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The influence of monomer ratios on the properties of copolymers of 3,3'-spirobiphthalide and bisphenol A diglycidyl ether

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SUMMARY

A spirobislactone, 3,3'-spirobiphthalide (SBP), has been copolymerized with the diglycidyl ether of bisphenol A (DGEBA), and the properties of the products have been evaluated and related to the proportion (1-15%) of SBP monomer used. Polymers were characterized by infrared spectral analysis, ^{13}C NMR, thermal analysis, and mechanical testing. Polymers containing SBP have lower glass transition temperatures and higher decomposition temperatures than DGEBA polymers cured with phthalic anhydride (PA). Materials with higher SBP content have higher T_{alpha} values. Mechanical properties of the SBP copolymers are similar to those of DGEBA-PA polymers.

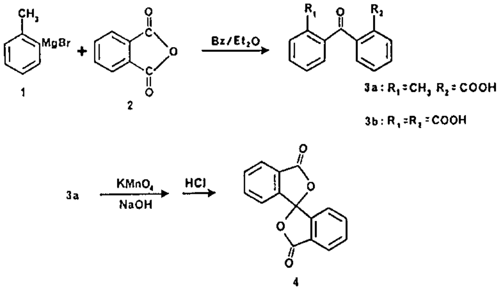
INTRODUCTION

3,3'-Spirobiphthalide, a spirobislactone, reacts with epoxy resins in a manner similar to that of acid anhydrides(1). During cure, hydroxy and oxirane groups in the epoxy resin attack and open both lactone rings in SBP, forming diaryl ketone and benzoate ester linkages which impart increased thermal stability to the polymer. In addition, multiple bond-breaking and ring-opening reactions compensate for some of the shrinkage that normally occurs when new bonds are formed during epoxy cure, because more than one bond is broken for each new covalent bond formed. Monomers containing more than one ring have been used previously to control the change in volume during polymerization of epoxy resins(2). This paper reports efforts to exploit multiple ring-opening reactions for the controlled synthesis of polymers with predetermined properties.

EXPERIMENTAL

Starting materials (Aldrich) were used as received without further purification. The diglycidyl ether of bisphenol A (DGEBA) was Epon 828 (Shell).

3,3'-Spirobiphthalide was prepared by a modification of an earlier procedure(3). *o*-Tolyl magnesium bromide (*1*), produced from *o*-bromotoluene and magnesium shavings in diethyl ether solution, was transferred under N_2 pressure into a dropping funnel and added slowly to a rapidly-stirred solution of excess phthalic anhydride (*2*) in 3:1 (vol) benzene : diethyl ether under continuous N_2 purge. The mixture was refluxed overnight, cooled, and hydrolyzed with ice. The organic layer was separated and extracted with 6 percent aqueous sodium bicarbonate solution, and the extracts were cooled in an ice bath. Ketoacid *3a* was precipitated by careful addition of 50% sulfuric acid solution. The raw product was recrystallized from xylene (technical grade) to give an off-white crystalline solid, mp 117°, in 65% yield. *3a* was dissolved in 10 percent aqueous sodium hydroxide and heated to reflux to remove xylene as its azeotrope with water. A 4 percent solution of aqueous potassium permanganate was added dropwise. The mixture was refluxed overnight, cooled, and filtered twice to remove precipitated manganese dioxide. Diacid *3b* was not isolated, but the filtrate was acidified with concentrated hydrochloric acid until strongly acidic, and boiled for 2 hours; during boiling, 3,3'-spirobiphthalide (*4*) precipitated from the solution as a white crystalline material. *4* was isolated in 80% yield by filtration, washed with cold 5 percent sodium bicarbonate solution until the washings were neutral, and washed with water to yield a crystalline solid, mp 212°.



Resins were polymerized using standard anhydride-epoxy procedures(4). DGEBA was heated to 120°, cooled to 80°, and mixed with SBP. The mixture was cooled to room temperature and one percent by weight of a catalyst [*tris*-(dimethylaminomethyl)phenol, "*tris*"] was added. The mixture was centrifuged for 10 minutes at 2200 rpm to remove gases, poured into molds treated with a fluorocarbon release agent, and allowed to stand one hour at room temperature under water aspirator vacuum to remove trapped air. Resins were cured for 18 hours at 130°, removed from the mold, and post-cured at 155° for 4 hours and then at 225° for 30 minutes. Standards for comparison were made from DGEBA alone and from solutions of 45 parts phthalic anhydride (PA) in 55 parts DGEBA cured under identical conditions.

Polymers under N_2 were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA) at scan rates of 10 °C/min (DSC, TGA) and 2.5 °C/min (DMA) using a DuPont 2100 Thermal Analyst with model 910 DSC, 951 TGA, and 982 DMA modules. A DuPont LNCA II cooling attachment was utilized for sub-ambient DMA scans. Reactions of resins between salt plates were followed with a Perkin Elmer model 1800 Fourier transform infrared spectrophotometer (FTIR) operated at a resolution of 2 cm^{-1}.

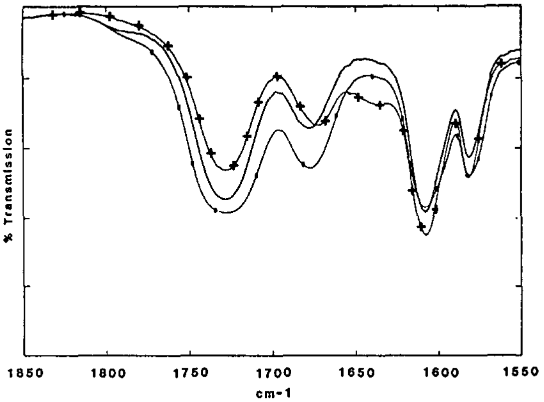


Figure 1. Typical FTIR spectra of materials cured with SBP: 5% SBP (—+—), 9% SBP (——), and 13% SBP (—◆—).

Solid state cross-polarized / magic angle spinning (CP/MAS) ^{13}C NMR spectra were obtained for powdered samples using a Bruker MSL 300 NMR spectrometer.

RESULTS AND DISCUSSION

Reaction mixtures containing from 1 to 15 percent by weight of SBP in DGEBA were studied. Solutions of up to 15 percent of SBP in DGEBA appear to be stable indefinitely at room temperature, and may be easily manipulated to produce products. Mixtures with more than 15 percent of SBP in DGEBA precipitated SBP upon standing at room temperature. Sublimation at curing temperatures and precipitation of the solute below 70° do not occur, as is the case when solutions of PA in DGEBA are used. At 1 to 4 percent SBP, cured polymers were very similar to the homopolymer of DGEBA produced by *tris* catalyst. Changes in polymer properties were apparent at the 5 percent level and reached a constant value at 13-15%. Cured polymers ranged in color from medium yellow (1% SBP) to dark orange (15% SBP).

The progress of the curing reaction was monitored by FTIR. The strong bislactone band at 1790 cm^{-1} disappeared and bands near 1728 cm^{-1} (benzoate ester) and 1677 cm^{-1} (diaryl ketone) formed. In materials with smaller amounts of SBP, a weak band was visible near 1636 cm^{-1} and the ketone band was shifted to 1675 cm^{-1}. A benzoate ester band was evident at 1728 cm^{-1} in all cured materials. Figure 1 shows typical carbonyl band positions and intensities for 5, 9, and 13 percent of SBP in DGEBA. The 9 and 13% systems display only benzoate and ketone bands, whereas in the 5% system the benzoate ester band shifts slightly to 1675 cm^{-1} and an additional band appears at 1636 cm^{-1}. This behavior may be due to *cis* and *trans* isomers of substituted allyl alcohols produced in a *tris*-catalyzed rearrangement of the glycidyl ether groups in DGEBA; such bands can be observed(5) at 1669 and 1637 cm^{-1} in the spectra of epoxies homopolymerized by *tris* alone. The band at 1669 cm^{-1} is obscured by the benzoate ester band, but is responsible for its slight shift. Figure 2 shows the spectra of a mixture containing 9 percent of SBP after catalyst addition, during cure, and completely cured. Initially, hydroxyl groups in DGEBA react with SBP, opening both rings and forming benzoate ester, diaryl ketone, and carboxylic acid groups. The acid reacts with epoxide rings to generate new hydroxyl groups. The

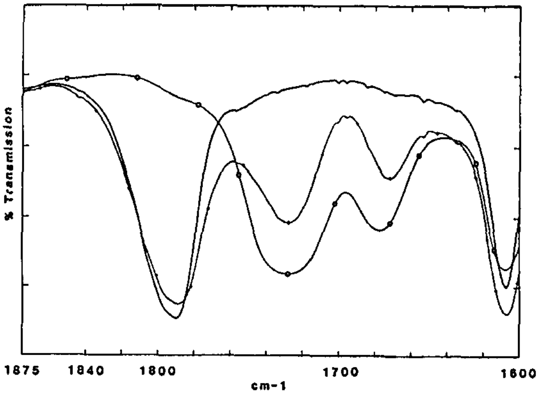


Figure 2. FTIR of a 9% SBP system during cure at room temperature: 30 minutes after *tris* addition (——), 2 days (—+—), final heat cured material (—o—).

reaction continues in this fashion until the SBP is exhausted. Full cure of the polymer is then attained by *tris*-catalyzed condensation of the remaining epoxy groups.

The CP/MAS ^{13}C NMR spectra of cured resins displays typical characteristics of cured epoxy resins. Absorption at 44 ppm which is reported(6) to be characteristic of epoxy rings is absent. The carbonyl peaks appear near 175 ppm, but are too poorly resolved to aid in structure determination.

Differential scanning calorimetry of SBP-DGEBA mixtures after addition of *tris* catalyst show multiple exotherms near 150 and 200°, and the amplitude of the peaks depends on SBP content. The peak near 150° is produced by the opening of the bislactone rings; this peak appears only in DSC scans of mixtures which contain bislactone carbonyl absorption in their FTIR spectra. The area of the DSC peak increases with higher amounts of SBP monomer (Figure 3). The broader peak around 200° is produced by epoxy homopolymerization and by esterification of the carboxylic acid produced in the ring-opening step. Heats of reaction for the bislactone ring-opening at 150° vary with the amount of SBP present.

Values for the glass transition temperature (T_g), measured at the midpoint of the DSC endotherm, typically fall between 110 and

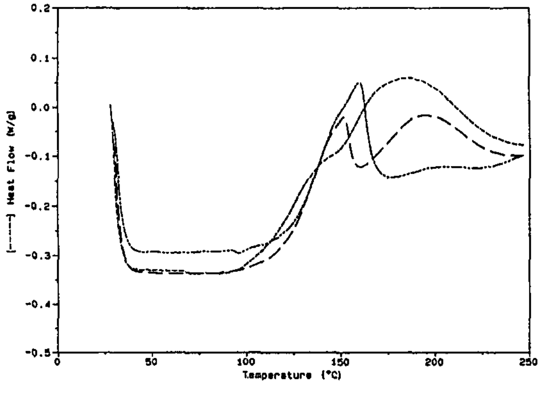


Figure 3. DSC scans of DGEBA:SBP mixtures immediately after addition of *tris*: 5% SBP (- - - -), 9% SBP (— —), and 13% SBP (— - -).

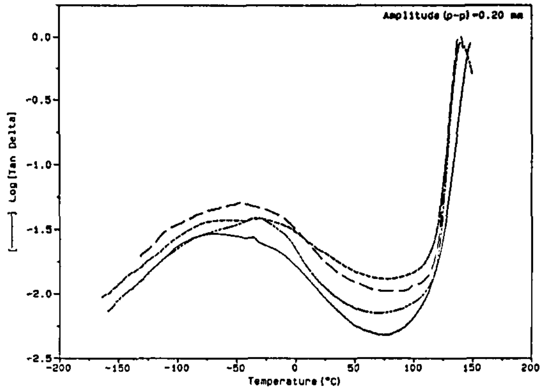


Figure 4. DMA scans of cured SBP samples: 5% SBP (— —), 9% SBP (----), 13% SBP (—--), and 15% SBP (——).

125°. The measurements are not sensitive enough to reveal a relationship between T_g and the amount of SBP in the mixture. Homopolymers produced with *tris* alone display T_g values near 105°, and solutions of PA in DGEBA cured under the same conditions form polymers with T_g values of 160 °C.

Thermogravimetric analysis of SBP copolymers show an onset of decomposition (T_{dec}) near 380-400°, depending on the amount of comonomer used. Polymers with 13 percent of SBP monomer show the highest decomposition temperature, 405°. Polymers with 15 percent of SBP produce materials with a higher char yield, but their T_{dec} values fall to near 380°.

Dynamic mechanical analysis demonstrates T_{alpha} values in the range of 137 to 147°; these values increase with the amount of SBP moiety in the polymer. The value of T_{alpha} for DGEBA:PA polymers is 165°. The broad T_{beta} peak, ranging from -150 to 0°, can be assigned(7) to the sum of localized mechanical relaxations. Molecular relaxations at -70° have been correlated with diester linkages (7), and those at -56° with hydroxyether linkages (8). In the log (tan delta) plot in figure 4, there is a general trend to higher temperatures as the percentage of SBP is decreased. The T_{beta} peak of DGEBA polymerized by *tris* is near -40 °C. A relationship between motion of the polymer backbone and the number of open-chain SBP moieties in the backbone, as measured by the area of the benzoate ester carbonyl absorption in FTIR spectra, could not be established.

Mechanical properties for all SBP copolymers are similar. The yield strength ranged from 80 to 85 MPa, and the initial moduli vary from 1.9 to 2.2 GPa. These values are similar to those obtained for polymers of DGEBA cured with phthalic anhydride. Polymers containing 13 percent of SBP are at the top of these ranges.

CONCLUSIONS

3,3'-Spirobiphthalide (SBP) is a useful monomer for the copolymerization of epoxy resins at baking temperatures. Solutions of up to 15 percent of SBP in DGEBA appear to be stable indefinitely at room temperature, and may be cured with heat and an aromatic tertiary amine catalyst to give polymers with properties which depend on the content of SBP. Both bislactone rings in SBP open during cure to produce thermally stable benzoate ester and diaryl ketone links in the cured polymer. The properties of the cured polymers are less sensitive than those of anhydride-cured materials to stoichiometric equivalency and to reaction conditions. The decomposition temperature of the SBP copolymers is higher than that of DGEBA cured with phthalic anhydride or homopolymerized with an amine catalyst. Mixtures containing 13 percent of SBP show the highest decomposition temperature, 405°, and the best mechanical properties.

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