



Influence of molecular weight of polymer matrix on the structure and rheological properties of graphene oxide/polydimethylsiloxane composites



Ran Niu ^{a, b}, Jiang Gong ^{a, b}, Donghua Xu ^{a, *}, Tao Tang ^a, Zhao-Yan Sun ^{a, *}

^a State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

^b University of Chinese Academy of Sciences, Beijing 100039, PR China

ARTICLE INFO

Article history:

Received 24 March 2014
Received in revised form
18 August 2014
Accepted 25 August 2014
Available online 2 September 2014

Keywords:

Graphene oxide
Polydimethylsiloxane
Molecular weight of polymer matrix

ABSTRACT

The structure and rheological properties of graphene oxide (GO)/polydimethylsiloxane (PDMS) composites are examined as the molecular weight of PDMS and concentration of GO are varied. Clusters formed by GO sheets get smaller and disperse better with increasing molecular weight of PDMS, which results in the higher critical concentration to form network (C_{cr}). Moreover, at GO concentration just above C_{cr} , the plateau modulus of samples decreases with the molecular weight of PDMS. During shear experiments, negative normal stress differences (ΔN) are observed in composites with PDMS molecular weight lower than critical entanglement molecular weight (M_c). However, positive ΔN is found in samples with PDMS molecular weight above M_c . It can be concluded that the vorticity alignment of GO clusters induces the negative ΔN based on the optical shear experiments. The possible mechanism for the positive ΔN is also proposed.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Inorganic particles are widely used to improve the thermal, electrical and mechanical properties of the suspending polymer matrix [1,2]. Recently, graphene and graphene oxide (GO) sheets have attracted great attention due to their large specific surface area, high Young's modulus, good electrical and thermal conductivity [1–4]. A lot of work have reported that graphene and GO can improve the properties of polymer matrix, such as mechanical, electrical, thermal and gas barrier properties [2–4].

It is well known that the dispersion state of nanoparticles in polymer matrix has apparent influence on the properties of composites [4,5]. Like other nanoparticles, it is also difficult to achieve good dispersion of graphene or GO in polymer matrix. Some methods have been used to improve the dispersion of graphene or GO in polymer matrix, such as changing processing method or surface functionality of graphene or GO [4,5]. As is well known, the molecular weight, viscosity and the size of polymer chain have great influence on the dispersion and aggregation behaviors of nanoparticles in polymer matrix, as reported for spherical C_{60} ,

polyhedral oligomeric silsesquioxanes (POSS), one-dimensional nanotube etc [6–11]. However, few work has studied the influence of molecular weight of polymer matrix on the dispersion of two-dimensional graphene-based particles, which is also quite useful and valuable.

Some interesting rheological properties of graphene/polymer or GO/polymer composites were reported previously [5,12–15], for example, reduction of viscosity [12,13], shear banding [14] and negative normal stress differences etc [15]. Among these rheological phenomena, the negative normal stress differences observed in GO/polycarbonate (PC) composites are very impressive [15]. However, the underlying mechanism for the negative normal stress differences remains ambiguous. Furthermore, a detailed study of the influence of polymer molecular weight on the rheological properties, especially the normal stress difference, of GO/polymer composites is still lacking.

In this work, the structure and rheological properties of GO/PDMS composites are studied. In particular, the influence of molecular weight of polydimethylsiloxane (PDMS) and concentration of GO on the structure and rheological properties of GO/PDMS composites is explored. Different characterization methods covering length scale from a few nanometers to several hundred of micrometers are used to explore the dispersion and structure of GO in PDMS. Linear and nonlinear rheological properties of GO/PDMS

* Corresponding authors. Tel.: +86 0 431 85262896; fax: +86 0 431 85262969.
E-mail addresses: dhxu@ciac.ac.cn (D. Xu), zysun@ciac.ac.cn (Z.-Y. Sun).

composites are also explored. By establishing the relationship between structure and rheological properties of GO/PDMS composites, the mechanisms for the positive and negative normal stress differences are proposed.

2. Experimental section

2.1. Materials

Graphene oxide (GO) was prepared by the improved Hummer's method [16]. Trimethyl-terminated polydimethylsiloxane (PDMS) with different molecular weights ($M_w = 6000, 14,000, 28,000, 63,000$ and $117,000$ g/mol) were supplied from Alfa Aesar, termed as PDMS6, PDMS14, PDMS28, PDMS63 and PDMS117, respectively. The critical entanglement molecular weight (M_c) of PDMS was reported to be $\sim 31,000$ g/mol [17], thus PDMS63 and PDMS117 behave as entangled polymers.

2.2. Sample preparation

GO/PDMS composites were prepared by solution blending method. A designed amount of GO was dispersed in tetrahydrofuran (THF) (0.1 wt %) under sonication. PDMS was dissolved in THF, and then mixed with different volume of GO/THF suspension to obtain desired concentration of GO in PDMS. The resultant mixtures were mechanically stirred for 1 h and then poured into Petri dish to dry. Finally, samples were further dried for 5 h in a vacuum oven at 25°C to remove residual solvent.

2.3. Characterization

The surface element composition of GO was characterized by X-ray photoelectron spectroscopy (XPS) with a VG ESCALAB MK II spectrometer using an Al K exciting radiation from an X-ray source operated at 10.0 kV and 10 mA.

The morphology of GO was observed by transmission electron microscope (TEM, JEM-1011) at an accelerating voltage of 100 kV. The dispersion of GO in PDMS117 is also observed by TEM by drop casting the composites in copper grid.

Wide-angle X-ray diffraction (WAXD) experiments of samples were carried out with a Rigaku model D max 2500 with a $\text{Cu K}\alpha$ radiation.

Small-angle X-ray scattering (SAXS) experiments were carried out with the aid of a semiconductor detector (Pilatus 100K, DECTRIS, Swiss) attached to a conventional Ni-filtered $\text{Cu K}\alpha$ X-ray source (GeniX3D Cu ULD, Xencos SA, France). The wavelength of the X-ray radiation is 0.154 nm. The sample-to-detector distance is 6000 mm, where the effective range of the scattering vector q ($q = 4\pi/\lambda\sin\theta$, where 2θ is the scattering angle and λ is the wavelength) is 0.02 – 0.2 \AA^{-1} . Each SAXS pattern obtained in the center of the sample was collected within 60 min; background was corrected and normalized using the standard procedure.

Optical observations under shear were carried out at 25°C using a Linkam CSS-450 shearing cell equipped with an Olympus BX-51 optical microscope under bright field and crossed-polarizer. The dispersion state of GO in PDMS without applied shear field was observed first. For the optical-flow experiments, optical micrographs were taken in the x - z plane with flow along the x axis, a constant velocity gradient along the y axis, and vorticity along the z axis. Samples were confined between two parallel quartz plates separated by a fixed gap (100 μm). The lower plate rotates at an angular speed that sets the shear rate, $\dot{\gamma} = \partial v_x / \partial y$, and a fixed point is used for observation. The samples were sheared at constant shear rates for 2 min to explore the structural change under shear.

Rheological measurements were performed on ARES G2 (TA instruments, strain controlled rheometer) with 25 mm parallel-plate geometry. After the sample was loaded on the geometry, the sample was squeezed with an axial force lower than 0.2 N. Before the measurements, the sample was left at rest for at least 10 min to wait for the decay of axial force ($\sim 10^{-3}$ N). Oscillatory strain sweep experiments were conducted at a frequency of 1 rad/s to determine the linear viscoelastic region. Linear oscillatory frequency sweeps were performed from 0.05 to 100 rad/s at appropriate strain in the linear region. Pseudo-steady shear (or steady shear) experiments were carried out from 0.01 to 100 s^{-1} . The reason to perform a pseudo-steady shear is that a steady state of shear stress is hard to be achieved for some GO/PDMS composites, and the condition for pseudo-steady shear experiments was that certain shear rate was fixed for 60 s and the last 20 s was used for data collection. For parallel-plate geometry, the measured normal stress is actually a difference of the normal stress differences, $\Delta N = N_1 - N_2$ (the normal stress differences N_1 and N_2 are defined as $(\tau_{11} - \tau_{22})$ and $(\tau_{22} - \tau_{33})$, respectively, where τ_{ii} represent the normal stresses acting along the flow (1), flow gradient (2) and vorticity (3) directions) [18]. All the experiments were conducted at 25°C .

3. Results

3.1. Characterization of GO and GO/PDMS composites

3.1.1. X-ray photoelectron spectroscopy (XPS)

The surface chemistry of GO was analyzed by XPS. Fig. 1a shows the XPS spectrum of GO sheets, which indicates the existence of

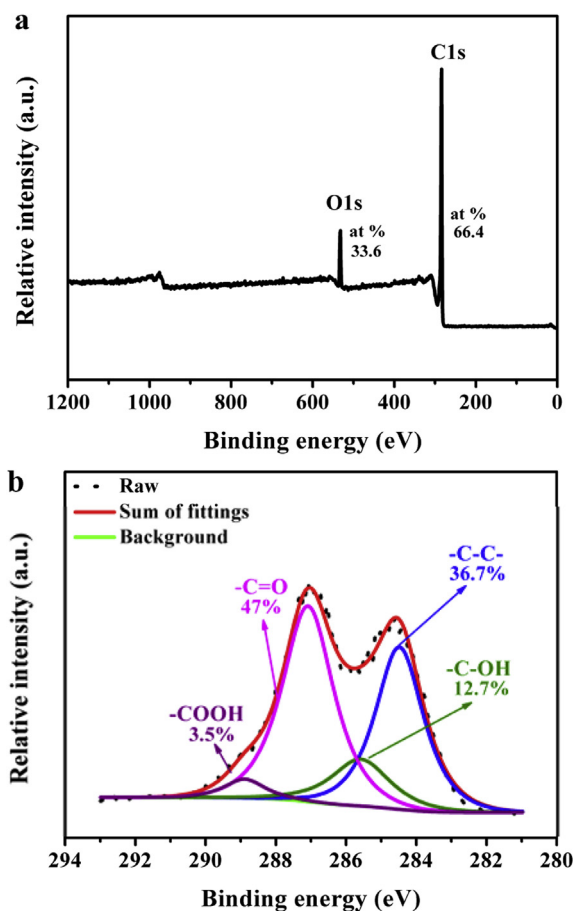


Fig. 1. XPS spectrum (a) and high resolution C1s spectrum (b) of GO sheets.

Download English Version:

<https://daneshyari.com/en/article/5180778>

Download Persian Version:

<https://daneshyari.com/article/5180778>

[Daneshyari.com](https://daneshyari.com)