Preparation and Characterization of Conductive blend composites of PP filled with ionic liquids treated-CNT

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Abstract. According to the facile melt blending method, a series of conductive blend composites based on polypropylene with the excellent electrical conductivity are prepared by Multi-walled carbon nanotube (MWCNT) and ionic liquid (IL). In light of the results of the FTIR and Raman, it was confirmed that the MWCNT was non-covalent modified by IL. The dispersion of MWCNT and the electrical conductivity of the composites are enhanced by the addition of a master-batch as a compatibilizer and IL as a modifier, respectively. With the adding of MWCNTs, the surface resistivity of the conductive blend composites was reduced by 4~6 orders of magnitude under the same IL loading.

1. Introduction
Conducting polymer composite is dispersions in which conductive filler is added to an insulating polymer matrix. Since they will combine the distinguishing feature of the matrix such as flexibility, low density, and processability with the electrical properties of the filler, this kind of material has been received great interest for recent several decades. Moreover, their ease of preparation, low cost, and tunable electrical properties make them become a promising material for different applications by using the appropriate amount of filler [1-2]. Nowadays, this field still worthy of special attention because of the recent development of new nanometric conducting fillers, such as carbon nanotube and graphene nanoplatelet, and new strategies for modifying and dispersing these fillers [3-6]. Therefore, new possibilities for developing such materials with excellent properties for new and more practical applications have been continually proposed.

The incorporation of a certain amount of conductive filler in a polymer matrix usually promotes an intense insulating-conducting transition. The filler particles begin to touch each other, even close to each other, thus taking shape conductive network, which is the reason for a jump in electrical conductivity values, in the filler concentration (known as the percolation threshold). It is generally accepted that The main purpose of adding conductive fillers is to build conductive pathways in the polymer matrix [7-8]. To attain a high level of conductivity of the corresponding conducting polymer composite, it is necessary to build an efficient conductive network, and thus the type and dispersion of the filler is particularly important.
2. Materials and Methods

2.1. Sample preparation
Polypropylene-grafted-maleic anhydride (PP-g-MA, 8-10 wt% of MA) with a weight-average molecular weight (Mw) of 9100 was obtained from Sigma-Aldrich. Multi-walled nanotubes (MWCNT) with diameter and length of about 5-15 nm and 10-30 μm were purchased from the Chengdu Institute of Organic Chemistry. All components were kept dried under vacuum at 60°C for 12h before processing. MWCNT (5 g) was reacted with 65 wt% HNO₃ (300 mL) in the three-necked flask, and the mixture was placed in an ultrasonic bath for 2h. Then, stirred for 8h under reflux at 80°C. The resulting mixture was diluted with deionized water and vacuum-filtered through 0.22 µm PTFE membrane. The obtained solid was washed with deionized water until the filtrate was neutral. After drying 12h under vacuum at 60°C, a solid powder was obtained and referred to as “A-CNT” by grinding in a mortar for about 5min.

Melting mixed with A-CNT/PP-g-MA (mass ratio 1:3) blend at 180°C in a counter-rotating twin-screw micro-compounder at 35hz for 20min. Then extruded pelletizing and stored in dry conditions. This resulting product was referred to as “MA-CNT”.

After that, the made MA-CNT was melting blended with PP and ionic liquid (IL) at 200°C and 60 rpm for 15min used the torque rheometer to prepare PP/MA-CNT/IL composites. And the corresponding PP/IL materials were also prepared for comparison. Finally, all the selective samples were prepared and stored in dry conditions before use.

2.2. Characterization
Fourier transform infrared spectroscopic measurements were performed using an FTIR spectrometer. The FTIR spectra were obtained in a transmittance mode by mixing a small amount of the materials in KBr pellets.

The Raman analysis was performed with a Raman spectrometer, which was equipped with an excitation wavelength of 532nm. The IL treated A-CNT was grinded in a mortar for about 20min.

Electrical conductivity was measured by a surface impedance tester, the temperature was 23±2°C and the relative humidity was 50±5%. The sample thickness was 500µm.

3. Results and discussion
Figure 1 exhibits the FTIR spectra for the A-CNT, PP-g-MA, and MA-CNT samples, respectively. The spectrum of PP-g-MA has an absorbance peak of polymaleic anhydride (1778 cm⁻¹) and carboxylic acid C=O stretch (1714 cm⁻¹) belonging to self-hydrogen-bonded carboxyl groups (COOH). After the melt blending, the absorbance of polymaleic anhydride stretch (1778 cm⁻¹) shifted to the lower wavenumber at the counterpart of MA-CNT, and its relative intensity is also reduced. This is due to hydrogen bond formation between polymaleic anhydride and A-CNT. And the hydrogen bond interaction between the PP-g-MA and A-CNT can enhance the interfacial interaction and improve the compatibility of the composites [9]. Therefore, the dispersion property of A-CNT could be heightened efficaciously by the melt blending with PP-g-MA.

![Figure 1 FTIR spectra of A-CNT, PP-g-MA and MA-CNT master-batch.](image-url)
Figure 2 shows Raman spectra of A-CNT and ionic liquid modified A-CNT. A-CNT generally exhibits two characteristic peaks. One is around 1339 cm⁻¹ (referred to as D-band). The other is around 1572 cm⁻¹ (referred to as G-band). The intensity ratio of D-band to G-band (ID/IG) can be used for assessment of the graphitic structure of A-CNT, defined to R-value. The selective samples display two visible bands, which supply affirmative evidence for the formation of so-called graphitic structures. Moreover, the D-band intensity is more intense than that of G-band in A-CNT (R₁=1.07) because of a great number of amorphous carbons. However, the ID/IG of ionic liquid modified A-CNT are approximately equal (R₂=0.98), which means that the amorphous carbon and lattice defects would be reduced by physical functionalization [10]. The R of the ionic liquid modified A-CNT is different from that of A-CNT, it could be due to the cation-π interaction between imidazolium groups and A-CNT.

![Raman spectroscopy of A-CNT and ionic liquid modified A-CNT](image)

Figure 2  Raman spectroscopy of A-CNT and ionic liquid modified A-CNT

Figure 3 shows the electrical conductivity of PP/IL blends and PP/MA-CNT/IL composites possessing with the mass ratio of 100:20 (PP/MA-CNT) as a function of IL loading. For comparison, all PP/IL blends, a decrease of the surface resistivity is observed as the IL is added in the range of 0.5~5 phr, and it is evident that PP/IL blends are static dissipative in this condition. There is no obvious change in the curve for the PP/IL specimens when the IL content is beyond 1 phr. Therefore, the optimum addition amount of IL is 1 phr, which will be applied to the subsequent experiments. However, it is astonishing that the surface resistivity of PP/MA-CNT/IL composites distinctly decreases with the addition of MA-CNT compared to that of PP/IL blends. At a constant content of 20 phr MA-CNT, when IL loading is 3 phr, the surface resistivity is lowest (4.8×10³ Ω/sq) among these samples. Beyond this, the curve gradually rises and trends gently. The PP/MA-CNT/IL composites exhibit excellent conductivity behaviors, different from those of the PP/IL blends. Thus, the addition of IL induces a significant enhancement of the electrical conductivity systems compared to the samples without IL, and the surface resistivity of the selective samples decreases with 1~3 orders of magnitude. Furthermore, under the same IL loading, the surface resistivity reduces with 4~6 orders of magnitude when MA-CNT is present in the samples.

![Surface resistivity of PP/IL blends and PP/MA-CNT/IL composites as a function of IL loadings](image)

Figure 3  Surface resistivity of PP/IL blends and PP/MA-CNT/IL composites as a function of IL loadings with PP/MA-CNT mass ratio of 100:20.
Figure 4 displays the surface resistivity of PP/MA-CNT/IL composites with the different A-CNT loading. The surface resistance slightly increases when the added amount of A-CNT is 1 phr. Beyond this, the curve gradually drops. The surface resistivity decreases about 5 orders of magnitude when the A-CNT loading is 5 phr, and the counterpart reduces about 6 orders of magnitude when the A-CNT loading is 7 phr. Both of them include in the conductive region. Moreover, for PP/A-CNT/IL composites, the prominent change trend occurs in the range of 3~5 phr A-CNT content for the surface resistivity.

![Figure 4](image_url)

**Figure 4** Surface resistivity of PP/MA-CNT/IL composites as a function of A-CNT contents with 1 phr IL

### 4. Conclusion

The MWCNT was dispersed in the polymer matrix to enhance the electrical conductivity of the composites by a facile melt blending. Under the same IL loading, the surface resistivity of composites was reduced with 4-6 orders of magnitude as a function of MWCNTs adding. Moreover, adding IL to the MWCNT composites, the surface resistivity was also decreased with 1~3 orders of magnitude as a function of IL loadings with PP/MA-CNT mass ratio of 100:20. It was confirmed that the MA-CNT master-batch can be successfully prepared and MWCNT was non-covalent modified by IL in light of the data of the FTIR and Raman, respectively.

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