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Acryloyl-group functionalized graphene for enhancing thermal and mechanical properties of acrylated epoxidized soybean oil UV-curable based coatings

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ABSTRACT

Recently, acrylate epoxidized soybean oil (AESO) has become one of the most important industrial, bio-based, UV-curable resins. To reinforce AESO-based UV-curable coatings, acryloyl-group functionalized graphene (*acr*-RGO) was successfully prepared and characterized using attenuated total reflection-Fourier transformed infrared spectroscopy, X-ray diffraction, Raman spectroscopy, and thermogravimetric analysis. The AESO/*acr*-RGO nanocomposite coatings were fabricated using UV-curing technology to covalently introduce graphene sheets into the AESO matrix. Real-time infrared and ATR-FTIR spectroscopy were used to monitor double-bond conversions and deep curing in the AESO/*acr*-RGO coating. Scanning electron microscope images revealed the homogeneous dispersion of *acr*-RGO in AESO. The thermal and mechanical properties of cured films were evaluated through thermogravimetric analysis, tensile testing, and dynamic mechanical analysis. The results revealed that the introduction of *acr*-RGO effectively enhanced the mechanical properties and the thermal stability of the host resin AESO. The optimal reinforcing effect was observed at 1.0 wt% *acr*-RGO loading, under which the tensile strength and storage modulus of the AESO/*acr*-RGO nanocomposite improved by 167% and 15%, respectively, compared with those of neat AESO. The initial degradation temperature of the AESO/*acr*-RGO nanocomposite was also sharply improved by 61 °C under a loading of 0.5 wt%. Additionally, a slight increase in the glass transition temperature of the AESO/*acr*-RGO nanocomposite from 29.6 to 36.1 °C was observed when *acr*-RGO was incorporated. Furthermore, introducing *acr*-RGO enhanced the coating properties. By contrast, the composite coating using amino-group functionalized graphene (AESO/*ami*-RGO) nanocomposites exhibited poorer mechanical properties and lower thermal stability than its *acr*-RGO counterpart. The remarkable property reinforcements are thus attributed to the acryloyl-group functionalization of graphene, which improved the compatibility and enhanced the interfacial adhesion of graphene with the AESO matrix.

1. Introduction

Because of the decline in petroleum reserves, the threat of global warming, and stringent environmental rules and regulations, renewable and environment-friendly materials, such as bio-based materials, are of considerable importance [1,2]. Among the various industrial bio-based materials, soybean oil (SYBO), with a global annual production of approximately 45 million tons, is one of the most widely used [3,4]. UV-curing is promising because of its unique economic and ecologic advantages, including a high curing rate, the absence of solvents, a broad formulation range, low energy consumption, and low space and capital requirements for curing equipment[5]. Acrylate epoxidized soybean oil (AESO) is one of the largest industrial bio-based UV-curable resins and is produced through the epoxidation of SYBO followed by the opening of the epoxide groups by using acrylic acid [6]. Due to its low volatile organic compound emissions, low cost, and high biodegradability, AESO can be used for UV-curable coatings [7]. However, the three long aliphatic chains of AESO often lead to poor mechanical and thermal properties which considerably limit its application in coatings [8]. To improve the thermal and mechanical properties of AESO, much focus has been placed over the past few years on preparing AESO composites that incorporate nanosized fillers. Nanomaterials such as glass fibers, clay, and carbon nanotubes are common toughening agents, which have been widely used in AESO matrices to prepare heat-curable nanocomposites [9–11]. Zhang et al. synthesized mercaptopropyl polyhedral oligomericsilsequioxane (POSS-SH) and then blended it with

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AESO to produce UV-curable hybrid coatings and reported significant improvements in the physical and mechanical properties of all cured samples [12].

Recently, because of its outstanding electronic, mechanical, and thermal properties, graphene has been widely employed as a toughening agent for fabricating polymer composites with enhanced properties [2,13,14].Although major progress has been achieved in this field, two practical challenges remain in realizing the maximum reinforcing force of graphene in composites. First, graphene sheets agglomerate or become stacked because of strong π–π interaction, inevitably leading to the low dispersion of graphene in polymer matrices. The high specific surface area of graphene [15,16] is also counteracted owing to the agglomeration. Second, the weak interfacial interaction between graphene and the polymer matrices, attributed to the inert surface of graphene, limits the load transfer from the polymer matrix to graphene. Therefore, the formation of a strong bond between polymer matrices and graphene is favored for efficiently improving the properties of composites. The chemical functionalization of graphene is an efficient solution for the aforementioned problems. The functionalization of graphene through covalent linking or noncovalent bonding not only immensely weakens the intermolecular interactions and prevents the aggregation of graphene sheets but also strengthens the interactions between graphene and polymer matrices [17–28]. For example, Ma et al. used *p*-phenylene diamine (PPD) to simultaneously functionalize and reduce graphene oxide (GO) and subsequently fabricated a PS/GO-PPD composite [25]. M. Kotal et al. grafted BIIR on GO-PPD surface and it showed that BIIR-g-GO-PPD filler was homogeneously distributed in the BIIR matrix to enhance mechanical, thermal and dielectric properties of the nanocomposites [17]. Wang et al. covalently functionalized graphene with 3-aminopropyl triethoxysilane (APTES) and used the amino-group functionalized graphene (*f*-GNS) to reinforce epoxy resins. The resulting epoxy composite exhibited a 52% increase in its tensile strength, owing to the homogeneous dispersion in the epoxy matrix and the covalent bonding between the *f*-GNS and the epoxy resins [20]. It is worth to mention that Hu et al. functionalized graphene using photosensitive double bonds and applied it to reinforce polyurethane acrylate through UV irradiation And a high-performance UV-curing nanocomposite was obtained [29]. These results indicate that functionalized graphene shows a grand potential as reinforcement material to fabricate nanocomposites. Inspired by the above works, we, added modified graphene with acryloyl-group to AESO matrix to enhance mechanical and thermal properties of AESO based nanocomposites.

In this study, to develop high-performance UV-curable AESO coatings, a UV-curable acryloyl-group functionalized graphene (*acr*-RGO) was fabricated and subsequently employed as a reinforcing filler in an AESO matrix by using UV-curing technology. The preparation procedure of the *acr*-RGO and nanocomposites is illustrated in Scheme 1. The grafting of the acryloyl-group onto the graphene surface enables the graphene sheets to covalently link with the AESO network, which is expected to improve the dispersion quality as well as strengthen interfacial graphene–AESO interaction. The mechanical and thermal properties and the coating performance of AESO/*acr*-RGO nanocomposites were investigated as a function of *acr*-RGO content.

2. Experimental

2.1. Chemicals and reagents

Graphite powder (GP) with an average size of 8000 mesh and a purity of > 99% was purchased from Shanghai Aladdin Industrial Co., Ltd., China. AESO was provided by Jiangsu San Mu Group Co., Ltd. (Wuxi, China). Potassium permanganate ($KMnO_4$, analytical reagent (AR) grade), sodium nitrate ($NaNO_3$, AR), hydrogen peroxide (H_2O_2, 30% aq.), sulfuric acid (H_2SO_4, 98%), hydrazine hydrate ($N_2H_4{\cdot}H_2O$, 85% aq.), ethanol (CH_3CH_2OH, AR), acetone (AR), and dimethylformamide (DMF, AR) were all used as received, and 4-methoxyphenol (MEHQ), dibutyltin dilaurate (DBTDL), and chloroform were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Aminopropyl triethoxy silane (APTES) was supplied by Sinopharm Chemical Reagent Co., Ltd. Isophorone diisocyanate (IPDI) and hydroxylethyl acrylate (HEA) was purchased from Dong-fang Chemical Co., Ltd. (Beijing, China) and was dried over 4 Å molecular sieves before use. In addition, 2-hydroxy-2-methyl-1-phenyl-1-propanone (darocur1173) and Phenylbis (2, 4, 6-trimethylbenzoyl) phosphine oxide (819) were kindly provided by Ciba Specialty Chemicals and were used as a photoinitiator.

2.2. Amino-group functionalization of GO

Graphene oxide (GO) was synthesized from graphite powder (GP) on the basis of the Hummers method [28]. In a typical procedure [26] for preparing *ami*-GO, GO (100 mg) was dissolved and exfoliated in 4.8 g of alcohol and 0.8 g of deionized water via ultrasonication with a SB-3200D ultrasonicator (Ningbo, China). Subsequently, APTES (500 mg) was added. The mixture was reacted with magnetic stirrer for 6 h at 60 °C and filtrated with a PTFE membrane with an average pore size of 0.45 μm. The filtrate cake was rinsed in ethanol with the aid of ultrasonication for 10 min and then filtrated. The rinsing-filtration process was repeated for a few times to remove the residual APTES. Finally, the filtrate cake was dried in an oven at 50 °C for 12 h.

2.3. Preparation of ami-RGO

Reduction of *ami*-GO was carried out in oil bath with mechanical stirring at 80 °C for 24 h [18] using hydrazine (mass ratio of *ami*-GO/hydrazine approximately 10:7). The resulting mixture was filtrated and washed for a few times with acetone to remove residual hydrazine. The reduced *ami*-GO (*ami*-RGO) was dried in a vacuum oven at 50 °C for 12 h.

2.4. Acryloyl-group functionalization of ami-RGO

Acryloyl-group functionalization of *ami*-RGO was done by reacting with a required amount of IPDI-HEA. Briefly, 500 mg of *ami*-RGO was dispersed in 200 mL of waterless DMF through ultrasonic treatment for 30 min. This dispersed *ami*-RGO was taken in a 250 mL four-necked round-bottom flask equipped with an additional funnel and a mechanical stirrer. Then, 5.0 g of IPDI-HEA was added dropwise into the reaction mixture. The reaction was continued for 24 h at a temperature of 30 °C to obtain *acr*-RGO. IPDI-HEA was synthesized on the basis of the previous report [30]. The product was filtrated and washed for a few times with acetone to remove residual IPDI-HEA. The *acr*-RGO was dried in a vacuum oven at 50 °C for 12 h prior to use.

2.5. Fabrication of UV-curable coatings

The formulation of the UV-curable coatings is displayed in Table 1. AESO/*acr*-RGO nanocomposite is designated as AESO/*acr*-RGO-X, where X represents the weight percentage of nanoparticles in the nanocomposites (X = 0.1, 0.5, 1.0). AESO/*acr*-RGO nanocomposite was prepared by solution blending [25,31]. Briefly, a certain amount of *acr*-RGO was dispersed in THF (approximately 0.1 g *acr*-RGO per 100 mL THF) by ultrasonic exfoliation for approximately 1 h by using a JYD-650 sonicator in an ice bath at 250 W. The resulting suspension was then combined with the AESO (70 wt%) and IBOA (30 wt%) mixture that was dissolved in THF (approximately 1 g mixture per 10 mL THF) at ambient temperature. Subsequently, the new mixture was homogenized and most of the THF was removed using an IKA T18 homogenizer (Germany) for approximately 3 h at 40 °C. The obtained nanocomposite was mixed with Irgacure1173 (3 wt%) and 819 (0.3 wt%) and coated on glass plates through leveling naturally. The nanocomposite was put in an oven at 40 °C for 2 h to degas and remove the