



# Microstructure and mechanical properties of aminated polystyrene spheres/epoxy polymer blends



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## ABSTRACT

Polystyrene (PS) spheres were chosen as soft fillers to toughen epoxy polymer. In order to weaken the aggregation of PS spheres in epoxy matrix caused by phase separation, amination treatment were firstly done on them. The results of FTIR, zeta potential test and TGA indicate that amine groups have been successfully grafted to the surface of PS spheres. SEM observation suggests that aminated PS spheres are monodisperse in prepared epoxy blends. The tensile strength and fracture toughness of the 15 wt% aminated PS spheres/epoxy polymer blends are 74.5 MPa and 2.23 MPa m<sup>1/2</sup>. Compared with cured pure epoxy polymer, they are increased by 25.6% and 84.3%, respectively. Excellent dispersion properties in epoxy matrix and increased interfacial force with epoxy matrix are responsible for the huge effect of the aminated PS spheres on toughening epoxy polymer.

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## 1. Introduction

Thermosetting epoxy polymers are widely used as engineering adhesives and matrices for composite materials [1–4]. Cured epoxy polymers typically possess high crosslink density, which results in good thermal stability, relatively high modulus and excellent adhesion properties. However, high crosslink density also leads to poor fracture toughness, which limit their application as engineering materials in many fields. A very successful route to improve the fracture toughness of epoxy polymers is to form epoxy composite materials via the introduction of rigid fillers (such as TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or carbon tubes) into epoxy polymer [5–12]. For example, Chen prepared  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/epoxy nanocomposites (ENCs) and investigated the influences of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles on the thermal and mechanical properties of the prepared ENCs [11]. Dittanet found that nanofillers with different size possess synergistic toughening effect. The increase degree of fracture toughness of the composite material toughened by different size filler is higher than the combination of that toughened by individual filler with same loading [12].

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In spite of the huge success of rigid fillers in toughening epoxy polymers, it is worth pointing out that this kind of rigid fillers/epoxy composite materials has become unable to meet the request of modern applications in some fields. Especially, with the rapid development of aerospace, large-scale cryogenic engineering and application of superconducting technology, epoxy polymers are required to adapt to low temperature even ultra-low temperature circumstance (e.g. liquid nitrogen temperature, –195.6 °C) [13]. However, the thermal physical properties of the common rigid fillers are significantly different from that of the epoxy polymer. At ultra-low or alternating high and low temperature circumstance, these rigid fillers not only fail to toughen the prepared epoxy composites, but also will play a role as stress concentration point and decrease their mechanical properties.

Soft fillers, which have similar thermal physical properties with epoxy polymer, are alternative fillers. Both rubber particles and thermoplastics are the potential toughening agent [14–22]. In most cases, the synthesis of these polymer blends is prepared starting from a homogeneous solution composed of precursors of epoxy polymer and the modifiers. Polymerization-induced phase separation (PIPS) during network formation is ineluctable [23]. As we all known, the ultimate properties of these materials is quite depend on the morphology generated during the build-up of epoxy matrix [24]. PIPS, which directly influence the morphologies development of the obtained epoxy composite materials, will indirectly

influence their ultimate properties. It is identified that excellent dispersion of the filler in epoxy matrix can greatly optimize the interactions between epoxy matrix and fillers and thus the mechanical properties of epoxy composites were fullest improved. Unfortunately, aggregation of filler resulted from PIPS usually occurs and leads to the dispersion of filler on the macroscopic scale, which weakens its toughening effect. Several experimental variables, which affect the thermodynamic and/or kinetic aspects of the PIPS process, have been studied. These variables include type and concentration of modifier, molecular weight of components, reactivity of cure agent and polymerization conditions (e.g. temperature, initial miscibility between the thermoset and the modifier, reaction rate et al.) [25–29].

Although the influences of experimental variables on the morphology and mechanical properties has been studied in the literatures for various thermoplastic–thermoset blends, these studies typically focused on the curing reaction of epoxy system. There are few publications that focused on the property of modifier. In this work, we prepared uniform polystyrene (PS) spheres with a diameter of 200 nm and used them as modifier to toughen epoxy polymer. The use of PS sphere can avoid usual drawbacks of rubber modification (i.e. reduction of yield strength, elastic modulus and glass transition temperature) [24]. Amination modification was firstly done on these PS spheres. The modified PS spheres were then introduced into epoxy system as the second and dispersed phase. The influences of the surface property and loading of PS spheres on the morphologies and mechanical properties of the prepared epoxy polymer blends were investigated in detail.

## 2. Experimental

### 2.1. Materials

Styrene, potassium persulfate, oleic acid, concentrated nitric acid, concentrated sulfuric acid, sodium hydroxide and sodium dithionite were obtained from Sinopharm Chemical Reagent Co. Epoxy resin (E-51, diglycidyl ether of bisphenol A) with an epoxide value of 0.51 and curing agent (593, adduct of diethylenetriamine and butyl glycidyl ether) were purchased from Tianyuan Group, Shanghai Resin Factory Co, China. All chemicals were used as received without any further purification.

### 2.2. Synthesis of PS spheres

The synthesis of PS spheres was based on our previous work [30]. Typically, 94  $\mu\text{L}$  oleic acid and 1.75 mL styrene were dissolved in 141 mL water, and then stirred at 60 °C for 1 h. After addition of 80 mg potassium persulfate, the solution was further heated to 70 °C accompanied with vigorous stirring for 5 h. The PS spheres were collected by centrifugation and washed for 3 times with deionized water. All steps were performed under argon.

### 2.3. Amination of PS spheres

The prepared PS spheres were firstly dispersed in 50 mL deionized water via sonication. Then, 16 mL concentrated nitric acid and 6 mL concentrated sulfuric acid were added into the solution. After reaction at 45 °C for 12 h, the product was obtained after centrifugal separation and washing with deionized water. Subsequently, the obtained product was dispersed in 50 mL sodium hydroxide solution (2 mol/L), and sodium dithionite powder (2 g) was added into the solution. After reaction at 75 °C for 4 h, the aminated PS spheres were collected by centrifugation and washed for 3 times with deionized water and one time with absolute ethanol.

### 2.4. Synthesis of PS spheres/epoxy polymer blends

For the synthesis of PS spheres/epoxy polymer blends, 10 g of E51 was firstly diluted by 2 g of acetone. Then, a predetermined amount suspend of PS spheres dispersed in acetone was added under vigorous stirring. The resulting mixture was continually stirred for 30 min and followed by ultrasonication for 20 min with the water bath temperature maintained at 30 °C. After removal of acetone by rotary evaporation (at 60 °C) and cooling down to room temperature, 2 g of curing agent 593 was added to the mixture. The obtained blend was mechanically stirred for 10 min and poured into Teflon molds and degassed in a vacuum oven to remove the bubbles. The final mixture was cured at 50 °C for 12 h at ambient pressure following the recommendation from the provider.

### 2.5. Characterizations

FTIR spectroscopy was collected on a Nicolet 6700 spectrometer. TGA was performed on a NETZSCH STA 449C thermobalance. The measurement was carried out under  $\text{N}_2$  with a heating rate of 10 °C/min. Zeta potential measurement was performed using a Zetasizer 3000 (Malvern Instruments). The sample of PS sphere was diluted to 1.0 mg/mL before measurements. The pH values of PS suspend were adjusted by adding ammonia solution or hydrochloric acid. TEM images of the samples were carried out with a Tecnai G220S-Twin electron microscope equipped with a cold field emission gun. SEM investigations were carried out with S4800 instrument to observe the morphologies of samples. A testing machine (Comten Industries, model 945KRC0300; Loading unit, PSB5000; Digit controller, DMC 026S) with C-Tap 3.0 software is used to test the tensile strength of the obtained epoxy polymer blends. The samples with dog-bone shape were shown in Fig. 1a. Specimens that fractured at some obvious fortuitous flaws or near a grip are discarded. A crosshead speed of 1.52 mm/min is used and strain (mm/mm) is calculated by dividing the crosshead displacement by the gage length. Fracture toughness ( $K_{IC}$ ) was determined using a single-edge notch bend (SENB) test, in accordance with the ASTM D5045 standard. A pre-crack was made by lightly tapping a fresh razor blade between adjoining plates, yielding a very sharp

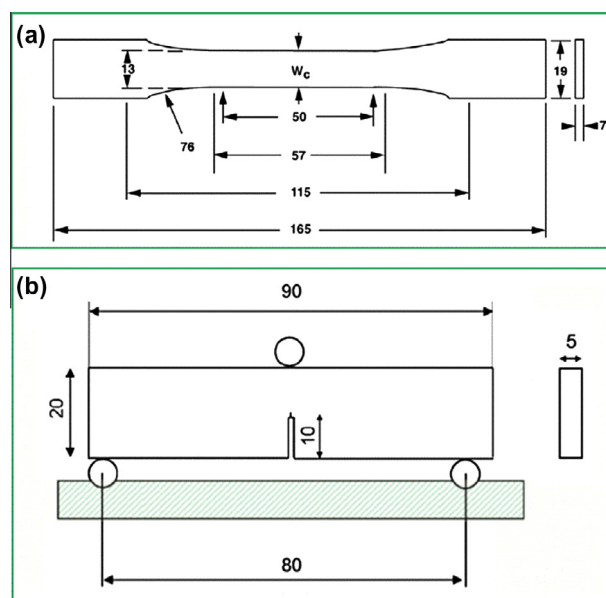


Fig. 1. Schematic of tensile specimen (a) and single-edge notched bending specimen (b), dimensions in mm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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