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Maleimido-functionalized spirobislactone having enhanced volumetric expansion on polymerization

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Abstract

An approach to enhancing the volumetric expansion on polymerization of spirobislactone is proposed. This approach suggests a molecular modification of spirobislactone through attaching a rigid pendant segment bearing maleimido group to its aromatic ring. An additional volumetric expansion is achieved from loose molecular packing in cured resins due to the steric hindrance effect among rigid pendent segments. Thus a new monomer, maleimido-functionalized spirobislactone (MFS), is prepared. In order to evaluate the volumetric expansion of MFS during curing, tetraglycidyl 4,4′-diamino diphenyl methane (TGDDM) is employed to cure with MFS. The volumetric expansion of MFS on curing is measured to be 12.3%, higher than that of net spirobislactone monomer. The existence of loose molecular packing in MFS/epoxy cured resins is demonstrated by morphology observation of the cured resin stained by the phosphotungstic acid (PTA), and the stained regions are observed to be nanoparticles. Such a cured resin, prepared from 20 mol% of MFS and 80 mol% of TGDDM epoxy resin, shows excellent toughness (Charpy impact strength 13,000 J/m^2) and good mechanical strength (flexural strength 120 MPa, storage flexural modulus 4.2 GPa). Its glass transition temperature by dynamic mechanical thermal analysis (DMA) attains 227 °C, much higher than that of the cured resin from net spirobislactone and epoxy resin. © 2002 Published by Elsevier Science Ltd.

Keywords: Spirobislactone; Volumetric expansion; Maleimide

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1. Introduction

Volumetric shrinkage during polymerization is an unavoidable consequence of the formation of new covalent bonds [1]. The change from van der Waals distance to the covalent bond length among monomer molecules is the primary cause for volumetric shrinkage during polymerization. Shrinkage during crosslinking reaction for a thermosetting resin causes internal stress in bulk materials and results in poor mechanical properties [2–5]. Shrinkage in optical adhesives induces residual stress, leading to optical distortion [4]. There have been several strategies available for reducing or eliminating the polymerization shrinkage. One is associated with employing 'expanding monomers', which was first developed by Bailey in 1972 [2]. The follow-up researches reveal that the 'expanding monomers' show potential in the application fields of optical adhesives, stress-free composites, dental restoratives, impression materials and photoresists [2–5]. Another one is related to hydrogen-bonding induced loose molecular packing, which was reported by Ishida et al. in their work of elucidating the volumetric expansion on polymerization of benzoxazine monomers [6,7].

Recently Brady et al. [8–14] have reported application of spirobislactone in abating the curing shrinkage of epoxy resin. Spirobislactone was demonstrated to be 'expanding monomer' by both dilatometric method [8–14] and density measurement [15]. Although the attempt for controlling shrinkage was failed due to consumption of spirobislactone monomers at the early stage of the curing procedure prior to gelation [10], it is impressed that the cured resins from spirobislactone and epoxy resin show good thermal stability [13]. Thus spirobislactones merit further investigation, especially the manipulation of the ring-opening reaction of spirobislactone to proceed throughout the whole curing procedure is worthy of investigation. To solve this problem, we attempt to modify spirobislactone by way of attaching a rigid pendant segment bearing maleimido group to its aromatic ring. We find that this modification of spirobislactone not only solves the above problem but also enhances its

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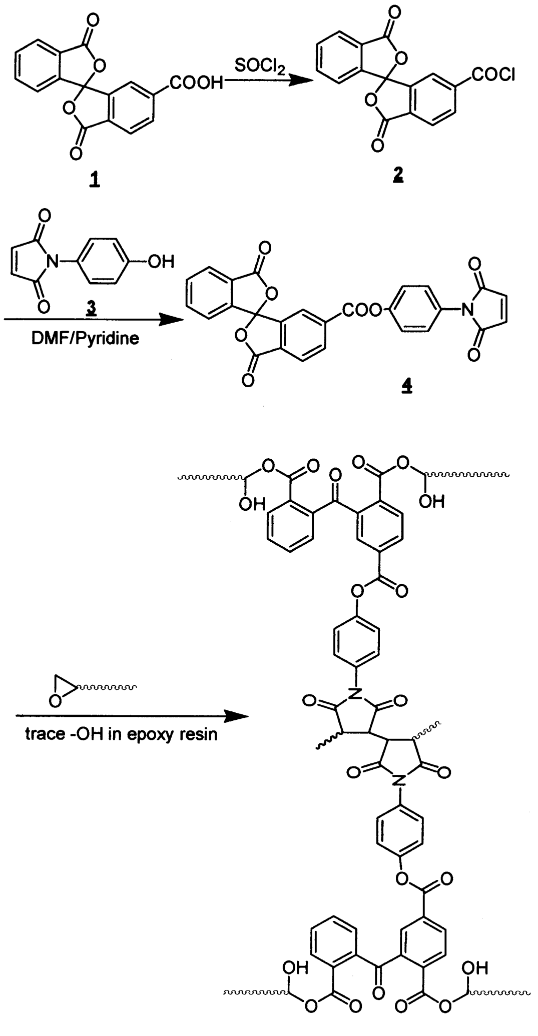

Scheme 1.

volumetric expansion during polymerization due to loose molecular packing among rigid pendent segments.

2. Results and discussion

As shown in Scheme 1, maleimido-functionalized spirobislactone (MFS) **4** was synthesized through esterification between *N*-(4-hydroxyphenyl) maleimide **3** and chlorocarbonyl containing spirobislactone **2** at room temperature according to Schotten–Baumann method [16, 17]. As-prepared MFS does not show apparent melting point. The aromatic spirobislactone **1** was synthesized by the procedure as reported by Brady et al. [13], and the *N*-(4-hydroxyphenyl) maleimide **3** was synthesized by the method as reported in the literature [18].

Tetraglycidyl 4,4′-diamino diphenyl methane (TGDDM) is selected to copolymerize with MFS to evaluate its volumetric expansion on polymerization. The curing reaction of MFS and epoxy resin comprises ring-opening copolymerization between spirobislactone and epoxy groups and free radical polymerization among maleimido groups, as shown in Scheme 1. The copolymerization of spirobislactone and epoxy groups was initiated from the trace hydroxyl groups attacking the spirobislactone groups. These trace hydroxyl groups was found to be pre-existed in the epoxy resin via IR measurement. If the spirobislactone consumed earlier than the epoxy group, the curing reaction would also include the polymerization among the epoxy groups. Fig. 1 shows the IR spectra of uncured and cured resins from MFS and TGDDM epoxy mixtures with the different molecular ratio. It is found that the cured resins with the MFS content higher than 30 mol% still contain unreacted spirobislactone groups, however, maleimido and epoxy groups are completely consumed in these cured resins. This implies that the volumetric expansion from ring-opening reaction of spirobislactone can be manipulated throughout the whole curing procedure after a certain modification of its molecule.

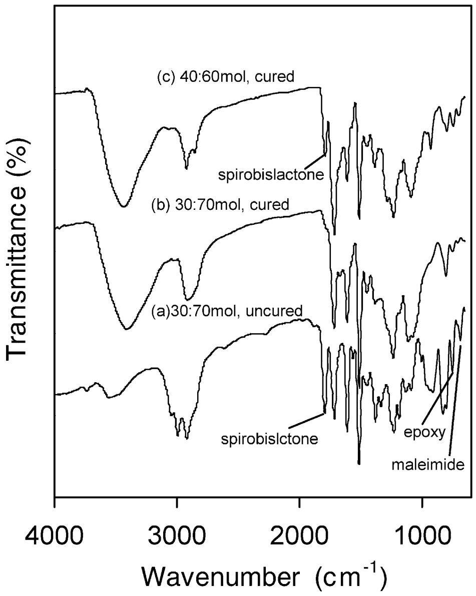

Fig. 1. The IR spectra of uncured and cured resins from MFS and TGDDM epoxy resin mixtures, where (a) uncured resin of 30:70 mol; (b) cured resin of 30:70 mol; (c) cured resin of 40:60 mol MFS and TGDDM epoxy resin mixtures.

The volumetric change of MFS and epoxy resin mixtures before and after curing is characterized by density measurement. Prior to density measurement, a complete degassing for MFS/epoxy mixtures was carried out at 60 °C under reduced pressure and MFS was ensured to dissolve in epoxy resin entirely. Care was taken to ensure that all cured samples were free of bubbles. Fig. 2 shows the plot of density variation as a function of MFS molecular content. The densities of uncured resins vary linearly with the MFS molecular content when their MFS contents are lower than 50 mol%. It should be noted that the MFS cannot completely dissolve in epoxy resins as its content surpasses 50 mol%, so the densities of uncured resins beyond 50 mol% MFS content were not measured. Correspondingly, the densities of cured resins also vary linearly with the

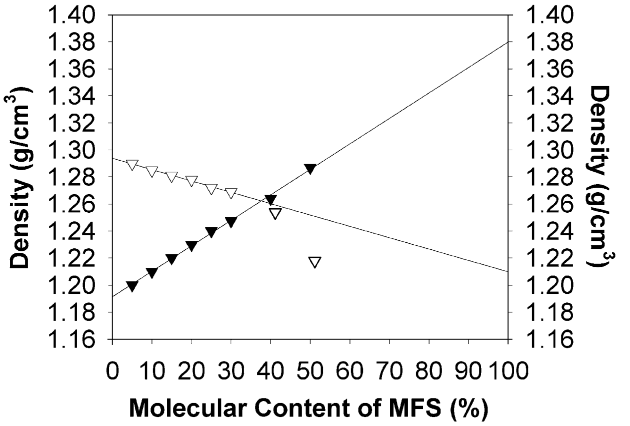

Fig. 2. The relationship of density vs. MFS molecular content, of which (▼) uncured resins of MFS/TGDDM epoxy; (▽) cured resins of MFS/TGDDM epoxy.

MFS molecular content if their MFS contents are lower than 30 mol%. However, such a relationship for cured resins deviates from linearity beyond the ken of 0–30 mol% MFS content. This may be resulted from the imperfect reaction of spirobislactone groups as mentioned above. In addition, it is observed that the density-content line of uncured resin intersects with that of cured resin at about 40 mol% MFS content, indicating a zero-shrinkage resin around this composition. By extending both density-content lines to the right *Y*-axis, the density of net MFS at the mixing state and the density of net MFS at the cured state are obtained from the intersection points of the uncured resin line/*Y*-axis and cured resin line/*Y*-axis. The density of net MFS is 1.38 g/cm^3 at the mixing state and 1.21 g/cm^3 at cured state, respectively. Based on both density values, the volumetric expansion of MFS is calculated to be +12.3%. This value is much higher than that of spirobislactone **1**, which was demonstrated to have a volumetric expansion on polymerization of +3.6% (see Appendix A). By the way, the volumetric change for net epoxy resin can be estimated by the density values at the intersection points of the density-content lines with the left *Y*-axis. It reveals that the TGDDM epoxy has a volumetric shrinkage of −7.2%.

The additional volumetric expansion of MFS except for the ring-opening contribution of spirobislactone is perhaps derived from loose packing of MFS molecules in the cured resin. This manner of loose packing structure is perhaps resulted from the steric hindrance effect of the maleimide rigid pendant segments. To demonstrate the existence of the loose packing structure of MFS in cured resins, a phosphotungstic acid (PTA) staining method according to the literature [19–23] is adopted to stain the MFS-concentrated domains in the cured resins. For the PTA staining, one common method is related to post-staining the sample sections embedded in cured epoxy resin, as a result of giant PTA molecules not to diffuse into the highly crosslinked epoxy resin. However, PTA can stain amorphous region of nylon because the PTA molecule was able to diffuse into loose packing region with low density [23]. The MFS molecules contain the similar polar amide structure just like nylon. If MFS-concentrated regions in the cured resins were loose packing regions, they should also be favorable for PTA molecules to diffuse. Fig. 3 is the morphology observation of PTA stained cured resin consisting of 20 mol% MFS and 80 mol% TGDDM epoxy with the aid of transmission electron microscopy (TEM). It is apparent that there are many nanoparticles in dimension of 20–50 nm in the cured resin, demonstrating the existence of loose packing structure in cured resin. Since the cured epoxy resin with high crosslinking density cannot be stained by PTA, the stained regions with nanodimension are deduced to be the loose-packed cured MFS.

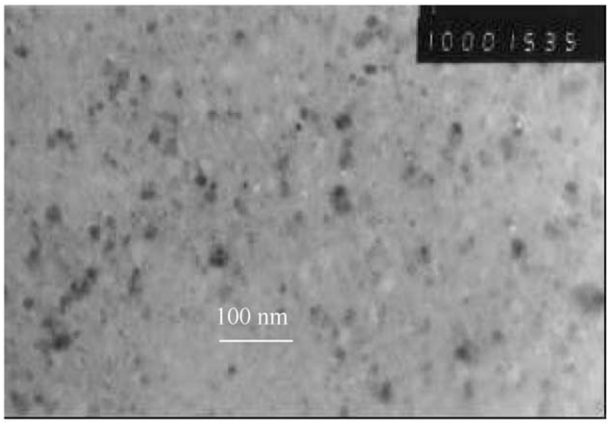

Fig. 3. The TEM observation of cured resin from 20:80 mol MFS and TGDDM epoxy resin mixture.

The mechanical properties of the cured resin from 20 mol% of MFS and 80 mol% of TGDDM epoxy were examined. This cured resin has a Charpy impact strength of 13,000 J/m^2, flexural strength of 120 MPa and storage flexural modulus of 4.2 GPa. Its glass transition temperature by dynamic mechanical thermal analysis (DMA) attains 227 °C, much higher than that of the previously reported resins [8–15,23] from net spirobislactone and epoxy resin. The excellent toughness may be caused by the formation of nanoparticles with the loose packing structure. However, the relationship between structure and mechanical properties needs further elucidation.

3. Experimental

3.1. Chemicals

Aromatic spirobislactone **1** was synthesized by the procedure as reported by Brady and Sikes [13], and the *N*-(4-hydroxyphenyl) maleimide **3** was synthesized by the method as reported in the literature [18]. MFS **4** was synthesized through esterification between *N*-(4-hydroxyphenyl) maleimide **3** and chlorocarbonyl containing spirobislactone **2** at room temperature according to

Schotten–Baumann method [16,17]. Epoxy resin, tetraglycidyl 4,4′-diamino diphenyl methane (TGDDM), was commercial product and used as received.

3.2. Curing procedure

The copolymerization was carried out via the following procedure: the monomer MFS/epoxy resin mixtures were degassed at 60 °C, and then they were annealed sequentially by 120 °C/24 h, 160 °C/5 h and 180 °C/2 h.

3.3. Density measurement

Density measurement was performed by pycnometer method using a 10 ml pycnometer at 40 °C for all samples. Dimethyl silicone oil was used as the standard. The samples immersed in silicone oil in pycnometer were sufficiently degassed at 40 °C before measurement. The volumetric change (ΔV) of a resin is calculated using $\Delta V = (d_m - d_p)/d_m \times 100\%$, in which d_m and d_p are the densities of uncured and cured resins, respectively.

3.4. Characterization

FTIR spectra were recorded on a Nicolet Magana-IR spectrometer 760 using KBr pellets. Phase structure was observed on a Japan JEM-100CXII transmission electron microscopy. The samples were prepared by ultrathin sectioning technique. PTA (2%) and benzyl alcohol (2%) in water were used as the stain solution. The sample sections on a specimen grid were floated on a drop of the mixed solution for 10 min and then washed with distilled water three times. DMA was tested using British Rheometric Scientific Corp. Dynamic Mechanical Thermal Analyzer MKIII. The measurement was performed in the three-point bending mode with a heating rate of 10 °C/min under N_2 atmosphere. The specimens dimension was 50 mm × 7 mm × 1 mm.

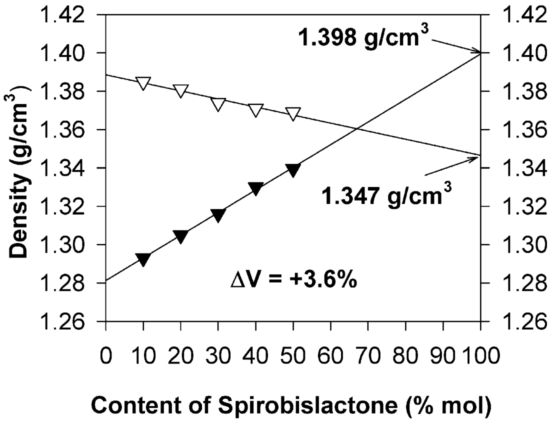

Fig. A1. The relationship of density and spirobislactone **1** content for cured and uncured spirobislactone 1/ODADE epoxy, where ODADE epoxy is 7-oxabicyclo [4,1,0]heptane-3,4-dicarboxylic acid diglycidyl esters.

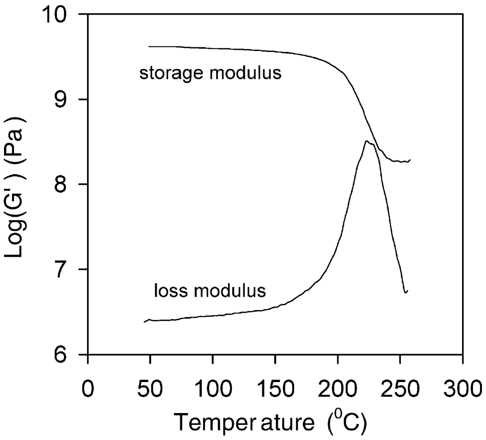

Fig. A2. The DMA spectrum of cured resin from 20 mol% MFS and 80 mol% TGDDM epoxy resin.

Appendix A. Supporting information

See Figs. A1 and A2.

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