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Epoxy toughening using self-assembled nanofibrillar scaffolds formed by organogels

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ABSTRACT

We propose a facile method for preparing toughening epoxies using self-assembled scaffolds formed by organogels. 1,3:2,4-dibenzylidene sorbitol (DBS) is a sugar derivative that is capable of self-assembling into a 3-D nanofibrillar network at relatively low concentrations in certain organic solvents to form organogels. In this work, we induced the formation of such nanofibrils in the most frequently used epoxy monomer, di-glycidyl ether of bisphenol A (DGEBA). Subsequently, we cured DGEBA in the presence of a curing agent with various amounts of DBS. The resulting materials were transparent and homogeneous epoxies with DBS nanofibrillar networks. The DBS nanofibrils in the epoxy matrix acted as reinforcing materials that enhanced the hardness and stiffness of the epoxies. Moreover, due to the entangled network structures, the toughness of the epoxies increased with increasing amounts of DBS (the maximum being an approximately 5-fold improvement). In addition, the thermal stability of the epoxies was improved by the addition of DBS, including the glass transition temperatures and thermal degradation temperatures.

1. Introduction

Epoxies or epoxy resins are widely used in industrial applications, such as coatings, adhesives, electronics and composite materials. However, the chemically cross-linked structures caused the epoxies to be brittle and easy to crack, limiting their applications. Therefore, improving the toughness of epoxies has been attracting a great deal of interest. The epoxy's toughness can be improved by either chemical or physical methods [1–6]. For example, the chemical modification of epoxy monomers and the use of curing agents (cross-linkers) have been discussed [1,2]. Conversely, physical methods, such as the addition of inorganic fillers, were likely used due to their cheaper and easier preparation [3–5]. In addition, organic compounds were added to enhance the elongation and impact toughness of the epoxies, which occurred due to an increase in the chain flexibility [6]. In recent years, block copolymers blended with epoxies have been prepared. Block copolymers can self-assemble into different nanostructures by changing the molecular weight, composition and block length [7–9]. Liu et al. showed that the wormlike (cylindrical) micelle structures can greatly improve the toughness of the epoxies [9].

1,3:2,4-dibenzylidene-D-sorbitol (DBS) is a butterfly-shaped amphiphile with two hydrophilic hydroxyl groups and two hydrophobic phenyl groups. It is derived from the sugar alcohol D-glucitol. The chemical structure of DBS is shown in Fig. 1. DBS and its derivatives are widely used as nucleating agents in certain crystalline polymers, such as polyethylene and polypropylene, to improve the crystallization rates and optical properties [10,11]. Recently, DSB and its derivatives were observed to exhibit self-assembly behaviors in a variety of organic solvents and liquid polymers at very low concentrations to form the organogels [12–15]. The DBS organogels were the result of the formation of 3-D nanofibrillar networks. The diameters of these nanofibrils ranged from 1 μm to 10 nm, as observed by electron microscopy, depending on the solvent polarity and DBS amounts [12–15]. The molecular interactions governed the gel formation of DBS. The intermolecular hydrogen bonding between the terminal hydroxyl groups of DBS molecules and acetal oxygens of neighboring DBS molecules caused DBS to self-assemble into nanofibrillar networks at relatively low concentrations, leading to the formation of gels [15]. DBS organogels can be used in many applications, such as

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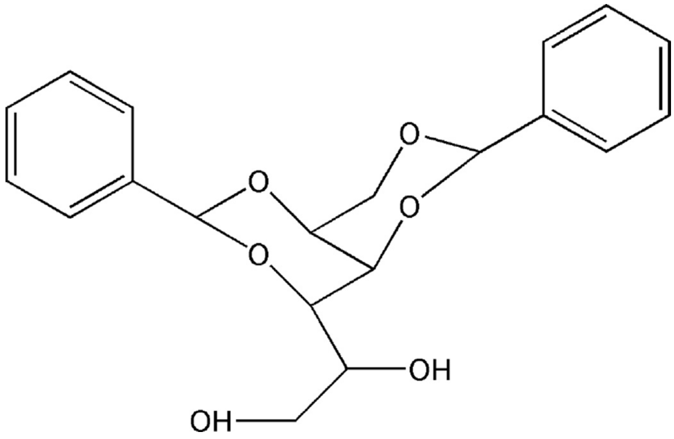

Fig. 1. Chemical structure of DBS.

battery electrolytes, drug-delivery systems, cosmetic products and template techniques [16–18]. In our previous study [19], in addition to the synthesis of porous polymers prepared using self-assembled templates formed by organogels, we kept these templates within polymers. The physical cross-linked DBS networks consisting of nanofibrils in a polystyrene (PS) matrix acted as the reinforcing materials [19]. The thermal and mechanical properties of PS improved by the addition of DBS. In addition, DBS and its derivatives were also observed to be added in certain thermoplastic polymers by melt blending to enhance the mechanical properties [20,21].

In this study, DBS organogels were used as self-assembled nanofibrillar scaffolds in the thermosetting polymers. We induced DBS nanofibrils in the most frequently used thermosetting epoxy monomer, di-glycidyl ether of bisphenol A. Next, the thermally cross-linking (curing) of the monomer was performed in the presence of thermal curing agent with differing amounts of DBS. After curing, the result was a series of novel epoxy materials with embedded DBS nanofibrils. To the best of our knowledge, this study is the first that uses organogels to prepare the epoxies. Our results showed that the addition of DBS significantly improves the thermal and mechanical properties, including the toughness of the epoxies. In addition, most strategies for epoxy toughening focused on the use of rubber and rigid particles [1–6], which usually suffered a decrease in glass transition temperature (T_g) or inhomogeneity. Here we added organic filler, DBS, to prepare the epoxies, trying to solve the problem. One of the advantage is that the amount of addition of DBS was small for the formation of organogel scaffolds within epoxies, and the increase of the toughness could be significant. Another advantage is that the "gel" formed in epoxy monomer could provide an additional method to tune the processability. Moreover, DBS is an inexpensive additive, suitable for industrial uses.

2. Materials and methods

2.1. Materials

1,3:2,4-dibenzylidene-D-sorbitol (DBS) was obtained from Milliken Chemicals Company. Di-glycidyl ether of bisphenol A (DGEBA) was purchased from Acros Company. Ancamine K61B cuing agent was obtained from Air Products Company. K61B is a mixture of 2,4,6-tri (dimethylaminoethyl)phenol and 2-ethylhexanoic acid salt with a mixing ratio of 1:3. Toluene was purchased from Acros Company.

2.2. Sample preparation

2.2.1. DBS organogel

The samples were prepared by dissolving various amounts of DBS (1–4 wt%) in DGEBA at 160 °C and 2 h on a hot plate under constant agitation. After the DBS had dissolved completely, the solution was removed from the hot plate and cooled to room temperature to induce the gelation. The gel samples were placed at room temperature for a week before the measurements.

2.2.2. Cured epoxy with DBS organogel

The samples were first prepared by dissolving different amounts of DBS (0–4 wt%) in DGEBA at 160 °C for 2 h on a hot plate. After the DBS was completely dissolved, K61B (10 wt%) was added as the curing agent to the samples. At this temperature, the K61B easily dissolved in the DBS/DGEBA within several seconds. Next, the samples were quickly removed from the hot plate and cooled to room temperature to suppress the curing. The samples were kept at room temperature until the DBS gels formed. Finally, the epoxies with DBS organogels were obtained after curing at 70 °C for 3 h.

2.3. Characterization

2.3.1. Rheological property of DBS organogel

The rheological properties of the DBS organogels were measured using an Anton Paar Physica MCR101 rheometer under an oscillatory shear. The frequency spectra were collected from 0.01 to 450 rad/s at 25 °C, and the strain amplitudes were maintained at 0.2%.

2.3.2. Chemical structure of cured epoxy with DBS organogel

The chemical structures of the samples were determined by a Nicolet Magna-IR 550 Fourier transform infrared spectrometer. The DBS organogel samples were prepared by spreading onto KBr plates and were placed in a vacuum oven at 60 °C for 12 h. The epoxy samples with DBS organogels were prepared by completely dissolving the DBS/DGEBA at high temperature on a hot plate and adding the curing agent in several seconds. The samples were then quickly removed from the hot plate and dropped onto KBr plates until the gels formed completely. Finally, the samples were cured at 70 °C for 3 h. Neat DBS samples were prepared by mixing with KBr and pelleting the mixture.

2.3.3. Initial curing time and glass transition temperature of cured epoxy with DBS organogel

The initial curing time and glass transition temperature of the epoxies with DBS organogels were determined by an Anton Paar Physica MCR101 rheometer under an oscillatory shear. The samples for the measurements were prepared as follows. DBS was first completely dissolved in DGEBA at high temperature on a hot plate. Next, the curing agent was quickly added into the DBS/DGEBA in several seconds. Second, the samples were quickly removed from the hot plate thereafter and dropped onto the parallel-plate geometry of the rheometer with the temperature setting at 70 °C. For the curing time measurement, the samples were maintained at 70 °C from 0 to 3 h. The initial curing time was defined as the onset of G'. For the glass transition temperature measurement, after 70 °C for 3 h, the samples were later heated from 70 to 130 °C with a heating rate of 3 °C/min. The frequency was maintained at 1 rad/s, and the strain amplitude was 0.2%.

2.3.4. Thermal degradation temperature of cured epoxy with DBS organogel

The thermal degradation temperature of the epoxies with DBS organogels was performed on a TA instrument Hi-Res TGA 2950