Mechanical and thermal properties of Polymer composites via the Synergistic effect of Carbon Nanotube and Ionic Liquid

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Abstract. A series of polymer composites based on Polypropylene (PP) are prepared by Multi-walled carbon nanotube (MWCNT) and ionic liquid (IL). The dispersion of MWCNT is investigated by FESEM measurements, and the tensile strength of composites are analyzed by tensile tests. The thermal properties of composites are also ameliorated by the results of differential scanning calorimetry (DSC) measurements.

1. Introduction
Carbon nanotube (CNT) is composed of one or more layers of graphene seamless hollow cylinders, which possess excellent thermal, electrical, mechanical properties and optical [1]. These properties are related to the incompatibility of the polymer matrices and facilitate their agglomeration. The surface functionalization of the nanoparticle is considered an effective way to avoid aggregation and improve the filler with the matrix [2-3]. Ionic liquid (IL) is organic salts composed of large organic cations and organic or inorganic anions that are poorly concerted. IL has also been reported as an excellent medium for dispersing inorganic particles, including carbon nanotubes [4-6]. According to a study by Fukushima et al., a small amount of single-walled carbon nanotubes (SWCNT) can interact with imidazolium-based ionic liquid to produce a solid material called a bucky gel [4].

In this work, a series of polymer composites based on Polypropylene (PP) are prepared by Multi-walled carbon nanotube (MWCNT) and IL. Mechanical and thermal properties of Polymer composites are investigated via the synergistic effect of carbon nanotube and ionic liquid.

2. Materials and Methods

2.1. Materials
Polypropylene (EPC30R-H) used was commercially available from Sinopec Group. Polypropylene-grafted-maleic anhydride was kindly provided by Sigma - Aldrich. MWCNT was purchased from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. 1-Hexadecyl-3-
methylimidazolium bromide was supplied by Shanghai Taitan Scientific Co., Ltd. All other solvents with AR grade were used as received.

2.2. Sample preparation
First, MWCNT was treated by 65 wt% HNO₃ under reflux at 80 °C for 8 h. A solid powder was obtained and named as “A-CNT”. Then A-CNT/PP-g-MAH (mass ratio 1:3) blends were prepared in a twin-screw compounder at 180 °C for 20 min. This resulting products was named “MA-CNT”. Finally, PP/MA-CNT/IL nanocomposites were obtained by using the torque rheometer (MIX-60, Harbin Harper Electric Technology Co., Ltd., China) at 200 °C and 60 rpm for 15 min. All the selective samples were prepared and stored in dry conditions before use.

2.3. Characterization
The microstructure of the cross-fractured surface of samples was observed using field emission scanning electron microscopy (FESEM, GeminiSEM 300-71-19, Germany). An acceleration voltage of 3 kV was used for the samples and the fractured surface was coated with a thin layer of gold.

Tensile tests were carried out using a universal tensile test machine (Model UTM4204, Shenzhen Sansi Vertical and Horizontal Technology Co., Ltd., China) at room temperature, using the standard dumbbell-shaped samples (75×12.5×2mm) with the crosshead speed of 5 mm/min.

Differential scanning calorimetry measurements were carried out by a differential scanning calorimeter (DSC, Q2000, USA). Operating in the range of 25-200 °C. After kept the sample at 200 °C for 5 min to eliminate previous thermal history, both the cooling and heating rates were 10 °C/min. The melting temperature ($T_m$) and crystallization temperature ($T_c$) were provided as the maximum of the $T_m$ and $T_c$ peak from the second heating and cooling processes, respectively.

3. Results and discussion
Figure 1 presents the microscopic morphology of the selective PP/MA-CNT and PP/MA-CNT/IL composite with the different magnification. From Figure 1A (observed under 1.00 KX), one can be seen that there are some large deformation in a jumble along the axial tension for the PP/MA-CNT composite. With the introduction of IL into the PP/MA-CNT matrix, this phenomenon can be apparently improved for PP/MA-CNT/IL composite (Figure 1B), showing the regular and compact arrangements in the matrix even after stretching. For the PP/MA-CNT without IL, it presents the layer separation peeling off the matrix, and the MWCNTs easily agglomerate and entangle are exposed on the surface of the matrix after stretching (Figure 1C). Compared with PP/MA-CNT, the agglomerates of MWCNTs in the PP/MA-CNT/IL sample become looser than that sample without IL and mostly embedded in the polymer matrix even after stretching (Figure 1D). It is illustrated that the introduction of IL would be helpful in improving the dispersion and the compatibility of MWCNTs in the polymer matrix.
Figure 1 FESEM images of PP/MA-CNT (A, C) and PP/MA-CNT/IL-1 phr (B, D) after stretching.

Figure 2 plots the tensile strength of the PP/MA-CNT/IL composites as a function of the IL loadings with the PP/MA-CNT weight ratio of 100/20. It is noting that as the IL loading increases, the tensile strength of the composite gradually decreases, then tends to be smooth, and finally rises slowly. The reason for this result may be that on the one hand IL mainly acts as a plasticizer in the polymer matrix [7], the force between the polymer segments becomes weak with the addition of IL, resulting in the decrease of the tensile strength. On the other hand, when the adding amount of IL proceed to increase into the polymer matrix, some IL could also be adsorbed on the surface of MWCNTs as well as play the part of a plasticizer in the polymer matrix, improving the interfacial adhesion between MWCNTs and the polymer matrix. When this interfacial adhesion is more obvious than plasticization, the tensile strength of the composites gradually rises.

Figure 3 demonstrates the DSC endotherms and exotherms changes of PP with the different IL loadings, and PP/MA-CNT, PP/MA-CNT/IL composites. From Figure 3A, it is apparent that the $T_m$ of PP/IL blends shift to a lower temperature than pure PP, and the corresponding temperature value is
166.7, 162.1, 162.8, and 163.3 °C for neat PP, PP/IL-1, PP/IL-3, and PP/IL-5, respectively. It is probably attributed to the influence of IL as a plasticizer in the polymer matrix [7], and the plasticizing effect decreases with the increase of IL. Therefore, this could be illustrated that when the force between the polymer segments weakens with the addition of IL, the polymer segments can easily migrate so that the \( T_m \) of the polymer is lowered. Furthermore, the addition of IL into the PP matrix will also reduce the area of the melting peak. It could be explained that IL plays a positive role in improving the perfect crystallization of the PP matrix. The \( T_c \) of all samples containing IL is higher than pure PP (Figure 3B), and with further increasing IL content, the \( T_c \) gradually changes to 117.1, 116.1, and 115.3 °C for PP/IL-1, PP/IL-3 and PP/IL-5, respectively.

Figure 3 DSC endotherms (A, C) and exotherms (B, D) of neat PP, PP/IL-1 phr, PP/IL-3 phr, PP/IL-5 phr, PP/MA-CNT, and PP/MA-CNT/IL composites as a function of temperature.

Furthermore, the \( T_m \) of neat PP is higher than PP/MA-CNT and PP/MA-CNT/IL, corresponding to the \( T_m \) value of 166.7, 162.3, and 163.3 °C, respectively (seen in Figure 3C). And the above results could be explicated that the presence of MWCNT has a crosslinking effect on PP segments [8]. However, as the temperature of PP/MA-CNT and PP/MA-CNT/IL increases, the crosslink segments has competent time to orderly align around the MWCNT and to give composites higher crystallinity (Figure 3D), so the \( T_c \) is 114.2, 123.3, and 123.3 °C for neat PP, PP/MA-CNT and PP/MA-CNT/IL, respectively. Based on the above results, the thermal properties of composites are ameliorated with adding MWCNT and IL into the polymer matrix, which could improve the processing and forming of materials for a wide range of applications.

4. Conclusions

PP/MA-CNT/IL nanocomposites were obtained by a facile melt blending. The addition of IL ameliorated the dispersion of MWCNTs in the polymer matrix through the observation of FESEM and tensile strength testing for the selective composite samples. In addition, we also found that MWCNT
and IL had an important effect on the crystallization properties of the polymer composites in the DSC investigations, which could be beneficial to the processing and forming of PP/MA-CNT/IL composites.

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