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Non-contact percolation of unstable graphene networks in poly(styrene-co-acrylonitrile) nanocomposites: Electrical and rheological properties

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Poly (styrene-co-acrylonitrile) (SAN)/chemically reduced graphene oxide (CRG) nanocomposites were prepared using a coagulation method. Due to the presence of SAN molecules that prevented CRG sheets from aggregation during reduction, CRG sheets were dispersed homogeneously in SAN. The electrical and rheological properties of the nanocomposites were systematically investigated to elucidate the structure of CRG electrical and rheological networks. With the incorporation of CRG sheets, both the electrical and rheological properties of the nanocomposites were remarkably changed. At higher CRG concentrations, the nanocomposites became electrically conductive and exhibited solid-like behaviors. According to the scaling power law, the electrical networks were constructed at a percolation threshold of 0.17 vol % compared to the rheological networks at 0.10 vol %. This discordance is attributed to the intrinsic difference in the network structure. Though both electrical and rheological networks were constructed through a non-contact mode, the rheological networks required SAN chains as bridges, while electrical networks did not. The CRG networks showed instabilities in both physical and chemical structure. Upon thermal annealing at 190 °C, the networks underwent self-improvement through disordering and thermal reduction of CRG sheets.

1. Introduction

Graphene, a two-dimensional (2D) monolayer or few-layer carbon material with excellent properties, has become a favorite filler in polymer nanocomposites. Since graphene differs greatly from polymer materials in its physical properties, its incorporation can impart exciting enhancements to the physical properties of polymers, especially electrical and rheological properties, when the graphene content exceeds a critical point. Taking advantage of percolation theory in multiphase material research, the enhancements have been related to the percolation of graphene networks and are well depicted by a scaling power law in the following equation:

$$X \propto (\varphi - \varphi_p)^t \tag{1}$$

where X represents properties (such as electrical conductivity and rheology properties), φ the volume fraction of graphene, φ_p the percolation threshold (i.e., the critical point) and t the critical exponent [1].

Benefitting from the construction of graphene networks for electron transportation, the electrical conductivity of polymer/graphene nanocomposites can increase by dozens of orders of magnitude. Depending on the content and properties of graphene (such as the aspect ratio and electrical conductivity) as well as its dispersion state in the polymer matrices, the reported electrical conductivity of the nanocomposites ranged from ~10^{-1}–~10^5 S/m

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[2–13]. Functionalized graphene sheets were first incorporated into polystyrene (PS), resulting in a dramatic improvement in electrical conductivity to ~1.0 S/m at 2.5 vol % [2]. In the following studies, the electrical conductivity of PS/graphene nanocomposites was further enhanced, e.g., 72.18 S/m at 2.45 vol % and even 1083.3 S/m at 4.8 vol % [5,6]. For epoxy/graphene films, an amazing conductivity value of 1.3×10^5 S/m was obtained at 20.0 vol % [10]. Due to the large aspect ratio and the 2D sheet structure of graphene, the graphene nanocomposites possess low percolation thresholds. When graphene was incorporated into homogeneous polymers through conventional methods, such as melt or solution mixing, the percolation threshold generally ranged from 0.1 to 1.0 vol % [2–10]. Using specific methods, the value could be significantly reduced to much lower values, such as 0.031 and even 0.007 vol % [12,13].

The percolation of graphene can also have great impacts on the rheological properties of the nanocomposite melt, since viscoelastic behavior, especially in the low-frequency region, is very sensitive to the microstructure of nanocomposites. At low frequencies, the viscoelastic behavior of homopolymers obeys typical terminal behavior, with a scaling law of $G' \sim \omega^2$ and $G'' \sim \omega^1$, where G' is the storage modulus, G'' is the loss modulus and ω is the frequency, respectively [14]. As graphene networks form in the polymer matrices, the scaling law is breached, and the non-terminal behavior with a “second plateau” appears, which is ascribed to the restraint of graphene networks on the relaxation of polymer molecules [3,15–18]. Incomplete relaxation, together with the enhancement effect of the rigid graphene, leads to an increase in nanocomposites by several orders of magnitude in the dynamic modulus or complex viscosity at low frequencies, signifying rheological percolation. To identify percolation behavior, a reliable percolation threshold can be given by the power law in Eq. (1), where the property X could be G', G'' and η^*, etc. Dominated by the aspect ratio and dispersion state of graphene, the rheological percolation threshold varied over a wide range between 0.05 and 2.0 vol % [17,19–21].

During the fabrication and processing of polymer nanocomposites, filler networks are established, but they might not be in a thermodynamically stable state, such as that found in CB and CNT systems [22–27]. Upon thermal annealing treatment, the unstable CB or CNT networks would experience self-improvement through aggregation, inducing a marked change in the electrical and rheological properties of the composites [22–27]. Similarly, the graphene network also exhibited instability [3,12,28]. In PC/graphene nanocomposites, an increase in G' with annealing time was found and was explained by restoration of the elastic networks disturbed by the squeezing flow during sample loading [3]. In polyester/graphene nanocomposites, due to network structure recovery during rheology testing, a lower electrical percolation threshold was obtained [28]. In our previous study of acrylonitrile-butadiene-styrene resin/graphene nanocomposites, after thermal annealing, electrical conductivity was increased, but the change in G' was confusing due to the structural complexity of the nanocomposites [29].

The influence of graphene networks on electrical and rheological properties has been widely investigated. However, few works have focused on the microstructure and the instability of graphene networks in the nanocomposites. In this work, CRG sheets were incorporated into SAN through a coagulation method. Based on the electrical and rheological behavior, the microstructure of electrical and rheological networks was investigated. To study the instability of CRG networks, the nanocomposites were annealed at 190 °C, and the evolution of network structure was monitored by studying the electrical and rheological properties of the nanocomposites.

2. Experiments

2.1. Materials

Natural flake graphite (NG) with an average size of 180 μm and a purity of >99% was supplied by the Beijing Invention Biology Engineering & New Material Co. Ltd. China. Poly (styrene-co-acrylonitrile) (SAN) with $M_w = 14.1 \times 10^4$ g/mol and $M_w/M_n = 2.08$, consisting of 28.4 wt % acrylonitrile component, was obtained from LG Chem Ltd. Of Korea. Potassium permanganate ($KMnO_4$, AR – analytical reagent grade), sodium nitrate ($NaNO_3$, AR), hydrogen peroxide (H_2O_2, 30% aq.), sulfuric acid (H_2SO_4, 98%), hydrochloric acid (HCl, 35% aq.), barium chloride ($BaCl_2$, AR), hydrazine hydrate ($N_2H_4 \cdot H_2O$, 80% aq.), and dimethyl formamide (DMF, AR) were all used as received.

2.2. Preparation of SAN/CRG nanocomposites

A stable dispersion of graphene oxide sheets (GrO) in DMF was prepared in our previous study [29]. To prepare SAN/CRG nanocomposites, the coagulation method was used. In detail, SAN particles were dissolved in the DMF/GrO dispersion under stirring. $N_2H_4 \cdot H_2O$ was dripped into the above dispersion under stirring at 90 °C to reduce graphene oxide sheets. After reduction for 4 h, the above mixture was gradually poured into a stirring bath containing a large volume of deionized water, and the nanocomposite was coagulated. This coagulation was filtered and washed repeatedly with deionized water. After drying in a vacuum oven at 80 °C for 24 h, SAN/chemically reduced graphene oxide (CRG) nanocomposites with varying CRG content were finally obtained. To convert filler content from wt % to vol %, the density used here is 2.20 g/cm^3 for CRG and 1.07 g/cm^3 for SAN.

Testing specimens of SAN/CRG nanocomposites were fabricated through compression molding in a vacuum hydraulic hot press at 10 MPa and 190 °C with a fixed dwell time of 10 min. Disk specimens with Φ25 mm × 1 mm were used for rheology tests, and rectangular specimens with 20 mm × 15 mm × 1 mm were used for direct current conductivity measurements. Isothermal annealing of the rectangular specimens was conducted in the vacuum oven at 190 °C.

2.3. Characterization

Atomic force microscopy (AFM) images were obtained using a DI Multimode 8 scanning probe microscope from the Bruker Corporation of Germany. The microstructure of the graphene oxide sheets was observed in tapping mode under ambient conditions at a scanning rate of 1 Hz. Samples for AFM images were prepared by dripping the dispersion of graphene oxide sheets onto a freshly cleaved mica surface and allowing free evaporation of solvent in open air.

The microstructure of CRG networks in the SAN nanocomposites was observed using an optical microscope (DMLP, Leica) under bright field and transmission electron microscopy (TEM, JEM-2100, JEOL, Japan). A very small piece of the SAN/CRG nanocomposite was hot-pressed between two glass slides for optical observations. Samples for TEM characterization were obtained by cutting SAN/CRG nanocomposites into ultrathin sections using a Leica microtome at room temperature, and collecting them onto copper grids.

X-ray diffraction (XRD) measurements were performed on a Rigaku D/max–2500 diffractometer using Cu Kα radiation ($\lambda = 0.154$ nm) under a generated voltage of 40 kV and current of 200 mA at a scanning rate of 4°/min in the 2θ region of 4°- 60°.

The direct current resistance of the nanocomposites was measured on a semiconductor characterization system (Keithley