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Synthesis and evaluation of Double-Decker Silsesquioxanes as modifying agent for epoxy resin

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A B S T R A C T

In this paper, we synthesized two types of epoxy group containing POSS derivatives: mono and poly Double-Decker Silsesquioxanes (mono DDSQ and poly DDSQ). The performance of epoxy resin with different DDSQ loading ratios was investigated, including curing kinetics, thermal, mechanical and surface properties. Both mono and poly DDSQ significantly improved thermal and mechanical properties of the epoxy thermosets. The mono DDSQ showed more flexible structure and toughened the epoxy resin better, while the branched poly DDSQ exhibited better thermal resistance. In addition, the DDSQ altered surface of the epoxy resin from hydrophilic to hydrophobic.

1. Introduction

Organic-inorganic hybrids have attracted great attention over the past decades for their combined properties of both organic and inorganic components. Recently, a new type of hybrid materials derived from polyhedral oligomeric silsesquioxane (POSS) becomes one of the research focuses. POSS is a cubic molecule edged with siloxane bond (Si-*O*-Si) and covered with organic groups such as methyl, phenyl and vinyl groups. Through changing the organic groups of POSS, the functionality and affinity of the hybrid materials can be easily regulated. Due to the distinctive structure and elemental composition, POSS offers many outstanding properties such as excellent thermal and mechanical properties, low dielectric constant, flame retardance, water resistance and so on [1–4]. Thence, the POSS based materials and their derivatives have been incorporated into various materials, like polyether [5], acrylics [2], polyurethanes [6], polyolefins [7,8], polybenzoxazine [9], epoxy resins [3,10–13] and so on, via grafting, polymerization and blending [14]. Axel H. E. employed POSS into the RAFT polymerization of organic/inorganic hybrid [15]. Jovan incorpated different types of POSS with epoxy group into polypropylene oxide nanocomposites to improve the dielectric relaxation [5].

Epoxy resins are widely used in our daily life, such as adhesives, composite materials and micro-electrical encapsulation, owing to their excellent overall performance in mechanical properties, corrosion resistance, adhesion between different matrixes [16–20]. However, epoxy resin is inherently brittle due to high crosslinking density and rigid phenyl groups. Further, it results in poor impact strength and is easy to crack. Epoxy resin usually requires toughening in applications. There are many methods to toughen epoxy resin, e.g., silicone [21], nano particles [22–24], thermal plastic elastomer resins [25], and so on.

Double-decker-shaped silsesquioxane (DDSQ) is a series of silsesquioxane containing two reactive end groups on diagonal position. With reactive end groups, it can be homogeniously dispersed and connected into polymer network [26,27]. Like POSS, DDSQ-modified hybrid polymers possess high thermal stability, good mechanical properties, low dielectric constant, excellent chain flexibility and softness, etc. [28,29] But DDSQ exhibit better molecular flexibility than POSS, which is helpful to further promote its dispersion and overall performance in polymer. The DDSQ can be designed as monomer to construct high performance polyimides:

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Kakimoto prepared DDSQ polyimides by reaction of dianhydride terminated DDSQ with 4,4′-Oxydianiline. The polycondensation of dianhydride terminated DDSQ in the matrix promoted dispersion of DDSQ, and lead to high performance of the polyimides: the highest break elongation rate of 6.0%, a good thermal stability at 5% weight loss in air over 490 °C, and water absorption of less than 1% [30]. Vuthichai Ervithayasupom prepared a novel type of polysiloxane with DDSQ as backbone. It exhibited higher glass transition temperature (around 15 °C), high transparency and hydrophobicity [27]. Sixun Zheng group incorporated DDSQ into the polybenzoxazine network (PBZ-DDSQ copolymer) by introducing dianilino DDSQ as functional monomer. The speherical DDSQ microdomains with a diameter of 10–20 nm were dispersed in the continuous polybenzoxazine matrix. The DDSQ enhanced the activation energy of polybenzoxazine's curing reaction. The copolymer displayed enhanced surface hydrophobicity and thermal stability [31].

In this paper, we synthesized two types of epoxy group containing Double-Decker Silsesquioxanes (DDSQs): mono and poly DDSQs (see Scheme 1). We incorporated the DDSQs into the matrix of epoxy and investigated their toughening effect on epoxy resin. Both mono and poly DDSQs possess aromatic groups and silicone segments, which are expected to improve mechanical properties and toughness of the epoxy resin. We studied DDSQ's affection on the curing mechanism, thermal and mechanical properties, and surface properties on the epoxy system. The results of this work provide good guidance and valuable mechanistic information for further investigation of DDSQ in thermosets modification.

2. Experiments

2.1. Materials

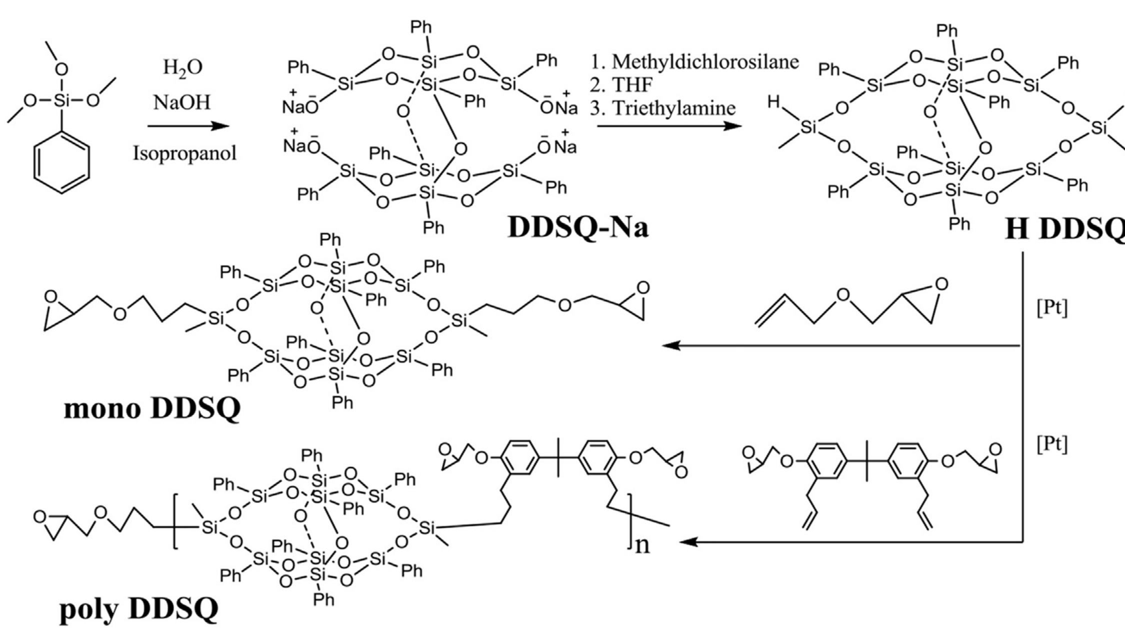
Tetrahydrofuran (THF), toluene, triethylamine and isopropanol were purchased from Aldrich (Shanghai, China) and processed with 4 Å molecular sieves to remove water before use. Epichlorohydrin, sodium hydroxide, methyldichlorosilane, tetramethylammonium bromide, diallyl bisphenol A, phenyltrimethoxysilane were also purchased from Aldrich (Shanghai, China) but used as received. Diglycidyl ether of bisphenol A (DGEBA) was obtained from Heli Resin Company (Suzhou, China) and it has an epoxy value of 5.1 mmol/g. The curing agent, 3,3′-diamino diphenyl sulfone (33DDS), was from Shanghai Regent Company Ltd. Both DGEBA and 33DDS were heated to 90 °C for 5 h to remove water before use.

2.2. Synthesis of DGEABA

To a 250 ml round bottom flask, diallyl bisphenol A (50 mmol, 15.4 g), epichlorohydrin (500 mmol, 46.0 g) and tetramethylammonium bromide (0.46 g, 1 wt%) were added and reacted at 115 °C under nitrogen for 2 h. The mixture was then cooled to 70 °C. 22 g NaOH solution (20 wt%, aq) was dropped into the mixture in a duration of 1 h. The mixture was then heated to 135 °C to remove water. The reaction was conducted at 70 °C for 24 h. The mixture was cooled to room temperature and washed with water to remove NaOH and NaCl for three times. The excessive epichlorohydrin was removed with a rotary evaporator to obtain pure DGEABA (yield 95%). Titration: [epoxy value] = 4.49 mmol/g and [double bond] = 4.88 mmol/g, respectively. ^{1}H NMR (ppm, $CDCl_3$): 1.58 [6H, $C(Ph)_2(C\mathbf{H}_3)_2$], 2.72, 2.81, 3.89, 4.07, 4.20[10H, epoxy group], 3.33 [4H, $-C\mathbf{H}_2-CH{=}CH_2$], 4.96[4H, $-CH_2-CH{=}C\mathbf{H}_2$], 5.93[2H, $-CH_2-C\mathbf{H}{=}CH_2$], 6.85, 7.04[6H, Ph-**H**].

2.3. Synthesis of H-DDSQ

H-DDSQ was synthesized following the procedure developed by Kakimoto [32]. To a 250 ml round bottom flask equipped with nitrogen inlet and condenser, phenlytrimethylsilane (242 mmol, 48 g), sodium hydroxide (160 mmol, 6.4 g), water (278 mmol, 5 g) and isopropanol were added. The mixture was stirred for 4 h under refluxing, and left at room temperature for 12 h. The precipitate was filtered and washed with 100 ml isopropenol, then dried in vacuum at 70 °C for 5 h to obtain DDSQ-Na. In a 250 ml three necked round bottom flask, DDSQ-Na (10 mmol, 11.6 g), triethylamine (30 mmol, 3.0 g) and THF (100 ml) were added under nitrogen. Methyldichlorosilane (30 mmol, 3.4 g) was dropped into the mixture at 0 °C. The mixture was kept for another 1 h. The product was dissolved in 100 ml toluene and washed with 50 ml water,



Scheme 1. Synthesis process of mono and poly DDSQ with epoxy group.