Effect of Various Carbon Nanotubes Contents on Surface Resistance and Thermal Degradation of Polypropylene/Polyamide 6/Glass Fiber Composite

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Abstract. The composite samples containing commercially available carbon nanotubes (CNTs), polypropylene (PP), polyamide 6/glass fiber composite (PA6/GF, 50%/50%) were prepared. They were (x%CNTs)/PP/(PA6/GF) (x/80/20, x% is the percentage of CNTs in the obtained composites, where x=0, 1, 2, 3, 4, 5, 6, respectively.). PA6/GF (50%/50%) and PP samples were also made as control. Surface resistance and thermal degradation for all the samples were measured. According to the resulting data, it is found that, with the increasing of carbon nanotubes contents, the surface resistance for the composite samples decreased, while the initial decomposition temperature increased. The result may be helpful to choose proper carbon nanotubes contents for antistatic and anti-degradation polymeric materials.

1. Introduction
The pursuit of high-performance polymer/carbon nanotubes (CNTs) composites has continued. Polypropylene (PP) is a commodity polymer widely used because of its low density, chemical resistance and good mechanical performances. Blending PP with an engineering polymer, such as polyamide 6 (PA6) or PA6/glass fiber (GF) composite, could bring excellent comprehensive performance and economic advantages. Here we introduce a composite based on PP (a nonpolar polymer) as matrix and PA6 (a polar polymer)/GF as dispersed phase, with low loadings of CNTs. They may be helpful to choose proper carbon nanotubes contents for antistatic and anti-degradation polymeric materials with lower price.

2. Experimental
2.1. Starting Materials
Multi-walled carbon nanotubes (CNTs) were obtained from Shenzhen Tuning Evolution Technology Co., Ltd. CAS number 308068-56-6, Purity >97%, Molecular weight 12.01, Tube diameter 3-15 nm, Tube length 15-30 µm, surface area 250-270 m²/g. Model S2040 polypropylene resin (PP) was provided by Xinjiang Dushanzi petrochemicals branch, PetroChina Company Limited. Model Ultrad® B3EG10 polyamide 6/glass fiber composite (PA6/GF, 50%/50%) was made by BASF Group, Germany.
2.2. Preparation of PPF Samples
CNTs, PP, PA6/GF were dried at 100 °C for 10 h before being used. The composite samples (x% CNTs)/PP/(PA6/GF) (x/80/20, x% is the percentage of CNTs in the obtained composites, where x=0, 1, 2, 3, 4, 5, 6, respectively.) by using a Thermo Scientific HAAKE™ Rheomix QC Laboratory Mixer (ThermoFisher Scientific) operating at 60 rpm and 240 °C for 10 min. To obtain the samples for measurement of surface resistance, length 100 mm × width 100 mm × thickness 1 mm samples for composites with various carbon nanotubes contents were prepared with a Compression Press (Model XLB-O 350x350, Zhejiang Huzhou Dongfang Machinery Co., Ltd.).

2.3. Measurement of Surface Resistance
The surface resistance (Ω) for the obtained (x% CNTs)/PP/(PA6/GF) composites was measured by a Model ZC36 (Shanghai Anbiao electronics Co., Ltd.) according to GB/T 1410-2006. Temperature (20±2) °C, Humidity (65±5) %, Electric voltage 500 V.

2.4. Measurement of Thermal Degradation
The thermal degradation for the obtained (x% CNTs)/PP/(PA6/GF) composites was measured by a Netzsch TG 209 F1 Thermal Gravimetric Analyzer. Sample mass ~ 5 mg, opening Al2O3 crucible, dry N2 flow 60 ml/min, heating rate 10 °C/min, temperature range 25 °C ~ 800 °C.

3. Results and Discussion
3.1. Effect of Carbon Nanotubes on Surface Resistance
Surface resistance values for various contents CNTs/PP/PA6/GF composites are shown in Table 1 and Figure 1. We can see that the surface resistance for the composite samples decreased normally with the gradual increasing of carbon nanotubes contents. The electrical conductivities measured exhibited a similar trend.

| Sample                  | 1     | 2     | 3     | 4     | 5     | Average   |
|-------------------------|-------|-------|-------|-------|-------|-----------|
| 0% CNTs/PP/PA6/GF       | 1.54×10^{15} | 1.74×10^{15} | 1.82×10^{15} | 2.11×10^{15} | 1.87×10^{15} | 1.82×10^{15} |
| 1% CNTs/PP/PA6/GF       | 1.41×10^{15} | 1.51×10^{15} | 1.49×10^{15} | 1.68×10^{15} | 1.42×10^{15} | 1.50×10^{15} |
| 2% CNTs/PP/PA6/GF       | 1.37×10^{15} | 1.39×10^{15} | 1.24×10^{15} | 1.51×10^{15} | 1.34×10^{15} | 1.37×10^{15} |
| 3% CNTs/PP/PA6/GF       | 1.05×10^{15} | 1.39×10^{15} | 1.14×10^{15} | 1.40×10^{15} | 1.17×10^{15} | 1.23×10^{15} |
| 4% CNTs/PP/PA6/GF       | 1.20×10^{15} | 1.23×10^{15} | 1.22×10^{15} | 1.32×10^{15} | 1.12×10^{15} | 1.22×10^{15} |
| 5% CNTs/PP/PA6/GF       | 1.24×10^{15} | 0.91×10^{15} | 0.86×10^{15} | 0.90×10^{15} | 0.78×10^{15} | 0.94×10^{15} |
| 6% CNTs/PP/PA6/GF       | 0.94×10^{15} | 0.90×10^{15} | 0.88×10^{15} | 0.91×10^{15} | 0.89×10^{15} | 0.90×10^{15} |

The values of surface resistance or electrical conductivity would be dominated by the formation of conductive network through physical interconnection among the dispersed CNTs and small CNT aggregates. [1] It was observed that sufficient conductive pathways were formed within the matrix at a CNTs loading fraction of 6 wt%, but mechanical properties decreased evidently.
Figure 1. Surface resistance values for various contents CNTs/PP/PA6/GF composites.

3.2. Effect of Carbon Nanotubes on Thermal Degradation

From the DSC curves (Figure 2), both PP and PA6 melting peaks are detected at their expected positions in the melting curves, which is typical for immiscible blends. [2-3]

Figure 2. Selected typical DSC heating thermograms of PP/PA6/GF and blend with CNTs.

It can be seen that the CNTs/PP/PA6/GF sample exhibits a strong main melting peak for PP (ca. 165°C) and a weak melting shoulder for the PA6 (ca. 220°C), while no peak for CNTs or GF. It could be deduced that the incorporation of CNTs had little effect on the melting behavior of the composite samples.
Figure 3. Thermal degradation (Residual mass percentage-Temperature) curves for various contents CNTs/PP/PA6/GF composites.

Thermal degradation (Residual mass percentage-Temperature) curves and derivative thermogravimetry curves for various contents CNTs/PP/PA6/GF composites are shown in Figure 3 and Figure 4, respectively. We can see that, with the increasing of CNTs contents, the initial decomposition temperature increased gradually.

Figure 4. Derivative thermogravimetry curves for various contents CNTs/PP/PA6/GF composites.

4. Conclusions
In this work, the composite samples containing commercially available carbon nanotubes (CNTs), polypropylene (PP), polyamide 6/glass fiber composite (PA6/GF, 50%/50%) were prepared. They were (x%CNTs)/PP/(PA6/GF) (x/80/20, x% is the percentage of CNTs in the obtained composites,
where \( x = 0, 1, 2, 3, 4, 5, 6 \), respectively.). PA6/GF (50%/50%) and PP samples were also made as control. Surface resistance and thermal degradation for all the samples were measured. According to the resulting data, it is found that, with the increasing of carbon nanotubes contents, the surface resistance for the composite samples decreased, while the initial decomposition temperature increased. The result may be helpful to choose proper carbon nanotubes contents for antistatic and anti-degradation polymeric materials.

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6. References
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