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Correlation between the free volume and thermal conductivity of porous poly(vinyl alcohol)/reduced graphene oxide composites studied by positron spectroscopy

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ABSTRACT

Light-weight porous poly(vinyl alcohol) (PVA)/reduced graphene oxide (rGO) composites were prepared by freeze-drying method. The effects of doping rGO nanosheets on the free volume and the thermal conductivity were systematically investigated. Experimental results indicated that the free volume decreased after addition of rGO due to the interfacial interaction between rGO and PVA, such as hydrogen bond. The thermal conductivity increased nearly linearly with rGO content. In order to understand the mechanism of thermal conductivity enhancement, the thermal conductivity was calculated using different kinds of models, including parallel model, series model and Maxwell-Garnett effective medium approximation (EMA), which were then compared with experimental result. The difference value between the experimentally measured thermal conductivity and the EMA theoretically calculated result was closely associated with interfacial interaction, revealing that the better the dispersion of rGO, the stronger the interfacial interaction, and the larger the thermal resistance and the lower the relative thermal conductivity. A direct relationship between the fractional free volume and the thermal conductivity has been obtained, suggesting that the interfacial free volume plays an important role in determining phonon scattering and the thermal conductivity of composites.

1. Introduction

Thermally conductive polymer composites have received much attention due to the rapid increasing of demand in effective thermal management systems and the enabling technology for high-performance electronics, thanks to the polymer advantages such as low cost, light weight, ease of processing and high durability. Nanofillers (such as Cu nanowires, Ag nanowires, carbon nanotubes, etc.) with high thermal conductivity were selectively added into polymer [1–3]. Recently, graphene, a monolayer of sp^2-hybridized carbon atoms arranged in a two-dimensional lattice, shows excellent thermal conductivity, as high as 3000–5000 W/mK when suspended in air, which will be an excellent candidate for thermal conductive filler [4–7]. However, contacting with a substrate could seriously affect the thermal transport properties of graphene because of phonons leaking across the graphene-support interface and strong interface scattering, and as a result, the thermal conductivity of monolayer graphene exfoliated on a silicon dioxide support decreased to about 600 W/mK at room temperature (still higher than Cu) [8]. What is more, this surface-induced disruption effect is limited to few layers of graphene, with a characteristic distance of approximately 2.5 nm at room temperature [9]. Later, it is proved that the residual polymer on graphene scatters phonons in a similar way as the SiO_2 support [10]. Hence, the mismatch of phonon delivery between graphene and polymer should be considered in investigating the thermal conductivity of graphene-based polymer composites. Though many theoretical papers reported that the interface and defect have an important effect on the thermal conductivity of polymer composites [1,10–13], the effects of the free volume and interfacial interaction on the thermal conductivity have never been reported. On the other hand, most of the studies adopted doping amount higher than 10 vol% to achieve a high thermal conductivity of the composite [11,14,15], and the details in low content is always ignored, which would be a lack of understanding the mechanism in thermal conductivity enhancement.

Positron annihilation lifetime spectroscopy (PALS) is the most reliable probe for atomic and molecular defects and interfacial

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properties as it has the versatility to reflect electronic environment around vacancy-type defects through measuring the changes in lifetimes of positron and positronium (Ps, a bound state of e+ and e−). In this technique, positrons from a radioactive source (^{22}Na) are injected in to a condensed medium like polymers and get thermalized rapidly by losing their energy. Following, the thermalized positrons diffuse in the medium, annihilating directly with electrons or indirectly by forming Ps. Usually, the Ps exists in two spin states: para-Positronium (*p*-Ps) in which particle spins are antiparallel and ortho-Positronium (*o*-Ps) in which the particle spins are parallel. In polymers, Ps are preferentially localized in the free volume cavity and according to the free volume model, the pick-off annihilation (annihilates with an opposite spin electron) lifetime of *o*-Ps, τ_3, is well correlated to the free-volume hole size. When the size of the free volume cavity increases, the electron density seen by the *o*-Ps decreases and thus *o*-Ps lives a longer lifetime. Although PALS has been widely employed to determine the free-volume, structural phase transformation, electronic and mechanics properties in polymeric system [16–23], the application on the thermal conductivity of polymer composites has been rarely reported. To the best of our knowledge, the defect evolution in the polymer/graphene composite with thermal conductivity remains unexplored [20–22,24,25].

In this paper, we chose poly(vinyl alcohol) (PVA) as the polymer matrix and reduced graphene oxide (rGO) nanosheets as the graphene fillers. The composites were prepared by directly freeze-drying the frozen PVA/rGO solutions. We systematically investigated the effects of doping rGO on the atomic free volume, interfacial interaction between rGO and PVA matrix, and the thermal conductivity of PVA composites at low content of rGO. The correlation between atomic free volume, interfacial interaction and thermal conductivity were studied.

2. Experimental

2.1. Materials

Flake graphite (460 mesh; purity >99.8%), poly(vinyl alcohol) (PVA, polymerization degree 1788 ± 50, AR), potassium permanganate ($KMnO_4$, AR), sodium nitrate ($NaNO_3$, AR), hydrochloric acid (HCl, 35% aq.), sulfuric acid (H_2SO_4, 98% aq.) and hydrogen peroxide (H_2O_2, 30% aq.) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All materials were used as received.

2.2. Preparation of graphite oxide and reduced graphene oxide

Graphite was oxidized to graphene oxide (GO) following a modified Hummers' method (see details in the Supporting information). The as-synthesized GO was diluted with deionized water to 1.0 mg/mL and sonicated in an ultrasonic bath (180 W, 0 °C) for 0.5 h to create a homogeneous GO dispersion. RGO was obtained via chemical reduction of GO with a probable portion of hydrazine hydrate (1:1 in mass ratio, 95 °C, 8 h). A portion of the GO and rGO solutions were freeze-dried for characterization.

2.3. Preparation of PVA/rGO composites

The porous PVA/rGO composite with 1.0 wt% rGO is used as an example to describe the preparation procedure. First, 3 g PVA (polymerization degree 1788 ± 50, AR) and 30 mL deionized water were added into 30 mL GO aqueous suspension (1 mg/mL) with mechanical stirring and then heated to 95 °C for 0.5 h to form a homogeneous aqueous solution. A probable portion of hydrazine hydrate (1:1 in mass ratio to GO) was added into the blending solution and stirred at 95 °C for another 8 h. Then the homogeneous PVA/rGO solution was achieved by ultrasonication to get rid of air bubbles. Finally water was removed by freeze-drying the frozen PVA/rGO solution. The mass fraction of rGO was adjusted as shown in Table S1. The produced porous material has a low density about 0.05 g/cm^3 and the density could be adjusted by changing the total volume of the blending solution.

2.4. Sample characterization

The morphologies and structures of GO, rGO and PVA/rGO composites were studied by scanning electron microscopy (SEM, FEI Nova Nano450) and high resolution transmission electron microscopy (HRTEM, Titan G^2 60-300 probe Cs corrector). The exfoliation of rGO in PVA/rGO composites was observed in ultrathin sections with TEM (HITACHI H-800, HITACHI Ltd, Japan). The ultrathin sections were got using an LEICA EM UC7 cryoultramicrotome (Leica Microsystems, Germany). Fourier transform infrared spectroscopy (FTIR) was obtained with a VERTEX 70 spectrometer (Bruker Company, Germany). The samples were directly analyzed as porous membranes with reflection components. The thermal conductivity of the composites was measured using a home-made thermal conductivity test equipment as illustrated in Fig. S1. Positron annihilation lifetime spectroscopy was carried out by a conventional fast–fast coincidence spectrometer with a time resolution 280 ps in room temperature. The positron source ^{22}Na (20 μCi) was sandwiched between two identical samples with a thickness over 1 mm. One million counts were recorded for each spectrum, which was resolved into three components by a commonly used positron annihilation fitting program. The third and longest lifetime component τ_3 (1.4–2.6 ns) is used to calculated the volume of free volume cavity (V_f) in a spherical hole model according to Eqs. (1) and (2):

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1} \quad (1)$$

$$V_f = \frac{4}{3}\pi R^3 \quad (2)$$

where R is the radius of the free volume cavity and ΔR = 1.656 Å derives from fitting the observed *o*-Ps lifetimes in molecular solids with known cavity sizes [26]. The formation probability of *o*-Ps, I_3, is correlated with the intensity of the free volume. The free volume fraction (f) was evaluated using Eq. (3):

$$f = AV_fI_3 \quad (3)$$

For convenience here, A could be approximately regarded as a constant, and we defined a relative free volume fraction (f_r) as $f_r = V_fI_3$.

3. Results and discussion

3.1. Structure and morphology

Fig. 1a shows the SEM image of rGO, which was got by reducing GO in water with hydrazine hydrate, presenting large area of nanosheets with less wrinkle and break comparing to GO nanosheets (Fig. S2) due to its strong mechanical strength [27]. The irreversible agglomeration and poor dispersibility in water or organic solvents has always been the challenge for achieving uniformly incorporating graphene nanosheets into polymer composites. It has been demonstrated that directly dispersing rGO into PVA water solution could not form an uniform composite [28]. In this work, we found that rGO nanosheets could be stably dispersed in