Preparation and Physical Properties of Polyethylene/Carbon Nanotubes/Nanosilver Composite

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Abstract. In this paper, nanosilver and carbon nanotubes was melt blended with HDPE and pet respectively to prepare HDPE/CNT/nanosilver and PET/CNT/nanosilver composites with antibacterial effect. After the preparation of samples, SEM, DSC, TGA, mechanical properties and antibacterial properties were tested. The possibility of preparing new materials by this method is studied. Compared with pure HDPE, when the content of CNT/nanosilver is 0.1 phr, the tensile strength of HDPE/CNT/nanosilver composite reach to the max value.

1. Introduction
Nanomaterial with polymer to prepare composites consist of a polymer matrix and nanofillers [1-2]. Research on nanocomposites of polar polymers with graphene and its derivatives has been widely studied. Few studies have been conducted on the addition of graphene and its derivatives to nonpolar polyolefins such as polystyrene [2] and polypropylene [3-4], because dispersing them in melt-blended nonpolar polymers is a major challenge—the nanosheets have thermodynamic tendencies to form aggregates [5]. As a result, the interfacial adhesion in nonpolar polymers is poor (unlike in the case of polar polymers). Therefore, surface modification of graphene is an essential strategy to effectively mix graphene with polyolefins.
Nanoparticles of metal oxides have high surface energies, small sizes, large surface atomic ratios, and large specific surface areas [6-7]. For these reasons, they have been widely used in many new fields such as photocatalysis [8], sunscreen makeup [9-10], antibacterial agents [11-13], and solar battery [12]. In this study, composites of HDPE and CNT/nanosilver had antibacterial properties with improving tensile properties.

2. Experimental
HDPE particles and CNT/nan silver melt blend, because of the characteristics of PE, do not need to dry before blending. The screw speed was set to 30 R/min and melt blending was carried out at 160
℃. HDPE/CNT/Ag composite samples were prepared by the automatic cutting mechanism of supercooled extrusion. Put the prepared pet particles into the vacuum drying oven for drying. Drying temperature 100 ℃, time 24 hours. After the moisture of pet is removed, the temperature of the hot press is raised to 270 ℃ to prepare for hot pressing. Put the granular material into the 18cm * 12cm mold with hot pressing pressure of 5 MPa, temperature of 270 ℃, and time of 5 min. PE particles of each component are directly put into the mould for hot pressing at 160 ℃, for 5 minutes, and the pressure is 5 MPa. Cut the pressed piece into dumbbell shape on the cutting machine. Each sample is cut into 3 pieces to ensure the accuracy of the mechanical test data. Put the prepared pet particles into the vacuum drying oven for drying. Drying temperature 120 ℃, time 24 hours. After the moisture of pet is removed, the temperature of the hot press is raised to 270 ℃ to prepare for hot pressing. PET particles of each component were directly put into Teflon and hot pressed at a pressure of 1 MPa, a temperature of 270 ℃, and a time of 1 min. Put PE particles of each component directly into Teflon membrane and conduct hot pressing with pressure of 1 MPa, temperature of 160 ℃ and time of 1 min. The main purpose of this study is to observe the surface and cross-section structure of the composite by scanning electron microscope (SEM) and EDS, and to observe the compatibility or distribution of pet and CNT/nanosilver by cross-section. First of all, spray gold with different proportions, and then observe the cross-section shape of the sample with the ratio of 1000 times and 10000 times respectively. Test parameter setting: start from -10 ℃ and heat up at the rate of 10 ℃ per minute until the constant temperature reaches 300 ℃. Cool down to room temperature at 10 ℃ per minute, measure the crystallization temperature of the sample, then rapidly raise the temperature to 300 ℃, keep the temperature constant for 3 minutes, suddenly cool to room temperature, and then raise the temperature to 300 ℃ at 10 ℃ per minute. The test data were analyzed by using the Origin software to do the temperature DSC diagram. At 25 ℃, heat up at the rate of 10 ℃ per minute until 750 ℃. Using the original software to do the temperature weightlessness scale diagram and temperature DTG diagram of the test data, and analyze the temperature at 95% weightlessness and 90% weightlessness, and the residual amount at 750 ℃. The main purpose is to test the physical and mechanical properties of different components of the composite, and analyze the relationship between the elongation at break, tensile strength, modulus and the components of the composite. Test standard ASTM D638, the test size of the sample is 100 mm × 10 mm in length × width, and the thickness depends on the sample made of different components, with the tensile rate of 50 mm/min.

3. Results and Discussion

3.1. SEM
Figure 1 shows the section morphology analysis of HDPE/CNT/nanosilver composite. It can be seen from figure 1 that the section of HDPE sample is relatively flat and slippery. After adding 0.1 phr of CNT/nanosilver, some defects appear on the composite section, which is most likely the trace left by the brittle fracture of HDPE/CNT/nanosilver soaked in liquid nitrogen. When CNT/nanosilver rises to 0.2 phr, the section begins to appear porous state, which may be due to the fact that CNT/nanosilver and HDPE are evenly divided in the substrate after compounding Scattered structure. When CNT/nanosilver was raised to 0.3 phr, the cross section of CNT/nanosilver was incomplete, which may be due to the agglomeration caused by too much CNT/nanosilver.

3.2. Tensile Properties
Figure 2a shows the tensile strength of HDPE and HDPE/CNT/nanosilver composite samples, and figure 2b shows the elongation at break of HDPE and HDPE/CNT/nanosilver composite samples. It can be seen from figure 2 that when the CNT/nanosilver content is 0.1phr, the tensile strength is higher than that of pure HDPE, and reaches the maximum value. When the CNT/nanosilver content is increased to 0.2 phr, the tensile strength returns to the same strength as that of pure HDPE, and then increases to 0.2 phr. At 3 phr, the tensile strength decreased significantly.
Figure 1. SEM images for (a) HDPE and (b) 0.1 (c) 0.2 (d) 0.3 phr composites.

Figure 2 shows the elongation at break of HDPE and HDPE/CNT/nanosilver composite samples. It can be seen from figure 2 that when the CNT/nanosilver content is 0.1 phr, the elongation at break increases from 120.6% of pure HDPE to 478.2%, when the CNT/nanosilver content is 0.2 phr, the elongation at break reaches the maximum value (650.9%), and with the CNT/nanosilver content increasing to 0.3 phr, the elongation at break decreases to close to that of pure HDPE. The results show that when CNT/nanosilver content is 1-2 phr, it is more suitable, but when CNT/nanosilver content is 0.3 phr, because of the agglomeration effect caused by the excessive content of nano silver doped carbon nanotubes, the tensile strength and the elongation at break decrease obviously [14].

3.3. Differential Scanning Calorimetry (DSC)
The DSC curves of HDPE/CNT/nanosilver composite samples are arranged in figure 3, the data list in tables 1 and 2. It can be seen from figure 3 and table 1 that when CNT/NANOSILVER is added, the crystallization rate of HDPE is only slightly increased (1-2 ℃). It can be seen from figure 3 that the melting points of all HDPE/CNT/nanosilver composite samples are close to those of pure HDPE samples. It can be seen from table 2 that when CNT/nanosilver is added to HDPE, the melting temperature does not change much. The crystallinity of each sample can be calculated from the crystallinity calculation formula, and the crystallinity of all samples can be arranged in table 1. It is further confirmed that CNT/nanosilver has little effect on the crystallization of HDPE and little effect on its processability. This is because the crystallization rate of HDPE is quite high, and the addition of CNT/nanosilver has no significant difference on the crystallization rate and crystallinity of HDPE.
Figure 2. Tensile properties of HDPE and composites: (a) tensile strength; (b) elongation at break.

Figure 3. DSC curve for HDPE and composites.

Table 1. DSC cooling data.

| Samples                        | Tc (°C) | ΔH (J/g) |
|--------------------------------|---------|----------|
| HDPE                           | 115.9   | 209.1    |
| HDPE/CNT/nanosilver<sub>0.1</sub> | 117.0   | 205.2    |
| HDPE/CNT/nanosilver<sub>0.2</sub> | 117.7   | 211.1    |
| HDPE/CNT/nanosilver<sub>0.3</sub> | 116.7   | 196.6    |
Table 2. DSC heating data.

| Samples                        | Tm (°C) | △H (J/g) | Xc (%) |
|-------------------------------|---------|----------|--------|
| HDPE                          | 139.1   | 215.3    | 79.73  |
| HDPE/CNT /nanosilver⁰.¹       | 138.8   | 210.6    | 77.77  |
| HDPE/CNT /nanosilver⁰.²       | 138.1   | 216.0    | 79.99  |
| HDPE/CNT /nanosilver⁰.³       | 139.1   | 203.1    | 75.21  |

3.4. TGA

Figure 4 are the thermal analysis data of HDP/nanosilver, and the changes of thermal cracking temperature and thermal weight loss are discussed. The temperature of HDPE at 5% weight loss is 404.9, while that nanomaterial content at 0.1-0.3 phr for composite at 5% weight loss is 421.9, 436.1 and 459.9, respectively. The temperature is significantly increased by 16 to 55 ℃, and the higher the content of cnt-ag, the higher the weight loss temperature is. In addition, the temperature trend of all composite samples is the same when the weight loss is 10% and 5%. In conclusion, CNT/NANOSILVER, as an additive of HDPE, can greatly improve the thermal stability of HDPE.

![Figure 4. (a) TGA and (b) DTG for HDPE and HDPE/CNT/nanosilver composites.](image)

4. Conclusion

In this experiment, polyethylene and CNT nano silver, polyethylene terephthalate and CNT/nanosilver were compounded respectively, and the effect of CNT/nanosilver with different proportion on HDPE was discussed. The tensile elongation of HDPE material will be greatly improved due to the reinforcement of carbon nanotubes, but it will obviously decrease with the increase of the amount. The mechanical properties of HDPE mainly depend on the HDPE material itself, and CNT/nanosilver has little effect on the tensile strength. At 750 ℃, the residual amount will increase with the increase of CNT/nanosilver content. CNT/NANOSILVER has little effect on the melting temperature of HDPE.

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