



Improving the fracture toughness of epoxy with nanosilica-rubber core-shell nanoparticles



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ABSTRACT

Nanocomposites from epoxy and nanosilica-rubber core-shell nanoparticles were fabricated. The soft shell was a copolymer synthesized from caprolactone and meso-lactide and was designed compatible with the cured epoxy system. The core-shell nanoparticles achieved a reasonably good dispersion in the matrix with minor aggregations. With the addition of the nanosilica based core-shell nanoparticles, the Young's modulus, maximum strength, and fracture toughness of the epoxy were all improved. The impact strength of the epoxy was improved by 39.4% with a loading of 2.0wt% nanofillers. The glass transition temperature of the epoxy was slightly decreased with the addition of nanofillers. The toughening mechanisms were investigated with the use of small angle X-ray scattering together with morphological observations. It was confirmed that crazing, microcracks formation and debonding of nanoparticles from the matrix were the main causes leading to the improvement of fracture toughness.

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1. Introduction

Aromatic epoxy resins have been widely used as adhesives, coatings and matrices in fiber reinforced composites for structural applications in a wide range of industries [1,2]. When cured with aromatic hardeners, aromatic epoxies are highly crosslinked, leading to some desirable properties such as high glass transition temperatures, high modulus and an undesirable property in that they are brittle and have a low resistance to crack initiation and propagation [3].

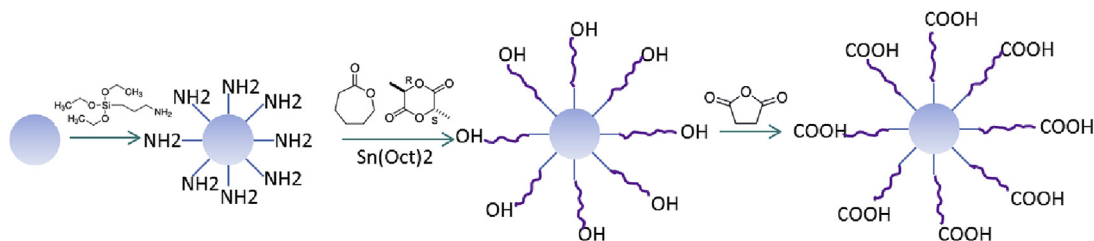
To improve the fracture toughness of epoxies, adding a rubber phase such as commercially available butadiene-acrylonitrile copolymers with different functional terminal groups has been well documented [4–6]. In general, the volume fraction of the toughening rubber phase varies from 5 to 20%. However, the addition of rubber phase increases the viscosity of the epoxy resin mixture, reduces the crosslink density, Young's modulus, tensile strength and dramatically reduces the glass transition temperatures of epoxies [4–6]. High performance thermoplastic engineering polymers such as poly(phenylene oxide), poly(ether sulfone) and

poly(ether imide) have also been used as toughening agents for aromatic epoxy resins [7–9]. The advantage of these thermoplastics modifiers is that their incorporation into epoxy resins does not result in much reduction in modulus and glass transition temperatures. However, thermoplastic modifiers have to be added into epoxy resins by solution or dissolution in epoxy resin at high temperatures. The viscosities of the modified epoxy resins are generally very high because of the high molecular weights and high viscosities of the toughening thermoplastics [7–10]. Hyperbranched poly(arylene ester)s of different molecular weights functionalized with carboxylic acid groups have also been added into diglycidyl ether bisphenol-A (DGEBA) epoxy resin to improve the fracture toughness [11]. It was found that higher molecular weight hyper branched polymers were effective in improving fracture toughness. However, they caused a sharp increase of viscosity to the resin mixtures.

Core-shell rubber (CSR) particles with a soft core such as polysiloxane, butadiene-styrene copolymers, or poly(butyl acrylate)s and a harder shell such as poly(methyl methacrylate) have been well studied for the improvement of fracture toughness of brittle epoxies [12–17]. It showed that the fracture toughness of epoxy was slightly improved when the loading of CSR particles was low [16], the yield strength and Young's modulus of epoxy decreased almost linearly with increasing CSR particle content although the glass transition temperature remained almost unchanged [14,16].

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Scheme 1. Route for the synthesis of silica-P(CL-mLA)-COOH nanoparticles.

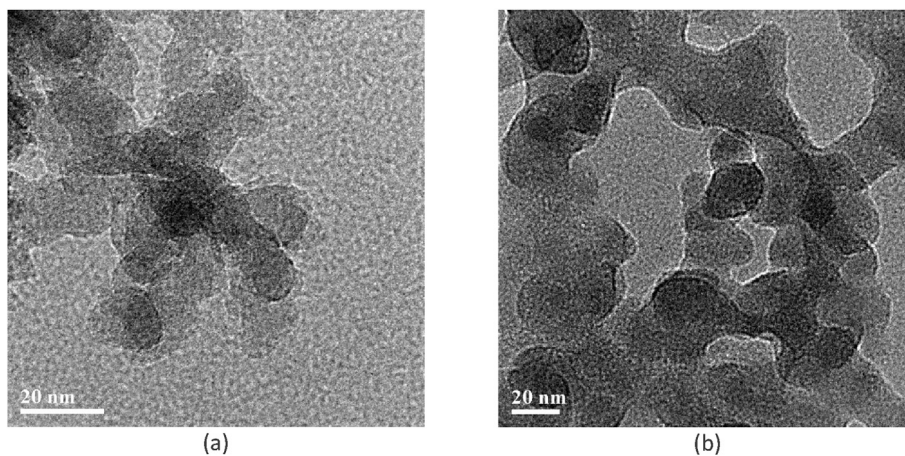


Fig. 1. TEM images of raw silica nanoparticles (a); and silica-P(CL-mLA)-COOH nanoparticles (b).

Furthermore, the viscosity of the epoxy system increased obviously when the loading of CSR particles was high [17].

Surface modified silica nanoparticles have been blended into DGEBA resin to improve its fracture toughness [18–24]. In general, a relatively high loading of nanosilica (up to 30 vol% [21]) is needed to achieve reasonable toughening effect. The high loading of silica nanoparticles would inevitably increase the viscosity of the resin mixtures. Investigation of particle size on the toughening effect of epoxy has generated controversy results [21,22]. In some cases, the particle sizes varying from 23 to 74 and 170 nm showed negligible effect on fracture toughness; while in other cases, smaller nanoparticles (12 nm) exhibited better effect in improving fracture toughness than the bigger ones (20 and 40 nm) [22]. Nanosilica particles in-situ formed from TEOS (tetraethyl orthosilicate) through sol–gel reactions showed good dispersion and particle size distribution in epoxy resin system [25]. However, the glass transition temperature of the modified epoxy showed an undesirable decrease with increasing silica loading.

There are also reports to improve the fracture toughness of epoxies with simultaneous addition of both hard nanosilica particles and soft rubber phase [26–29]. It was found the nanosilica particles and micro-sized rubber particles showed synergies in improving the fracture toughness of the epoxy resins when the nanoparticle concentration was low [26–28].

In all these reports, a relatively high loading of toughening agents (>10 wt%) is needed to achieve reasonable improvement in fracture toughness. High loading of toughening agents generally means higher viscosity of the resin mixtures, which is a great disadvantage for processing. It is therefore desirable that the fracture toughness of high temperature DGEBA epoxy could be improved by using only a small amount of nanoparticles (less than 2 wt%), while the physical and mechanical properties of the cured epoxy will not be impaired because of the addition of such

nanoparticles. In this paper, we report the use of silica based nanoparticles with a hard silica core and soft rubbery grafts as toughening agents for epoxy. The low loading of such nanoparticles will not result in an obvious increase in viscosity of the liquid resin mixtures while the mechanical property enhanced significantly.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A epoxy (DGEBA, D.E.R. 332) was purchased from Dow Chemicals. The hardener, diethyltoluenediamine (Ethacure 100-LC), was supplied from Albemarle. Fumed

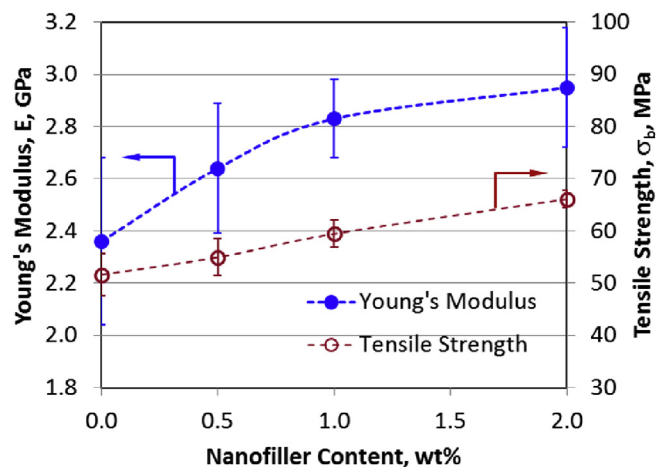


Fig. 2. Effect of nanofiller content on the tensile properties of epoxy/silica-P(CL-mLA)-COOH nanocomposites.

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