High thermal conductivity and stretchability of layer-by-layer assembled silicone rubber/graphene nanosheets multilayered films

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ABSTRACT

Thermally conductive silicone rubber composites used for heat removal from electronic devices have attracted great attention. A facile spin-assisted layer-by-layer assembly approach was used to fabricate highly thermally conductive multilayered silicone rubber/graphene films. The films exhibit highly ordered lamellar structure with the high orientation of graphene which provides continuous thermally conductive pathways in horizontal direction. A multilayered film with 40 assembly cycles has the thermal conductivity of 2.03 W/(m·K) in in-plane direction. Moreover, the film can be highly twisted to any angle and has the elongation at break of 325%, which is rarely achieved in previously reported graphene-based multilayered films. Even up to 500 stretch-recovery cycles at 50% strain, the change of the thermal conductivity was negligible, indicating the high durability, excellent flexibility and stretchability of the film. The films with high thermal conductivity and stretchability have potential applications in flexible electronics, wearable devices and electronic skin.

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1. Introduction

Thermally conductive silicone rubber composites used for heat dissipation have attracted considerable recent attention due to the ongoing trend for miniaturization and integration of electronics. Owing to high softness and elasticity, optical transparency, electrical insulation, thermal stability, chemical inertness and durability, silicone rubber (SR) has been applied in fabricating electronic materials [1,2]. However, SR exhibits low thermal conductivity ($\sim$0.16 W·m^{-1}·K^{-1}) [2]. To increase the thermal conductivity of the silicone rubber composites, aluminum oxide, zinc oxide, silicon nitride, silicon carbide and aluminum nitride [3] are commonly used. For above-mentioned fillers, only when the filling proportion is over 50% can the thermally conductive composites with randomly dispersed fillers obtain high thermal conductivity [4,5]. The high filler content inevitably leads to deterioration of mechanical properties because of some rigid particles acting as defects in the polymer matrix, which impedes the application of thermal conductive composites. Moreover, the high filler loading greatly influences the rheological behavior of the composites, leading to further composites processing or mixing difficult. [6] Graphene, with a unique 2D honeycomb-shaped layered structure, is one of the most promising candidates in improving the thermal conductivity of sil-

icone rubber composites at a low content due to its intrinsic ultra-high thermal conductivity ($\sim$5000 W·m^{-1}·K^{-1}) [7,8].

Several studies have reported that silicone rubber composites with aligned particles exhibited superior performance compared with that with randomly dispersed particles at the same content. The fillers can orient in silicone rubber under shear force [9,10], magnetic [11–13] and electric fields [14–16], which provide effective thermally conductive pathways at low filling fraction. Li et al. [13] reported that graphene nanoplates (GNPs) oriented in SR under magnetic fields, promoting the enhancement of thermal conductivity. The thermal conductivity of GNPs/SR composite with 3 wt% GNPs content increased from 0.327 to 0.488 W/(m·K) after GNPs orientation. The orientation of boron nitride nanosheets (BNNSs) in silicone rubber was achieved under shearing on a two-roll mill and led to the increase in thermal conductivity from 1.56 to 5.47 W/(m·K) at the BNNSs loading of 30.8 vol% [10]. Linear alignment of BNNSs was also achieved under electric field, resulting in the thermal conductivity increment of approximately 3 times compared with the silicone rubber with randomly distributed BNNSs at 15 vol% filling content [16].

However, it is difficult to achieve high orientation degree of particles by aforementioned methods. Layer-by-layer (LBL) assembly, as a technique used to prepare laminated nanocomposites, is a promising approach to fabricate composites with high thermal conductivity [17]. The composites prepared via LBL assembly have the characteristics of planar orientation and highly ordered multi-

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layer architectures, providing channels for heat transport at an extremely low loading [17,18]. Zhu et al. [19] proved that LBL-assembled graphene-based composites have more pronounced alignment compared with vacuum-assisted flocculation composites due to the higher accuracy of the LBL deposition process. Furthermore, this commercially feasible method can be applied to large-scale production applications through 3D printing.

The process of LBL assembly can be implemented by spin coating, spray coating, dipping, and Langmuir–Blodgett method [20]. Among these approaches, spin-assisted LBL assembly is a simple, efficient and inexpensive process, through which the structure of composites can be designed by tailoring the thickness of polymeric and inorganic layers under high-speed centrifugal force and changing composition of hierarchical composites [17,21]. Xiong et al. [17] assembled 1D cellulose nanocrystal with the flexible 2D graphene into nanomembranes by a spin coating technique. The membrane with 56.8 wt% RGO content exhibited high electrical conductivity around 5000 S m^{-1} and outstanding ultimate stress of 655 MPa, resulting from highly ordered "brick and mortar" structure.

Herein, we used a facile, versatile and low-cost spin-assisted LBL assembly method to fabricate highly ordered silicone rubber/-graphene multilayered films. The highly oriented and layered arrangement of graphene nanosheets in multilayered films were expected to lead to high thermal conductivity. Generally, polyvinyl alcohol (PVA) [13,19,22–24] and cellulose [18,25–27] were often used to prepare multilayered films by LBL assembly. To our best knowledge, silicone rubber, as one of components, has rarely been used for LBL assembly. In this work, silicone rubber was chosen to endow composites with high elasticity, outstanding flexibility and stretchability, temperature resistance and moisture resistance. Furthermore, we demonstrated silicone rubber/graphene laminated films have potential applications in flexible, stretchable and transparent electronics, wearable devices and electronic skin.

2. Experimental

2.1. Materials

Addition liquid silicone rubber (SR) and Pt catalyst were made by China Bluestar Chengrand Co., Ltd., China. GO (purity: 99 wt%; thickness: 0.8–1.5 nm; lateral dimension: 0.5–5 μm) was made by Suzhou Tanfeng Graphene Technology Co., Ltd., China. Polyethylene glycol monododecyl ether was made by TCI (Tokyo, Japan) and used as received. All other reagents were used as received without further purification.

2.2. Preparation of SR/Graphene multilayered films by layer-by-layer assembly

Silicon wafers were cleaned by "Piranha" solution and rinsed with deionized water, then dried in nitrogen atmosphere. Addition liquid silicone rubber (1.87 g), Pt catalyst (10 ppm based on rubber) and polyethylene glycol monododecyl ether (0.03 g) were dissolved in tetrahydrofuran (THF, 40 ml) and stirred in a beaker for 1 h to obtain 5 wt% SR solution at ambient temperature. Polyethylene glycol monododecyl ether was used to reduce surface tension of SR solution. GO (20 mg) was dispersed in THF (40 ml) to obtain 0.5 mg/ml GO dispersion under sonication for 30 min at ambient temperature. For spin-assisted LBL assembly, the multilayered films were deposited on a sacrificial layer of polyethylene glycol monododecyl ether on silicon wafer. SR/GO multilayered films were fabricated by sequential repetition of the following steps at ambient temperature: the SR solution and GO dispersion were alternatively spun on the silicon substrate at 500 rpm for 6 s fol-

lowed by 3000 rpm for 30 s. For simplicity, SR/GO multilayered films were named in following format: (SR/GO)$_n$, where n is the number of deposition cycles. After LBL assembly, pure liquid silicone rubber was spun on SR/GO films in order to obtain free standing films. The solvent in films was slowly evaporated at ambient conditions for 2 h. Then, the films were cured at 60 °C for 30 min. The films were separated from substrates after being immersed in boiling water for 10 min. Afterward, the reduction of the multilayered films was carried out in hydrazine solution at 90 °C for 2 h. The resultants were named (SR/RGO)$_n$.

2.3. Characterization

The morphology was examined with a Nova NanoSEM 450 scanning electron microscope (FEI, USA). X-ray diffraction (XRD) patterns of the films were recorded with a BRUKER D8 ADVANCE using Cu Kα radiation (λ = 1.54 Å) under a voltage of 40 kV and a current of 40 mA. Raman spectra were obtained by using a DXR Raman spectrometer with 633 nm laser excitation. The RGO content and thermal stability were measured through thermogravimetric analysis (TGA) in nitrogen atmosphere at a heating rate of 20 °C·min^{-1} from 50 °C to 800 °C by using a TA Instruments Q5000IR. The stress–strain curves were measured by using a tensile machine (Instron 4465, USA) at a crosshead speed of 5 mm/min at room temperature. The rectangular samples were prepared with dimension of 20 mm × 4 mm. The in-plane and through-plane thermal diffusivity (α) were determined by using a laser flash method on a NETZSCH LFA447 laser flash analyzer. The thermal conductivity was calculated by the following formula:

$$\lambda(T) = \alpha(T) \cdot Cp(T) \cdot \rho(T)$$

where $Cp(T)$ is specific heat capacity and $\rho(T)$ is density of the film. The density of films was measured by using the buoyancy method on a PRECISA XS 225A-SCS electronic balance.

3. Results and discussion

A spin-assisted layer-by-layer deposition process of silicone rubber and GO nanosheets was employed to prepare the laminated films, followed by curing and chemical reduction processes, as illustrated in Fig. 1a. Enormous active adsorption sites on both edges and basal plane of GO, resulting from the huge specific surface area of GO nanosheets, can interact with silicone rubber. The primary driving force of LBL-assembled thin films is considered to be hydrogen bonds between the —OH/—COOH of GO nanosheets and the —O— on silicone rubber [28,29]. In addition, hydrophobic interactions and van der Waals forces can also make contributions on the interactions for bridging SR to GO nanosheets.

The SEM image of the surface of graphene on SR (Fig. 1b) reveals huge area of graphene layers because of the overlapping of substantial oriented graphene nanosheets, even larger than 200 μm in diameter, providing effective thermally conductive channels along graphene layers. The localized wrinkles in GO layers deposited on SR also can be observed in Fig. 1b. The SEM image of the cross-section of the (SR/RGO)$_{40}$ multilayered film shows that highly ordered RGO nanosheets and SR are alternately stacked with the densely well-defined lamellar structure, as presented in Fig. 1c. The high orientation of graphene was achieved by high-speed centrifugal force through spin coating. The ordered laminated structure could maximize the efficiency of phonon heat transfer because heat mostly transport along graphene layers. The thickness of SR/RGO multilayered films is nearly proportional to the number of cycles, as shown in Fig. 2. After 10 deposition cycles, the thickness of the film is 7.3 μm. The average thickness is 0.73 μm for every deposition cycles. The average thicknesses of each