

Properties and Toughening of Heat-Resistant Thermosets Based on Unsaturated Ester Resins

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Received 2 August 2001; Accepted 20 December 2001

ABSTRACT: We describe our investigations of the curing chemistry and properties of heat-resistant thermosets comprised of unsaturated ester resins. We suggest a mechanism for the rearrangement of the cured matrix and volatile evolution during the curing process. We employed dielectric spectroscopy (DES) as a tool for monitoring the extent of cure, determining glass-transition temperatures, and evaluating electrical properties of the resins. We compare and contrast results obtained by DES to results obtained by dynamic mechanical analysis (DMA). Fracture testing showed that improvements were made in the toughness of

these materials by blending the uncured resin with impact modifiers such as hydrocarbon or silicone reactive rubber adducts or poly(arylene ether sulfone)-based thermoplastic oligomers. We determined the effects of the thermoplastic toughening additive's molecular weight, concentration, and endgroup functionality on the phase separation, thermal stability, and fracture toughness of the blend. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 821–843, 2002

Key words: polyesters; blends; mechanical properties; fracture; dielectric properties

INTRODUCTION

Polymers with good thermal stability (temperature $>200^{\circ}\text{C}$) are needed for a variety of specialty applications ranging from microelectronics to high-performance composites and adhesives. However, improvements in the processing and performance of resins for high-temperature applications must be made before large markets can develop for these materials.¹ Although significant advances in the development of these materials have been made in the past 30 years, processing issues such as solvent removal, volatile evolution, and extremely high cure temperature are still common problems. Therefore, the realization of epoxy-like processability is a major challenge for the development of new, more versatile high-temperature adhesives.² In addition, many of the materials used as high-temperature thermosets suffer from inherent performance limitations in load-bearing applications because they are extremely brittle. For these types of materials to find wide commercial applicability, their toughness must be improved via a method that does not simultaneously sacrifice their high-temperature performance.

Unsaturated polyester resins that provide a unique combination of room-temperature processability in

the uncured state and high-temperature ($>200^{\circ}\text{C}$) stability in the cured state have been the subject of several reports.^{3–9} These resins are mixtures of various compositions of oligomers and difunctional aromatic monomers with styrenic or methacrylic functionality (Fig. 1). The mixtures result from the two-step, one-pot reaction of bis[4-(1-hydroxyethyl)phenyl] ether with methacrylic acid in the presence of a *para*-toluenesulfonic acid catalyst.⁹ The relative amounts of each compound in the mixture can be controlled by changing the reaction conditions.⁹ Depending on the mixture composition, the resulting resins range in physical state from liquids (with a very wide range of viscosities) to solids (with liquification points ranging from 25 to 115°C). The formation of a crosslinked matrix from the resin mixture with either thermal or catalytic curing has been studied in detail.^{4–6} Typically, the resins were hardened with very lengthy (>24 h) curing regimes with gradual increases in temperature.⁶

Although most of the reported work involved complex resin mixtures, some of the pure compounds were isolated and their curing behavior was studied independently. For example, the curing kinetics of pure bis(4-vinylphenyl) ether monomer (**M1**) was reported.¹⁰ In addition, preparative scale gel permeation chromatography (GPC) was employed to isolate the asymmetrically substituted monomer (**M2**) and its thermal polymerization was monitored by IR spectroscopy and calorimetry.³

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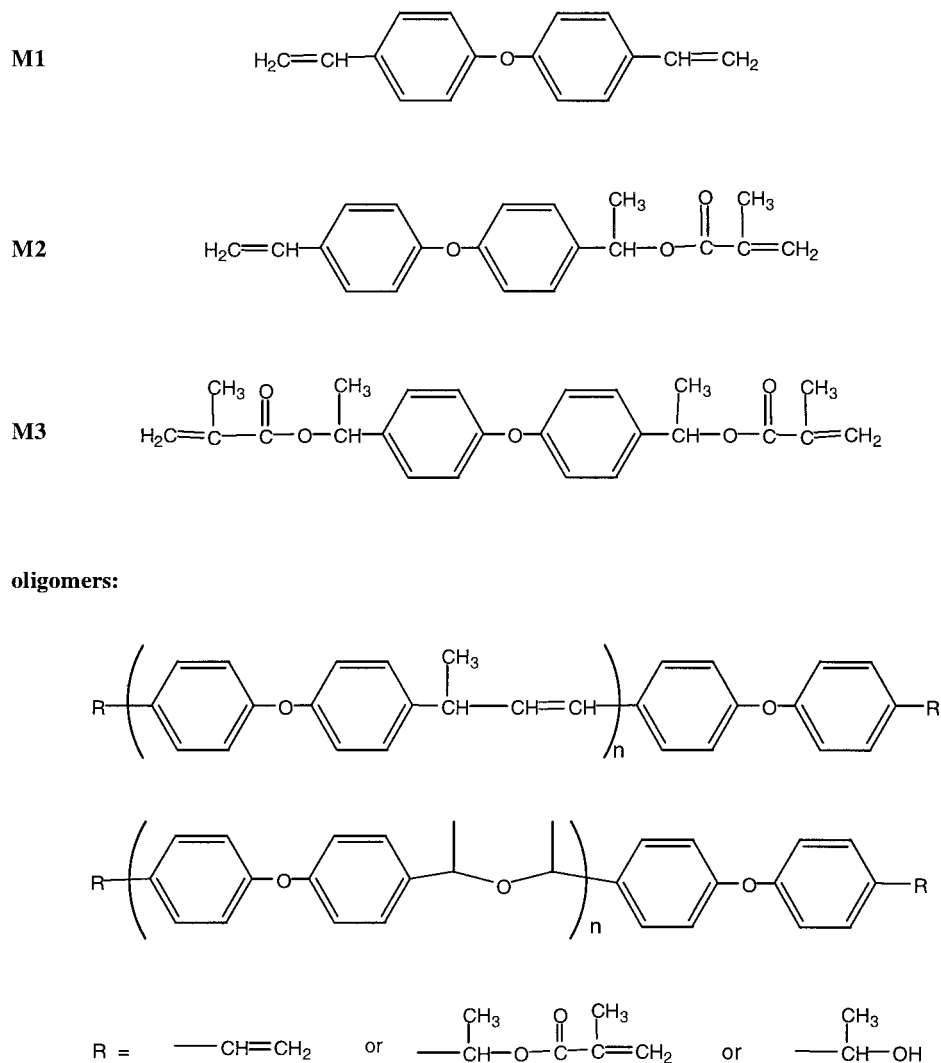


Figure 1 Structures of compounds comprising polyester resin mixtures.

In addition to prior work that focused on details of the polyester resin synthesis and cure kinetics, the thermal and physical properties of the cured resins have been reported. Several types of composites (using glass,¹¹ carbon,¹² polyimide,¹³ or Kevlar¹³ fibers) were prepared, tested, and compared to samples constructed with an epoxy matrix. In general, the performance of the polyester-based composites was shown to be superior to the epoxy-based composites at high temperatures (>350°C) on the basis of measurements of Young's modulus (E'), tensile strength, and rupture strain. However, at room temperature, the polyester-based composites showed inferior performance because of accelerated formation of the zone of failure, which results from low resistance to brittle crack propagation in the matrix.¹² Composites have also been prepared with blends of polyester resins and epoxy resins in an effort to improve the low-temperature performance of the composites while maintaining good thermal stability.^{14,15} Because the epoxy resins

combined with the liquid polyester resins in all proportions, preparations of these blends was facile. Although phase separation was observed during the thermal hardening to give an interpenetrating polymer network, an extensive interphase region was noted that resulted from the reaction of the polyester resin's ester, acid, and anhydride groups with the epoxy. The composites fabricated from epoxy/polyester blends showed increased heat resistance when compared to those made from neat epoxies.

Herein, we report results from investigations of the fracture mechanics, thermal stabilities, electrical properties, and mechanical properties of cured polyester resins and blends. Improvements were made in the toughness of these materials by the blending of uncured resin with impact modifiers such as hydrocarbon or silicone reactive rubber adducts or poly(arylene ether sulfone) (PSf)-based thermoplastic oligomers. The effects of the thermoplastic toughening additive's molecular weight, concentration, and

endgroup functionality on the phase separation, thermal stability, and fracture toughness of the cured blends were determined.

EXPERIMENTAL

Materials

We prepared polyester resins by acid-catalyzed dehydration of bis[*p*-(1-hydroxyethyl)phenyl] ether using procedures described in the literature.^{3,9} Araldite GY6010 epoxy resin (Ciba Geigy, Tarrytown, NY), Dyhard 100S (SKW Chemicals, Marietta, GA), and Ancamine 2014FG (Air Products, Allentown, PA) were used as received. Bis(4-fluorophenyl)phenyl phosphine oxide (99.9%) was kindly provided by Zeneca (Wilmington, DE) and was used as received. Benzoyl peroxide (97%), cumene hydroperoxide (80%), 4-*tert*-butyl catechol (97%), *N,N*-dimethylformamide (99%), potassium carbonate (+99%), bis(4-chlorophenyl) sulfone (98%), bisphenol A (+99%), tetrabutylammonium hydrogen sulfate (97%), magnesium sulfate (99%), sodium hydroxide pellets (99.998%), hydrochloric acid (1M), toluene (anhydrous), *N,N*-dimethylacetamide (DMAc; anhydrous), and PSf [number-average molecular weight (M_n) \approx 16,000 g/mol] were purchased from Aldrich (Milwaukee, WI) and were used as received. Irgacure 184 (1-hydroxycyclohexyl phenyl ketone; Ciba) and Darocur 1173 (2-hydroxy-2-methyl-1-phenyl-1-propanone; Ciba) were used as received as photoinitiators. Methanol (EM Science, Gibbstown, NJ) and chloroform (JT Baker, Phillipsburg, NJ) were used as received for the purification of the PSf oligomers. Tetrahydrofuran (THF; Mallinckrodt, Phillipsburg, NJ) was used as the extraction solvent and eluent for GPC. The endcapping agents used for the PSf syntheses were *trans*-4-hydroxystilbene (98%; Acros, Geel, Belgium) and vinylbenzyl chloride (mixture of \sim 70% meta-substituted and \sim 30% para-substituted; Fluka, Milwaukee, WI). Methylbenzylidene-cyanoacetate-capped oligomers, R45-HT rubber, and poly(dimethylsiloxane) were synthesized at Lord Corporation following a procedure described elsewhere.¹⁶ Poly(dimethylsiloxanes), poly(methylphenylsiloxanes), and poly(diphenylsiloxanes) homopolymers or reactive adducts with vinyl or methacrylic functional groups of various molecular weights were purchased from United Chemical Technologies (Bristol, PA) or Gelest (Morrisville, PA) and were used as received.

Synthesis and functionalization of PSf oligomers

The PSf oligomers were synthesized via well-established step growth polymerization methods involving the reaction of bisphenols with activated aromatic dihalides.¹⁷ The chemical functionality of each oligomeric product was confirmed by ¹H-NMR and Fourier

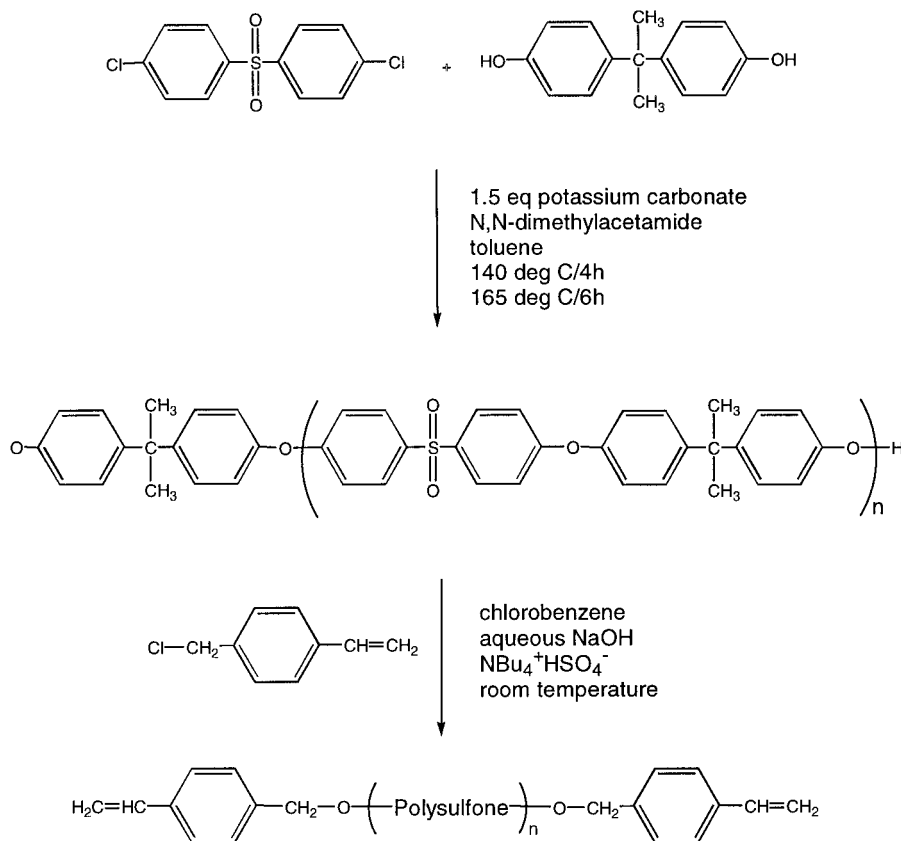
transform infrared spectroscopy. The degree of polymerization was determined by two independent methods: ¹H-NMR and GPC.

PSf with phenolic endgroups

To prepare the PSf oligomers with phenolic functional groups on the chain ends (Scheme 1, step 1), we quantitatively charged bis(4-chlorophenyl) sulfone, bisphenol A, potassium carbonate, toluene, and DMAc to a three-necked, round-bottomed flask under nitrogen flow. To ensure that the endgroups were phenolic functional groups and to target the desired degree of polymerization, we calculated a precise excess of bisphenol A using standard equations.¹⁸ For example, to prepare the oligomer with a target number average molecular weight of 2000 g/mole, we used 1.637 equivalents of bisphenol A for each equivalent of bis(4-chlorophenyl) sulfone. The reaction vessel was purged with nitrogen and equipped with a nitrogen bubbler, an overhead stirrer, a Dean-Stark trap fitted with a condenser, and a heating mantle controlled by a digital temperature controller and thermocouple. The reaction mixture was dehydrated via toluene azeotrope for 4 h at a reaction temperature of 140°C; then, the remaining toluene was removed by distillation, the temperature was increased, and the solution was heated for an additional 6 h at 165°C. The reaction mixture was cooled to room temperature and filtered to remove potassium chloride and residual potassium carbonate. We isolated the solid polymer product by adding the reaction mixture dropwise to a large excess of an 80/20 methanol/water mixture, collected it by vacuum filtration over a Hirsch funnel, and dried it *in vacuo* at room temperature overnight. The next day, we redissolved the polymer to make a 25 wt % solution in chloroform; we filtered the solution to remove any remaining residual salts, and the filtrate was added dropwise to a five-fold excess of methanol. This time, the polymer precipitated as a fine, white powder. The product was collected by vacuum filtration over a Hirsch funnel and dried *in vacuo* at room temperature until it reached a constant weight. The purified product was recovered at 86% yield.

PSf with styrenic endgroups

To prepare this type of material, we followed the general procedure of Auman and colleagues (Scheme 1, step 2).^{19,20} We ground the PSf oligomer with phenolic endgroups into a fine white powder using a mortar and pestle. A 25 w/v% solution of the oligomer in chlorobenzene was stirred until it was clear, colorless, and homogeneous. We added tetrabutylammonium hydrogen sulfate (a phase-transfer catalyst) and a two-fold excess of the vinyl benzyl chloride to the reaction mixture with stirring. Then, 10 v/v% of a

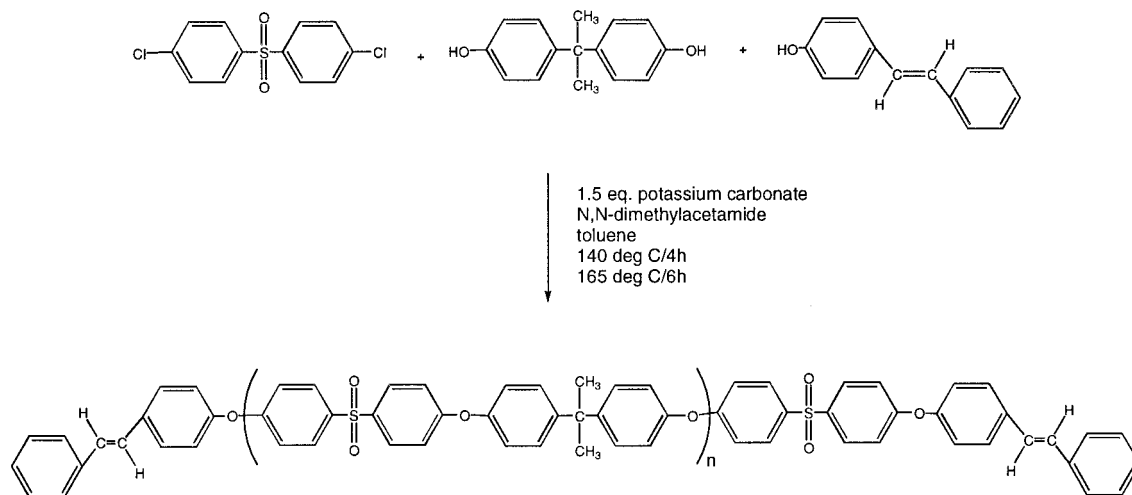


Scheme 1 Synthesis of phenol-terminated and styrene-encapped PSf oligomers.

12.5N NaOH solution was slowly added to the reaction mixture. After about 30 s, the reaction mixture changed to a deep blue and then a deep purple color while a white precipitate (sodium chloride) formed. The reaction mixture was put under a nitrogen blanket and allowed to stir at room temperature overnight. The reaction mixture went through several more color changes from dark grey to dark green, and the next day it was a medium golden brown color. We filtered the reaction mixture to remove the insoluble salts and washed the filtrate with three portions of 1M HCl and then two portions of water. The organic layer was dried over magnesium sulfate and filtered. We isolated the product by adding the organic layer dropwise to a large excess of acidic methanol. The off-white precipitate (polymer product) was collected by vacuum filtration over a Hirsch funnel and dried *in vacuo* overnight. The next day, the product was redissolved in chloroform and precipitated again into methanol, collected by vacuum filtration, and dried *in vacuo* to constant weight. The purified product was recovered at 70.0% yield. ¹H-NMR indicated that the conversion of the endgroups to the styrenic functionality was complete and that no residual solvent or starting material was present.

PSf with stilbene endgroups

We prepared and purified the stilbene-terminated oligomers (Scheme 2) using the same general procedure described previously for the PSf with phenolic endgroups. In this case, the *trans*-4-hydroxystilbene endcapping agent was added directly to the reaction vessel before the polymerization. For example, to achieve a target M_n of 15,000 g/mol, we quantitatively charged 25.000 g (0.087 mol) of bis(4-chlorophenyl) sulfone, 19.874 g (0.087 mol) of bisphenol A, 1.035 g (0.00528 mol) of *trans*-4-hydroxystilbene, 18.05 g (0.131 mol) of potassium carbonate, 150 mL of toluene, and 200 mL of DMAc to a 500 mL three-necked round-bottom flask. Before heating, the reaction mixture was bright yellow and transparent with a small amount of undissolved white solid (potassium carbonate). The toluene/water azeotrope was gradually removed from the reaction vessel by distillation over 5 h. During the 11 h of total reaction time, the solution color evolved from pale yellow to yellow green to bright yellow, and near the end of the reaction time, a viscosity increase was observed. A second batch of this material was made on a three times larger scale. In both cases, the product was recovered at high yield (>95%).



Scheme 2 Synthesis of stilbene-terminated PSf oligomer.

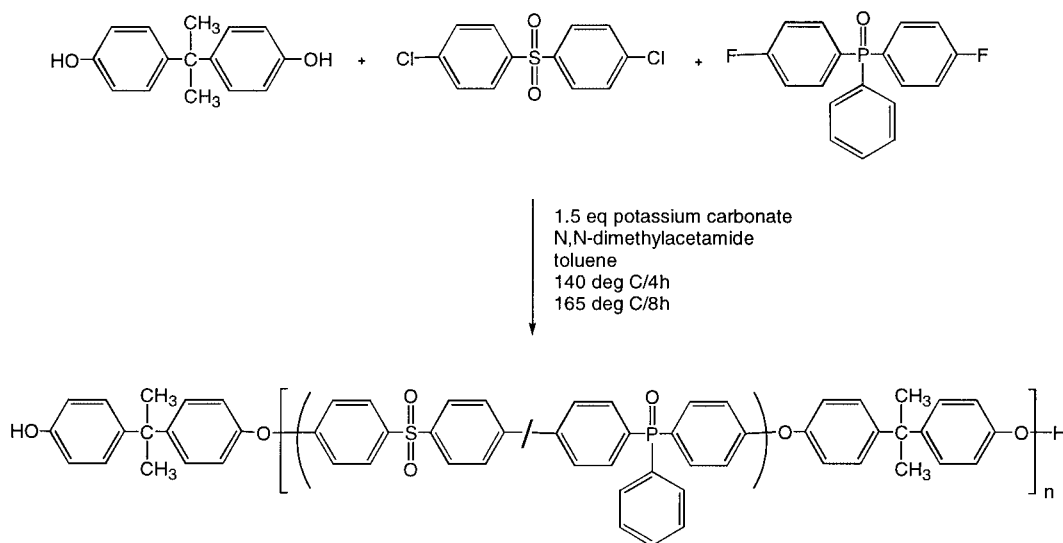
Poly[arylene ether(phenyl phosphine oxide-co-sulfone)]

We prepared and isolated a random copolymer with 50 mol % sulfone units and 50 mol % phenyl phosphine oxide units (Scheme 3) following the same general procedure for the phenolic endcapped PSf homopolymer outlined previously. In this case, three monomers were initially charged: bisphenol A (1.0 eq), bis(4-chlorophenyl sulfone) (0.47 eq), and bis(4-fluorophenyl)phenyl phosphine oxide (0.47 eq). The slight excess of bisphenol A was used to target an M_n of 16,000 g/mol. After removal of the water by toluene azeotrope for 4 h at 140°C, the reaction mixture was allowed to proceed at 165°C for 8 h. $^1\text{H-NMR}$ was used to confirm the structure of the product, which was isolated at 93% yield (GPC versus polystyrene

standards: $M_n = 4550$ and polydispersity index of the molecular weight distribution (PDI) = 2.38).

Thin film preparation

The resins, which can be either solids or liquids at room temperature, were processed into thin films by two different techniques: melt pressing or direct casting. For the direct casting technique, we made solutions by adding Irgacure 184 (2.2 w/w%) and Darocur 1173 (2.2 w/w%) to the liquid resins. We mixed the solutions on a roll mill until homogeneous, and then we cast films onto glass or Teflon-coated aluminum plates using an adjustable casting knife with a 10- or 20-mil gap. We photocured the thin liquid films using the AETEK (Romeoville, IL) ultraviolet-curing proces-



Scheme 3 Synthesis of 50/50 random copolymer: poly[arylene ether(phenyl phosphine oxide-co-sulfone)].

sor (two consecutive lamps at 300 W each, belt speed = 15 ft/min, nitrogen atmosphere, one pass through unit.) The photocured films lifted easily off of the fluoropolymer-coated plates, and a water soak was used to gently remove films from the glass plates (the films were subsequently allowed to dry at room temperature.) The films were then postbaked at 170°C for 30 min and at 250°C for varying amounts of time. In contrast, the solid resins were melt pressed at 150°C and 31 psi for 1 h. We then postbaked these films at 170°C and 250°C to parallel the processing of the photocured films.

Preparation of blends

To prevent premature cure during the blending process, we initially added 1 wt % 4-*tert*-butyl catechol to the resins and stirred them until homogeneous. After the inhibitor was dissolved, the toughener (polyimide, PSf, functionalized PSf's, silicone, or butadiene-based rubber adduct) was added to the solution. In most cases, the solution was kept under a nitrogen blanket, stirred with a magnetically coupled stir bar, and heated in a boiling water bath to speed up the dissolution of the toughener. The silicones and rubber adducts were liquids, and they mixed well with the liquid polyester resin at ambient temperature. Then, about 1.1 v/v% cumene hydroperoxide was added with stirring, and the solution was degassed *in vacuo* for 15 min. The warm, degassed solutions were then quickly poured into the large bar sample mold (see later).

Thermally cured disk preparation

Solutions were prepared by adding benzoyl peroxide (0.4 g) to resin (20.0 g) and mixed on the roll mill at room temperature overnight. We prepared disks by pouring the resin into a Teflon mold (diameter = 29 mm, thickness = 3 mm) and baked them for 2 h cycles at the temperatures indicated (170, 190, 210, 230, and/or 250°C), which resulted in a total cure time ranging from 2 to 10 h.

Thermal curing and fracture mechanics sample preparation

Large molded bars (dimensions = 0.5 × 2.6 × 30.5 cm) were made in open-topped, Teflon-coated, stainless steel molds. We thermally cured the resin samples or blends in a vented oven by slowly increasing the temperature from 125 to 250°C over 6 h. We cut samples into the appropriate geometry (1 × 5 cm pieces) using a ceramic tile saw. Two rectangular samples and scrap pieces from each bar were set aside for dynamic mechanical analysis (DMA) and thermal gravimetric analysis (TGA), respectively, and the remaining eight

samples were machined with notches for fracture studies.

One-part epoxy

For comparison, a one-part epoxy resin with a latent amine curing agent was also tested. Araldite GY6010 (100.0 g) was mixed with Dyhard 100S (6.5 g) and Ancamine 2014FG (11.0 g). After determining the optimum curing conditions using differential scanning calorimetry, we prepared a large resin bar as described previously by thermal curing at 175°C for 1 h and 200°C for 2 h. We cut the large bar into pieces (about 5 × 1 × 0.5 cm each) and tested them following the same procedures that were used for the polyester resins.

Extraction of blends

To determine the amount of residual monomer in the pure, thermally cured resin samples, we extracted weighed pieces from the thermally cured disks with THF (a good solvent for the monomers) for 18 h. The extract was analyzed for monomer by gas chromatography (GC). We dried the extracted resin samples *in vacuo* overnight and then weighed them to determine the mass of extracted material. To determine the extent of phase separation on the fracture samples of the cured blends, Soxhlet extractions with THF (a good solvent for PSf) were conducted for 48 h. We then dried the samples *in vacuo* at room temperature overnight, and the fracture surfaces were analyzed via scanning electron microscopy (SEM). Six samples were extracted: four blends and two pure polyester resin controls.

Characterization

¹H-NMR spectra were recorded on a Bruker (Rheinstetten, Germany; model 250 MHz); chemical shifts were references to internal tetramethylsilane (TMS). For the uncured resins, we determined the relative molar concentrations of the functional endgroups and the presence of various types of oligomers using peak ratios in the ¹H-NMR spectra. We used this technique to distinguish three types of end groups: benzyl alcohol [$\delta = 4.90$, 1H], methacrylate esters [$\delta = 1.95$, 3H (methyl); $\delta = 5.55$, 1H (vinyl); $\delta = 5.95$, 1H (benzyl); $\delta = 6.15$, 1H (vinyl)], and styrenic groups (vinyl peaks: $\delta = 5.20$, 1 H; $\delta = 5.65$, 1 H; $\delta = 6.70$, 1 H]. We also used ¹H-NMR to identify chain-extending groups: benzyl ethers [two diastereomeric peaks: $\delta = 4.25$, 2H, and $\delta = 4.50$, 2H] and styrene dimer [$\delta = 3.60$, 1H (benzyl methane); $\delta = 6.35$, 2H (olefin)]. With a good sample properly run, all of these groups were well resolved. The greatest difficulty arose in quantification from poor integration of weak signals because of baseline noise. Therefore, multiple signals representing the

same moiety were weighted appropriately for the number of protons involved and averaged. The average of the individual functional group peaks were calculated as follows:

$$\langle \text{Sty} \rangle = (I_{5.20} + I_{5.65} + I_{6.70})/3 \quad (1)$$

$$\langle \text{MA} \rangle = [I_{5.55} + I_{6.15} + I_{5.95} + (I_{1.95}/3)]/4 \quad (2)$$

$$\langle \text{BE} \rangle = (I_{4.25} + I_{4.50})/2 \quad (3)$$

$$\langle \text{Sty Dimer} \rangle = [(I_{6.35}/2) + I_{3.60}]/2 \quad (4)$$

where $\langle \text{Sty} \rangle$ is the average intensity of the styrenic group hydrogen peaks, $\langle \text{MA} \rangle$ represents the methacrylate group, $\langle \text{BE} \rangle$ represents the benzyl ether group, and $\langle \text{Sty Dimer} \rangle$ represents the internal olefin produced when the styrenic groups dimerize.

The number-average degree of chain extension was also estimated from these integrated values as two times the appropriately weighted number of chain-extending moieties divided by the number of terminal moieties. The percentage endgroups was calculated as follows:

$$\% \text{Sty} = [\langle \text{Sty} \rangle / (\langle \text{Sty} \rangle + \langle \text{MA} \rangle + \langle \text{BA} \rangle)] \quad (5)$$

$$\% \text{MA} = [\langle \text{MA} \rangle / (\langle \text{Sty} \rangle + \langle \text{MA} \rangle + \langle \text{BA} \rangle)] \quad (6)$$

$$\% \text{BA} = [\text{BA} / (\langle \text{Sty} \rangle + \langle \text{MA} \rangle + \text{BA})] \quad (7)$$

where BA is the intensity of the benzyl alcohol endgroup peak. The average degree of chain extension, $\langle X_n \rangle$, was calculated as follows:

$$\langle X_n \rangle = (\text{Number of Chain Extenders}) / [0.5(\text{Number of Chain Ends}) + \langle \text{Sty Dimer} \rangle + \text{Total BE}] / [0.5(\langle \text{Sty} \rangle + \langle \text{MA} \rangle + \langle \text{BA} \rangle)] \quad (8)$$

Viscosities were determined with a Brookfield (Middleboro, MA) DV-III+ cone and plate rheometer. Measurements were made at 25°C; the reported value for the viscosity is the average of two separate measurements.

Single-edge notch-bending fracture experiments were conducted according to ASTM D5045 using a Dynastat instrument built by Dynastatics Instrument Corp. (Troy, NY). In general, five to eight samples were tested for each resin, and the average values are reported. Average sample dimensions were 41.13 × 10.42 × 4.32 mm. The experiments were conducted at a constant crosshead rate of 0.1 mm/s at room temperature (25.0 ± 2.3°C). For every sample, we initiated a sharp crack in the notch by scoring the sample with a razor blade immediately before the run.

Thermal stability studies were conducted with thermogravimetric analysis (Perkin-Elmer TGA 7, Shelton, CT). The temperature was ramped from 50 to 750°C at 20°C/min under either an air or a nitrogen atmosphere. The evolved gas analysis using gas chromatography in concert with mass spectroscopy (GC/MS) was conducted at Materials Analytical Services.²¹ A Hewlett Packard 5890-II GC-5985 mass spectrophotometer with a CDS Analytical model 2000 Pyroprobe with 1500 valved interface was used with a J&W DB-5ms capillary column (15 m × 0.25 mm-inner diameter (id) × 1 μ film, 8 psig for approximately 1.6 mL/min helium at 35°C). The oven was held at 35°C for 0.5 min, ramped to 323°C at 12°C/min, and held for 1.5 min. Mass spectra were acquired at 1.4 scans/s, mass range 25–225 u from 0–6 min and 35–400 u for the remainder, with a sensitivity change to maintain the scan rate. Part of the coil of the analytical column was placed in liquid nitrogen during the operation to cryofocus poorly retained analytes before the beginning of the GC/MS program. We used a different Hewlett Packard 5890 Series II plus gas chromatograph to determine the amount of residual monomer in the polyester resin disks that were thermally cured at 170°C for 2 h. In this case, HP-5ms (30 m × 0.25 mm, 0.25 μ) columns were used. Samples were held at 200°C for 1.5 min and then ramped to 325°C at 15°C/min.

Data for Young's modulus (E') and the thermal transitions were collected using a TA Instruments (New Castle, DE) dynamic mechanical analyzer (model 2980) in dual cantilever bending mode. Temperatures were scanned from –100 to 325°C at a rate of 20°C/min, and mechanical deformations were made at a frequency of 1 Hz. GPC was used to determine the molecular weights and molecular-weight distributions for the uncured resin mixtures and the PSf samples. The eluent was THF, and the samples were compared to a polystyrene universal calibration curve. GPC analysis easily detected oligomers in some samples for which the NMR analysis outlined previously yielded no integrable signal for chain-extending moieties. SEM was performed with a JEOL (Peabody, MA) 6400FE microscope at North Carolina State University.

Dielectric spectroscopy (DES) data were collected with a Novocontrol (Hundsangen, Germany) GmbH broadband dielectric spectrometer. We prepared the samples by coating the disks with a thin gold layer using a Denton Vacuum Large Desk II cold sputter/etch unit. Samples were fixed in a 22-mm diameter mask and placed in the sputter coater at 60 mTorr and 40 milliamps (mA) for 120 s on each side. Under these conditions, a gold layer with a thickness of about 1000 Å was deposited on each side of the film. Before placing the thin films in the sample cell, we measured their thicknesses in several places using a micrometer. The thicknesses of the ether-based resin films ranged from 0.128 to 0.428 mm, with the average thickness

TABLE I
Uncured Resin Compositions (Determined with ¹H-NMR)

| Resin sample | Physical state at 25°C | Viscosity at 20 rpm (cP) | End groups | | | Chain extension | | |
|--------------|------------------------|--------------------------|------------|---------|---------|-----------------|-----------|-----------|
| | | | MA (%) | Sty (%) | ROH (%) | Degree (n) | Dimer (%) | Ether (%) |
| A | Liquid | 340 | 47 | 53 | 0 | 0.30 | 0 | 100 |
| B | Liquid | 350 | 41 | 59 | 0 | 0.00 | 0 | 0 |
| C | Liquid | 770 | 51 | 45 | 4 | 0.34 | 0 | 100 |
| D | Liquid | 950 | 55 | 42 | 2 | 0.37 | 0 | 100 |
| E | Liquid | 2000 | 53 | 43 | 4 | 0.41 | 0 | 100 |
| F | Liquid | 2300 | 53 | 45 | 2 | 0.38 | 0 | 100 |
| G | Liquid | 3500 | 48 | 52 | 0 | 0.14 | 31 | 69 |
| H | Liquid | 9300 | 58 | 25 | 17 | 0.65 | 14 | 86 |
| I | Solid ^a | NA | 56 | 24 | 20 | 1.03 | 0 | 100 |
| J | Solid ^a | NA | 27 | 73 | 0 | 3.14 | 100 | 0 |
| K | Solid ^a | NA | 22 | 78 | 0 | 0.35 | 100 | 0 |
| L | Solid ^b | NA | 0 | 100 | 0 | 0.00 | 0 | 0 |

MA = methacrylic functional groups; Sty = styrenic functional groups; ROH = alcoholic functional groups; NA = not applicable.

^a Amorphous solid.

^b Crystalline solid, melting point = 89–90°C.

being 0.297 mm. The hydrocarbon-based resin films were noticeably thinner, with a range of 0.035 to 0.164 mm and an average of 0.0934 mm. DES measurements were made every 5° from –100 to 325°C at frequencies ranging from 10² to 5 × 10⁶ Hz.

RESULTS AND DISCUSSION

Uncured resins: compositions and properties

To pursue the objective of determining structure–property relationships for the cured matrices, the relative concentrations of functional groups and oligomers in the uncured resin mixtures must be known. However, the GPC method previously reported^{22,23} gives only an estimation of the resin composition because of peak overlap. ¹H-NMR proved to be a much more precise method for the determination of the relative molar concentrations of the functional endgroups and the presence of various types of oli-

gomers. These compositions, the physical states of the resins, and the viscosities (for liquids resins) are listed in Table 1. Two factors, monomer functionality and degree of oligomer chain extension, clearly make major contributions in the determination of the physical state of the uncured resin. As an illustration, resins A through G combined high ratios of acrylic functionality to hydroxyl functionality with relatively low degrees of chain extension, and as a result, these resins were liquid. Resins H and I, which had relatively high percentages of hydroxyl functionality and moderate degrees of chain extension, were more viscous or even solid at room temperature despite the high levels of acrylic functionality. Finally, the relatively high concentration of styrenic functionality in resins J and K clearly contributed to their solid physical states. Resin L was a pure, crystalline solid sample of M1.

In general, for applications such as composites where a liquid binder is often preferred, the relative

TABLE II
TGA Data for Thermally Cured Resins

| Resin sample | Cure temperature (°C) | Primary onset of weight loss (°C) | Change in weight (wt %) | Secondary onset of weight loss (°C) | Change in weight (wt %) | Char yield (wt %) |
|--------------|-----------------------|-----------------------------------|-------------------------|-------------------------------------|-------------------------|-------------------|
| A | 170 | 296 | 8.3 | 447 | 72 | 18 |
| B | 170 | 276 | 6.6 | 474 | 75 | 19 |
| D | 170 | 296 | 11 | 465 | 68 | 20 |
| K | 170 | 298 | 3.6 | 474 | 75 | 21 |
| L | 170 | 501 | 76 | | | 24 |
| A | 170,250 | 472 | 77 | | | 23 |
| B | 170,240 | 460 | 79 | | | 21 |
| D | 170,250 | 479 | 77 | | | 23 |
| K | 170,240 | 460 | 74 | | | 26 |

Samples were baked for 2 h at each of the temperatures indicated. TGA was conducted in a nitrogen atmosphere. Reported char yields were at 750°C under a nitrogen atmosphere.

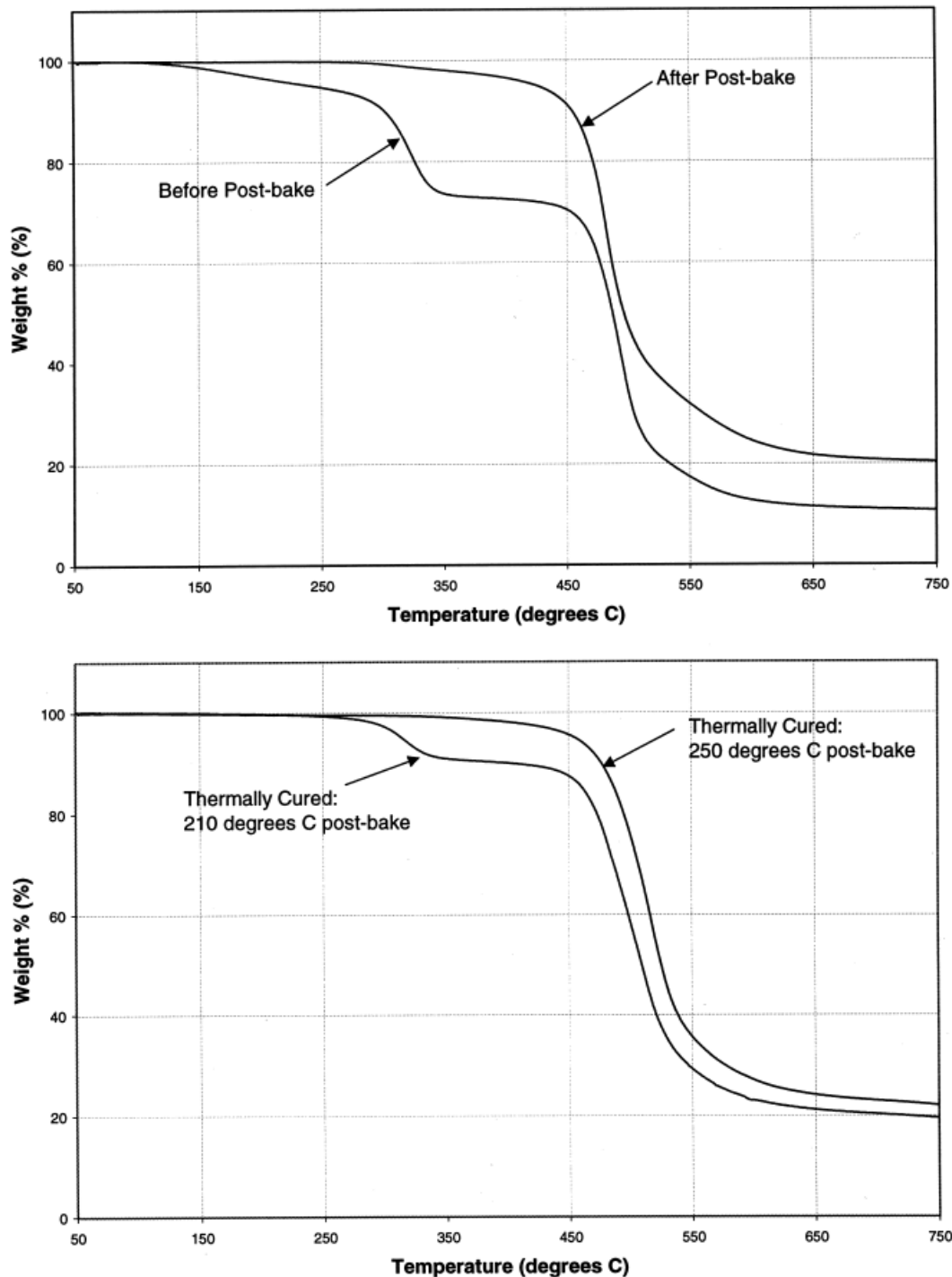


Figure 2 Illustrative TGA results before and after 250°C postbake for (top) photocured thin film and (bottom) thermally cured disk. Samples-cured polyester resin D.

amounts of the asymmetric monomer (M2) and the bis(methacrylic ester)-substituted monomer (M3) need to be maximized, whereas the amounts of the styrenic functional monomer (M1), hydroxyl functionality, and oligomer need to be minimized. Pure M1 was a crystalline solid with a melting point of 89–90°C, whereas the ester-containing monomers, M2 and M3, were liquids under ambient conditions. As

expected, the resin mixtures reduced the tendency of M1 to crystallize, but resins that had relatively high concentrations of M1 and/or oligomers existed as solids at room temperature. In addition, in some cases, the liquid resins phase-separated during storage at 4°C, resulting in a solid phase suspended in the liquid matrix; these solids could easily be redissolved by agitation. This phase separation was most likely due

TABLE III
Effect of Thermal Curing Schedule on the Thermal Stability of Polyester Resins

| Description and curing procedure | Primary onset of weight loss (°C) | Change in weight (wt %) | Secondary onset of weight loss (°C) | Change in weight (wt %) | Char yield (wt %) |
|----------------------------------|-----------------------------------|-------------------------|-------------------------------------|-------------------------|-------------------|
| Polyester resin A | | | | | |
| 170°C | 296 | 8.3 | 447 | 72 | 18 |
| 170 and 190°C | 293 | 8.2 | 460 | 70 | 20 |
| 170, 190, and 210°C | 288 | 7.2 | 463 | 71 | 19 |
| 170, 190, 210, and 230°C | 467 | 77 | | | 22 |
| 170, 190, 210, 230, and 250°C | 466 | 78 | | | 20 |
| 170 and 210°C | 291 | 7.0 | 471 | 72 | 19 |
| 170, 210, and 250°C | 467 | 77 | | | 22 |
| 170, and 250°C | 472 | 77 | | | 23 |
| Polyester resin D | | | | | |
| 170°C | 296 | 11 | 465 | 68 | 20 |
| 170 and 190°C | 295 | 13 | 469 | 72 | 16 |
| 170, 190, and 210°C | 284 | 7.6 | 461 | 71 | 19 |
| 170, 190, 210, and 230°C | 286 | 8.0 | 463 | 70 | 20 |
| 170, 190, 210, 230, and 250°C | 461 | 77 | | | 23 |
| 170 and 210°C | 291 | 9.2 | 465 | 69 | 19 |
| 170, 210, and 250°C | 462 | 77 | | | 22 |
| 170 and 250°C | 479 | 77 | | | 23 |

TGA program = hold for 1 min at 50°C, heat from 50 to 750°C at 20.0°C/min. Atmosphere = N₂.

to crystallization of the M1 monomer. Finally, the presence of oligomers, of course, generally increased the viscosity of the fluid. Other factors, such as hydrogen bonding between residual alcoholic groups, also influenced the viscosity of some of the resins.

Curing and thermal stability

Previous reports cited thermal curing schedules for these polyester resin blends requiring very long times (up to 33 h) and increasing temperatures until a final cure temperature of 250°C was reached.⁵ From a practical standpoint, the time and temperature required to

obtain a cured resin with reasonable properties should be determined. For this purpose, TGA studies were used to determine extent of cure and to evaluate the thermal and thermo-oxidative stability of cured samples (Table II). Sample L, which did not contain any ester functionality, showed very good thermal stability after a 2-h cure cycle at 170°C. In contrast, the other samples that were thermally cured at 170°C lost 4–10% of their total weight at an onset temperature below 300°C. The sample weights then leveled out until the onset of a second degradation at >450°C. When these samples were treated with a second post-cure cycle at 240–250°C and then analyzed by TGA,

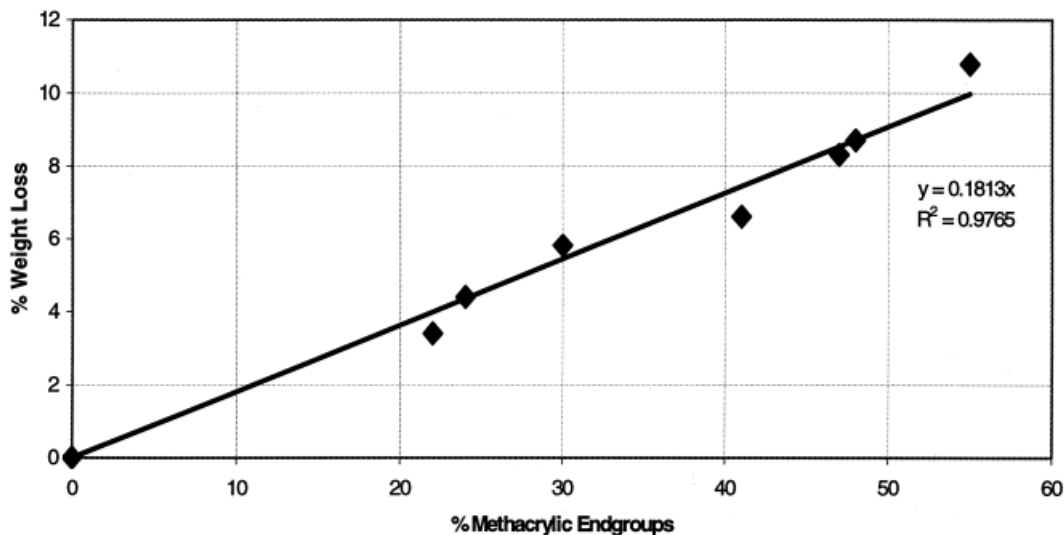


Figure 3 Correlation between the amount of methacrylic endgroups in the resin and the amount of weight loss observed at temperatures below 350°C during a dynamic TGA scan of the cured resin.

TABLE IV
GC/MS Results: Volatile Decomposition Products that Were Collected from the Heating of Cured Polyester Resin (Sample D from Table I) to Temperatures up to 325°C

| Relative amount | Identity | Comments |
|-----------------|-------------------------------------|--|
| 86% | Bis(vinylphenyl) ether ^a | From cleavage of crosslink groups (see Fig. 1 and Scheme 4) |
| 9% | Methacrylic acid | Residual acid from synthesis or cleavage product from M2 and M3 monomers |
| 3% | Benzoic acid | Benzoyl peroxide decomposition by-product |
| 0.7% | Toluene | Residual solvent from monomer synthesis |
| 0.7% | <i>N,N</i> -dimethylformamide | Residual inhibitor |
| <0.5% | Water | |
| <0.5% | Acetone | |
| <0.5% | Benzene | |
| <0.5% | Other aromatics | |

^a Molecular weight = 222–224.

they had good thermal stability at temperatures above 300°C in either a nitrogen or an air atmosphere.

TGA also showed that the samples photocured at room temperature lost a larger percentage of weight at the lower temperatures than those that were thermally cured, suggesting that the photocured samples did not cure completely due to vitrification of the matrix. However, a postbake thermal treatment at 250°C afforded these thin film samples with the same good high-temperature stability as described previously. In all cases, the degradation onset temperatures were relatively insensitive to atmosphere (air or nitrogen), and the char yields were very low: 0–23% in nitrogen and 0% in air. Figure 2 shows illustrative TGA traces of samples before and after the 250°C thermal treatment. When an appropriate curing regimen was used, the thermooxidative stability of this family of resins

rivalled that of other high-performance polymeric materials such as cyanate ester resins. Results for char yield were lower than those for competing materials such as high-temperature epoxies, cyanate ester polymers, and toughened bismaleimides, which give values between 30 and 50% in nitrogen.²⁴

A more in-depth study on the effect of curing schedule on the thermal stability of polyester resins showed that curing temperatures of at least 230°C were needed to afford materials that did not show weight losses with onsets below 300°C (Table III). In the case of resin sample D, an even higher curing temperature of 250°C was necessary. This weight loss below 300°C probably resulted from either residual monomer (incomplete cure due to vitrification) and/or volatile compounds formed during heat-induced structural rearrangements.^{3,5} Figure 3 shows the relationship be-

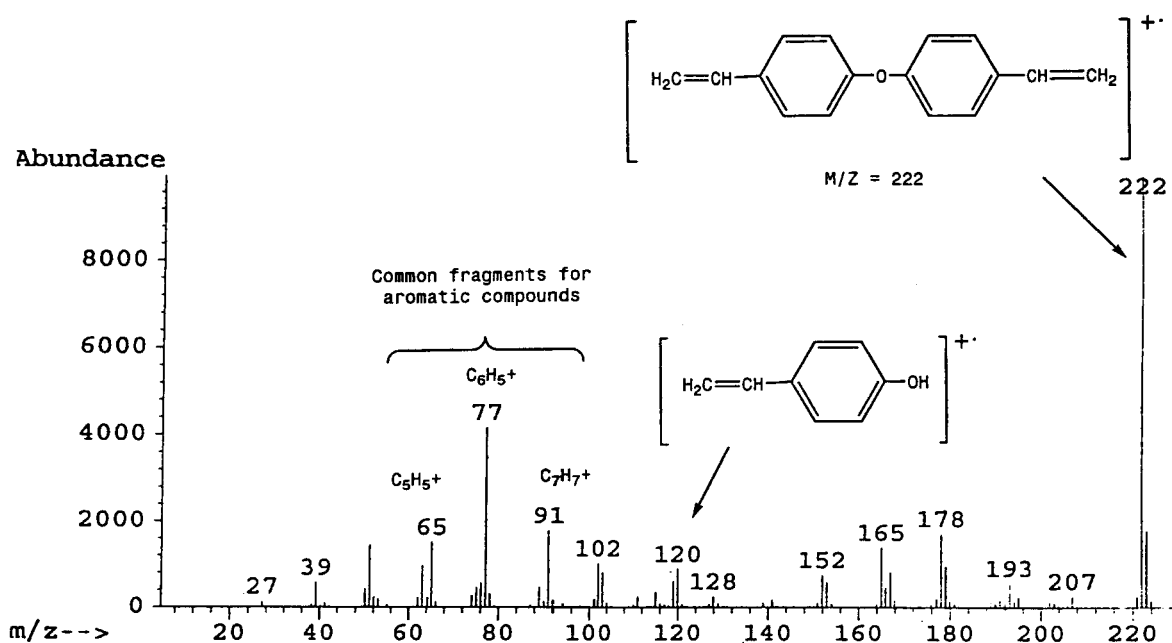
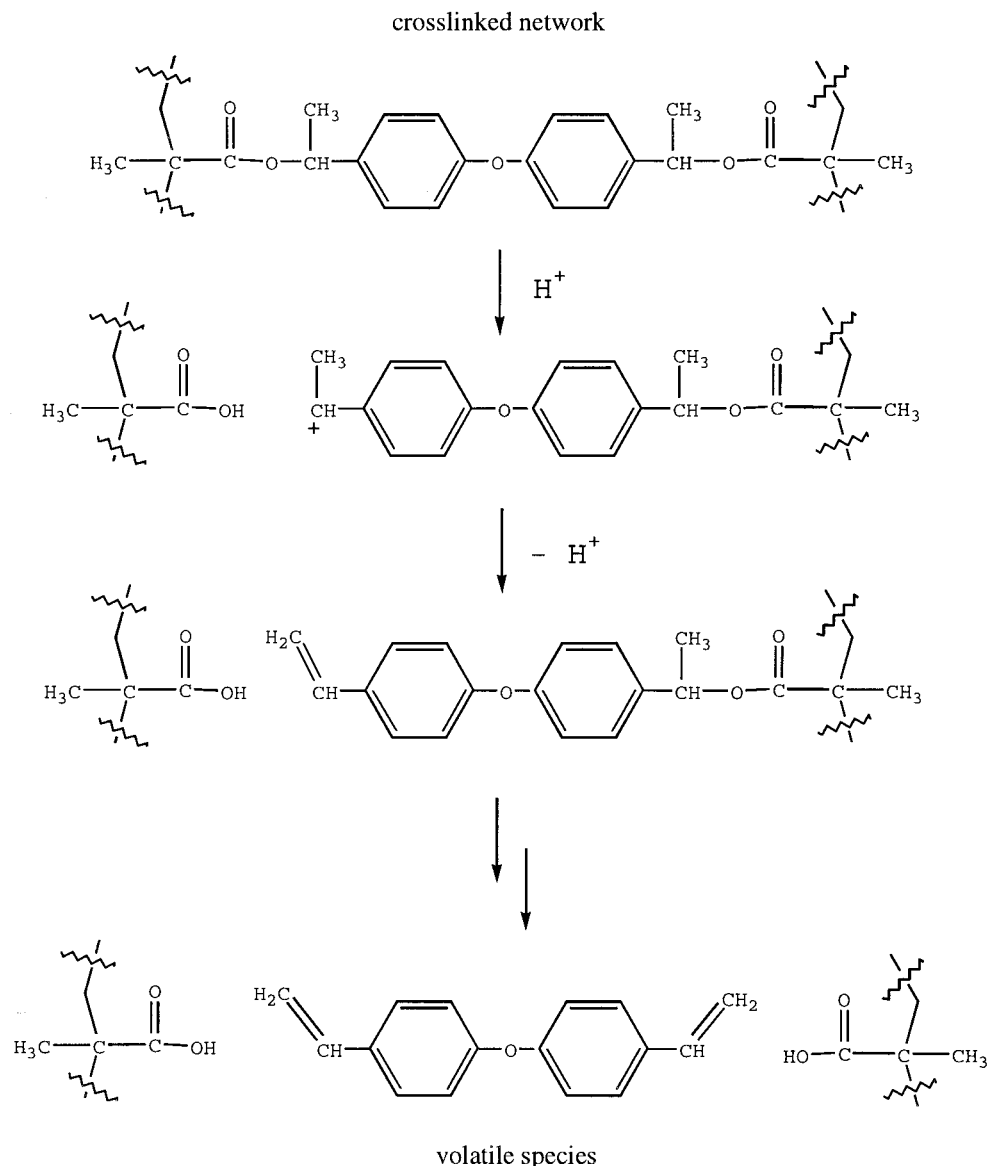


Figure 4 Mass spectrum for primary volatile product from low-temperature decomposition of thermally cured (170°C/2 h) polyester resin (sample D from Table I).



Scheme 4 Pathway for decomposition of a crosslinked structure at 250°C to produce **M1** derivative as a volatile by-product.

tween the amount of ester functionality in the resins and the weight loss observed at temperatures below 350°C. The linear relationship strongly supports the hypothesis that thermal decomposition of the ester linkages produced the observed weight loss.

The identities of the volatile components that evolved during the low-temperature weight loss (observed for polyester resin samples cured at temperatures below 230°C) were determined with GC/MS. We used this technique to separate and identify the compounds as they evolved during a temperature ramp up to 325°C (Table IV). Resin sample **D** was thermally cured at 170°C for 2 h before analysis. The mass spectrum for the primary volatile product, **M1**, is shown in Figure 4. A route for the generation of this species through acid-catalyzed bond cleavage is shown in Scheme 4. This confirmed a reported obser-

vation that the ester groups of a model compound, 4,4'-bis(1-acetoxyethyl)diphenyl ether, were catalytically cleaved at temperatures of $\geq 230^\circ\text{C}$ or greater to give the vinyl functional monomer and acetic acid.²³ Other volatile products, such as methacrylic acid (residual either from synthesis or from decomposition) and benzoic acid (from benzoyl peroxide decomposition), were also present. Extracting the cured resin with THF and performing GC on the extract revealed that only minute traces of unreacted monomer were present after a 2 h thermal cure at 170°C. The amount of residual monomer was more than two orders of magnitude lower than the amount that would be required to account for the observed weight loss. This result confirms the theory that the **M1** obtained in the GC/MS experiment was the by-product of the decomposition of the crosslinked matrix and not simply residual monomer.

TABLE V
DES Data for Ether-Based Cured Polyester Resin Thin
Films over a Wide Range of Compositions

| Resin | Endgroups ^a | | | ϵ' ^b | T_g ^c |
|-------|------------------------|---------|---------|--------------------------|----------------------|
| | MA (%) | Sty (%) | -OH (%) | | |
| L | 0 | 100 | 0 | 3.1 | Unclear ^d |
| B | 41 | 59 | 0 | 3.3 | 280°C |
| G | 49 | 51 | 0 | 3.4 | 235°C |
| F | 53 | 45 | 2 | 3.5 | 260°C |
| D | 55 | 42 | 2 | 3.6 | 290°C |
| I | 56 | 24 | 20 | 4.4 | 285°C |
| H | 58 | 25 | 17 | 4.5 | 250°C |

^a Resin compositions were estimated previously by ¹H-NMR. Please see Table I.

^b Reported ϵ' values were measured at 25°C and 1 MHz.

^c T_g was determined from the maximum in the $\tan \delta$ curve at a frequency of 1 MHz.

^d This material was not polar enough to produce a clear peak.

The observed weight losses for the polyester resins were much lower than the calculated values for the decomposition of all of the difunctional ester linkages. Indeed, some of the styrenic groups must have reacted with the matrix either before the other side of the molecule was cleaved or during the diffusion of the molecule through the matrix. In the latter case, the amount of volatiles that actually escaped from the resin would be very sensitive to the ratio of the surface area of the article to its volume. Therefore, larger molded parts are not expected to exhibit as much

weight loss as the very small castings and thin films tested herein.

DES

DES is a powerful technique for the determination the dielectric constant, or permittivity, of a material by measurement of the orientation of molecular dipoles in a restricted environment under the influence of an electric field.²⁵ By varying the frequency of the oscillating electric field and the temperature over wide ranges, we studied time- and temperature-dependent molecular motions of the cured polyester resin films. Just as the modulus of a material can be separated into storage (real) and loss (imaginary) components with DMA, the complex dielectric constant (ϵ^*) can be separated into dielectric storage (ϵ') and dielectric loss (ϵ'') with DES. Therefore, the glass-transition temperature (T_g) and secondary relaxations of these polymers with polar functional groups could be measured.

The DES results demonstrated the expected relationship between chemical composition and ϵ' (Table V). The measured ϵ' was lowest for the resins that were almost entirely **M1** monomer, and it increased as the concentration of polar methacrylic or alcoholic groups in the resin increased. In particular, resins with high alcohol endgroup content (which occurred from the incomplete reaction of the diol starting material during resin preparation) had the highest ϵ' values of the samples analyzed.

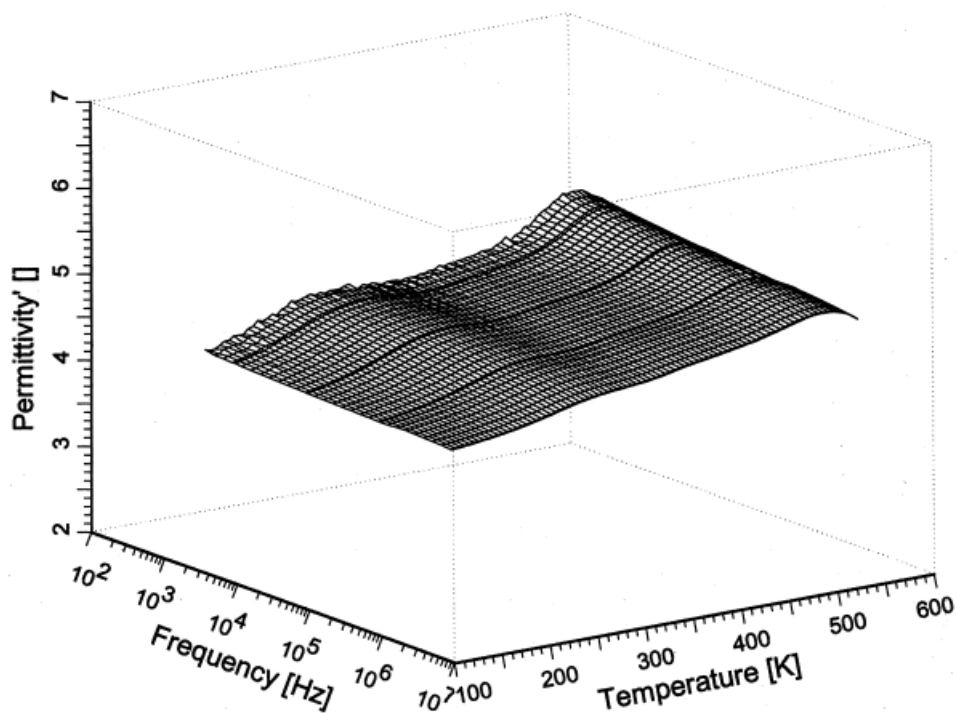


Figure 5 ϵ' as a function of temperature and frequency for a crosslinked polyester film (made from resin sample E).

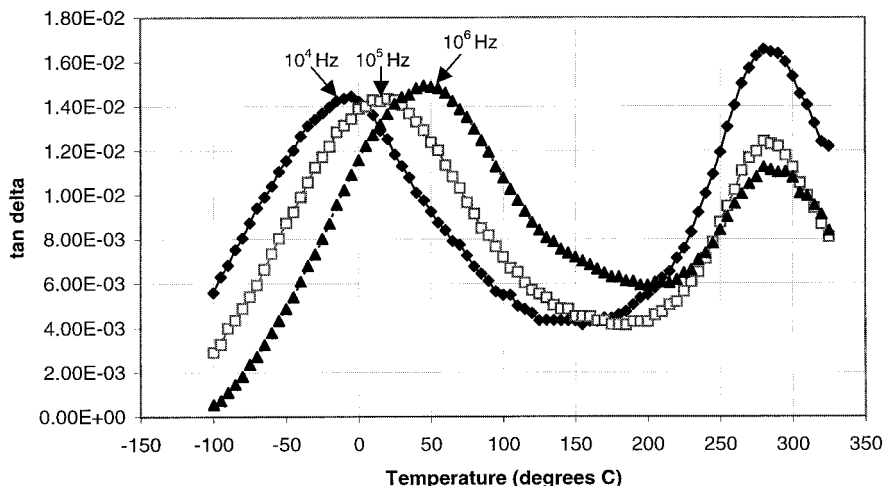


Figure 6 Frequency dependence of the β -transition for a cured polyester resin thin film with methacrylic functionality (sample D from Table I, photocured then postbaked at 170°C/30 min and 250°C/4 h).

For many microelectronics applications, the material's ϵ' needs to be stable (either always low or always high) over a wide temperature range. However, ϵ' is fundamentally temperature related as an indirect result of density and polar interactions.²⁶ For nonpolar polymers, ϵ' decreases with an increase in temperature because density decreases as temperature increases. Another factor influencing the dielectric behavior of a material is its chemical structure, which directly affects the charge distribution and statistical thermal motion of polar groups. Therefore, for most polar polymers, changes in intramolecular and intermolecular interactions cause ϵ' to increase as temperature increases. In general, ϵ' values for the thin polyester films studied here did not show much variation over a wide range of temperatures and frequencies (Fig. 5). Indeed, this result was not surprising because copolymers of styrene and methacrylate are known to

have ϵ' values that are fairly independent of temperature because the contributions of the nonpolar styrene groups are balanced by the contributions of the polar methacrylate groups.²⁶ T_g , taken as the highest temperature peak maximum in the dielectric loss tangent ($\tan \delta$) versus temperature curve, was constant over the range of frequencies studied. However, the β -transition (T_β), which was most likely due to the crankshaft rotation of the methacrylate functional group, was very sensitive to frequency (Fig. 6).

DES was also used to monitor the extent of cure of the films. Figure 7 illustrates that the duration of the postbake cycle affected $\tan \delta$. As the curing progressed, the low-temperature β -transition increased from 35 to 45°C, and T_g increased from 245 to 280°C (the longer the postbake, the higher the loss tangent). This was caused by the loss of chain mobility resulting from the higher degree of crosslinking obtained by

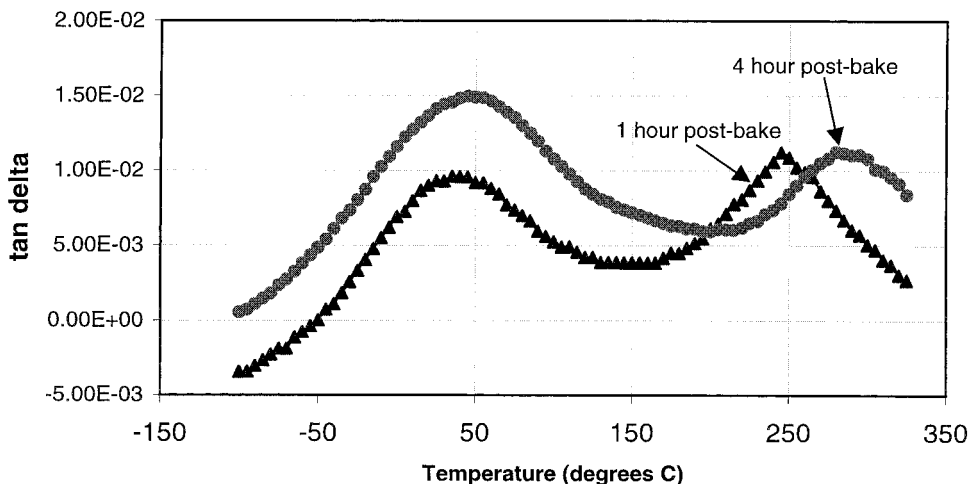


Figure 7 $\tan \delta$ as a function of temperature for cured polyester resin (sample D from Table I) thin films that were photocured and then postbaked at 250°C for various amounts of time. As the stiffness of the chain (due to structural rearrangements) or degree of crosslinking increased with time, T_g also increased. Frequency = 1 MHz.

TABLE VI
Data from DES Measurements on Polyester Thin Films

| Cure time at 250°C (h) | Measurements at 25°C and 1 MHz | | |
|---------------------------|--------------------------------|------------------------------|-------------------------------|
| | ϵ' (± 0.2) | ϵ'' (± 0.005) | $\tan \delta$ (± 0.001) |
| 1 | 3.4 | 0.032 | 0.009 |
| 2 | 3.6 | 0.038 | 0.011 |
| 3 | 3.6 | 0.046 | 0.013 |
| 4 | 3.6 | 0.046 | 0.013 |

Thin films were made from resin sample **D** and were photocured and postbaked at 170°C for 30 min and at 250°C for various times.

further curing the film. The maximum cure at 250°C was obtained by 3 h of reaction time, as illustrated by the data in Table VI. As the temperature increased, ϵ' increased slightly for all of the films. In many of the samples, a small minimum was observed in the ϵ'' value at a frequency of 2×10^5 Hz. The location of the peak was very close to the β -transition peak that is observed for poly(methyl methacrylate),²⁷ and therefore, it most likely arose from the incorporation of the methacrylic functionalized monomers, **M2** and **M3**.

The results from DMA were compared to results from analysis of the same samples by DES (Fig. 8). Thermal transitions such as T_g and higher order transitions can be obtained by either analytical method. However, in this case DES could provide complementary data, clearly revealing transitions that were difficult to observe with DMA. Due to the broad range of frequencies scanned by DES, the β -transition caused

by the motion of side groups around the main backbone of the resin could be seen much more clearly in a dielectric spectrum as shown in Figure 8. The T_g data from both DMA and DES for the same film corresponded relatively well. T_g results from the DMA analysis were consistently slightly lower (15–30°C) than those obtained by DES. This could have resulted from the substantially longer DES run time (10 h vs. ~2 h for DMA); therefore, the DES samples could have continued to postcure for a longer amount of time during the actual analysis. In addition, the samples were tested at very different frequencies (1 MHz for DES and 1 Hz for DMA), so the observed difference in T_g was likely to have resulted from the inherent time dependence of these techniques.

Fracture analysis of unreinforced resins

We determined the thermal and mechanical properties of unreinforced, cured polyester resins quantitatively to provide baseline values for the toughening studies. A one-part epoxy was also tested to provide a second frame of reference. The results from the fracture, DMA, and TGA experiments on these materials are summarized in Table VII. These results can be compared to literature values for other commercially available, high-temperature resistant materials such as polyimides²⁸ and cyanate ester resins.²⁴ Polyimides, such as General Electric's thermoplastic Ultem, have even better thermal stability than the resins investi-

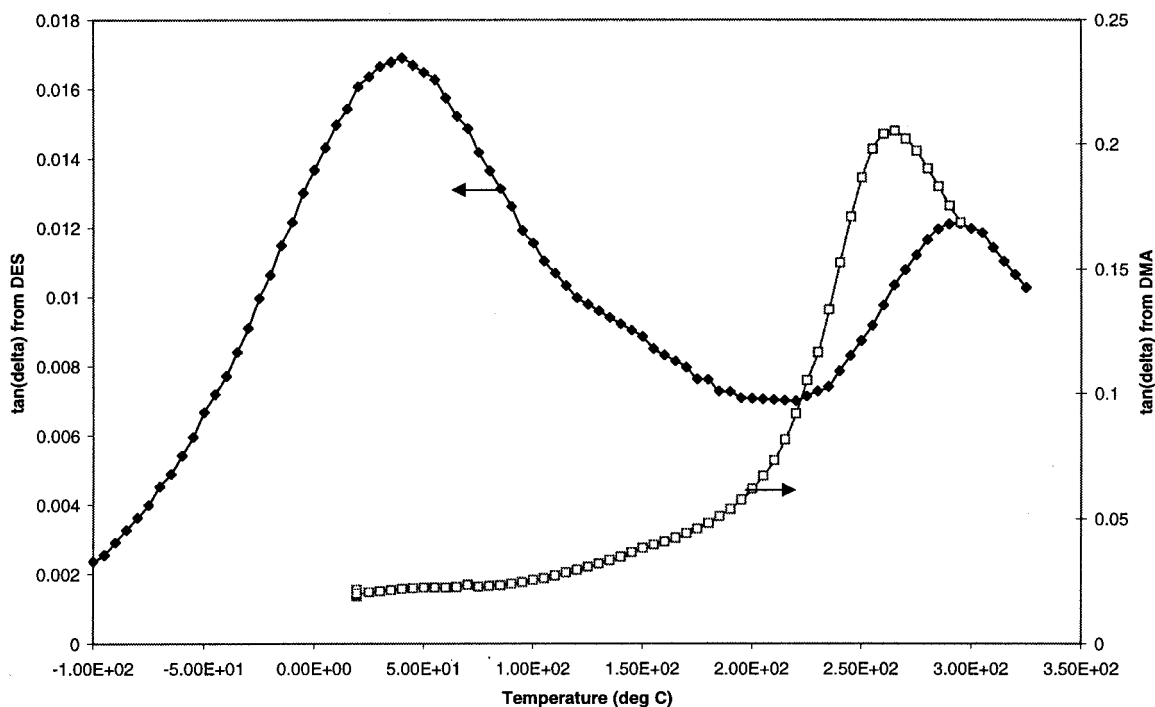


Figure 8 Comparison of DES (frequency = 1 MHz) and DMA (frequency = 1 Hz) data for the same cured polyester resin thin film (resin sample **E**, photocured and then postbaked at 170°C/30 min and 250°C/4 h).

TABLE VII
Summary of Data from the Characterization of Mechanical Properties and Thermal Stabilities of Polyester Resins and an Epoxy

| Resin ^a | 5% Weight loss temperature ^b | E' at 25°C (MPa) ^c | E' at 200°C (MPa) ^c | T_g (°C) ^d | K_{IC} (MN/m ^{3/2}) | G_{IC} (J/m ²) |
|--------------------|---|---------------------------------|----------------------------------|-------------------------|---------------------------------|------------------------------|
| Epoxy | 380 | 675 | 10 | 168 | 1.28 ± 0.05 | 613 ± 75 |
| L | 490 | 879 | 228 | 232 | 0.14 ± 0.01 ^e | 9.1 ± 0.2 ^e |
| G | 450 | 792 | 388 | 219 | 0.38 ± 0.04 | 57 ± 13 |
| E | 450 | 628 | 280 | 189 | 0.30 ± 0.05 | 43 ± 19 |

^a Please see Table I for chemical structures and compositions of polyester resins.

^b Determined by TGA under nitrogen.

^c E' as determined by DMA with dual cantilever fixture (frequency = 1 Hz).

^d T_g was determined by DMA with the temperature at the maximum in tan δ .

^e These values are the average of experiments on two specimens rather than the standard of five. This material was so brittle that most of the other samples broke prior to measurement during zeroing of the instrument's displacement.

gated herein, but this property is obtained at the expense of the processability. The polyimides must be processed at very high temperatures or made from the amic acid precursor, which gives off large amounts of water during cure. Cyanate ester resins, on the other hand, offer processing advantages such as a volatile-free curing pathway and relatively low melting temperatures when compared to other traditional high-temperature-resistant materials.

Epoxyes are one of the toughest classes of thermosetting resins, and this was reflected in the experimental results, as shown in Table VII. In contrast, the relative brittleness of the polyester resins was demonstrated by the low-plane strain fracture toughness (K_{IC}) and fracture energy (G_{IC}) values. These values were a function of the high crosslink density, and they were comparable to those reported for many other types of thermosets such as unreinforced phenolic resins.²⁹ Therefore, to make these resin systems commercially viable for adhesive applications including weld or rivet replacement, the polyester resins needed to be toughened in a manner analogous to the way phenolic resins are typically rein-

forced with rubber. For the polyester resins, the key was to reach the goal of a tougher material while maintaining the high temperature stability and facile processability.

Toughening strategies

Traditional methods for improving the toughness of a rigid thermoset include decreasing the crosslink density of the material, introducing flexible linkages to the rigid structure, or adding an impact modifier such as an elastomer, a thermoplastic, rigid particulate fillers, or core-shell particles. The latter approach of adding a toughening agent to the resin matrix was chosen for this system. The additives that were tested include poly(butadiene) and silicone-reactive rubber adducts, a commercially available high-performance thermoplastic, and some analogous low-molecular-weight, thermally stable oligomers. The oligomers were used both as prepared and functionalized to improve reactivity with the resin.

TABLE VIII
Summary of Data from Experiments to Determine the Effect of Blending Polyester Resins with Poly(butadiene)-Based or PDMS-Based Rubber Adducts

| Material ^a | 5% weight loss temperature ^b | E' at 25°C (MPa) ^c | T_g (°C) ^d | K_{IC} (MN/m ^{3/2}) | G_{IC} (J/m ²) |
|--------------------------------|---|---------------------------------|-------------------------|---------------------------------|------------------------------|
| Resin L | 490 | 879 | 232 | 0.14 ± 0.01 ^e | 9.1 ± 0.2 ^e |
| Resin L + polybutadiene adduct | 450 | 668 | Unclear | 0.21 ± 0.03 | 24 ± 8.3 |
| Resin G | 450 | 792 | 219 | 0.38 ± 0.04 | 57 ± 13 |
| Resin G + polybutadiene adduct | 350 | 461 | 218 | 0.53 ± 0.05 | 227 ± 30 |
| Resin C | 420 | 1150 | 239 | 0.35 ± 0.06 | 45 ± 11 |
| Resin C + PDMS adduct | 410 | 1040 | 206 | 0.43 ± 0.04 | 118 ± 16 |

^a Please see Table I for a key to the polyester resin compositions. Polybutadiene and PDMS adducts were benzylidene-cyano acetate functionalized.

^b Determined by TGA under air.

^c E' as determined by DMA with dual cantilever fixture (frequency = 1 Hz).

^d T_g was the temperature of maximum tan δ in the DMA trace.

^e These values are the average of experiments on two specimens rather than the standard of five. This material was so brittle that most of the other samples broke prior to measurement during zeroing of the instrument's displacement.

TABLE IX
Data from Synthesis and Functionalization of PSf Oligomers

| PSf oligomer endgroups | Targeted M_n (g/mol) | Observed M_n^a (g/mol) | GPC results | | |
|------------------------|------------------------|--------------------------|-------------|--------|------|
| | | | M_n | M_w | PDI |
| Stilbenic | 15,000 | NA ^b | 7,100 | 21,900 | 3.08 |
| Stilbenic | 15,000 | NA ^b | 6,170 | 21,700 | 3.51 |
| Phenolic | 8,000 | 8,600 | 5,050 | 11,500 | 2.28 |
| Styrenic | 8,000 | 8,800 | 6,150 | 17,600 | 2.86 |
| Phenolic | 2,000 | 2,000 | 2,340 | 3,330 | 1.43 |
| Phenolic | 2,000 | 2,000 | 2,410 | 3,570 | 1.48 |
| Styrenic | 2,000 | 2,200 | 2,607 | 3,890 | 1.49 |

M_w = weight-average molecular weight; NA = not analyzed; PDI = polydispersity index of the molecular weight distribution.

^a We estimated molecular weights by using the ratio of endgroups to aromatic repeat units on the ¹H-NMR.

^b Because of the relatively high weights of these oligomers, the ¹H-NMR endgroup signals were too small to integrate accurately.

Hydrocarbon and silicone rubber adducts

One of the most widely utilized strategies for improving the toughness of an inherently brittle, highly crosslinked thermoset such as a phenolic resin is the addition of rubber or a reactive rubber adduct. The rubber phase separates to form “soft” domains, which can relieve stress and dissipate energy through cavitation and shear yielding. We used this methodology as the first strategy for toughening the polyester resins. Up to 20 wt % of a functionalized polybutadiene was added in an effort to improve the K_{IC} and G_{IC} values. The results from these experiments are summarized in Table VIII. Some significant increases in the fracture values were obtained, with K_{IC} increasing by 40–50% and G_{IC} increasing by 250–400%. However, as expected, the thermal stability and E' decreased with the addition of the poly(butadiene)-based material.

To overcome the reduction in thermal stability observed with the use of a traditional hydrocarbon rubber toughener, we explored silicone rubbers as a class of alternative, thermally stable toughening additives. Several studies in the literature have shown that silicone elastomers can be used to improve the toughness of high-performance epoxies^{30–33} and polyimides.^{34–36}

To this end, we evaluated a range of different silicone resins with vinyl, methacrylate, or benzylidene cyanoacetate functional endgroups or sidegroups as thermally stable toughening additives for the polyester resins. We hoped that the reactive groups on the silicones would prevent the low-surface-energy materials from migrating out of the matrix during cure. Poly(dimethylsiloxane) (PDMS)-, poly(methylphenylsiloxane)-, and poly(diphenylsiloxane)-based materials, including homopolymers and reactive adducts of a range of molecular weights, were all screened for compatibility and reactivity. However, in many cases the incompatibility of the resins with the silicones resulted in gross phase separation during cure. Alternative curing conditions may alter the kinetics of phase separation of these materials to give the desired results, but this avenue has not yet been fully explored. The only sample that provided small enough silicone domains for a meaningful fracture test was the benzylidene-cyanoacetate-functionalized PDMS, and the results from this test are shown on Table VIII. A toughening effect was observed when this blend was compared to the pure polyester resin, and the thermal stability and E' decreased slightly but not as dramatically as with the butadiene blends.

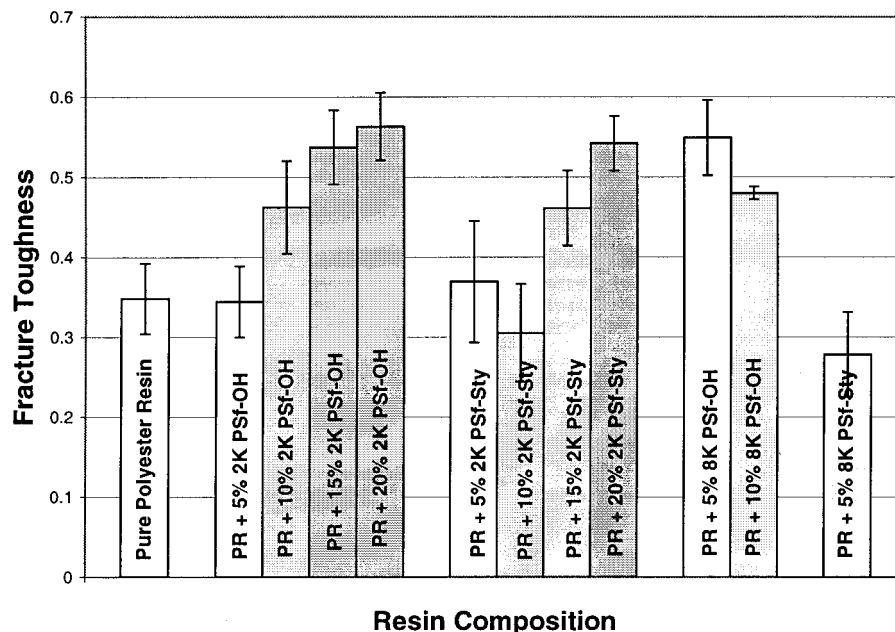
TABLE X
Summary of Preliminary Experiments to Determine the Effects of Blending Polyester Resin (Sample G from Table I) with PSf Toughening Additives of Various Molecular Weights and Chain-End Functionalities

| Toughening additive | | 5% weight loss Temperature ^b | E' at 25°C (MPa) ^c | K_{IC} (MN/m ^{3/2}) | G_{IC} (J/m ²) |
|-----------------------------|------|---|---------------------------------|---------------------------------|------------------------------|
| Identification ^a | wt % | | | | |
| None | 0 | 450 | 790 | 0.38 ± 0.04 | 57 ± 13 |
| 15K PSf–stil | 5 | 430 | 1780 | 0.46 ± 0.1 | 109 ± 26 |
| 2K PSf–OH | 15 | 410 | 670 | 0.61 ± 0.1 | 143 ± 47 |
| 2K PSf–sty | 15 | 410 | 920 | 0.65 ± 0.09 | 180 ± 40 |

^a 15K PSf–stil = PSf oligomer with stilbene endgroups and M_n = 15,000 g/mol; 2K PSf–OH = PSf oligomer with phenolic endgroups and M_n = 2000 g/mol; 2K PSf–sty = PSf oligomer with styrenic endgroups and M_n = 2000 g/mol.

^b Determined by TGA under air.

^c E' = as determined by DMA with dual cantilever fixture (frequency = 1 Hz).



| KEY: | abbreviation | composition | endgroups | M_n (g/mol) |
|------|--------------|-----------------|-----------|---------------|
| | PR | polyester resin | | |
| | 2K PSf-OH | polysulfone | phenolic | 2,000 |
| | 2K PSf-sty | polysulfone | styrenic | 2,000 |
| | 8K PSf-OH | polysulfone | phenolic | 8,000 |
| | 8K PSf-sty | polysulfone | styrenic | 8,000 |

Figure 9 Effect of PSf oligomers of various molecular weights and endgroup functionalities on K_{1C} ($\text{MN}/\text{m}^{3/2}$) of thermally cured polyester resin (sample C from Table I) and blends.

Commercially available poly(arylene ether sulfone)

Another strategy that has shown promise for toughening a brittle thermoset for high-temperature applications involves the incorporation of a nonreactive, commercially available, high-performance thermoplastic as a toughening additive. With this in mind, high molecular weight, commercially available PSf was screened for solubility in the polyester resins. This material has excellent thermal stability, with a 5% weight loss temperature of 550°C (in air). Although this thermoplastic did demonstrate some solubility in the resin at low loadings, the viscosity of the mixture became extremely high as the concentration of the PSf was increased to levels that would be necessary to observe any toughness enhancement. In an effort to improve the solubility of the PSf thermoplastic, we prepared a random copolymer with sulfone and phenyl phosphine oxide linkages (Scheme 3). McGrath and coworkers have shown that these materials effectively toughen vinyl ester networks that are somewhat similar in structure to the polyester resins described

herein.³⁷ In addition, the bulky phenyl sidegroups should improve the solubility of the copolymer when compared to pure PSf. Unfortunately, in this case, the random copolymer did not have improved solubility in the polyester resin when compared to the PSf homopolymer. Because the increase in viscosity made this method less attractive from a processibility standpoint, this approach was abandoned in favor of the oligomer approach described next.

Thermoplastic oligomers

Because the high-molecular-weight thermoplastics demonstrated limited solubility in the polyester resins without the use of a cosolvent, lower molecular weight PSf oligomers were synthesized and evaluated. The functionalization of the chain ends of these toughening oligomers provided a route to reactive adducts. Two different approaches were used for the preparation of oligomers with reactive functional groups on the chain ends. For the first attempt, *trans*-4-hydrox-

TABLE XI
Summary of the Thermal, Mechanical, and Fracture Data for Polyester Resin (Sample C from Table I)
Blended with PSf-Based Oligomers

| Toughening additive ^a | 5% weight loss temperature ^b | E' at 25°C (MPa) ^c | E' at 200°C (MPa) ^c | T_g (°C) | K_{IC} ^d (MN/m ^{3/2}) | G_{IC} (J/m ²) |
|----------------------------------|---|---------------------------------|----------------------------------|------------|--|------------------------------|
| None (control) | 420 | 1150 | 906 | 239 | 0.346 | 45.1 |
| None (control) | 410 | 1270 | 1290 | 230 | 0.350 | 51.8 |
| 5% 2K PSf-OH | 430 | 1250 | 656 | 214 | 0.344 | 53.7 |
| 10% 2K PSf-OH | 420 | 1690 | 765 | 226, 186 | 0.462 | 80.6 |
| 15% 2K PSf-OH | 450 | 1260 | 1050 | 234, 171 | 0.537 | 107.6 |
| 20% 2K PSf-OH | 460 | 1370 | 980 | 215, 166 | 0.563 | 130.9 |
| 20% 2K PSf-OH ^d | | 1750 | 1280 | 216, 167 | | |
| 5% 2K PSf-sty | 430 | 1370 | 1210 | 242 | 0.369 | 63.5 |
| 10% 2K PSf-sty | 450 | 1680 | 1410 | 275 | 0.305 | 46.5 |
| 15% 2K PSf-sty | 440 | 1800 | 1640 | 217 | 0.461 | 82.3 |
| 20% 2K PSf-sty | 450 | 1970 | 1770 | 226 | 0.542 | 115.1 |
| 5% 8K PSf-OH | 450 | 1200 | 927 | 236, 191 | 0.549 | 114.9 |
| 10% 8K PSf-OH | 450 | 977 | 597 | 227, 198 | 0.480 | 92.7 |
| 10% 8K PSf-OH ^d | | 899 | 553 | 221, 198 | | |
| 5% 8K PSf-sty | 450 | 1360 | 1180 | 238 | 0.278 | 39.6 |

^a 2K or 8K PSf-OH = PSf oligomer with phenolic endgroups and $M_n = 2000$ or 8000 g/mol, respectively; 2K or 8K PSf-sty = PSf oligomer with styrenic endgroups and $M_n = 2000$ or 8000 g/mol, respectively.

^b Determined by TGA under air.

^c E' as determined by DMA with dual cantilever fixture (frequency = 1 Hz).

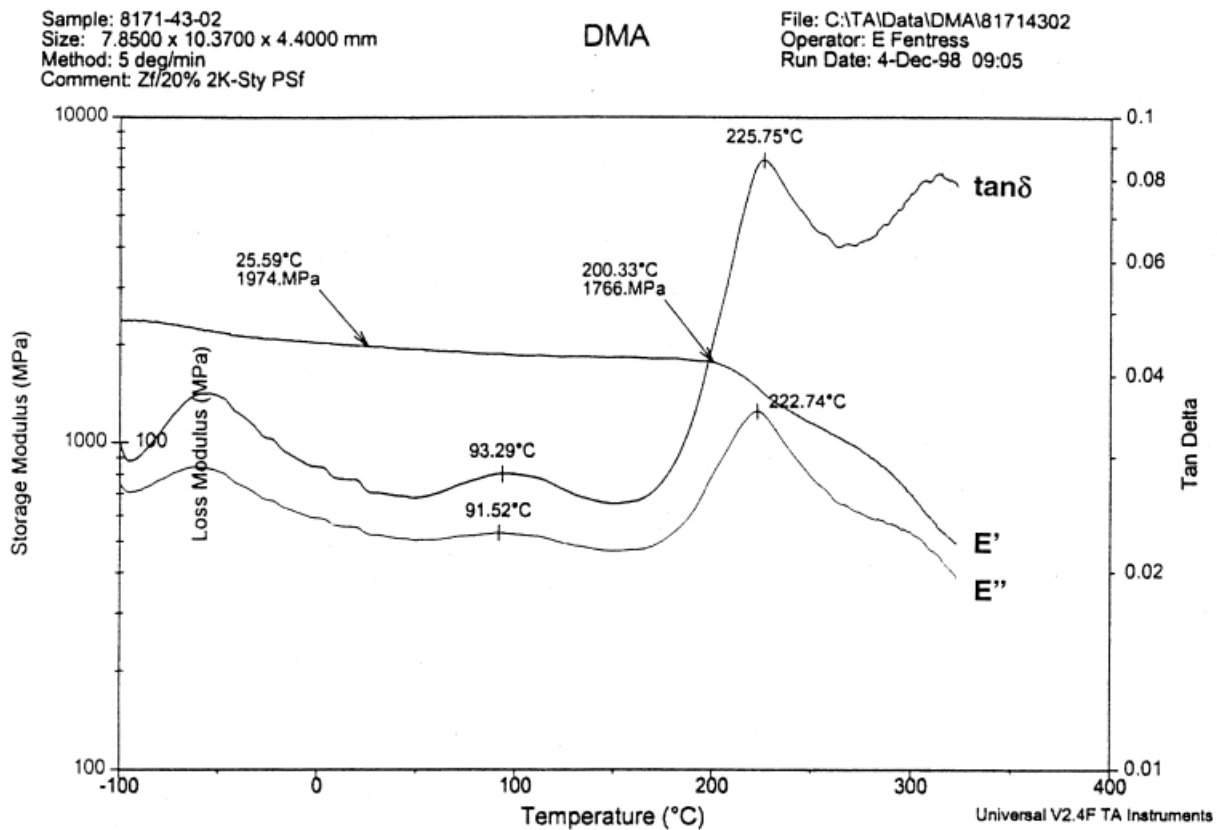
^d DMA experiment was repeated to verify results.

ystilbene, which was used as an endcapping agent, was charged directly to the reaction mixture before the polymerization (Scheme 2). This compound was chosen because of its high boiling point, commercial availability, and ability to copolymerize³⁸ with the styrenic and methacrylic functionality of the polyester resins. The molecular weight of the oligomeric product was controlled by the amount of monofunctional monomer, which created a stoichiometric imbalance. In the second approach, we synthesized PSf oligomers with phenolic endgroups (PSf-OH) by adding a precise excess of bisphenol A (Scheme 1). The ratio of bisphenol A to bis(4-chlorophenyl) sulfone was also used to control the molecular weight of each oligomer. In a second step, we converted a portion of each batch of oligomer from phenolic endgroups to styrenic endgroups using vinylbenzyl chloride and a phase-transfer catalyst (Scheme 1).^{19,20} The results from the syntheses of PSf oligomers are contained in Table IX.

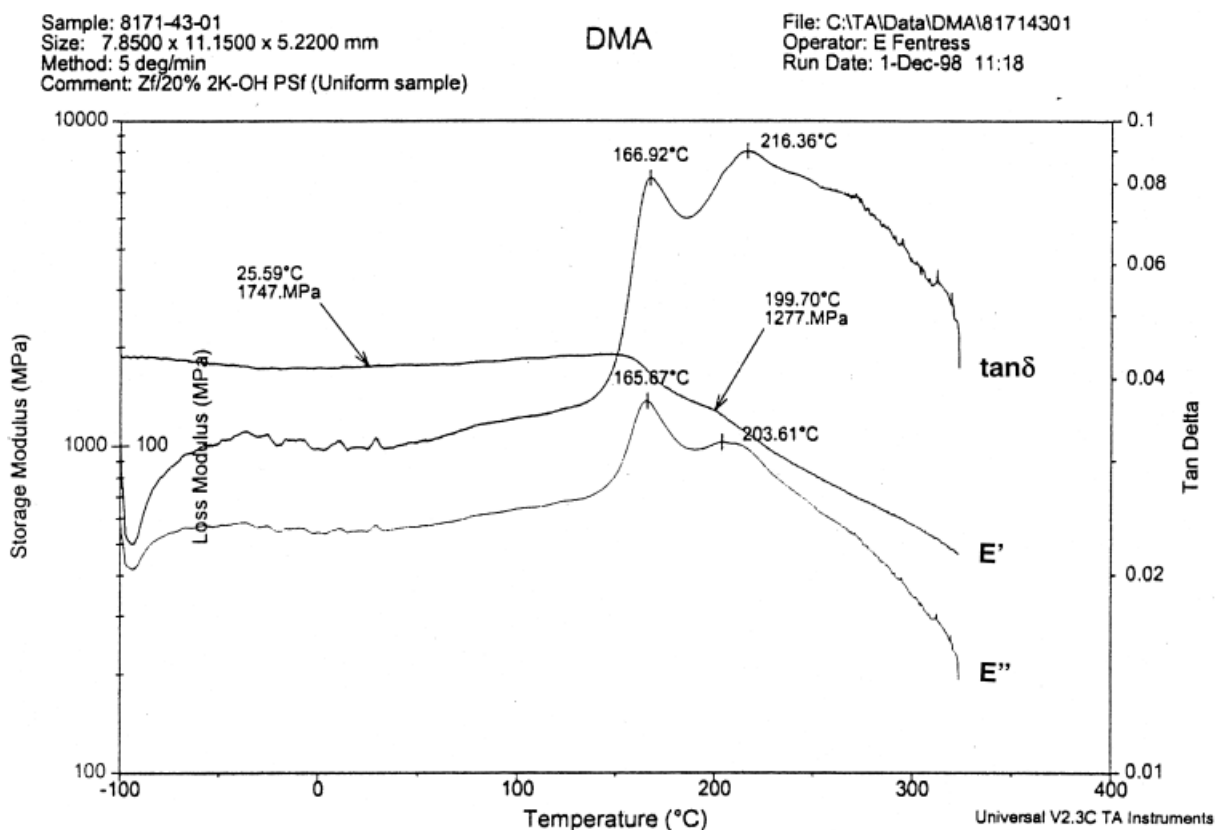
Paralleling the commercially available PSf resin, the medium molecular weight ($M_n = 15,000$ g/mol) PSf with reactive stilbene endgroups (PSf-stil) had limited solubility in the polyester resins. Although 5 wt % of this material could be dissolved in the uncured resins to give a homogeneous solution, attempts to make more concentrated solutions resulted in some phase separation and extremely high viscosities. Therefore, lower molecular weight ($M_n = 2000$ g/mol) PSf oligomers were prepared and blended with the polyester resins. Preliminary screening studies (Table X) revealed that the addition of 15 wt % PSf oligomer with styrenic reactive endgroups (PSf-sty) resulted in significant increases in the fracture values, with a nearly

twofold increase in K_{IC} and a threefold increase in G_{IC} . The blend of the oligomer with unreactive phenolic endgroups with the polyester resin also showed significant improvements when compared to the neat resin. In addition, these improvements were made without a significant decrease in the thermal stability or E' of the material. Indeed, from the standpoint of improving the fracture toughness without decreasing the high-temperature performance, blends with the PSf oligomers were superior to the blends with the reactive polybutadiene-based rubber adducts. On the basis of these results, a systematic study of the effect of PSf molecular weight, endgroup functionality, and percentage loading as an additive on the toughness of the polyester resins was conducted.

Summaries of the data from this systematic study of the toughening of polyester resins with PSf oligomers are shown in Figure 9 and Table XI. We prepared and analyzed duplicate sample sets of the unreinforced polyester resins to verify the reproducibility of the data. Clearly, K_{IC} and G_{IC} could be improved substantially without a detrimental loss of the thermal stability and mechanical properties. We obtained the best results by blending the resin (sample C) with 20% of either 2000 g/mol PSf oligomer. Comparison of the 2000 g/mol oligomers with different endgroup functionalities confirmed that the reactive styrenic endgroups were not necessary to improve the toughness of the material. In fact, the preponderance of the data suggests that the phenolic functional, nonreactive oligomers were more effective. These blends had K_{IC} values that were about 60% higher than the unreinforced control and G_{IC} values that were 230–260%



(a)



(b)

Figure 10 DMA traces for polyester resin (sample C from Table I) blends with 2000 g/mol PSf oligomers with (a) reactive styrenic endgroups and (b) nonreactive phenolic endgroups.

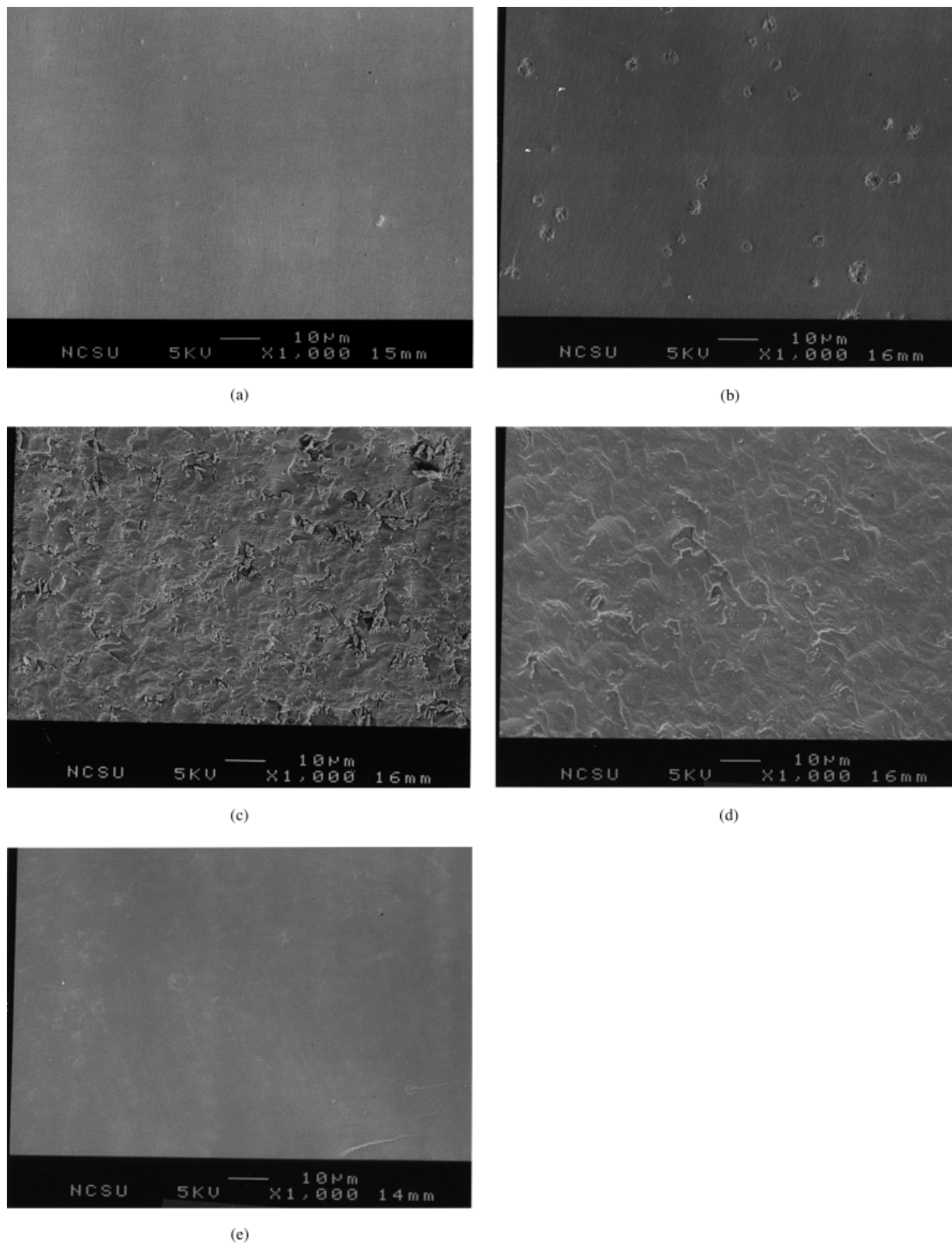


Figure 11 SEM photographs of fracture surfaces of cured samples: (a) pure polyester resin G after THF extraction (control), (b) blend polyester resin G with 5 wt % PSf-stil before THF extraction, (c) blend polyester resin G with 5 wt % PSf-stil after THF extraction, (d) blend polyester resin G with 15 wt % PSf-OH after THF extraction, and (e) blend polyester resin G with 15 wt % PSf-sty after THF extraction.

higher than the unreinforced control. The improvements in the toughness were made without sacrifice of the thermal stability of the material. Moreover, the blends had slightly better thermal stability than the unreinforced, pure polyester resin control (Table XI). Much lower amounts (5%) of the higher molecular weight (8000 g/mol) oligomer additive were needed to obtain similarly good results. Attempts to dissolve 10 or 15% of the 8 K 8000 g/mol oligomers were difficult or unsuccessful due to large viscosity increases (even when the solution was heated to $\sim 100^\circ\text{C}$).

The DMA data showed that E' generally increased slightly when the polyester resin was blended with the PSf oligomers. More importantly, the stiffness at a high temperature (200°C) remained satisfactory for the blends. The data for T_g of the blends indicated that more macrophase separation occurred for the phenolic functional oligomers than for the styrenic functional oligomers (Fig. 10). Two T_g 's were evident in all of the samples with relatively high concentrations of the PSf oligomers with phenolic endgroups. In contrast, the samples containing the PSf oligomers with styrenic endgroups showed a single T_g , indicating that phase separation occurred only on a very small scale.

The effect of the PSf endgroup functionality on the morphology of the blends was also probed with SEM. The surfaces of cured samples from fracture studies were analyzed both before and after extraction with THF, which was a good solvent for PSf. Analysis of the fracture surfaces showed significant qualitative differences between the extracted and unextracted blends and the pure, unreinforced polyester resin (Fig. 11). The rough surfaces of the extracted blend samples containing the PSf with the stilbenic or phenolic endgroups showed that these thermoplastics could be selectively removed from the polyester matrix with THF [Fig. 11(c, d)]. It also confirmed that these relatively unreactive endgroups led to cured blends with large phase-separated areas, which gave rise to the dual T_g 's that were observed by DMA. In contrast, the smooth surface from the sample containing the PSf with the styrenic endgroups indicated that this material could not be extracted from the polyester matrix [Fig. 11 (e)]. This provided further evidence for the chemical reaction of the styrenic-functionalized oligomer, in particular, with the resin monomers during cure. For comparison, control samples of the pure polyester resin, which were fractured and extracted by the same procedure as the blends, showed very smooth surfaces [Fig. 11 (a)].

CONCLUSIONS

The thermosetting unsaturated ester resins described herein provide a combination of room-temperature processibility for B-staging and heat resistance for

harsh environments. TGA revealed a linear relationship between the cured polyester resin composition and weight loss due to decomposition of ester linkages during the required postbake cycle. The volatile compounds that resulted from this process were identified, and a mechanism for their formation was proposed. After appropriate processing at high temperatures, these polyester resins did not have any significant weight loss at temperatures below 300°C in an air or nitrogen atmosphere. DMA and DES were used to determine that the cured polyester resins exhibited the following major thermal transitions: $T_g = 200\text{--}300^\circ\text{C}$ and $T_\beta = -5$ to 45°C . The temperature of these transitions depended on the resin composition, the extent of cure, and the oscillation frequency. The β -transition arose from rotation of the polar pendant groups.

Fracture studies revealed that the unreinforced polyester resins were brittle when thoroughly cured. The resins with relatively high percentages of ester linkages had higher K_{IC} and G_{IC} values than those with high percentages of styrenic functional groups. Blending low-molecular-weight PSf oligomers with the polyester resins resulted in substantial increases in the K_{IC} and G_{IC} values. These improvements were made with neither significant reduction in thermal stabilities and high-temperature mechanical properties of the blends that was observed for the butadiene-based rubber blends nor the phase incompatibilities observed for the silicone-based blends. In addition, the facile room-temperature processibility for B-staging of the resins was maintained for the polyester-PSf blends. The PSf oligomers did not need reactive functional groups on the chain ends to toughen the polyester resins effectively. Therefore, the synthetic step of converting the polysulfone chain ends from phenolic to styrenic groups was unnecessary.

Comparison of PSf oligomers with two different molecular weights, 2000 and 8000 g/mol, showed that higher molecular weight PSf provided the same degree of toughness at a much lower concentration. The blends with PSf oligomers containing phenolic or stilbenic chain end functional groups gave more macrophase separation during cure than the blends with the styrenic endcapped oligomers. Cured blends of the polyester resins with polybutadiene-based reactive rubber adducts showed increased K_{IC} and G_{IC} values when compared to the neat resins. Unfortunately, as expected, these improvements were accompanied by a moderate loss in thermal stability and stiffness. Cured blends of the polyester resins with a silicone-based reactive rubber adduct showed increased K_{IC} and G_{IC} values when compared to the neat resins. Although the thermal stabilities of the cured polyester-silicone blends were excellent, phase separation problems were significant.

The authors extend their appreciation to Boris Zaitsev and Irina Shvabskaya of the Russian Academy of Sciences for useful technical discussion. They also thank Fran Dennis, who conducted the GC and GPC analyses, and Jeff Hatcher, who synthesized the benzylidene cyanoacetate rubber and silicone adducts. Rick Clark and Sonya Mims-Barnette are thanked for technical assistance; Bruce Adams, Mike Brown, Marlene Hontz, and Richard Wilder are thanked for training in the operation of various analytical instruments.

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