PREPARATION AND PROPERTIES OF GRAPHITE NANOPLATELETS (GNPs) HYDRID POLYMER NANOCOMPOSITES

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Preparation and Properties of Graphite Nanoplatelets (GNPs) Hybrid Polymer Nanocomposites
納米石墨填充聚合物基納米復合材料的制備與性能

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ABSTRACT

This work tries to study the preparation, morphology and properties of graphite nanoplatelets (GNPs) hybrid polymer nanocomposites, and explore their potential applications in areas such as electromagnetic interference (EMI) shielding. The main results are as follows:

The GNPs were successfully prepared by a “chemical intercalation-hot expansion-ultrasonication” process: acid-intercalated expandable graphite (GICs) were heated at high temperature to obtained worm-like structure expanded graphite (EG), and then dispersed in *N*,*N*-dimethylformamide (DMF) solvent and treated in an ultrasonic bath to obtain stable and evenly dispersed exfoliated GNPs. The GNPs prepared possessed a thickness of less than 100 nm, which could be confirmed by SEM and TEM results. XRD results showed that the sharp (002) diffraction peak remained the same in the EG and GNPs compared with that of GICs, indicating that the heating and ultrasonic treatment had no effect on the carbon crystal layer spacing. Oxygen-containing groups were found on the GNPs from the FTIR results, which was beneficial to the interaction between the GNPs and polymers.

Two kinds of polymers were used to prepare GNPs filled polymer nanocomposites here, one was thermoplastic polyurethane (TPU), and the other was a thermosetting polymer, epoxy. A facile solution method was introduced to prepare GNPs/TPU nanocomposites: TPU/DMF solution was mixed with the GNPs/DMF suspension, and after ultrasonic treatment the GNPs/TPU/DMF mixture was added into a large ethanol-

bath to get GNPs/TPU nanocomposites aggregations. SEM images showed a well dispersion of GNPs in the TPU matrix, and XRD results implied that the TPU molecular chains could only enter the spaces between the graphite sheets. The addition of GNPs could significantly improve tensile and dynamic mechanical properties of the materials, resulting in the significantly improvements in the tensile modulus, the storage modulus (E') and glass transition temperature (T_g) of the nanocomposites. The cone calorimeter testing showed that the GNPs could act as intumescent flame retardant and improved the flame retardancy of the material. The electrical conductivity of the nanocomposites was greatly improved by GNPs, and the maximum value was 3.4×10^{-3} S/cm at the GNPs content of 6.8 vol%. With the increasing GNPs content, the nanocomposites showed a transition from insulator to semiconductor in both d.c and a.c conditions, and the percolation threshold (Φ_c) were found to be 2.1 and 2.2 vol%, respectively. There was a high positive temperature coefficient (PTC) effect followed by a sharp negative temperature coefficient (NTC) effect for the nanocomposites around Φ_c, due to the breakage and the reformation of the conducting networks. A nonlinear to linear transition in the I-V characteristics was observed when the nanocomposites underwent insulator-conductor transition, and the conduction mechanism was referred to tunneling-hopping model. The dielectric constant and dissipation factor of the nanocomposites increased dramatically around Φ_c and exhibited strong dependency on frequency, due to the Maxwell-Wagner-Sillars (MWS) polarization mechanism. The EMI shielding test showed that GNPs/TPU nanocomposites could be used as an EMI shielding material.

The GNPs/epoxy nanocomposites were successfully prepared through solidification process by the aid of ultrasonication. SEM images showed that GNPs dispersed uniformly in the epoxy matrix, and the XRD results showed that graphite crystal structure was not changed during the intercalation of the epoxy molecular chains. The thermal stability of the materials became worse, due to the existence of the residual solvent and unreacted small molecules. The a.c conductivity of the nanocomposites increased with the increase of frequency and GNPs content, and the dielectric constant increased with the GNPs content but decreased with frequency due to the polarization.

A facile method was applied to prepare GNPs/silver nanoparticles (SPs)/polymer nanocomposites, the SPs were *in situ* reduced successfully and anchored uniformly on the GNPs surface. The SEM and FEG-SEM confirmed the formation of the SPs and their evenly dispersion. XPS and XRD results further proved the reduction of SPs by this process. The GNPs/SPs/TPU and GNPs/SPs/epoxy nanocomposites were prepared *via* two different processes, and the SEM showed that the SPs were still anchored on the graphite surface. However the silver diffractions did not shown in XRD patterns of the two nanocomposites, due to the low concentration of the SPs in polymer matrix. The addition of the GNPs/SPs hybrids resulted in the greatly reduction of $T_{10\%}$ and deterioration in the thermal stability of the GNPs/SPs/epoxy nanocomposites due to the residual solvent. The GNPs/SPs/polymer nanocomposites are expected to have wide potential applications such as EMI shielding and so on.

OUTLINE

LIST OF FIGURES

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