

무수 말레익산이 그래프트된 폴리프로필렌을 상용화제로 사용한 아이소택틱 폴리프로필렌/세균성 셀룰로오스 복합체의 기계적/유변학적 물성

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Mechanical and Rheological Properties of Isotactic Polypropylene/Bacterial Cellulose Composites: Maleic Anhydride Grafted Polypropylene as a Compatilizer

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Abstract: To improve the mechanical performance of isotactic polypropylene (iPP), the iPP/bacterial cellulose (BC) composites were prepared. The tensile and impact strength of the composites were maximized (38.21 MPa and 2.812 KJ/m²) when maleic anhydride grafted polypropylene (MAPP) content was 7 wt%, the tensile modulus was increased with the higher MAPP content and the maximum value was 1858.39 MPa. Compared with pure iPP, the tensile strength, impact strength and tensile modulus increased by 6.32 MPa, 0.75 KJ/m², and 279.68 MPa, respectively. Compared with the control group (the sample which added BC but no MAPP added), the tensile strength, impact strength and tensile modulus increased by 5.61 MPa, 0.692 KJ/m², and 11.24 MPa, respectively. Moreover, the elongation at break of the composites was decreased. Besides, the rheological results and SEM photographs indicated that with the addition of MAPP, the compatibility of the composites was improved greatly, which demonstrated the increase of the mechanical properties of the composites.

Keywords: bacterial cellulose, isotactic polypropylene, mechanical and rheological properties, compatibility.

Introduction

Polymer composites is compounded with fillers which have, low additive quantity, good scattering and good interfacial adhesion in the polymer matrix.¹ And the mechanical properties are the most important properties of the polymer composites. In recent years, many studies are concentrated various kinds of composites with excellent mechanical properties by added different kinds of fillers (fibers, particles).²⁻⁵

Isotactic polypropylene (iPP) has a lot of useful properties

such as low density, electrical resistance, and chemical resistance. iPP has been particularly studied and widely used in automotive, packaging materials and other industries. However, poor impact property limits its extensive use in industries.⁶⁻⁹ In recent years, there are more and more interests in using fibers as reinforcement in iPP composites.^{10,11} These materials are characterized as easy processibility, good dimensional stability, and excellent mechanical performance.¹² The fibers used for reinforcement in iPP are divided into natural and synthetic one, but both of them have advantages and drawbacks. Synthetic fiber reinforced iPP composites have better mechanical properties, but they are not environmentally friendly.¹³ Moreover, as a synthetic biodegradability polymer, bacterial cellulose (BC) has great potential in the application of

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materials, food and medicine.¹⁴ The structure and properties of BC is similar with natural fibers, and has many superior properties such as high purity, high crystallinity, high young's modulus, and excellent mechanical properties.¹⁵ Based on those functions, BC has the benefits of both natural and synthetic fibers for reinforced iPP.¹⁶ Whereas, there is few study on using BC for iPP reinforce. In such composites, BC may be used for the reinforcement and the main source of strength for iPP, while the iPP matrix keeps them in the desired location and orientation and protects them from damages.

Unfortunately, the frequent incompatibility between polar BC and non-polar iPP due to the molecular chain of BC has lots of hydrophilic hydroxyl group. Thus, the stress cannot be effectively transmitted at the interface and the degree of dispersion is poor of the BC in iPP matrix.¹⁷ Meanwhile, rheology,^{17,18} scanning electron microscope,¹⁹ and dynamic mechanical thermal analyses²⁰ are the most common methods to investigate the compatibility of polymer and its filler. It was reported that the maleic anhydride grafted polypropylene (MAPP) can be used to provide compatibility between filler and immiscible polymers matrix through reduction of the interfacial tension.²¹

In this study, iPP/BC composites were prepared by twin screw extruder. The effects of MAPP content on the mechanical properties changes of the composites were investigated. And the rheological properties of the composites were characterized by rotational rheometer.

Experimental

Feedstock Sources. iPP (S1003), with a melt flow index (MFI) of 3.6 g/10 min was supplied by Sinopec Beijing Yan-shan Company (China). MAPP (CMG9801), percent grafting 1% was purchased from Nantong Sunny Polymer New Material Technology Co., Ltd (China). The BC film (Hainan Yida Food Industry Co., Ltd. China) was flushed with deionized water to neutral, dried by freeze-drying machine, then milled into powder (20–200 nm).

Preparation of iPP/BC Composites. The iPP, MAPP, and BC were mixed with a twin screw extruder (Nanjing Jieya Extrusion Equipment CO., Ltd. SHJ-20, China), the extruder temperature of each division were 170, 185, 195, and 200 °C, respectively. The standard test specimens of iPP/BC composites were finally molded by an injection machine (Fomtec Machinery Co., Ltd., FT-150, China) with an injection pressure of 15.5 MPa and 170 °C. The pure iPP notes for 1#, control

group adding 3 wt% BC, but no MAPP adding for 2#, adding 3 wt% MAPP for 3#, adding 5 wt% MAPP for 4#, adding 7 wt% MAPP for 5#, adding 5 wt% MAPP for 6#, adding 10 wt% MAPP for 7#. The iPP content of each sample was 100 wt%, and the BC content of sample 2-7# was 3 wt%.

Mechanical Properties Test. Tensile properties of the composites were evaluated using universal testing machine (Z020, Zwick Roell Group, Germany) at a crosshead speed of 20 mm/min at room temperature according to GB/T 1040-2006. The charpy notched impact strength of the composites was notched for depth 2 mm on the narrow side of the specimens using a notching machine (Ceast AN50, Instron Company, USA), and measured by impact tester (Ceast 9050, Instron Company, USA) with 1 J capacity at maximum pendulum height (150°) at room temperature according to GB/T 1043.1-2008. Ten samples were tested individually and the average results were recorded.

Rheological Properties Test. The melt rheological properties of the samples were determined by rotational rheometer (Malvern Instruments Ltd., Kinexus ultra+, UK) in the oscillatory mode. The measurements were performed in the dynamic mode and 25 mm parallel plate geometry with gap setting of about 2 mm. The strain was kept constant at 2%. The temperature was 200 °C with the scanning frequency between 100–0.1 Hz.

Scanning Electron Microscopy. Samples 2# and 5# were viewed via SEM (Quanta 250 FEG, FEI, Oregon, USA) at an accelerated voltage of 10 kV in order to observe the compatibility at the tensile fractured surfaces of the composites.

Results and Discussion

Mechanical Properties of iPP/BC Composites. Mechanical properties of each sample (Figures 1-4) were determined and the mean value of the property was plotted against sample number. Figure 1 shows that the tensile strength of the composites. It is observed that 7 wt% MAPP gave the best results for the composites. And there was a tremendous increase in the tensile strength of the composites (nearly 20% compared to pure iPP and 17% compared to control group). This result may attribute to the increasing of interface bond between iPP and BC. This is because the MAPP branches may react with hydroxyl groups of BC which provide stress transfer between the iPP and BC.²² Such similar behavior has been reported by many researchers.²³ However, with a further increase in the content of MAPP from 7 to 10 wt%, the tensile strength of the

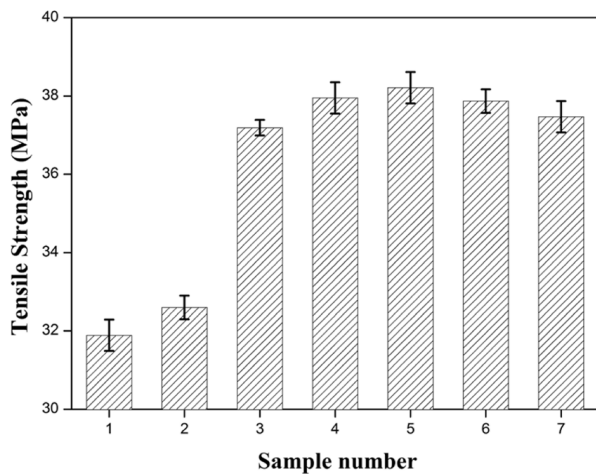


Figure 1. Tensile strength of the iPP/BC composites.

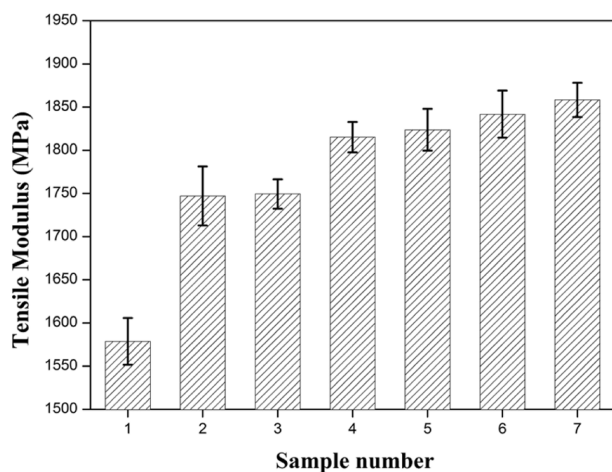


Figure 2. Tensile modulus of the iPP/BC composites.

composites decreased. The main reason might be that MAPP has a lower molecular weight compared to iPP which possibly hindered the plasticizing effect.²⁴ The tensile modulus (Figure 2) increased with the MAPP content of the composites (nearly 18% compared to pure iPP and 7% compared to control group). The main reason of this result might be that when MAPP was added, surface crystallization dominates over bulk crystallization and a transcrystalline layer can be formed around the BC. Crystallites have much higher moduli as compared to the amorphous regions and can increase the modulus contribution of the polymer matrix to the composites modulus.²⁵ In comparison with pure iPP, a dramatic loss in elongation at break was observed for all samples (Figure 3). The BC in the iPP matrix results in the stiffening and hardening of the composites, so the decay in resilience and toughness are observed.²⁶ The impact energy is an indication of both crack

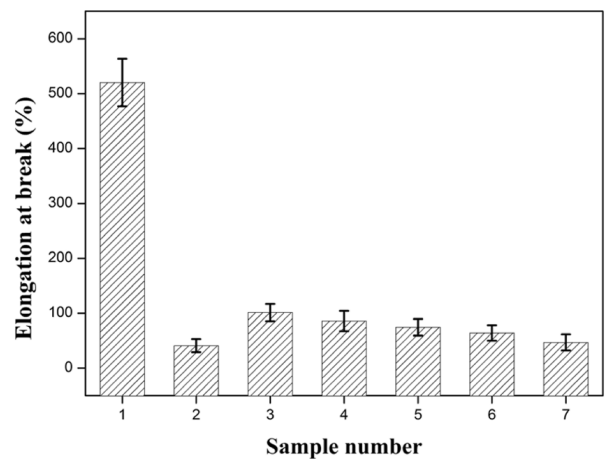


Figure 3. Elongation at break of the iPP/BC composites.

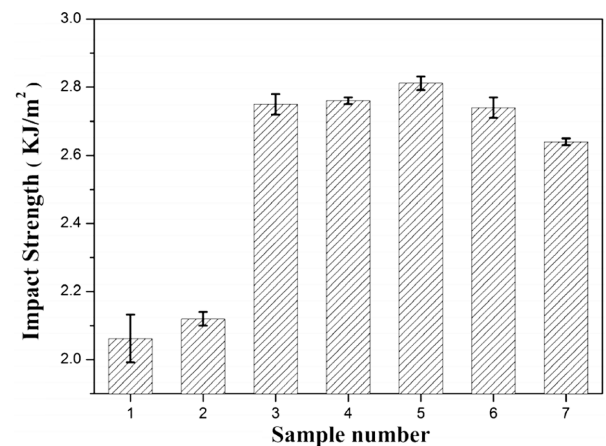


Figure 4. Impact strength of the iPP/BC composites.

initiation and propagation. The crack initiation energy is a function of matrix properties, adhesion between filler and the matrix and it tends to dominate the fracture process. As shown in Figure 4, 7 wt% MAPP also gave the best results for the impact strength of the composites (nearly 27% compared to pure iPP and 25% compared to control group). The main reason of this result might be that the interfacial adhesion of the composites became better, the high impact strength was expected. Mohanty *et al.* reported that the impact strength of the polyolefin cellulosic fiber composites was found to be increased after treating the fiber surface with MAPP.²⁷ However, this could only be beneficial at low fiber content.

Rheological Properties of iPP/BC Composites. The increase in mechanical properties is due to the compatibility in the presence of BC. It can results in more efficient stress transfer between the iPP and BC. The rheological properties of iPP/BC composites were characterized in order to study the com-

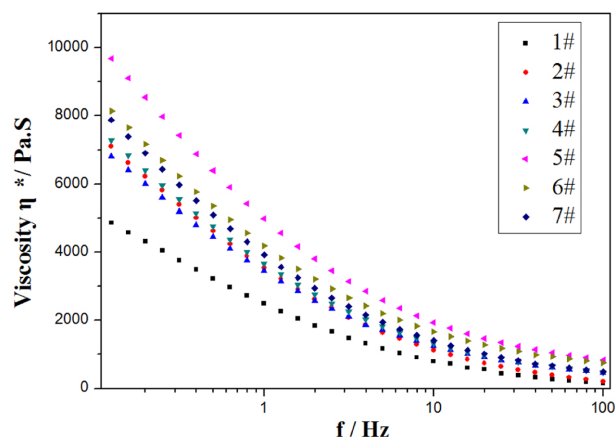


Figure 5. Viscosity of iPP/BC composites.

patibility of the composites.

On the one hand, the increase of the viscosity depends on the concentration, particle size, particle size distribution and shape of the filler.²⁸ The presence of BC particles perturbs normal polymer flows and hinders the mobility of chain segments. Therefore, the worse the dispersion of the BC in iPP, the viscosity of the composites can be decreased. As shown in Figure 5, all the samples show non-newtonian pseudo plastic behavior. In the range of high shear rates, shear-thinning behavior of the melt was observed and all the samples exhibited nearly the same viscosity. This phenomenon is probably due to alignment of the BC at high shear rates along the tube axis thereby decreasing BC fiber to BC fiber collisions.²⁹ Meanwhile, it is evident that the dynamic viscosity of the composites increased progressively with the increase in MAPP loading from 3 to 7 wt%, but the value decreased with more MAPP addition. This is because in the composites, the BC perturbs the normal flow of the polymer and hinders the mobility of the chain segments in the direction of flow,²⁹ and with the increase of MAPP addition, the compatibility of the composites was improved greatly, so the melt flow rate was accelerated.

On the other hand, the elastic properties of the composites depend on energy storage mechanisms at the interphase. The relaxation of the dispersed phase itself is often longer than the relaxation of the polymer chains of the individual components.³⁰ It can be seen from Figure 6 that the storage modulus of the composites was higher with the MAPP content increased from 3 to 7 wt%, but the value decreased with more MAPP addition. This similar behavior with viscosity of the composites can be explained by the fact that the BC restricts deformation in the same manner.²⁶ It also means that with the MAPP addition, the dispersion of BC in the composites is

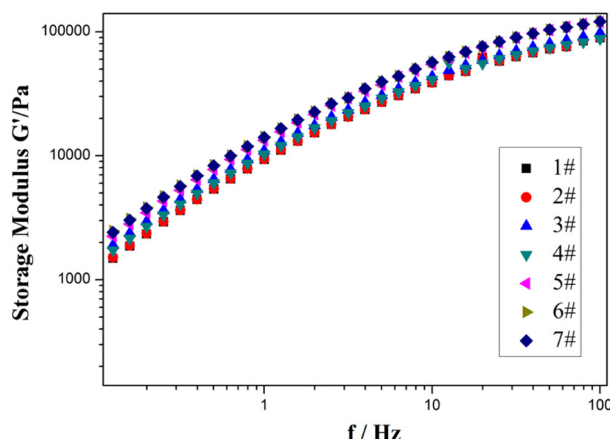


Figure 6. Storage modulus of iPP/BC composites.

more uniform. The compatibility between iPP and BC was improved greatly.

Scanning Electron Microscopy Observations. Figure 7 shows the SEM photographs of the composites tensile fractured surface. It can be seen that the tensile fractured surface of the composites was divided into two phrases, BC and iPP. Conversely, with not added to the MAPP, the dispersion of the BC in the iPP was poor. However, when MAPP was added, the remaining holes were smaller, which illustrated improved compatibility. The good compatibility between the iPP/BC

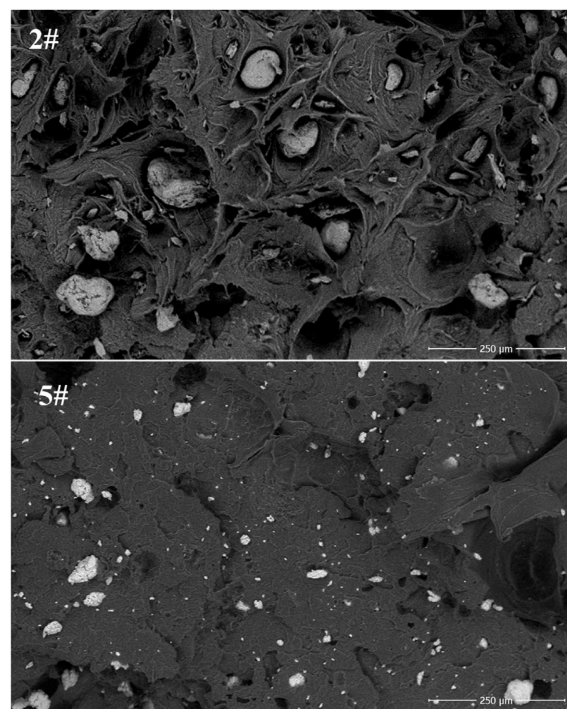


Figure 7. SEM photographs of the iPP/BC composites tensile fractured surface.

composites resulted in better stress transfer and superior mechanical properties. As expected, by adding MAPP, the interface compatibility improved, and the iPP could effectively adhere to the BC surface. The good compatibility between the iPP and BC contributed to forming a strong interfacial layer that altered the local stress distribution.³¹ This explained why the mechanical properties of the iPP/BC nanocomposite were better when the MAPP was added.

Conclusions

The mechanical properties of iPP/BC composites were improved greatly with the addition of MAPP. The tensile strength and impact strength of the composites were maximized when MAPP content was 7 wt%, the tensile modulus was increased with the higher MAPP content and the maximum value was 1858.39 MPa. Compared with pure iPP, the tensile strength, impact strength and tensile modulus increase by 20%, 27%, 18%. Compared with the control group (the sample which added BC but no MAPP added), the tensile strength, impact strength and tensile modulus increase by 17, 25 and 7%). Moreover, the elongation at break of the composites was decreased. The higher MAPP content causes the sufficient increase in the viscosity of the iPP/BC composites, and when the content of MAPP was higher than 7 wt% the value decreased. The storage modulus of the composites shows the similar behavior with the viscosity of the composites. Rheological results indicated that with the addition of MAPP, the compatibility of the composites was improved greatly, which demonstrated the changes of mechanical properties of the composites. The SEM photographs of the composites showed improvements for the interface compatibility, and dispersion of iPP and BC changed when the MAPP was added. This phenomenon provided evidence to explain why the mechanical properties of the of iPP/BC nanocomposite improved greatly when MAPP was added.

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