



Balanced electrical, thermal and mechanical properties of epoxy composites filled with chemically reduced graphene oxide and rubber nanoparticles



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ABSTRACT

Epoxy composites filled with 2D chemically reduced graphene oxide (CRGO) sheets and preformed 3D powdered rubber (PR) nanoparticles were fabricated to investigate the effect of hybrid nanofillers on the electrical, thermal and mechanical properties as well as fracture toughness. As expected, the presence of CRGO sheets endows epoxy with electrical conductivity and enhances its thermal properties, stiffness and toughness; while the addition of PR results in significant reductions in thermal stability and stiffness, but produces dramatic improvements in fracture toughness. Compared with the binary composites, the ternary composites containing hybrid 2D CRGO and 3D PR fillers provide a good balance among electrical conductivity, thermal stability, glass transition temperature, stiffness, strength and fracture toughness, which cannot be achieved by independent single-phase fillers. Based on the morphologies of the fracture surfaces and damage zones around the crack tip, various toughening mechanisms such as crack-bridging by GO sheets, sheet/sheet delamination and sheet/matrix debonding, rubber cavitation and matrix shear banding, were identified and correlated with the fracture toughness of the hybrid composites studied. Results obtained disclosed suppression of deformation and/or cavitation of the PR nanoparticles after the incorporation of CRGO, which explained the moderate improvement in fracture toughness of the hybrid composites.

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1. Introduction

Epoxy polymers are being widely used as matrices in state-of-the-art applications due to many useful properties like high specific strength and stiffness, chemical resistance, processability, environmental stability and relatively low cost [1]. Cured epoxies with tight three-dimensional molecular network structures have relatively high thermal stability and glass transition temperature (T_g); however, they exhibit inherent brittle fracture behavior and poor crack growth resistance, thus limiting their general usage in mechanical components. Therefore, toughening of epoxy without sacrificing its thermal properties is mandatory if epoxy-based

composites are targeted for load-bearing applications.

During the past decades, numerous attempts were made for improving the brittleness and fracture energy of epoxies by blending with soft rubber particles [2] and rigid nanofillers, such as silica [3], alumina [4] and carbon nanotubes (CNTs) [5]. It is well-established that rubber particles can produce the desired effect on toughening brittle epoxy, but they usually cause deterioration of other important properties, such as elastic stiffness, strength and T_g [6], especially thermal stability [2]. The principal toughening mechanisms involve rubber debonding/cavitation and massive matrix shear banding. Comparatively, although rigid nanoparticles can improve the toughness and stiffness simultaneously without loss in the thermal properties, they usually provide a relatively mild toughening efficiency. Rigid nanofillers mainly toughen epoxy via crack pinning and deflection, filler/matrix debonding and subsequent matrix shear yielding or plastic deformation [4,5].

To further balance the mechanical and thermal properties,

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epoxy composites reinforced/toughened with hybrid fillers have gained extensive interests in both academia and industries. By combining different scales and/or types of particles, it is possible to improve certain key mechanical and other important properties simultaneously [7–10]. Our early studies utilized several hybrid fillers (e.g., sub-micron rubber and nano-silica [11], rubber or silica and CNT [12], submicron-rubber and powdered nano-rubber [13]) to toughen epoxy; and the mechanical properties including stiffness, strength and toughness, and thermal properties could be tailored by adjusting the weight ratio of the hybrid fillers. More importantly, some studies revealed that selective combinations of soft rubber particles and rigid nanofillers (e.g., layered clay and core-shell rubber [7], liquid rubber and nano-silica [8]) were more effective in toughening epoxy than single-phase fillers, i.e., existence of synergistic toughening. However, there are still conflicting reports concerning the influence of hybrid fillers on dispersion and microstructure [9,11], T_g [12,14], stiffening and strengthening efficiency [7,15], and toughness and ductility [8,9,11]. These results reflect complicated interactions between two different types of hybrid fillers that co-exist in the composites.

Graphene, two-dimensional layer of sp^2 -bonded carbon with single layer thickness less than 1 nm, has generated great interest during the past several years owing to its intriguing and unparalleled physical properties [16]. After proper surface modification and processing, graphene and its derivatives can be well-dispersed and exfoliated in a polymer matrix, producing significant improvements in thermal and mechanical properties at relatively small graphene loadings (<1.0 wt.%) [17], even effectively increasing the toughness of brittle epoxies [18]. In our previous studies [19–22], significant effort was made to prepare epoxy composites incorporated with low loading (0.1–0.5 wt.%) of graphene oxide (GO) or reduced graphene oxide (RGO) and analyze their structural, thermal, mechanical and fracture behaviors. In particular, in Ref. [19], the test results revealed that highly-dispersed RGO with a corrugated morphology led to a substantial interphase zone with the matrix and thus constrained the mobility of the polymer chains. Meanwhile, RGO sheets were also observed to bridge micro-cracks and debond/delaminate during the fracture process due to the poor filler/matrix and filler/filler interfaces, thus triggering and promoting local matrix plastic deformation to dissipate fracture energy. As a result, incorporation of 0.2 wt.% highly-dispersed RGO into epoxy provided $\sim 11^\circ\text{C}$ and $\sim 52\%$ increase in T_g and fracture toughness (K_{IC}), respectively. Hence, the combined use of graphene and rubber hybrid fillers is promising for further optimization and balance of mechanical and thermal properties of epoxy. However, until now, research on the mechanical and thermal properties of epoxy resin filled with graphene-based hybrid fillers is scarce. Furthermore, to determine unambiguously how graphene and other fillers influence the fracture behaviors of epoxy, it requires that the complicated interaction between the hybrid fillers on toughening epoxy should be clarified and understood.

Since nano-scale rubber toughens epoxy without any significant loss of other important properties, e.g., T_g and tensile strength, when compared to the traditional toughener such as liquid rubber [23], herein, we also chose preformed rubber nanoparticles as the second-phase filler and prepared graphene/rubber/epoxy hybrid composites. The main focus of this work is to elucidate the fracture behaviors and the toughening mechanisms in epoxy-based binary and ternary composites. Special emphasis is given to observe how the second soft PR particles interact with graphene and affect the crack growth in epoxy. Approaches to achieve good balance of electrical, thermal and mechanical properties in epoxy composites are also discussed.

2. Experimental work

2.1. Materials

Epoxy resin used was standard diglycidyl ether of bisphenol-A epoxy (DGEBA, Wuxi Resin Factory of Bluestar New Chemical Materials Co., Ltd., China), and the hardener employed was a mixture of 4-methylhexahydrophthalic anhydride (MHHPA, Puyang Hui-cheng Chemicals Co., Ltd., China) and a trace (100:1/w:w) of N, N-Benzylidimethylamide (Sinopharm Chemical Reagent Co., Ltd., China). The chemical structures of epoxy and hardener used in this work are shown in Fig. S1.

Natural graphite flakes (Huadong Graphite Factory, China), potassium chlorate (Fuchen Chemical Reagents, China) and other materials including concentrated sulfuric acid, concentrated nitric acid and hydrochloric acid (Beijing Chemical Factory, China) were used. Graphite oxide was prepared by oxidizing natural graphite flakes in a solution of sulfuric acid, nitric acid, and potassium chlorate for 96 h [24]. Dried graphite oxide was suspended in deionized water with strong stirring and ultra-sonication for 12 h to obtain a highly exfoliated GO solution. Hydrazine hydrate (weight ratio: hydrazine hydrate/GO = 1) was then added into the solution at 80°C for 12 h by stirring and ultra-sonication. After that, the samples were immediately isolated through filtration, and washed with deionized water for 4–5 times, and then dried in an oven at 60°C for 24 h to obtain 2D¹ chemically reduced graphene oxide (CRGO) sheets with dimensions of several micrometers. The structural characterizations of CRGO are given in Fig. S2. Preformed 3D¹ powdered rubber (PR) nanoparticles (Narpow VP-501) were carboxylic nitrile-butadiene preformed rubber latex particles supplied by SINOPEC Beijing Research Institute of Chemical Industry [13,25]. As shown in Fig. 1a, the 3D PR nanoparticles are usually agglomerates. Similar clusters of PR nanoparticles with an average size of ~ 90 nm were also observed after being dispersed in ethanol (Fig. 1b).

2.2. Fabrication of composites

The general procedure for preparing epoxy-based composites has been described in detail in earlier studies [19,26]. Typically, the CRGO and/or PR fillers were first dispersed in ethanol by sonication for ~ 0.5 h, and epoxy was then added and dispersed in a sonication bath for ~ 0.5 h to obtain a stable mixture. The mixture was further dispersed by a planetary ball mill (PM 400, Retsch) at 250 rpm for ~ 6 h. After degassing at 80°C for 20 h and room temperature for 6 days to remove the solvent, the hardener with a resin-to-hardener weight ratio of 185:170 was incorporated into the above dispersion by using mechanical mixing (~ 1500 rpm for ~ 0.5 h). After second degassing at 60°C for ~ 0.33 h, the blend was poured into preheated steel moulds and cured in an oven with no applied pressure. A four-step curing procedure was used: from room temperature to 90°C for 0.5 h, then at 120°C for 1 h, afterwards from 120°C to 160°C for 0.5 h and finally at 160°C for 2 h. The cured samples were allowed to cool slowly in the oven to room temperature. Fig. 1c shows the processing steps used to fabricate the composites. For easy reference, the samples are designated as RxGy, where R and G represent nano-sized PR and CRGO, respectively; x and y stand for the weight content of the relevant components in this formula. For example, R3G0.5 represents composites containing 3.0 wt.% PR and 0.5 wt.% CRGO.

¹ 2D and 3D are used to indicate the dimensions of the fillers. Hereafter, these prefixes will be dropped.

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