

# Latent nucleophilic initiators for melt processing phenolic–epoxy matrix composites

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## Abstract

Phenolic–epoxy matrix compositions have been investigated for preparing tough, flame retardant fiber reinforced composites. Melt composite fabrication with these materials requires latent initiators for the curing reaction due to the high viscosities of the matrix resins. The objective is to provide a means for ensuring stability (i.e. no reaction) of the phenolic–epoxy matrix resins at  $\sim 140^\circ\text{C}$  while the matrix is applied to the fiber preforms, then to effect rapid reaction at the cure temperature of  $\sim 180\text{--}200^\circ\text{C}$ . We have investigated the strategy of embedding the initiators for matrix cure within the fiber sizing to achieve this goal. The cure times can be significantly reduced since high initiator levels can be employed with this approach. Reaction kinetics were investigated by differential scanning calorimetry to predict composite cure times. Monomeric initiators such as tris(2,4,6-trimethoxyphenyl)phosphine encapsulated in thermoplastic polyimide fiber sizings yielded promising results. Composite toughness and fatigue properties of these flame retardant composites are excellent. © 2000 Published by Elsevier Science Ltd.

*Keywords:* Phenolic; Epoxy; Latent

## 1. Introduction

Phenolic resins are of great interest in the composite industry in view of their excellent flame retardance and cost effectiveness [1–4]. However, the common procedure for curing phenolic Novolac resins, e.g. by reaction with hexamethylenetetramine (HMTA), releases volatiles during the cure, producing networks with numerous voids and high crosslink densities. This results in materials which lack the toughness necessary for structural applications [5–9]. An alternative to curing with HMTA is to crosslink the phenolic Novolac resin with epoxy reagents [10–12]. This reaction proceeds by nucleophilic addition without the release of any volatiles, thereby creating a void-free network (Fig. 1) [13,14].

Networks prepared with high compositions of epoxies crosslinked with phenolic Novolacs are used in microelectronics packaging applications [15]. However, these materials are not flame retardant due to the large offset of the flammable epoxy component. By contrast, flame retardance can be achieved by using a stoichiometric (and weight)

excess of the phenolic component [16]. Network densities can also be controlled to maximize both toughness and stiffness by tailoring the stoichiometry and functionality of the reagents [17,18]. Fracture toughness and stress relaxation tests show that networks prepared with phenolic novolac oligomers having an average functionality of  $\sim 7.1$  and with a stoichiometric offset of about three phenolic hydroxyl groups per epoxide have better toughness (higher  $K_{1c}$ ) than commercial untoughened aerospace epoxy networks [18].

Due to high viscosities of the phenolic–epoxy resins, melt composite fabrication is challenging. The resin must be heated to  $\sim 140\text{--}145^\circ\text{C}$  to achieve sufficiently low viscosity ( $\sim 5\text{ Pa s}$ ) for efficient fiber preform impregnation in melt processes, and the resin viscosity must remain stable at those temperatures for an extended period. In addition, it is desirable for the resin to react rapidly at cure temperatures of about  $180\text{--}200^\circ\text{C}$  to prepare composite components within a few minutes. Embedding the cure initiators in the fiber sizing allows both of these seemingly paradoxical requirements to be met. Since the initiator is not in contact with the resin in the processing “resin pre-bath,” stable viscosity can be maintained during this stage. Also, relatively high initiator concentrations can be placed in the fiber sizings to achieve rapid matrix cure at elevated temperatures.

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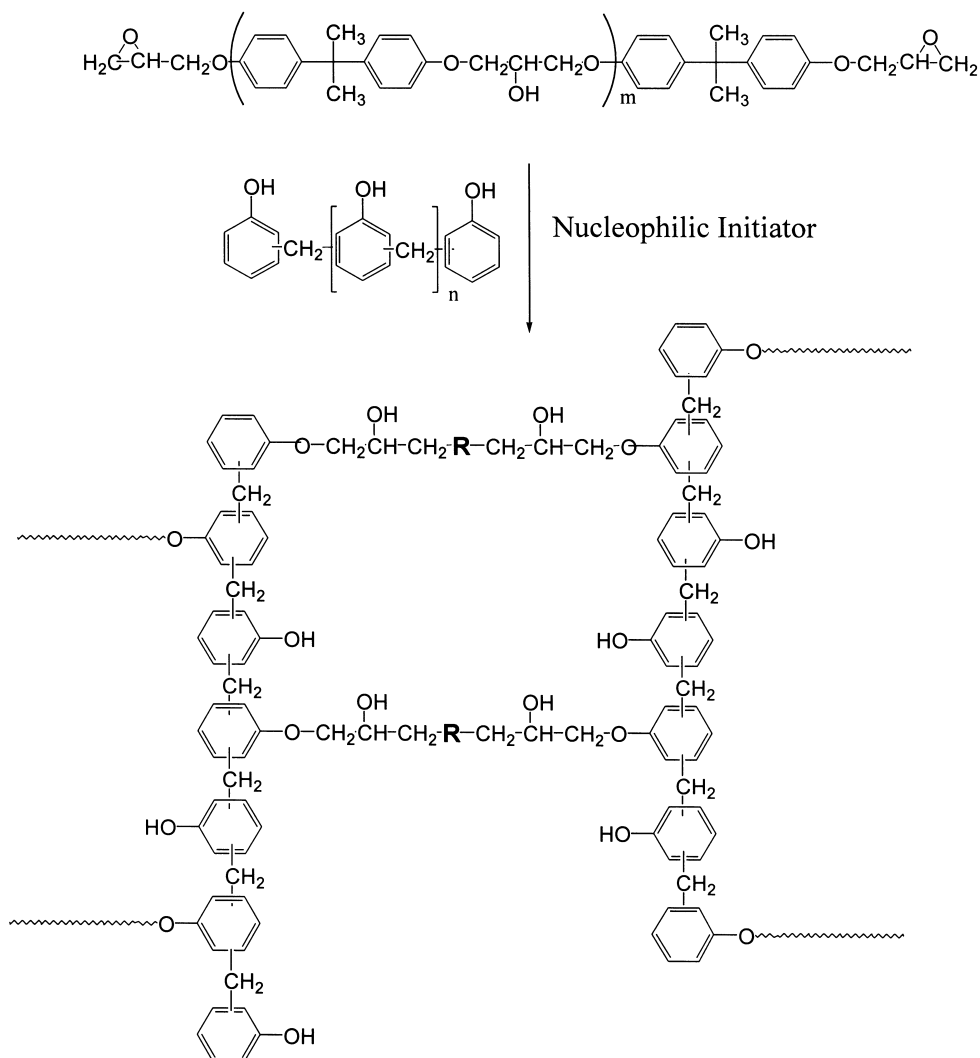


Fig. 1. Phenolic/epoxy network formation.

This paper focuses on an investigation of the kinetics of the phenolic–epoxy curing reaction with different types of initiators as well as the effects of placing the initiators within the fiber sizings. Several initiators were investigated to determine the effects of initiator structure on the cure rates at elevated temperatures. Composite panels were prepared by melt prepegging the sized fibers, followed by curing in a press for the appropriate cure cycles (determined by kinetic analysis). Composites prepared with the latent initiators embedded on the fibers (cured relatively rapidly) vs. those made without initiator (and cured for long times at higher temperatures) exhibited comparable properties.

## 2. Experimental

### 2.1. Materials

AS-4 unsized but surface treated 12 K tow fibers and  $G'$

(Hexcel's proprietary sizing) sized 12 K tow fibers, were obtained from Hexcel. Tetrahydrofuran (EM Sciences) was refluxed over sodium with a small amount of benzophenone as an indicator for dryness and distilled immediately prior to use. The poly(hydroxyether) and the "commercially modified poly(hydroxyether) sizing" were donated by Phenoxy Associates, Rock Hill, SC. Phthalic anhydride was obtained from Aldrich and sublimed prior to use. Succinic anhydride was obtained from Aldrich, and stored under nitrogen prior to use. Dimethylaminopyridine (DMAP) was obtained from Aldrich and used as received. 2,2'-Bis [4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (bisphenol A dianhydride), obtained from General Electric, was recrystallized from toluene and acetic anhydride four times, then washed with toluene and *n*-heptane. The purified bisphenol A dianhydride was dried in the vacuum oven at 140°C overnight immediately prior to use. *Meta*-phenylene diamine (Aldrich) was sublimed using an 80°C oil bath prior to use. Tripropylamine was obtained

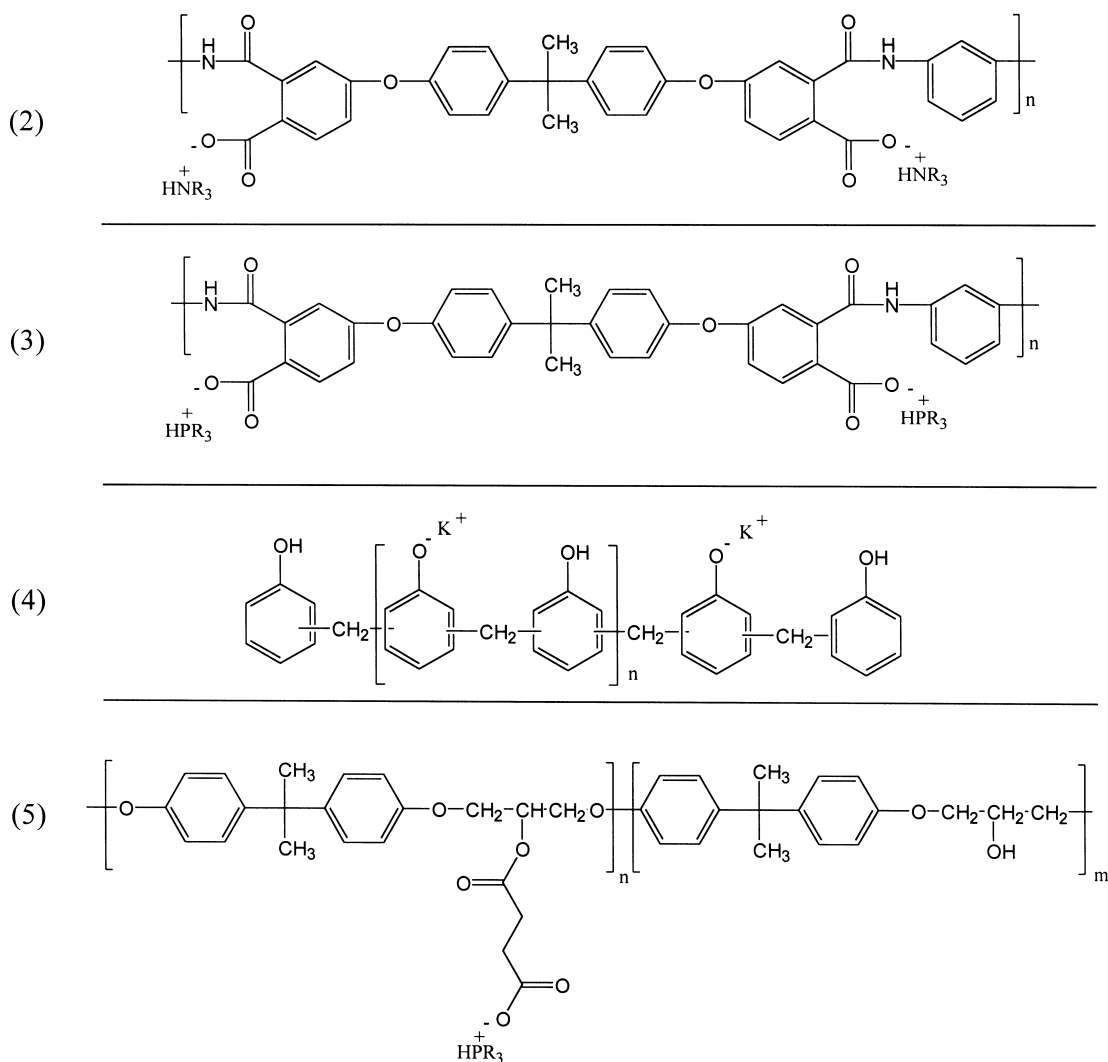


Fig. 2. Poly(amic acid) control (2) and latent initiator (3–5) sizing materials.

from Aldrich and used as received. The commercial phenol–formaldehyde novolac resin was provided by the Georgia Pacific Corp., Decatur, GA (Product #GP-2073). The molecular weight by proton NMR was 760 g/mol. Epon 828 epoxy resin was obtained from Shell Chemical. Triphenylphosphine (TPP) and tris(2,4,6-trimethoxyphenyl)phosphine (TMOPP) were obtained from Aldrich and used as received. Sodium acetate, rubidium acetate and cesium acetate were obtained from Aldrich and used as received. Acetic acid was obtained from Aldrich and used as received.

## 2.2. Resin preparation by melt mixing (for DSC samples and pre-pregging)

To a three neck round bottom flask equipped with a vacuum tight mechanical stirrer and a vacuum adapter was added phenolic novolac (65 wt.%). The flask was heated in an oil bath to 170°C. When the novolac began to

liquefy at 170°C, mechanical stirring was initiated, and a heat gun was used to facilitate the process. Once all the novolac was liquefied, a slight vacuum was applied for about 3 min to partially degas the novolac. The epoxy cross-linking component (35 wt.%), which had been degassed in a vacuum oven at ~60°C, was then added to the novolac. The flask was sealed and a vacuum was applied incrementally to prevent the material from swelling into the vacuum line. Once full vacuum was achieved (2–5 Torr) the solution was stirred for 2 min to degas the blend. The hot melt was then poured into aluminum pans and cooled in a dry ice/isopropanol bath. The resin was stored at room temperature prior to use.

## 2.3. Solvent mixing for rheology measurements

To a 100 ml round bottom flask was added ~2–3 g epoxy resin (35 wt.%), novolac (65 wt.%) and initiator (triphenylphosphine). The solids were dissolved in acetone (~30% by

wt.) with stirring. The solvent was evaporated first by a Rotovap and then in a vacuum oven at room temperature for 2–3 days until all the acetone had been removed. Samples were stored at ambient temperature and pressure until used.

#### 2.4. Sample preparation for DSC

The novolac and epoxy were melt mixed as described above with no added initiator, then ground to a powder. The initiator was crushed to a powder and mixed with the novolac–epoxy powder. For the kinetic comparisons between initiators, 2.0 mol% initiator was used based on the equivalents of epoxy in the resin. For determination of composite cure cycles, the initiator concentration was determined by the weight percent sizing in the composites, to model the kinetic behavior of the composite panels.

#### 2.5. Synthesis of Ultem™ type poly(amic acid)

Bisphenol A dianhydride (51.3032 g, 0.0986 mol) was weighed into a dry 500 ml round bottom flask with a stir bar. The flask was then sealed with a rubber septum and purged with nitrogen. Dry THF (250 ml) was added to the flask by cannula. Phthalic anhydride (0.7524 g, 0.0051 mol) and *m*-phenylene diamine (10.9313 g, 0.1011 mol) were added to a 100 ml round bottom flask. This flask was also sealed with a rubber septum and purged with nitrogen. Dry THF (50 ml) was added to the 100 ml flask by cannula and the mixture was stirred for about 10 min, until all monomers had dissolved. The solution was then added to the heterogeneous bisphenol A dianhydride solution by cannula. The 100 ml flask was rinsed twice with ~25 ml of dry THF, and the wash solution was added to the reaction flask by cannula. After 24 h the polymer solution was poured into a Teflon dish, placed inside a covered glass container equipped with a nitrogen sweep, and was exposed to a brisk nitrogen flow at room temperature for about 48 h to evaporate the solvent. The poly(amic acid) was then placed in a vacuum oven at 20°C to remove more of the solvent. The weight percent THF remaining in the poly(amic acid) was determined, by proton NMR, to be about 20% for all samples. This was used to obtain an accurate weight of the poly(amic acid) for poly(amic acid) salt formation.

#### 2.6. Synthesis of Ultem™ type poly(amic acid) salt with tripropylamine

To a 1000 ml beaker was added methanol (600 ml) and tripropylamine (11.65 ml). A 10 mol% excess of base was added relative to carboxylic acid groups to assure 100% conversion to the poly(amic acid) salt. To this solution was added Ultem™ type poly(amic acid) and stirring was initiated. The beaker was covered with parafilm and the mixture was stirred until all poly(amic acid) had dissolved (about 5 h), indicating formation of the salt. The solution

was then poured into a Teflon boat and the solvent was evaporated.

#### 2.7. Synthesis of Ultem™ type poly(amic acid) salt with tris(2,4,6-trimethoxyphenyl)phosphine (TMOPP)

To a 2000 ml beaker with a magnetic stir bar was added THF (1000 ml), methanol (500 ml), and TMOPP (52.300 g, 0.0982 mol), a 10% excess relative to carboxylic acid groups. Once the TMOPP had dissolved, poly(amic acid) (28.062 g, 0.0893 mol) was added. The solution was stirred for about 6 h (all poly(amic acid) had dissolved within 5 h), then poured into a Teflon boat to evaporate the solvent.

#### 2.8. Modification of the commercial polyhydroxyether (Fig. 2, number 5)

##### 2.8.1. With phthalic anhydride

To a 500 ml round bottom flask was added polyhydroxyether (15.21 g, 0.0535 mol), phthalic anhydride (8.318 g, 0.05616 mol), and dry tetrahydrofuran (300 ml). A 5 mol% excess of phthalic anhydride, based on hydroxyl groups, was used to promote high conversion. The mixture was stirred until all particles had dissolved (about 3 h), then a catalytic amount of dimethylaminopyridine (DMAP) (0.327 g, 0.00267 mol) was added. The solution was refluxed under nitrogen for 18 h. The modification reaction was monitored by infrared and nuclear magnetic resonance spectroscopies to determine the percent conversion of hydroxyl groups to pendant acid groups. The solution was then poured into a Teflon boat and the solvent was evaporated. After 24 h, the modified polyhydroxyether was placed in a vacuum oven at room temperature for 24 h, then 60°C for 24 h to remove most of the remaining solvent. After drying, about 7% by weight THF remained in the sample, determined by NMR. The conversion was calculated by NMR to be 82%.

##### 2.8.2. With succinic anhydride

To a 500 ml round bottom flask was added polyhydroxyether (40.353 g, 0.1419 mol), succinic anhydride (11.363 g, 0.1135 mol), and dry THF (250 ml). The mixture was stirred under nitrogen until all particles had dissolved (about 3 h), then a catalytic amount of DMAP (0.869 g, 0.0071 mol) was added. The reaction was monitored by NMR to achieve the desired 50% conversion. After stirring at room temperature under nitrogen for 20 h the reaction was quenched by adding a few drops of water to convert the remaining anhydride to acid. The polymer solution was precipitated into a 50/50 acetone/water solution to remove unreacted succinic acid, then dried in a vacuum oven at room temperature for ~72 h. After drying, ~11% by weight THF remained in the sample, determined by NMR. The conversion was calculated by NMR to be 63%.

## 2.9. Synthesis of the polyhydroxyether salt of TMOPP

### 2.9.1. From phthalic anhydride (82% modification)

To a 500 ml beaker was added modified polyhydroxyether containing some phthalic acid (7.546 g, 0.0205 eq. acid) and TMOPP (12.000 g, 0.0226 mol). A 10% molar excess of the TMOPP was added to promote full conversion of the acid to the salt. THF (250 ml) and methanol (250 ml) were added to the beaker, and the solution was stirred for 3 h, then poured into a Teflon boat and the solvent was evaporated. The film was placed in a vacuum oven and dried at room temperature for 24 h then 60°C for 24 h. The resulting material was soluble in methanol, indicating conversion to the salt.

### 2.9.2. From succinic anhydride (63% modification)

To a 500 ml beaker was added the modified polyhydroxyether (4.439 g, 0.0072 eq acid) and TMOPP (4.022 g, 0.0076 mol). A 5% molar excess of TMOPP was added to promote full conversion of the acid groups to the salt. THF (200 ml) was added to the beaker, and the solution was stirred for 3 h, then poured into a Teflon boat and the solvent was evaporated. The film was placed in a vacuum oven and dried at room temperature for 48 h then heated to 60°C for 24 h. The resulting material was soluble in methanol, indicating conversion to the salt.

## 2.10. Preparation of Na<sup>+</sup> phenolate salts of a novolac for kinetic analysis of a curing reaction

To a 100 ml beaker was added novolac (5.5234 g, 0.0531 eq phenolic hydroxyl), sodium hydroxide (1.0622 g, 0.0266 mol), and methanol (50 ml). The mixture was stirred for about 4 h then poured into a Teflon boat to evaporate the solvent. All particles had dissolved within one hour and a dark red color appeared. The phenolate was then dried in a vacuum oven at 60°C for 24 h.

## 2.11. Sizing materials

Six different fiber sizings were investigated, two control sizings with no initiator and four latent initiator sizing materials (Fig. 2). Sizing (1) was a commercial  $G'$  sizing obtained from Hexcel. Sizing solution (2) was prepared by dissolving a 2 wt.% solution of the poly(amic acid) salt from tripropylamine in methanol. Sizing solution (3) was prepared by dissolving a 2 wt.% solution of the poly(amic acid) salt from TMOPP in methanol. Sizing solution (4) consisted of a 1.5 wt.% aqueous solution of the potassium salt of a novolac with 50% conversion of the phenolic hydroxyl groups to the salt. The sizing solution was prepared by adding the novolac (15.000 g, 0.1442 eq phenolic hydroxyl) to 1000 ml of water containing potassium hydroxide (4.046 g, 0.0721 mol). A small amount of acetone (80 ml) was added to dissolve the novolac, then evaporated before the sizing process. Sizing solution (5) consisted of a 2 wt.% dispersion of the modified polyhydroxyether

(from phthalic anhydride) in a 50/50 NMP/water solution. This was prepared by dissolving the modified polyhydroxyether in NMP, then slowly adding the water to the solution. Initially the solution appeared soluble but after several hours became cloudy. The dispersion was stable with stirring for 2 weeks. Sizing solution (6) consisted of a 2 wt.% dispersion of a commercially modified polyhydroxyether in water.

## 2.12. Fiber sizing

### 2.12.1. Sizing solutions (2 and 3)

Fiber tow was sized on a custom made small scale sizing line from 2 wt.% solutions in methanol. The tows were dried by passing through a vented hood at room temperature, then wound onto a spool. The tow was then passed back through the vented hood heated to 260°C at a speed that produced a total of 3 min in the heated “drying” tower on the sizing line. This allowed for rapid on-line imidization of the poly(amic acid) salt sizing.

### 2.12.2. Sizing solution (4)

Fiber tow was sized on a custom made small scale sizing line from the 1.5 wt.% solution in water. The tow was dried by passing through a vented hood at about 180°C, then wound onto a spool.

### 2.12.3. Sizing solutions (5 and 6)

Fiber tow was sized on a custom made small scale sizing line from the 2 wt.% solution in NMP/water for sizing (5) and a 2 wt.% solution in water for sizing (6). The tow was dried by passing through the vented hood heated to 230°C at a speed that produced a total of 5 min in the tower, then wound onto a spool. This resulted in light crosslinking of the polyhydroxyether sizings.

## 2.13. Measurements

Rheological experiments were carried out on a Bohlin VOR rheometer in continuous oscillation mode with a frequency of 1 Hz. Temperature control was accomplished with a Bohlin HTC. The auto-strain was set to control the torque to 25% of the maximum torque allowed. The maximum strain for the instrument was 0.25. Samples of about 0.7 g of dry powder were pressed into pellets then placed between the preheated 25 mm diameter parallel plates of the rheometer. The gap was closed to ~1 mm and the sides were scraped to remove excess sample before the run was begun. The samples used in these tests were prepared by solvent mixing.

In order to determine the weight percent sizing on the fiber for sizing solutions 2–4, the sized fiber (before imidization in the case of sizings 2 and 3) was cut into sections, placed in 3 separate aluminum pans and weighed. The fibers were washed five times with methanol to remove all sizing material, dried in a vacuum oven at ~80°C for 3 h then reweighed. The weight percent sizing in the composite, and the mole percent initiator based on epoxy content, were

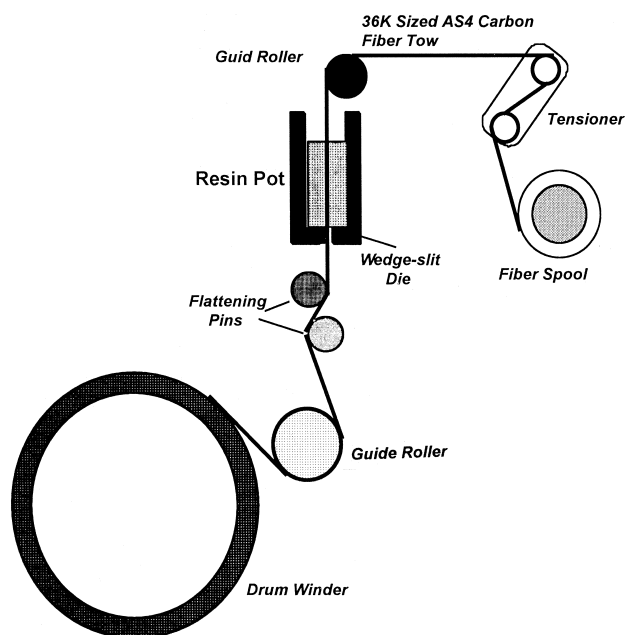


Fig. 3. Hot-melt prepregging schematic.

calculated based on a predicted fiber volume fraction of 60% and the densities of the resin (1.23 g/ml) and fiber (1.80 g/ml). These calculations were used to determine the cure times needed to achieve 100% conversion.

In order to determine the weight percent sizing on the fiber for sizing solutions 5 and 6, the fibers were weighed, then heated to 600°C for 30 min under nitrogen. The fibers were then re-weighed to determine the weight loss. In addition a small sample of sizing was analyzed by TGA under the same conditions (600°C for 30 min under nitrogen) to determine the percent weight loss of the sizing under these conditions. From this analysis a corrected weight percent sizing on the fiber was determined.

A Perkin–Elmer DSC-7 was used for differential scanning calorimetry measurements. The DSC was calibrated with indium and zinc standards, and ice water was used as the coolant. Samples of ~15–20 mg were sealed hermetically in aluminum pans. Isothermal analyses were conducted by loading the samples at room temperature and heating to the load temperature at 300°C/min. The area of the exotherm was integrated to determine percent conversions from partial areas. Dynamic scans were performed at systematically varied heating rates (5–20°C/min) from 50 to 270°C. Activation energies were obtained following ASTM E 698, with correction for the influence of heating rate on temperature. The correction was calculated by the deviation in the melting point of indium from the accepted value of 156.6°C. Half-life analyses according to the ASTM standard were conducted to determine the validity of the kinetic parameters. For the samples in which the half-life analysis proved the kinetic parameters to be invalid, rate constants were determined from isothermal scans. For half-life analyses, the samples were heated isothermally

in the DSC at a time and temperature that was calculated, using the kinetic parameters, to promote 50% conversion. Temperature scans were then performed on both the isothermally aged sample and uncured sample at 10°C/min from 50 to 270°C. The peak heights divided by the sample weights of the partially cured samples were compared to those of the uncured samples, in order to confirm or refute the validity of the apparent activation energies.

In order to determine the glass transition temperatures of the polyimides, samples were scanned from 50 to 300°C at 10°C/min then cooled rapidly (200°C/min), and scanned a second time from 50 to 300°C at 10°C/min. The glass transition temperatures were measured from the second heating scans.

#### 2.14. Hot-melt prepregging and composite fabrication

A lab scale Model 30 prepregger manufactured by Research Tools Corporation, Ovid, Michigan was used for composite preparation (Fig. 3). In this apparatus, a 12 K sized AS-4 carbon fiber tow was passed through a wedge-slit die at the bottom of a heated resin pot containing the matrix resin. The wetted tow was then passed between a pair of flattening pins and around a guide roller before being wound on a drum. The flattening pins and the guide rollers were independently heated. Unidirectional carbon fiber prepregs were prepared with 65/35 wt/wt novolac–epoxy resin (without added initiator), with the series of sizing materials, using the hot-melt technique. The set-point temperature of 140°C for the resin pot, flattening pin, and roller was determined by viscosity data. This high temperature was necessary to achieve a low enough melt viscosity to process the materials. Low melt viscosity of the resins was

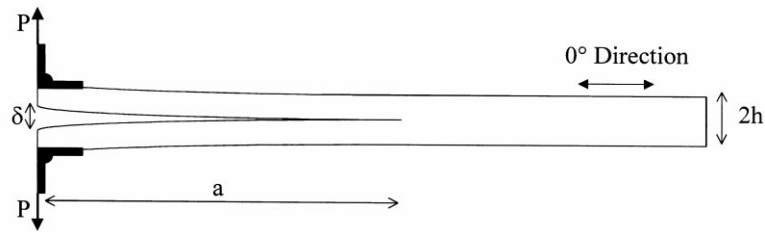


Fig. 4. Loading geometry for mode I toughness.

critical to permit good wet-out of the reinforcing fiber tows and yield uniform resin content. The prepregs were then cut and placed in a metal mold and cured under pressure using a thermal cycle determined by the kinetic parameters.

#### 2.15. Composite fabrication for $G_{1c}$ and $G_{2c}$ tests

Panels for  $G_{1c}$  and  $G_{2c}$  tests were prepared by aligning 10–14 plies unidirectionally with a 0.05 mm Teflon delamination tab placed midway through the laminate, with a length of 50.8 mm (2 in.) from the outside of the panel. The number of plies was determined based on the ply thickness after prepregging to achieve a specimen thickness close to 3.18 mm. The samples were then cured in a metal mold with a thermal cycle determined by the kinetic parameters. The  $15.2 \times 15.2$  cm ( $6 \times 6$  in.<sup>2</sup>) panels were cut to six  $12.7 \times 2.0$  cm ( $5 \times 0.79$  in.<sup>2</sup>) specimens. Prior to testing an initial crack was generated about 1 mm past the Teflon delamination tab through the resin rich region. This crack was generated by placing the sample in a vice with the sample clamped approximately 1–2 mm below the end of the Teflon. A thin wedge was then placed in the crack and tapped lightly with a hammer until the crack propagated through the resin rich region (evidenced by a soft cracking noise). For the  $G_{1c}$  samples, piano stock hinges were adhered to the samples to facilitate loading. The piano hinges allowed free rotation and minimal stiffening of the specimens. The weight fraction of fibers in the composites ranged from 0.72 to 0.78.

#### 2.16. Composite fabrication for fatigue testing

Panels for quasi-static compression and fatigue tests were prepared by orienting 7 plies in a  $(0^\circ/90^\circ)_7$ s lay-up with sizings (1) and (6). The samples were cured in the metal mold with a thermal cycle determined by the kinetic parameters. The  $15.2 \times 15.2$  cm ( $6 \times 6$  in.<sup>2</sup>) panels were then cut to five  $15.2 \times 2.54$  ( $6 \times 1$  in.<sup>2</sup>) specimens with a 6.35 mm (0.25 in.) diameter hole in the center. Prior to testing, aluminum tabs with a spacing of exactly 2.54 cm (1 in.) were adhered to the samples to allow for attachment of the extensometer. The weight fraction of fibers in the composites ranged from 0.65 to 0.70.

#### 2.17. Composite panel characterization

The composite panels were C-scanned for overall quality using a Sonix model HF 1000 by a pulse–echo arrangement using a 15 MHz transducer with a focal length of 38.1 mm. Scanning electron photomicrographs, obtained from an ISI SX-40 SEM, were used to establish the void free nature of the composites and to confirm good resin distribution and fiber wet-out.

Dynamic mechanical analyses were used to determine the glass transition temperatures of the cured composite panels. These measurements were performed using a Perkin–Elmer dynamic mechanical analyzer, model DMA-7. The  $T_g$ 's were measured from the peaks in the  $\tan \delta$  curves. The tests were conducted using a 3-point bend set-up with rectangular specimens. The tests were run with tension control set at 120% using an amplitude of 9  $\mu$ m. Samples were heated at 5°C/min from 25 to 200°C. Two samples of each material were tested and averaged.

#### 2.18. $G_{1c}$ testing

A double cantilever beam set-up with piano hinge tabs was used to measure  $G_{1c}$  of the composite panels according to ASTM D 5528-94a. The specimens were placed in the grips of the Instron with a 1000 lb. load cell. Prior to loading, the sides of the specimens were painted white to facilitate analysis of the crack as it progressed along the length of the specimen. The specimens were then loaded at a cross-head rate of 0.5 mm/min to allow crack propagation to be followed and recorded easily (Fig. 4). The crack tip was marked and recorded as a function of the load and displacement. The crack length was measured using a lighted magnifying glass and marked with a pencil. The crack propagation was recorded in  $\sim 2$  mm increments for the first 15 mm, followed by  $\sim 5$  mm increments until the crack had propagated at least 60–65 mm from the starter film. The samples were then unloaded at 5 mm/min.

#### 2.19. $G_{2c}$ testing

$G_{2c}$  tests were conducted with the end notched flexural specimen geometry in three-point bend loading according to the protocol for interlaminar fracture testing by the European group on fracture [19]. Initially the uncracked portion of each sample was tested using the three-point

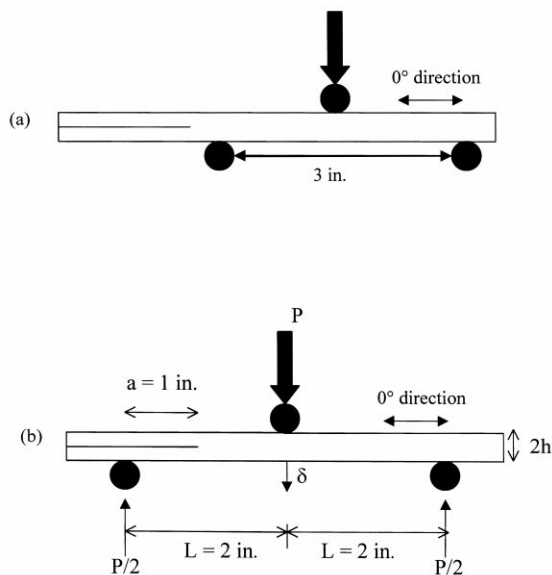


Fig. 5. Loading geometry for mode II toughness: (a) initial compliance measurement; and (b) loading to failure.

bend setup to determine the compliance (Fig. 5a). For the initial compliance test of the uncracked length, a span of 75.8 mm was used with a testing rate of 0.5 mm/min. The load/deflection data was obtained up to 0.25 kN to determine the compliance and this value was used in the calculation of bending stiffness for each specimen. Following the initial compliance measurement, the span was changed to 101.1 mm and the sample was positioned to give  $a/l = 0.5$ , where ( $a$ ) was the pre-crack length and ( $l$ ) was half the span. The sample was then loaded at 0.5 mm/min until the crack propagated to the center of the sample (Fig. 5b).

### 2.20. Quasi-static compression and fatigue testing

Quasi-static compression and fatigue tests were conducted on notched cross-ply specimens using an MTS test frame to assess composite strength and durability. Quasi-static compression tests were conducted with a loading rate of 200 pounds per second. Fatigue tests were conducted using a sinusoidal mode in fully reversed tension–compression ( $R = -1$ ) at a frequency of 10 Hz. A 5.08 cm (2 in.) test gauge length was used to ensure that

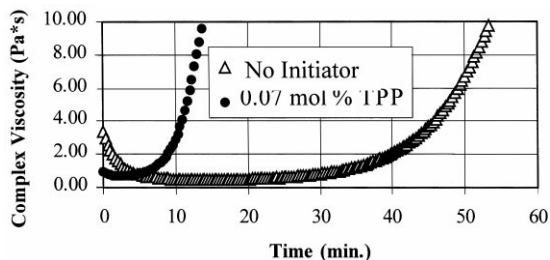


Fig. 6. Isothermal rheology at 145°C of an initiated vs. uninitiated 65/35 wt phenolic/epoxy reaction.

buckling would not influence failure. The specimens were loaded into the grips at a grip pressure ranging from 1300 to 1700 psi depending on the composite thickness. Specimen alignment was ensured with a spirit level. Emory cloth (100 grit) was wrapped around the grip sections of the specimens to prevent slip and protect the sample. An MTS Model 632 extensometer with a gauge length of 12.7 mm (0.5 in.) and a maximum strain limit of 4% was used to monitor strain. Aluminum extensometer tabs were used to hold the extensometer's knife edges and the signal from the extensometer was amplified using a 2310 Vishay Measurements Group amplifier. Lab View™ was used to acquire data on load, stroke, strain, and number of cycles.

### 3. Results and discussion

Previous work has demonstrated that these phenolic–epoxy networks with a ratio of three equivalents phenol to one equivalent epoxy (65 wt.% novolac–35 wt.% epoxy) have excellent mechanical properties [16–18]. Because of the void free nature of these materials combined with tailored crosslink densities, these thermosets have toughness comparable to or exceeding untoughened aerospace epoxies (bisphenol A based epoxy cured with diaminodiphenylsulfone) while maintaining flame retardant properties approaching those of the pure phenolic materials [18]. Therefore the processing of these materials by commercial means such as prepregging and pultrusion is of great interest. Although solution processing from acetone is achievable, due to the high viscosity of the resin and the tendency toward premature curing in the processing step, a latent initiator is required for melt processing.

Melt processing requires the resin to have a viscosity of less than  $\sim 5$  Pa s to achieve good wet-out of the reinforcing fiber tows and yield uniform resin content. The temperature necessary to reach this low viscosity, determined by complex viscosity measurements, is 140–145°C. At these high temperatures, the resin cures quickly even with only small amounts of initiator (Fig. 6). For example, the time below 5 Pa s is only about 10 min with a triphenylphosphine concentration of 0.07 mol% (based on moles of epoxy). In addition, this amount of catalyst requires a cure time of about 2 h at 180°C to achieve 100% conversion. On the other hand, the resin without added initiator had a much longer processing window, greater than 1 h (Fig. 6), but required very long cure times at high temperatures to achieve complete cure (220°C for 4 h).

In order to prevent premature curing during the processing stage, followed by rapid reaction during the curing stage, several latent initiators have been investigated. These initiators were designed to either be encapsulated into a fiber sizing in relatively high concentrations or grafted onto a polymer that was then sized onto the fiber. During melt prepregging, the hot resin is in contact with the fibers for less than 5 s before it is cooled. Therefore, initiators



Table 1  
Half-life analyses of phenolic/epoxy melts (65 wt.% phenolic novolac/35 wt.% epoxy) with latent nucleophilic initiators

Latent nucleophilic initiators	Initiator type	Percent conversion (with target 50%)	Validity of kinetic parameters
Triphenylphosphine	Monomer	52	Valid
Polyimide encapsulated TMOTPP	Encapsulated monomer	48	Valid
Acetic acid salt (Na <sup>+</sup> )	Monomer	48	Valid
Acetic acid salt (TMOTPP)	Monomer	56	Valid
Modified polyhydroxyether salt (TMOTPP)	Polymer	63	Not Valid
Phenolate (Na <sup>+</sup> )	Monomer	48	Valid
Novolac phenolate (Na <sup>+</sup> )	Oligomer	38	Not Valid

embedded in the fiber sizings do not cure the resin significantly during this processing stage, and thus, high concentrations of initiator can be used. This leads to rapid reaction in the cure cycle. This method may also be sufficient for other melt processes such as pultrusion.

### 3.1. Preparation of latent initiators

Three types of latent initiators to be introduced as fiber sizings have been investigated to assess the feasibility of melt processing phenolic–epoxy matrix resins. Tris(2,4,6-trimethoxyphenyl)phosphine (TMOPP) initiator was dispersed in a 22,000 g/mol ( $M_n$ ) Ultem™ type polyimide. In this system the TMOPP was reacted with an Ultem™ type poly(amic acid) to form a poly(amic acid) salt. The salt was soluble in methanol and dispersible in a 15/85 wt/wt NMP/water mixture and thus the sizing operation could be conducted with either of these systems. TMOPP was chosen as the base due to its sufficiently strong basicity to quantitatively form the poly(amic acid) salt and also because of its high vaporization temperature. The poly(amic acid) salt eliminated the phosphine and cyclized to the corresponding polyimide when heated at 260°C for 3 min. Therefore the phosphine initiator became sequestered in the high molecular weight polyimide sizing material. Complete encapsulation is probably not important, because the initiator has minimal contact with the resin prior to the curing stage.

A second initiator type was the TMOPP salt of a commercial bisphenol A based polyhydroxyether modified with carboxylate grafts (Fig. 2). The salt was soluble in methanol and dispersible in a 50/50 NMP/water mixture. At high temperatures (230°C for 5 min) the polyhydroxyether salt lightly crosslinks. This sizing/initiator combination was of particular interest since similar polyhydroxyether sizing materials have been shown to improve composite properties in other systems [20].

The third initiator investigated was the phenolate salt of a novolac ( $M_n \sim 760$  g/mol) resin. This material is cost effective and does not require co-solvents or high temperatures during the sizing process. The novolac phenolate with 1phenolate/1phenol is soluble in water and therefore was sized from an aqueous solution.

### 3.2. Kinetics

It was necessary to study kinetic parameters of the phenolic–epoxy network forming reactions to relate effects of initiator structure to the rates. A detailed understanding of the kinetics with different initiator systems was important for the design of latent initiators as well as for determining appropriate cure cycles for the composite panels cured with the latent initiators.

Kinetic parameters were calculated from dynamic DSC data using the procedure outlined in ASTM E 698. The standard is based on a method developed by Ozawa [21] for determining apparent activation energies, and relates the heating rate ( $B$ ) to the temperature of maximum reaction rate ( $T_{max}$ ). Activation energies were calculated at the appropriate catalyst concentrations using Eq. (1) where  $d(\log B)/d(T_{max})$  was determined from linear regression. The activation energies were refined until self-consistent using a process outlined in the ASTM standard. Pre-exponential factors ( $A$ ) were calculated based on a method outlined by Kissinger (Eq. (2)) [22]

$$E_a = (-2.303R/D)d(\log B)/d(T_{max}) \quad (1)$$

$$A = BE_a/RT_{max}^2(\exp(-E_a/RT)) \quad (2)$$

With these kinetic parameters, rate constants were calculated utilizing the temperature dependence of  $k'$  (Eq. (3)).

$$k' = A \exp(E_a/RT) \quad (3)$$

The percent reaction conversion versus time was predicted over a range of temperatures based on the kinetic parameters for each initiator.

The validity of the kinetic parameters ( $E_a$  and  $A$ ) for each type of initiator was established by half-life analyses according to the ASTM standard. Samples were reacted to a predicted 50% conversion at a temperature at which the reaction rate was relatively slow to allow good control of the reaction. The times and temperatures needed to achieve 50% conversion were determined from the rate constants which were calculated from the activation energies and pre-exponential factors. According to the standard, samples achieving within 10% of the desired 50% conversion based

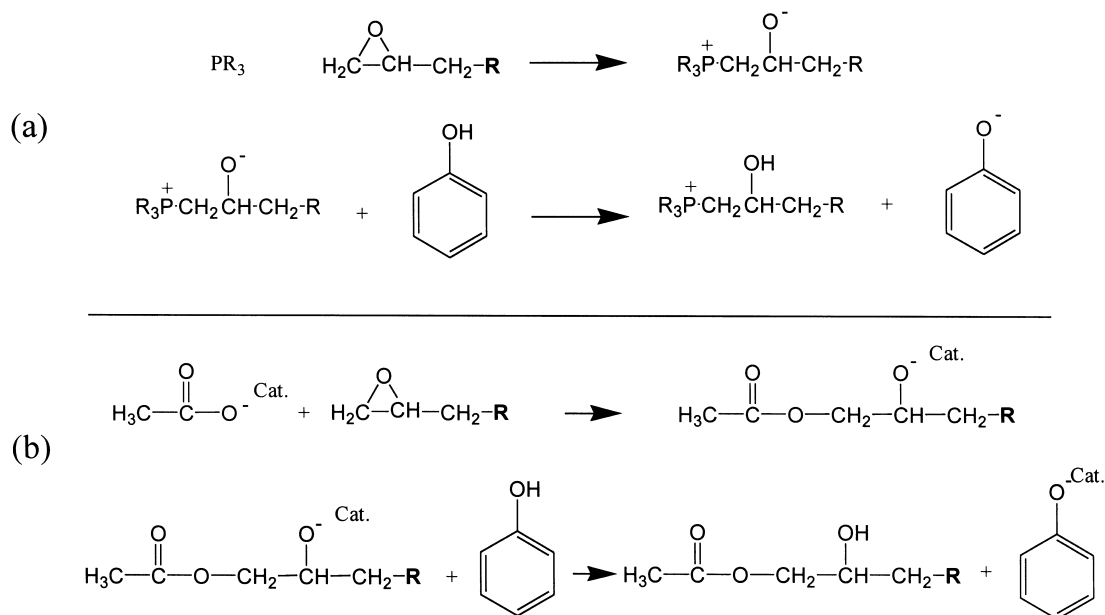


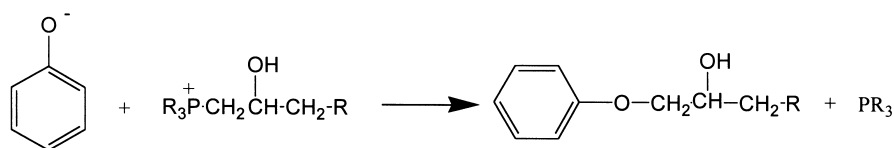
Fig. 7. Phenolic/epoxy reaction initiation: (a) initiated by triphenylphosphine; and (b) initiated by a carboxylate anion.

on peak heights, are considered to have valid kinetic parameters (Table 1). For the samples in which the  $E_a$  and  $A$  were determined to be invalid, isothermal reactions were used to determine the rate constants and reaction conversion versus time.

The reaction mechanism of a phenolic novolac with epoxy in the melt initiated by triphenylphosphine has been investigated previously for electronic applications [13]. In this reaction the triphenylphosphine can ring open the epoxy generating a zwitterion. In the presence of phenol groups, a

rapid proton transfer from the phenol to the secondary hydroxyl occurs, generating a phenolate ion (Fig. 7a). This phenolate ion can then react with the electrophilic carbon to regenerate the triphenylphosphine or with another epoxy group (Fig. 8) [13]. The phenolate nucleophile is the propagating species of the reaction, and its concentration is assumed to be constant once all the initiator has reacted. It is reasonable to expect TMOPP to react by a similar mechanism as the triphenylphosphine. Another type of initiator for the phenolic–epoxy reaction is the salt of a carboxylic acid.

#### Mechanism 1



#### Mechanism 2

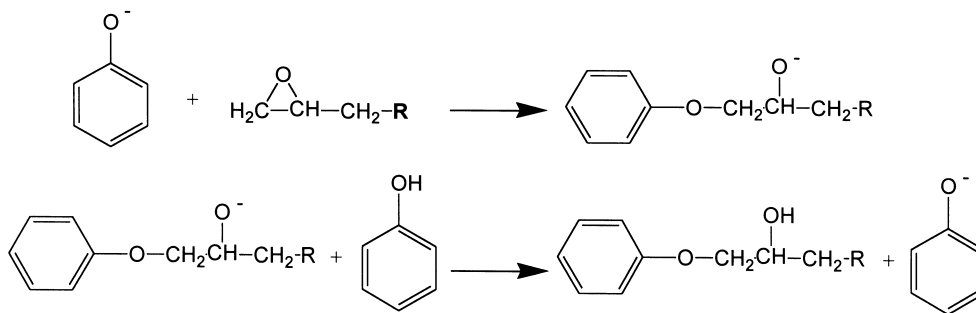


Fig. 8. Phenolic/epoxy reaction propagation.

Table 2  
Kinetic parameters for phenolic/epoxy melts (65 wt.% phenolic novolac/35 wt.% epoxy) containing 2.0 mol% initiator based on moles of epoxy

Initiators	$E_a$ (KJ/mol)	$k$ ( $s^{-1}$ ) at $T = 180^\circ\text{C}$	Time to 99% conversion at $T = 180^\circ\text{C}$ (min)
TMOTPP	70	$2.0 \times 10^{-2}$	4
Polyimide encapsulated TMOTPP	69	$8.3 \times 10^{-3}$	9
Acetic acid salt ( $\text{Na}^+$ )	66	$5.3 \times 10^{-3}$	15
Acetic acid salt ( $\text{Rb}^+$ )	63	$4.9 \times 10^{-3}$	16
Acetic acid salt ( $\text{Cs}^+$ )	68	$5.4 \times 10^{-3}$	14
Acetic acid salt (TMOTPP)	66	$1.1 \times 10^{-3}$	7
Modified polyhydroxyether salt (TMOTPP)	–	$2.5 \times 10^{-3}$	31
Phenolate ( $\text{Na}^+$ )	63	$6.6 \times 10^{-3}$	12
Novolac Phenolate ( $\text{Na}^+$ )	–	$3.2 \times 10^{-3}$	24

The carboxylate can ring open the epoxy creating a zwitterion, then rapid proton transfer from a phenolic group to the secondary hydroxyl will generate the phenolate nucleophile (Fig. 7b).

The kinetics of the latent initiators are strongly dependent on the initiator structure. Both the counterion type and the number of initiation sites per chain can affect the kinetics of the phenolic epoxy reaction. These two effects were analyzed by studying a series of different initiators.

A series of four similar initiators with different counterions were used to investigate the effect of counterion size and type on the kinetics. These included the acetate salts of sodium, rubidium, cesium, and TMOPP-H. There was no apparent effect of the counterion size on the activation energies or rate constants within the series of inorganic counterions investigated (Table 2). On the other hand, the rate constants were significantly higher with the phosphonium counterion, although the activation energies were similar. This could be a result of the very large increase in counterion size or a difference in charge distribution creating a weaker ion pair once the phenolate propagating species is formed.

Several types of latent initiators were investigated for the phenolic–epoxy matrix composites, ranging from partially encapsulated small molecules (e.g. encapsulated TMOPP) to oligomeric (e.g. novolac phenolate) and polymeric (e.g. succinic acid modified polyhydroxyether) species. Reaction kinetics with the oligomeric and polymeric initiators, which also had multiple initiator sites on the same chain, were directly compared with monomeric analogues. In addition, effects of encapsulation were probed by comparing rates with TMOPP embedded in polyimides versus free TMOPP.

A comparison of the rate of reaction at  $180^\circ\text{C}$  with the sodium salt of novolac versus the sodium salt of phenol indicated that the reaction rate was slower for the oligomeric material at the same anion concentration (Fig. 9). With 2.0 mol% initiator, the material initiated by the sodium salt of phenol reached 99% conversion in 12 min, whereas it took 24 min for the material initiated by the sodium salt of novolac to reach 99% conversion. In addition, doubling the concentration of the oligomeric initiator shows a slight rate increase, but the rate does not double as would be expected for a monomeric initiator. A similar comparison between the TMOPP salt of the carboxylic acid modified

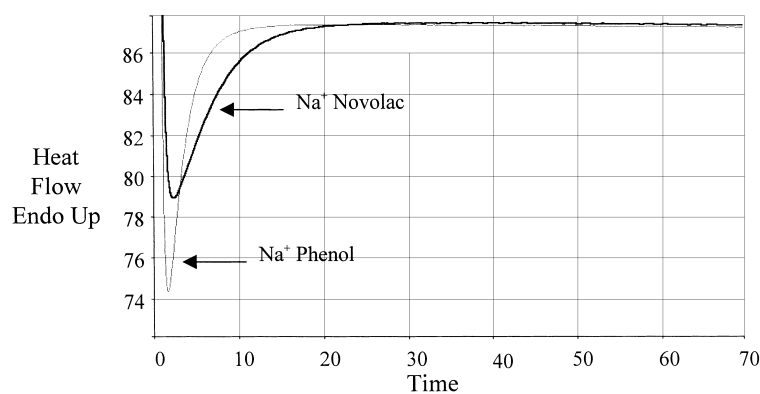


Fig. 9. Isothermal DSC kinetics of the phenolic epoxy reaction initiated by 2.0 mol% of: (a) the sodium salt of phenol; and (b) the sodium salt of novolac.

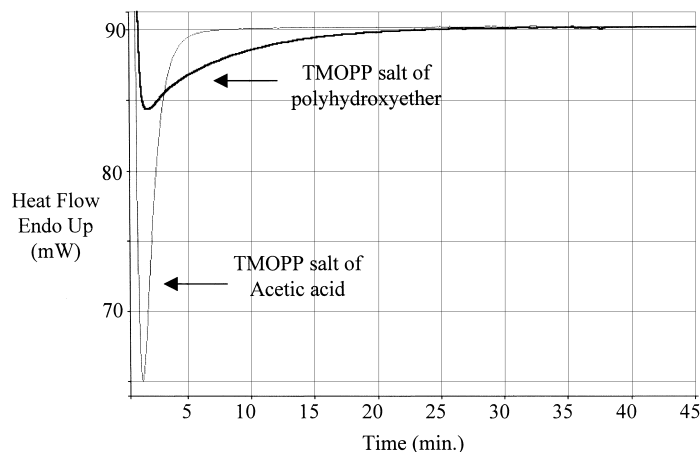


Fig. 10. Isothermal DSC kinetics of the phenolic epoxy reaction initiated by 2.0 mol% of: (a) the TMOPP salt of acetic acid versus; and (b) the TMOPP salt of modified polyhydroxyether.

polyhydroxyether and the TMOPP salt of acetic acid indicates that this reaction rate is also much slower with the polymeric initiator (Fig. 10). With 2.0 mol% initiator the material initiated by the TMOPP salt of acetic acid reached 99% conversion in 7 min, whereas the material initiated by the TMOPP salt of the modified polyhydroxyether required 31 min to reach 99% conversion.

It should also be noted that kinetic parameters (determined from the ASTM method previously described) were “invalid” with the oligomeric or polymeric initiators (Table 1). This also indicates that there is some effect on the kinetics when a polymeric initiator is used as opposed to a monomeric initiator of the same type and concentration. For this reason, kinetics with the polymeric initiators were investigated by isothermal DSC analysis as opposed to the dynamic method.

The comparison between the polyimide encapsulated TMOPP and the free TMOPP indicated some drop in the rate due to the encapsulation but no significant change in the activation energy (Table 2). This is probably a result of the low  $T_g$  of the polyimide blended with high initiator concentrations. The  $T_g$  of the polyimide (22,000 g/mol) with 1 mol of TMOPP per imide group is plasticized from 213 to 98°C. This should allow significant diffusion of the TMOPP at the 180–200°C cure temperatures of the phenolic epoxy networks.

### 3.3. Diffusion

An important consideration in understanding effects of embedding the matrix cure initiators in the fiber sizing are diffusion issues. The time required for an initiator to diffuse from its initial location at the fiber surface throughout the matrix resin at the cure temperature becomes a critical parameter. The DSC cure kinetics described above were conducted on mixtures of initiator and resin powders. During the kinetic measurements, these heterogeneous

powder mixtures were heated (without shear mixing) to afford homogeneous melts. The kinetic analyses with the polyimide encapsulated monomeric TMOPP initiator suggested that this initiator rapidly diffuses into the matrix resin at 180°C. This is evident by the fact that the rate constant with the *encapsulated* TMOPP is only slightly lower than with the *free* TMOPP and the activation energies are equivalent (Table 2).

Diffusion rates of both a monomeric initiator (TMOPP) and a polymeric initiator (the TMOPP salt of modified polyhydroxyether) were estimated from the Lusis–Ratcliffe Eq. (4) [23]. The total time for diffusion over the predicted distance between fibers (assuming 8  $\mu\text{m}$  diameter fibers and 60 vol.% fiber in the composite and 5  $\mu\text{m}$  between fibers) was estimated to be 5 s for the monomeric initiator and 41 s for the polymeric initiator at the cure temperature of 180°C. This suggests that initiators may effectively diffuse throughout the resin during composite processing at early stages of the cure cycle.

$$D_{AB}^{\circ} = \frac{(8.52 \times 10^{-8} T)}{\eta_B V_B^{1/3}} \left[ 1.4 \left( \frac{V_B}{V_A} \right)^{1/3} + \frac{V_B}{V_A} \right]. \quad (4)$$

Resin parameters for a 65/35 wt/wt novolac/epoxy composition were assumed as follows: the average molecular weights of the epoxy and novolac components were 374 and 750 g/mol, respectively, resulting in an average molecular weight of  $(0.65)(750) + (0.35)(374) = 618$  g/mol. Assuming the density of the resin (uncured) was 1.1 g/cm<sup>3</sup>, the molar volume ( $V_B$ ) of the resin is  $(618 \text{ g/mol}) / (1.1 \text{ g/cm}^3) = 562 \text{ cm}^3/\text{g}$ . Tris(2,4,6-trimethoxy phenyl)phosphine has a molecular weight of 540 g/mol and the density was assumed to be 1 g/cm<sup>3</sup>. This affords a molar volume of TMOPP ( $V_A$ ) of  $(540 \text{ g/mol}) / (1 \text{ g/cm}^3) = 540 \text{ cm}^3/\text{g}$ . The resin viscosity at 453 K ( $\eta_B$ ) was assumed as 1000 cps and the cure temperature ( $T$ ) considered was 453 K. This results in estimation of the diffusion coefficient ( $D_{AB}^{\circ}$ ) for the TMOPP through the resin at this temperature

Table 3  
Kinetic predictions for composites based on the calculated mol% initiator in the composite

Sizing	Sizing Sol. (Wt.%)	Wt.% Sizing on fiber	Mol% initiator in composite	Time to 99% conversion ( $T = 180^\circ\text{C}$ ) (min)
3	2.0	1.62	3.2	5
4	1.5	0.63	5.2	15
5	2.0	0.74	1.5	41
6	2.0	1.38	–	43

to be  $1.15 \times 10^{-8} \text{ cm}^2/\text{s}$ . The following parameter were used to estimate a diffusion time for a carboxylate modified polyhydroxyether through the novolac/epoxy resin. The polyhydroxyether molecular weight was assumed to be 49,000 g/mol and the polymer density was estimated at  $1 \text{ g/cm}^3$ . The molar volume ( $V_A$ ) was then calculated as  $(49,000 \text{ g/mol})/(1 \text{ g/cm}^3) = 49,000 \text{ cm}^3/\text{g}$ . The viscosity of the resin at 453 K ( $\eta_B$ ) was assumed as 1000 cps and the cure temperature ( $T$ ) of 453 K was used to estimate the diffusion coefficient ( $D_{AB}^\circ$ ) of  $1.53 \times 10^{-9} \text{ cm}^2/\text{s}$ .

In an idealized model of a fiber reinforced composite with 60 vol.% fiber and a fiber diameter of  $8 \mu\text{m}$ , there is about  $5 \mu\text{m}$  between fibers. If one assumes that an initiator has to travel half the distance between fibers at the widest point, then it has to travel  $2.5 \mu\text{m}$ . Diffusion time ( $t_{\text{diff}} = (\text{distance})^2/(D_{AB}^\circ)$ ) so the predicted required time for the initiator to diffuse over this distance is: (TMOPP) $t_{\text{diff}} = (2.5 \times 10^{-4} \text{ cm})^2/1.15 \times 10^{-8} \text{ cm}^2/\text{s} = 5.4 \text{ s}$  and (carboxylate modified polyhydroxyether)  $t_{\text{diff}} = (2.5 \times 10^{-4} \text{ cm})^2/1.53 \times 10^{-9} \text{ cm}^2/\text{s} = 41 \text{ s}$ . One assumption is that the fiber volume fraction before curing is close to that after curing. This is true if only minimal amounts of resin are squeezed out during the cure.

These calculations suggest that the slower curing rates of the phenolic–epoxy network with polymeric initiators are not a result of slow diffusion of the initiators. The polymer should be dispersed throughout the resin within 41 s.

Table 4  
Cure cycles and glass transition temperatures of composites with varied sizing materials

Sizing	Mol% initiator	Cure cycle	$T_g$ ( $^\circ\text{C}$ )
1	None	200°C (1 h) 220°C (3 h)	132
2	None	200°C (1 h) 220°C (3 h)	132
3	3.2	180°C (20 min) 200°C (10 min)	130
4	5.2	180°C (30 min) 200°C (30 min)	135
5	1.5	180°C (20 min) 200°C (20 min)	135
6	–	180°C (1 h) 200°C (1 h)	128

Therefore the slower rate may be a result of a localized initiation around the polymer, as opposed to random initiation throughout the resin.

### 3.4. Sizings

Control panels were fabricated from 12 K  $G'$  commercially sized fiber from Hexcel. All sizing solutions were sized onto 12 K AS-4 unsized carbon fibers from Hexcel. Composite panels were fabricated with six different sizing materials to study the effects of the latent initiators on the thermal and mechanical properties of the composites. The following sizing materials were used in composite fabrication: (1) a commercial  $G'$  sizing material; (2) a 22,000 g/mol polyimide with no initiator; (3) a 22,000 g/mol polyimide with 3.2 mol% initiator; (4) a potassium salt of phenolic novolac with 5.2 mol% initiator; (5) a modified polyhydroxyether with 1.5 mol% initiator; and (6) a commercially modified polyhydroxyether with an unknown initiator concentration.

The cure cycles for panels from each type of sized fiber were determined by kinetic analysis based on the initiator concentration (Table 3). The  $T_g$ 's of the cured panels were measured to confirm that the panels were fully cured with the designated cure cycles (Table 4). All of the panels with the latent initiator systems were fully cured with significantly shorter cure times than the control uncatalyzed panel. With no initiator, a cure cycle of 1 h at  $200^\circ\text{C}$  and 3 h at  $220^\circ\text{C}$  was required to reach full conversion. Uncatalyzed panels cured for only 3 h showed a significantly lower  $T_g$  than both the catalyzed panels and the uncatalyzed panels cured for 4 h. There was no significant change in the  $T_g$ 's of catalyzed panels when post cured for an additional 1 h at  $200^\circ\text{C}$ , indicating that all composites were fully cured.

Mode I fracture toughness of the composite panels with sizings (1)–(3), were analyzed (Table 5). The corrected crack length ( $a + \Delta$ ), for each sample, was determined from a plot of the cube root of compliance versus the measured crack length, based on the corrected beam theory.  $G_{1c}$  values were calculated for the entire range of crack lengths by Eq. (5) according to ASTM D5528-94a. The values reported were

$$G_{1c} = 3P\delta/2b(a + \Delta) \quad (5)$$

$P$  = applied load;  $\delta$  = displacement;  $b$  = specimen width;  $a$  = crack length; and  $\Delta$  = correction factor for the crack

Table 5

Mode I composite toughness of unidirectional AS-4 carbon fiber reinforced phenolic/epoxy composites from sizings 1, 2, and 3

Sizing	Mol% initiator	Cure cycle	Fiber vol. Fraction (%)	$G_{1c}$ (J/m <sup>2</sup> )
1	None	200°C (1 h) 220°C (3 h)	67.6	573 ^ 46
2	None	200°C (1 h) 220°C (3 h)	71.1	695 ^ 83
3	3.2	180°C (20 min) 200°C (10 min)	64.2	542 ^ 92

length taken from the region of stable crack growth of each sample indicated by the plateau in the plot of  $G_{1c}$  versus corrected crack length.

Mode I toughness of the phenolic–epoxy panels, both with and without initiators, is significantly higher than for untoughened epoxy/carbon fiber composites and equivalent to toughened epoxy/carbon fiber composites [24–27]. The slight differences in the values between the three panels may be a result of small differences in fiber volume fractions. There were no significant differences in toughness between the panels from sizings (1) and (2) and in the panel from the polyimide encapsulated TMOPP sizing (3). This demonstrates that the desired properties of the novolac/epoxy resin system can be retained with a much shorter cure time (30 min instead of 4 h) and lower cure temperatures (180–200°C as opposed to 200–220°C).

Mode II fracture toughness using end-notched flexural (ENF) geometry on unidirectional composites with the same three sizing materials was measured. Before testing each sample, the compliance was measured from the region of the sample with no crack, using three-point bend testing with a span of 7.62 cm (3 in.). This compliance was used to determine the flexural modulus (Eq. (6)). The flexural moduli were later used

$$E_{\text{flex}} = L^3/4bC'h^3 \quad (6)$$

$L$  = half the span;  $b$  = specimen width;  $C'$  = compliance of the sample with no pre-crack; and  $h$  = half the specimen height in the calculations for the corrected crack lengths. Each sample was loaded in three-point bend geometry with a span of 10.16 cm (4 in.) and a crack length of 2.54 cm (1 in.). This was necessary to meet the requirement that  $a = 1/2 l$ . The corrected crack length was calculated by Eq. (7)

then used in the calculation for  $G_{2c}$  (Eq. (8)).

$$a_{\text{corr}} = [8E_{\text{flex}}Cbh^3/3]^{1/3} \quad (7)$$

$C$  = compliance of the pre-cracked sample

$$G_{2c} = 9\Delta a_{\text{corr}}^2 P/2b(2L^3 + 3a_{\text{corr}}^3) \quad (8)$$

$\Delta$  = displacement at failure and  $P$  = load at failure.

Trends in the mode II composite toughness for the composites with the three different sizing materials are similar to the mode I results in that there is no significant difference between those prepared with initiators embedded in the fiber sizings and those prepared at higher temperatures and in longer cure cycles without any added initiator (Table 6). All of these phenolic–epoxy composites have relatively high mode II toughness, equaling the values of toughened epoxies [24,25] and exceeding the toughness of untoughened carbon fiber/epoxy composites [25–27]. In addition, the  $G_{2c}$  values are close to twice the  $G_{1c}$  values, as would be expected.

Composite panels (0°/90°)<sub>7s</sub> prepared from sizings (1) and (6) were tested in fully reversed ( $R = -1$ ) notched fatigue to determine the effects of the fiber–matrix interphase material on the composite fatigue performance. Robertson et al. [20] have previously shown the composite fatigue results to be particularly sensitive to changes in the fiber–matrix interface. Improved fatigue performance is noted by a decrease in the slope of the S–N curve and increase in the stress level that defines the fatigue limit, i. e. the stress level at which the material survives 10<sup>6</sup> cycles. There was no significant difference in the fatigue limits of composite panels prepared from sizing (1) and (6) (Fig. 11). This demonstrates that the performance of the composite panel is not dependent on

Table 6

Mode II composite toughness of unidirectional AS-4 carbon fiber reinforced phenolic/epoxy composites from sizings 1, 2, and 3

Sizing	Mol% Initiator	Cure cycle	Fiber vol. fraction (%)	$G_{2c}$ (J/m <sup>2</sup> )
1	None	200°C (1 h) 220°C (3 h)	66.4	1410 ^ 302
2	None	200°C (1 h) 220°C (3 h)	70.4	1254 ^ 64
3	3.2	180°C (20 min) 200°C (10 min)	69.0	1224 ^ 250

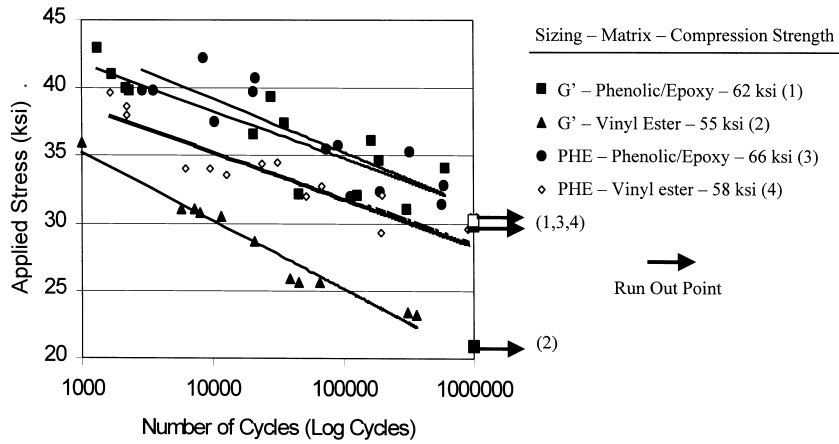


Fig. 11. Applied stress vs. number of cycles of phenolic/epoxy composites from sizings (1) and (6) compared with vinyl ester composites [20].

whether the sizing material contains the initiator. Therefore, good fatigue performance can be achieved with lower cure times and temperatures using these latent initiator systems.

Fatigue properties of these phenolic/epoxy panels were also compared to similar panels with vinyl ester matrices, since vinyl ester matrices are well established in the composite industry. Both vinyl ester panels prepared with the *G'* sizing (1) and vinyl ester panels with an improved interface (polyhydroxyether (PHE) sizing) were investigated. The vinyl ester network composition was derived from 70 wt.% of a methacrylate terminated vinyl ester oligomer ( $M_n = 700$  g/mol) co-cured with 30 wt.% styrene, and the fibers were stitched prior to composite fabrication by resin film infusion [20]. The phenolic/epoxy composites studied herein have improved fatigue limits and compression strengths relative to the vinyl ester composites with the commercially sized (*G'*) fibers and equivalent fatigue limits relative to the vinyl ester composites with the improved interface (Figs. 11 and 12). This probably reflects properties of both the matrix resins and also their interactions with the interphase materials (between fiber and matrix).

#### 4. Conclusions

Phenolic/epoxy composites with high phenolic compositions (65 wt.% phenolic/35 wt.% epoxy) are difficult to process in the melt due to the high viscosities of the resins. Temperatures at which the viscosities are in a processable range cause premature curing with even very small initiator concentrations. However high initiator concentrations are required for rapid cure at elevated temperatures. The approach of embedding the initiator in a fiber sizing allows for high initiator loadings, which results in rapid cure in the cure stage (99% conversion in less than 5 min) with minimal premature curing during the processing step. The kinetic analyses indicate that sizing materials containing monomeric organic initiators (such as TMOPP) encapsulated into polymeric sizings allow for the fastest cure times of the initiators investigated. Both initiators with inorganic cations and polymeric initiators resulted in slower cure rates and therefore were not as desirable for use as sizing encapsulated initiators.

Composite toughness, compression strength, and fatigue

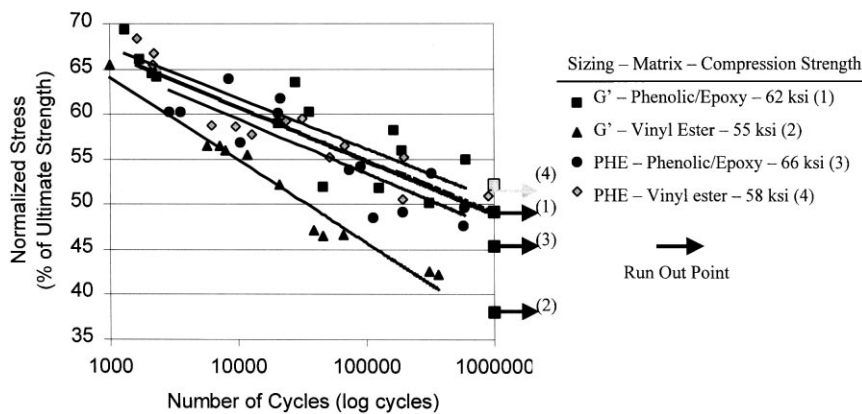


Fig. 12. Normalized stress vs. number of cycles of phenolic/epoxy composites from sizings (1) and (6) compared with vinyl ester composites [20].

were investigated both to determine the effects of the sizings on these properties and to determine the feasibility of phenolic/epoxy composites for infrastructure applications. The properties of the composite panels prepared from sizing materials with and without initiator were equivalent, indicating that embedding the initiator in the fiber sizing does not diminish the composite properties. In addition, the phenolic/epoxy composites had equivalent toughness when compared to toughened epoxies, and equivalent fatigue when compared to a vinyl ester composite with an improved interface. This is important since flame retardant phenolic composites are typically extremely brittle.

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