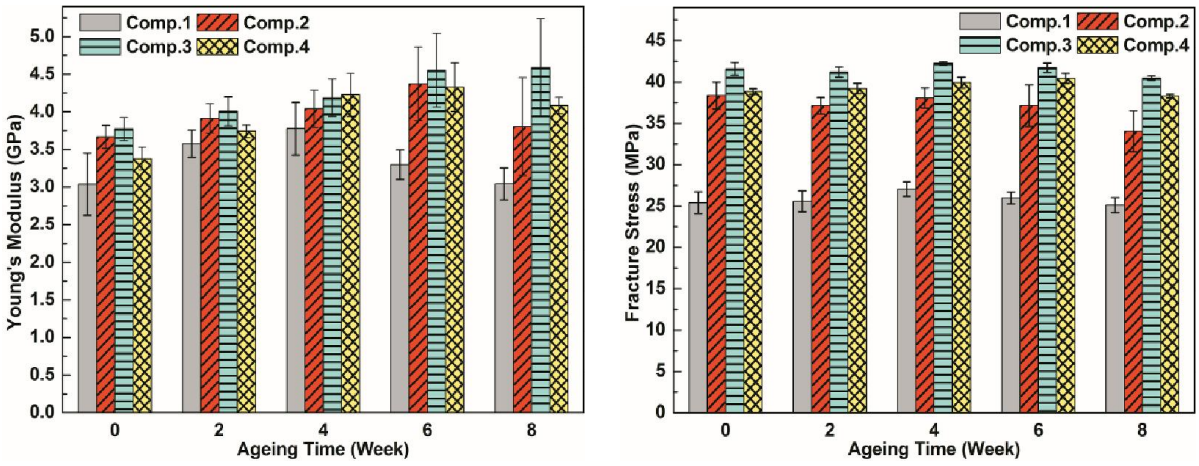

Figure 2. Young's modulus and fracture stress of composites after humidity ageing.

The tensile properties of PP composites reinforced with untreated fiber (Comp.1 and Comp.2), water treated fiber (Comp.3) and alkali treated fiber (Comp.4) are shown in figure 2. The tensile properties of these composites were affected considerably by humidity ageing. Interestingly, it's observed that Young's modulus increased significantly in initial ageing process. From figure 2, Young's modulus increased 24.3 % (Comp.1, after 4 weeks), 19.2 % (Comp.2, 6 weeks), 21.7 % (Comp.3, 8 weeks) and 28.2 % (Comp.4, 6 weeks). The fracture

stress also enhanced slightly 6.5% (Comp.1 after 4 weeks), 1.6 % (Comp.3 after 4 weeks) and 4.1% (Comp.4 after 6 weeks). Generally, the tensile strength of elementary hemp fiber decreases directly [8]. Thus, this increase can be explained like that the fiber swollen due to water absorption increases the interface pressure, thus results the enhancement of composites mechanical properties. In addition, it's seemed that stronger interfacial adhesion strength retards the decrease of Young's modulus, such as the Comp.1 and Comp.2 began to decrease after 4 weeks and 6 weeks, respectively. However, Comp.3 did not decrease until 8 weeks because of its stronger interfacial adhesion.

After 8 weeks humidity ageing, the fracture stress decreased 1.1 % (Comp.1), 11.3% (Comp.2), 2.6 % (Comp.3) and 1.4 % (Comp.4). Due to the interfacial adhesion of Comp.1 is very weak initially; we can't found obviously diminution of fracture stress caused by interface degradation. PP-g-MAH has effectively improved the interfacial adhesion strength of Comp.2. While the untreated fiber in Comp.2 covered with a layer of roughness water-soluble polysaccharide, which is sensitive to water. With the water penetrates into the interface of fiber/matrix, this polysaccharide begins to decompose causing the interface debonding and weakening along. Therefore, the evident decrease of fracture stress occurs in Comp.2. In contrast, after water or alkali treatment of hemp fiber, the water-soluble polysaccharide was completely removed resulting stronger interfacial adhesion of composites. This clean fiber surface and stronger interfacial adhesion are favorable to effectively inhibit the interface absorbing water and retarding the interface degradation. Thus, the fracture stress of Comp.3 and Comp.4 decreased slightly after 8 weeks ageing.

3.2 Water uptake

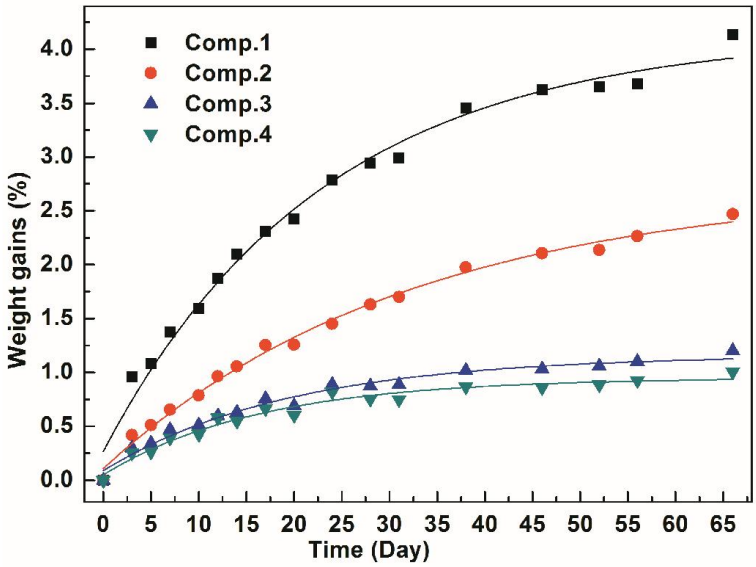

Figure 3. Weight gains of composites.

The figure 3 shows the water uptake percentage of composites at room temperature. The weight of each composite increased initially, followed by saturation or an equilibrium state indicated by a plateau region. The higher water uptake is observed in Comp.1, which is reinforced with untreated fiber. With the addition of PP-g-MAH, Comp.2 exhibits lower water absorption values compared with Comp.1. Besides, the water and alkali treatment is beneficial to reduce the hemp fiber water uptake ability of Comp.3 and Comp.4. This

indicates that the amount of water uptake dramatically decreased with the improving of interfacial strength.

The level of water uptake of natural fiber is largely dependent on the amount of accessible hydroxyl groups, which can form hydrogen bonds with water molecules. The higher amount of hydroxyl groups, the higher level of water uptake. Alkali treatment could effectively eliminate the higher hydrophilic components, such as hydroxyl groups of hemicellulose and lignin in amorphous regions reducing the water uptake of natural fiber. Therefore, the water uptake of Comp.4 is lower than Comp.3 in figure 3.

3.3 Fracture surface observation

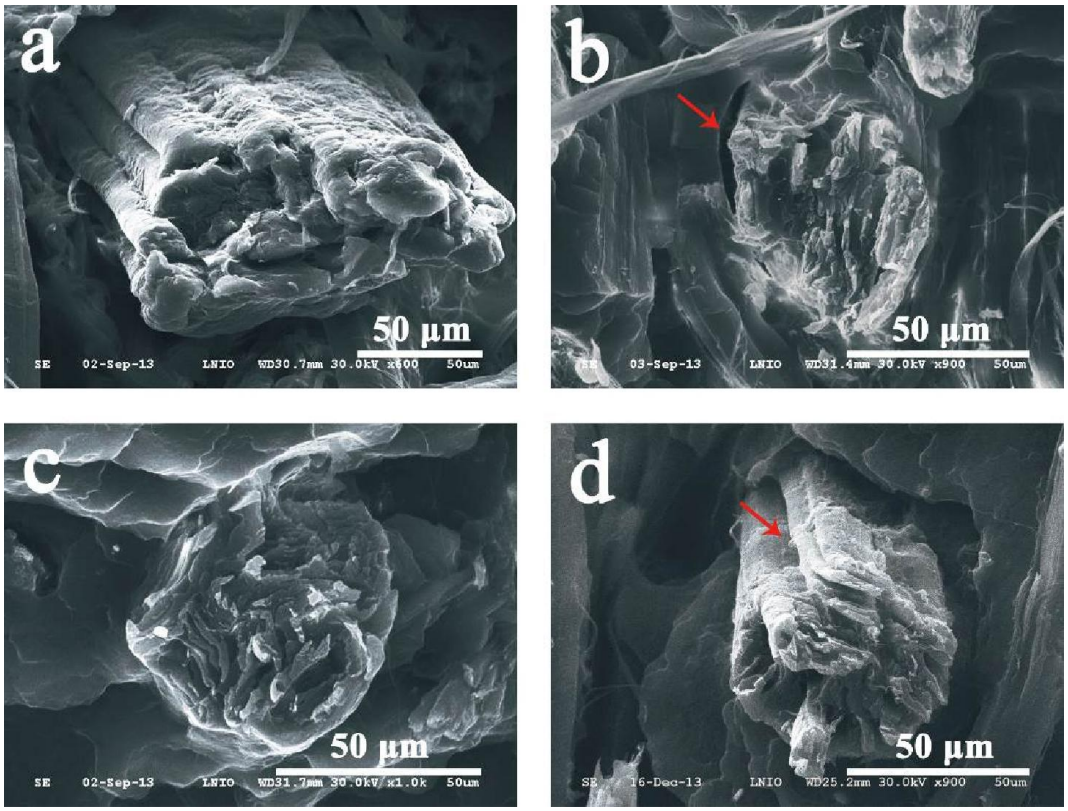

Figure 4. SEM micrographs of composites fracture surface after 8 weeks humidity ageing: (a), Comp.1 (untreated fiber); (b), Comp.2 (untreated fiber, PP-g-MAH); (c) Comp.3 (water treated fiber, PP-g-MAH); (d), Comp.4 (alkali treated fiber, PP-g-MAH).

Figure 4 displays SEM images of composites fracture surface after tensile tests for 8 weeks humidity ageing. For the composites reinforced with untreated fiber (figure 4a), it's observed that the hemp fiber was pulled out directly because of the poor fiber/matrix interfacial adhesion. For other three composites, with adding MAH-g-PP (figure 4b,c,d), the fiber were all broken after tensile test. In figure 4b, it seems that the large gap between fiber and PP was caused by the degradation of water-soluble polysaccharide on the surface of untreated fiber. In figure 4c,d, because of water or alkali treatment eliminated this water-soluble polysaccharide, there is no obviously degradation of fiber/matrix interface. The fiber and PP still connected very well. While, in figure 4d, it's observed that the fiber surface is not smooth because of alkali treatment partly removed hemicellulose and lignin causing damages of elementary fiber and forming voids in internal fiber. The composites structures are presented in figure 5.

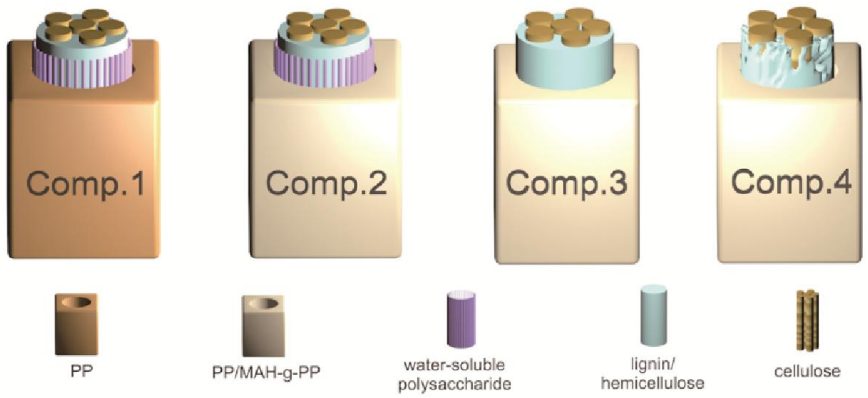

Figure 5. schemes of composites structure.

3.4 Composites swelling

The composites swell with the water uptake process of fiber, which has negative affect to the composites dimensional stability. Figure 6 presents the cross-section swollen of specimens in the humidity ageing process (scatter) and the calculated cross-section swelling from the composites weight gains (red line).

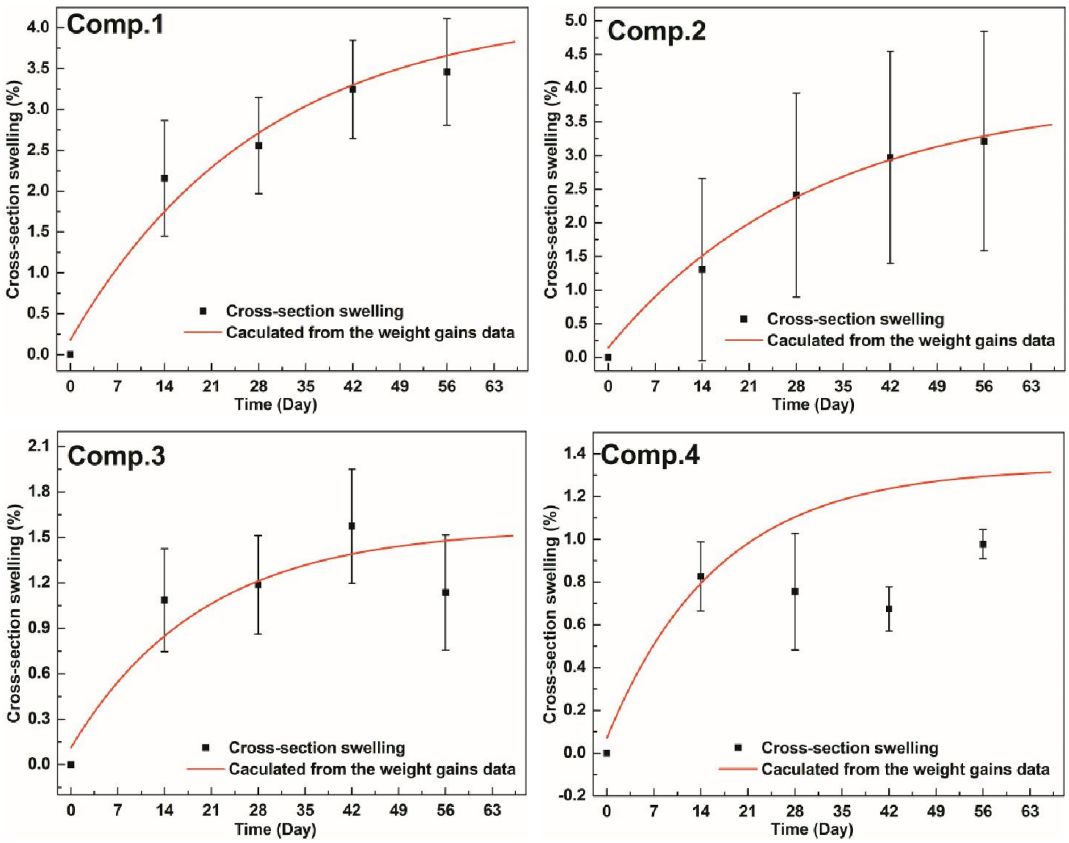

Figure 6. Cross-section expansion of composites specimens: a, Comp.1; b, Comp.2; c, Comp.3; d, Comp.4.

As shown in figure 6, the cross-section swelling of calculated results corresponded very well with the determined one, especially in Comp.1, Comp.2 and Comp.3. It proves that the assumptions of that fiber in specimens oriented along the injection directions and the fiber mainly swelling in radial direction. For Comp.4, the calculated swelling rate is higher than the experimental determined one after 2 weeks ageing. It suggests that Comp.4 absorbed certain quantities water but its volume didn't increase. As we analysed in previous section, alkali

treatment destroyed the fiber structure forming voids or defects in the composites. Due to this, hemp fiber absorbed water and swollen to fill these void with the process of ageing. Thus composites apparently didn't swelling. By comparing Comp.1, Comp.2 and Comp.3, it's concluded that the dimension stability could be significantly improved by enhancing the composites interfacial adhesion strength.

4. Conclusion

The humidity ageing mechanism of hemp fiber reinforced PP composites has been studied in this paper. It shows that the fiber swelling due to the water absorption increases the interface pressure resulting to the improvements of composites mechanical properties in the initial periods of humidity ageing. With the process of ageing, the absorbed water will cause the degradation of fiber/matrix interface and hemp fiber itself decreasing the composites mechanical properties. The stronger interfacial adhesion of fiber/PP matrix effectively retards the decrease of composites mechanical properties and improves the dimension stability by inhibiting the water absorption behaviour of composites.

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