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Thermal, mechanical and electrical properties of polyurethane/(3-aminopropyl) triethoxysilane functionalized graphene/epoxy resin interpenetrating shape memory polymer composites

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ABSTRACT

Functionalized graphene (FG) was successfully synthesized by treating graphene oxide with (3-aminopropyl) triethoxysilane (KH-550) and then reduced by hydrazine hydrate. Subsequently, significant reinforcement of polyurethane/epoxy resin (PU/EP) composites in situ synthesized on the FG is prepared. Morphologic study shows that, due to the formation of chemical bonding, the FG was dispersed well in the PU/EP matrix and the mechanical performance is improved. Meanwhile, the thermal degradation temperature was enhanced almost 50 °C higher than that of PU/EP. The conductivity of PU/FG/EP nanocomposites was 82.713×10^{-6} S/m at 2.0 wt% loadings. The resulting composites exhibited 96% shape fixity, 94% shape recovery, enhanced shape recovery force to realize thermo-electric dual-responsive property. Comparing with the results in literature, the composites used in this study have shown a progress between electrical conductivity and shape memory property.

1. Introduction

In the field of material design, the composites often show all kinds of outstanding performance. Polymer composites, compared with the pure polymer matrix, possess better mechanical properties and thermodynamic performances [1–3]. Shape memory polymers (SMPs) are intelligent materials that can respond to an external stimulus; they have been widely researched due to their facile processability, low cost, appreciable shape recovery, and broad range of shape recovery temperatures [4–6]. Nishikawa et al. conducted periodic-cell simulations of the thermo mechanical cycle of thermally activated shape memory polymer (SMP)-based composites [6]. In particular, polyurethane (PU) has many applications such as fiber, coating, adhesives and smart actuators [7,8]. But its good deformability, low stiffness and tensile strength may limit its application in some field. Epoxy resins (EP) are associated with high modulus and strength, which have been widely studied and used in many kinds of structural composites. Dong et al. have prepared shape memory silica/epoxy composites by hydrolysis of tetraethoxysilane (TEOS) within the epoxy matrix via latex, freeze-drying, and hot-press molding method [9]. However, epoxy resins are generally brittle polymers, which restrict their application [9–11]. To conquer these problems, the formation of interpenetrating polymer networks (IPNs), which consist of two polymer networks holding together by permanent covalent entanglement, is an effective way to combine the respective outstanding properties of different polymer materials [12,13]. The excellent synergistic effect in mechanical properties has been achieved in PU/EP IPNs due to their good compatibility between polyurethane and epoxy [14,15].

In the past few years, carbon materials, including zero-dimensional fullerene, one-dimensional carbon nanotubes, and three-dimensional diamond, have been widely applied in polymer composites [16–18]. Graphene nanosheet (GNS) is a new type of carbon material which was discovered by Konstantin Novoselov and Andre Geim in recent years [19]. Graphene nanosheet has emerged as an exciting, new nanocarbon, because it has novel properties: an electrical conductivity of 10^8 S/m, a basal plane elastic modulus of 1 TPa, a thermal conductivity of 5000 W/m·K, a high aspect ratio, and a large specific surface area of 2600 m^2/g [20–23]. Modified graphene can be synthesized through a reduction of functionalized oxidation graphene. Based on the characteristic of graphene oxide (GO), a lot of functional organic substances were grafted to the graphene forming the functionalized graphene, which greatly improved the dispersibility of graphene in the

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polymer matrix [24,25]. Pokharel et al. reported that the segmental length correlating properties of polyurethane (PU) in its nanocomposite system with graphene oxide (GO) were investigated [26]. Han and Chun fabricated high-performance polyurethane nanocomposites with surface-functionalized, nano-layered graphene sheets, which showed greater shape memory properties up to 98% shape fixity and a 94% shape recovery ratio after four cycles than the reduced graphene/PU composites [27]. Xia et al. reported that graphene-oxide-hybrided polyurethane/epoxy interpenetrating polymer networks were prepared through an in-situ polymerization which showed the better mechanical performance due to the formation of chemical bonds [28]. Li et al. reported the significant reinforcement of polyurethane/epoxy resin (PU/EP) composites in situ synthesized on the graphene oxide nanosheets (GONS) [29]. With the incorporation of 0.066 wt% of GONS, the tensile modulus of composites increased from 218 MPa to 257 MPa, the tensile strength and elongation at the break increased by more than 52% and 103%, respectively.

In the current work, an in situ polymerization method to obtain the polyurethane/KH550-functionalized graphene/epoxy resin nanocomposites (PU/FG/EP) has been developed. As is well-known, the PU/EP IPNs is applied more and more widely, but few studies have focused on the conductivity and the shape memory property. In this paper, the (3-aminopropyl) triethoxysilane functionalized graphene was synthesized which could react with isocyanate group of pre-PU and curing reaction of PU/EP IPNs. The formed PU/FG/EP composite provided outstanding thermal and mechanical properties and thermo-electric dual-responsive shape memory property. The facile and feasible method provides a potential way to design a new class of graphene based polymer nanocomposites and use them in various applications.

2. Experimental

2.1. Materials

Graphite flakes (325 mesh, purity 99%) were purchased from Qingdao Haida Graphite Co., Ltd, China. Silane coupling agent, (3-aminopropyl)triethoxysilane (KH-550), Nanjing forward Chemical Co., Ltd. 2,4-/2,6-Toluene diisocyanate (TDI) was purchased from Chengdu Kelon Chemical Reagent Limited, China. Polyoxytertramethylene (PTMG) with molecular weight of 3000 g/mol was received from Qingdao Huayuan Polymer Co., Ltd. Epoxy resin (E-51, epoxide number 0.48–0.54 eq/100 g) was purchased from Hunan Yueyang Baling Petrochemical Co., Ltd. Epoxy resin curing agent (593, amine value 550–700 mg KOH/g) was received from Shanghai Chemical Industry Co., Ltd. The 4A molecular sieve with globular $\varnothing$3 – 5 mm was purchased from Shanghai Runhai Rapid Chemical Reagent Co., Ltd. Dimethyl formamide (DMF) was dried with CaH_2 for 24 h and freshly distillated before use. Hydrazine Hydrate was purchased from Tianjin Kermel Chemical reagent plant. The chemicals included potassium permanganate ($KMnO_4$), concentrated sulfuric acid (98%), hydrochloric acid and hydrogen peroxide (30%) and others are all reagent grade.

2.2. Synthesis of (3-aminopropyl) triethoxysilane functionalized graphene (FG)

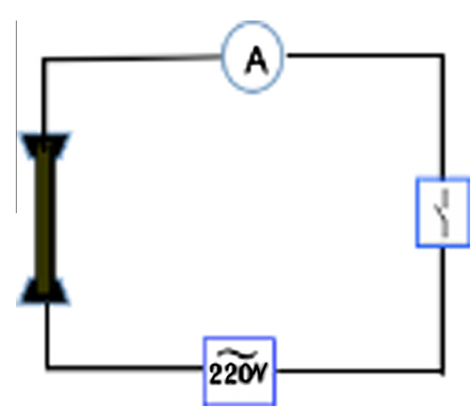
The synthesis process of KH550 - functionalized graphene was as follows: First of all, in a typical step, GO was prepared from a method of modified Hummers' method [1]. 100 mg of GO was loaded into a 250 mL round-bottom flask in 150 mL of DMF/water solution (9:1 v/v) by ultrasonication dispersion. At the same time, 0.5 mL hydrazine hydrate was drop wise added into the solution in the beaker and kept at 98 °C and stirred for 7 h. The mixture was filtered under vacuum with a PTFE filter (0.22 μm pore size), and dried at 80 °C for 12 h to yield a solid black material. Then adjusting pH about 3.5–5.0, 1.00 g of KH-550 was added into the flask equipped with stirring for 12 h at 75 °C. The slurry reaction mixture was filtered and washed with anhydrous ethanol in order to remove redundant KH-550.

2.3. Fabrication of polyurethane/KH550-functionalized graphene/epoxy resin nanocomposite (PU/FG/EP)

The procedure for preparing PU/FG/EP was presented in Scheme 1: First of all, the FG had been produced; Secondly, in situ polymerization of TDI and PTMG in the presence of FG. Briefly, the preparation of the sample containing 0.5 wt% FG called PGE-0.5 was as follows: 6.348 mg of FG was dispersed in DMF with the assistance of ultra-sonication at room temperature. Then, 3 g of PTMG was added into the above FG suspension at 70 °C for 2 h protected by N_2. Afterwards, 0.174 g of TDI was added into the flask and the mixture was stirred at 80 °C for another 2 h to in situ preparing polyurethane prepolymer on the FG (pre-PU/FG); Thirdly, 3.174 g epoxy resin was introduced into the homogeneous mixture which was stirred 1.5 h and 0.576 g amine curing agent was introduced and degassed under a vacuum at 80 °C until thicken. Then, the mixture was poured into pre-heated molds made from Teflon; Finally, the PU/FG/EP nanocomposites were obtained via in situ thermal polymerization; Other samples containing 0.0 wt% to 2.0 wt% FG were synthesized by the same procedures. The final samples were labeled PGE-0.1, PGE-0.2, PGE-0.3, PGE-0.4, PGE-0.5, PGE-0.6, PGE-0.8, PGE-1.0, PGE-1.2, PGE-1.4, PGE-1.5, PGE-1.8 and PGE-2.0, respectively.

2.4. Characterization

Fourier-transform infrared (FTIR) spectra were collected on a Nicolet Fourier spectrophotometer, using KBr pellets (Perkon-Elmer1700, USA). X-ray diffraction (XRD) patterns were recorded on a TD-300 X-ray diffractometer using Cu Ka radiation (λ = 1.54 Å) as the X-ray source. Thermo-gravimetric analysis, using the Germany NETZSCH TG 209 types of differential thermo-gravimetric analyzer, was used to measure the thermal stability of the materials at a heating rate of 10 °C/min in a N_2 atmosphere from 0 to 700 °C. X-ray photoelectron spectroscopy (XPS) measurements were performed using a monochromic Al Ka (1486.6 eV) source at 15 kV and 10 mA on the Kratos Axis Ultra DLD spectrometer. The Raman spectra of the graphene were recorded with a Raman spectrometer (WITec, Alpha 300R)



Scheme 1. Schematic representation for the measurement of electrical resistivity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)