Effect of hyperbranched polymer modified on the impact strength of epoxy resin at cryogenic temperature

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Abstract. In order to investigate the effect of hyperbranched polymer modified on impact strength of epoxy resin at 77K. One modifier called H204 was employed to methyl nadic anhydride (MNA) cured diglycidyl ether of bisphenol A (DGEBA) epoxy resin system. The impact strength at 77 K was studied and the results indicated that introduction of modifier used in this study can enhance the impact strength at cryogenic temperature. The 58.57% increase was obtained by addition of 10 wt% H204 into the epoxy matrix. Furthermore, scanning electron microscopy (SEM) was used to investigate the fracture mechanism and strengthening effect.

1. Introduction
Epoxy resins and its composite materials are increasingly used in the cryogenic engineering fields as impregnating materials or adhesives[1, 2]. For example, in fusion reactors, such as the International Thermonuclear Experimental Reactor (ITER), large quantities of epoxy composite was used as thermal insulation, electrical insulation and structural support for superconducting magnets[3]. However, epoxy resins would become brittle at cryogenic temperature due to thermal shrinkage. And the engineering application of epoxy resins is generally limited by their brittleness[4-6].

In cryogenic engineering, epoxy resins are often exposed to 77 K even to 4.2 K and subjected to thermal cycling[7]. As the temperature is decreased down to cryogenic levels, the impact strength would decrease because of their brittleness. Thus, improvement of toughness and strength of epoxy...
resin at low temperatures are desirable for its application in cryogenic engineering. Many researchers have explored some effective methods to enhance the impact strength at room temperature (RT), such as using rubber elastomer to toughen epoxy resins and improve their impact strength\(^{[8-10]}\).

Cryogenic mechanical behaviors of epoxy composites are generally different from those at room temperature. Therefore, it may not be useful to improve the impact strength of the composites at cryogenic temperatures by methods which are used to enhance the impact strength at room temperature. There are few publications concerning the improvement of their impact strength at low temperatures.

In this work, the effect of hyperbranched polymer (H204) modified on the impact strength of epoxy resin at cryogenic temperatures is presented. Methyl nadic anhydride (MNA) cured diglycidyl ether of bisphenol A (DGEBA) epoxy resin system were employed as polymer matrix, modified by the introduction of H204. The impact strength of the modified epoxy resin at 77 K were investigated and their fracture surfaces were examined by scanning electron microscopy (SEM) to explain the impact strength results.

2. Experiment

2.1 Materials
The resin used in this study was a commercially available diglycidyl ether of bisphenol A epoxy resin (DGEBA, DER332) supplied by Shanghai King Chemical, China. The curing agent was a liquid aromatic amine, methyl nadic anhydride (MNA) supplied by Shanghai Macklin Biochemical Co., Ltd, China. The accelerator was 2,4,6-tris (dimethylaminomethyl) phenol K54 from Changzhou Mingyao Chemical New Material Co. Ltd, China. The hyperbranched polymer used in this work was polyester H204 from Wuhan HyperBranched Polymers Science&Technology Co. Ltd, China.

2.2 Specimen preparation
Firstly, the H204 was added into the DER332/MNA mixture. The mixture was stirred and heated at 130°C for 2h until a homogenous mixture was observed. The content of H204 in the mixture varied from 0 to 10% in weight. A stoichiometric amount of accelerator K54 was added to the H204/epoxy mixtures at 60°C. Then the clear homogeneous solution was degassed by a vacuum rotary pump at 60°C for 2h. After the air bubbles were completely removed, mixture was poured into a preheated steel mold at 80°C, then cured at 80°C for 16 h, 100°C for 4 h, and post cured at 125°C for 6 h.

2.3 Impact strength test
The impact strength of the cured specimens was measured with a PTM1200-AL Impact Tester according to ASTM D-256. The impact specimens were prepared with the size of 4 mm (thickness)×10 mm (width)×80 mm (length). Impact testing at 77K was performed with the specimens dipped in a liquid nitrogen filled cryostat for over 10 minutes, and it was quickly completed within a couple of seconds after taking the specimens out from the cryostat. At least five specimens were tested for each composition.

The fracture surfaces of the impact specimens were observed by scanning electron microscopy
(SEM) using a HITACHI S-4800 microscope (Japan). Prior to examination, the fracture surfaces were cleaned with alcohol and spray coated with a thin layer of evaporated gold to improve conductivity.

3. Results and discussion

Fig. 1 plots the impact strength of the composites at RT and 77 K as a function of H204 content. It is shown in Fig. 1 that the content had different influences on the impact strength of H204/epoxy composites at RT and 77 K. It shows that the cryogenic impact strength is higher than the RT strength for modified resin. Moreover, impact strength at RT (RT impact strength) doesn’t change apparently until H204 content is increased to 7.5 wt% at which the RT impact strength is increased from 11.61 kJ/m² for the pure epoxy resin to 14.75 kJ/m² for the modified system. And then RT impact strength reaches the maximum value 16.46 kJ/m² with the H204 content increased to 10 wt%. The impact strength at 77 K increases with increasing the H204 content and reaches the maximum value 18.41 kJ/m² for the modified system with 10 wt% H204, showing an improvement of 58.57% over that for the pure epoxy resin. The impact strengths at RT and 77 K are discussed below. It is generally expected that the impact strength of epoxy resins at 77 K should be lower than that at RT since epoxy resins become normally more brittle at low temperature \( ^{[11]} \). However, it is interesting to note that the impact strength at 77 K of the modified epoxy systems is higher than that at RT for the same H204 content.

The RT impact strength is first discussed. The flexible groups (namely ester segments in H204) can dissipate the impact energy by their segmental motion in molecular chains, which contributes to the increase of impact strength at RT. The free spaces (the unoccupied spaces within the molecules) and free volumes (the unoccupied spaces between molecules in three-dimensional epoxy networks) can also absorb much energy by distorting themselves and providing motion space for the molecules in the network during impacting. Thus, as the content of H204 reaches a certain level, the impact strength of cured epoxy resin increases at room temperature.
At 77 K, the flexible ester segments in H204 are not completely frozen and can dissipate the impact energy by their segmental motion. And the free volumes and free space would become smaller due to thermal shrinkage but still exist in the cured epoxies when the temperature goes down to 77 K\textsuperscript{[12, 13]}. That’s because of the hyperbranched polymers have a unique spherical structure, and molecular chains do not tangle with each other (Fig. 2). They can also absorb much energy by distorting themselves and providing motion space for the molecules in the network during impacting at 77 K. Both of these factors will increase the cryogenic impact strength of the cured system by introduction of H204. Furthermore, it is also observed that the impact strength at 77 K of the cured systems is not lower than that at RT except for the pure epoxy resins. Because at 77 K, free volume and free space still exist due to thermal shrinkage, only become smaller (Fig.2). And the cohesive strength of the molecule did not increase too much, the out-of-plane vibration of the chemical bond still exists, not completely frozen. Then the hydrogen bonds and chemical-bonds would become shorter. The stronger hydrogen bonds because of the presence of large numbers of hydroxyl groups from H204 and hence higher intermolecular forces at 77 K will make a much larger contribution than at RT to the impact strength at 77 K, leading to the higher impact strength at 77 K than at RT.

Fig 2. Hyperbranched polymer toughened epoxy resin model
Fig 3. SEM micrographs of fracture surfaces after impact testing with different H204 contents (a) 0 wt%, RT; (b) 0 wt%, 77 K; (c) 2.5 wt%, RT; (d) 2.5 wt%, 77 K; (e) 5 wt%, RT; (f) 5 wt%, 77 K; (g) 7.5 wt%, RT; (h) 7.5 wt%, 77 K; (i) 10 wt%, RT; (j) 10 wt%, 77 K.

For better understanding the role of H204 modification, the impact behavior of the cured epoxies can be examined in terms of the morphology observed by SEM. Scanning electron micrographs of the representative fracture surfaces at RT and 77 K are shown in Fig. 3(a)-(j). The smooth and glassy surfaces as shown in Fig. 3(a) and (b) are substantial evidence of brittle failure of the pure epoxy resin. The fracture surfaces for the H204-modified epoxies with 2.5-10 wt% of H204 in Fig. 3(c)-(j) were quite different from those of the pure epoxy. As for the modified systems, the fracture surfaces show
relatively rough and irregular appearance. A lot of ‘‘protonema’’ have been observed in SEM micrographs of H204-modified epoxy resins. The ‘‘protonema’’ is the indication of the characteristics of toughening fracture. So, an improvement in impact strength has been observed by the addition of 2.5–10 wt% H204. In addition, no second phase can be found in the SEM images in Fig. 3(c)–(j), indicating that H204/epoxy systems are homogeneous.

4. Conclusion
In this study, methyl nadic anhydride (MNA) cured diglycidyl ether of bisphenol A (DGEBA) epoxy resin system was modified by introduction of H204. The effect of H204 on the impact strength at RT and 77 K of epoxy resin was investigated. The results show that addition of H204 of proper amounts can improve the impact strength of the epoxy resin whatever at room temperature or at 77 K. The maximum impact strength at 77 K is obtained for the modified system with 10 wt% H204. The observed ‘‘protonema’’ by SEM on fractured surfaces of modified epoxy resins is used to explain the RT and cryogenic impact strength for the H204-modified epoxy resins. The data at 77 K provide valuable information for using hyperbranched polymers in modifying epoxy resins for cryogenic engineering applications.

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