



# The effect of hyperbranched polyester and zirconium slag nanoparticles on the impact resistance of epoxy resin thermosets



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## ARTICLE INFO

### Article history:

Received 28 November 2014

Received in revised form

23 March 2015

Accepted 29 April 2015

Available online 8 May 2015

### Keywords:

B. Fracture toughness

A. Polymer-matrix composites (PMCs)

E. Cure

A. Particle-reinforcement

B. Impact behaviour

## ABSTRACT

A hyperbranched polyester (HBP) was synthesized through a polymerization of AB<sub>2</sub> approach with succinic anhydride and diethanolamine. The effect of HBP and Zirconium slag nanoparticle (ZSN, a kind of solid waste in Zirconium industry) content on the toughness enhancement and morphology of diglycidyl ether of bisphenol A epoxy resin (DGEBA) thermosets was studied. The results indicated that HBP can greatly improve the impact strength (IS) of epoxy thermosets, but the flexural strength (FS) was decreased with increasing the HBP content. The IS of epoxy thermosets modified with ZSN was also improved, and the FS decreases as increase of ZSN. The thermosets modified with both HBP and ZSN showed excellent IS and FS. The toughening enhancement mechanism was also discussed.

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## 1. Introduction

Epoxy resins are known to be common used for many industrial applications such as adhesives, coatings, electronics, mechanic, and structural applications [1–4]. Moreover, many curing agents available for their curing such as 4, 4'-methylenedianiline (DDM), 4, 4'-diaminodiphenyl sulfone (DDS), m-Phenylenediamine (m-PDA), isophorone diamine (IPDA), phthalic anhydride, tetrahydrophthalic anhydride (THPA), triethylenetetramine (TETA) etc [5–8], is an important reason for its wide applications. When polymerized by curing agents, epoxy resins are highly crosslinked materials and this microstructure results in several unique properties, such as a high thermal stability, great modulus, low creep, and excellent flexible and tensile strength [4,9]. However, their high crosslink density leads to materials with a poor impact resistance [10]. Hence their brittleness is one of their major drawbacks. Moreover, shrinkage during epoxy curing is another major drawback, because shrinkage may lead to generating micro-cracks and/or internal stress, which can result in a loss of mechanical properties of epoxy resins [11,12].

There are many approaches to improve toughness of epoxy resins [13–21]. One typical route is the addition of rubbers such as

amine-terminated butadiene acrylonitrile (ATBN) [22], polybutadiene [23], carboxy-terminated butyronitrile (CTBN) [12], liquid rubbers [4,24], and rubber nano-particles [25], to the uncured epoxy system and obtain the rubber particles that can absorb energy, which dispersed in the epoxy matrix. The disadvantage of this route is that the flexural modulus, shearing and yield strength, thermal resistance, and glass transition temperature are effectively lowered by the incorporation of a rubber [26,27]. Another approach is the addition of inorganic fillers [10,25,28–33] especially montmorillonite (one kind of layered clay mineral) nanostructure particles [34,35]. The unique characteristics of montmorillonite/epoxy nanocomposites are due to the nanometer size of the montmorillonite, its high aspect ratio, high surface area and the extent of filler adhesion to the epoxy matrix [36]. The advantage of this section is that montmorillonite as toughness reinforcement is highly attractive because of its relatively low cost, excellent thermal inertness, environment-friendly and ready availability characteristics. However, montmorillonite nanofillers tend to form aggregate during preparation of epoxy/montmorillonite composites, which result in decreasing the overall properties of epoxy cured system.

In the last decade, hyperbranched polymers (HBPs) have been widely investigated [37–47]. HBP materials as a subfamily of dendritic polymers, are highly branched macromolecules with three-dimensional architecture and multiple numbers of functional groups on the terminal of branch [48]. Because of their unique structure, HBPs exhibit lower melting and solution viscosities than

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linear polymers of the same molar mass [48]. A significant advantage of HBPs is the high density of functional terminal/end groups, such as hydroxyl, amine, anhydride, isocyanate, carboxylic, and epoxy groups, which can enhance the compatibility between HBPs and other polymeric matrixes. Another excellent characteristic of HBPs is that they have a lot amount of free volumes and spaces in their networks, which can greatly improve the toughness of epoxy resins when HBPs are used as modifiers [49,50]. Moreover, the unique spherical structure of HBPs, which can stretch after terminal groups interacting with functional groups of epoxy resins and/or curing agents, can reduce the shrinkage of epoxy resins thermosets [50–52].

In the present work, diglycidyl ether of bisphenol A epoxy resin (DGEBA) was modified with Zirconium slag nanoparticles, a kind of solid waste in Zirconium industry, as nano-fillers, and hyperbranched polyester, synthesized by the polycondensation of succinic anhydride and diethanolamine, a toughness modifier. The cured materials were fully characterized and toughness was evaluated by impact resistance test.

## 2. Experiment section

### 2.1. Materials

The epoxy resin used in this work was the diglycidyl ether of bisphenol A (DGEBA, E51), purchased from Hangzhou Wujingang Adhesive Co., Ltd (Hangzhou, China), which had an epoxy value of 0.48–0.54, and an epoxide equivalent weight of 185–200. Polyamide 650 with an amine value of 200–240 (mg KOH gm<sup>-1</sup>) was used as curing agent, which was supplied by Wuxi Resin Factory (Wuxi, China). The Zirconium slag particles with an average diameter of 300 nm (which is calculated based on SEM micrograph, see supporting materials S1) were obtained from Yixing Xinxing Zirconium Co., Ltd (Yixing, China).  $\gamma$ -Aminopropyl triethoxysilane ( $\gamma$ -APS, KH-550) purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) was used as a coupling agent. Toluene was obtained from Nanjing Chemical Reagent Co., Ltd (Nanjing, China). Aqueous solution of H<sub>2</sub>O<sub>2</sub> (30 wt %), N, N-dimethylacetamide (DMA), succinic anhydride (SA), and diethanolamine (DETA) were supplied from Chengdu KeLong Chemical Reagent Company (Chengdu, China). Unless otherwise specified, all the chemicals were analytical grade and used as-received.

### 2.2. Modification of zirconium slag nanoparticles

Three steps were used to modify Zirconium slag nanoparticles:

Step 1. Pre-treatment of as received Zirconium slag nanoparticles.

The received Zirconium slag nanoparticles had strong acidity. It would not be directly used before neutral treatment. The treatment process was as follows: Zirconium slag nanoparticle was added into distilled water and washed several times until pH value of the solution detected by a pH meter was about 7. Then the solution was filtrated and dried overnight under vacuum at 80 °C. The dried sample was milled by a planet milling-ball at 400 rpm for 30 min. The Zirconium slag nanoparticle after neutral treatment was named as ZSN.

Step 2. Hydroxylation of ZSN.

ZSN was hydroxylated and functionalized according to a previously described procedure [53]. 15 g of ZSN were added into 80 mL of an aqueous solution of H<sub>2</sub>O<sub>2</sub> (30 wt %) in a round-bottomed flask. The mixture was sonicated for 30 min and then was refluxed at 105 °C for 4 h. The nanoparticles were recovered by filtration. The resulting products were washed with deionized water three times, and then dried under vacuum at 80 °C for 12 h. The obtained hydroxylated ZSN nanoparticles were named as ZSN-OH.

Step 3. Functionalization of ZSN-OH.

10 g of ZSN-OH were first added into 80 mL of toluene in a round-bottomed flask and sonicated for 30 min, and then 5 g  $\gamma$ -APS was added and the mixture was heated to 80 °C for 24 h under air flow. The nanoparticles were recovered by filtration. The resulting products were washed with deionized water three times, and then dried under vacuum at 80 °C for 12 h. The obtained functionalized ZSN-OH nanoparticles were named as ZSN-APS. The structure of ZSN-APS particles is shown in Scheme 1.

### 2.3. Synthesis of hyperbranched polyester

The synthesis of HBP was followed an AB<sub>2</sub> approach. Typically, 1.57 g of succinic anhydride was added into 5 mL of DMA in a 25 mL three-necked round-bottomed flask with a thermometer. The mixture was heated up to 70 °C and stirred until succinic anhydride was all dissolved. Then, 1.50 g of diethanolamine was added and stirred for 30 min. The mixture was heated to 120 °C and stirred under Nitrogen for 6 h. Then this system was vacuumed for 2 h. The structure of succinic anhydride, diethanolamine and HBP are shown in Scheme 2.

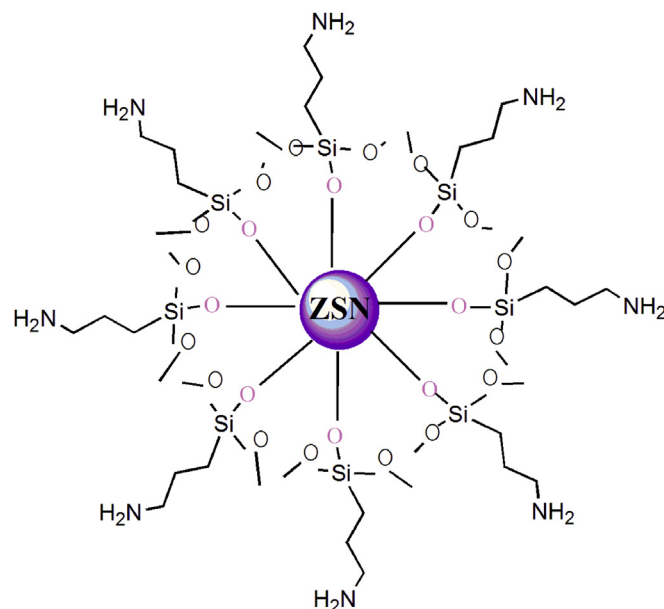
### 2.4. Preparation of DGEBA/HBP/ZSN-APS thermosets

For the preparation of DGEBA/HBP/ZSN-APS, appropriate amounts of ZSN-APS (0–5 phr) was mixed with DGEBA with sonicated for 30 min. Then 0–20 phr HBP was added and under mechanical stirred for 10 min. After that, appropriate amounts of polyamide 650 (DGEBA/polyamide 650, 1:1 wt/wt), which was pre-heated up to 60 °C, was added and the resulting mixture was also homogenized. Finally, the formulations were placed in stainless steel templates (also pre-heated to 60 °C) and cured at 60 °C for 48 h in an oven. The preparation process of epoxy thermosets modified with HBP is shown in Scheme 3.

### 2.5. Characterization

#### 2.5.1. Attenuated total internal reflectance Fourier-transform infrared spectroscopy (ATR-IR)

ATR-IR spectra were conducted with a Tensor 37 instrument (Germany, Bruker). Each sample was scanned with a resolution of



Scheme 1. The structure of ZSN-APS particles.

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