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Novel Matrix Resins for Composites for Aircraft Primary Structures

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PREFACE

NASA Langley Research Center awarded The Dow Chemical Company, in April 1989, a research and development contract (NAS1-18841) as a part of its Advanced Composite Technology Program. The objective of the contract is to develop novel matrix resins with improved properties and processability for primary aircraft structures. The contract comprises an initial phase of three years and three option years, and is monitored by Paul M. Hergenrother as the Technical Representative of the Contracting Officer. This report describes the work of Phase One covering the period of April 1989 to March 1992. Brief descriptions of the individual tasks and major accomplishments are provided in the Executive Summary Section.

More than forty people in Dow have participated to various extents and for various durations as contract work evolved from resin synthesis to composite panel fabrication and testing. In addition to the authors of this report, significant contributors are:

> James Bertram in the development of CET chemistry;
>
> William Shiang, Daniel Scheck, Jerry Kolb, Kurt Bell, and Lisa Wujkowski in the synthetic work of Tasks 2,3, and 4;
>
> Dan Murray and Frank Chen in cyclic oligomers;
>
> Philip Yang, Charles Lee, Mike Groleau, Scott Laman, Brian Allen, Carl Raeck, Derrick Wetters, and Donald Foye in all aspects of polymer testing, prepregging, composite processing and testing;
>
> Pamela Foster, Ronald Graunke, and Gary Buske in AB-BCB-maleimide monomer scale-up.

Acknowledgments are also due to Larry Laursen and Thomas Wells, leaders of the composite and scale-up operations respectively, whose cooperation and support have been critical to the success of this contract.

Edmund Woo
Principal Investigator

EXECUTIVE SUMMARY

The contract has five main tasks. Task One has as its objective the development of resin formulations with improved toughness and processing characteristics for resin injection molding. Emphasis is on near-term availability and, accordingly, all formulations are based on commercial or near-commercial materials. The objective of Task Two is to develop a damage tolerant prepreg composite system capable of 177°C (350°F)/wet performance based on Dow's experimental cyanate resin XU 71787.02. Task Three's objective extends Task Two's temperature performance to 400°F/wet. Task Four is more exploratory in nature and calls for the study of Diels-Alder polymerization of benzocyclobutene-based monomers with other functional groups with the expectation that these low molecular weight, low viscosity monomers would yield polymers with thermoplastic-like toughness during parts fabrication. This concept is further explored in Task Five which involves the synthesis and polymerization of cyclo-oligomeric arylene ethers.

To maximize contract productivity, it was decided at the outset to evaluate all resins against a set of screening criteria comprising processability, fracture toughness, modulus at ambient condition and at elevated temperatures, and to eliminate from further consideration those failing the screen. As a result of this selection process, parts of Task One and Task Four, and, the whole of Task Three and Task Five were terminated with the approval of the Technical Representative of the Contracting Officer. Because of the wide variety of resin chemistries involved, it was also decided that at most one or two promising candidates of the same chemistry will be evaluated in composite forms. Specific accomplishments of Phase One contract work are summarized below.

<u>Task One</u>

After screening a variety of resin chemistries, two systems have been identified as potentially useful matrix resins for composites for aircraft primary structures.

The first system comprises two RTM formulations and a powder prepreg formulation based on crosslinkable epoxy thermoplastic (CET) chemistry. All formulations yield composites with good damage tolerance (CAI ~ 40 ksi) and 180-200°F/wet mechancial performance. The RTM formulations are processable at 220-250°F. Sixty-eight pounds of CET resins have been delivered to NASA and NASA contractors for evaluation at no additional cost to the contract.

The second system is based on Dow's experimental cyanate XU 71787.02. The two RTM formulation show improved CAI over standard epoxy resins and 300°F/wet performance.

Task Two

A prepeg system capable of 350°F/wet performance and CAI of 40 ksi resulted from an in-depth study of toughening Dow's experimental cyanate XU 71787.02 with thermoplastics. The unique feature of this system is its resistance to aging as evidenced by the maintainence of fracture toughness and compressive interlaminar shear strength after exposure to air at 360-400°F for 4000 hours. Seventy-five pounds of prepreg were delivered to McDonnell Aircraft for HSCT evaluation through an addition to the contract.

Task Four

A resin with the processability of a thermoset and the toughness of a thermoplastic has been the desire of many composite scientists. The AB-BCB-maleimide resin developed in this contract is the closest approximation of this lofty goal. It has water-like viscosity upon melting (~110°C), cures without giving off volatile materials to a polymer with fracture toughness similar to many thermoplastics. Composite panels fabricated via RTM show CAI of about 50 ksi, 350°F/wet mechanical performance, and ≥90% retention of mechanical properties after aging in air at 400°F for 4000 hours. As an add-on to the contract, 32 panels were fabricated by RTM for evaluation at McDonnell Aircraft under NASA Contract NAS1-18862. Development of conventional prepreg and adhesive product forms are in progress.

The above technologies were introduced to the composite community at a Dow Plastics press briefing during the 36th International SAMPE Symposium & Exhition (Anaheim, CA, Arpil 1992). Experimental CET-3 resin XU71992.00 (see p 5) and experimental cyanate resin XU71787.09 (see p. 40) are now available from Dow for developmental purposes.

If Phase One may be likened to sowing and weeding, then the first option year will be a period for cultivating and nurturing. The CET resins will be further characterized with respect to the relationship between composite performance and processing conditions. The AB-BCB-maleimide resin will be the subject of a scale-up campaign to provide material for product form development and additional fundamental studies.

This report is divided into five sections, each covering one of the five main tasks of the contract. The sections are self-contained so that each section may be read independent of the others. A Table of Content and Lists of Tables and Figures are provided in the next few pages to facilitate quick assess to the data of interest to the readers.

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TASK 1. RTM COMPOSITE SYSTEMS

The objective of this task is to develop affordable RTM composite resin systems with improved processability and/or toughness for 93-149°C (200-300°F)-wet applications. Because resin cost is an important factor for fabrication of lower cost composite structures, the technical approach focuses on the development of new formulations of commercial or near-commercial resins that will have processing characteristics suited for RTM.

1.1. SUMMARY

Cyanate Resin Systems. Two cyanate resin formulations were identified for composite evaluation during the first year of the contract from neat resin data. The uniweave composite data obtained from RTM plaques confirms the utility of the cyanate resin system as suitable for RTM applications at 149°C (300°F)-wet operating conditions. They also exhibit fair damage tolerance (CAI values of 28 - 30 ksi).

Vinyl Ester Resin Systems. One vinyl ester formulation was selected from neat resin data and has been evaluated in composite form. The uniweave composite data indicated that it was marginally suitable for applications at 121°C (250°F)/wet. The presence of volatile (styrene) resin components and the marginal performance of the composite at elevated temperatures led to the termination of this task.

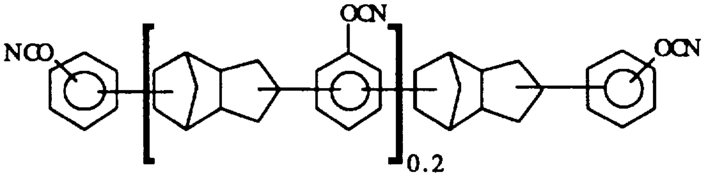
Crosslinkable Epoxy Thermoplastic (CET) Resin Systems. Two experimental CET formulations have been selected for RTM applications. XU71992.00 and XU71992.01 polymers have excellent thermal, mechanical, and processing characteristics. The first resin formulation has a higher density (1.35 g/cc vs. 1.26 g/cc, respectively) and has slightly better modulus and elevated wet performance than the second formulation. A version suitable for powder prepreg was also developed at NASA's request. All formulations give composite with excellent property retention at 82.2°C (180°F)/wet and CAI of about 40 ksi. Approximately seventy pounds of resins were produced and sampled to NASA and NASA contractors for evaluation at no additional cost to the contract.

High Temperature Epoxy-Based Resin Systems. This task was terminated after a series of resins were evaluated and determined to possess properties short of the stated goals of a tough 149°C (300°F)/wet RTM system.

1.2. RESULTS AND DISCUSSION

1.2.1. Evaluation of Cyanate Resin (Task)

Experimental cyanate resin XU71787.02, the product of several years of research effort in Dow, was originally targeted for circuit board applications. Its structure was chosen for reasons of processability, low moisture absorption, high T_g, and excellent electric properties. All references to cyanate in this report are specific to this resin unless otherwise noted. Investigation of cyanate resin as a system for use in resin transfer molding applications was begun at Dow with IR&D funding. Initial work used 20% of vinyltoluene as a diluent to reduce resin viscosity. This high concentration of vinyltoluene produces lower viscosities but also reduces polymer performance.



Experimental Cyanate XU71787.02

This work examined formulations with reduced vinyltoluene content and also the possibility of improving composite damage tolerance by adding rubber. The rubber chosen was an in-house developed material with the acronym of GRC. It comprised an elastomer core of copoly(styrene-butadiene) and a polymer shell of styrene-methylmethacrylate-acrylonitrile. The composition of the latter was selected for its compatibility with the cyanate resin such that the rubber particles dispersed in the resin would remain so after the cure. The average particles size was about 0.1 micron and the size distribution was very narrow. Formulations containing either 3% or 5% GRC, and 5%, 10%, and 15% vinyltoluene were produced and characterized for viscosity and polymer mechanical properties. Two formulations were selected for composite work: a) an unmodified cyanate Experimental Product XU-71787.02 and b) a rubber modified cyanate containing 3 wt % GRC rubber. Both cyanate systems were catalysed with 300 ppm of $Co(AcAc)_3$ and diluted with 5 wt % vinyltoluene. The clear cast mechanical properties for these resin systems are reviewed in Table 1.1.

With addition of GRC, significant toughening of the unmodified XU71787.02 polymer was achieved while incurring a 10% reduction in modulus. At 250 J/m^2, the fracture toughness of the rubber toughened formulation is 50% higher than 3501-6 (G_{1c} = 130 J/m^2), a commercially competitive system. The increased polymer fracture toughness is translated into a small improvement in compressive strength after impact (CAI 28.5 ksi for the unmodified version *vs* 30.5 ksi for rubber modified) as shown in Table 1.2.

Both resin formulations were used to prepare composite panels for analysis. More information on the composite manufacturing process can be found in the experimental section. The fiber volume of the composites tested was 60%, as measured by acid digestion. The flexural and tensile values on both resin formulations are shown in Table 1.3. Where multiple composite panels were tested, the values in brackets are the 90% confidence interval of the mean. The mean was determined from the averaged test values from each composite panel. Where only one panel was tested, the values in parenthesis are the standard deviation of the test data.

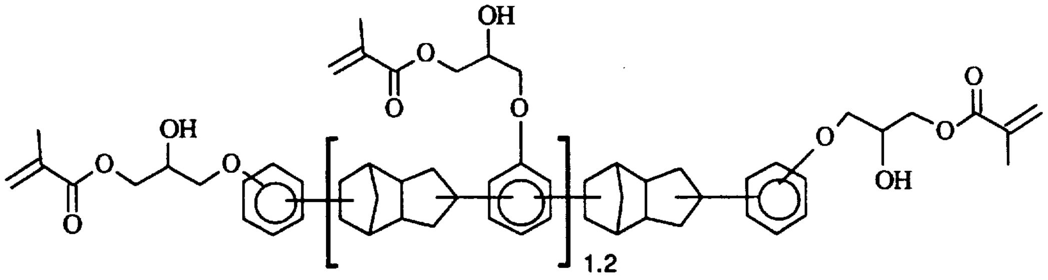
The tensile, flexural, and compressive properties show that rubber toughened formulations produced composites equivalent to the unmodified analog. The increase in toughness and decrease in flexural modulus of the resin, shown in Table 1.1, are not manifested in the flexural, tensile, or compressive composite properties in Tables 1.2 and 1.3. Indeed, the 0° flexural data of both formulations compares favourably to industry standard prepreg systems like 3501-6/AS4 (strength 300 ksi, modulus 18.5 ksi). The 0° tensile strength is lower than that observed for 3501-6/AS4 (strength 315 ksi, modulus 21 msi), but this is not a surprising result since the RTM composite preforms are made using a unidirectional fabric. The fill fibers that hold the fabric together cause the 0° fibers to have a sinusoidal oscillation. This is in contrast to 3501-6 prepreg tape, which does not have fill fibers. Accordingly, the 90° tensile values are similar to those of 3501-6/AS4 (strength 7.8 ksi, modulus 1.4 msi), indicating that the fiber-matrix adhesion obtained in the RTM process utilizing AS4 unidirectional fabric is as good as the fiber-matrix adhesion obtained in 3501-6 prepreg using AS4 fiber.

Retention of flexural and compressive modulus at 149°C (300°F)/wet of the rubber toughened formulation shown in Table 1.2 and 1.3 is indistinguishable from its unmodified analog. The 15% drop in compressive strength is probably caused by the 15% lower modulus of the rubber toughened resin at 300°F/wet, shown in Table 1.1. Both the strength and modulus retention of the rubber toughened XU71787.02 are superior to those of 3501-6/AS-4. The rubber toughened XU71787.02 retains 76% of its compressive strength at 300°F compared to 76% at 82.2°C (180°F) for 3501-6/AS4. The rubber toughened XU71787.02 retains 99% of its compressive modulus at

300°F compared to 90% at 104.4°F (220°F) for 3501-6/AS4. However, the actual strength and modulus values of 3501-6/AS4 at 180°F (190 ksi and 20 msi, respectively) and the modulus at 220°F (18.0 msi) are higher than the corresponding rubber toughened XU71787.02 compressive properties.

1.2.2. Evaluation of Vinyl Ester Resin.

The strategy used in executing this task was to develop a toughened vinyl ester resin by reformulating standard epoxy resins with rubber and converting them to vinyl ester resin (VER). Vinyl ester resins have been studied extensively. The characteristics for which they are most noted are their low viscosity, ease and versatility of cure, and excellent mechanical properties and corrosion resistance. These characteristics make vinyl esters excellent candidates for use in structural composites made via RTM. Production of a vinyl ester that has high modulus, low water uptake, a high glass transition temperature, and good toughness would provide an excellent RTM resin. Since the alicyclic structure of cyanate XU71787 appears to make positive contributions to the properties of the resulting polymer, it was decided to examine a vinyl ester of similar structure, namely the vinyl ester derived from Tactix® 556. Four vinyl ester systems were produced from blends of this material with 18% or 25% of the vinyl ester of a bisphenol A epoxy. Toughening was approached by adding to the base resins 3% CTBN, 5% CTBN, and 5% DAR. DAR, an acronym for dispersed acrylic rubber, is made by the graft polymerization of 2-ethylhexyl acrylate in a bisphenol A diglycidyl ether. It may be viewed as a core-shell rubber with an elastomeric acrylate core and a bisphenol A glycidyl ether shell. Clear cast mechanical properties showed that DAR was superior to CTBN in enhancing the fracture toughness of the VER. However, the 40% retention of initial flexural modulus of moisture saturated samples at 121.1°C (250°F) with the



Vinyl Ester Derived from Tactix® 556

DAR modified VER was unacceptably low. Higher post cure temperature (350°F) was found to improve the modulus retention (55%) and further investigation has identified three other formulations that retain greater than 50% of their room temperature-dry flexural modulus at 250°F/wet. The clear cast mechanical data for some of these formulations are discussed below and shown in Table 1.4. Four changes in the formulation from the baseline system (formulation A) were evaluated: 1) reducing the styrene concentration to 25% (formulation B), 2) reducing the styrene concentration to 16% while adding 20% vinyltoluene (VT) (formulation C), 3) changing the reactive diluent to paramethylstyrene (PMS) (formulation D), and 4) and increasing the Vinyl Ester Derived from Tactix® 556 ratio in the formulation (formulation E). The first, second, and third changes were made in response to Federal regulatory activities which concern reducing styrene exposure in the work place. The fourth change was an attempt to improve the retention of flexural properties at 250°F/wet. None of the new formulations exceeded the mechanical properties of the original styrene formulation (column A), which itself does not exceed the mechanical properties of 3501-6. Because of the regulatory activity concerning styrene, the 36% *p*-methylstyrene vinyl ester formulation was chosen to investigate further.

Eight ply unidirectional composite panels were made with formulation D for compression testing. The Boeing compressive strength values obtained at ambient and 250 °F/wet are in Table 1.5. The initial compressive strength is comparable to that of the rubber toughened XU71787.02. However, the compressive strength retention of moisturized samples at elevated temperatures is low. In view of the mediocre performance of the PMS vinyl ester resin, and with concurrence of the NASA Technical Representative of the Contracting Officer, the vinyl ester task was terminated.

1.2.3 Evaluation of Crosslinkable Epoxy Thermoplastics (CET).

The concept of CET resin was originally developed at Dow nearly a decade ago. Briefly, the chemistry involves chain extension and crosslinking in a controlled manner so that the best compromise in heat resistance and toughness can be achieved. Our commercial product, Tactix® 695, is an aromatic amine-cure system designed for prepreg applications. As such, it does not have the rheological profile suitable for RTM. The strategy was to develop a one-pot RTM resin system that had sufficiently low viscosity over a period of time for resin injection. The thermal, mechanical, and processing characteristics of more than fifty CET formulations were evaluated. The formulation that possessed the best mechanical properties initially identified, herein referred to as CET-2, had a high density (1.75g/cc) compared with an industry standard resin such as 3501-6 (1.27 g/cc). With concurrence of the Technical Representative of the Contracting Officer, work on the CET-2 system was terminated, while development of a lower density CET formulation was to continue. The search for the optimum formulation that produced the best compromise of mechanical properties, resin density, and processability identified two resins that were suitable for RTM applications, herein referred to as XU71992.00 resin and XU71992.01 resin. The clear cast properties of TACTIX 695, CET-2, XU71992.00, and XU71992.01 resins are reviewed in Table 1.6.

CET resins are solids at room temperature and processing these materials requires that they must be heated to lower the viscosity (<500 cps). However, heat also increases the rate of reaction of the resin which builds viscosity faster by advancing the CET resin. Therefore, there exists an optimum processing temperature for the CET resins. The viscosity behavior of the XU71992.00 and XU71992.01 resin systems is shown in Figure 1.1. XU71992.01 resin has a higher viscosity than XU71992.00 resin. Both resins have to be heated in excess of 220°F to reduce the viscosity to a point where they can be used in RTM. The effect temperature has on the viscosity build of these two resins is shown in Figures 1.2 and 1.3. XU71992.00 resin maintains a viscosity below 500 cps for 3 hours at 250°F. XU71992.01 resin, because of its slightly higher viscosity, must be processed at 127-132°C (260-270°F) where approximately two hours molding time is available.

As shown in Table 1.6, most of the clear cast mechanical properties of XU71992.00 and XU71992.01 resins are equivalent or superior to TACTIX 695 resin; only the tensile modulus and elongation are lower. The fracture toughness is 50% higher than that of 3501-6 ($G_{1c} = 130$ J/m^2) and is translated into the improved CAI strength shown in Table 1.7. The CAI strength of 39 ksi for the CET resin is almost twice as high as that of 3501-6/AS4 (22 ksi).

The data on modulus and strength retention of moisture saturated samples at elevated temperatures for XU71992.01 and XU71992.00 is shown in Figure 1.4 and 1.5, respectively. The modulus of the lower density formulation drops off faster at high temperature. Both formulations are suitable for 200-220°F/wet applications.

Prior to terminating work on the CET-2 formulation composite panels and the mechanical properties on uni weave AS-4 (3K, Hercules®) were obtained and are reviewed in Table 1.8 along with comparable composite data for XU71992.00. The IITRI compression strength of both CET-2 and XU71992.00 are equivalent to 3501-6/AS4. Also, the fiber-resin interface as judged by the 90° flexural strength of CET-3 is comparable to that of 3501-6/AS4 (7.8 ksi).

In the course of this work, we undertook the additional task of developing a powder prepreg version of CET-3 resin at the request of NASA Langley. Because there is no need to attain low viscosity for liquid processing, a different formulation was chosen which was advanced partially to a non-sintering powder with a T_g (before cure) of about 60°C (140°F). The properties of this resin (with an experimental resin designation XU 71991.00) and its polymer is given in Table 1.9. Composite panels were prepared by the same method using a batch of resin before partial advancement. Data generated on these panels are compared to those of the RTM versions in Table 1.10. Viscosity profiles of the powder version are provided in Figures 1.6 and 1.7.

Fifty-five pounds of XU 71992.01 and thirteen pounds of XU 71991.00 were produced and sampled to NASA and NASA contractors for evaluation at no additional cost to the contract.

1.2.4. Evaluation of High Temperature Epoxy-Based Resin Systems.

The strategy employed to develop an RTM resin system that produces tough composites with 300°F-wet performance began with TACTIX* 742 and TACTIX* 556 epoxy resins. To develop a material that performs at 300°F following moisture saturation, it is necessary to produce a material that has a glass transition temperature substantially higher than 300°F and has low moisture absorption. Because moisture absorption depresses both polymer modulus and Tg, the more moisture the final polymer absorbs the higher the initial dry T_g and modulus must be. The logic of choosing TACTIX 742 is that it produces a polymer with an exceptionally high T_g (572°F) when cured with 4,4'-diaminodiphenylsulfone (DDS) and Tactix® 556 produces a polymer with low moisture absorption (approximately 2% moisture absorbed at equilibrium when cured with DDS).

DDS is a commonly used epoxy curing agent in many high performance prepreg materials. The advantages of this hardener is that it typically forms polymers with flexural moduli >450 ksi and $T_g > 204$°C (400°F). However, its high melting point (350°F) makes this solid material very difficult to use in RTM formulations. The use of DDS in a two part RTM system, would result in heating the hardener side to at least 350°F in order to pump this material. If instead, a one part system was formulated with DDS hardener it would suffer from the same sort of viscosity instability problems that effect typical epoxy prepregs, especially as the temperature of the mix is increased to allow molding. Hence, the desirable polymeric properties produced by curing an epoxy with DDS (see Tables 1.11 -1.13) are not available because of the lack of RTM processability of this material.

Diethyltoluenediamine (DETDA) is used commercially as an epoxy curing agent in RTM formulations. The advantages provided by this low viscosity aromatic amine are good processability and production of a polymer with a high glass transition temperature [Tg > 191°C

(375°F)]. However, curing a variety of epoxy resins with DETDA always produced polymers with modulus values less than 400 ksi. As a result, a one or two part resin system using DETDA curative will form a material that is processable, has an acceptably high Tg, but has insufficient modulus to meet the minimum value of 450 ksi (see Tables 1.11 1.13). Attempts to increase the modulus of the polymer by DETDA cure of higher functionality epoxy resins was unsuccessful (see Table 1.11).

Phenol-formaldehyde novolacs are not typically used to cure epoxy resins. The cure rate of an epoxy with a novolac is too fast to be useful in RTM applications when using the typical amine, imidazole, ammonium, or phosphonium catalysts. Controlling the cure rate of the reaction between a novolac and epoxy is the most difficult part of this chemistry. With a latent catalyst that is thermally activated, novolac cured epoxies could form very useful RTM systems. The modulus of polymers produced in this reaction are typically 410-460 ksi with a high strain to yield/failure (>7%) and low moisture absorption. However, the polymers formed generally have a fairly low T_g (121-170°C). Epoxy resins from difunctional to multifunctional when cured with a novolac produced glass transition temperatures with a maximum of 170°C (338°F) (see Tables 1.11 to 1.13). These one-pot novolac cured epoxy resin systems have good RTM processability and a sufficiently high polymeric modulus is obtained, but the glass transition temperatures of polymers is not high enough to produce a 300°F/wet material.

1.3 CONCLUSIONS

1.3.1. Cyanate Resin Chemistry.

In the composite tests performed there was no significant improvement in properties observed for the rubber toughened XU71787.02 composite as compared to those of XU71787.02. Composites of cyanate resin made by RTM are similar to those of 3501-6 except the cyanate has a higher use temperature and is somewhat more impact resistant: CAI of about 29 ksi *vs* 22 ksi for 3501-6. The data obtained on both neat resin and composites indicate that the cyanate will be useful at 275-300°F/wet.

1.3.2. Vinyl Ester Resin Chemistry.

Federal regulatory activities concerning styrene exposure in the work place focused the reformulation efforts to identify alternative reactive diluents for vinyl ester resins. *p*-Methylstyrene was identified as the best styrene replacement material, even though its mechanical properties were reduced. Regulatory activities coupled with the marginally acceptable mechanical properties led to the termination of this task.

1.3.3. CET Resins.

The CET-2 resin which was originally produced for this task has been replaced with XU71992.00 and XU71992.01, new lower density formulations. Composite parts on both uni-weave and fabric have been fabricated with the new formulations via RTM and look very promising. The data collected on both clear cast polymer and composite indicate that following equilibrium moisture saturation the material will be useful at 200-220°F. The polymer generated on cure is a very tough material and produces composites with CAI values of 38-40 ksi. This resin processes easily at 250°F with over a two hour window for molding. This combination of processability and thermal and mechanical properties provides an ideal resin for RTM applications forming composites for subsonic aircraft. A version of CET-3 suitable for powder prepreg has been developed. Fifty-five pounds of the powder version and thirteen pounds of the RTM version were produced and sampled to NASA and NASA contractors for evaluation.

1.3.4. High Temperature Epoxy-Based Resins.

Work on this task was terminated when it was determined that the goal of a tough epoxy-based RTM resin that will maintain useful properties at 300°F following moisture saturation was unrealistic. Standard amine curatives such as DDS and DETDA provided epoxy formulations that were not processable or had insufficient modulus, respectively. Use of phenol-formaldehyde novolac as a curative provided good processability and polymeric modulus but low T_g.

1.4. FUTURE WORK

Being the most promising system developed in this Task, the CET-3 resins will receive further attention in the first option year of the contract. As pointed out above, samples of both versions have been made available to various people associated with the ACT Program, and, therefore, much of the work to be done will depend on the nature of the feedback. It is also planned to study the microcracking resistance of CET-3 composite panels to determine if its improved toughness would translate into improved resistance to microcracking during temperature cycling. Some detail aspects of CET-3 resin chemistry related to storage stability and the influence of minor stoichiometric changes on polymer properties will also be examined.

1.5. EXPERIMENTAL

Cyanate formulations. XU71787.02 cyanate resin is heated to ca. 80°C to liquefy, and the 300 ppm CoAcAc (cobaltacetylacetonate) dissolved in vinyltoluene (5 wt%) is slowly poured into the liquid cyanate with good stirring.

Rubber modified cyanate formulations. XU71787.02 cyanate resin is heated to ca. 80°C to liquefy and blended with 1/3 the amount of XU71787.07. Three hundred ppm CoAcAc dissolved in vinyltoluene (5 wt%) is slowly poured into the cyanate blend with good stirring.

Cyanate unreinforced clear cast panel preparation. 300 g of cyanate formulation is degassed and poured into a mold (approximately 12" x 12" x 0.125") made from two aluminium plates. The resin is cured for 2 hours at 160°C, 2 hours at 180°C (356°F), and postcured for 2 hours at 240°C (464°F). Frekote® 44 was used as the mold release agent.

Synthesis of vinyl ester resin. A 20-liter reactor is charged with 1047 g of D.E.R.® 383 liquid epoxy resin and 3140 g of experimental epoxy XP 71756.00. The mixture is heated and stirred under nitrogen until the solid resin is melted. When the temperature is 90-95°C (194-203°F), the nitrogen sparge is replaced with an air sparge. Hydroquinone is added and immediately followed by a stoichiometric equivalent of glacial methacrylic acid. When the temperature returns to 90°C, reaction catalysts are added. The temperature is gradually increased to 118°C (244°F) and the reaction is continued until the acid concentration is less than 1.1 % as COOH. The reaction is stopped with the addition of oxalic acid dihydrate, styrene, and inhibitor.

Synthesis of 5% DAR-modified vinyl ester resin. A 20-liter reactor is charged with 544 g of D.E.R.® 383 liquid epoxy resin, 1256 g of XU71790.04 (a 40 weight percent dispersion of acrylate rubber in liquid epoxy resin), and 3231 g of XP71756.00. The mixture is heated and stirred under nitrogen until the solid resin is melted. When the temperature is 90-95°C, the nitrogen sparge is replaced with an air sparge. Hydroquinone is added and immediately followed by a stoichiometric equivalent of glacial methacrylic acid. When the temperature returns to 90°C, reaction catalyst are added. The temperature is gradually increased to 118°C, and the reaction is continued until the acid concentration is less than 1.1% as COOH. The reaction is stopped with the addition of oxalic acid dihydrate, styrene and inhibitor.

Vinyl ester resin and clear casting test methods. Kinematic viscosity was determined by the methods of ASTM D-445 and D-2515. Density was determined using a Mettler-Paar Densitometer Model DMA46 as described in ASTM D-4052. Gel time at 25°C (77°F) was measured with an American Analog gelometer using 100 grams of resin catalysed with 1.83% HiPoint 90 (methyl ethyl ketone peroxide, Witco) and 0.5% cobalt naphthenate (6% cobalt). SPI 180°F gel time was performed by addition of 1% benzoyl peroxide (BPO) as resin catalyst.

One-eighth inch clear castings were prepared by addition of 0.3% cobalt naphthenate and 1.22% HiPoint 90 (MEKP) into 300 grams of vinyl ester resin and mixed thoroughly. The resin was degassed and poured into aluminium molds. The resin was cured for 16 hours at 25°C and postcured two hours at 177°C (350°F). Use of Mylar® release film aided in removal of the casting from the mold.

Composite panel fabrication by RTM. 16 plies of 3K AS-4 uniweave fabric, obtained from Textiles Technology, was laid up with meticulous detail to fiber alignment. Figure 1.8 shows the RTM equipment used to make the composite panels. The resin is pushed by nitrogen gas (60 psi) from the heated pressure pot, through the heated transfer line to the fan gate of the mold. Once the resin is in the mold as shown in Figure 1.9, it travels around the preform and out through the resin exit port. After this port is closed, the resin is forced through the length and width of the preform, moving toward the center, and out through vent ports on the top of the mold. This process typically takes between one and two hours.

The quality of the composite panels made is ascertained by ultrasonic non-destructive evaluation techniques, otherwise known as "C-scan". Composite panels were scanned using a Dupont NDT Systems Ultrascan 333 Inspection System with multisonic/PC scan control, ultrasonic instrument and data acquisition and imaging software. 10 MHz focused (3" focal length, 0.5 crystal diameter) transducers were used to scan all composite panels. Through transmission was used to identify large defects. Once identified, defects type and location were clarified using pulse echo. Finally, three 3" x 3" areas of the panels were scanned in the pulse-echo mode to determine the void volume. With our instrument, resolution scanning 9 sq.in. using a 10 MHz transducer is on the order of the wavelength of the sound inside the composite panel, i.e. 0.1 mm. Defects smaller than 0.1 mm in diameter will not be identified. With this resolution an estimate of void volume was obtained. Only composite panels with less than 1% void volumes were tested.

The 16 ply uni composite panels provided enough test specimens to perform 0° and 90° flexural and tensile testing as well as compression specimens for analysis by the IITRI method. Eight-ply uni-composite panels were made to determine the compression (RTD and ETW) properties by SACMA recommended tested method SRM 1-88.

Sample preparation and conditioning. Samples were cut from prepared panels using a Micromatic Precision Slicing & Dicing Machine made by Micromech Manufacturing Corporation. This diamond wheel cutting device insured that the samples had parallel sides and exact dimension. Before mechanical tests were conducted, samples identified as ambient-dry were dried thoroughly in a oven for at least 16 hours at 120°C (248°F).

Moisture saturation conditioning. Flexural specimens were used to determine the moisture absorption of cured clear cast and composite panels. Both the clear cast and composite samples were dried for at least 16 hours at 120°C, cooled over dessicant, and weighed prior to moisture treatment. The clear cast samples were placed in boiling water for 14 days, the time to reach moisture saturation. The composite samples were place into a Blue M temperature/humidity chamber at 180°F-95 RH for 4-8 weeks, the time to reach moisture saturation. The percentage weight gain due to water absorption was determined by reweighing the flexural samples during periodic removal from moisture treatment, until the sample weights were stabilized.

Elevated temperature flexural test conditions. All clear cast and composite moisture saturated samples were removed from the moisture treatment, dried with a paper towel, weighed, and placed into room temperature deionized water until they were tested. The temperature of the specimen during the test was estimated by using a thin film detector embedded in a flex test sample, which was placed adjacent to the sample being tested. The thermocouple used was an OMEGA® thin film detector (2 mm X 3 mm X 2 mm, catalogue No. A2105). The oven used during testing was a Thermotron hot/wet environmental chamber.

The precision of elevated temperature testing is effected by the ability to provide the same thermal history to each specimen tested. By monitoring the temperature of the embedded thermocouple during testing, the estimated thermal history of each sample can be documented and the time it takes the sample to "come to temperature" can be optimised, reducing the amount of water lost prior to testing. Water loss will have an adverse affect on both the accuracy and precision of the data obtained. However, since water will be lost during testing above 100°C (212°F), the accuracy of elevated temperature testing will be a rough estimate of the "true" value. The same estimated thermal history can be accurately reproduced from sample to sample, thus increasing the precision of the test.

Flexural testing of clear cast samples. The flexural tests were performed using the three point bending procedure described in ASTM D-790. The sample dimensions were 3.0" x 0.5" x 0.125".

The support span was 2.00", which made the support span to sample thickness ratio for this test 16:1. The crosshead rate of motion was 0.05"/minute. Five samples were tested at each test condition.

Flexural testing of composite samples. The 0° and 90° flexural tests were performed using the three point bending procedure described in ASTM D-790.

a. The sample dimensions were 7.3" x 1.0" x 0.09" for 0° flex specimens. The corresponding support span was 5.63", which made the support span to sample thickness ratio for this test 60:1. The crosshead rate of motion was 0.56"/minute. Five samples were tested at each test condition.

b. The sample dimensions were 2.5" x 1.0" x 0.09" for 90° flex specimens. The corresponding support span was 1.5", which made the support span to sample thickness ratio for this test 16:1. The crosshead rate of motion was 0.04"/minute. Five samples were tested at each test condition.

Tensile testing of clear cast samples. The reference standard for this test was ASTM D-638. Samples for tensile testing measured 8.5" x 0.5" x 0.125". Instron model 4505 was used to perform the tensile test. Instron model 2630-037 axial strain gauge extensometer that has 2" gauge length and a 50% range and a Instron model A1439-1014 transverse strain extensometer that has 2.5 mm range were used to measure the strain during the tensile test. Five specimens were tested at each test condition.

Tensile testing of composite samples. The 0° and 90° tensile tests were performed using ASTM D-3039. The conditions for each test are shown below. The conditions for each test are shown below.

a. The sample dimensions were 9" x 0.5" x 0.09" for 0° flex specimens. The gage length was 5.0".The crosshead rate of motion was 0.02"/minute. Five samples were tested at each test condition.

b. The sample dimensions were 6.5" x 1.0" x 0.09" for 90° flex specimens. The gage length was 5.0". The crosshead rate of motion was 0.02"/minute. Five samples were tested at each test condition.
Strain gages (350Ω) were used to measure the strain during both 0° and 90° tensile tests. Strain gages and installation procedures that were followed are available from Measurements Group, Inc., P.O. Box 27777, Raleigh, North Carolina 27611.

Tab material was made of an epoxy/glass electrical laminate (for room temperature testing) purchased from Norplex-Oak Co., 505 King Street, LaCrosse WI. The tab dimensions were 1.75" x 0.058" and the tapered angle (10°) was machined into the tab using a jig attached to a belt sander.

The test panel was cut large enough so that all 0° or 90° tensile specimens could be cut from it after the tapered-tab material was affixed to the test sample. The tab material was adhered to the test sample using FM123-2 (thickness of 0.01"), a room temperature adhesive film made by American Cyanamid Co., Bloomingdale Areospace Products, Havre Degrace, Maryland, 21078. The four tapered tabs were placed onto the test sample with a jig to ensure proper front-to-back tab alignment as well as to ensure that the tapered edge of the tab was perpendicular to the uni fibers of the test sample. The jig had an adjustable cavity depth that could be customized to the exact dimensions of the tabbed sample. By design, the tab-specimen sandwich was slightly taller than the cavity depth. The jig compressed the tab-specimen sandwich while the adhesive was curing(two hours at 100°C), causing a small amount of the film adhesive to flow out from under the tab material. This eliminated thickness gradients and air pockets in the cured adhesive and resulted in an adhesive thickness of 0.008". After the adhesive was cured, the samples were cut from the tabbed-test sample using the Micromatic Precision Slicing & Dicing Machine.

Plane strain fracture toughness testing. Testing was performed using the compact tension geometry as described in the ASTM E399 test method. Samples had a nominal sample geometry of 1.02"x1.06"x0.125". A sharp notch introduced by a new razor blade produced a sharp crack ahead of the starter notch. The typical ratio of initial crack length to specimen width is about 0.3 to 0.4. The sharpness and the quality of these initial cracks were verified by the excellent agreement between initial and subsequent crack propagations. Only specimens that had crack length (a) to width (W) ratios between 0.3 and 0.6 were used for data analysis; this included multiple crack data. Furthermore, only data from those samples whose crack surface remained in the plane normal to load direction were used to calculate K_{IC}. The crosshead rate of motion was 0.02" per minute. An Instron Model 1127 using a 1000 pound load cell was used. The data acquisition software used was Automated Materials Testing System Series IX v4.09a. Only peak load values were obtained from this software since actual crack lengths were measured after the test was performed. K_{IC} were averages of at least 10 specimens, with two or more crack lengths for each specimen. Relative standard deviations were generally ± 2%.

Compression testing. Three different test methods were used to determine compressive properties, IITRI, SRM 1-88, and SRM 2-88. The conditions for each test are shown below.

The test method used for IITRI compression testing is ASTM D-3410. The sample dimensions are 0.5" x 5.0" x 0.09". The gauge section was 0.5". These samples were tabbed using the same tabbing procedure described in the composite tensile test above. Test samples were run on an Instron model 1127 using a 20,000 lbs load cell.

The SACMA recommended test method SRM 1-88 test method was used. This test procedure is similar to ASTM D-695. The modulus sample dimensions are 0.5" x 3.0" x 0.045" and the strength samples dimensions are 0.5" x 3.188" x 0.045". The samples for strength determination were tabbed (0.188" gauge section), whereas the modulus samples were not.

The test method used for compression after impact testing is SRM 2-88. The sample dimensions are 4.0" x 6.0" x 0.21". The impact energy level is 1500 in-lbs/in resulting in a drop weight of 12.4 lbs and a tup diameter of 5/8". The damage area was determined by C-Scan. Test samples were run on an Dynatup 8200 using a steel test fixture.

1.6 TABLES AND FIGURES

Table 1.1. Mechanical Properties of Clear Cast Panels Made of Unmodified XU71787.02 and Rubber Toughened XU71787.02 Resins Diluted with Vinyltoluene (5%)

Mechanical Test	Mechanical Property	Unmodified XU71787.02	Rubber (3% GRC) Toughened XU71787.02
Fracture	K_{1c} (psi $\sqrt{in}$)	530(9)	845(18)
Toughness	G_{1c} (J/m^2)	85(3)	250(11)
Flex	25°C (77°F)-Dry		
	Strength (ksi)	17.4(0.5)	18.1(1.6)
	Modulus (ksi)	500(2)	440(6)
	Strain (%)	3.5(0.1)	4.3(0.5)
	149°C (300°F)-Wet		
	Strength (ksi)	11.9(0.2)	10.3(0.2)
	Modulus (ksi)	310(7)	265(2)
	Strain (%)	10(1)	12(1)
	Retention		
	Strength (%)	70(-)	57(-)
	Modulus (%)	62(-)	60(-)
Tensile	25°C (77°F)-Dry		
	Poisson's Ratio	0.40(0.01)	0.39(0.01)
	Strength (ksi)	10.0(0.3)	11.3(0.5)
	Modulus (ksi)	480(6)	430(20)
	Elongation (%)	2.4(0.1)	3.5(0.2)

All average mechanical values for both formulations of Experimental Product XU71787.02 represents one clear cast panel.
() Standard deviation represents only one clear cast panel.
The cure schedule on clear cast panels is 2 hrs @ 160°C and 2 hrs @ 180°C, followed by a post cure schedule of 2 hrs @ 230°C.

Table 1.2. Composite Compressive Properties of Unmodified XU71787.02 and Rubber Toughened XU71787.02 Resins

Mechanical Test	Mechanical Property	Unmodified XU71787.02	Rubber Toughened XU71787.02
0° Compression by IITRI[a]	25°C (77°F)-Dry		
	Strength (ksi)	$180[15]_2$	$188[8]_2$
0° Compression by SRM 1-88[b]	25°C (77°F)-Dry		
	Strength (ksi)	171(10)	$180[22]_2$
	Modulus (ksi)	$15.9[1.1]_2$	$16.4[0.2]_2$
	149°C (300)°F Wet		
	Strength (ksi)	$162[39]_2$	$137[15]_2$
	Modulus (ksi)	$16.3[1.2]_2$	$16.0[0.3]_2$
	Retention		
	Strength (%)	100(-)	$76[18]_2$
	Modulus (%)	$100[0]_2$	$99[3]_2$
Compression After Impact[c]	25°C (77°F)-Dry		
	Strength (ksi)	28.5(0.7)	30.5(0.3)

$[]_n$ 90% confidence interval for mean value generated from n different composite panels.
() Standard deviation represents only one composite panel.
The cure schedule on all composite panels is 3 hrs @ 165°C followed by a post cure schedule of 2 hrs @ 240°C.
All composite mechanical properties reflect a 60% Fiber Volume.

[a] 16 Ply uni weave AS-4 (3K, Hercules®). The test method followed was ASTM D-3410 procedure B.

[b] 16 Ply uni weave AS-4 (3K, Hercules). The test method followed was SACMA recommended test method 1-88. This procedure is very similar to the Boeing modification of ASTM D-695.

[c] 16 Ply 8 HS AS-4 (3K, Hercules). The test method followed was SACMA recommended test method 2-88.

Table 1.3. Flexural and Tensile Properties of 16 Ply AS-4 Uni Weave Composites Made With Unmodified XU71787.02 and Rubber Toughened XU71787.02 Resins

Mechanical Test	Mechanical Property	Unmodified XU71787.02	Rubber Toughened XU71787.02
0° Flex	25°C (77°F)-Dry		
	Strength (ksi)	$298[15]_3$	$249[26]_4$
	Modulus (msi)	$19.8[1.5]_3$	$18.6[0.6]_4$
	Strain (%)	$1.70[0.02]_3$	$1.5[0.1]_4$
	149°C (300°F)-Wet		
	Strength (ksi)	$142.5[4.6]_2$	$126[25]_2$
	Modulus (msi)	$15.7[0.8]_2$	$14.8[0.6]_2$
	Strain (%)	$0.98[0.01]_2$	$0.9[0.1]_2$
	Retention		
	Strength (%)	$47[2]_2$	$55[12]_2$
	Modulus (%)	$76[6]_2$	$81[7]_2$
90° Flex	25°C (77°F)-Dry		
	Strength (ksi)	$12.4[0.3]_3$	$11.3[1.3]_4$
	Modulus (msi)	$1.47[0.02]_3$	$1.37[0.08]_4$
	Strain (%)	$0.8[0.1]_3$	$0.9[0.2]_4$
	149°C (300°F)-Wet		
	Strength (ksi)	$6.0[1.1]_2$	$7.0[0.5]_2$
	Modulus (msi)	$0.70[0.01]_2$	$0.56[0.06]_2$
	Strain (%)	$1.00[0.06]_2$	$1.5[0.3]_2$
	Retention		
	Strength (%)	$49[9]_2$	$63[26]_2$
	Modulus (%)	$47.8[0.3]_2$	$44[13]_2$
0° Tensile	25°C (77°F)-Dry		
	Strength (ksi)	$220[43]_2$	$189[9]_2$
	Modulus (msi)	$18.6[0.9]_2$	$19.8[4]_2$
	Elongation (%)	$0.8[0.1]_2$	$1.05[0.01]_2$
90° Tensile	25°C (77°F)-Dry		
	Strength (ksi)	$7.1[1.2]_2$	$8.49[0.03]_2$
	Modulus (msi)	$1.55[0.06]_2$	$1.4[0.3]_2$
	Elongation (%)	$0.5[0.1]_2$	$0.71[0.06]_2$

□$_n$ 90% confidence interval for the mean value generated from n different composite panels.
The cure schedule on all composite panels is 3 hrs @ 165°C followed by a post cure schedule of 2 hrs @ 240°C.
All composite mechanical properties reflect a 60% Fiber Volume.

Table 1.4. Mechanical Properties of Clear Cast Panels Made With Rubber (5% DAR) Modified Vinyl Ester Resin

Mechanical Test	Property	A Low HEN 36% STY	B High HEN 25% STY	C High HEN 20% VT 16% STY	D High HEN 36% PMS	E High HEN 36% STY
Fracture Toughness	K_{1c} (psi √in)	630	640	605	530	635
	G_{1c} (J/m^2)^a	145	140	140	115	140
Flex	77°F-Dry					
	Strength (ksi)	17.0	17.0(	18.0	17.5	18.5
	Modulus (ksi)	460	455	470	460	450
	Strain (%)	4.5	5.0	4.5	4.5	5.
	250°F-Wet					
	Strength (ksi)	4.5	4.1	4.5	5.5	4.9
	Modulus (ksi)	248	205	217	251	248
	Strain (%)	3.9	3.7	3.5	4.1	3.7
	Retention					
	Strength (%)	26	24	25	31	26
	Modulus (%)	54	45	46	55	55
Tensile	77°F-Dry					
	Strength (ksi)	9.0	9.5	9.0	9.5	10.0
	Modulus (ksi)	420	450	420	375	445
	Elongation (%)	3.0	3.0	3.	3.5	3.5

The cure schedule on all clear cast panels is 16 hrs @ 77°F, followed by a post cure schedule of 2 hrs @ 350°F.

[a] Calculated using tensile modulus and a Poisson's Ratio of 0.35.

HEN --- Vinyl ester from Tactix® 556
PMS--- *p*-Methylstryrene
VT --- Vinyltoluene
STY --- Styrene

Table 1.5. Compressive Properties on 8 Ply Uni Weave AS-4 Composites Made With Rubber (5% DAR) Modified Vinyl Ester Resin Containing *p*-Methylstyrene

Mechanical Test	Mechanical Property	High HEN 36% PMS
0° Compression by SRM 1-88[a]	77°F-Dry	
	Strength (ksi)	175(15)
	Modulus (ksi)	16.6(0.9)
	300°F-Wet	
	Strength (ksi)	85(7)
	Modulus (ksi)	18.4(0.3)
	Retention	
	Strength (%)	49(-)
	Modulus (%)	100(-)

() Standard deviation represents only one composite panel.

The cure schedule on all clear cast panels is 16 hrs @ 77°F, followed by a post cure schedule of 2 hrs @ 350°F.

[a] The test method followed was SACMA recommended test method 1-88. This procedure is very similar to the Boeing modification of ASTM D-695.

Table 1.6. Physical Properties of Clear Cast Panels Made With CET (Crosslinkable Epoxy Thermoplastic) Resins

Test	Property	Tactix® 695	CET-2	XU71992.00	XU71992.01
Fracture Toughness	K_{1c} (psi $\sqrt{in}$)	630[50]$_3$	835[166]$_2$	835(52)	711(46)
	G_{1c} (J/m^2)	137[20]$_3$	220[62]$_2$	245(30)	192(25)
Flex	77°F-Dry				
	Strength (ksi)	18.5[0.6]$_3$	22.5[5.5]$_2$	21.1(0.6)	19.0
	Modulus (ksi)	443[13]$_3$	563[155]$_2$	496(20)	460
	Strain (%)	>5[0]$_3$	≥5[0]$_2$	>5(0)	>5
Tensile	77°F-Dry				
	Strength (ksi)	13.2[0.3]$_2$	13.3[0.5]$_2$	13.0(0.9)	13.3[1.2]$_2$
	Modulus (ksi)	444[2]$_2$	490[55]$_2$	441(29)	407[19]$_2$
	Elong. (%)	8.3[0.9]$_2$	6[2]$_2$	5(2)	5.5[0.3]$_2$
Density	(g/cc)	1.50	1.75	1.36	1.26
Water Uptake[a]	(wt%)	1.62[0]$_2$	0.73[0.02]$_2$	1.40(0.01)	1.37[0.05]$_3$
Glass Transition	DMA Tan d, °C	164.7[0.6]$_3$	155[3]$_2$	155(-)	164.3[0.6]$_2$

() Standard deviation represents only one clear cast panel.

[]$_n$ 90% confidence interval for the mean value generated from n different clear cast panels.

The cure schedule for all clear cast panels was 4 hrs @ 150°C followed by a post cure schedule of 2 hrs @ 200°C.

[a] Moisture content after immersion in boiling water for two weeks.

Table 1.7. Mechanical Properties of 8HS G30-500 Composites Made With XU71992.00 and XU71992.01 Resins

Mechanical Test	Mechanical Property	XU71992.00	XU71992.01
Compression After Impact	77°F-Dry Strength (ksi)	39.0	36-40
Open Hole Compression	77°F-Dry Strength (ksi)	38.0	36.4
	180°F-Wet Strength (ksi)	34.4	33.3
Compression by SRM 1-88[a]	77°F-Dry Strength (ksi)	113	108

The cure schedule on all composite panels is 4 hrs @ 165°C (329°F) followed by a post cure schedule of 2 hrs @ 200°C (392°F).

[a] The test method followed was SACMA recommended test method 1-88.

Table 1.8. Mechanical Properties on Composite Made With CET Resins on Uni Weave AS-4

Mechanical Test	Mechanical Property	CET-2	XU71992.00
0° Flex	77°F-Dry		
	Strength (ksi)	$215[15]_2$	$220[31]_2$
	Modulus (msi)	$17.5[1.5]_2$	$17.3[0.8]_2$
	Strain (%)	$1.5[0]_2$	$1.5[0]_2$
90° Flex	77°F-Dry		
	Strength (ksi)	$10.5[1.5]_2$	$13[0]_2$
	Modulus (msi)	$1.2[0.2]_2$	$1.30[0.15]_2$
	Strain (%)	$1.0[0]_2$	$1.0[0]_2$
0° Compression by IITRI[a]	77°F-Dry		
	Strength (ksi)	$175[15]_2$	$198[38]_2$
	Modulus (msi)	Not Available	20.0(2.5)
0° Compression by SRM 1-88[b]	77°F-Dry		
	Strength (ksi)	$178[8]_2$	Not Available
	Modulus (msi)	$17.3[2.3]_2$	
	225°F-Wet		
	Strength (ksi)	$105[0]_2$	Not Available
	Modulus (msi)	$16.3[0.8]_2$	
	Retention		
	Strength (%)	$59[3]_2$	Not Available
	Modulus (%)	$94[8]_2$	

() Standard deviation represents only one clear cast panel.

$[\,]_n$ 90% confidence interval for the mean value generated from n different composite panels.

The cure schedule on all composite panels is 4 hrs @ 165°C followed by a post cure schedule of 2 hrs @ 200°C.

[a] The test method followed was ASTM D-3410 procedure B.

[b] The test method followed was SACMA recommended test method 1-88. This procedure is very similar to the Boeing modification of ASTM D-695.

Table 1.9. Properties of CET-3 Resin for Powder Prepreg

Tensile	Strength (ksi)	13
	Modulus (ksi)	410
	Elongation (%)	5
Flexural	Strength (ksi)	21
	Modulus (ksi)	450
	Strain (5)	7
Density	Polymer (g/cc)	1.27
H_2O Pick-up	Weight %	1.35
Thermal	T_g (Tan delta °C)	164

Table 1.10 Composite Properties of CET-3 Formulations

	XU71992.00 RTM	XU71992.01 RTM	XU71991.00 Powder
0° Tensile Strength (ksi)	139	--	136
0° Tensile Modulus (msi)	9.9	--	8.8
0° Flexural Strength (ksi)	152	128	137
0° Flexural Modulus (msi)	7.9	8.3	8.3
Short Bean Shear (ksi)	9.9	9.7	9.9
0° Compressive Str. (ksi)	113	108	109
CAI (ksi)	38.7	36, 40	37.5
Open Hole Comp. Str.			
RTD (ksi)	37.8	36.4	37.5
180°F/wet (ksi)	34.4	33.3	33.8

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[a] SACMA Standard except open hole compression. G30-500 3K 8HS. All panels are 59-62% fiber volume.

Table 1.11. Effect of Hardener on Modulus of Tactix Resins and Blends

Resin Formulation	Hardener Modulus (ksi)		
	DDS	3.2 F Novolac Epoxy	DETDA
TACTIX 123	480	413	365
TACTIX 556	450	446	370
TACTIX 742 TACTIX123	480	418	388
DEN* 438	495	456	---
XP71756/ TACTIX 123	455	434	380
TACTIX 556/ DEN 438		453	

The acronym DEN refers to Dow Epoxy Novolac.

Table 1.12. Effect of Hardener on Strain at Yield/Failure of Tactix Resins and Blends

	HARDENER Strain (%)		
Resin Formulation	DADS	3.2 F Novolac Epoxy	DETDA
TACTIX 123	5	735	4.5
TACTIX 556	7	13	8.5
TACTIX 742 TACTIX 123	5	8.3	5.4
DEN* 438	7	9	---
XP71756/ TACTIX 123	---	7	4.5
TACTIX 556/ DEN 438		10	

The acronym DEN refers to Dow Epoxy Novolac.

Table 1.13. Effect of Hardener on Glass Transition Temperature of Tactix Resins and Blends

Resin Formulation	Hardener Tg (°C) DADS	3.2 F Novolac Epoxy	DETDA
TACTIX 123	218	123	194
TACTIX 556	210	149	204
TACTIX 742 TACTIX 123	299	169	250
DEN* 438	246	148	---
XP71756/ TACTIX 123	205	154	214
TACTIX 556/ DEN 438		149	

The acronym DEN refers to Dow Epoxy Novolac.

Figure 1.1. Viscosity Profiles of XU71992.00 and XU71992.01 Resins

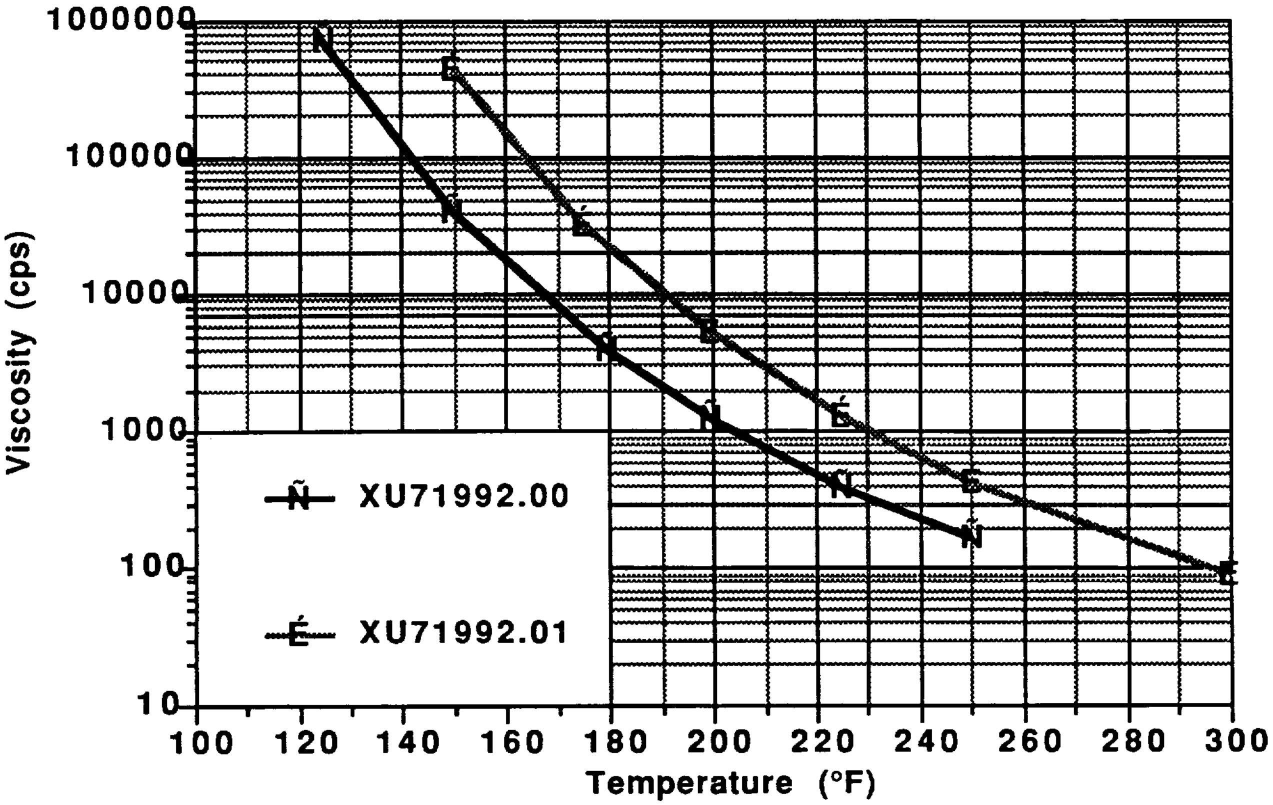


Figure 1.2. Isothermal Viscosity Profiles of XU71992.00 Resin

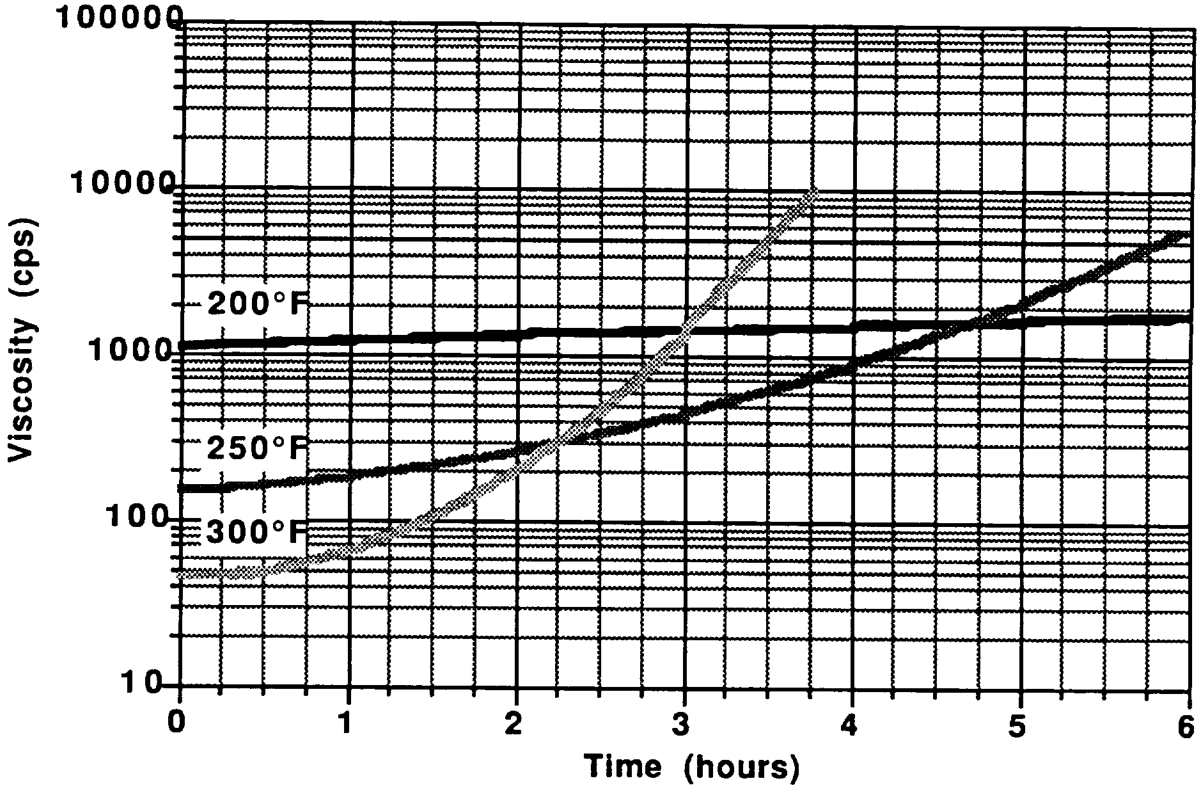


Figure 1.3. Isothermal Viscosity Profiles of XU71992.01 Resin

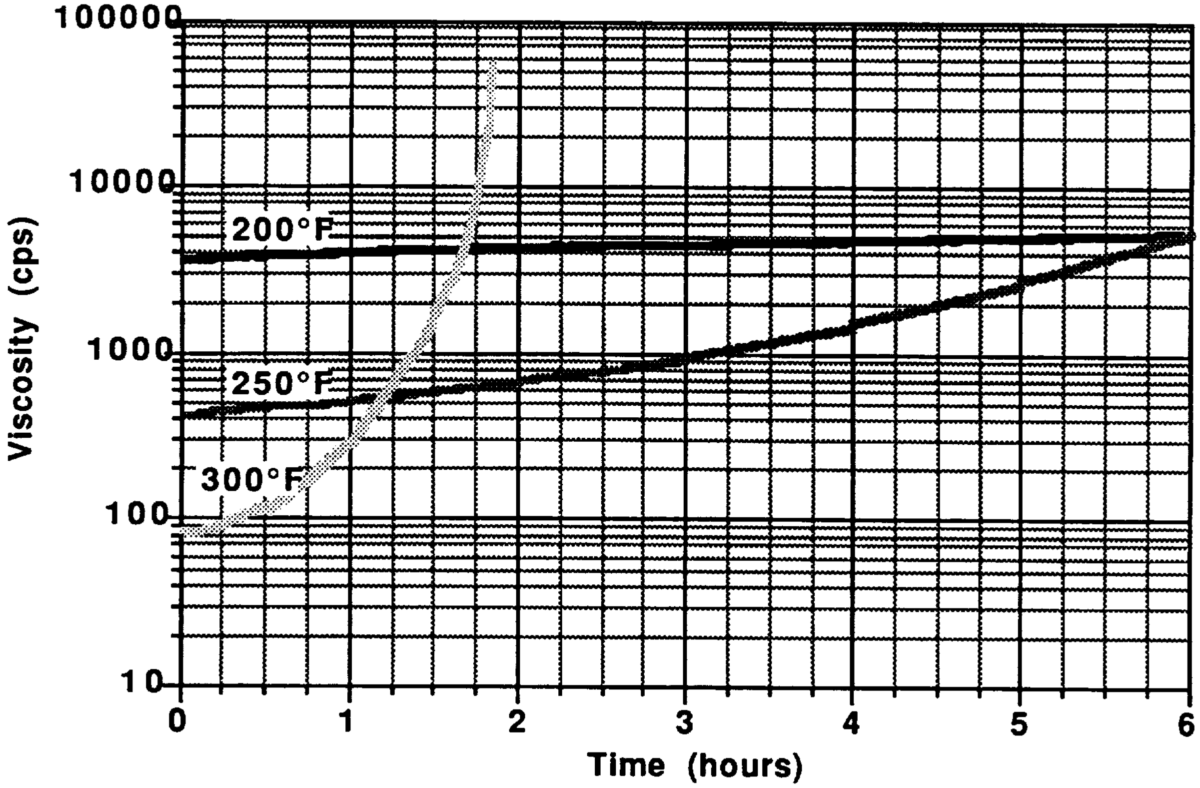


Figure 1.4. Flexural Modulus and Strength Retention of Clear Cast Panels Made With XU71992.01 Resin

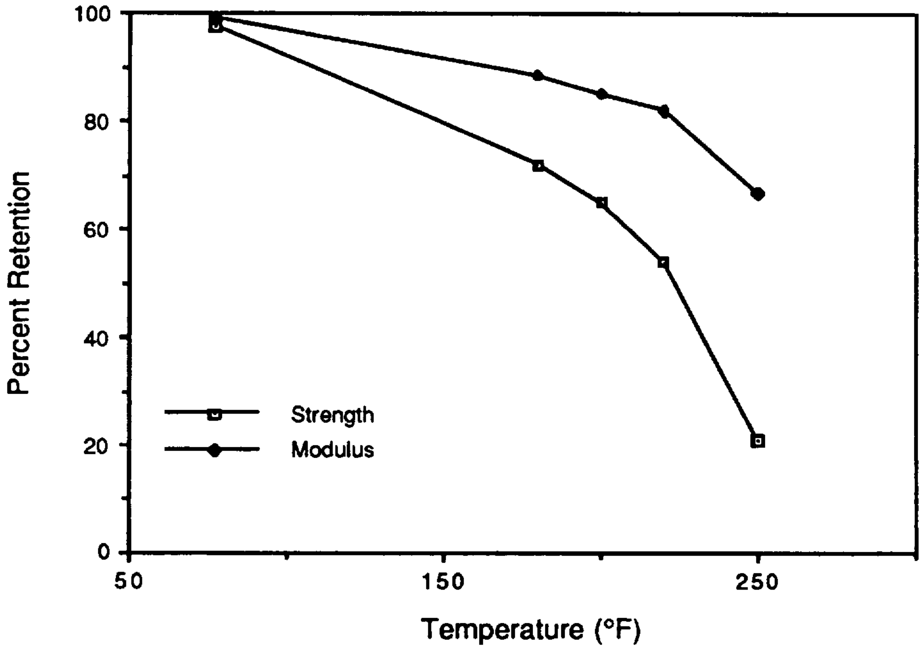


Figure 1.5. Flexural Modulus and Strength Retention of Clear Cast Panels Made With XU71992.00 Resin

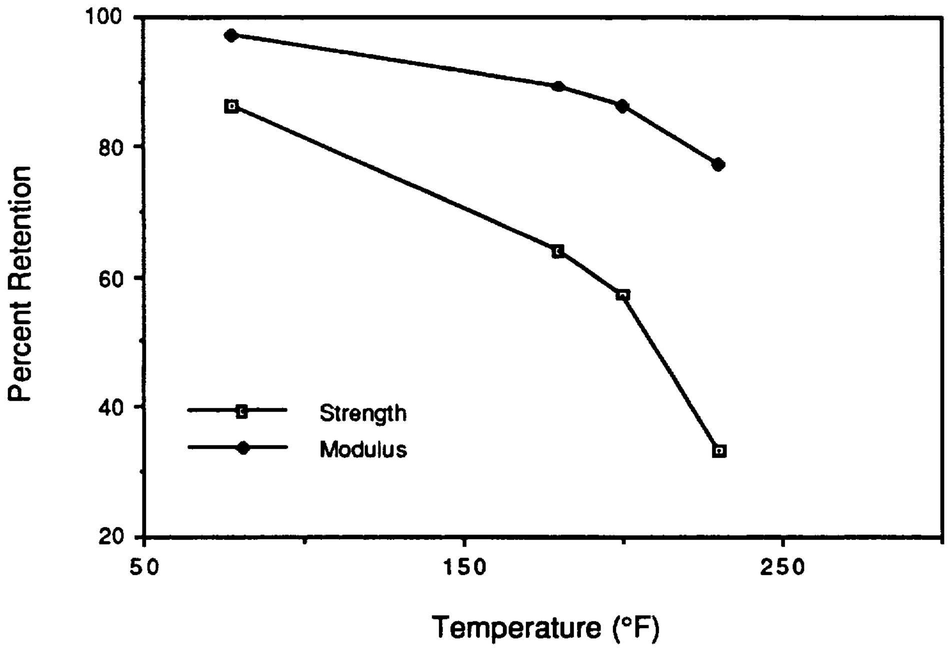


Figure 1.6. Viscosity of CET-3 Powder *vs* Temperature

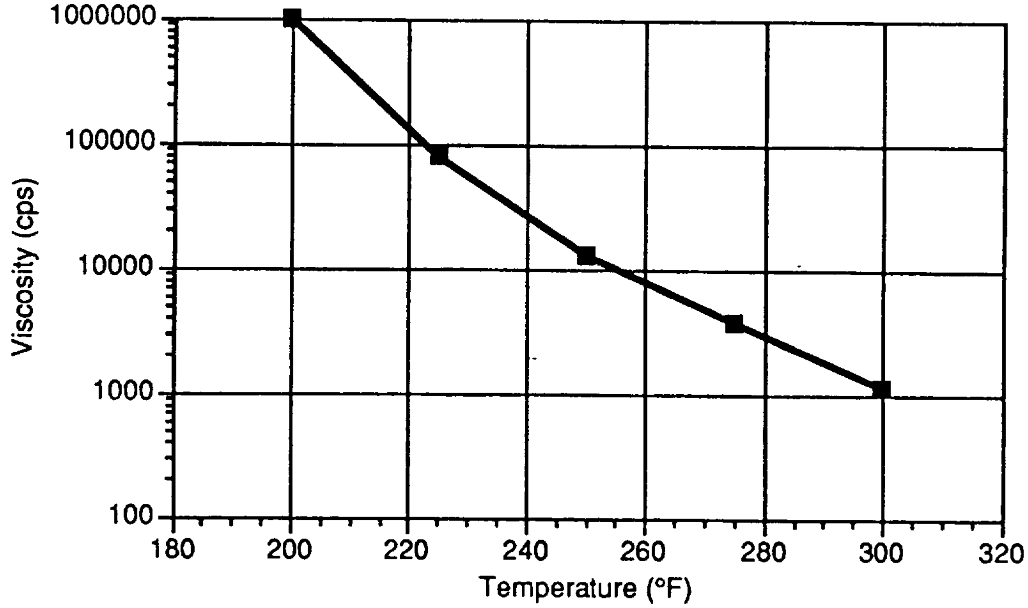


Figure 1.7. Viscosity of CET-3 Powder at 150°C *vs* Time

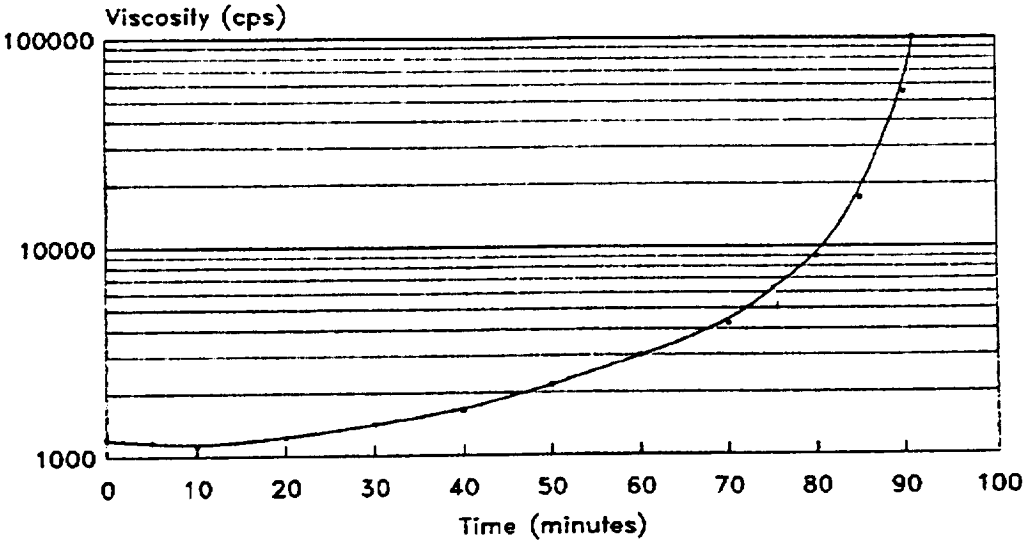


Figure 1.8. Resin Transfer Molding Equipment

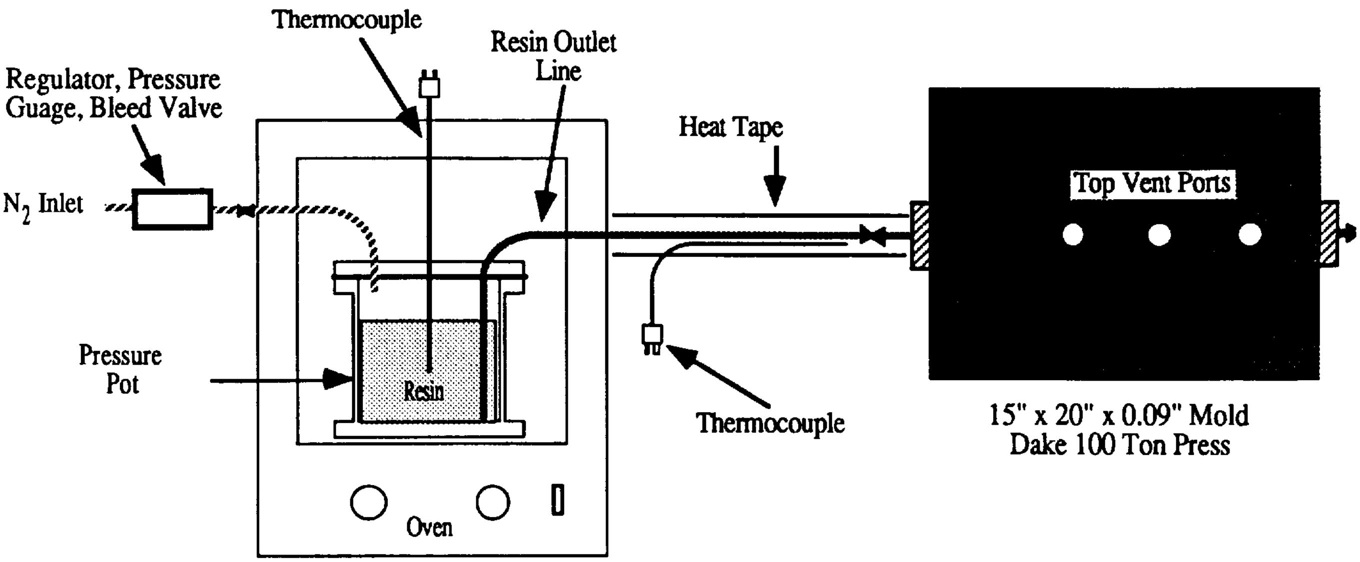
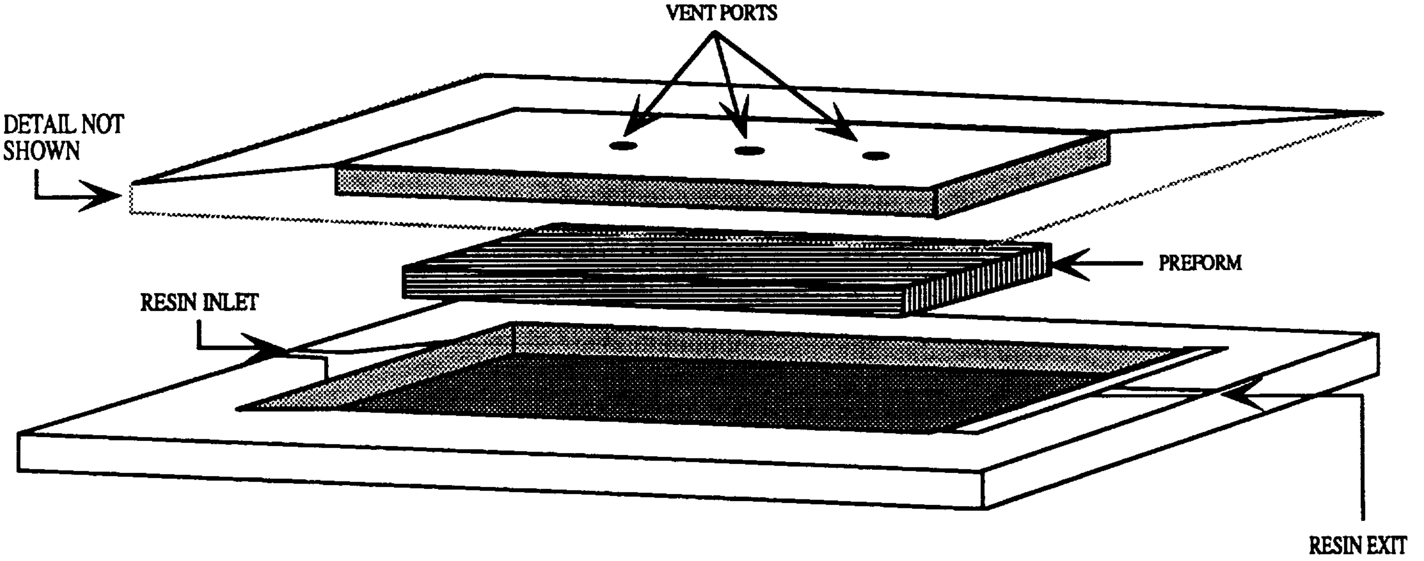


Figure 1.9. RTM Mold Design.



SECTION 2

TASK 2. CYANATE COMPOSITE TECHNOLOGY

The objective of this Task is to develop prepreg-composite systems based on cyanate XU71787 with improved processability and toughness suitable for ≥177°C (350°F) application. Three technical approaches have been taken for toughness: toughening with a core-shell rubber, toughening with cyanate-capped poly(ether ether ketone)s (PEEK) from bisphenol A and 4,4'-difluorobenzophenone, and toughening with thermoplastics having high glass transition temperatures.

2.1. SUMMARY

Selection of Fiber. Previous IR&D study indicated that AS 4G and Apollo 43 carbon fiber were compatible with cyanate XU71787. In light of the withdrawal of Apollo 43 from the market an effort to find an alternate intermediate modulus fiber was implemented. The best alternative is G40-800 which shows equivalent CAI to IM 7 but superior 10° off-axis, edge delamination, and open-hole compressive strengths.

Toughening with Core-Shell Rubber. The family of core-shell rubbers developed as a part of in-house research and development (IR&D) program has been shown to be very effective in toughening cyanate resin XU71787 at 5-10% loading levels. This improvement in toughness is translated into enhanced composite damage tolerance: compressive strength after 6.7 kJ/m (1500 in lb/in) impact improves from 172 MPa (25 ksi) to 227 MPa (33 ksi).

Hot/Wet Mechanical Properties. The mechanical properties of G40-800 composite derived from cyanate XU71787 modified with 5% of rubber were determined at room temperature/dry, 177°C/dry and 177°C/wet. The results suggest that this system is capable of 177°C/wet short-term performance.

Toughening with PEEK Oligomers. The highest toughness ($G_{1C} \sim 1 kJ/m^2$) was obtained from a blend containing 30% of cyanate-capped PEEK (M_w 24,000). Unfortunately, all the blends with significantly improved toughness show thermoplastic-continuous morphology and, therefore, poor mechanical properties at elevated temperatures. Accordingly, this approach has not been extended to composite study.

Toughening with Thermoplastics. After screening a variety of thermoplastics (including commercially available and in-house polymers), the powder form of a commercially available poly(ether imide) was selected on the basis of fracture toughness, modulus at elevated temperatures, and processability. Composite panels derived from this formulation showed a CAI of about 40 ksi, 87% retention of room temperature dry open hole compressive strength at 310°F wet and excellent resistance to solvents and thermal aging. Seven-five pounds of prepreg were submitted to McDonnell Aircraft for High Speed Civil Transport (HSCT) evaluation.

2.2. RESULTS AND DISCUSSION

2.2.1. GRC-Toughened Cyanate Composite (Task 2.1). Previous IR&D work has demonstrated the toughening efficiency of GRC for cyanate XU71787. (For a brief description of the cyanate resin, the GRC rubber and toughening work, refer to p 2-5 of this report and reference 2.) Unfortunately, before the question of the translation of resin toughness to composite damage tolerance could be thoroughly addressed, the preferred intermediate modulus carbon fiber (Apollo 43) was withdrawn from the market. Accordingly, the initial effort was focused on selecting a fiber.

Fiber selection. The ability to transfer stress applied to a composite specimen to the fiber is mainly determined by the nature of the resin-fiber interface. However, there is no consensus in the literature on a preferred method of measuring the interface. Furthermore, optimizing the resin-fiber combination for a certain mechanical performance sometimes deleterious affects other mechanical properties. The methodologies described in the literature for interfacial study are very diverse, from single fiber-type measurements to 90° tension, to the more complex edge delamination strength. Systematic correlations between the results of one test to those of others are, unfortunately, lacking. Since the primary emphasis of this task is damage tolerance, it seemed most efficient in the whole to study the variations of the composite compressive strengths after impact as a function of fiber. To this end, four intermediate modulus carbon fibers were selected for prepregging.

Prepregs of 5% GRC-modified cyanate on Torayca® T800, Celion® G40-800, Thornel® T650-42, and Magnamite® IM7 were prepared by YLA Inc. via a hot-melt process. Composite panels were prepared by a standard vacuum bag procedure (see Experimental). Compressive strength after impact (CAI) test was conducted according to Boeing BBS 7260. Impact of 6.7 KJ/m (1500 in-lb/in) was effected by a Dynatup instrument. The data, presented in Table 2.1, indicate that the selection of fiber plays a major role in the composite damage tolerance. The CAI value of 227 MPa

(33 ksi) from G40-800 and IM7 panels are equivalent to those of the toughened BMIs and cyanates systems recently reported in SAMPE meetings. There is also a good correlation between CAIs and damage area: G40-800 showed the smallest damage area while T800R with the lowest CAI showed the largest.

Since the G40-800 and IM7 panels gave the same CAI, comparative evaluation was extended to other "toughness-related" tests, namely, edge delamination strength, open-hole compressive strength, and 10° off-axis strength. In all cases, the G40-800 panels showed superior performance (Table 2.1). These performance data are again comparable to those reported in recent literature.

Composite Evaluation. Having resolved the issue of fiber selection, about 36 Kg of prepreg were prepared by YLA Inc. The property profile of this system was characterized and summarized in Table 2.2. The retention of room temperature/dry properties at 177°C/wet is greater than 60% for those properties that are resin dependent, namely, 0° flexural strength and compressive strength, and short beam shear strength. Accordingly, the short-term service wet temperature of this system is better than 177°C, which is 15-25°C higher than the recently reported systems of comparable CAI values. The only property that is in need of improvement is the 0° compressive strength. The relative low values may be attributed to the adverse effect of the rubber on the modulus of the resin. Although the rubber loading is only 5%, it causes the resin's flexural modulus to drop from 3.31 MPa (480 ksi) to 2.76 MPa (400 ksi).

Processability. One attractive feature of this resin is its processability. As can be seen from the viscosity-temperature curve (Figure 2.1), its viscosity drops rapidly to about 1000 cps upon warming to about 80°C, making it ideal for hot-melt prepregging operation. Since the cure rate may be controlled by the concentration and the nature of the catalyst, this resin can be readily formulated to suit various processing schedules. A typical formulation for prepregging is a blend of the resin with cobalt acetylacetonate (~250 ppm cobalt) dissolved in divinylbenzene. Prepregs with excellent fiber wet-out, drape and tack are obtained.

Autoclave curing of lay-ups involves a simple straight-up/hold/straight-down schedule without any intermediate steps. A representative cure schedule is given in Figure 2.2. A free-standing 2-h postcure at 232°C (450°F) is sufficient to complete the cure for most purposes.

2.2.2. Toughening with Poly(ether ether ketone) oligomers and polymers. The deficient 0° compressive strength of the GRC-toughened system highlights the critical importance of resin modulus. One option, widely reported in the literature, is to employ a tough thermoplastic as the toughening agent. Since the moduli of thermoplastics are normally 10-50 times that of most elastomers, the moduli of the resulting polymeric blends should not be compromised much.

Synthesis of cyanate-capped poly(ether ether ketones). Poly(aromatic ketones) are generally noted for their toughness. A particular tough polymer is the poly(ether ether ketone) derived from bisphenol A and 4,4'-difluorobenzophenone. It is, therefore, a good starting point.

Phenolic-terminated poly(ether ether ketones) (PEEK) of nominal M_n 5000, 8000, and 12000 were prepared by heating a mixture of the appropriate amounts of bisphenol A, 4,4'-difluorobenzo-phenone, and potassium carbonate in dimethylacetamide. The polymers were characterized by standard spectrocopic, solution viscosity, and GPC techniques. The higher molecular weight samples appeared to have the bimodal distribution, commonly observed in poly(arylene ethers). Consequently calculation of polydispersity is flawed with uncertainty. A representative sample of each molecular weight was subjected to laser light scattering for absolute molecular weight determination. From this and GPC analysis the M_w values are determined to be 11000 (11K), 16000 (16K), and 24000 (24K). A summary of the data are given in Experimental Section.

The direct detection of phenolic end-groups proved to be elusive. Spectroscopic analysis and potentiometric technique were considered but deemed unreliable because of the very low concentration of the end-groups. An indirect method was employed as a last resort. ^{19}F NMR measurement with the aid of an internal standard was used to provide a lower limit of fluoride concentration in the polymers. It was concluded with a reasonable degree of confidence that less than 1% of the polymer chains were fluoride capped. Or, the polymer chains were at least 99% capped with phenolic end-groups.

Similar difficulty was encountered in our attempts to quantify the conversion of phenolic end-groups to cyanate. Consequently, a large excess of cyanogen bromide was used in each case to ensure that the conversion was as complete as possible.

Copolymers of Cyanate and Cyanate-Capped PEEK. Each cyanate-capped PEEK was blended with the cyanate resin at 10%, 20%, and 30% level, providing a total of 9 different copolymers. Blending was accomplished in methylene chloride to ensure homogeneity. Copolymers containing 10% and 20% PEEK were prepared by standard casting technique while those containing 30% PEEK had to be compression molded.

Dynamic Mechanical Spectra. Plots of shear moduli *vs* temperature of all nine copolymers are given in Figures 2.3, 2.4, and 2.5. All spectra indicate the occurrance of phase separation as evidenced by a drop in moduli centered at about 150°C, the T_g of the thermoplastic phase. At 10 and

20% loading levels, equlibrium moduli at >250°C were observed which may be due to a thermoset-continuous morphology. In contrast, an equilibrium modulus was not seen in any of the 30% copolymers; the modulus drops precipitously past the T_g of the thermoplastic. This is indicative of a thermoplastic-continuous morphology. The addition of PEEK has no appreciable effect on the room temperature modulus of all the copolymers.

SEM Analysis. The morphological picture suggested by DMS were confirmed by SEM analysis of fracture surfaces. Representative micrographs are reproduced in Figures 2.6 to 2.10. With 10% PEEK the thermoplastic dispersed phase exists as fine spherical particles regardless of the molecular weight (Figure 2.6).

With 20% PEEK, the molecular weight of the thermplastic has a significant effect on the morphology. For the 11K PEEK (Figure 2.7), large particles of thermoplastic are dispersed in the thermoset continuous phase, but finer structures can be seen within these particles. These fine structures appear to be absent in the 16K copolymer sample (Figure 2.8). The morphology of the 24K copolymer is complex and irregular; thermoplastic particles of different sizes are found (Figure 2.9).

The classical ball-socket type morphology is seen in all copolymers with 30% PEEK regardless of molecular weight (Figure 2.10). The dispersed phase is believed to be the thermoset. Unlike the other copolymers, debonding between phases is observed.

Effect of Morphology on Properties. The copolymers were characterized for their fracture toughness, MEK uptake, and flexural properties. The fracture toughness data, presented in Figure 2.11, are consistent with the expectation that copolymers with thermoplastic-continuous morphology would be much tougher, and that the toughness, at the same loading, will increase with molecular weight.

Solvent resistance is a necessary feature for any matrix material for composite application. As a general screen, we chose MEK as a representative solvent and studied the uptake of MEK as a function of time. The % uptake after a 2-week immersion is given in Figure 2.12. At 10% loading of PEEK there is little difference in MEK uptake among the copolymers of 3 different molecular weights. This is not entirely unexpected since they have have the same thermoset continuous morphology. At 30% loading, MEK uptake increases with increasing molecular weight. At 20% loading, the results are easily explained and are probably reflective of the vastly different morphologies of these copolymers. At any rate, the overall picture is discouraging: the control sample only absorbed 2.7% while the copolymers absorbed about 9%, as much as >300% more.

The DMS analysis portends to poor high temperature properties for the 30% copolymers. Since they exhibit fracture toughness values in the desired range, it seemed appropriate to complete the evaluation with flexural property testing. The copolymer containing 30% PEEK of 24K M_w showed rather promising room temperature values: 142 MPa (20.6 ksi) flexural strength, 3.00 GPa (436 ksi) modulus, and 6% strain at break. However, it was too soft to test at 177°C.

In light of the poor solvent resistance and elevated temperature mechanical properties, it was proposed to the Technical Representative of the Contracting Officer (TRCO) that no further work should be done on this resin system. This task was discontinued with his approval.

2.2.3. Toughening with High Molecular Weight Thermoplastics. At a review in May 1990 at NASA Langley, it was agreed to modified the Statement of Work making it more consistent with the research nature of the contract and to take into account NASA's emerging interest in HSCT. The modified program entailed a three-pronged approach: a study of the thermo-oxidative stability of the base resin, a study of its hot/wet mechanical performance and a toughening effort.

Hot/Wet Mechanical Performance of Base Resin Composite. Cyanate XU71787.02/G40-800 unidirectional panels were prepared according to the cure profile of Figure 2.2. Specimens for flexural properties and short beam shear strength were machined and a porton of them humidity aged at 170°F, 90% humidity to saturation. A moisture uptake of 0.34% at saturation was measured after 16 days. The specimens were tested at RTD, RTW, 400°F/dry and 400°F/wet (see Table 2.3). The better than 60% retention of flexural strength and 50% retention of short beam shear strength at 400°F were considered acceptable.

Thermo-oxidative Stability of Base Resin and Composite. Thermo-oxidative aging at 400°F in air was conducted with neat resin castings and short beam shear strength specimens. Near resin casting specimens of Compimide® 353 and Compimide®TM121 of the same dimensions were used as reference. Composite aging was conducted with pre-cut short beam shear specimens. The data for casting aging and composite aging are provided in Tables 2.4 and 2.5 respectively indicate that the cyanate-based casting was significant more resistant to heat aging than a typical bismaleimide and that this resistance is reflected in a better than 95% retention of short beam shear strength after 2000 hours of exposure to air at 400°F. It is worth noting that the short beam shear specimen aging very likely represent the worst case scenerio since the specimens had very high surface area to volume ratio.

Toughening with Thermoplastics. At the outset, it was decided to focus on commercially available high T_g thermoplastics and to avoid undertaking any chemical modifications so that a successful technical development would also be economically viable. Several thermoplastics were blended by use of a solvent with cyanate XU71787.02 and the resulting blends compression molded into plaques for testing. Table 2.6 lists the morphology (by SEM) and fracture toughness. Except the PPO blends, the morphology of the blends was thermoplastic continuous resembling "eggs in a carton" with the cured cyanate forming the eggs embedded in a continuous thermoplastic phase. Scanning electron micrographs of these blends are almost indistinguishable from the one depicted in Figure 2.10. These polymer plaques disintegrated when exposed to methylene chloride.

The PPO blends, however, were more resistant to methylene chloride and SEM showed a very different morphology (see Figure 2.13) which is loosely described here as co-continuous. The micrograph reveals a rather homogenous composition with very fine domain size. The fracture toughness of the 30% PPO blend was also higher than all the others. This composition would have been a good choice for further work but unfortunately it only retained about 50% of its RTD flexural modulus at 400°F which is far short of our target.

In our last attempt with this approach, Matrimide® 5218 (a soluble polymide with a very high T_g) was studied. Although the solvent resistance of the blends was excellent, there was little improvement in fracture toughness.

Toughening with PEI Particles. While the above work was in progress, we began exploring the concept of using finely ground particles of thermoplastic. We postulated that the cure schedule could be used to control the dissolution of the thermoplastic particles such that only partial dissolution would take place thus creating a co-continuous (in a macro sense) morphology which provide, at once, high temperature properties and enhanced toughness. To this end, PEI [Ultem® 1000] particles (diameter <40 microns) was blended with cyanate XU71787.02 and was heated on a hot-stage microscope. Heating the sample at 1°C per minute from 80° to 177°C led to very little dissolution of the PEI particles. There appeared, however, a trace of dispersed phase in the cyanate domain presumbly due to the phase separation of the small amount of dissolved PEI. Changing the heating rate to 5°C per minute gave an entirely different result. The PEI particles clearly dissolved in part forming a connected network structure. In Figure 2.14 the bright spots are the partially dissolved PEI particles and they are clearly embedded in a network structure of primarily thermoplastic. There is also evidence of a finely dispersed PEI phase in the thermoset domain. With this discovery in hand, we proceeded to study the fracture toughness and the dynamic mechanical properties of castings of several compositions at different heating rates. Castings containing 20% and 30% of PEI were prepared. Solvent blending and compression molding of the blends were done in a similar manner as described for the aforesaid PEEK blends. The particles blends were made by mixing the particles with the cyanate resin at 80°-100°C and then subjected to standard casting procedure. Heating rates between 1°C/min to 5°C/min were used to mimic the conditions of the hot-stage microscopy work.

The different behaviors of the casting to exposure to methylene chloride immediately pointed out a difference in morphology. The solvent blend casting disintegrated in several seconds when immersed in methylene chloride while the particle blend castings showed little or no visible change after 5 minutes. Consistent with this observation were the shear moduli at 203°C. The dramatic differences are shown in Table 2.7. At 20% PEI level, the solvent blend casting had a shear modulus of 5.8 dyne-cm^2 x 10^9 while the particle blend's modulus was 9.4. At 30% PEI level, the deleterious effect of the continuous PEI phase on modulus was highlighted by the very low modulus at 203°C. The co-continuous morphology of the particle blend castings helped to preserve the eleveated temperature modulus at a useful level. The last three entries in Table 2.7 demonstrate the effect of heating rate (or changes in morphology) on fracture toughness. The higher the heating rate, the higher was the fracture toughness measured. It was shown earlier that at a heating rate of 1°C per minute, very little dissolution of the PEI particles would have occurred and therefore we would expect the least improvement in fracture toughness.

The fracture surfaces of the particles blends were examined by SEM to ascertain the correlation between the desirable properties observed and morphology. Representative micrographs are reproduced in Figures 2.15a to 2.15c. Figure 2.15a is a low magnification (80X) micrograph of a 30% PEI particle blend showing clearly the interconnected network structure with the thermoset-rich phase appearing darker. The particulate nature of the PEI-rich network is also clearly evident. A higher magnification (2000X) look at the border area between the two phases (Figure 2.15b) shows that while the PEI particle retains its shape to a large degree, it is also infiltrated by the thermost resin such that the morphology within the outline of the particle is best described as thermoplastic continuous. Surrounding the particle is the thermoset-rich phase containing very fine particles of phase separated PEI. Figure 2.15c is a very high magnification (20,000X) look into the PEI particle showing the continuous membrane-like thermoplastic network and small (< 1micron) spheres of thermoset nested within.

The improved solvent resistance and better retention of modulus at 203°C noted for the particle blends can be readily attributed to the co-continuous thermoset-rich phase in the interconnecting network. It is not difficult to imagine that the co-continuous thermoplastic-rich phase could inhibit crack growth, providing improved fracture toughness.

Composite Properties of PEI-Particle Toughened Cyanate. Celion® G40-800 prepregs were prepared at YLA, Inc. After several unsuccessful attempt to obtain good quality prepregs of particle blends by the standard hot-melt technique, we resorted to prepare the prepregs in two stages. First a resin-poor (about 26% resin content) cyanate prepreg without additive was made by hot melt. Then a film of cyanate containing 18% PEI was coated onto release paper and the coating paper laminated in-line onto the resin-poor prepreg, giving an overall PEI concentration of about 10% in the resin. Although this method provided prepregs of acceptable quality, the resin content was typically about 42% and therefore requiring a significant amount of bleeding during autoclave cure. The need for considerable bleeding had caused some problems. At the beginning, panel quality was rather erratic leading to a large variability in compressive strength after impact. It was found after a considerable effort that debulking between plies was the key to consistently good quality panels. It is clear that additional work on reducing the prepreg resin content and optimizing the autoclave schedule is necessary. Nonetheless, good quality panels were obtained by autoclaving under the following conditions:

Apply full vacuum at the start
Heat at 2°F/min to 200°F
Apply pressure at 180°F to 75 psi at 5.0 psi/min
Release vacuum when pressure reaches 75 psi
Hold at 200°F for 10 min
Heat at 4-7°F/min to 350°F
Hold at 350°F for 120 min
Heat at 4-7°F/min to 450°F
Hold at 450°F for 60 min
Coll to 140°F at 2°F/min
Vent pressure. No additiona post-cure is necessary

Following the HSCT material development guideline (D6-55587) of Boeing, distributed in June 1991, we selected 310°F as the material evaluation temperature. The data are compiled in Tables 2.8 to 2.10. The performance of the system appears to be quite good, with a CAI of about 40 ksi, and better than 85% retention of RTD open hole compressive strength at 310°F/wet (see Table 2.8). The system also showed good solvent resistance (see Table 2.9) although the in-plane shear strengths were lower than desired. Thermo-oxidative stability was measured by aging compressive interlaminar shear specimens for 4000 hours at 360°F and 400°F and tested at 77°F and at the aging temperature. It can been seen from Table 2.10 that the compressive interlaminar shear strengths were essentially unaffected by aging and the aged samples had better high temperature strengths probably due to additional cure. To determine the effect of aging on fracture toughness, castings were also aged at 360°F in air. Figure 2.16 is a graphic representation of fracture toughness *vs* time and it clearly shows that fracture toughness is unaffected by aging.

2.3. CONCLUSIONS

The GRC-toughened cyanate/G40-800 composite system has been shown to exhibit 177°C/wet service temperature, and excellent processability and damage tolerance.

The PEEK-modified cyanate compostions, though possessing high fracture toughness, suffer from all the disadvantages of a thermoplastic-continuous morphology. Consequently this portion of the contract was terminated with the agreement of the TRCO.

The PEI-toughened system shows excellent compressive strength after impact and retention of open hole compressive strength at elevated temperature. Aging study at 360° and 400°F up to 4000 hours indicates that the system has excellent thermo-oxidative stability. Additionally, the fracture toughness of the polymer is unaffected by aging. The system as it stands requires considerably more optimization of the prepregging process and autoclave cure schedule. There is no further plan to conduct the optimization work under this contract.

2.4. EXPERIMENTAL

GRC-modified cyanate. The preparation of the resin has already been discussed in Section 1. To prepare neat resin castings, a quantity of the resin was degassed in vacuum at 120°C for 30 min and then poured into a 125°C preheated stainless steel parallel plate mold which had been pretreated with Teflon® mold release. The mold was then heated in an oven at 175°C for 2 h, 225°C for 1 h and 250°C for 1 h. The casting was removed after the mold was allowed to cool.

GRC-modified prepregs and composite preparation. The resin for prepregging was formulated with 200 ppm cobalt acetylacetonate. Actual prepregging was done by YLA, Inc. Lay-ups for various tests are specified in Table 2.2 and the cure schedule as illustrated in Figure 2.2.

Preparation of poly(ether ether ketone) oligomers. The following is the procedure for the synthesis of 5000 M_n (nominal) oligomer. To a 1-L three necked round bottom flask fitted with a thermometer, mechanical stirrer, Dean Stark trap/condenser/nitrogen inlet was added bisphenol A (61.90 g, 0.2712 mol), difluorobenzophenone (54.55 g, 0.25 mol), potassium carbonate (56.23 g, 0.4068 mol), toluene (160 mL), and dimethylacetamide (335 mL). The mixture was stirred and heated to reflux (~140°C) for 3.5 h during which ~ 8 mL of water was collected in the Dean Stark trap. The toluene was then distilled out over a 1.5 h period during which time the reaction temperature increased to 158°C. The reaction mixture was then maintained at 158°C for 18. 5 h. The mixture was filtered hot through Celite® filter aid. The filtrate was diluted to ~500 mL with tetrahydrofuran.

This solution was then added dropwise to 3.5 L of methanol containing a small amount of glacial acetic acid. A white solid precipitated which was isolated by vacuum filtration and rinsed with methanol. The solid was then suspended in 2.5 L of methanol and allowed to stand overnight. The polymer was isolated by filtration, rinsed with methanol, and dried in vacuo overnight at 60°C to give 89.5 g (90% yield) of an off white solid. Analysis by ^{1}H and ^{13}C-NMR confirmed the formation of the desired poly (ether ether ketone) oligomer. Analysis by Gel Permeation Chromatography calibrated using polystyrene standards indicated a M_n= 7912 g/mole and M_w=16796 g/mole. A 0.25 g sample dissolved in 50 mL of chloroform was analyzed by capillary viscometry at 25°C indicating an inherent viscosity of 0.22 dL/g.

The other molecular weight poly(ether ether ketone) oligomers were prepared analogously. A number of runs were performed for each molecular weight. The runs were all analyzed by ^{1}H-NMR, ^{13}C-NMR, GPC (PL-Gel Mixed bed, 5um, 300 mm X 7.5 mm ID, THF as solvent, calibrated against polystyrene standards), and inherent viscosity ($CHCl_3$, 25°C) then blended together.

5K M_n Run	M_n g/mole	M_w g/mole	Dispersity	η_{inh} dL/g
1	7912	16796	2.12	0.22
2	7564	17231	2.28	0.23
3	7491	17493	2.34	0.22
4	7311	16814	2.30	0.23
5	7339	16687	2.27	0.22
6	6873	15266	2.22	0.21
7	73781	6799	2.28	0.18
Blend	7114	16723	2.35	

8K M_n Run	M_n g/mole	M_w g/mole	Dispersity	η_{inh} dL/g
1	9100	25533	2.8	0.28
2	8904	24903	2.8	0.28
3	9070	25501	2.8	0.28
4	9096	26412	2.9	0.29
5	8805	25114	2.85	0.28
6	8924	24890	2.8	0.28
Blend	8772	25108	2.86	

12K M_n Run	M_n g/mole	M_w g/mole	Dispersity	η_{inh} dL/g
1	10594	36217	3.42	0.35
2	10541	37310	3.54	0.38
3	10300	35115	3.41	0.35
4	10820	35902	3.32	0.34
5	10469	35712	3.41	0.35
6	10469	35712	3.41	0.36
Blend	9952	35296	3.55	

The oligomers were also analyzed by laser light scattering.

5K	Run 7	M_w = 10600 g/mole±10%
8K	Run 1	M_w = 16400 g/mole ±10%
12K	Run 2	M_w = 23500 g/mole ±10%

All references to these oligomers will be based on the M_w from laser light scattering.

Cyanation of poly (ether ether ketone) oligomer. To a 3-L three necked round bottom flask fitted with a mechanical stirrer, addition funnel, and thermometer was added 200 mL of methylene chloride. The solvent was cooled to -30°C in a dry ice/isopropanol bath. To this cold solvent was then added cyanogen bromide (38.13 g, 0.36 mol). After 15 min a solution of 5000 M_n poly (ether ether ketone) oligomer (300 g, 0.06 mol), triethylamine (36.43 g, 0.36 mol), and methylene chloride (900 mL) was added dropwise at a rate so as to keep the reaction mixture at -30°C. After the addition was complete (~1 h) the mixture was stirred for 1 h at -30°C then allowed to warm to room temperature. To the reaction flask was then added 0.1 N HCl (aq.) (200 mL) and the mixture stirred for 5 min. The mixture was transferred to a separatory funnel and the organic layer removed. The organic layer was then washed twice with water and dried over magnesium sulfate. The mixture was filtered and the filtrate was diluted with 500 mL of tetrahydrofuran. This solution was then added dropwise to methanol (2 L) with vigorous stirring precipitating a white solid. The solid was isolated by filtration and dried in vacuo at 25°C overnight to give 261.1 g of cyanated PEK oligomer. Analysis of the product by ^{13}C-NMR indicated the introduction of the cyanate groups and no indication of phenol terminated groups was present.

The other MW oligomers were cyanated in an analogous fashion and analyzed by ^{1}H-NMR, ^{13}C-NMR, FT-IR, and GPC.

Sample	M_n g/mole	M_w g/mole	Dispersity
5K-1	8348	16770	2.01
5K-2	7931	16729	2.11
8K-1	9795	25218	2.57
8K-2	9328	25196	2.70
12K-1	11066	35359	3.20
12K-2	11923	35440	2.97

Preparation of a 30% 24K Oligomer/ cyanate XU71787 Blend. To a 2-L round bottom flask was added XU71787 polycyanate resin (455 g) and methylene chloride (100 mL). The mixture was stirred until a homogeneous solution was formed. Separately 24K oligomer (195 g) was dissolved in methylene chloride (1 L). The oligomer solution was then added to the XU71787 solution and the solvent removed using a rotary evaporator. A solution of cobalt(III) acetylacetonate in acetonitrile (100 ppm Co in final product) was added and most of the remaining solvent removed on the rotary evaporator. The mixture was then poured into an aluminum pan and degassed in a vacuum oven at 60°C and 2 mm Hg for 1 h. The resulting material was frozen in liquid nitrogen and cryogenically ground to a fine powder. The product was then dried in vacuo at 25°C for 2 days.

Molding of 30% 24K oligomer/ cyanate XU71787 resin blend. To a 4.5" x 4.5" compression mold was added 75 g of a 30% 24K oligomer/ cyanate XU71787 resin blend prepared as described above. The mold was placed in a heated press preheated to 80°C. The material was compress with 30 ton force then the force was lowered to 5 ton. After 40 min the force was increased to 30 ton for 1 min then lowered to 5 ton. The press was then heated to 125°C for 1 h during which time some flash formed. The temperature of the press was then increased to 175°C for 1 h. The force was then increased to 30 ton then lowered to 5 ton. The press was then heated to 200°C for 1 h then to 250°C for 1 h. The mold was then removed and allowed to cool to <80°C. The mold was then opened and a well consolidated, void free plaque was obtained.

Preparation of the cyanate of tris(hydroxyphenyl) methane (tris-cyanate). To a 5-L 3 necked round bottom flask fitted with a mechanical stirrer, addition funnel, and a thermometer was added acetone (1 L) and tris(hydroxyphenyl) methane (450 g, 1.54 mol). The material was stirred until dissolved then cooled to -30°C using a dry ice/ethylene glycol-water bath. When the reaction mixture was at -30°C cyanogen bromide (538.07 g, 5.08 mol) was added and the mixture allowed to stir for 15 min. Triethylamine (708 mL, 5.08 mol) was then added dropwise at a rate so as to keep the reaction temperature near -30°C (approximately 1.25 h). After the addition was complete the reaction mixture was stirred at -30°C for 1 h, then allowed to warm to room temperature. The triethylamine hydrobromide salt was filtered off and the filtrate was transferred to two 2-L separatory funnels. The reaction mixture was diluted with methylene chloride and washed three times with water. The organic layer was dried ($MgSO_4$) and solvent removed in vacuo to give 327.37 g (57% yield) of tris-cyanate. Analysis by ^{1}H-NMR, ^{13}C-NMR, and FT-IR indicated the introduction of the cyanate group. Some diethylcyanamide and acetone remained.

1.5 TABLES AND FIGURES

Table 2.1. Laminate Properties of 5% GRC-Cyanate

	G40-800	IM7	T650-42	T800R
CAI (MPa)	227.7	227.7	186.3	149.0
Damage Area (cm^2)	8.06	10.19	20.32	25.39
Edge Delamination Str. (MPa)	299.0	208.4		
Open-Hole Comp. Str. (MPa)	310.0	275.3		
10° Off-Axis Str. (MPa)	59.3	48.3		

Table 2.2. Properties of 5% Rubber-Modified Cyanate Composites

	RTD	RTW[a]	350°F/Dry	350°F/Wet
0° Flex. Strength[b], GPa	1.41	1.30	0.98	0.87
0° Flex. Modulus, GPa	144.9	142.1	140.8	138.7
0° Flex. Strain, %	0.984	0.927	0.693	0.630
0° Tensile Strength[c],GPa	3.22	3.18	2.86	2.87
0° Tensile Modulus, GPa	170.4	164.2	161.5	162.2
0° Strain, %	1.78	1.86	1.76	1.82
Short Beam Shear, MPa	86.3	82.8	59.3	53.8
0° Comp. Strength[d], GPa	1.26	1.46	0.84	0.77
0° Comp. Modulus, GPa	151.8	160.8	146.3	151.1
Edge Delam. Str., MPa	299			
Open-hole Tension[e], MPa	601.7			
Open-hole Comp., MPa	310.0			
10° Off-axis Str., MPa	59.3			
In-plane Shear Str., MPa	62.1		35.2	
CAI[f], MPa	227.7			

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[a] Humidity saturation at 170°F, 90% humidity; equilibrium moisture uptake of 0.273% reached after 36 days.

[b] Void content of 1.79% by acid digestion.

[c] Void content of 2.92% by acid digestion.

[d] Boeing modified ASTM D695.

[e] $(+45/0/-45/90)_{2S}$, 0.250" hole, 1.500" width.

[f] Boeing BBS 7260, 6.7 KJ/m (1500 in-lb/in) impact.

Table 2.3. Properties of cyanate XU71787/G40-800 composite samples

	RTD	RTW[a]	400°F/Dry	400°F/Wet[a]
0° Flex. Strength., ksi	194	222	132	117
0° Flex. Mod., msi	18.7	19.4	18.7	18.5
0° Flex. Strain, %	1.04	1.11	0.68	0.61
Short Beam Shear, ksi	14.9	14.0	8.04	7.11

[a] Humidity saturation at 170°F, 90% humidity; moisture uptake of 0.343% reached after 16 days.

Table 2.4. 400°F Aging of Cyanate and BMI Castings in Air

	100 hr	500 hr	1250 hr	2000 hr
XU71787.02	+0.09	-0.31	-0.91	-1.42
Compimide™ 353	-0.41	-0.85	-18.60*	-25.7*
Compimide™ 353/TM121	-0.20	-0.97	-2.06	-2.82

*Specimens cracked extensively and pieces broken off.

Table 2.5. 400°F Aging of Cyanate Composite In Air

Hours	SBS Strength (ksi)	Wt. Loss (%)
0	14.8±0.1	--
100	15.1±0.4	0.08
500	14.6±0.3	0.31
1250	14.1±0.5	0.71
2000	14.1±0.5	1.18

Table 2.6. Thermoplastic-Cyanate XU71787.02 Solvent Blends

Thermoplastic	%	Morphology	K_{IC} psi x in$^{1/2}$
Udel® Polysulfone	20	Egg-in-carton	699
Udel® Polysulfone	30	Egg-in-carton	745
Ardel® Polyarylate	30	Egg-in-carton	978
Ultem® PEI	10	Egg-in-carton	707
Ultem® PEI	20	Egg-in-carton	979
Ultem® PEI	30	Egg-in-carton	1014
PPO	20	Co-continuous	1150
PPO	30	Co-continuous	1500

Table 2.7. Properties of PEI-Cyanate Castings -- Solution *vs* Particle Blends

% PEI	Heating Rate to 175°C	Shear Modulus[a] at 203°C	K_{IC} psi x in$^{1/2}$
20% Solvent		5.8	939
20% Particle	1.67°C/min	9.4	737
20% Particle	5°C/min	8.6	1234
30% Solvent		2.3	1014
30% Particle	1°C/min	--	1209
30% Particle	2.7°C/min	8.6	1477
30% Particle	5°C/min	9.1	1680

[a] Shear moduli in dune-cm^2 x 10^9

Table 2.8. PEI-Toughened Cyanate Composite Properties

Open-hole compressive strength, RTD	43 ksi
Open-hole compressive strength, 310°F dry	39 ksi
Open-hole compressive strength, 310°C wet	37.6 ksi
Open-hole tension strength, RTD	67 ksi
Open-hole tension modulus, RTD	7.14 msi
CAI (aluminum base plate)	42 ksi
CAI (steel base plate)	38 ksi

Table 2.9. PEI-Toughend Cyanate In Plane Shear Properties

Condition[a]	Modulus (ksi)	Strength (ksi)	% Wt. Gain
Control	0.624	15.5	--
MEK	0.581	15.3	0.42
Jet Fuel	0.590	16.4	0.12
Skydrol	0.545	14.5	0.39
Water	0.605	14.8	0.29

[a] Immersion in MEK at RT for 24 hours, all others at 160°F for 14 days.

Table 2.10. CILS of PEI-Cyanate Composite Panels *vs* Aging

Aging Temp. °F	Test Temp. °F	Wt. Loss (%)	CILS (ksi)
None	77	none	9.44
None	77	none	9.79
None	360	none	7.11
None	400	none	7.51
360	77	0.245	11.8
360	360	0.245	8.3
400	77	0.623	9.9
400	400	0.623	6.9

Figure 2.1. Viscosity-Temperature Profile of GRC-Cyanate

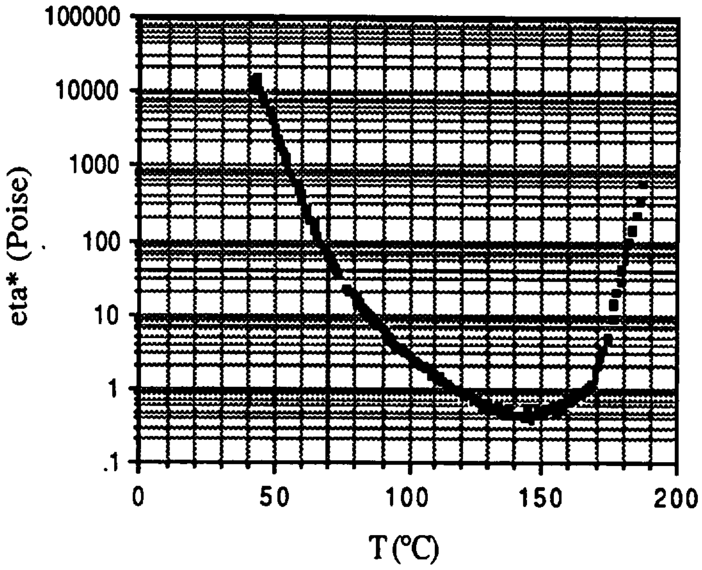
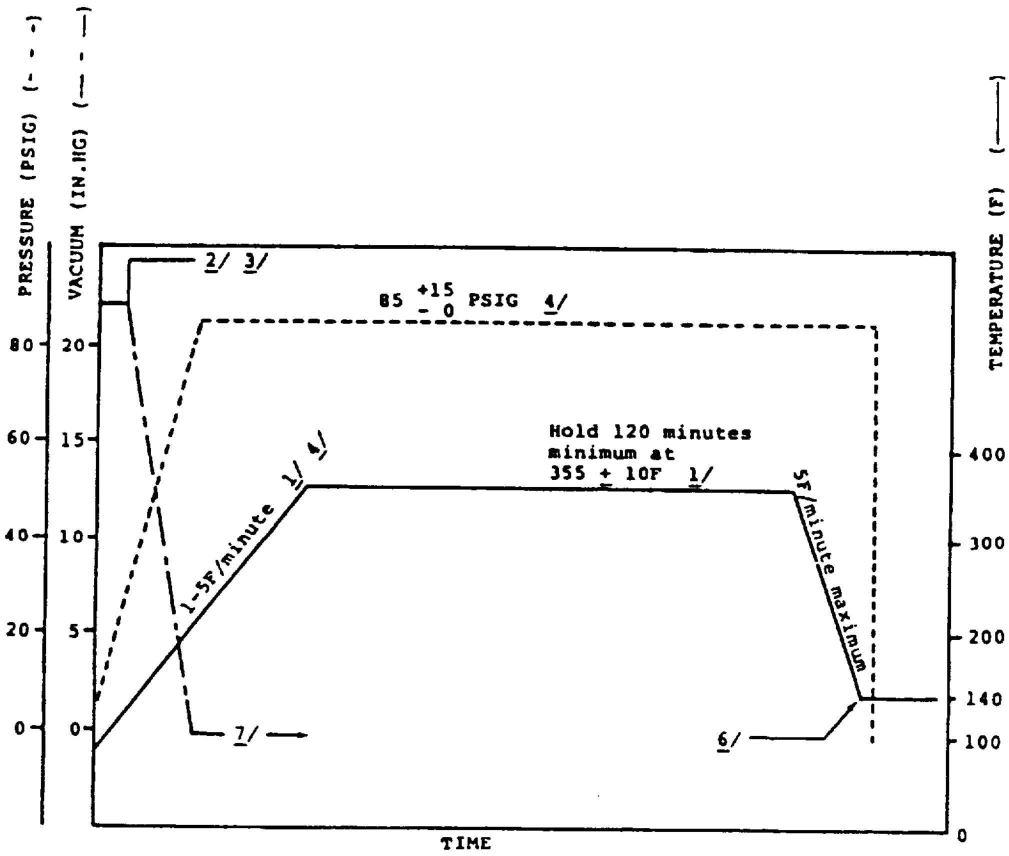


Figure 2.2. Cure Schedule of Cyanate Prepregs



1/ Temperature based on lagging thermocouple
2/ Apply 22 inches Hg vacuum minimum to vacuum bag
3/ Vent vacuum bag to atmosphere when pressure reaches 20 psig
4/ A minimum heat-up rate of 0.3°F/minute is acceptable
5/ Apply 85± 15 psig pressure
6/ Below 140°F release pressure and remove part
7/ The vacuum within the bag must remain at 0-5 inches Hg throughout

Figure 2.3. DMS of 10% PEEK-Modified Cyanate

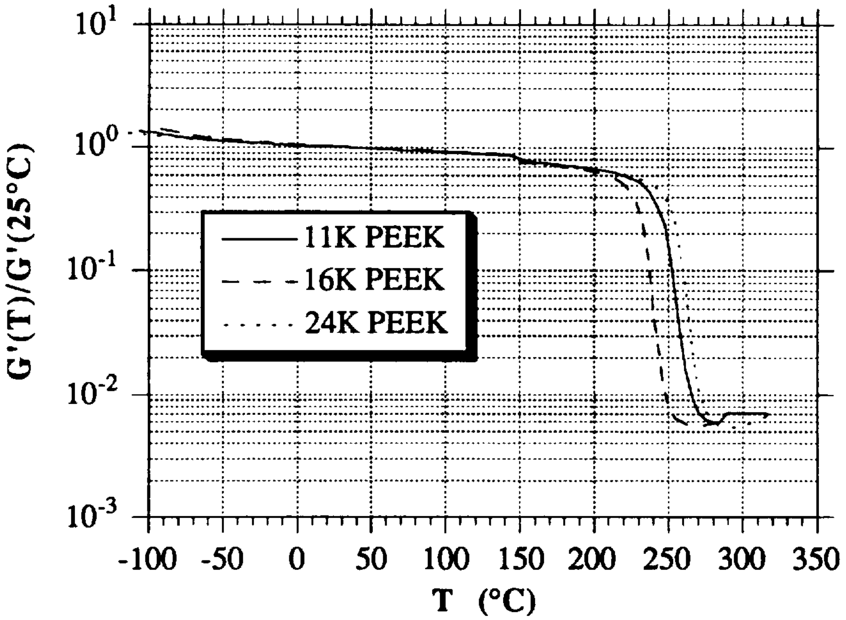


Figure 2.4. DMS of 20% PEEK-Modified Cyanate

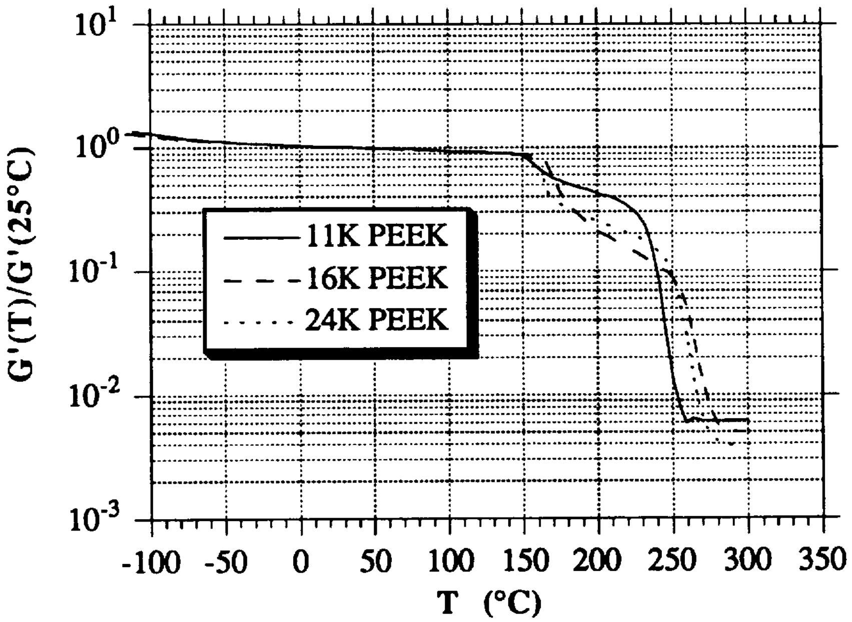


Figure 2.5. DMS of 30% PEEK-Modified Cyanate

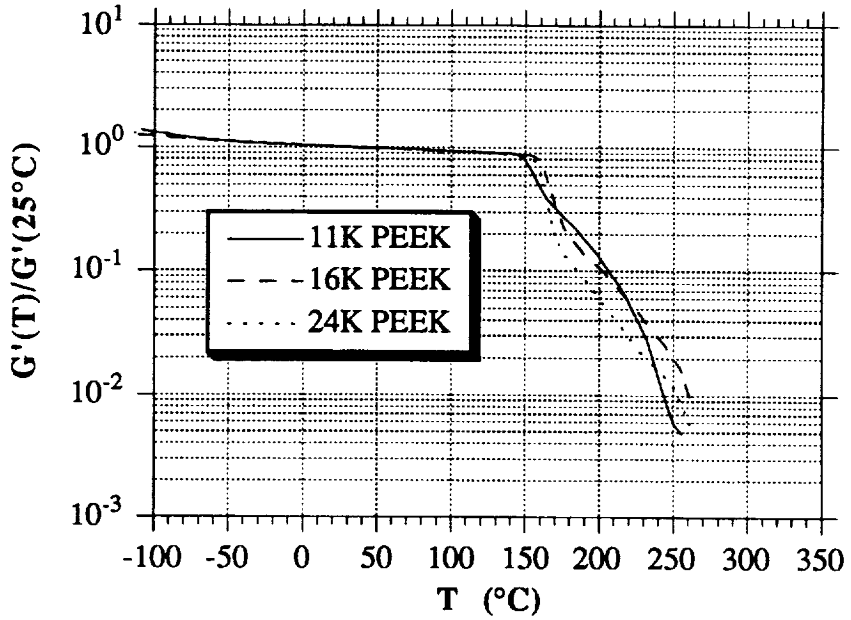


Figure 2.6. 10% PEEK (M_w 11K) in Cyanate XU71787

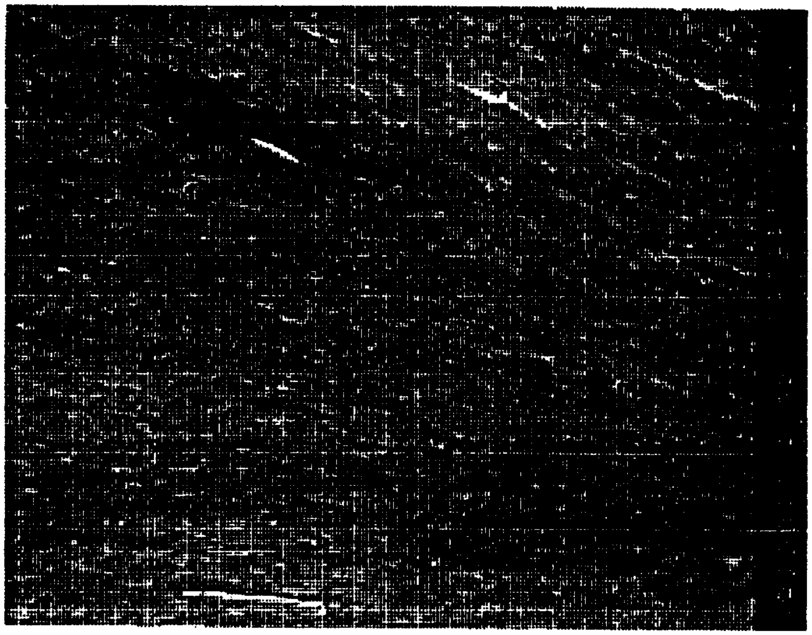


Figure 2.7. 20% PEEK (M_w 11K) in Cyanate XU71787

Figure 2.8. 20% PEEK (M_w 16K) in Cyanate XU71787

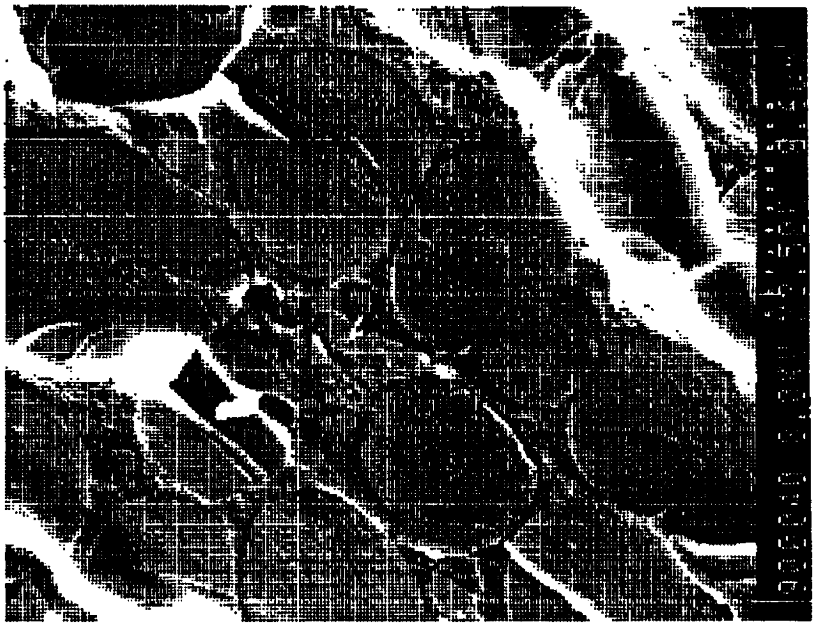


Figure 2.9. 20% PEEK (M_w 24K) in Cyanate XU71787

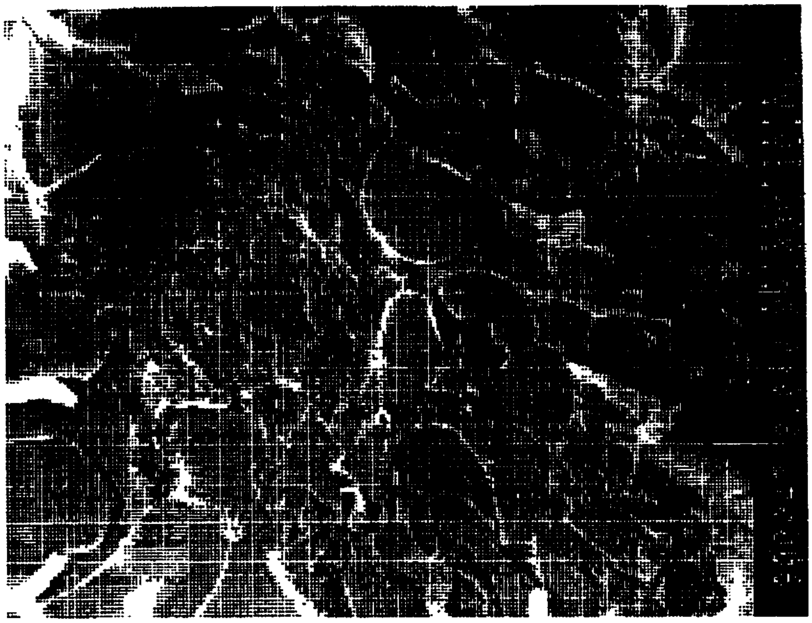


Figure 2.10. 30% PEEK (M_w 24K) in Cyanate XU71787

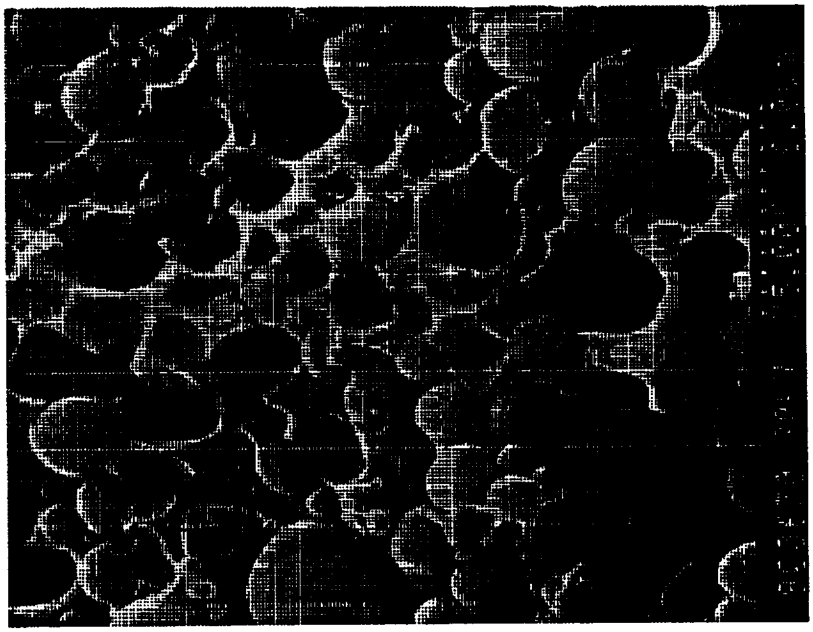


Figure 2.11. Fracture Toughness of PEEK-Cyanate Copolymers

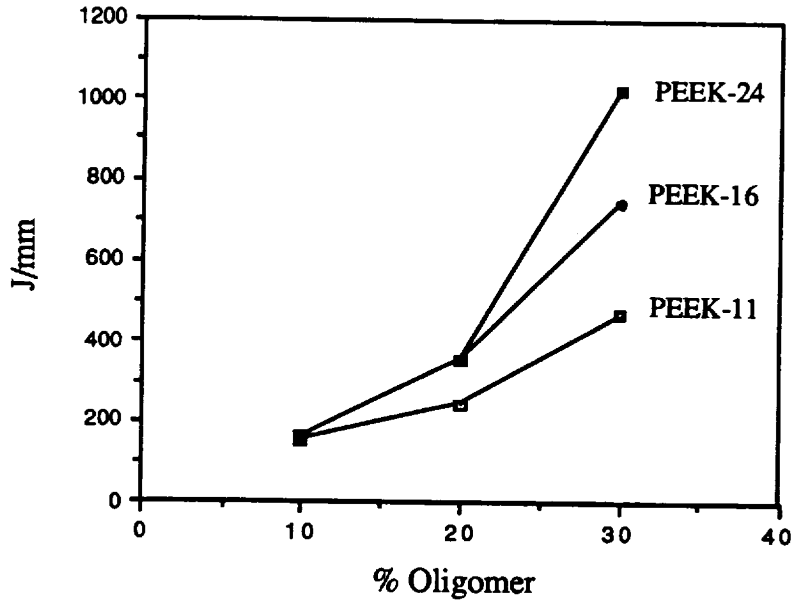


Figure 2.12. MEK Uptake of PEEK-Cyanate Copolymers

2-Week Immersion (Unmodified Cyanate = 2.7%)

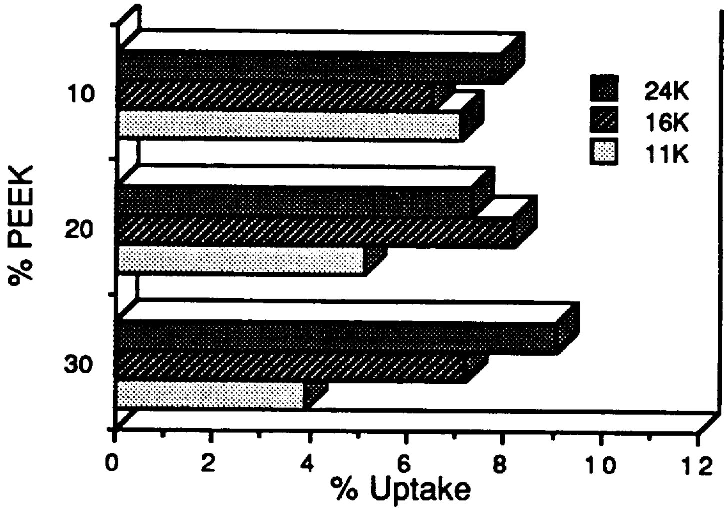


Figure 2.13. SEM of PPO (30%)-Cyanate Casting

Figure 2.14. Optical Micrograph (Partly Polarized of 20% PEI-Cyanate Heated from 80°-177°C at 5°C/min

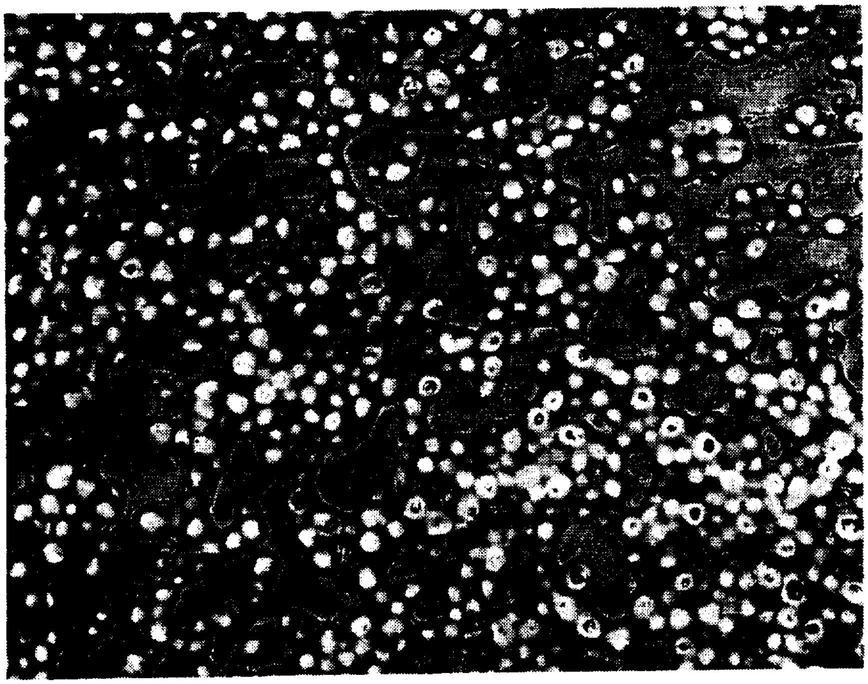


Figure 2.15a. SEM of 30% PEI-Cyanate Casting

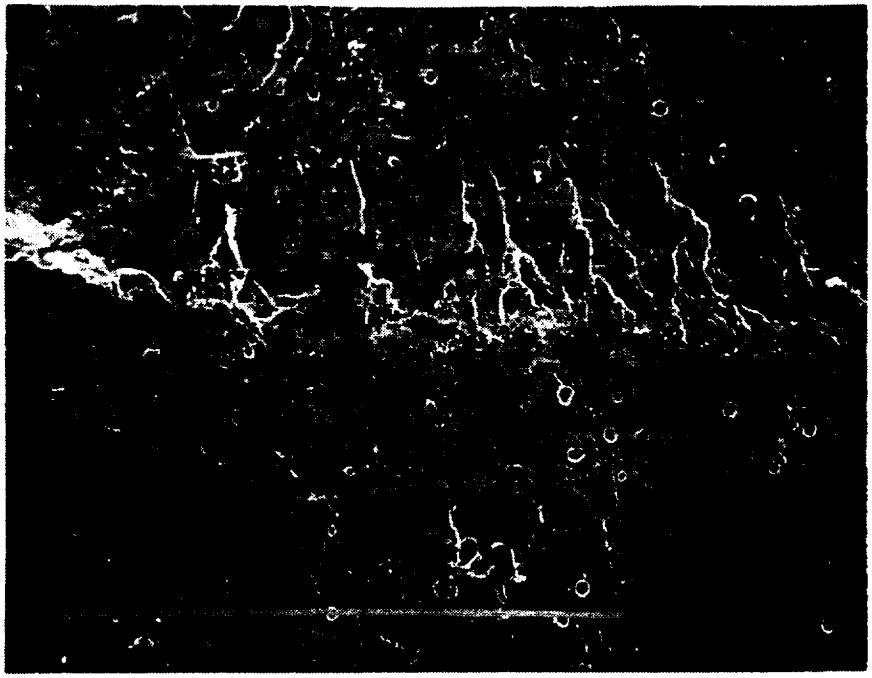


Figure 2.15b. SEM of 30% PEI-Cyanate Casting

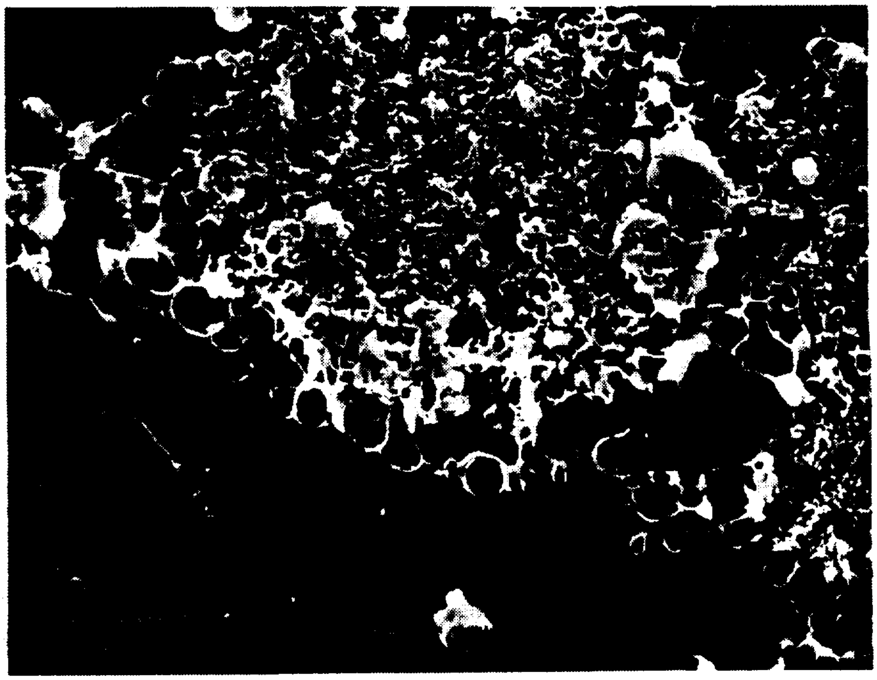
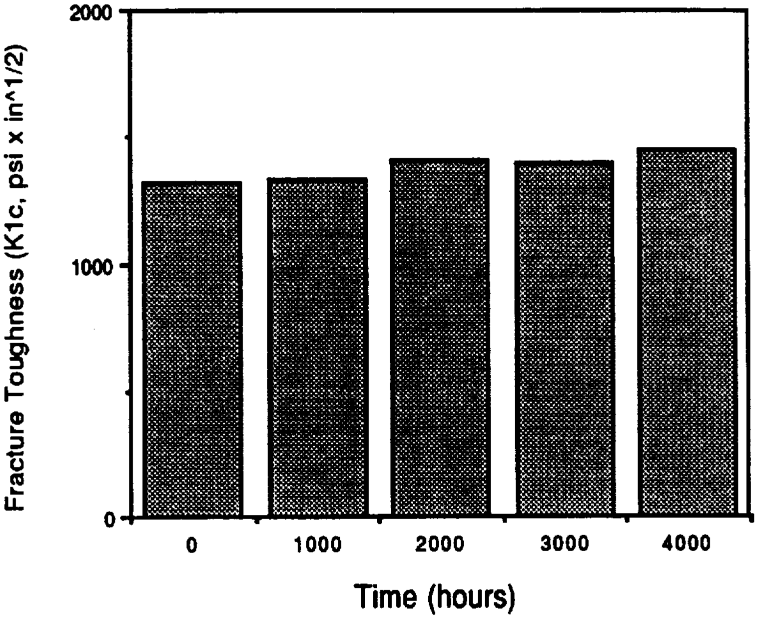


Figure 2.15c. SEM of 30% PEI-Cyanate Casting

Figure 2.16. Fracture Toughness of PEI-Cyanate *vs* Aging at 360°F in Air



SECTION 3

TASK 3. ACETYLENE-CHROMENE-TERMINATED RESIN COMPOSITE SYSTEM

The objective of this task is to develop a prepreg composite system with ≥232°C (450°F)/wet service temperature and ≥40 ksi compressive strength after impact. The technical approach is to select a resin based on the acetylene-chromene chemistry which is capable of ≥232°C/wet performance and then to apply the knowledge on thermoplastic toughening gained in Task 2 to optimize toughness and composite damage tolerance.

3.1. SUMMARY

Resin Preparation. About twenty pounds of the acetylene-chromene-terminated (ACT) resin were prepared for use in toughening and RTM study.

Thermoplastic Toughening. The morphology and fracture toughness of a number of ACT-thermoplastic blends were characterized. Toughness improvement was only modest at thermoplastic levels of less than 30%.

RTM Composite Properties of Unmodified Resin. Properties were as expected from a highly crosslinked resin. Panels, unfortunately, also had a significant amount of microcracks.

Task Termination. Due to the tendency for the unmodified resin to yield composite panels with microcracks and its lack of response to toughening additives, this task was terminated with the approval of the Technical Representative of the Contracting Officer.

3.2 RESULTS AND DISCUSSION

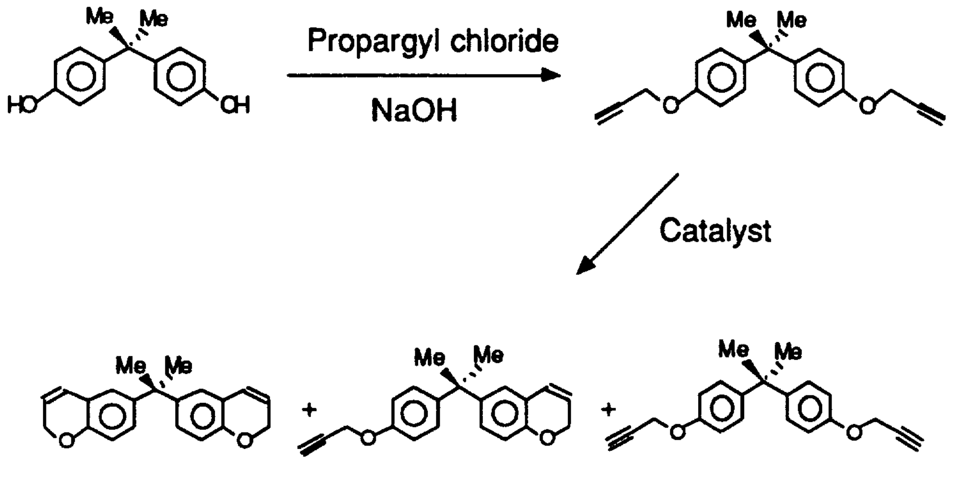
Resin Chemistry. The synthesis of propargyl ethers of phenolic materials is known int the literature.[1,2] Typically, however, a number of problems often occur including the formation of both O-alkylated and C-alkylated products. Further, the literature teaches the use of propargyl bromide whose shock sensitivity represents a serious barrier to industrial use. Before the inception of this Contract, we have developed a phase-transfer process which uses no solvent and the shock insensitive propargyl chloride instead of the chloride. The process yields the propargyl ethers of a number of phenolic materials in high purity and high yields.[3]

Attempts to prepare neat resin castings from the bis-propargyl ether of bisphenol A, though alluded to in the literature[2], invariably resulted in cured parts that were full of voids, depression due to shrinkage, and extensive cracking. We then turned to B-staging as a means to minimize these problems. Reactive chemical studies, however, shows that the polymerization of the bis-ether is extremely exothermic (about 1100 J/g) so that run-away exothermic reactions is very likely.

We suspected that the polymerization might involve the intermediacy of the corresponding chromene[4] and that the rate of the Claisen rearragement to chromene is competitive to the polymeriztion of the resulting chromene. In a model compound study, we found that the heat of reaction for the Claisen rearragement is several times that of the chromene polymerization. Therefore, if a way could be found to convert the bis-propargyl ether to the corresponding chromene without significantly advancing the resin then the problem of exothermicity and shrinkage might be solved.

We discovered prior to the beginning of the Contract that very high conversion to chromene can be achieved by heating (180°C) the bis-propargyl ether of bisphenol A in *o*-dichlorobenzene and a catalytic amount (50 ppm) of cuprous chloride. At the preferred conversion of about 60% a low viscosity (about 100 cps at 80°C) resin with epoxy-like thermochemistry is obtained. Since this resin contains acetylene and chromene terminal groups, it has been given the acronym of ACT. About 20 lb of ACT resin have been prepared using the above procedure (Scheme I).

SCHEME I



Resin and polymer properties. ACT resin is a dark brown substance which is pourable at room temperature, though with some difficulty. Its viscosity as a function of temperature is shown in Figure 3.1. As can be seen, the viscosity drops rapidly as the temperature increases: about 300 cps at 40°C and about 200 cps at 60°C. The ACT resin is perhaps the lowest viscosity high temperature thermoset when compared to commercially available bismaleimides. This unique feature makes it a very desirable candidate for RTM and as a base resin for thermoplastic modifications.

Initial evaluation of the hot/wet properties of the polymer indicates at least a 204°C (400°F) performance (Figure 3.2). Moisture conditioning was conducted in at 90% humidity and 170°F. The moisture uptake as a function of time is shown in Figure 3.3. Castings were exposed to air at 204°C to determine its thermo-oxidative stability. For comparison, samples of Compimide® 353 and Compimide® 353/TM121 were included. These reference samples were chosen because they are well-characterized materials and recommended cure schedule are available from the manufacturer. As can be seen in Table 3.1, the ACT casting held up to aging better than both bismaleimide resins, although there were some surface cracks. The casting of Compimide® 353 were extensively cracked by the aging process to the point of partially disintegration.

Thermoplastic Toughening. The approach taken was based on two working hypotheses. First, a more compatible system (of the cured resin and the thermoplastic) will give more effective toughness improvement. Second, compatibility is determined by a close match of solubility parameters to a first approximation. Accordingly three commercially available thermoplastics [polyphenylene oxide (PPO), Ultem® 1000 (PEI), Matrimide® 5218 (polyimide)] and two research polycarbonate samples were selected on the basis of their calculated solubility parameters for toughening study (see Table 3.2). These selections covered a reasonably wide solubility parameter range to compensate for the inherent inaccuracy in solubilility parameter calculations.

The morphology of the various blends containing 20% thermoplastic may be divided into two groups. The first comprises the the blends with the two polycarbonates (see Figures 3.4 and 3.5) which appeared to be thermoset-continuous with a dispersed thermoplastic phase. Unfortunately, these castings were extremely brittle and were eliminated from further consideration. The second group comprises Ultem® PEI, PPO and Matrimide® 5218. The SEM micrographs (Figures 3.6 to 3.8) clearly showed a smooth, featureless, and presumably thermoset region, alongside a phase-separated mixed region suggesting that increasing the thermoplastic content might force the system to one morphology. This was, indeed, found in the blends with 40% PEI and Matrimide® (see Figure 3.9 for micrograph of Matrimide® blend).

Next, we studied the fracture toughness and modulus retention by dynamic mechanical analysis of a few of the above blends (see Table 3.3). The PEI blends at 20% and 40% did not have the marked increase in fracture toughness needed and the shear modulus at 450°F of the 40% blend was only 18% of that at 77°F. Therefore, these blends could not meet our objective. The 40% Matrimide® blend with good modulus retention and marginally acceptable fracture toughness was considered worth additonal attention. The challenge was to find a way to make a prepreggable system out of a resin blend with such a high level of thermoplastic. The obvious approach was to use particles instead of a solution blend in light of the success of this approach in the cyanate task. To this end, many attempts were made but none was successful. Each time when the resin and the thermoplastic particles mixture was warmed to effect mixing and degassing, the particles aggregated into a solid mass.

In light of the lack of real success in toughening, this task was terminated with the approval of the Technical Representative of the Contracting Officer.

3.3. CONCLUSIONS

3.4. EXPERIMENTAL

Preparation of Aromatic Propargyl Ethers. To a 500-mL round bottom flask were added 45.6 g (0.2 mol) of bisphenol A, 200 mL of 20% aqueous sodium hydroxide, and 3.22 g (0.01 mol) of tetrabutylammonium bromide. To this stirred mixture was added 34.27 g (0.46 mol) of propargyl chloride over a 10 min period. The mixture was stirred at room temperature for 16 h. The reaction mixture was filtered to remove the white product which was rinsed twice with 200 mL of water and rinsed twice with 50 mL of isopropanol. The product was dried in vacuo to yield 57.9 g (95% yield) of the bispropargyl ether of bisphenol A of 99.7% purity, as determined by gas chromatography, with a melting point of 83°C.

Conversion of the Bispropargyl Ether of Bisphenol A to an ACT Resin. To a stirred mixture of the bispropargyl ether of bisphenol A (153 g) and *o*-dichlorobenzene (455 mL) under a nitrogen blanket was added 60 microliters of a solution of cuprous chloride in concentrated hydrochloric acid (1g/4 mL) (100 ppm, 0.01%). The mixture was stirred and heated to reflux for 4 h. Analysis of an aliquot by gas chromatography showed 13% bispropargyl ether, 42.6% monopropargyl ether/monochromene, and 43.9 % bischromene (area percents) in the mixture. Solvent was removed *in vacuo* to give a viscous oil (153 g, 100% yield).

Polymerization of ACT Resins. A sample of acetylene-chromene terminated resin prepared above was degassed in a vacuum oven at 180°C for 1.0 h. The degassed resin was then poured into preheated (205°C) stainless steel parallel plate molds which had been pretreated with Teflon® mold release agent. The material was then cured in an oven at 205°C for 2 h followed by 250°C for 2 h. A hard, dark brown polymer resulted.

3.5. REFERENCES

1. A. S. HAY, U.S. Patent 3,594,175.
2. L. Picklesimer, U.S. Patent 4,226,800
3. M. Inbasekaran and S. Dirlikov, U.S. Patent 4,885,403.
4. The Chemistry of the Carbon-Carbon Triple Bond, Part 1, Ed. S. Patai, John Wiley & Sons, 1978, page 423.

3.6. TABLE AND FIGURES

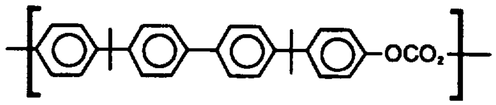
Table 3.1. ACT Casting Weight Change at 204°C in Air

	100 hr	500 hr	2000 hr
ACT	+0.038%	-0.40%	-1.75
Compimide® 353	-0.41%	-0.85%	-25.7
Compimide® 353/TM 121	-0.20%	-0.97%	-2.82

Table 3.2. Properties of Thermoplastic for Toughening of ACT

Polymer	Solubility Parameter $(J/cc)^{0.5}$	T_g (°C)
ACT Resin	20.1	>300
PPO	19.4	210
Polycarbonate A	20.6	192
Polycarbonate B	21.6	282
Matrimide® 5218	22.4	282
Ultem®1000	23.7	215

Polycarbonate A



Polycarbonate B

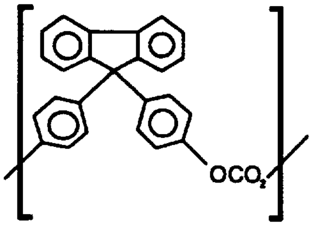


Table 3.3. Properties of Thermoplastic-ACT Blends

Thermoplastic	%	K_{IC} psi x $in^{0.5}$	G' at 450°F/G' at 77°F
None	0	444	
PEI	20	507	
PEI	40	710	0.184
Matrimide®	40	1050	0.670

Figure 3.1. Viscosity of ACT Resin

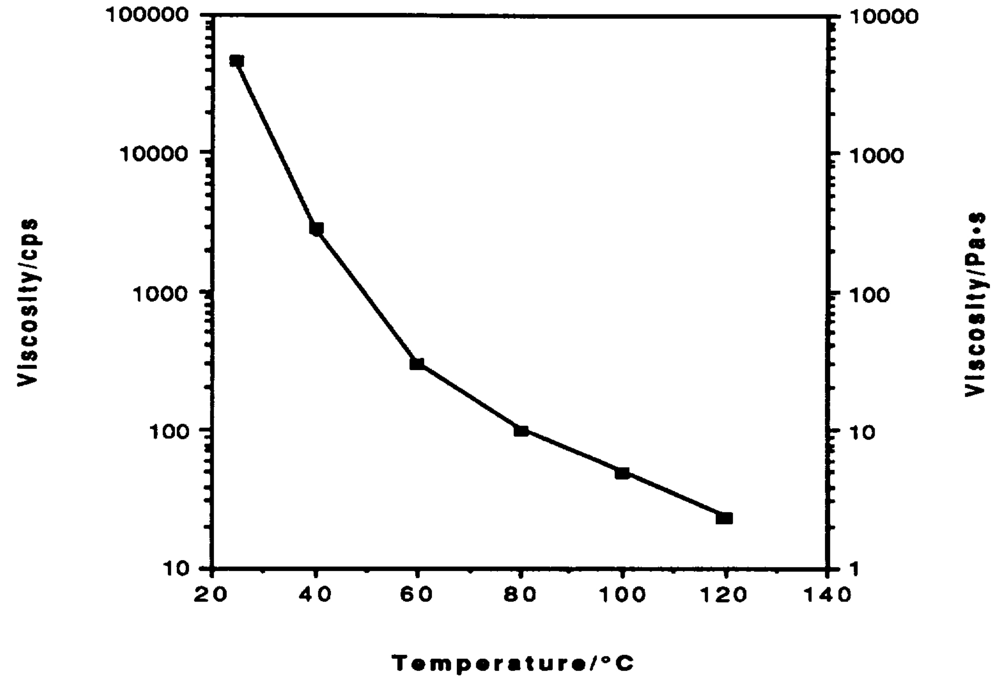


Figure 3.2. Flexural Modulus of ACT Polymer

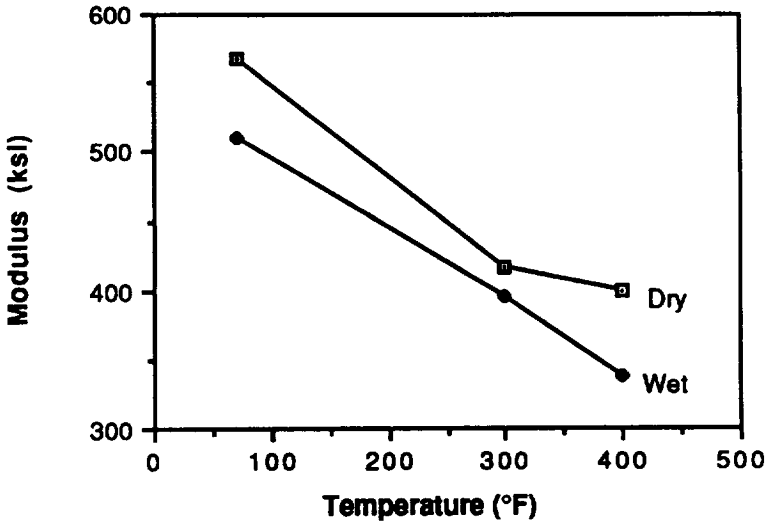


Figure 3.3. Moisture Pick-up of ACT Polymer

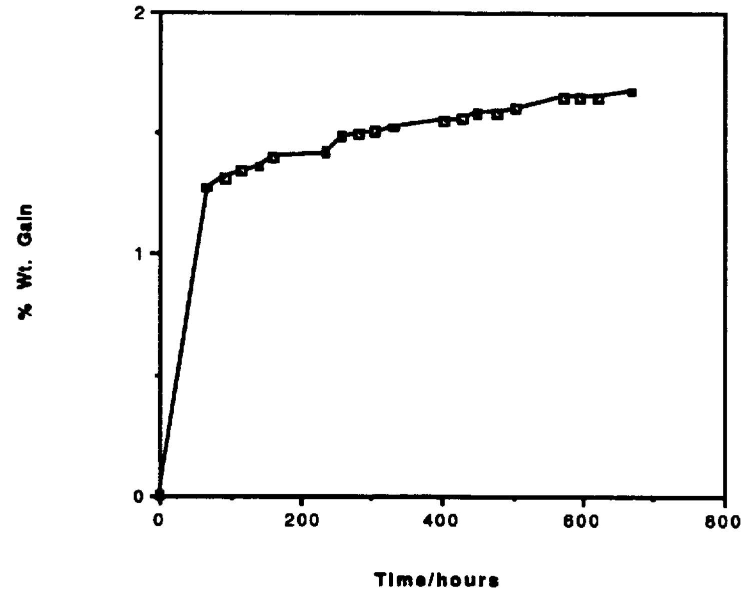


Figure 3.4. SEM of ACT Casting Containing 20% FBP

Figure 3.5. SEM of ACT Casting Containing 20% BPBA

Figure 3.6. SEM of ACT Casting Containing 20% PPO

Figure 3.7. SEM of ACT Casting Containing 20% Matrimide®

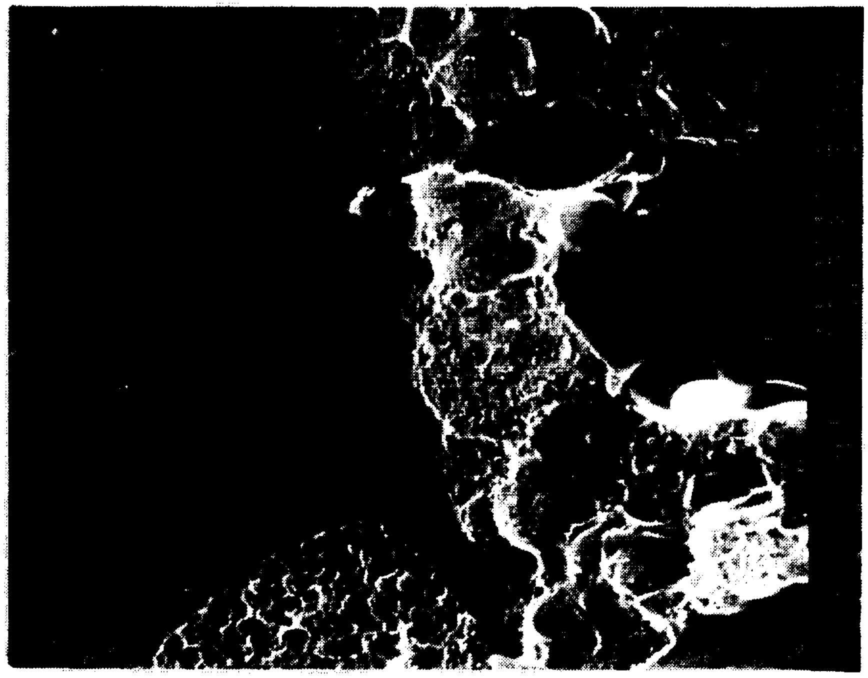


Figure 3.8. SEM of ACT Casting Containing 20% Ultem®

Figure 3.9. SEM of ACT Casting Containing 40% Matrimide®

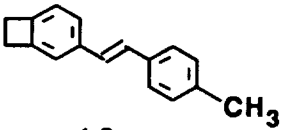
SECTION 4
TASK 4. BENZOCYCLOBUTENE TECHNOLGY

The objective of this task is to explore the Diels-Alder reaction of benzocyclobutene (BCB) with acetylenes and maleimides. AABB- and AB-type polymers will be evaluated for heat resistance, modulus and fracture toughness and the most promising polymeric candidate will be studied as a matrix material for carbon fiber-reinforced composites.

4.1. SUMMARY

BCB-Acetylene Copolymers. The complex product mixture obtained from the reaction of BCB and phenylacetylene indicated that Diels-Alder reaction was not a major reaction pathway. Two AB type monomers containing BCB and acetylene functionalities were studied but their high exothermicity prevented the preparation of good quality castings. This work was terminated with the approval of the Technical Representative of the Contracting Officer.

Monobenzocyclobutene-Bismaleimide Copolymers. Copolymers in various mole ratios of p-vinyltoluenebenzocyclobutene (p-VTBCB, **10**) and Compimide® 353 were prepared and their thermal and mechanical properties characterized. The copolymers had excellent glass transition temperature and modulus, but did not have good retention of hot-wet properties and displayed poor fracture toughness. This work was terminated with the approval of the Technical Representative of the Contracting Officer.



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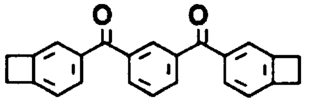
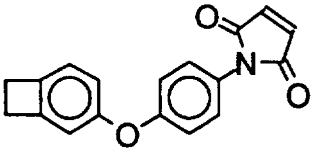
Bisbenzocyclobutene-Bismaleimide Copolymers. The 1:1 copolymer of methylenedianiline bismaleimide and the bisbenzocyclobutene **11** was prepared.



11

While the copolymer had a high T_g and flexural modulus, it also exhibited a low flexural strength and more importantly a low fracture toughness (G_{1c}=130 J/m^2). Attempts to improve the toughness by incorporating radical inhibitors led to the formation of copolymer parts that had voids or phase separation problems. This work was terminated with the approval of the Technical Representative of the Contracting Officer.

AB-Benzocyclobutene-Maleimide Polymers. Several new monomers and polymers have been prepared. These polymers have been characterized for thermal and mechanical properties. The monomer (6) chosen for further study was the subject of a 50-pound scale-up campaign and extensive work on polymerization fundamentals.



(6)

AB-Benzocyclobutene-Maleimide Composite Evaluation. Composite panels of 6 were fabricated using Dow's proprietary resin flow molding technique. Internal evaluations using G30-500 8HS fabric as the reinforcement showed a compressive strength after impact (CAI) of about 49 ksi, excellent resistance to solvents and 350°F hot/wet performance. Aging of open hole compressive strength specimens at 400°F for 4000 hours yielded less than 10% drop in strength and about 0.5% weight loss. Thirty uniweave panels (IM 7) were also fabricated for evaluation at McDonnell Aircraft. In addition to rating this system as the number one candidate for High Speed Civil Transport, McDonnell Aircraft also reported a CAI of more than 55 ksi.

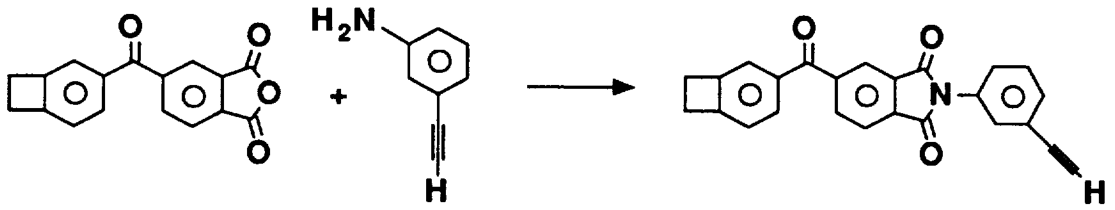
4.2. RESULTS AND DISCUSSION

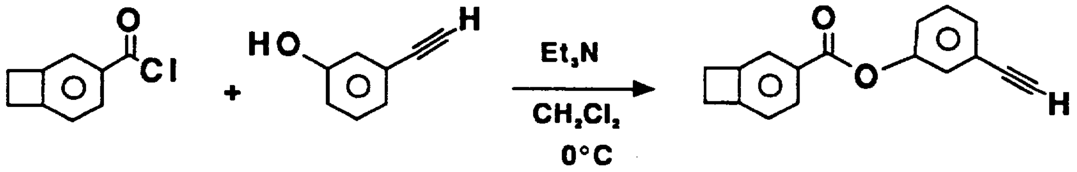
4.2.1. Technical Approach. In keeping with the exploratory nature of this task, a variety of monomers was synthesized and polymerized, and the resulting polymers screened for glass transition temperature, modulus at ambient and elevated temperatures, and fracture toughness. The desired property profile was a T_g >225°C (preferably >250°C), flexural modulus >450 ksi, and G_{IC} ≥700 J/m^2. Also considered were the ease of the synthetic route and ease of processing. The most promising candidate was studied extensively with respect to its polymerization kinetics, rheology, composite fabrication, and composite properties.

4.2.2. Reaction of BCB with Acetylenes.

Model study. The reactions of the parent BCB compound with phenylacetylene and diphenylacetylene were examined under a variety of condidtions. In each case the reaction gave a very complex mixture indicating that Diels-Alder cycloadditon was not the predominant reaction pathway.

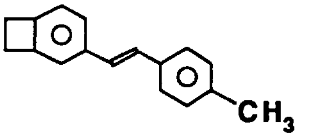
AB-type monomers and polymers. The two monomers shown below were prepared.



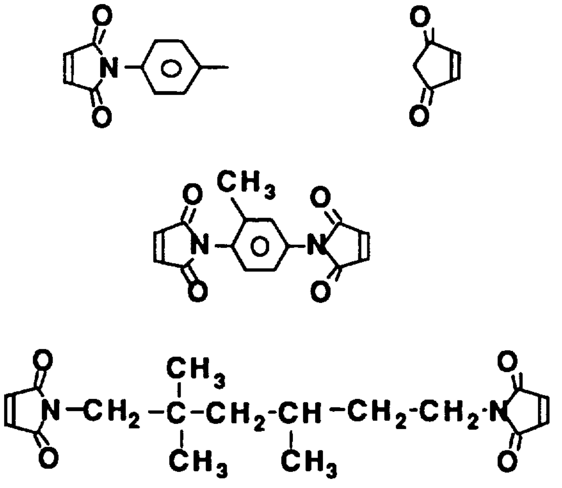


The monomer containing the phthalimide moiety had a melting point of 216°C which overlapped the polymerization exotherm of both of the functional groups. Therefore, melt polymerization of this material to a good quality casting appeared unlikely. Nonetheless an attempt was made to polymerize a small amount in a glass tube but the resulting polymer plug was full of voids. The monomer containing an ester linkage had a melting point of 82°C and became water-like when melted. It also had a very large energy of polymerization (65.6 kcal/mole) which meant that processing to form a polymer must be carried out carefully over a long period of time to allow dissipation of the energy released. Several attempts at polymerization resulted in extremely brittle castings which broke into pieces when the mold was cooled to room temperature. This work was terminated with the approval of the Technical Representative of the Contracting Officer.

4.2.3. MonoBCB with Bismaleimide. Several different copolymers were prepared based upon the reaction of a monobenzocyclobutene (p-VTBCB) and Compimide® 353 which is a eutectic mixture of bismaleimides. The mole ratios of p-VTBCB to Compimide® 353 ranged from 2:1 to 1:2 and all compositions provided homogeneous mixtures when heated at 110°C that could be easily poured into a steel mold. The monomer mixtures were thermally cured using the following cycle: 140°C/30 minutes, 160°C/60 minutes, 180°C/60 minutes, 200°C/60-120 minutes, 220°C/60 minutes, 250°C/60 minutes. At the end of the last step the plaque could be removed immediately, or cooled to approximately 100°C before removing from the mold. The plaques were in general clear dark amber parts that had no voids. Analysis by DSC indicated that there was a residual exotherm present usually around 300-330°C. If the plaque was heated at 330°C for 90 minutes the exotherm was no longer present and in general the T_g was higher than that obtained directly after initial cure at 250°C. The plaques were cut using a diamond saw to give the test specimens required. Table 4.1 contains the results of several of the analyses of the copolymers prepared. Ultem® 1000 was included in the testing as a calibration of the results. All of the experimental copolymers after post cure at 330°C showed high T_gs ranging from 273°C to 322°C along with good values for flexural modulus, as determined by DMA (dynamic mechanical analysis). As was to be expected, the copolymer which contained the greater amount of p-VTBCB also showed the least amount of moisture absorption (1.19%), as well as having the lowest T_g (273°C). While the copolymers displayed good processability and very good thermal and room temperature dry flexural properties, they were very brittle. Consequently, it was decided to terminate further work on this copolymer system.

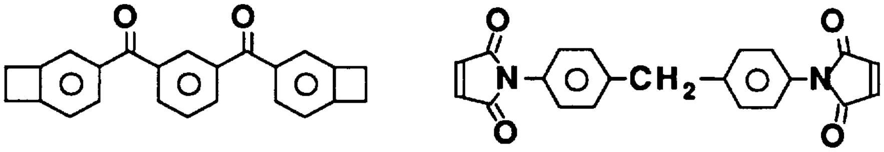


p-VTBCB



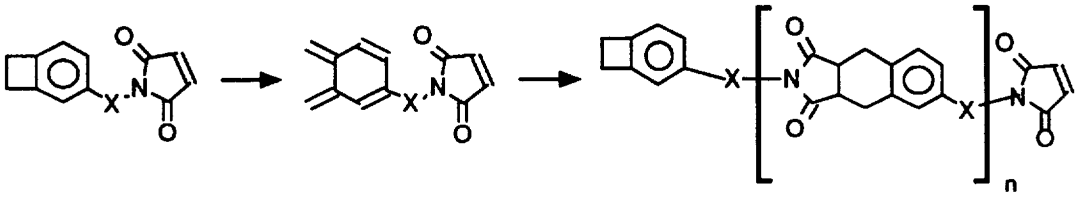
Compimide® 353

4.2.4. Bisbenzocyclobutene-Bismaleimide Copolymers. The monomers chosen for this work were BCB-diketone and the bismaleimide of methylenedianiline. BCB-diketone was



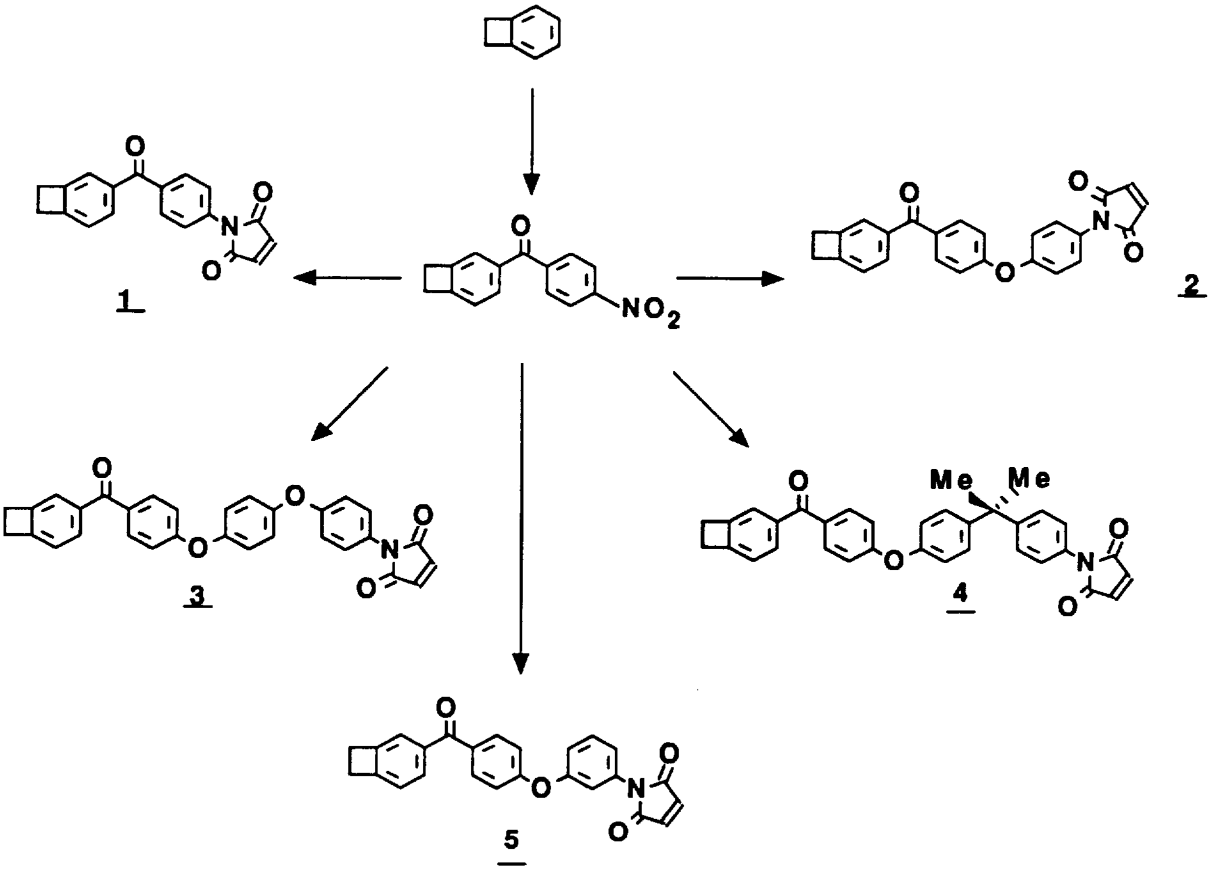
obtained from our IR&D program and the BMI was purchased from a commercial source. The first attempts to form a copolymer of BCB-diketone with a BMI were based upon using Compimide® 353 as the bismaleimide. When the two components were melted together they initially formed a homogeneous misicible liquid. However, upon standing at temperatures greater than 110°C, a phase separated material was observed. Polymerization of a 1:1 comonomer mixture provided plaques that were nonhomogeneous. Additionally, there was a problem of stress cracks forming in the plaque during the molding operation. It was decided at that time to shift to the pure BMI based on MDA. In this case the formation of the copolymer is a more difficult process because of the melting point 154-156°C of the BMI. Once it was melted, it could not be held for prolonged periods of time without some formation of a gelatinous phase. Small plaques of the copolymer (2"X3"X1/8" or 3"X3"X1/8") could readily be formed and were of satisfactory quality for further evaluation of thermal and thermomechanical properties. These properties are summarized in Table 4.2. The copolymer has a high T_g (306°C by DMS) along with 530 ksi ambient flexural modulus. The fracture toughness of the copolymer was not as good as was hoped for. The G_{1C} turned out to be 130 J/m^2 which was far lower than our selection criterion. Accordingly, this work was terminated.

4.2.5. AB-BCB-Maleimide Monomer Synthesis. Several years ago as a part of a patent application a small amount of the AB-BCB-maleimide monomer **1** (see next page for structure) was synthesized. In light of the difficulties encountered in the other systems, it was decided to examine the AB system in greater depth. It was hypothesized that AB-type monomers would not tend to phase separate and would polymerize to more linear (tougher) polymers because there is always an exact balance in stoichiometry. The idealized structure of the polymers is shown below.

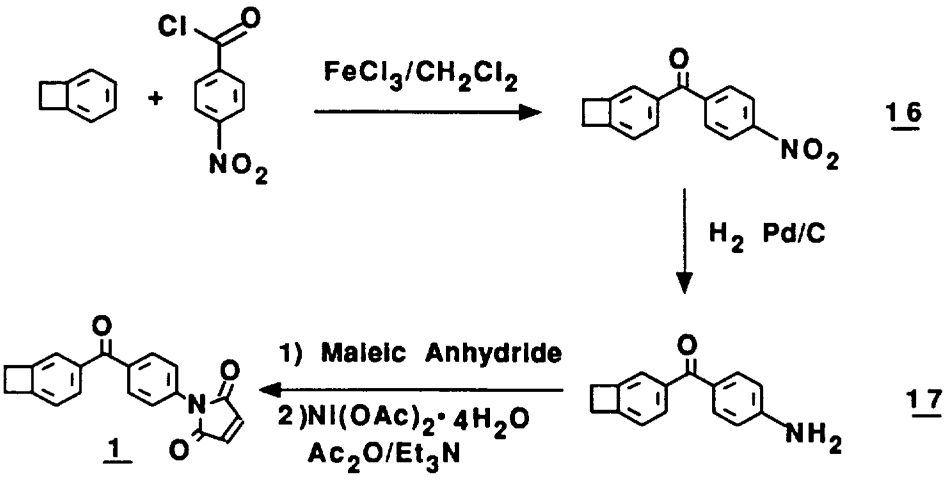


The AB benzocyclobutene maleimide monomers that have been prepared can be basically separated into two distinct families based upon the chemistry used to prepare them plus the type of linking group present. The first family, shown below, starts with the BCB hydrocarbon and its subsequent reaction with 4-nitrobenzoyl chloride under Friedel-Crafts conditions to afford the key intermediate in the preparation of all of the monomers shown. All of these monomers have either keto- or keto ether linking groups.

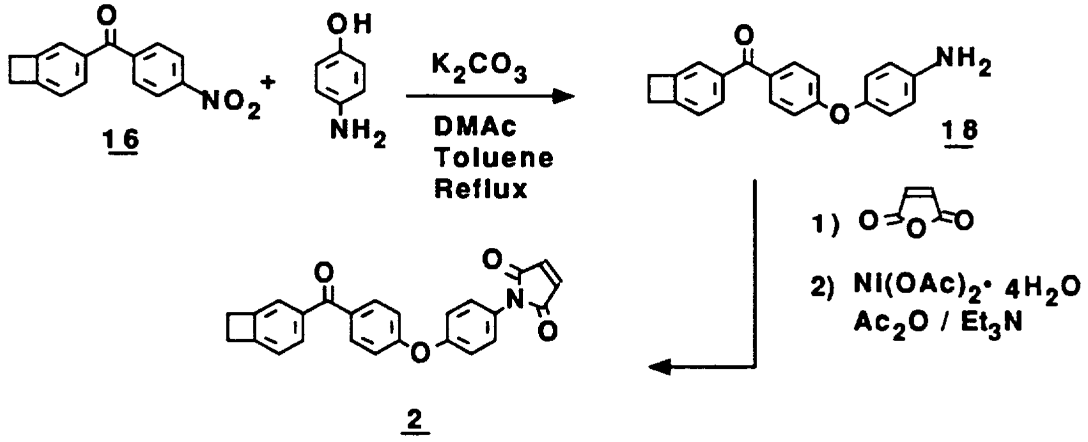
FAMILY I



<u>Synthesis of Monomer 1</u>. The first monomer, first prepared prior to the inception of the contract, was accessed by the route outlined below. It melts at about 151°C.

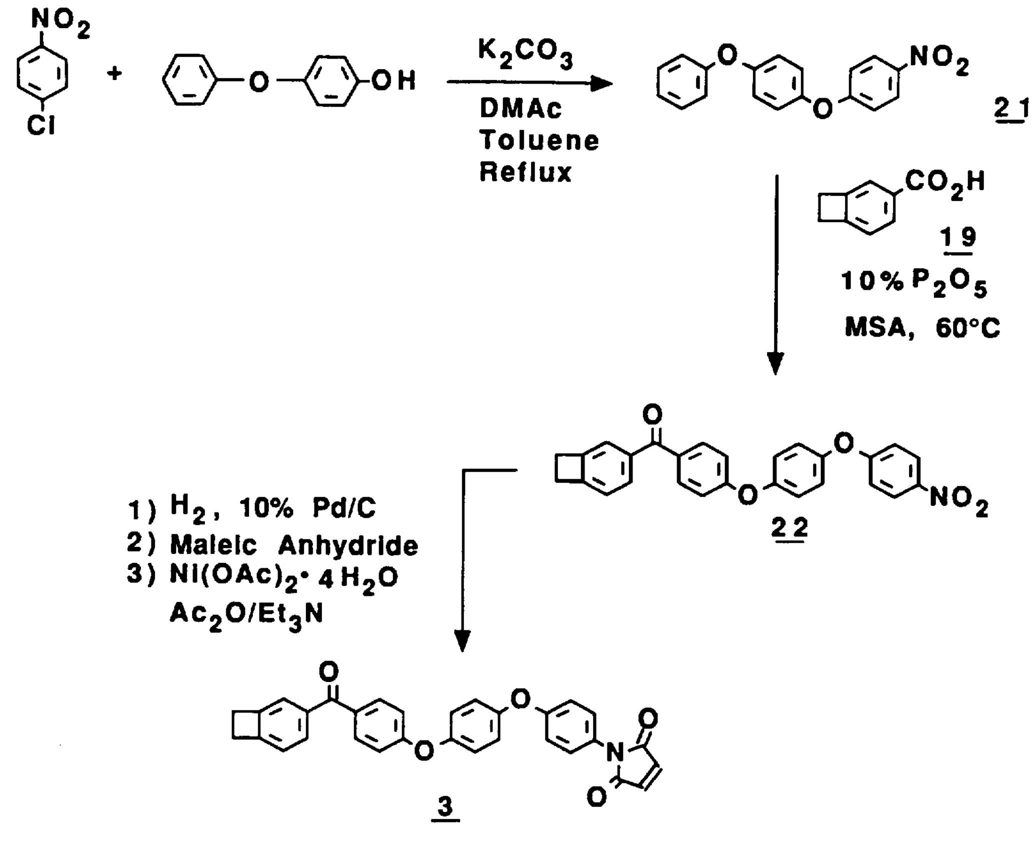


Synthesis of Monomer 2. The scheme below outlines the best synthesis of monomer 2.

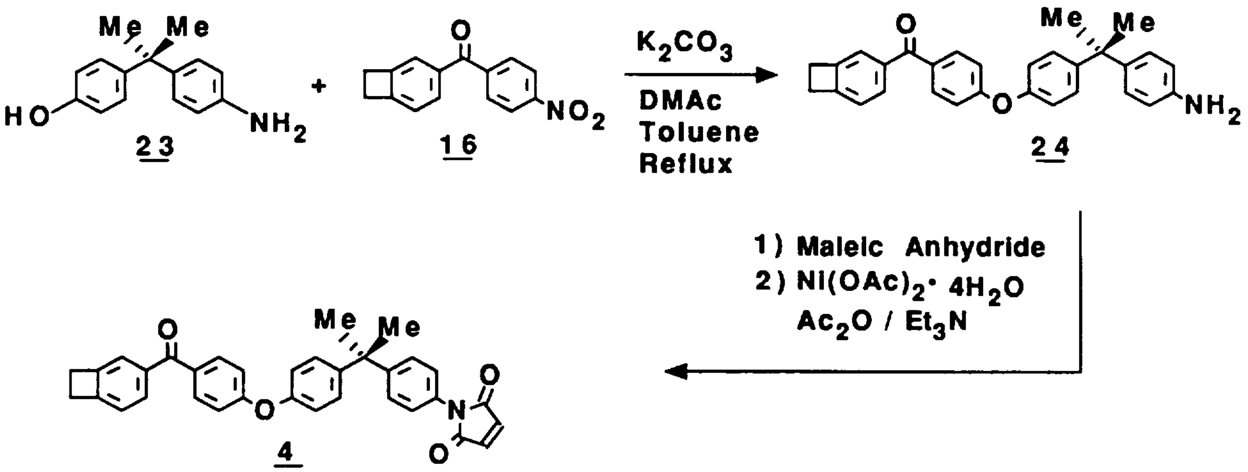


Monomer 2 was obtained after silica gel chromatography as a crystalline solid which melts at 158°C.

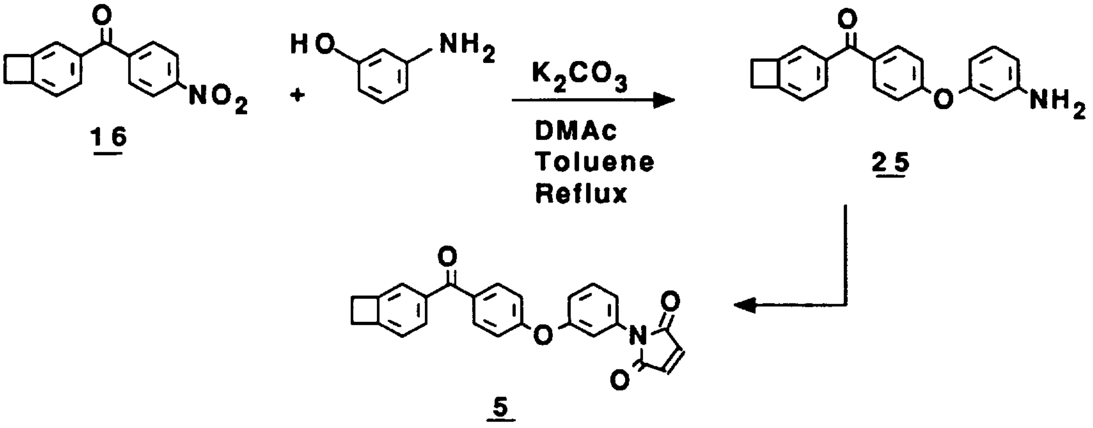
Synthesis of Monomer 3. The scheme on the next page details the sequence of reactions used for its preparation. Monomer 3 had a melting point of 177°C.



Synthesis of Monomer 4. Monomer **4** was prepared in an identical manner as both **2** and **3** by carrying out a phenate displacement upon **16**. It does not have a melting point but rather a T_g of 118°C by DSC.

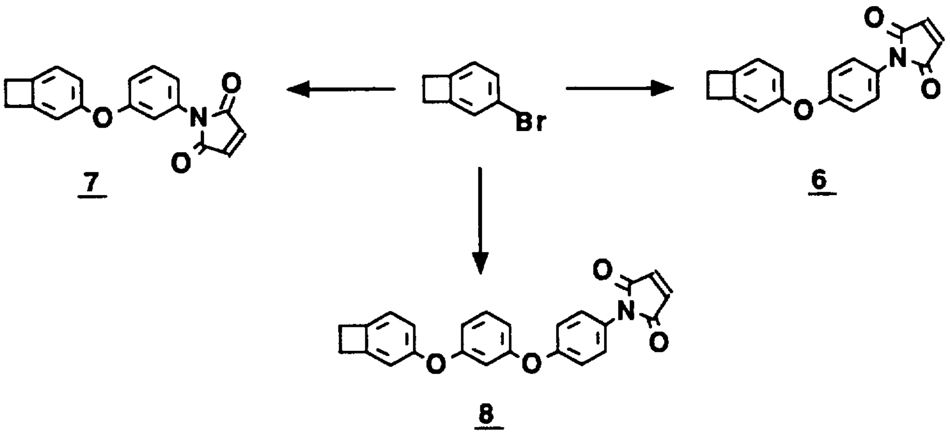


Synthesis of Monomer 5. This material was prepared in an almost identical fashion to that detailed earlier for monomer 2. Rather than starting with 4-aminophenol, the starting material was the meta substituted isomer. The melting point of this monomer was 95°C.

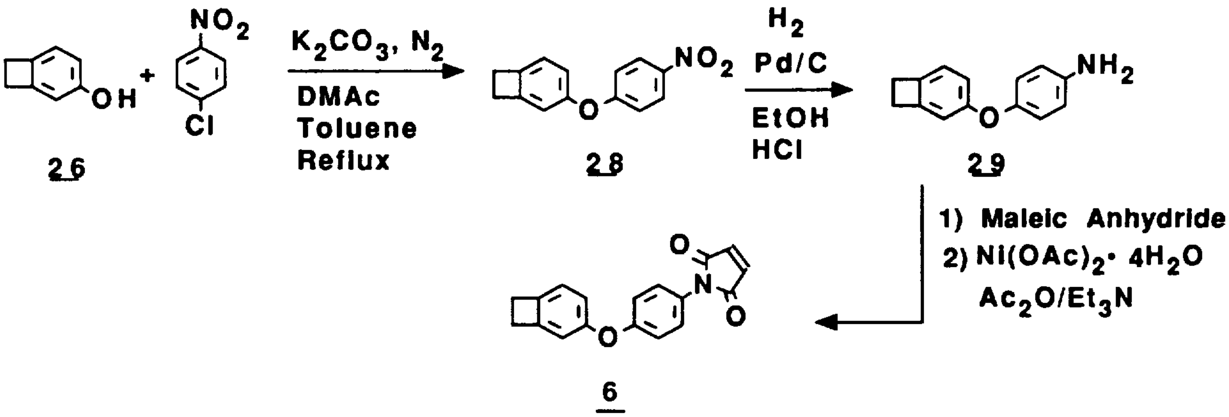


A second family of monomers containing aryl ether groups as the only linking groups were also prepared to further evaluate structure-property relationships.

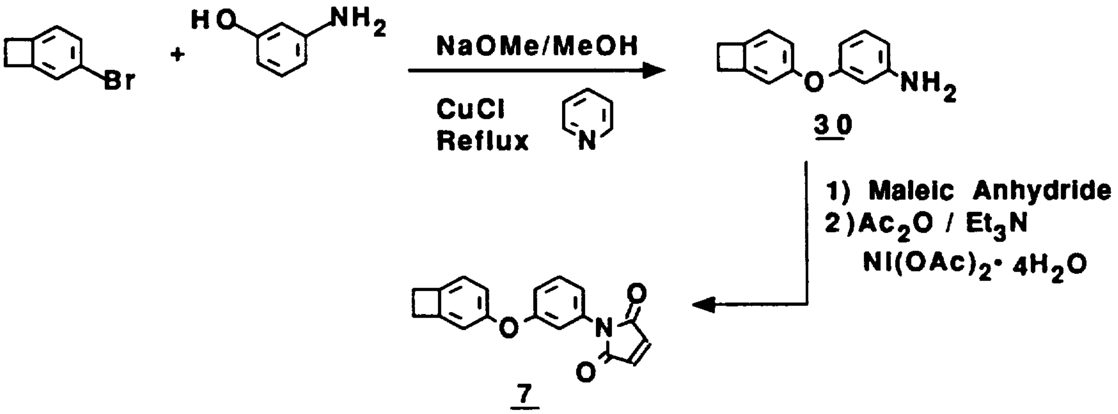
FAMILY II



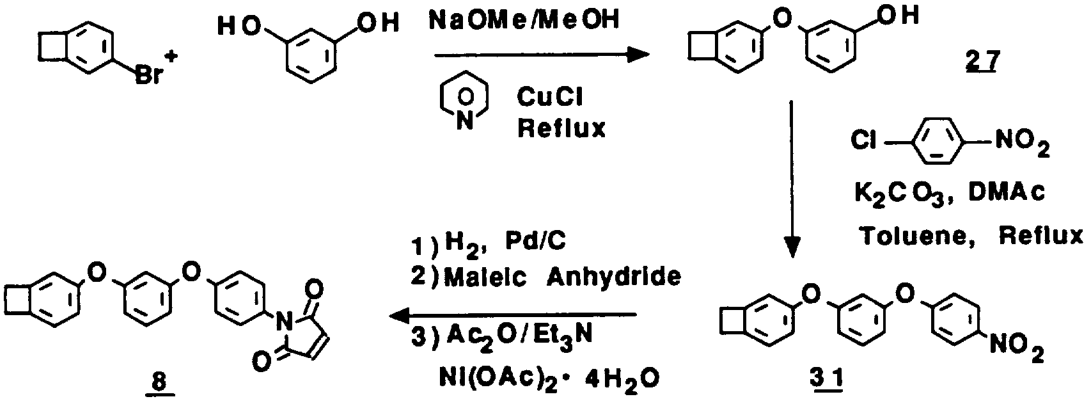
Synthesis of Monomer 6. The synthesis of monomer 6 involved the displacement of the activated chloride from *p*-chloronitrobenzene by hydroxy-BCB.



Synthesis of Monomer 7. The synthetic sequence shown on the next page was used to prepare monomer 7. Monomer 7 was obtained as a yellow solid, m.p. 103°C.



Synthesis of Monomer 8. The following reaction sequence was used to prepare monomer 8 (m.p. 126°C)



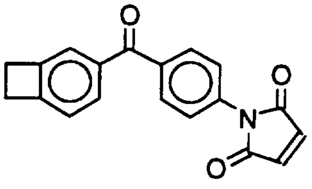
4.2.6. Curing of AB-BCB-Maleimide Monomers and Properties of Polymers.

Preliminary screening of monomers and polymers. The following general procedure for preparation of polymer castings was used for all monomers for the initial screening process. A quantity of monomer was melted and degassed under vacuum. The liquid was then poured into a steel mold and the mold heated at one-hour intervals at 160°C, 180°C, 200°C, 220°C and finally at 250°C. The resulting polymer plaque was removed after it had cooled to ambient temperature and then subjected to a post-cure at 300°C for 90 minutes.

All the monomers/polymers were evaluated to the same extent. The screening sequence involved first a DSC scan to determine its melting point, onset of polymerization, and T_g of the polymer upon rescan. Then a small casting was made to measure its dynamic mechanical properties and fracture toughness. Flexural properties were measured only if the above properties were promising (see Table 4.3 for compilation of data). The structures of all the monomers are shown on the next page to facilitate the reading of this report. The processability of monomer **3** was considered unsatisfactory because its melting point (177°C) was very close to the onset of polymerization so it was not evaluated further. The trend in fracture toughness is **8** ~ **5** > **6** > **2** ~ **4** > **1** > **7**. The toughness of polymers of **5** and **8** was so high as to exceed the limit of the compact tension test; consequently only lower limit values were reported. However, the glass transition temperatures of these polymers were too low to be useful for 350°F applications. Monomer **6**, with the most desirable combination of T_g, fracture toughness and flexural modulus, was selected for scale-up and further evaluation.

Fracture toughness *vs* molecular structures. There is no apparent correlation between the observed fracture toughness and molecular structures. Monomers **5** and **2** form an isomeric pair. Since **5** is much tougher than **2**, one may be attempted to conclude that the presence of a *meta* linkage enhances toughness. Yet, in the isomeric pair of **6** and **7** the *meta*-isomer is the least tough of all. Monomer **8** has two flexible ether linkages and may be expected to be very tough -- and indeed it was. Monomer **4**, with an ether and an isopropylidene linkage was only modestly tough. One possible explanation may lie in the degree of crosslinking of the polymers, a topic to be discussed later.

Glass transition temperatures *vs* molecular structures. Differences in T_g are consistent with expected effects of monomer structure. For example, for the isomeric pairs (**2** vs **5**; and **6** vs **7**) the change of a *para-* phenylene to *meta-* phenylene ring results in a drop in T_g. Monomer **8**, which has two ether linkages (flexible), and one *meta-* phenylene ring, has the lowest T_g.



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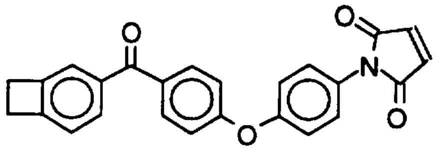

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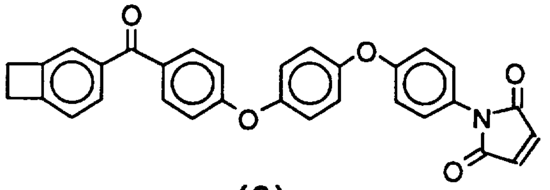

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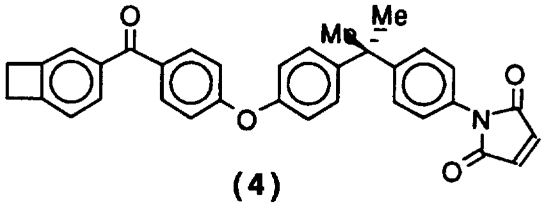

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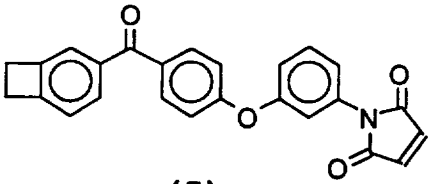

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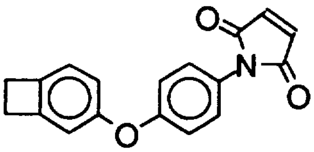

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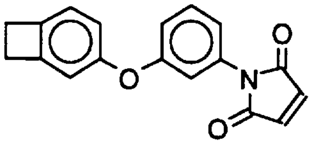

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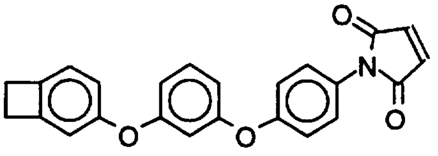


(8)

Everything else being the same, keto-links provide higher T_g than ether which is higher than isopropylidene. Thus, replacing the ether of **6** with a carbonyl group (**1**) raises the T_g by 40°C; replacing the isopropylidene of **4** with an ether (**3**) raises the T_g by 17°C. Another general trend is that monomers with longer spacers between the BCB and the maleimide have lower T_g. This is in accordance with the expectation that the more polar and rigid imide group is an important contributor to polymer T_g and longer spacers reduce the density of imide group in the polymer backbone.

Cure Viscosity Profiles of AB BCB-MI Monomers. Changes in resin viscosity at a constant heating rate (i.e., cure viscosity profile) give an indication how that resin will process. Cure viscosity profiles have been obtained for different monomers synthesized under this contract. For all monomers, the minimum viscosity is reached at about the same temperature, ≈ 200°C. Above this temperature, cure proceeds rapidly enough to cause the viscosity to increase. Monomer structure affects the value of the minimum viscosity; for example, the minimum viscosity of monomer **6** is ≈ 2 cP, whereas that of monomer **4** is ≈ 20 cP. It also affects the temperature at which a given viscosity is reached in the cure portion of the curve; for example, temperatures at which $\eta^* = 1$ P (100 cP) and $\eta^* = 100$ P (10^4 cP) vary with structure (Table 4.4). Monomer viscosity depends on structure through: overall length; the flexibility of the divalent linkages (i.e., ether versus ketone versus isopropylidene); and whether the phenylene moieties are 1,3- or 1,4-substituted. Since BCB-MI monomers cure at the same rate, regardless of structure, then a higher viscosity monomer will reach a given viscosity at a lower temperature and lower conversion than will a lower viscosity monomer. A typical cure viscosity profile, for monomer **4** at a heating rate of 2°C/min, is shown in Figure 4.1 (complex viscosity, η^*). In cure viscosity profiles, the temperature where G' and G" crossover, that is, where G' = G" ($\tan \delta = G''/G' = 1$), is often taken as the gel point. For these BCB-MI resins, however, crossovers (when seen) are not due to gelation, since gelation leads to insolubility, but partially cured resins at the end of these tests were still soluble in methylene chloride. Crossovers for these BCB-MI resins are instead due to an increase of T_g during cure. When the difference between test temperature and T_g gets sufficiently small, G' will exceed G" (i.e., crossover). This type of crossover is often seen for linear polymer melts.

Dynamic Mechanical Properties of AB BCB-MI Castings. Investigation of structure-property relationships for these BCB-MI monomers included dynamic mechanical testing. This provided information on how monomer structure affected room temperature modulus, retention of modulus at elevated temperatures, T_g, secondary mechanical relaxations, and level of cross-linking. Dynamic mechanical properties were determined for polymers from monomers **2**, **4**, **5**, **6**, **7**, and **8**, over a wide range of temperature, at constant frequency. Polymer castings were prepared by the procedure and cure schedule given earlier; these were the same castings used for toughness (K_{IC}) measurements.

All these BCB-MI polymers show three transitions. These are illustrated in Figure 4.2 for monomer **6** (G" = shear loss modulus). The glass transition (α-relaxation) varies from fairly sharp, as in this example, to broad or even bimodal for some of the castings; the location, that is, T_g, varies significantly with monomer structure. BCB-MI polymers all show a broad β-relaxation, with a maximum at T ≈ 0-25°C. Details of the β-relaxation (e.g., location, breadth) also vary with structure. A γ-relaxation is seen at still lower temperature. The elastic modulus (G') decreases over temperature ranges corresponding to the loss peaks (Figure 4.3). This linear plot of G'(T) shows the rather significant decrease in modulus associated with the γ- and β-relaxations; however, the modulus is relatively flat between the β-relaxation and T_g. Of course, the elastic modulus falls even more drastically at T_g. A well-defined plateau in G' at $T > T_g$ is generally seen. This rubbery plateau is characteristic of cross-linked polymers. Because G' in the rubbery state is only about 10^7 dynes/cm^2 for these BCB-MI polymers, the plateau isn't evident on a linear scale (e.g., Figure 4.3).

Room temperature modulus appears roughly correlated with T_g for these BCB-MI polymers: the higher the T_g, the higher the modulus (see Table 4.5). Retention of shear modulus G' at elevated temperatures depends to a large extent on T_g: the higher the T_g, the better the retention at elevated temperatures. However, other factors that affect modulus retention for these BCB-MI polymers are the breadth of the glass transition, and also the magnitude of the modulus drop associated with the lower temperature β-relaxation. Table 4.5 also shows the large drop in modulus associated with the γ-relaxation (i.e., retention at –100°C). The % retention of dynamic properties at elevated temperatures doesn't directly correspond to % retention of transient mechanical properties (e.g., flexural modulus), because of viscoelastic effects. Toughness also appears correlated with T_g for these BCB-MI polymers: higher T_g polymers tend to have lower toughness.

Stress relaxation, at temperatures well above T_g, was used to try to characterize the extent of cross-linking in these BCB-MI polymers. Typical thermosets show a rapid decay of the relaxation modulus, G(t), to a steady value, the equilibrium modulus G_e, from which the cross-link density can be calculated. For these BCB-MI polymers, however, modulus generally doesn't decay to a plateau G_e (Figure 4.4); instead, stress continues to relax at long times, which implies fairly low levels of cross-linking. The stress relaxation curves are essentially parallel, with the approximate ranking, **7** > **6** > 2 > **5** > **8**; this corresponds roughly to the ranking of toughness, and T_g and other properties.

<u>Cure Kinetics and Cure Rheology of AB BCB-MI Monomers: Overview</u>. Data have been generated on the cure kinetics and cure rheology of AB BCB-MI monomers. Monomer **6** (4-benzocyclobutenyl-4'-maleimidophenyl ether) has been used for most of the polymerization studies. The results of these cure studies have been used to develop cure schedules for making neat resin castings and composite laminates; and to develop methods to B-stage monomer **6** into forms more suitable for composite fabrication. The polymerization rate constant has been

C-2

determined from 170-220°C, using both DSC (residual heat of polymerization), and liquid chromatography (residual monomer). Rate constants, although measured for monomer **6**, apply to all BCB-MI monomers, since polymerization kinetics is independent of monomer structure. The dominant reaction in cure of BGB-MI monomers is a Diels-Alder reaction between maleimide and ring-opened benzocyclobutene, making it mainly a step-growth polymerization. This leads to slower increase in molecular weight and viscosity, and gelation at much higher conversion, compared to typical thermosets. Viscosity increase during isothermal cure has been investigated using parallel plate rheometry, which has also been used to look at the rheology of B-staged materials. Cure viscosity, B-staged viscosity, and T_g versus conversion results are specific to monomer **6**, although some of the conclusions are generally applicable.

Polymerization Kinetics for BCB-MI Monomers. Knowledge of the polymerization rate as a function of temperature is valuable in developing methods for B-staging and cure. A number of variables changed from experiment to experiment: different samples of monomer **6**; polymerization under nitrogen versus under air; and polymerization with or without a radical inhibitor, phenothiazine. Because these changes do not affect the polymerization rate, all results were combined to determine the Arrhenius dependence of polymerization rate. (However, they do affect other aspects of the polymerization.) Almost all work was with 6-benzocyclobutenyl-4'maleimidophenyl ether (i.e., monomer **6**). However, "single point" kinetic results (i.e., conversion reached after given time and temperature) for other BCB-MI monomers demonstrate that the polymerization rate is independent of structure, making these kinetic results useful for BCB-MI monomers as a class.

Cure kinetics were followed by analyzing partially polymerized samples: residual heat of reaction, by differential scanning calorimetry (DSC); and residual monomer, by size exclusion chromatography (SEC). Analysis by both techniques indicates that overall cure kinetics are first order. Further, evolution of the molecular weight distribution with conversion indicates the polymerization is predominantly step-growth. For the kinetic analysis of DSC data, the relationships between residual heat, fractional conversion (p), and first order rate constant (k_1) are:

$$(1-p) = \frac{\Delta h_p(t)}{\Delta h_p(0)} = e^{-k_1 t} \qquad (1)$$

where $\Delta h_p(0)$ is the specific heat of polymerization (J/g) for monomer (i.e., cured for time = 0), and $\Delta h_p(t)$ is the residual specific heat of polymerization for partially cured material (i.e., cured for time = t). For the kinetic analysis of SEC data, the relationships between weight fraction of monomer (w_1), fractional conversion, and first order rate constant (k_2) are:

$$(1-p)^2 = w_1 = e^{-k_2 t} \tag{2}$$

where, by comparison of Eqns (1) and (2), the rate constant k_2 from SEC should be related to the rate constant k_1 from DSC as:

$$k_2 = 2\,k_1 \tag{3}$$

Rate constants have been determined over the temperature range 170-220°C, by the approaches just described. Data are consistent with first order kinetics over this entire range, within experimental error. Rate constants are collected in Tables 4.6 (k_1, from DSC) and 4.7 (k_2, from SEC). Table 4.8 gives the ratio k_2/k_1. The average for all these experiments is $k_2/k_1 \approx 2$, which is the ratio expected for a step-growth polymerization following first order kinetics. These rate constants were fit to an Arrhenius expression (Table 4.9):

$$k = Z \cdot \exp\left(\frac{-E_a}{RT}\right) \tag{4}$$

where Z is the prefactor, E_a the activation energy, R the gas constant, and T the temperature (°K). These fits were performed for: (1) data at all temperatures; (2) lower temperature data only, $T \leq 202°C$; and (3) higher temperature data only, $T \geq 204°C$. Despite the high correlation coefficients (r) for the fits, values for activation energy, and especially the prefactor, vary significantly. A large part of the reason is that for exponential fits such as these, a number of combinations of prefactor and activation energy will fit the data nearly equally well. For example, a small change in activation energy will lead to a significant change in prefactor, but with nearly identical statistical quality of fit. As a consequence, caution should be used against over-interpreting the specific parameters from such fits.

An Arrhenius plot of the data (Figure 4.5), with different symbols for different polymerization conditions, shows that the polymerization rate is basically unaffected by atmosphere (i.e., air versus nitrogen) or by the radical inhibitor phenothiazine. Linear least squares fits over the entire temperature range appear to fit the data quite well (Figure 4.6). However, closer examination suggests that there is some upward curvature in the Arrhenius plot of the rate constant on going to lower temperature. This shows up in the fit results as a lower activation energy for fits restricted to lower temperature data. The averages of the activation energies from the fits to various subsets of the data by temperature (Table 4.10) show this trend. This curvature is consistent with an increase in the relative rate of non-Diels-Alder reactions (e.g., free radical) to Diels-Alder reaction at lower temperatures, and results in a significant enhancement of rate at lower temperatures, relative to what would be predicted based only on high temperature data. For purposes of predicting conversion versus time, it is better to use the Arrhenius expression appropriate for the temperature under consideration, instead of the expression obtained by fitting all data.

Isothermal Cure Viscosity for Monomer **6**. Knowledge of how the viscosity increases during isothermal cure helps to detemine when in the cure schedule to apply pressure for part consolidation. These experiments were performed at approximately the same temperatures as the kinetic experiments. Because polymerization rate depends strongly on temperature, the time to reach a given viscosity varies widely with temperature (Figure 4.7). A more meaningful comparison results from plotting viscosity versus conversion (Figure 4.8), using first order rate constants to convert times into conversions. At a given conversion, the viscosity decreases with increased cure temperature. Certainly much of this vertical shift is simply because the viscosity is being measured at different temperatures. However, the remainder of this vertical shift is due to differences in the molecular weight distribution of polymer being produced at different cure temperatures. Cure at lower temperature leads to more high molecular weight polymer, which in turn results in a higher viscosity at a given conversion and measurement temperature. Free radical inhibitors reduce the molecular weight of polymer produced. This shows up as a slower increase in viscosity vs conversion when phenothiazine, a radical inhibitor, is present (e.g., Figure 4.9). The chemical structure of the BCB-MI monomer also affects the rate of viscosity increase (Figure 4.10). A stiffer structure (monomer **1**, keto-1,6-phenylene linked) results in much more rapid increase compared to a more flexible structure (monomer **6**, ether-1,6-phenylene linked).

The isothermal viscosity curves for these BCB-MI monomers differ from those for more highly cross-linked thermosets. Compare the results for a difunctional BCB resin (Figure 4.11) to those for BCB-MI monomer 6 (Figure 4.12). For the difunctional BCB resin, the rapid rise in viscosity corresponds to gelation, as indicated by the crossover in G' and G" (conversion $p_{GEL} \approx 0.52$, with $\eta^*_{GEL} \approx 3300$ P), and by insolubility of the material at the end of the test. For the BCB-MI resin, although the viscosity and conversion at the completion of the test ($\eta^* \approx 40{,}000$ P, conversion $\approx$ 0.8) are much higher than at the gel point of the difunctional BCB resin, the material is still not cross-linked: it is soluble, and G" still remains above G'. For these BCB-MI monomers, this relatively rapid increase in viscosity, which precedes gelation, is likely due to the T_g of the resin approaching the cure temperature, T_{cure} (see Figure 4.13). This explains why "stiffer" BCB-MI monomers, with higher T_g's at a given conversion, show an earlier increase in viscosity than "flexible" BCB-MI monomers.

This difference in isothermal cure viscosity behavior, between BCB-MI resins and typical highly cross-linked thermosets, translates into a potential processing advantage. For BCB-MI resins, there is a much larger window for applying pressure for part consolidation, between where the resin viscosity is high enough to support application of pressure and where the resin gels and is thus incapable of flow.

To be able to use these data for cure schedule modeling, empirical expressions for isothermal cure viscosity as a function of conversion were found. First, isothermal cure viscosity data were parametrized in terms of conversion, instead of time, as the independent variable (see Eqn (1)). The following functional form does a reasonable job in matching the shape of the curves; no attempt here is made to theoretically justify this expression.

$$f(p) = \ln\left\{ \ln \eta(t) - \ln \eta(0) \right\} = a + b \cdot p \tag{5}$$

The viscosity can then be calculated as a function of conversion, by inverting Eqn (5):

$$\eta(t) = \eta\{p(t)\} = \exp\left\{ \exp\{a+bp(t)\} + \ln \eta(0) \right\} \tag{6}$$

The results of such fits for monomer **6** at three temperatures are given in Table 4.11. Note that all three parameters are correlated with temperature. If more extensive data were collected, then the temperature dependence of these parameters could be determined; this would aid in better being able to predict viscosity increases during arbitrary cure schedules.

Glass Transition Temperature vs Conversion for Monomer **6**. How the glass transition temperature varies with conversion gives an idea of up to what conversion will B-staged materials be tacky; and also where in cure will vitrification occur. In polymerization of these BCB-MI monomers, the glass transition temperature (T_g) increases primarily due to an increase in molecular weight, secondarily due to introduction of cross-links. Figure 4.14 shows T_g as a function of conversion for monomer **6**. A second order polynomial fit (empirical; no theoretical basis) does a reasonable job of describing the data:

$$T_g = 12 - 34p + 272p^2 \tag{7}$$

and gives the limits $T_g \approx 12°C$ ($p = 0$) and $T_g \approx 250°C$ ($p = 1$). The lower conversion limit is reasonable, since amorphous monomer **6** is quite sticky at room temperature, implying a low T_g. Normally crystalline monomer **6** is readily made amorphous, by cooling it fairly quickly from the melt. B-staged monomer **6**, with conversion up to about 0.15-0.2, is also tacky at room temperature. All these tacky, low T_g materials tend to recrystallize. The rate of recrystallization increases with temperature; decreases with conversion; and increases with nucleating agents (e.g., solid impurities, physical disturbances, surfaces, etc.). Monomer **6** itself appears to recrystallize completely, although some samples have remained amorphous for days. Once the conversion of B-staged monomer **6** reaches about 0.15-0.2, it appears to be relatively stable against recrystallization. However, this observation is qualitative; no study of melt crystallization rate as a function of temperature and conversion has been made. Composition, as determined by B-staging temperature and blending operations, also has been seen to affect melt crystallization rate. The higher conversion limit ($T_g \approx 250°C$ at $p = 1$) is also reasonable, with the following explanation. This value is lower than is typically measured ($T_g \approx 260\text{-}270°C$) for fully cured polymer from monomer **6**. However, it has been shown that gelation occurs at high conversion; thus, the effects of cross-linking on T_g is only seen at very high conversion. Almost all the data in Figure 4.14 are for non-cross-linked samples and thus do not include any "contribution" to T_g from cross-links. Therefore, this plot is of little value in understanding ultimate T_g of fully cured samples, due to this neglect of cross-linking. Its main use is in knowing how the T_g of B-staged monomer **6** depends on conversion.

By solving the quadratic Eqn (7) for conversion as a function of T_g, one can estimate when in cure vitrification will occur:

$$p = \frac{34 + \sqrt{34^2 - 4 \cdot 272 \cdot (12 - T_g)}}{2 \cdot 272} \qquad (8)$$

where T_g is in °C. Figure 4.15 is an isothermal time-temperature-transformation diagram for monomer **6**, where the isoconversion curves are calculated from cure kinetics, and vitrification curves are calculated using Eqn (8).

<u>Rheology of B-Staged Monomer **6**</u>. Data for how viscosity depends on temperature and conversion can aid in developing B-staged versions of BCB-MI monomer **6** more suitable for composite processes (e.g., hot melt prepregging, resin transfer molding, etc.) than the monomer itself. Monomer **6**, like most BCB-MI monomers, is highly crystalline; however, many composite

processes require a more typical amorphous type resin. Also, once melted, BCB-MI monomers are very low in viscosity ($\eta \approx 10$ cP); such low viscosity is unacceptable for many composite processes. For these reasons, a substantial effort has been put into B-staging of monomer **6**, then determining the viscosity of the B-staged materials as a function of temperature and conversion. The results in this section demonstrate the versatile processability of monomer **6**, and, by extension, other BCB-MI monomers. By B-staging to different extents, BCB-MI monomers can be converted into resins to satisfy the requirements of different composite fabrication techniques. Many of these requirements are viscosity (η) related, for example: an upper viscosity limit for melt prepregging, $\eta \approx 10^5$ cP (below this to get good impregnation of fiber bundles); an upper viscosity limit for resin transfer molding, $\eta \approx 500$ cP (below this to get good filling of the fiber preform); and a lower limit to viscosity reached during autoclave curing, $\eta \approx 1000\text{-}2000$ cP (above this to avoid excessive loss of resin due to flow).

One study was aimed at assessing the effects of B-staging temperature (172, 192, and 208°C) on viscosity, due to variation in polymer molecular weight. B-staging was carried out under nitrogen, making three samples at each temperature, each with different conversion (Table 4.12; SEC conversions are more accurate). For the two extreme temperatures, the conversions match up closely. (Knowledge of how the polymerization rate depends on temperature allows for prediction of conversion versus time, thus for good design of B-staging experiments.) Viscosity profiles, generated at a heating rate of 2°C/min, are shown in Figures 4.16 (172 vs 208°C) and 4.17 (192°C). At lower conversions ($p \approx 0.1$ and 0.2) the viscosity profile is nearly independent of B-staging temperature. However, at higher conversion ($p \approx 0.35$), the material B-staged at lower temperature has a higher viscosity.

One important finding is that the viscosity profiles have nearly the same shape regardless of conversion. With increasing conversion, the viscosity profile is merely shifted horizontally. This horizontal shift is due primarily to an increase in T_g with increased conversion. For these BCB-MI monomers, the viscosity profiles don't turn upwards, due to further cure, until about 210°C (at the heating rate of these experiments, 2°C/min).

From these results, it is seen that the viscosity requirement for resin transfer molding ($\eta < 5$ P) can be easily satisfied by monomer **6**, at fairly low temperatures, at a variety of conversions. Here the key issue, not yet investigated, is the stability of monomer **6**, or B-staged versions thereof, against recrystallization from the melt. (Early indications are that conversions greater than about 0.15-0.2 are stable against recrystallization.) The viscosity of monomer **6** itself (determined from steady shear experiments at $T > T_m$) is shown in Figure 4.18, in comparison to that for B-staged material with $p = 0.10$. (The solid line is an Arrhenius fit to the monomer data, which is reasonably good at temperatures of the measurements and above. At lower temperatures, the monomer viscosity actually probably curves upward in typical WLF fashion, just like the B-staged sample. However, the monomer viscosity at lower temperatures couldn't be measured, since at $T < T_m$, the amorphous monomer tends to crystallize.)

From these results, it is also seen that the viscosity requirement for hot melt prepregging ($10^2 < \eta < 10^3$ P) can be readily satisfied by B-staged monomer **6**, at a variety of conversions, with the temperature required for prepregging depending on the conversion. However, other requirements may also need to be satisfied by a hot melt prepreg resin, depending on the nature of subsequent processing steps. For example, requirements for autoclave processing are discussed later in this section, along with an estimate of the conversion that is required for B-staged monomer **6** to satisfy the requirements of autoclave processing.

For B-staged monomer **6** to possess tack at room temperature, the upper limit for conversion is about 0.15-0.2 (see the preceding section, on T_g versus conversion). Looking at the viscosity profiles for samples with conversion $p \approx 0.2$, it can be seen that at about 100°C they reach a viscosity $\eta \approx 10$ P, which is roughly the minimum viscosity which is desired in autoclave processing. Since the cure rate at 100°C is negligibly slow, it appears that it would not be possible to get tack at room temperature, together with a high enough minimum viscosity for autoclave processing, without some sort of formulation.

Since this initial investigation, the focus has been on B-staging of monomer **6** to a viscosity that would allow for autoclave processing. This ideally requires that the viscosity during cure stay above a minimum of about 1000-2000 cP (10-20 P), to prevent excessive resin flow. Further, in order to have reasonably short cure cycles in an autoclave, the B-staged material can't reach this minimum viscosity until a temperature of about 185°C, preferably somewhat higher . If it reached the minimum viscosity at a lower temperature, the time required to advance it sufficiently to prevent flow would probably be considered too long to be practical. Satisfying these requirements for autoclave processing requires relatively high conversion. At the conversions required, B-staging temperature can have a significant effect on viscosity.

Viscosity profiles for several B-staged materials that are close to meeting the requirements for autoclave processing are shown in Figure 4.19. These results indicate that a conversion of about 0.5-0.6 will be required; this is well short of the gel conversion (≈ 0.9). Work continues to better home in on the target.

Lastly, blends of high conversion B-staged resins with monomer were investigated, to see if that might lead to a different shape to the viscosity profiles. A flatter curve would be desirable for autoclave processing. Monomer **6** was B-staged at 200°C to conversions of 0.34 (parent A) and 0.82 (parent B, fairly close to the gel point). These were melt blended with monomer **6** to give nominal conversions of 0.09 and 0.21 (daughters A1 and A2); and of 0.05, 0.14, 0.23, and 0.27 (daughters B1-B4). The results (Figure 4.20) don't indicate any significant change in viscosity profile shape. The blends from the high conversion parent B are much higher in viscosity than either blends from the lower conversion parent A or directly B-staged materials, at a given nominal conversion. Aside from requiring an additional step to make, another potential disadvantage of these blends was seen, namely, a greater tendency towards crystallization, especially for the blends from parent B, compared to materials directly B-staged to the same conversion.

4.2.7. AB-BCB-Maleimide Composite Study.

Based on its good combination of properties, monomer **6** was selected as the best candidate to be carried on to the formation of a composite panel. The composite properties measured to date show a combination of exceptional toughness, with good strength and stiffness. Retention of properties under hot/wet test conditions, or after heat aging, or after solvent exposure, is excellent.

Resin-fiber adhesion. In order to ensure an appropriate choice of carbon fiber, the strength of the resin-fiber interface was determined for polymer from **6** with a variety of fibers and surface treatments, prior to moving on to making composites. The interface strength ranging from 9.4 to 10.5 ksi, as measured by the microdrop method, was comparable to that of epoxy-carbon fiber for all the fiber types examined (Table 4.13). The specimens on G40-800 fiber after aging under nitrogen at 400°F for 1000 hours did not show any drop in interfacial shear strength. This portends to excellent long-term thermal stability of the system because of the large surface area to volume ratio of the specimens (droplets of resins of about 50 microns in diameter on a single fiber).

Composite panel fabrication. Composite panels were fabricated directly from the monomer, using Celion G30-500 (3K, G105/ 42"/8HS) fabric, via a technique dubbed resin flow molding. (**a**) Load the mold with the required amount of monomer. On top of the monomer, place a fiber mat with the desired layup (edge stitched to hold it together). Close the mold and apply vacuum for 30 min. at room temperature. (**b**) Heat from room temperature to 130°C at 8.3°C/min, and hold for 15 min. During this step, the top plate is off and vacuum is continued. This step serves to melt and degas the monomer and strip any volatiles. (**c**) Put on the top plate (this provides a small pressure on the resin and fiber), then heat to 200°C at 1.7°C/ min, and hold for 60 min. Vacuum is continued during this step. (**d**) Turn off the vacuum and hold for an additional 60 min at 200°C while applying a force of 600 pounds. (**e**) Heat to 230°C at 1.7°C/min and hold for 30 while applying a force of 3000 pounds. (**f**) Heat to 260°C at 1.7°C/min and hold for 10 min under a force of 5000 pounds. (**g**) Hold for an additional 60 min at 260°C while increasing the force to 7000 pounds. (**h**) Cool to room temperature at 2.8°C/min under a force of 7000 pounds. Some panels were made using minor variations in heating rates and/or the force profile from the previous schedule. Ram force was varied to keep the pressure (i.e., psi) the same for different size panels. However, the time-temperature profile was always the same. Prior to testing, all laminates were examined for quality using standard procedures such as fiber volume fraction and examination for voids by C-scan. All panels were of good quality. The same basic procedure was use for the formation of 8, 16 and 32 ply composite panels.

Composite properties. We used Boeing's HSCT Material Development D6-55587 document as the guide for selection of tests and followed SACMA procedures for lay-up and testing. The data collected were based on different panels with different fiber contents and were not normalized. In general the fiber volume of the panels was about 60% unless otherwise identified. Table 4.14 summarizes the more routine type composite properties. The two more outstanding properties are flexural strength and compressive strength even after making allowance for the high fiber content of this panel. The expectations of high toughness and 350°F/wet performance are also realized as evidenced by the compressive strength after impact fo 48-49 ksi (two separate panels) and the 70% retention of RTD open hole compressive strength at 350°F/wet (see Table 4.15).

Solvent resistance was characterized by measuring the in-plane shear strength before and after exposure to solvents (see Table 4.16). In general, the shear strength was only minimally affected with Skydrol yielding the most pronounced effect.

Next we turned our attention to the thermo-oxidative stability of the composite. This was evaluated by exposure of flexural and open hole compressive strength specimens to air at 400°F for 4000 hours. As can be seen in Tables 4.17 and 4.18, the weight loss was about 0.5% in both cases. There was a drop of about 10% in flexural strength after aging but no appreciably loss in open hole compressive strength. It is believed that the data represent the worst case situation since the specimens for aging were very small --- smaller than 4" x 6" --- and hence had a relative large surface area.

4.3. CONCLUSIONS

1. After exploring a variety of different monomers which could potentially undergo Diels-Alder polymerization, the AB-BCB-maleimide family of resins were found superior, exhibiting excellent toughness, T_g and mechanical properties.
2. The AB monomer, 4-benzocyclobutenyl-4'-maleimidophenyl ether, in which the BCB moiety is linked to the N-phenylmaleimide moiety by an ether group was selected for scale-up and further evaluation on the basis of the processability of the monomer and the properties of the polymer. Composites based on it show remarkably high damage tolerance (CAI about 50 ksi), resistance to long-term exposure to air at 400°F and excellent solvent resistance. The latter is somewhat unexpected in light of the predominantly linear nature of the polymer.
3. An extensive study on the polymerization of **6** and other AB monomers (to a lesser extent) has provided in-depth fundamental understanding of the polymerization reaction. The reaction is primarily step-growth in nature and the key kinetic parameters are independent of molecular structure. This indicates that BCB ring opening is the rate controlling step under most circumstances.
4. The cure rheology of **6** was also characterized extensively such that the conversion and viscosity can be predicted given input of time and temperature. This predictive capability should be valuable in refining fabrication parameters.
5. An addition to the contract required Dow to fabricate composite panels (32 panels, 12" x 18") based on **6** for HSCT evaluation by McAir. The task was completed in November. McAir rated this system as one of the most promising candidates and measured a CAI of 55 ksi.
6. Finally, **6** is the subject of a scale-up campaign. The target of 50 pounds has been met. About one-half of the material was used for panel fabrication for McAir and the rest will be used for prepreg development.

4.4. FUTURE WORK

In light of the excellent processability and properties of the AB-BCB monomer **6**, Dow has been informed by NASA of its intention to exercise the first of three option years. The general plan is as follows:

1. Conduct optimization of the chemical process for this monomer.
2. Conduct another scale-up campaign with the goal of producing about 200 pounds of monomer.
3. Carry out additonal fundamental studies on polymerization and fabrication.

4. Support the development of prepreg and adhesive product forms.

4.5. EXPERIMENTAL

Preparation of 4-Nitrophenyl-4-Benzocyclobutenyl Ketone (16). Into a 3L, 3-neck flask, equipped with an overhead air stirrer, thermometer, and a Claisen Head with and equilibrating addition funnel and a reflux condenser with N_2 inlet, was placed 103 g (0.635 mol) of ferric chloride. In one portion was added 116 g (0.625 mol) of 4-nitrobenzoyl chloride in 1000 mL of CH_2Cl_2. The mixture was stirred vigorously at room temperature for 45 minutes before cooling to -10°C. Began adding 100 g (0.962 mol) of benzocyclobutene, dropwise, with care to not let the temperature rise above -7°C. After all of the benzocyclobutene was added, the reaction was continued at bath temperature for 1 hour before allowing to warm slowly to room temperature. Stirred at room temperature for 1 hour. The reaction mixture was poured into 1000 mL of 3N HCl with vigorous stirring. The two phase mixture was transferred to a separatory funnel and the organic layer removed. The organic phase was washed with 3N HCl (3X800 mL); H_2O (1X1000 mL); 1M NaOH (2X500 mL); H_2O (2X1000 mL) before drying ($MgSO_4$). Filtration through celite followed by removal of the volatiles *in vacuo* afforded 197 g of a brown gummy solid. The crude product was recrystallized from hexane/EtOAc (2:1, vol/vol) and decolorizing charcoal. The product, an off white solid was isolated by filtration and weighed119 g (75% yield). Melting point = 115°C. ^{1}H-NMR, 300 MHz, ($CDCl_3$, TMS) 8.32 (d,2), 7.90 (d,2), 7.68 (d,1), 7.48 (s,1), 7.18 (d,2), 3.28 (s,4). ^{13}C-NMR ($CDCl_3$, reference 77.00 ppm) 195.43, 152.85, 149.75, 146.42, 143.74, 135.38, 130.67, 129.85, 124.29, 124.21, 124.13, 123.49, 122.72, 77.42, 77.00, 76.57, 29.82, 29.26. DSC (10°C/minute to 400°C) MP=115°C, Exotherm #1, 265°C (614.8 J/g); Exotherm #2, 330°C (760 J/.g); Exotherm #3, 372°C (198 J/g). The product was >95% pure by gas chromatography and was of sufficient purity to be carried on to the next step.

Preparation of 4-Aminophenyl-4-Benzocyclobutenyl Ketone (17). Into a 1L Parr Pressure Bottle was placed 50 g (0.1975 mol) of 4-nitrophenyl-4-benzocyclobutenyl ketone and 200 mL of EtOH. Added 2.1 g of 10% Pd/C (1.975 mmol; 1 mol%) followed by 250 mL of EtOH and 50 mL of concentrated HCl. The hydrogenation was carried out at room temperature under 55 psi of H_2. After 90 minutes the pressure had dropped to 19 psi and the reaction was stopped at this time. The catalyst was removed by filtration. The filtrate was cooled in an ice bath and 200 mL of 1N NaOH added dropwise and quickly. An off white solid comes out of solution and after stirring for 15 minutes was isolated by suction filtration. After drying in air for 1 hour the product was recrystallized from 2-propanol and decolorizing charcoal and provided 37.76 g (85.8% yield) of a yellow crystalline solid which was >96.6% pure by gas chromatography. Melting point=173-175°C. ^{1}H-NMR ($CDCl_3$, TMS) 7.65 (d,2), 7.55 (d,1), 7.37 (s,1), 7.15 (d,1), 6.65 (d,2), 4.97 (bs,2), 3.25 (s,4). ^{13}C-NMR ($CDCl_3/DMSO_{d6}$, reference 77.00 ppm) 195.68, 151.56, 149.68, 145.22, 137.62, 132.57, 128.41, 126.52, 123.31, 121.72, 113.01, 77.43, 77.00, 76.57, 29.17, 28.85. DSC (10°C/minute to 400°C) MP=175.22°C, Exotherm, 263.5°C, 500 J/g.

Preparation of **4-N-Phenylmaleimido-4-Benzocyclobutenyl Ketone (1)**. Into a 1L, 3-neck roundbottom flask equipped with a magnetic stir bar, reflux condenser with a N_2 inlet, thermometer, and stopper was placed 50 g (0.2241 mol) of 4-aminophenyl-4-benzocyclobutenyl ketone in 400 mL of acetone. To the vigorously stirring solution was added 21.98 g (0.2241 mol) of maleic anhydride in several portions over a period of 30 minutes. After one half of the maleic anhydride was added a dense yellow solid began to come out of solution.. After all of the maleic anhydride was added the reaction was continued at room temperature overnight. To the vigorously stirring mixture was added 2.24 g (0.009 mol) of $Ni(OAc)_2 \cdot 4H_2O$, 59 g (0.578 mol) of acetic anhydride, and 45.35 g (0.4482 mol) of triethylamine. As the triethylamine was added the reaction becomes a homogeneous solution. Reaction was continued at room temperature overnight. The reaction flask was cooled in an ice bath and 300 mL of saturated $NaHCO_3$ was added dropwise and slowly. The reaction was transferred to a separatory funnel and extracted with $CHCl_3$ (2X500 mL). The combined organic layers were washed with 10% HCl (4X500 mL); H_2O (3X500 mL) and brine (1X500 mL). After drying ($MgSO_4$) and filtering through celite, the solvent was removed *in vacuo* to provide 116 g of a gummy white solid. The crude product was recrystallized from 2-propanol and decolorizing charcoal to afford 54.24 g (79.8 % yield) of the product as a pale yellow solid. MP=151°C. ^{1}H-NMR ($CDCl_3$, TMS) 7.85 (d,2), 7.68 (d,1), 7.55 (m,3), 7.17 (d,1), 6.85 (s.2), 3.25 (s,4). ^{13}C-NMR ($CDCl_3$, reference 77.00 ppm) 196.40, 169.30, 151.81, 146.07, 137.22, 136.37, 134.75, 134.55, 130.93, 129.71, 125.20, 124.26, 122.45, 77.43, 77.00, 76.57, 29.73, 29.25. DSC (10°C/minute to 400°C) MP=150.5°C, Exotherm 260.45°C, 657 J/g.

Preparation of **4-Amino-4'-Benzocyclobutenoyldiphenyl Ether (18)**. Into a 2L 3-neck round bottom flask equipped with an overhead stirrer, thermometer, and Dean Stark water separator with reflux condenser and N_2 inlet was placed 50 g (0.1974 mol) of 4-nitrophenyl-4-benzocyclobutenyl ketone, 21.54 g (0.1974 mol) of 4-amino-1-phenol, 54.56 g (0.3948 mol) of K_2CO_3, 500 mL of dimethylacetamide (DMAc), and 250 mL of toluene. The vigorously stirring mixture was heated to reflux and the water continuously removed via the Dean Stark Trap. Reflux was continued overnight. Began to distill out the toluene under N_2. Collected 220 mL of toluene before cooling to room temperature. The reaction mixture was poured into 1L of distilled water with vigorous stirring. After 10 minutes added 400 mL of $CHCl_3$ and transferred to a separatory funnel. Collected the organic layer and dried ($MgSO_4$). Filtration through celite followed by removal of the volatiles *in vacuo* provided a dark brown liquid containing residual DMAc. The DMAc was removed by bulb to bulb distillation under vacuum and the crude product obtained as a brown solid. The NMRs (^{1}H- and ^{13}C-) indicated that the crude product was of sufficient purity to be carried on to the next step without further purification. ^{1}H-NMR ($CDCl_3$, TMS reference) 7.75 (m,2), 7.65 (d,1), 7.45 (s,1), 7.12 (d,1), 6.95-6.85 (m,4), 6.65 (m,2), 3.72 (bs,2), 3.22 (s,4). ^{13}C-NMR ($CDCl_3$, reference 77.00 ppm) 196.35, 162.91, 150.97, 147.02, 145.78, 143.85, 137.03, 132.43, 131.57, 129.28, 123.98, 122.19, 121.72, 116.20, 115.89, 77.43, 77.00, 76.59, 29.57, 29.17.

Preparation of 4-N-Maleimido-4'-Benzocyclobutenoyldiphenyl Ether (2). Into a 1L, 3-neck roundbottom flask equipped with an overhead stirrer, stopper, and reflux condenser with a N_2 inlet was placed 61 g (0.1935 mol) of 4-amino-4'-benzocyclobutenoyl diphenyl ether and 400 mL of acetone. To the vigorously stirring solution was added 18.96 g (0.1935 mol) of maleic anhydride in several portions over a period of 15 minutes. A dense yellow solid developed within 10 minutes during the addition. Reaction was continued overnight. The solid was isolated by filtration and washed with acetone that had been cooled previously in the refrigerator. The amic-acid was taken up in 500 mL of acetone and treated with 39.6 g (0.3879 mol) of acetic anhydride, 1.48 g (0.006 mol) of $Ni(OAc)_2{\bullet}4H_2O$, and 30.91 g (0.3055 mol) of triethylamine. The homogeneous reaction was stirred at room temperature for 48 hours. The flask was cooled in an ice bath and 300 mL of 1N NaOH was added dropwise. The entire reaction mixture was transferred to a separatory funnel and diluted with 400 mL of $CHCl_3$. The organic phase was separated from the aqueous layer and the aqueous layer extracted with $CHCl_3$ (1X200 mL). The organic layers were combined and washed with 10% HCl (3X200 mL); water (3X500 mL); 10% $NaHCO_3$ (3X200 mL) and water (3X200 mL) before drying ($MgSO_4$). Filtration through celite followed by removal of the volatiles *in vacuo* provided 73.1 g of a light brown solid. The crude product was passed through a column of silica gel (600 g) using $CHCl_3$ as the mobile phase and the yellow band which eluted through was collected. Removal of the solvent on a rotary evaporator provided 48 g (63%) of the product **2** as a bright yellow crystalline solid. MP (DSC)=158°C; Exotherm 261°C (571 J/g). ^{1}H-NMR ($CDCl_3$, TMS reference) 7.72 (d,2), 7.55 (d,1), 7.39 (s,1), 7.29 (m,2), 7.11-7.05 (m,3), 6.99 (d,2), 6.78 (s,2), 3.16 (s,4). ^{13}C-NMR ($CDCl_3$, 77.00 reference) 196.27, 169.73, 160.76, 155.53,151.32, 145.95, 136.85, 134.34, 133.21, 132.59, 129.45, 127.80, 127.27, 124.10, 122.35, 120.33, 117.80, 77.42, 77.00, 76.57, 29.68, 29.25. Gas chromatography indicated the presence of only one component.

Preparation of **4-Nitro-4'-Phenoxydiphenylether (21)**. Into a 250 mL 3-neck roundbottom flask equipped with a magnetic stir bar, thermometer, Dean Stark Trap with reflux condenser and N_2 inlet, and stopper was placed 21.18 g (0.1344 mol) of 4-chloro-1-nitrobenzene, 25 g (0.1344 mol) of 4-phenoxyphenol, 37.15 g (0.2644 mol) of K_2CO_3, 80 mL of DMAc and 40 mL of toluene. Heated the vigorously stirring mixture to reflux with continuous removal of water (140°C). Continued reaction overnight. Distilled the toluene away from the reaction mixture and then cooled to room temperature where the reaction mixture was poured into 400 mL of vigorously stirring water. A light brown solid came out of solution. The entire mixture was taken up in 300 mL of $CHCl_3$ and transferred to a separatory funnel where the organic phase was removed from the aqueous layer. Dried ($MgSO_4$) the organic layer. Filtration through celite followed by removal of the volatiles *in vacuo* provided a brown liquid (DMAc still present). The residual solvent was removed by bulb to bulb distillation at 1mm Hg pressure and the product which remained in the distillation pot was a brown fluffy solid. The crude product was recrystallized from 1200 mL of EtOH and decolorizing charcoal to yield 37.02 g (89.7%) of a light tan solid. ^{1}H-NMR ($CDCl_3$, TMS reference) 8.19 (m,2), 7.35 (m,2), 7.15 (m,1), 7.05-6.90 (m,8). ^{13}C-NMR ($CDCl_3$, 77.00 ppm reference), 163.90, 157.25, 154.87, 150.06, 142.70, 130.02, 126.06, 123.72, 122.03, 120.42, 118.95, 116.78, 77.43, 77.00, 76.58. IR (KBr disk) no -OH present, 3100 ,1610, 1520,1495, 1375, 870, 755 cm^{-1}.

Preparation of **4-(4-Nitrophenoxy)-4'-Benzocyclobutenoyl Diphenyl Ether (22)** Into a 100 mL 3-neck roundbottom flask equipped with a thermometer, reflux condenser with N_2 inlet, glass stopper and magnetic stir bar was placed 2.00 g (6.5 mmol) of 4-nitro-4'-phenoxydiphenyl ether, 0.91 g (6.5 mmol) of benzocyclobutene-4-carboxylic acid and 30 mL of 10% P_2O_5 in methane sulfonic acid (MSA). The vigorously stirring mixture was heated at 60°C for 6 hours. Cooled the reaction to room temperature and carefully poured into 200 mL of ice cold water with vigorous stirring. After 10 minutes added 100 mL of $CHCl_3$ and transferred to a separatory funnel. Removed the aqueous layer and washed the organic phase with 10% $NaHCO_3$ (3X50 mL); and water (2X50 mL) before drying over Na_2SO_4. Filtration through celite followed by removal of the solvent *in vacuo* provided 1.84 g (65%) of the desired product. Recrystallized the product from 2-propanol and obtained 1.62 g (56.8% yield). MP (DSC)=130.7°C; Exotherm #1, 263.6°C (210.4 J/g); Exotherm #2, 343.7°C (381.2 J/g). ^{1}H-NMR ($CDCl_3$, TMS reference) 8.22 (dd,2), 7.85 (dd,2), 7.66 (d,1), 7.48 (s,1), 7.19-7.0 (m,9), 3.26 (s,4). ^{13}C-NMR ($CDCl_3$, 77.00 ppm reference) 196.35, 163.66, 161.28, 153.24, 151.41, 151.23, 146.03, 136.93, 133.10, 132.76, 132.67, 129.52, 126.18, 124.17, 122.42, 122.27, 121.84, 117.32, 117.23, 117.07, 117.02, 77.43, 77.00, 76.58, 29.75, 29.32. IR (KBr), 3090, 2910, 1705, 1650, 1590, 1510, 1400, 1310, 1265, 1160, 840 cm^{-1}.

Preparation of 4-(4-Aminophenoxy)-4'-Benzocyclobutenoyl Diphenyl Ether. Into a 1L Parr Pressure Reactor was placed 38.0 g (0.0870 mol) of 4-(4-nitro-1-phenoxy)-4'-benzocyclobutenoyl diphenyl ether, 400 mL of EtOAc, and 1.08 g (0.001 mol) of 10% Pd/C. Hydrogenation was carried out at 55 psi for 24 hours. The catalyst was removed by filtration through celite and the filtrate concentrated *in vacuo* to yield 33.0 g (93.2%) of the crude amine. The NMRs indicated that the product was of sufficient purity to be carried directly to the formation of maleimide. ^{1}H-NMR ($CDCl_3$, TMS reference) 7.82 (d,2), 7.65 (d,1), 7.45 (s,1), 7.15 (d,1), 7.05-6.65 (m,10), 3.32 (bs,2), 3.27 (s,4). ^{13}C-NMR ($CDCl_3$, 77.00 reference).

Preparation of 4-(4-Maleimidophenoxy)-4'-Benzocyclobutenoyl Diphenyl Ether (3) Into a 500 mL 1-neck roundbottom flask equipped with a magnetic stir bar and N_2 inlet was placed 33.0 g (0.0811 mol) of 4-(4-aminophenoxy)-4'-benzocyclobutenoyl diphenyl ether and 350 mL of acetone. To this solution was added 7.95 g (0.0811 mol) of maleic anhydride in several portions over a period of 15 minutes. Approximately half way through the addition of maleic anhydride a yellow solid began to come out of solution. After all of the anhydride was added reaction was continued at room temperature overnight. The amic-acid solid was isolated by filtration and washed with acetone which had been previously chilled, until the washes were colorless. The bright yellow solid was resuspended in 400 mL of acetone and treated with 16.5 g (0.1622 mol) of acetic anhydride, 0.619 g (2.51 mmol) of $Ni(OAc)_2 \cdot 4H_2O$, and 12.95 g (0.1279 mol) of triethylamine. The reaction was stirred at room temperature for a total period of 48 hours. The acetone and other volatiles were removed on a rotary evaporator and provided the crude product as a viscous liquid. Dissolved the product in 300 mL of $CHCl_3$ and transferred to a separatory funnel where it was washed with 10% HCl (2X100 mL); water (1X100 mL); 10% $NaHCO_3$ (2X100 mL); water (1X100 mL). After drying ($MgSO_4$) followed byfiltration through celite and removal of the solvent *in vacuo* there was obtained 21.6 g (54.7% yield) of a yellow solid. Recrystallization of the product from acetone afforded an impure material as determined by NMR and DSC. The product was passed through a silica gel column with $CHCl_3$ as the eluent. The product was isolated as a bright yellow band from the column. Removal of the solvent afforded 14.84 g (37.6% yield) of the AB maleimide. MP (DSC)=177°C. ^{1}H-NMR ($CDCl_3$, TMS reference) 7.72 (d,2), 7.65 (d,1), 7.47 (s,1), 7.32-7.25 (m,2), 7.18-7.0 (m,7), 6.86 (s,2), 3.25 (s,4). ^{13}C-NMR ($CDCl_3$, 77.00 reference).

Preparation of 4-(4-Nitrophenoxy) Benzocyclobutene (28) Into a 2L 3-neck round bottom flask equipped with a thermometer, overhead stirrer and a Dean Stark Trap with reflux condenser and N_2 inlet was placed 40 g (0.333 mol) of 4-hydroxybenzocyclobutene, 52.52 g (0.333 mol) of 4-chloro-1-nitrobenzene, 92.2g (0.667 mol) of K_2CO_3, 300 mL of toluene and 600mL of DMAc.

Heated the vigorously stirring mixture to reflux and began to remove water in the Dean Stark Trap. Reflux was continued for18 hours. The water/toluene was drained from the trap and began to distill out the toluene via the trap. Temperature rises from 133°C to 155°C at which point heating is ceased and the reaction cooled to room temperature. The reaction was poured into 1L of vigorously stirring water and after 10 minutes transferred to a separatory funnel where it was extracted with $CHCl_3$ (3X500 mL). The combined extracts were washed with 10% HCl (4X500 mL) and water (4X500 mL) before drying ($MgSO_4$). Filtration through celite followed by removal of the solvent *in vacuo* provided a 121 g of a brown liquid. The excess DMAc was removed by bulb to bulb distillation under vacuum (100°C at 0.6 mm/Hg) and the product remained as a solid in the distillation bulb. The solid was taken up in EtOH and decolorizing charcoal, heated to boiling and filtered. The product crystallized upon cooling. Filtration followed by drying in a vacuum oven at 60°C overnight afforded 70.5 g (87.7% yield) of the pure nitro ether product. MP (DSC)=68°C. ^{1}H-NMR ($CDCl_3$, TMS reference) 8.17 (dd,2), 7.08 (d,1), 6.97 (dd,2), 6.92 (d,1), 6.81 (d,1), 3.18 (s,4). ^{13}C-NMR ($CDCl_3$, 77.00 reference) 164.39, 154.01, 147.57, 142.96, 142.46, 125.99, 124.58, 124.48, 119.81, 116.71, 115.88, 115.81, 77.43, 77.00, 76.58, 28.91, 28.85. By gas chromatography the product is 98.6% pure. DSC (10°C/minute to 400°C) MP=68.04°C; Exotherm#1, 266.65°C (543 J/g); Exotherm#2, 328.6°C (949 J/g).

Preparation of 4-(4-Aminophenoxy) Benzocyclobutene (29) Into a 1L glass Parr Pressure vessel was placed 50 g (0.2075 mol) of 4-(4-nitrophenoxy) benzocyclobutene, 2.21 g (2.1 mmol Pd) of 10% Pd/C and 450 mL of EtOAc. Hydrogenation carried out at 55 psi H_2. At the end of 8 hours pressure had dropped to 21 psi. The catalyst was filtered away from the reaction and the EtOAc concentrated in vacuo to afford 31.47 g of the product. The gas chromatograph indicated that the product was a mixture of starting nitro compound and the amine product (82:18). Both the ^{1}H- and ^{13}C-NMR clearly showed the presence of the starting material. The product was carried on at this time to the formation of the amic-acid where the nitro compound can be readily removed.

Preparation of 4-(4-N-Maleimidophenoxy) Benzocyclobutene (6). Into a 1L 3-neck roundbottom flask equipped with an overhead stirrer, stopper, and reflux condenser with N_2 inlet was placed 31.47 g (82% amine=25.49g; 0.1208 mol) of 4-(4-aminophenoxy) benzocyclobutene in 300 mL of acetone. To this solution was added 11.87 g (0.1210 mol) of maleic anhydride in several portions over a period of 15 minutes. A dense yellow solid began to come out of solution. Reaction continued at room temperature for 18 hours.The amic-acid was isolated by filtration and washed with cold acetone until the washes were colorless. Resuspended the amic-acid in acetone (400 mL) and added 0.917 g (3.70 mmol) of $Ni(OAc)_2 \cdot 4H_2O$, 24.7 g (0.2416 mol) of acetic anhydride, and 19.07 g (0.1884 mol) of triethylamine. Reaction continued at room temperature for

24 hours. Cooled the flask in an ice bath and added 200 mL of 1N NaOH dropwise. Added 300 mL of $CHCl_3$ and transferred the mixture to a separatory funnel where the aqueous phase was removed. Washed the organic layer with 10% HCl (3X300 mL); water (2X300 mL); 10% $NaHCO_3$ (2X300 mL) and water (2X300 mL) before drying ($MgSO_4$). Filtration through celite followed by removal of the volatiles *in vacuo* afforded 32 g of a dark yellow solid. Recrystallization of this material from EtOH and decolorizing charcoal provided 25.5 g (71.6% yield) of the product which was one peak by gas chromatography. ^{1}H-NMR ($CDCl_3$, TMS reference) 7.25 (d,2), 7.05 (m,3), 6,88 (dd,1), 6.83 (s,2), 6.78 (d,1), 3.15 (s,4). ^{13}C-NMR ($CDCl_3$, 77.00 reference) 169.98, 158.33, 155.71, 147.14, 141.46, 134.34, 127.73, 125.42, 124.12, 119.19, 118.31, 115.14, 77.42, 77.00, 76.57, 28.84, 28.74. DSC (10°C/minute to 400°C) MP_1=105°C; MP_2=114.2°C; Exotherm, 262.6°C (742 J/g).

Preparation of **2-[(4-Benzocyclobutenoylphenoxy)-4-Phenyl]-2-[(4-Aminophenyl Propane (24)** Into a 1L 3 neck round bottom flask equipped with a thermometer, overhead stirrer and Dean Stark Trap with reflux condenser and N_2 inlet, was placed 75 g (0.2963 mol) of 4-nitrophenyl-4'-benzocyclobutenyl ketone, 67.26 g (0.2963 mol) of 2-(4-hydroxyphenyl)-2-(4-aminophenyl) propane, 81.84 g (0.5926 mol) of potassium carbonate, 150 mL toluene and 300 mL of dimethylacetamide. The Dean Stark Trap was filled with toluene and the vigorously stirring reaction mixture brought to reflux under N_2. Reflux was continued overnight (18 h). After this time, 7.0 mL of water had been collected in the trap. The Dean Stark Trap and condenser were replaced with a vacuum distillation head and the toluene removed by distillation at atmospheric pressure. After the reaction had cooled to room temperature it was poured into 1000 mL of distilled water with vigorous stirring. After stirring for 10 minutes, 250 mL of $CHCl_3$ was added and the two phase mixture transferred to a separatory funnel. The organic layer was removed and the aqueous layer extracted with $CHCl_3$ (1 x 250 mL). The combined organic phases were dried ($MgSO_4$) and then filtered through celite. The volatiles were removed (rotary evaporator) and the product was obtained as a viscous liquid which was subjected to bulb to bulb distillation at reduced pressure (0.5 mmHg) to remove the residual DMAc (@20 mL). The product weighed 124 g (96% yield) and was a viscous dark yellow liquid. Analysis of the ^{1}H- and ^{13}C-NMRs indicated that the product was of sufficient purity to be carried on to the imidization step. ^{1}H-NMR, 300MHz, ($CDCl_3$, TMS reference, ppm) 7.75 (dd,2), 7.65 (d,1), 7.45 (s,1), 7.25 (dd,2), 7.13 (d,1), 7.08-6.90 (m,6), 3.55 (bs,2), 3.23 (s,4), 1.65 (s,6). ^{13}C-NMR, ($CDCl_3$, 77.00 ppm reference) 196.35, 161.79, 153.31, 151.1, 147.80, 145.85, 144.30, 140.61, 137.03, 132.56, 132.40,132.31, 129.48, 129.30, 128.54, 128.32, 128.14, 127.77, 127.68, 127.55, 127.49, 124.19, 123.97, 122.42, 122.14, 119.66, 119.58, 119.46, 119.38, 117.25, 117.12, 116.98, 116.84, 114.91, 114.83, (77.00), 41.64, 30.73, 29.64, 29.23.

Preparation of 2-[(4-Benzocyclobutenoylphenoxy)-4-Phenyl]-2-(4-Maleimidophenyl) Propane (4). Into a 2L 3 neck round bottom flask equipped with a thermometer, reflux condenser with N_2 inlet and an overhead stirrer was placed124 g (0.2863 mol) of 2-[(4-benzocyclobutenoylphenoxy)-4-phenyl]-2-(4-aminophenyl)propane and 1000 mL of acetone. To this stirring solution was added in several portions over a period of 20 minutes, 28.06 g (0.2863 mol) of maleic anhydride. A bright yellow solid came out of solution as the anhydride was added. This mixture was stirred at room temperature overnight. The amic-acid product was isolated by suction filtration and washed with several portions of cold acetone. The amic-acid was resuspended in 1000 mL of fresh acetone in the 2L flask and treated with 58.43 g (0.5726 mol; 54 mL) of acetic anhydride, 44.3 g (0.4380 mol; 61 mL) of triethylamine and 2.27 g (8.6 mmol) of nickel acetate tetrahydrate. The reaction mixture was stirred at room temperature for 48 hours. The reaction was cooled in an ice bath and 550 mL of 5M NaOH was added slowly. The volatiles were removed on a rotary evaporator and the remaining material in the flask was transfered to a separatory funnel where it was extracted with $CHCl_3$ (500 mL). The $CHCl_3$ layer was washed with water (2 x 500 mL) before drying over $MgSO_4$. Filtration through celite followed by removal of the solvent *in vacuo* afforded 124 g (84.4%) of a viscous yellow liquid. DSC of the monomer: Small Tg 118°C, exotherm at 261°C (388.9 J/g, 47.6 kcal/mole); Rescan of DSC: Tg 231°C. ^{1}H-NMR ($CDCl_3$, TMS, ppm) 7.79 (d,2), 7.64 (d,1), 7.47 (s,1), 7.35 (d,2), 7.37-7.24 (m,4), 7.13 (d,1), 7.01 (t,4), 6.82 (s,2) 3.23 (s,4), 1.71 (s,6). ^{13}C-NMR 196.29, 169.88, 161.61, 153.71, 151.11, 150.42, 146.48, 145.86, 137.01, 134.31, 132.49, 132.45, 129.40, 128.94, 128.52, 127.64, 125.67, 124.08, 122.28, 119.66, 117.09, 77.43, 77.00, 76.57, 42.38, 30.56, 29.64, 29.23.

Preparation of 3-Amino-4'-benzocylcobutenoyldiphenyl Ether (25). Into a 2L 3 neck roundbottom flask equipped with an overhead stirrer, thermometer and a Dean Stark Trap with relux condenser and N_2 inlet was placed 100 g (0.3949 mol) of 4-nitrophenyl-4'-benzocyclobutenyl ketone, 43.04 g (0.3949 mol) of 3-hydroxyaniline, 109.15 g (0.7898 mol) of K_2CO_3, 800 mL of dimethylacetamide (DMAc) and 400 mL of toluene. The Dean Stark Trap was filled with toluene and the vigorously stirring reaction mixture was heated to reflux with concurrent removal of water. Reflux was continued overnight. A total volume of 15 mL of water was collected. The heating was stopped and the reaction cooled to a lower temperature. The Dean Stark Trap was replaced with a distillation head and the toluene distilled off at atmospheric pressure under N_2. The reaction mixture was cooled to room temperature and poured into 2000 mL of vigorously stirring distilled water. After stirring for 20 min., $CHCl_3$ (600 mL) was added and the two phases transfered to a separatory funnel. The organic layer was removed and the aqueous phase extracted with $CHCl_3$ (1 x 500 mL). The extracts were combined and washed with water (2 x 500 mL) before drying ($MgSO_4$). Filtration through celite followed by removal of the volatiles *in vacuo* afforded a dark brown liquid which was subjected to bulb to bulb distillation at reduced pressure. The material remaining in the distillation bulb was a dark brown semi solid and weighed 121 g (97%). ^1H-NMR ($CDCl_3$, TMS, ppm) 7.77 (dt,2), 7.64 (d,1), 7.47 (s,1), 7.17-7.11 (m,2), 7.02 (dt,2), 6.51-6.39 (m,6), 3.78 (bs,2), 3.23 (s,4). ^{13}C-NMR ($CDCl_3$, 77.00 ppm reference) 196.45, 161.58, 156.99, 151.19, 148.50, 145.91, 127.04, 132.46, 130.72, 129.42, 124.11, 122.31, 117.32, 111.29, 109.88, 106.64, 77.42, 77.00, 76.57, 29.68, 29.26. The product was of sufficient purity to be carried on to the formation of the maleimide.

Preparation of 3-Maleimido-4'-Benzocyclobutenoyldiphenyl Ether (5). Into a 3L 1 neck roundbottom flask equipped with a magnetic stir bar and reflux condenser with N_2 inlet was placed121 g (0.3841 mol) of 3-Amino-4'-benzocylcobutenoyldiphenyl ether and 1500 mL of acetone. To this stirring solution was added 37.64 g (0.3841 mol) of maleic anhydride in several portions over a period of 20 minutes. The reaction was stirred at room temperature overnight. To the stirring reaction was added 93.34 g (0.9143 mol, 86.3 mL) of acetic anhydride, 65.3 g (0.6149 mol, 85.7 mL) of triethylamine and 3.00 g (0.0122 mol) of nickel acetate tetrahydrate. The reaction was stirred at room temperature for 48 hours under N_2. The flask was cooled in an ice bath and 700 mL of 10% $NaHCO_3$ was added dropwise. Transfered the reaction mixture to a separatory funnel and added 1000 mL of $CHCl_3$. Removed the organic layer and extracted the aqueous phase with $CHCl_3$ (1 x 500 mL). Combined the organic extracts and washed with 10% $NaHCO_3$ (2 x 500 mL), 10% HCl (2 x 500 mL) and water (1 x 500 mL) before drying ($MgSO_4$). Filtration through celite followed by removal of the solvent *in vacuo* afforded 170 g of a tacky dark brown solid. The crude product was subjected to column chromatography on silica gel with $CHCl_3$ as the eluent. Collected the bright yellow fraction as it came off the column. Removal of the solvent afforded 87.8 g (58%) of the desired product. MP 95°C. ^1H-NMR ($CDCl_3$, TMS, ppm) 7.82 (d,2), 7.67 (d,1), 7.47 (m,2), 7.39-7.05 (m,6), 6.85 (s,2), 3.22 (s,4). ^{13}C-NMR ($CDCl_3$, 77.00 ppm reference) 196.33, 169.40, 160.70, 156.50, 151.31, 145.95, 136.87, 134.41, 133.19, 132.84, 132.57, 132.44, 130.48, 129.45, 124.11, 122.36, 121.68, 119.09, 117.73, 117.54, 117.27, 77.42, 77.00, 76.57, 29.68, 29.26.

Preparation of 3-Hydroxyphenyl-4'-benzocyclobutenyl Ether (27). Into a 3L 3 neck roundbottom flask equipped with an overhead stirrer, thermometer and a reflux/distilling head with a N_2 inlet was placed 566 g (5.14 mol) of resorcinol and 1500 mL of pyridine. To this vigorously stirring solution was added 470 mL (25% by weight in MeOH, 111.11 g, 2.05 mol) of sodium methoxide in methanol. The solution was heated to reflux and the MeOH distilled out until the temperature at the distilling head was 114°C. Cooled the reaction slightly and added 190 g (1.04

mol) of 4-bromobenzocyclobutene in 200 mL of pyridine followed by 10 g (0.101 mol) of CuCl. The reaction mixture was heated to reflux and continued for three days. The pyridine was distilled out at atmospheric pressure and the flask cooled in an ice bath. To the cold reaction mixture was added concentrated HCl until the mixture was acidic to pH paper. The product mixture was taken up in toluene (500 mL) and transfered to a separatory funnel and the layers separated. The aqueous layer was extracted with toluene (3 x 300 mL). Combined the toluene extracts and washed with water (3 x 500 mL) and brine (1 x 500 mL) before drying ($MgSO_4$). Filtration through celite and removal of the volatiles in vacuo afforded 215 g of a brown viscous liquid. Bulb to bulb distillation under vacuum provided 157.6 g (71.4%) of the product as an amber liquid which also contained @ 1% toluene (by GC). ^{1}H-NMR ($CDCl_3$, TMS reference, ppm) 7.35-6.4 (complex multiplets,7), 5.37 (bs,1), 3.18 (s,4). The material was of sufficient purity to be carried on to the next step.

Preparation of 1-(4-Benzocyclobutenoxy)-3-(4-Nitrophenoxy)Benzene (31). Into a 2L 3 neck roundbottom flask equipped with an overhead stirrer, thermometer and Dean Stark Trap with reflux condenser and N_2 inlet was placed 157 g (0.7402 mol) of 3-(4-benzocyclobutenoxy)phenol, 116.54 g (0.7402 mol) of 4-chloro nitrobenzene and 204 g (1.48 mol) of K_2CO_3 in 700 mL of DMAc and 350 mL of toluene. The Dean Stark Trap was filled with toluene and the reaction mixture brought to reflux under N_2. Reflux continued overnight. The reaction mixture was cooled slightly and the Dean Stark Trap was replaced with a distilling head and receiver. The toluene was distilled away at atmospheric pressure and the reaction cooled to room temperature where it was filtered. The solid was washed with $CHCl_3$ (1000 mL) and the combined filtrate was transfered to a separatory funnel where it was washed with water (4 x 500 mL), 10% HCl (3 x 500 mL) and water (2 x 500 mL) before drying over $MgSO_4$. Filtration through celite followed by removal of the volatiles *in vacuo* afforded 234.2 g (95%) of a brown viscous oil. The crude product was recrystallized from EtOH and decolorizing charcoal to provide 192.3 g (78%). ^{1}H-NMR ($CDCl_3$, TMS reference, ppm) 8.18 (d,2), 7.32 (t,1), 7.02 (d,3), 6.91-6.66 (m,5), 3.18 (s,4). ^{13}C-NMR, $CDCl_3$, 77.00 ppm reference) 162.98, 160.18, 146.99, 142.08, 141.41, 130.77, 125.94, 123.97, 118.99, 117.14, 114.97, 114.42, 113.98, 109.58, 77.42, 77.00, 76.58, 29.01, 28.91.

Preparation of 1-(4-Benzocyclobutenoxy)-3-(4-Aminophenoxy)-Benzene. Into a 1L Parr Pressure Bottle was placed 35 g (0.1051 mol) of 1-(4-benzocyclobutenoxy)-3-(4-nitrophenoxy) benzene, 450 mL of EtOAc and 1.11 g (1.05 mmol) of 10% Pd/C. Hydrogenation was carried out at 55 psi of H_2. After 6 hours of shaking at room temperature the pressure had dropped to 22 psi. The solution was filtered away from the catalyst and the filtrate concentrated on a rotary evaporator to provide 30.02 g (94.3%) of the amine. ^{1}H-NMR ($CDCl_3$, TMS reference, ppm) 7.15 (t,1), 6.98 (d,1), 6.87 (d,3), 6.75 (s,1), 6.61 (dd,5), 3.58 (bs,2), 3.13 (s,4). Gas chromatography (15 M, DB-5 column, 0.25u diameter, 0.1u film thickness) indicated that the product was >95% pure.

Preparation of **1-(4-Benzocyclobutenoxy)-3-(4-Maleimidophenoxy)-Benzene (8)**. Into a 2L 3 neck roundbottom flask equipped with an overhead stirrer, thermometer and reflux condenser with a N_2 inlet was placed 110 g (0.3630 mol) of 1-(4-benzocyclobutenoxy)-3-(4-aminophenoxy) benzene in 1200 mL of acetone. To this stirring solution was added 35.58 g (0.3630 mol) of maleic anhydride in several portions over a period of 20 minutes. After all of the anhydride was added reaction was continued at room temperature for 8 hours. At the end of this time there was added 88.72 g (0.8691 mol; 82 mL) of acetic anhydride, 59.2 g (0.5847 mol; 81.5 mL) of triethylamine and 3.0 g (0.0122 mol) of nickel (II) acetate tetrahydrate. Reaction was continued at room temperature for 18 hours. Added 500 mL of 10% $NaHCO_3$, dropwise to the reaction and then transfered to a separatory funnel. Added 500 mL of $CHCl_3$ and separated the layers. The organic phase was washed with 10% $NaHCO_3$ (2 x 300 mL), 10% HCl (2 x300 mL) and brine (2 x 300 mL) before drying over $MgSO_4$. Filtration through celite followed by removal of the volatiles *in vacuo* afforded 130 g (93.5%) of a yellow solid. This was recrystallized from 1500 mL of hot EtOH and decolorizing charcoal. After filtration and drying the product weighed 117 g (84.2%). MP = 126°C. ^{1}H-NMR ($CDCl_3$, TMS reference, ppm) 7.22 (m,3), 7.08 (d,2), 7.01 (d,1), 6.88 (d,1), 6.84 (s,2), 6.70 (m,4), 3.16 (s,4). ^{13}C-NMR ($CDCl_3$, 77.00 ppm reference) 169.53, 159.82, 157.61, 156.55, 155.37, 146.80, 141.10, 134.14, 130.34, 127.55, 126.03, 123.91, 119.01, 118.91, 114.87, 113.09, 113.00, 109.07, 77.42, 77.00, 76.58, 29.01, 28.89.

Preparation of **3-Aminophenyl-4'-Benzocyclobutenyl Ether (30)**. Into a 500 mL 3 neck roundbottom flask equipped with a reflux/distilling head with a N_2 inlet, thermometer, equilibrating addition funnel and a magnetic stir bar was placed 20 g (0.1835 mol) of 3-aminophenol in 100 mL of pyridine. To this stirring solution was added 41.9 mL (9.913 g; 0.1835 mol) of a 25% by weight solution of NaOMe in MeOH. The reaction mixture was heated to reflux and the MeOH and pyridine distilled out until the temperature at the distilling head was 115°C. Heating stopped and after 20 minutes added 33.6 g (0.1835 mol) of 4-bromobenzocyclobutene in 20 mL of pyridine, in one portion, followed by 1.82 g (0.0185 mol) of CuCl. The reaction mixture was brought to reflux and continued until analysis by gas chromatography no longer indicated the presence of starting materials (48 hours). Distilled away the pyridine and took the material remaining up in 200 mL of EtOAc and transfered to a separatory funnel. Washed the organic phase with 10% HCl (2 x 100 mL) and water (2 x 100 mL) before drying ($MgSO_4$). Filtration through celite followed by removal of the solvent *in vacuo* afforded 39.1 g (>100%) of a gummy brown solid which had a distinct pyridine smell. Recrystallization from EtOH and decolorizing charcoal provided 21.47 g (55.5%) of a white solid which by NMR was consistant with the structure of the product. MP(DSC) 70.4°C. ^1H-NMR ($CDCl_3$, TMS reference, ppm) 7.10-6.96 (m,2), 6.87 (dd,1), 6.76 (d,1), 6.35 (m,2), 6.27 (t,1), 3.64 (bs,2), 3.14 (s,4). ^{13}C-NMR ($CDCl_3$, 77.00 ppm reference) 159.89, 156.33, 148.10, 146.95, 140.75, 130.38, 123.83, 118.92, 114.85, 109.95, 108.34, 104.90, 77.43, 77.00, 76.57, 29.82, 29.70.

Preparation of 3-Maleimidophenyl-4'-Benzocyclobutenyl Ether (7). Into a 500 mL 3 neck roundbottom flask equipped with an overhead stirrer, thermometer and a reflux condenser with N_2 inlet was placed 19 g (0.090 mol) of 4-benzocyclobutenyl-3-aminophenyl ether and 200 mL of acetone. To this stirring solution was added 8.83 g (0.090 mol) of maleic anhydride in several portions over a period of 15 minutes. A dense yellow precipitate developed and reaction was continued at room temperature overnight. The reaction mixture was treated with 18.38 g (0.180 mol; 17 mL) of acetic anhydride, 14.2 g (0.1404 mol; 19.6 mL) of triethylamine and 686 mg (0.0028 mol) of nickel (II) acetate tetrahydrate. Stirred at room temperature overnight. The reaction was transfered to a separatory funnel and $CHCl_3$ (300 mL) added. Washed with water (1 x 300 mL), 10% HCl (3 x 200 mL), water (1 x 300 mL), 10% NaOH (2 x 200 mL) and water (2 x 200 mL) before drying ($MgSO_4$). Filtration through celite followed by removal of the volatiles *in vacuo* provided 24.7 g (94.3%) of a gummy yellow solid. The crude product was passed through a column of silica gel with $CHCl_3$ as the eluant. Removal of the solvent provided 18.9 g (72%) of a bright yellow solid. MP(DSC)102.8°C. ^1H-NMR ($CDCl_3$, TMS reference, ppm) 7.36 (t,1), 7.04-6.86 (m,6), 6.78 (s,2), 3.13 (s,4). ^{13}C-NMR ($CDCl_3$, 77.00 ppm reference)169.51, 159.11, 155.57, 147.08, 141.36, 134.27, 134.18, 132.43, 130.03, 129.95, 124.06,120.03, 119.07, 117.25, 115.75, 115.02, 77.43, 77.00, 76.58, 28.80, 28.68. Analysis by gas chromatography indicates that the product is >95% pure.

4.6. TABLES AND FIGURES

Table 4.1. Properties of Vinyltoluene-BCB/Compimide®353 Copolymers.

	p-VT/C-353			
	2:1	1:1	1:2	Ultem 1000
DSC				
T_m (°C)	79	78	82	
Exotherm: T_{max} (°C)/Δh_p (J/g)	253/518	248/275	251/462	
T_g (°C)	ND	ND	ND	219
TMA				
T_g (°C)	225/273*	257/314**	252/322**	217
CLTE (ppm)	59	58	51	
DMA				
Flexural Modulus, Dry/RT (ksi)	501	565	577	534
Flexural Modulus, Wet/RT (ksi)	516	656	samples broke	528
Flexural Modulus, Dry/450°F (ksi)	334	408	358	4.1
Flexural Modulus, Wet/450°F (ksi)	177	441	samples broke	20
T_g (°C), dry	250	298	294	221
T_g (°C), wet	268	305	samples broke	218
% Water Gain	1.3	2.51	3.92	1.02
Flexural Strength, Dry/RT (ksi)	9.78	10.3	10.5	
Flexural Strength, Wet/450°F (ksi)	0.94	3.9	samples broke	
Hot/Wet (ksi)				
Flexural Modulus, Dry/RT (ksi)	484	509	538	
Flexural Modulus, Wet/450°F (ksi)	30.6	192	samples broke	
Elongation, Dry (%)	1.92	2.02	1.98	
Elongation, Wet (%)	2.72	2.03	samples broke	
K_{Ic} (psi-in$^{1/2}$)	288	286	288	

Notes:
* = post cure 300°C/90 min/air
** = post cure 330°C/90 min/air
ND = Not Detectable

Table 4.2. Properties of 1:1 BCB-Diketone/MDA-BMI Copolymer.

T_g (°C)	
from TMA	294
from DMA	306
DMA Flexural Modulus (ksi)	
RT/Dry	536
232°C/Dry	410
300°C/Dry	270
Equilibrium Moisture Pick-up (%)	3.49
K_{Ic} (psi-in$^{1/2}$)	667
G_{Ic} (J/m^2)	130
Tensile Elongation (%)	4.0

Table 4.3. Properties of AB-BCB-Maleimide Monomers and Polymers

Monomer	**M.P. (°C)**	**T_g (°C)**	**K_{IC} (psi x in$^{0.5}$)**	**G_{IC} (J/m^2)**	**Flex. Str. (ksi)**	**Flex. Mod. (ksi)**
1	148	317	1450	780	30.2	471
2	157	270	1650	1037	25.3	458
3	177	247	--	--	--	--
6	105	277	> 2110	> 1560	26.3	508
4	None	230	1690	1110	20.3	447
5	95	220	> 2900	> 2940	--	--
7	103	265	1150	463	--	--
8	126	202	3590	4200	23.9	538

Table 4.4. AB BCB-MI monomers: cure viscosity data summary.

Monomer	Temperature (°C) where $\eta^* \approx$ 1 P (100 cP)	Temperature (°C) where $\eta^* \approx$ 100 P (10^4 cP)
2	236	248
3	212	233
6	235	248
4	220	235
5	228	241
8	238	250

Table 4.5. Dynamic mechanical test results for AB BCB-MI polymers.

Monomer	T_g (°C)	G' (GPa) @ 25°C	% modulus retention (vs at 25°C)				K_{Ic} psi-in$^{1/2}$
			-100°C	350°F	400°F	450°F	
2	278	1.29	132	86	84	80	1650
6	277	1.35	132	83	81	69	2110
4	246	1.18	133	85	80	43	1690
5	225	1.52	123	83	71	9	2900
7	262	1.86	120	79	75	69	1150
8	201	1.36	128	83	41	1	3590

Notes:

T_g taken as maximum in G", 2nd scan, $\omega = 1$ rad/s.

G' values from 1st scan, 5°C/min, $\omega = 1$ rad/s.

Table 4.6. Rate constant (from DSC) for polymerization of BCB-MI monomers.

T (°C)	k_1 (min^{-1})	±	σ (min^{-1})	$(\sigma/k_1)\cdot 100\%$
170	4.69E–4	±	0.18E–4	3.8
188	2.305E–3	±	0.082E–3	3.6
191	3.278E–3	±	0.100E–3	3.1
200	5.97E–3	±	0.44E–3	7.4
202	--	±	--	--
202	--	±	--	--
204	8.652E–3	±	0.236E–3	2.7
206.5	9.893E–3	±	0.339E–3	3.4
206.5	1.156E–2	±	0.076E–2	6.6
207	1.099E–2	±	0.033E–2	3.0
219	3.244E–2	±	0.144E–2	4.4
221	4.155E–2	±	0.090E–2	2.2

Table 4.7. Rate constant (from SEC) for polymerization of BCB-MI monomers.

T (°C)	k_2 (min^{-1})	±	σ (min^{-1})	$(\sigma/k_1)\cdot 100\%$
170	8.962E–4	±	0.223E–4	2.5
188	5.417E–3	±	0.065E–3	1.2
191	6.243E–3	±	0.135E–3	2.2
200	8.49E–3	±	0.56E–3	6.6
202	1.716E–2	±	0.018E–2	1.0
202	1.588E–2	±	0.074E–2	4.7
204	1.170E–2	±	0.026E–2	1.5
206.5	1.998E–2	±	0.059E–2	3.0
206.5	2.002E–2	±	0.021E–2	1.0
207	2.334E–2	±	0.051E–2	2.2
219	6.890E–2	±	0.193E–2	2.8
221	8.724E–2	±	0.174E–2	2.0

Table 4.8. Comparison of DSC and SEC rate constants.

T (°C)	k_2/k_1
170	1.91
188	2.35
191	1.90
200	1.42*
202	--
202	--
204	1.98
206.5	2.02
206.5	1.73
207	2.12
219	2.12
221	2.10
mean	2.03
± σ	± 0.18
* Omit from average	

Table 4.9. Arrhenius fits to polymerization rate data.

Constant	T range	Z (min^{-1})	E_a/R (°K)	E_a (kcal/mol)	r
Linear least squares fit					
k_1	all	1.020E15	18278	36.3	0.9982
k_1	≤ 202°C	2.139E14	18010	35.8	0.9963
k_1	≥ 204°C	7.632E16	20822	41.4	0.9993
k_2	all	2.898E15	18885	37.5	0.9968
k_2	≤ 202°C	4.679E15	19087	37.9	0.9973
k_2	≥ 204°C	1.810E18	22017	43.7	0.9992
Weighted non-linear least squares fit					
k_1	all	1.413E16	19991	39.7	0.9994
k_1*	≤ 202°C	1.113E13	16623	33.0	0.9951
k_1	≥ 204°C	1.095E17	21001	41.7	0.9997
k_2	all	1.849E17	20895	41.5	0.9962
k_2	≤ 202°C	1.444E15	18519	36.8	0.9990
k_2	≥ 204°C	2.056E18	22084	43.9	0.9993
* Poor fit visually.					

Table 4.10. Temperature dependence of activation energy for polymerization.

T range	E_a (kcal/mol)
170-221°C	38.8 ± 2.3
170-202°C	35.9 ± 2.1
204-221°C	42.7 ± 1.3

Table 4.11. Fit parameters for isothermal cure viscosity of monomer 6 (Eqn (5)).

T (°C)	a	b	ln $\eta(0)$
188	−0.5405	4.329	−3.55
200	−0.6856	4.447	−3.65
219	−1.562	4.788	−3.75

Table 4.12. B-staging of monomer 6 at several temperatures.

B-stage T = 172°C			B-stage T = 192°C			B-stage T = 208°C		
Conversion p			Conversion p			Conversion p		
SEC	DSC	Test #	SEC	DSC	Test #	SEC	DSC	Test #
0.09	0.13	391	0.23	0.24	392	0.10	0.12	394
0.18	0.17	395	0.46	0.46	397	0.19	0.19	396
0.35	0.38	398	0.56	0.55	400	0.34	0.37	399

Table 4.13. Resin-Fiber Interface Strength by Microdrop Method for Monomer 6.

Fiber	Interface strength (ksi)
Celion G30-500	9.7
Hercules AS-4	9.4
Hercules AS-4G	10.1
Hercules IM-7G	10.2
Celion G40-800	10.5

Table 4.14. Composite Properties: Monomer 6 on Celion G30-500 (3K, G105/8HS).

Fiber volume %	66
T_g (°C)	278
Tensile strength (ksi)	156.6
Tensile modulus (ksi)	10.35
Tensile strain (%)	1.5
Compressive strength (ksi)	124
Short beam shear strength (ksi)	13.26
Flexural strength (ksi)	190.2
Flexural modulus (Msi)	9.9
Flexural strain (%)	1.94

Table 4.15. Open Hole Compression and Compression After Impact on 6/G30-500 Composite.

Test Condition	**CAI (ksi)**	**OHC* (ksi)**
Room Temperature	48, 49	42.4
275°F/Wet**		32.5
310°F/Wet**		32.9
350°F/Wet**		29.6
400°F/Wet**		26.4

* Northrop test method, using 1" x 3" specimens.

** Wet = 14 days at 160°F and 95% relative humidity.

Table 4.16. In-Plane Shear Solvent Resistance of Monomer 6/G30-500 Composite.

Condition	Modulus (ksi)	Strength (ksi)	% Wt Gain
Control	0.796	17.3	____
MEK	0.738	15.6	0.45
Jet Fuel	0.811	17.4	0.39
Skydrol	0.644	16.9	0.52
Water	0.721	16.1	0.78

Table 4.17. Aging Study of Monomer 6/G30-500 Composite at 400°F in Air: Flexural Properties and Weight Loss.

Aging time (hours)	Flexural strength (ksi)	Flexural modulus (Msi)	Weight loss (%)
0	168	9.27	----
500	162	9.31	0.009
2000	158	9.32	0.273
4000	151	9.19	0.535

Table 4.18. Aging Study of Monomer 6/G30-500 Composite at 400°F in Air: Open Hole Compression.

Time (hours)	Weight loss (%)	Test condition	OHC (ksi)
0	0	RTD	42.4*
4000	0.54	RTD	46.7
		350°F/dry	39.3

* Data obtained from several months earlier from a different panel.

Figure 4.1. Viscosity versus temperature, monomer 4.

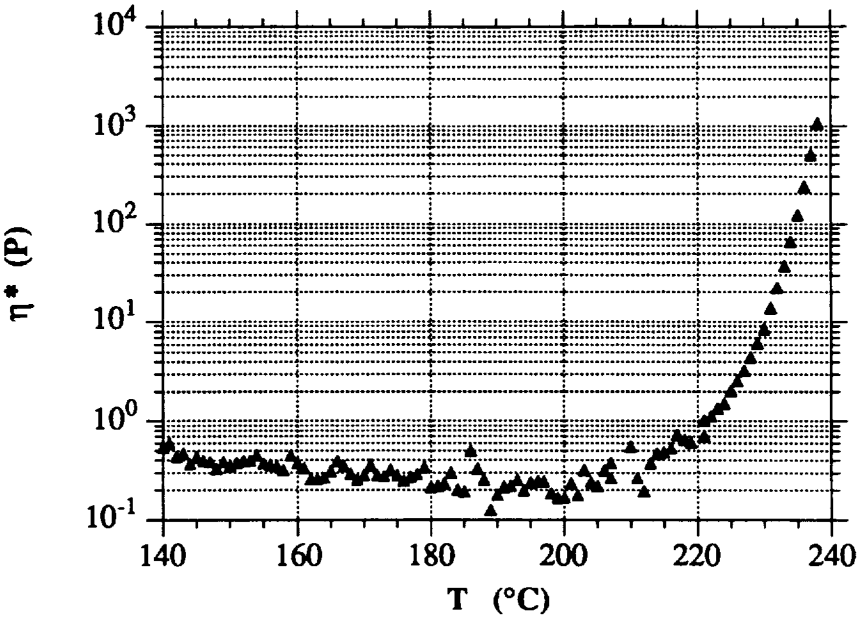


Figure 4.2. Transitions (G", shear loss modulus) for polymer 6.

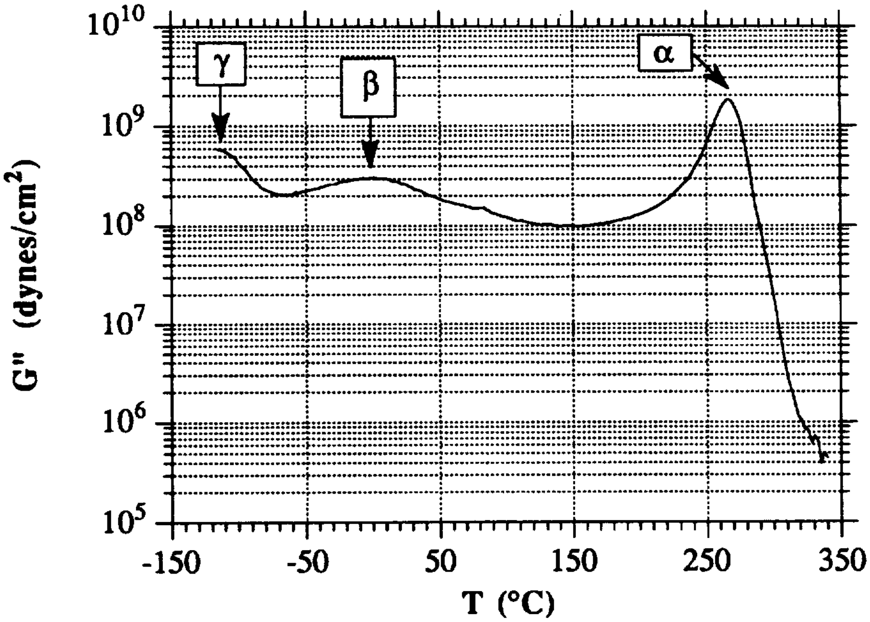


Figure 4.3. Transitions (G', shear storage modulus) for polymer 6.

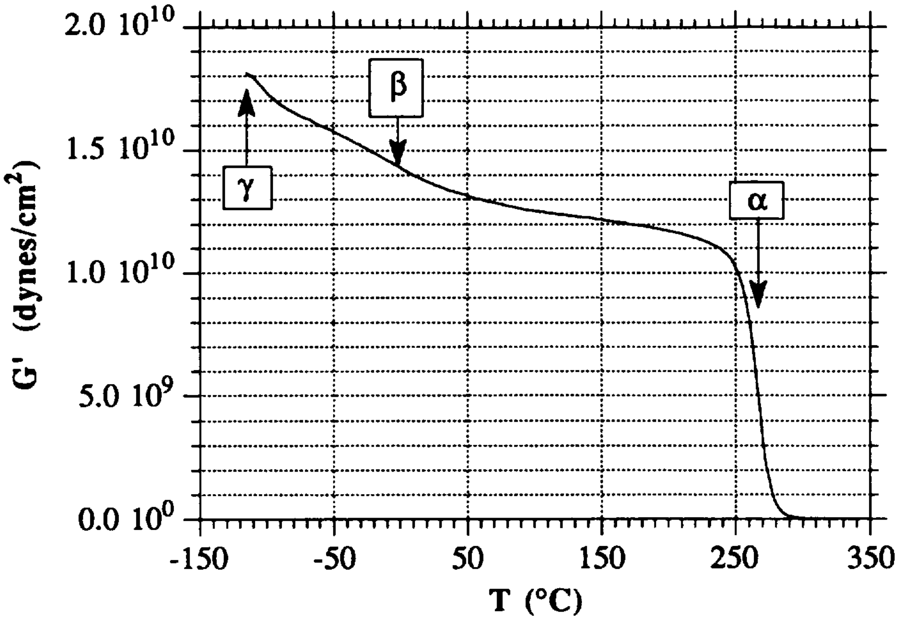


Figure 4.4. Stress relaxation for BCB-MI polymers, ε = 2%, T = 345°C.

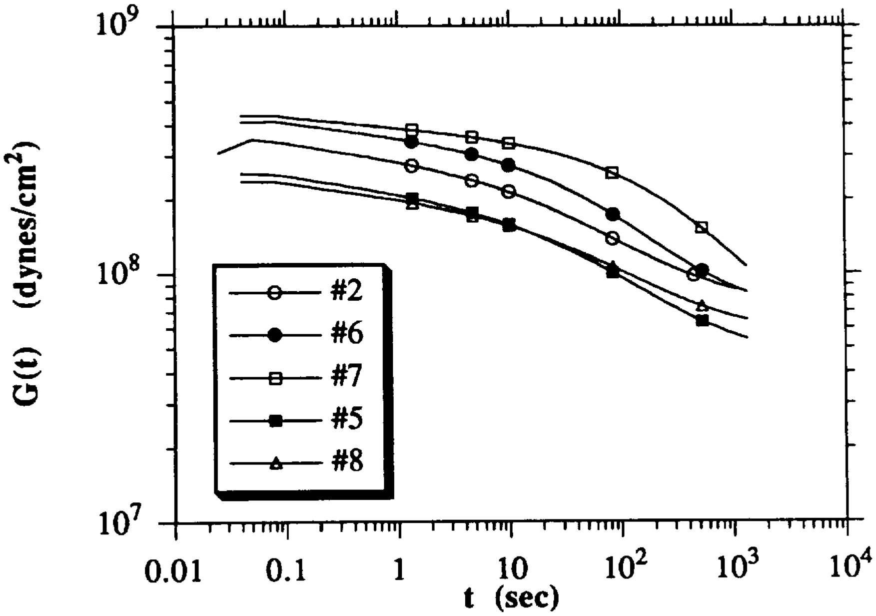


Figure 4.5. Polymerization rate constant for BCB-MI monomer 6.

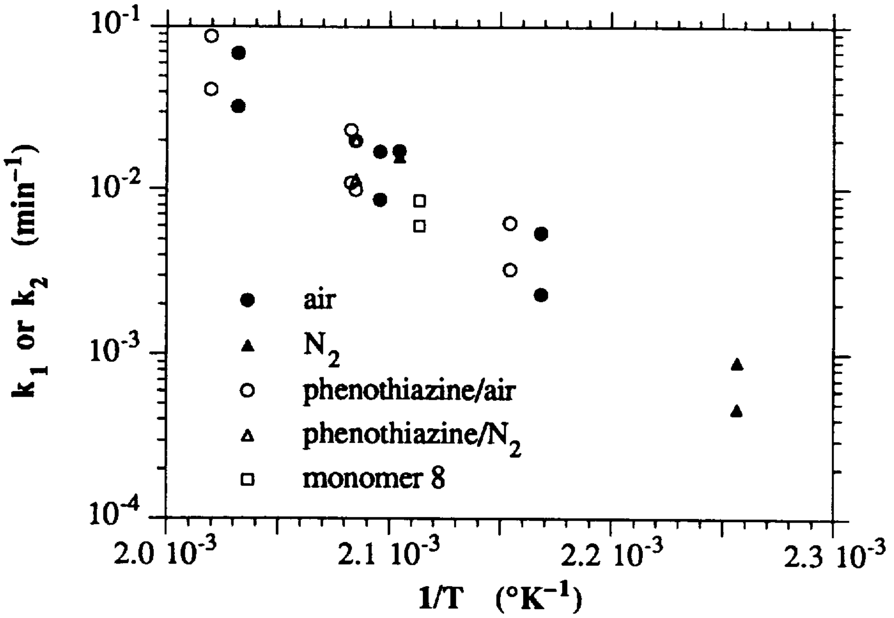


Figure 4.6. Arrhenius plot of polymerization rate constant, BCB-MI monomer 6.
Lines are linear least squares fits to all data.

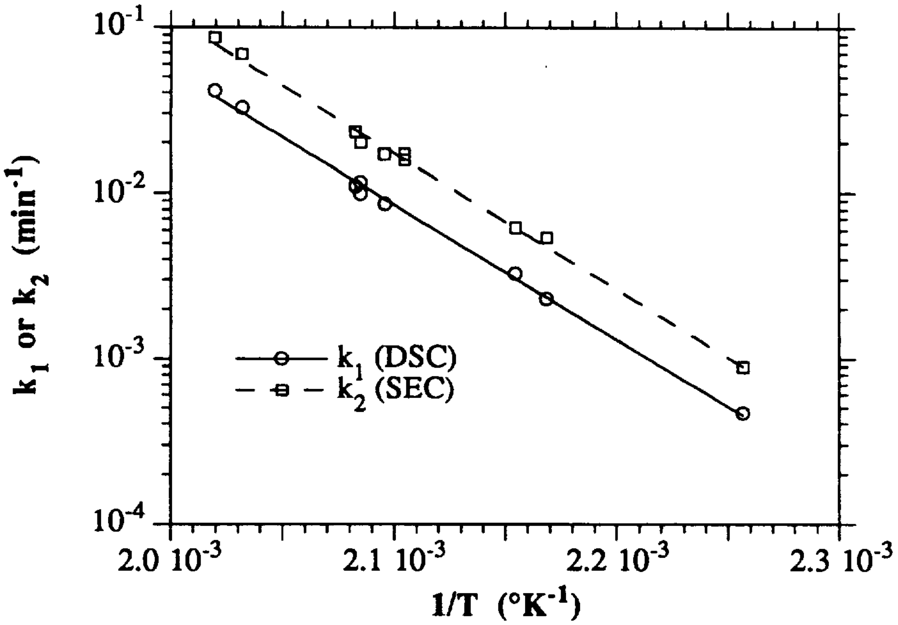


Figure 4.7. Effect of temperature on isothermal cure viscosity, monomer 6.
Composite curves: steady shear, $\eta(\dot{\gamma})$ (< 1 P); and dynamic, $\eta^*(\omega)$ (> 1P)

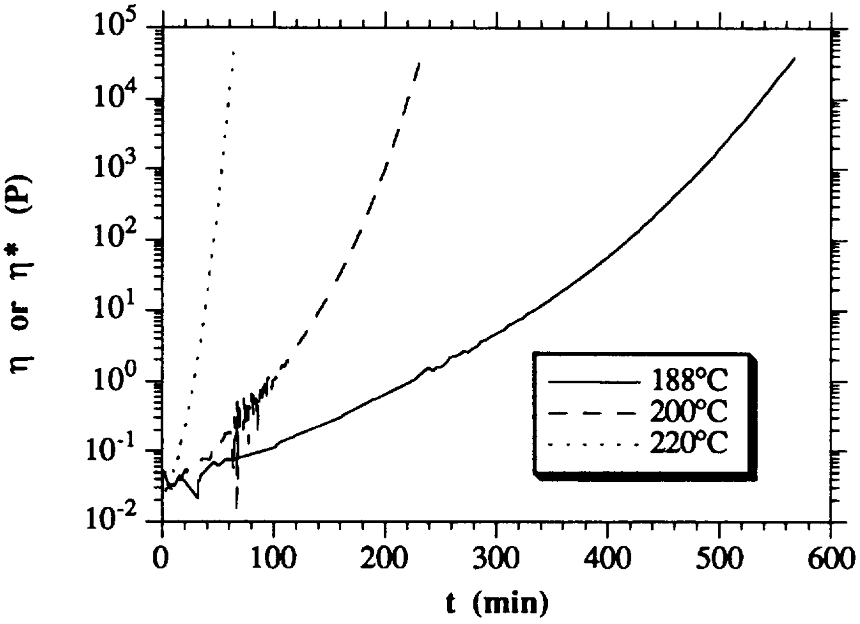


Figure 4.8. Isothermal cure viscosity vs conversion, several T, monomer 6.
Composite curves: steady shear, $\eta(\dot{\gamma})$ (< 1 P); and dynamic, $\eta^*(\omega)$ (> 1P)

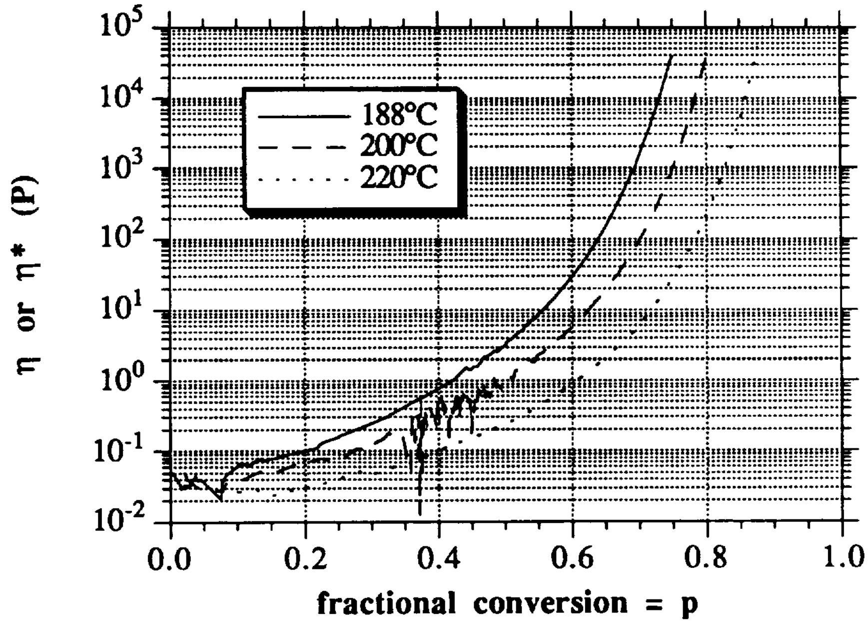


Figure 4.9. Effect of radical inhibitor on cure viscosity of monomer 6 (188°C).

Composite curves: steady shear, $\eta(\dot{\gamma})$ (< 1 P); and dynamic, $\eta^*(\omega)$ (> 1P)

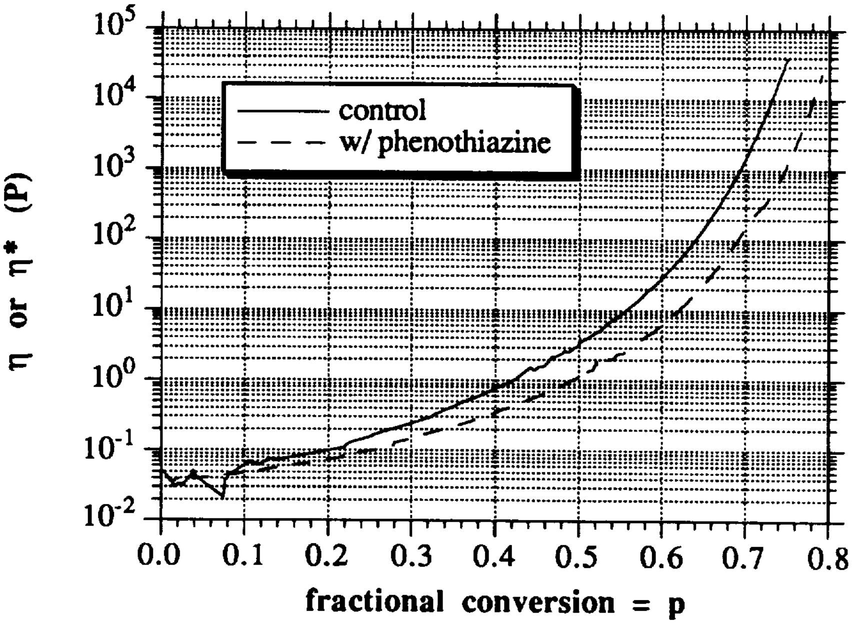


Figure 4.10. Effect of monomer structure on isothermal cure viscosity (200°C).

Composite curves: steady shear, $\eta(\dot{\gamma})$ (< 1 P); and dynamic, $\eta^*(\omega)$ (> 1P)

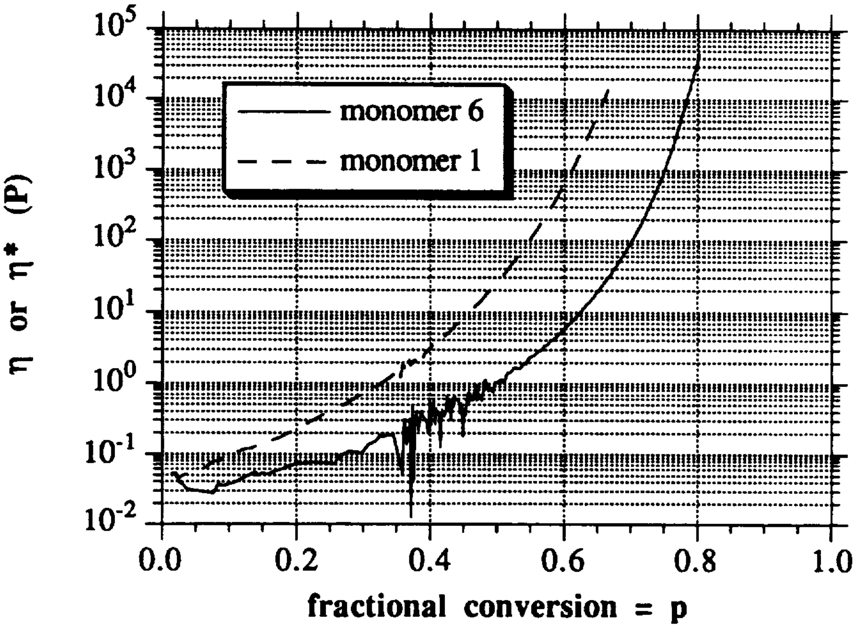


Figure 4.11. Cure of difunctional BCB resin at 200°C, showing gelation.
Measurements at $\omega = 1$ rad/s, hence $\eta^* \approx G''$.

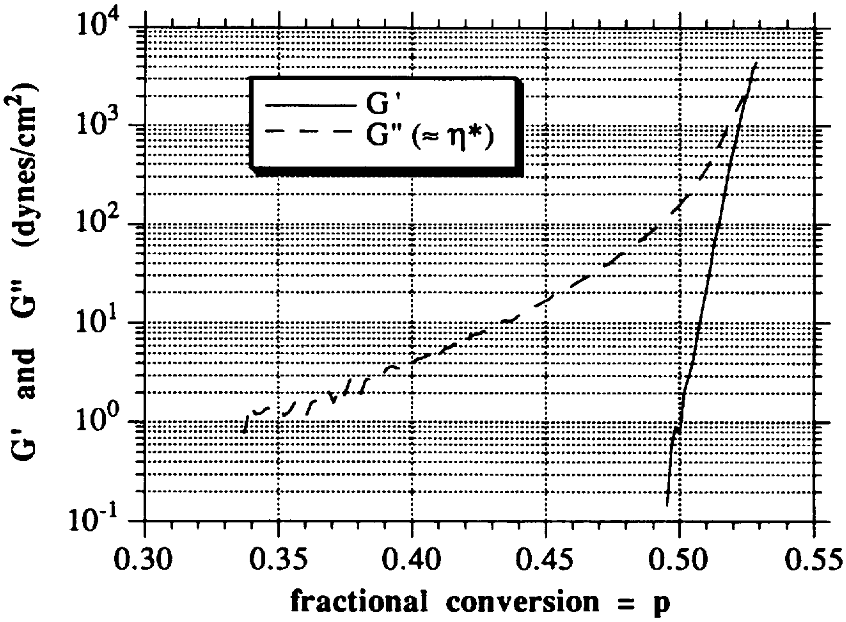


Figure 4.12. Cure of BCB-MI resin at 200°C, showing absence of gelation.
Measurements at $\omega = 10$ rad/s, hence $\eta^* \approx G''/10$.

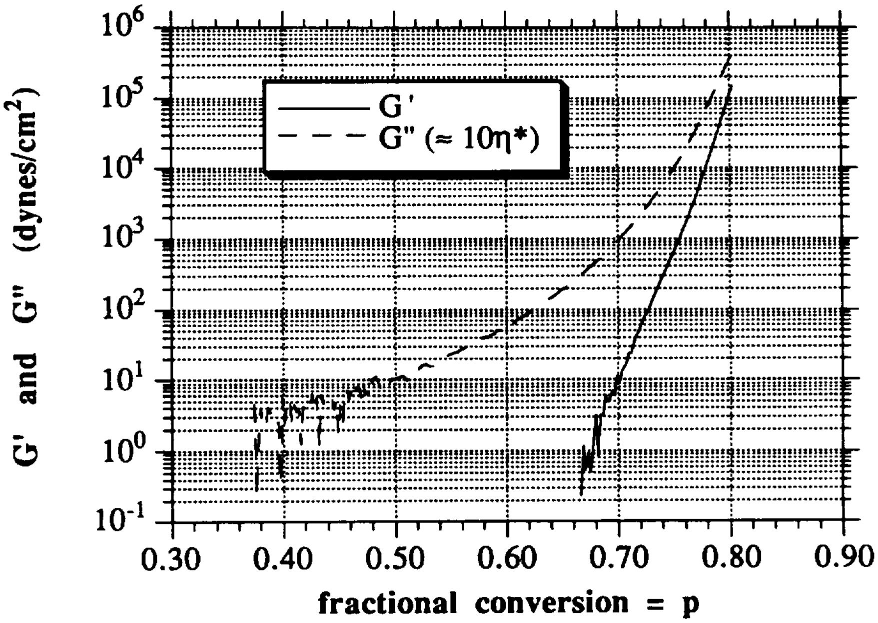


Figure 4.13. Effect of increasing T_g during cure on isothermal viscosity, for BCB-MI monomer 6 at 200°C.

Composite curve: steady shear, $\eta(\dot{\gamma})$ (< 1 P); plus dynamic, $\eta^*(\omega)$ (> 1P)

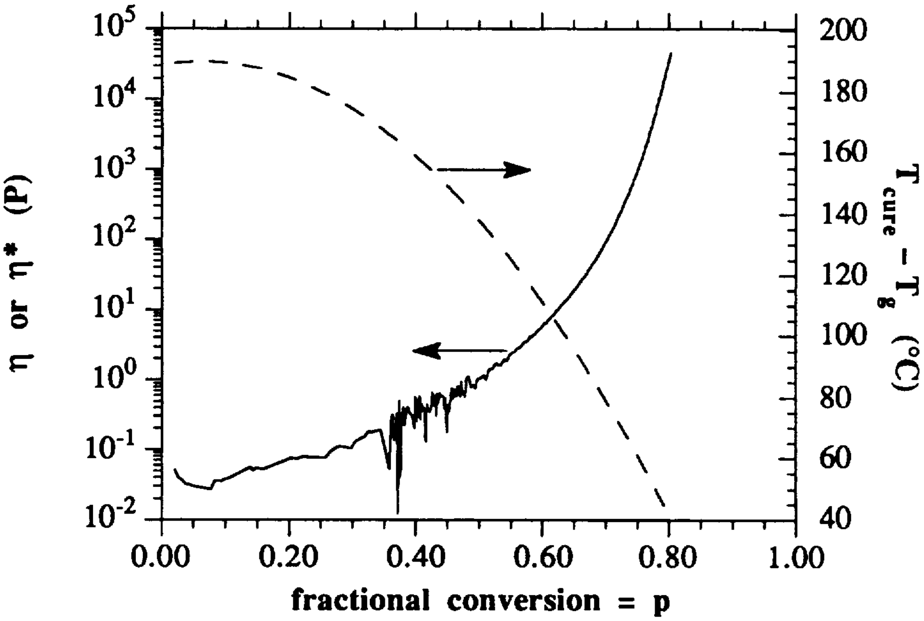


Figure 4.14. T_g versus conversion for BCB-MI monomer 6.

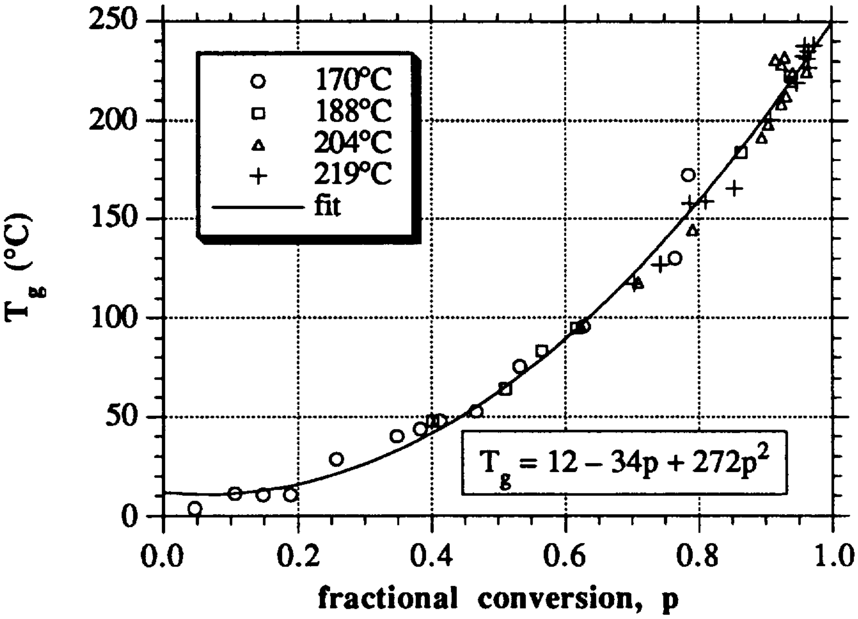


Figure 4.15. Time-temperature-transformation diagram for BCB-MI monomer 6. See text for details.

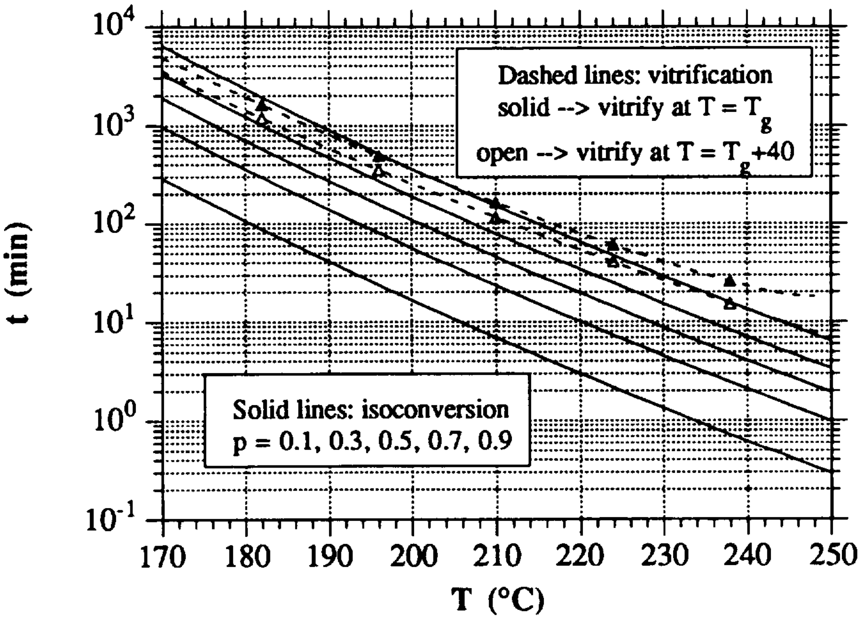


Figure 4.16. Effect of B-stage temperature (172 vs 208°C) on viscosity. Data for monomer 6. Key: B-stage temperature/fractional conversion by SEC.

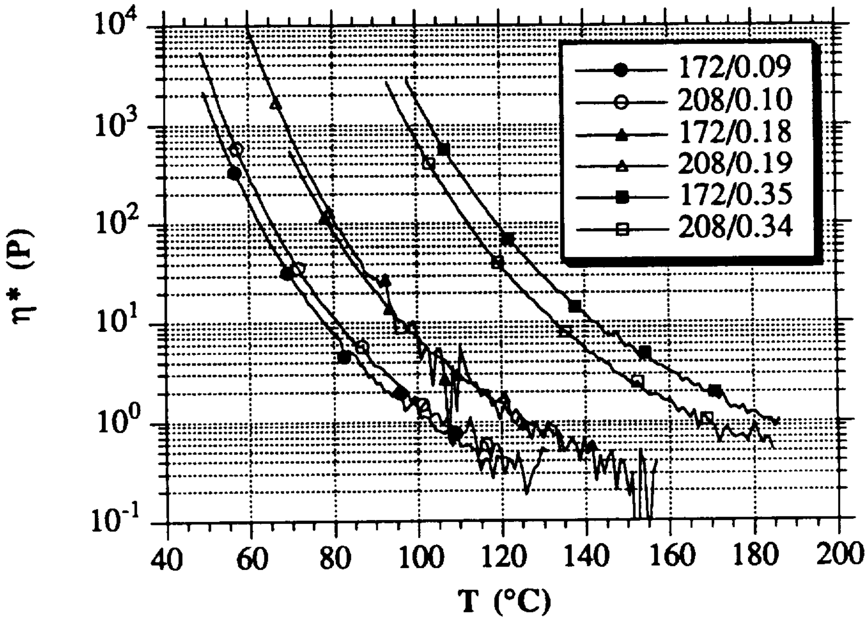


Figure 4.17. Viscosity profiles for B-stage temperature 192°C.
Data for monomer 6. Key: B-stage temperature/fractional conversion by SEC.

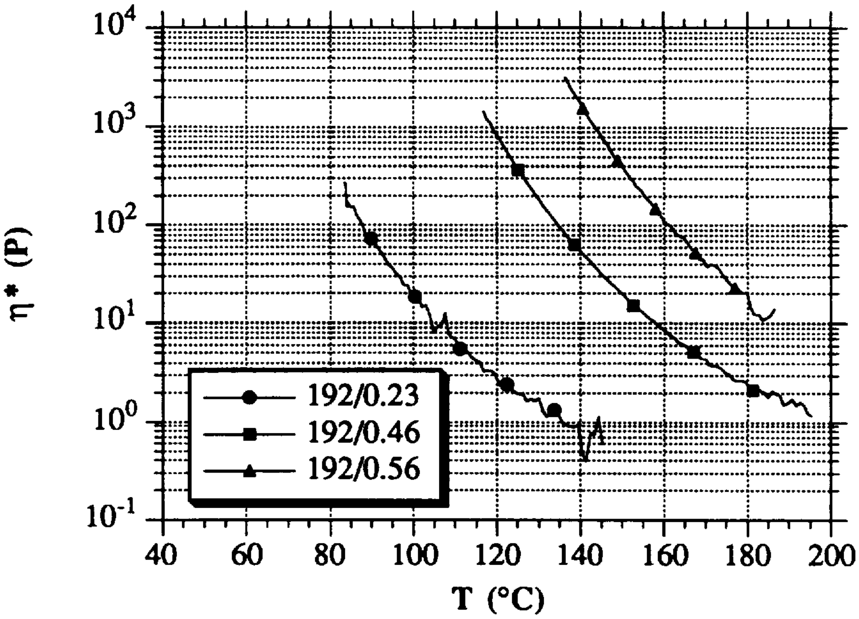


Figure 4.18. Viscosity of monomer 6, vs low conversion B-staged sample.
See text for explanation of fit to monomer data.

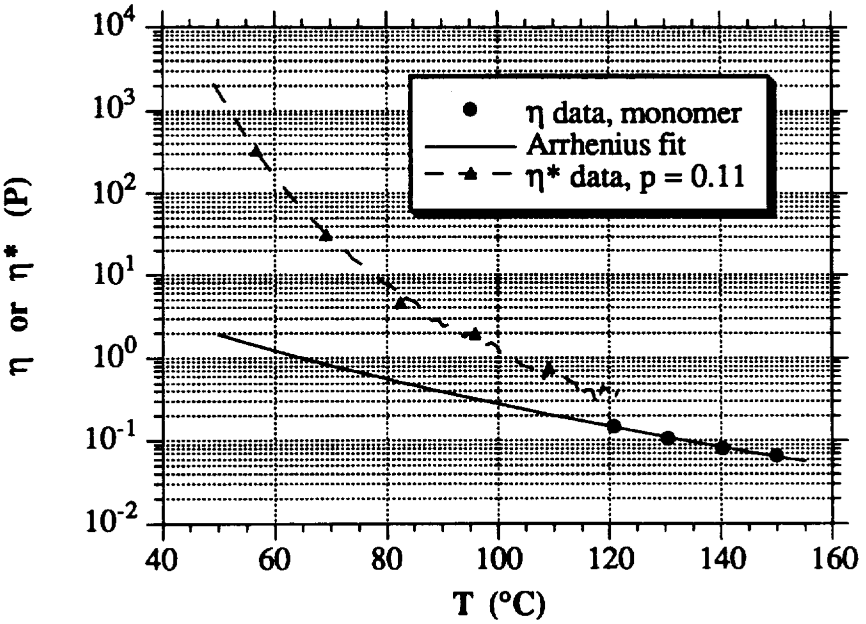


Figure 4.19. Viscosity of B-staged monomer 6 (autoclave processable).
Key: B-stage temperature/fractional conversion by SEC.

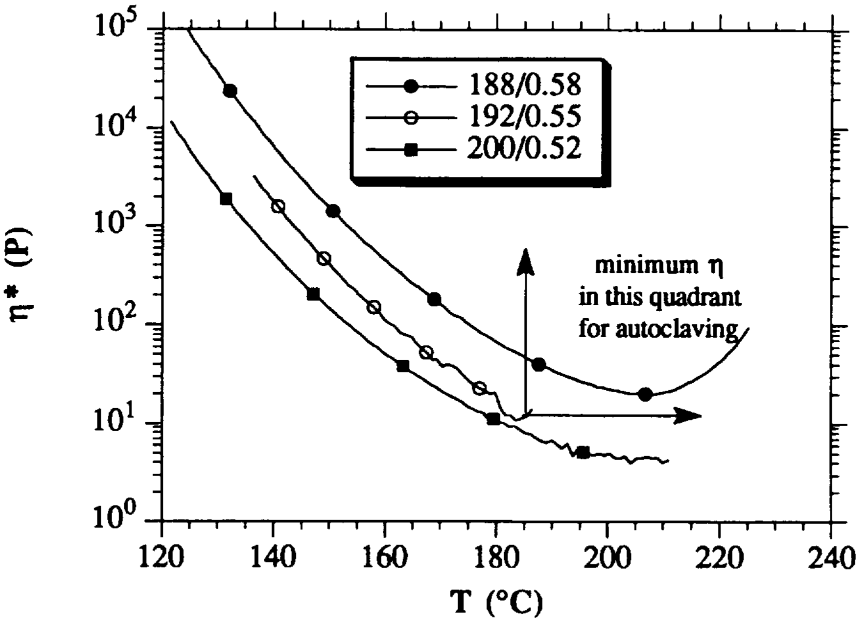
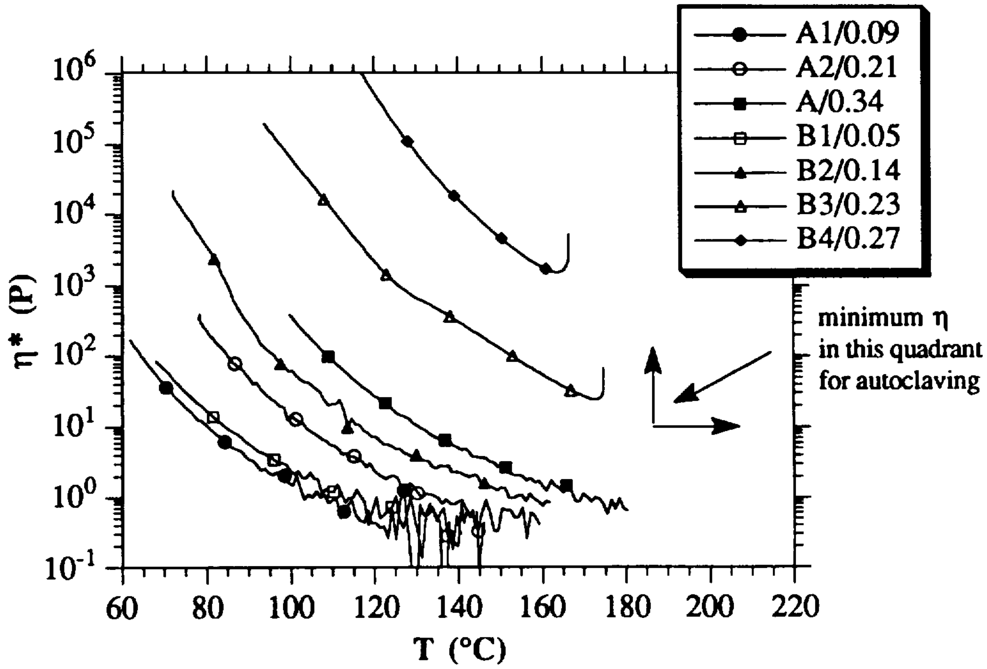


Figure 4.20. Viscosity of blends (monomer 6 + B-staged monomer 6).
Blends An from parent A (p=0.34, also shown). Blends Bn from parent B (p=0.82, not shown).



SECTION 5

TASK 5. CYCLIC OLIGOMERS

The objective of this task is to determine the feasibility of preparing cyclic arylene ether oligomers and their polymerization to high molecular weight, linear polymers.

The catalyzed polymerization of cyclic monomers to high molecular weight, linear polymerization is practiced widely and polymers from oxiranes, tetrahydrofuran, and caprolactam are of commercial importance. These polymers, however, do not have the required properties for advanced composite applications. The recent report by Brunelle, *et. al.*[1] on the preparation of a series of bisphenol A cyclic carbonate oligomers and the polymerization to high molecular weight polymers brings us closer to the vision of fabricating thermoplastic advanced composites via RTM but the material is still deficient in T_g, solvent resistance, and other mechanical properties. Poly(arylene ethers) possess the desired properties and there are scattered reports of the isolation of aryl ether cyclooligomers. Monomers such as 4-chlorophenyl-2-hydroxyphenyl sulfone[2] and a polycyclic spirobiindanediol[3], which are forced to adopt a "bent" configuration, are prone to cyclooligomer formation. Also, cyclooligomers containing biphenyl groups have been obtained from the reductive coupling of aryl halides with $NiCl_2/Zn/Ph_3P$ in dilute solution[4]. Poly(phenylene sulfide) cyclooligomers formed in trace quantities during the preparation of high molecular weight polymers have been isolated[5]. During the past year poly(ether nitrile) cyclooligomers were described in a Japanese patent[6].

5.1 SUMMARY

Preparation of Cyclic Oligomers. Cyclic oligomers whose repeating units contain aromatic ether imide, aromatic ether nitrile, and aromatic ether benzoxazole were prepared and characterized. The best isolated yield obtained was 69% after a reaction time of less than 24 hours.

Polymerization Catalyst. A variety of nucleophilic species was examined as ring opening polymerization catalysts. Cesium phenolate gave the fastest rate but also partially insoluble polymers. The catalyst of choice was cesium fluoride.

Polymerization. None of the cyclic oligomers could be polymerized to high molecular weight, soluble polymers because of their high melting points. However, a mixture of ether imide cyclics and ether sulfone cyclics was successfully polymerized to a block copolymer with short block lengths.

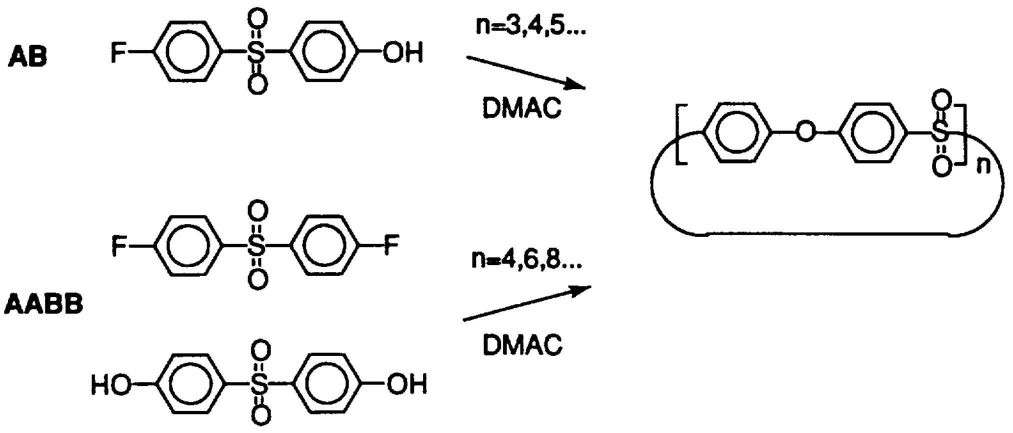
Rheology. The rheology profile as a function of temperature of several cyclic oligomers were studied. It was shown that the arylene ether cyclics would require temperatures of about 350°C or high to reduce their viscosity to ≥ 1000 cps. Since decomposition becomes an important competing reaction at these temperatures, it appeared unlikely that these materials would be suitable for RTM processing. This task was terminated with the approval of the Technical Representative of the Contracting Officer.

5.2. RESULTS AND DISCUSSION

5.2.1. Technical Approach. Our contract work is restricted to those cyclooligomers which were judged suitable for the RTM process and which ring-opened to a high performance matrix. One important resin requirement for adequate composite compressive strength is high modulus. We adopted the value of 450 ksi which has been described by Johnston and Hergenrother[7] as a minimum acceptable value. Also, for the amorphous poly(aryl ethers) under consideration, we arbitrarily set a lower limit for the glass transition temperature of 200°C. The maximum viscosity of the cyclooligomers tolerable for the RTM process is (set rather generously at) ~1000 centipoise (cP). Finally we chose a maximum processing temperature of 300°C. With the above property profile in mind, our next task was to select among numerous candidate structures. Our first consideration was ease of cyclooligomer synthesis and analysis. Relatively simple repeat units with numerous "bent" groups (ethers, m-phenylene, etc.), which favors cyclization over polymerization, were considered first. The properties of the candidate polymers which were not known were estimated using a computer program developed at Dow. The next step was to synthesize the high molecular weight linear polymers using conventional techniques, and determine whether the polymer met our target properties. Cyclooligomers with the same repeat units as the candidates which survived these screens were then synthesized, and the ring-opening polymerization was investigated.

5.2.2. Poly(ether sulfone) and the Corresponding Cyclooligomers. Prior to the introduction of this task into the contract, there had been a considerable internal research effort on the ether sulfone system. Some of our IR&D results are included in this report to help clarify the reasons for the technical work done under the contract.

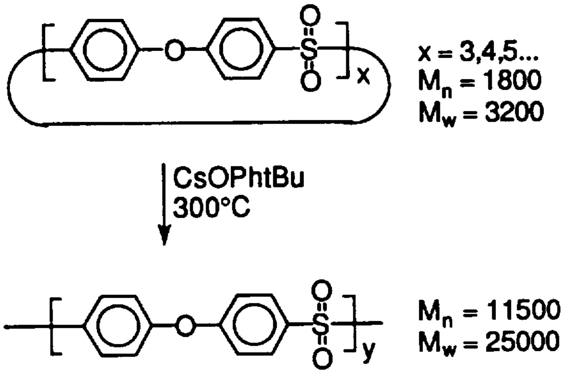
Poly(ether sulfone) -- Cyclooligomer synthesis. With a proper choice of process conditions, aryl ether cyclooligomers are surprisingly easy to prepare. Two methods for the preparation of cyclooligomers of poly(ether sulfone) are shown below. Even membered cyclooligomers with 4 or more repeat units are obtained when the AABB starting materials are used. A mixture of even and odd cyclooligomers (n = 3,4,5...) can be obtained from the AB monomer[8]. These reactions are best conducted by adding the monomer (or monomers) continuously to a suspension of K_2CO_3 in dimethyl acetamide (DMAC) at temperatures from 130° to 140°C. At temperatures greater than 140°C the cyclics undergo cleavage reactions, and the yield is reduced. Typical yields of isolated product are a function of the M_n desired: M_n 2040, 43% yield; M_n 3200, 75% yield. An analysis of the liquid chromatogram of the crude product before workup by liquid chromatograph is shown in Figure 5.1. Individual cyclooligomers with 3 and 4 repeat units have been isolated and thoroughly characterized. The individual cyclooligomers are extremely high melting solids (trimer, 447°C; tetramer, >450°C). Despite this, the crude mixture is amorphous, and begins to flow at ~230°C.



There are numerous factors which determine the yield of cyclooligomer relative to linear polymer. The primary consideration is to maintain the concentrations of electrophilic and nucleophilic ends as low as possible. This is best done by slow addition of starting materials, maintenance of the correct stoichiometry, and choosing conditions where the displacement reaction is as fast as possible (high temperatures, use of fluoride instead of chloride). The process to prepare ether sulfone cyclooligomers was studied extensively. The rates of displacement and cyclization of the various species with 5 and fewer repeat units have been obtained. Although it is beyond the scope of this report to discuss these data in detail, we reached some important conclusions about this chemistry which apply to the other cyclizations and also to the commonly used aromatic nucleophilic displacement processes to prepare high molecular weight poly(aryl ethers).

Most importantly, it is necessary to reduce the concentrations of water to the lowest possible levels. Water is harmful in several ways. The rate of displacement is decreased by several orders of magnitude when significant levels of water are present. This is particularly detrimental to the yields of cyclooligomers. In addition to lowering the rate of these reactions, we have found that water slowly converts the aryl fluorides to phenols, resulting in a stoichiometric imbalance. Analyses by HPLC of aliquots taken during the cyclization process show that the linears with two phenolic ends predominate when the reaction is insufficiently dry. The formation of cyclics gradually halts as the ratio of aryl fluoride to phenolics drops to zero. We attribute this to nucleophilic attack by hydroxide on the aryl fluoride. Finally, it is critical to perform the cyclizations in such a way that the concentration of low molecular linears is small at the end of the reaction. These linears, which are difficult to separate from the cyclooligomers, limit the ultimate number average molecular weight attainable on ring opening polymerization.

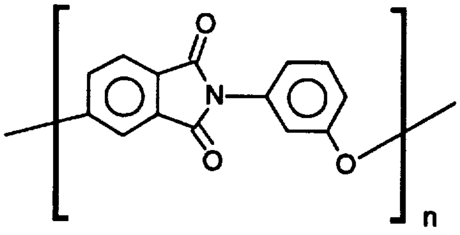
Ring-opening polymerization of ether sulfone cyclooligomers. These cyclooligomers can be induced to polymerize in the melt in the presence of catalysts which reversibly cleave the activated carbon-oxygen bonds joining the rings. A similar reversible nucleophilic aromatic substitution process has been proposed as the mechanism for randomization of block poly(ether sulfone ketone) copolymers[9].



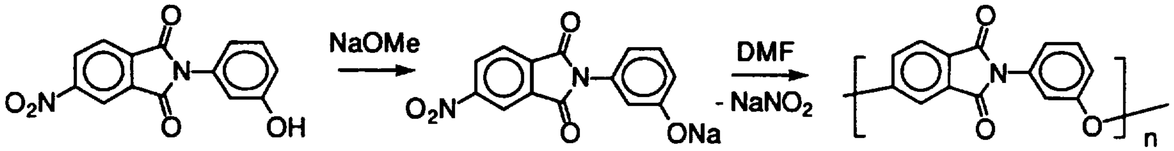
A variety of catalysts, particularly phenoxides and fluorides, may be used. It is also possible to titrate the residual phenolics with hydroxide, converting them to phenoxides. When the concentration of residual linears is low it is possible to achieve reasonably high molecular weights (M_n

11,500, M_w 25,000). For comparison, the molecular weight of Victrex® PES 3600 as determined by gel permeation chromatography under identical conditions is: M_n 10,500, M_w 24,000.

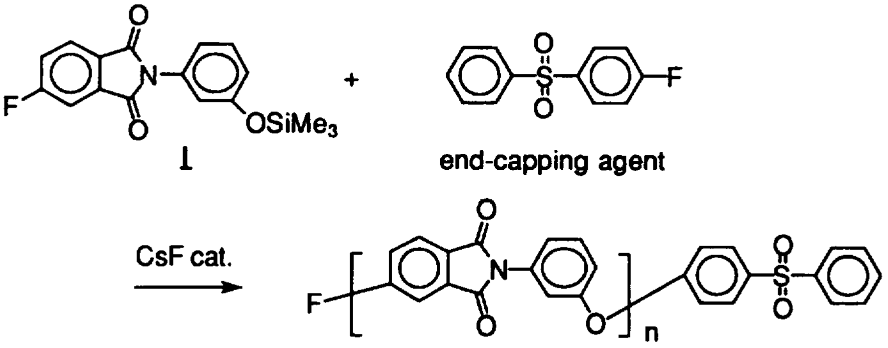
5.2.3. Poly(ether imide) and the Corresponding Cyclooligomers. The poly(ether imide) with the structure shown below was chosen for several reasons. Based on the known mechanical properties of Ultem® and other phthalimide polymers, this polymer should have properties which meet the targets set initially. An computer based estimate predicted that the tensile modulus would be 500 ksi, with a T_g of 229°C. For comparison, this same program predicts a tensile modulus of 477 ksi and a T_g of 215°C for Ultem®. Another attractive feature of this structure is that the displacement kinetics for leaving groups attached to phthalimide rings are particularly fast[10], which should favor cyclooligomer formation.



Synthesis of high molecular weight poly(ether imide). In keeping with the strategy stated in our work statement, out first task was to synthesize the high molecular weight polymer and determine whether further effort was justified. There are two reports[11, 12] of the synthesis of a low molecular weight polymer with this structure using the chemistry shown below.

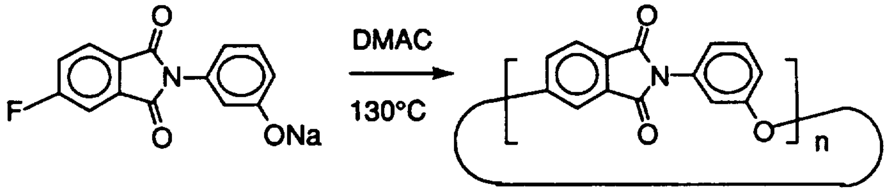


We were unable to increase the molecular weight above that reported using this chemistry. Several variations were tried, such as replacement of the nitro group with fluorine and the use of K_2CO_3 in place of the NaOMe, but little improvement was observed (η_{inh} < 0.20 dL/g in DMAc at 25.0°C). The reasons for this are unclear, but a contributing factor is the formation of a surprising high percentage (~5-10%) of cyclooligomers. The use of polymerization chemistry first described by Kricheldorf[13] was more successful (see the scheme below). This condensation polymerization is conducted at high temperatures (330°C), optionally in the presence of a high boiling solvent, such as diphenyl sulfone. In contrast to the above mentioned problem of too low a molecular weight, we needed to add an end-capping agent to reduce the molecular weight typically obtained using the high temperature method. In the example below, a monofunctional aryl fluoride is used for this purpose.



We managed to compression mold a tough, clear, void free film (0.030" thickness) from this poly(ether imide). The mechanical properties were determined from microtensile bars which were machined from the film. This polymer has a high tensile modulus (548±11 ksi), much higher than Ultem® (459±8 ksi), which was tested at the same time using the same specimen dimensions. The glass transition temperature (209°C) will allow this material to be used at high temperatures while still allowing it to be melt processed at reasonable temperatures. This combination of excellent mechanical properties and solvent resistance make it well suited for composite applications.

<u>Synthesis of ether imide cyclooligomers</u>. The conditions we chose were similar to the conditions used for ether sulfone cyclooligomers. To summarize the results of many experiments, our best process was to slowly add a solution of the sodium salt of the AB monomer to hot DMAC as shown below.



This cyclization proceeds more quickly and in better yield than we obtained for ether sulfone cyclooligomers. In less than 24 hours a 69% isolated yield of product (16 g) was obtained using 750 mL total solvent. The remainder of the product is high molecular weight polymer, which is probably linear.

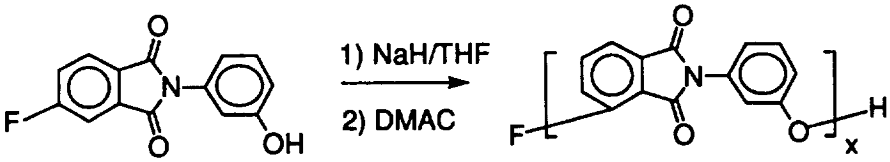
The analysis cyclooligomer mixtures is difficult. We approached this problem using a combination of methods. First, the two smallest cyclooligomers ('n' = 3 and 4) were isolated and characterized. Mass spectroscopy is particularly useful, as the cyclic structure causes the proportion of parent ion to be unusually high. Secondly, we developed an NMR method for analysis of residual phenolic and aryl fluoride groups, which allows us to determine the ratio of repeat units to end-groups in the product. Finally, gel permeation chromatography (GPC) in NMP was used to obtain relative molecular weights. We have occasionally had problems with unusually sharp high molecular weight peaks in the GPC analysis which we attribute to aggregation of charged groups (salts of amic acids?) in the backbone of the polymers. This was overcome by adding low levels of LiCl to the NMP eluent.

As is the case with ether sulfone, the individual cyclooligomers are extremely high (>400°C) melting crystalline solids. The challenge was to isolate an amorphous mixture of cyclooligomers from the mixture of linear products. The high molecular weight (Mw > 4000) products are efficiently removed using selective solvent precipitation. Low molecular weight linear impurities are much more difficult to remove. We therefore adjusted our process conditions to minimize the concentrations of low molecular weight linears to acceptably low levels. This was done using the techniques which were effective for ether sulfone, namely extreme care in reducing the concentration of water and dimethyl amine in the DMAC used as solvent.

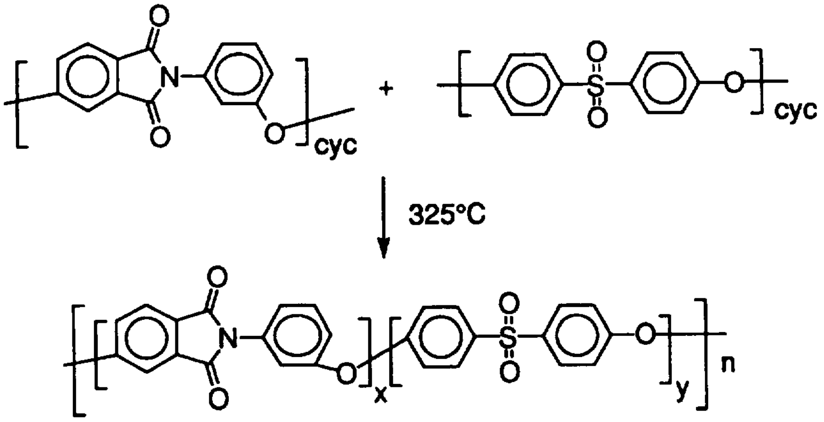
Similar to our experience with ether sulfone cyclooligomers, the fraction soluble in CH_2Cl_2 contained subtantial amounts of residual salt (1.1% sodium), despite several water washings. The presence of inorganic salt was found to cause premature polymerization of cyclooligomers at elevated temperatures. It was possible to reduce the sodium level to 100 ppm simply by quickly passing the solution through a column ion exchange beads (Dow MSC-1H, crosslinked sulfonated polystyrene in the acid form). This procedure also works well on the DMAC solution in which the cyclooligomers are synthesized. The sodium ion concentration in the solids obtained after evaporation of the DMAC solution was reduced from more than 7 wt% to 120 ppm. We also succeeded in reducing the amount of linear contaminants to tolerable levels. According to our ^1H and ^{19}F NMR analysis, the molar ratio of ether imide repeat units to phenolic and fluoride ends is >100, indicating that the ultimate M_n achievable on polymerization should be >20,000.

Ring-opening polymerization of ether imide cyclooligomers. The ring-opening polymerization was investigated next using cesium phenoxide (1 wt %) and other catalysts at temperatures up to 350°C. In all but one case, which could not be reproduced, incomplete reaction occured. Analysis of the products by HPLC showed that a portion of the predominant cyclooligomer in the starting mixture ('n' = 3) remained in the product. Wide angle X-ray diffraction was used to show that this particular cyclooligomer crystallized selectively from the melt of the amorphous mixture.

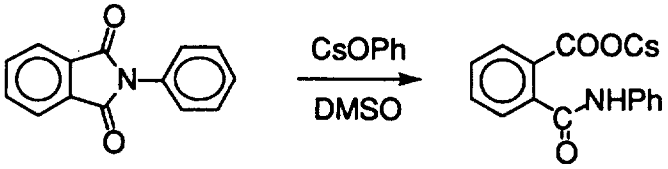
Three methods were tried to overcome this problem. The first method was to synthesize a low molecular weight (M_n~2000) AB oligomers which would serve both as a catalyst for ring opening and as a melting point depressant. The molecular weight was controlled by using a slight deficiency of base (NaH). The M_n was measured by two NMR techniques. First, the ratio of aryl fluoride to number of repeat units was quantified by ^{19}F NMR, which gave an M_n of 1955±200. The oligomers were then acetylated, and the ratio of acetates to repeat units was measured by ^{1}H NMR, which gave a similar M_n of 1965±200. This mixture of linear oligomers was then converted to the sodium salt with NaH, and mixed in with the cyclooligomer mixture in a 10/90 (w/w linear/cyclic) ratio. Although the linear oligomers were useful as catalysts for the ring-opening process, they did not prevent the crystallization problem.



A second method which was more successful was to use a mixture of ether imide and ether sulfone cyclooligomers. Somewhat surprisingly, the lower ether imide cyclooligomers do not crystallize from a 50/50 (w/w) mixture. A reasonably high molecular weight block copolymer results (η_{inh} 0.54 dL/g in NMP) which contains no residual cyclooligomers as indicated by gel permeation chromatography (M_w 28,000; M_n 8,700; narrow polystyrene standard, NMP solvent). The cyclooligomers were heated to 325°C for 30 minutes using CsF as catalyst (1.0 mole%, ~0.08 wt % fluoride).



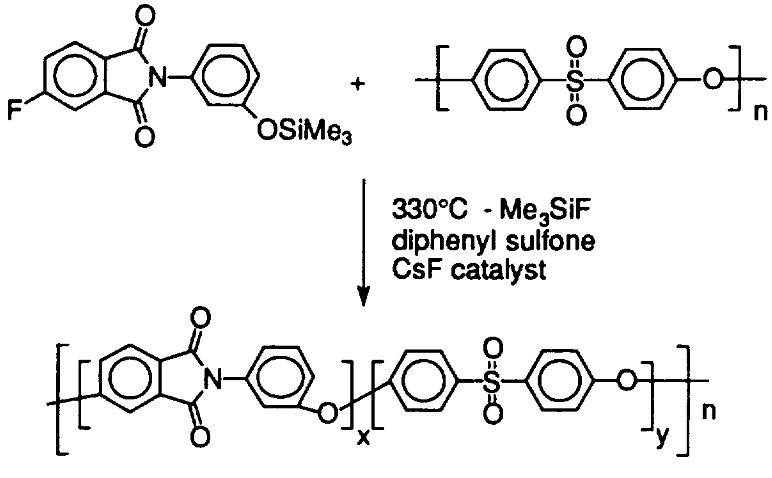
The use of cesium phenoxide as catalyst gave fast polymerization rates, but produced a product which was partially insoluble in DMAC. In order to determine the source of this insolubility, we have investigated the model chemistry shown below. Approximately 75% of the starting material was converted to the amic acid after an hour at room temperature, and none of the anticipated phenyl ester was produced.



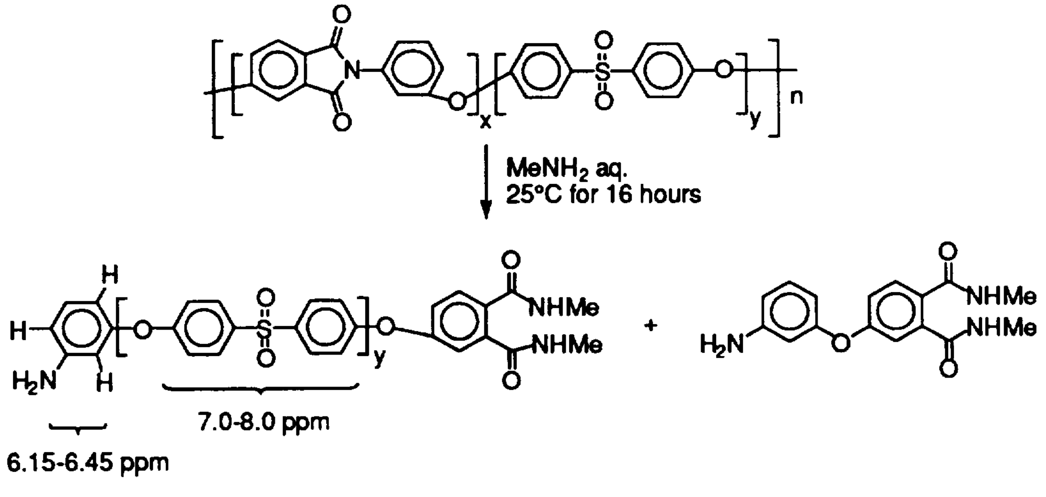
This result indicates that traces of water can exchange with the phenoxide, producing hydroxide which quickly attacks the phthalimide. When CsF is added in place of CsOPh, no reaction was observed. Finally, no reaction occurred when phenyl phthalimide was treated with NaOPh prepared from NaH and phenol in tetrahydrofuran. These results lead us to suspect that the insolubility we observe when the cyclooligomer mixtures are polymerized with phenoxide is the result of ionic aggregation of polyamic acid salts. If this is true it is probably not a serious problem. In any case a small amount of crosslinking may be acceptable and perhaps even desirable for composite applications.

We were concerned that the block copolymer would not have sufficiently good properties to meet the criteria previously stated. Relatively large quantities of polymer were required for testing. Rather than scaleup the cyclooligomer synthesis, we sought to synthesize the polymer independantly and measure the mechanical properties. Although it would have been simple to prepare a random copolymer from a mixture of the AB monomers, we were concerned that the block copolymer would have different properties. Poly(aryl ether) block copolymers are surprisingly rare[14]. It is known that the high temperature melt processes commonly used induce ether-ether exchange reactions which result in random copolymers[15].

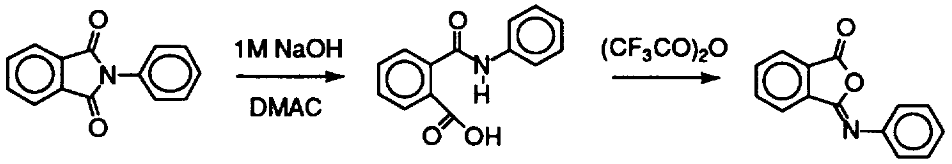
The method shown below was successfully used. We speculate that the initial reaction is a homopolymerization of the AB ether imide monomer, which is complete in a few minutes. Ether-ether interchange between the poly(ether imide) and the poly(ether sulfone), which produces a block copolymer, occurs more slowly during the 60 minute reaction. The properties of the copolymer product from our best run are shown in Table 5.1. Data which we have determined for Ultem® are shown for comparison. The molecular weight is not optimum, as evidenced by the 0.28 dL/g inherent viscosity (0.5 dL/g at 25°C in CH_2Cl_2). Nevertheless, the properties are quite good, and our original target properties (>450 ksi tensile mod., >200°C Tg) are met by this copolymer.



We were interested in confirming that the products from the ring-opening polymerization of the mixture of cyclooligomers and the melt polymerization were indeed block copolymers. Also, we have observed in previous work that the mechanical properties of block copolymers are often different from the weighted average of the properties of the parents[16]. The ^{13}C NMR spectra suggest block lengths for both product polymers of 5-10 repeat units, but a more accurate determination was not possible. We next attempted to degrade the phthalimide groups and leave a short poly(ether sulfone) segment terminated by the fragments from the imide. Attempts to do this with hot aqueous hydroxide or acid were not completely successful. The method which worked surprisingly well was overnight treatment with aqueous $MeNH_2$ at room temperature, as shown below. From the ^{1}H NMR it was possible to determine that the number average block length of the poly(ether sulfone) from the mixture of cyclooligomers was 3.9 repeat units, while that from the Kricheldorf synthesis was 6.4.

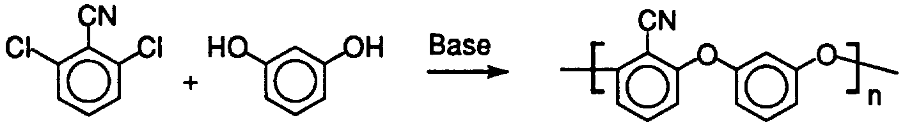


One other method for overcoming the cyclooligomer crystallization problem was briefly investigated. If a portion of the imide groups could be isomerized to isoimides, perhaps the tendency for crystallization would be reduced. It is known[17] that isoimides thermally isomerize to the more stable imides. This chemistry was investigated using the model shown below.



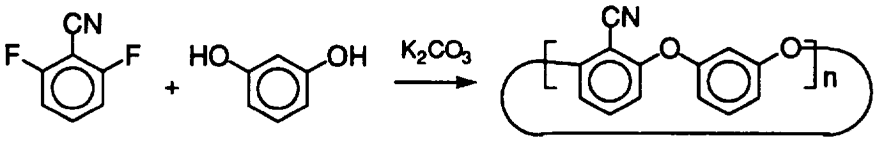
The hydrolysis of N-phenyl phthalimide proceeds quickly at room temperature. After acidification the amic acid can be isolated in nearly quantitative yield. Trifluoroacetic anhydride worked best for the ring closure to the isomide[18]. The hydrolysis of the ether imide cyclooligomer with 4 repeat units proceeds cleanly as evidenced by a single HPLC peak. Our attempts to reclose the resulting amic acid to the imide or the isoimide using conditions which have been applied to our model have resulted in complex mixtures. Work on this process was abandoned as the data from parallel plate rheometry indicated that the viscosity of the cyclooligomer melts would be too high for resin transfer molding.

5.2.4. Poly(Ether Nitrile) and the Corresponding Cyclooligomers. Unlike the other polymers considered for our program which were new compositions, the poly(ether nitrile) is a semi-commercial polymer prepared using the displacement process shown . The properties of the



polymer are described in a patent assigned to Idemitsu[19]: T_g 148°C, Tm 340°C, tensile modulus 437 ksi. Although the tensile modulus claimed for this polymer is slightly lower than our target (450 ksi) this polymer appeared suitable for our purposes.

In addition to the desirable polymer properties, we suspected that cyclooligomers would readily form due to the flexible backbone. This was indeed the case although the process conditions were

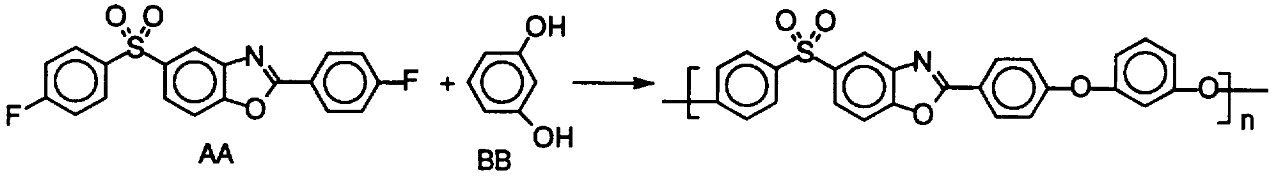


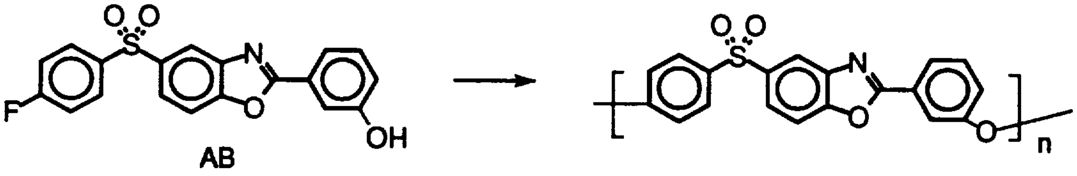
critical to obtaining cyclooligomers in reasonable selectivity. It was found that temperatures above 150°C caused the initially formed cyclooligomers to ring open to high molecular weight polymer. This detrimental process also occurred much more readily when the diol was present in slightly greater than stoichiometric amounts. This was avoided by using a slight excess (0.5 to 1 mole%) of the difluoride. In the HPLC trace (Figure 5.2) the largest peak is the cyclooligomer with 3 repeat units. Individual cyclooligomers with 3 and 4 repeat units have been isolated and thoroughly characterized. The individual cyclooligomers are extremely high melting solids (trimer, 447°C; tetramer, >450°C). Despite this, the crude mixture is amorphous, and begins to flow at ~230°C.

As in all of these syntheses, we first proceeded to isolate and characterize the smallest individual oligomers. This was done for the cyclooligomers with 3 (cPEN3) and 4 (cPEN4) repeat units. These crystalline solids had surprisingly poor solubility in a number of solvents, and had very high melting points (cPEN3: 451°C, cPEN4: 397°C). Mixtures were isolated which appeared to melt at 350°C. In the presence of various catalysts (CsF, $PhONa{\cdot}3H_2O$) ring opening polymerization occured as evidence by disappearance of the cyclooligomers. The product polymers were crosslinked, as evidenced by insolubility and swelling in hot p-chlorophenol. In order to determine if this crosslinking occurs as a result of ring-opening, or whether it is an inherent problem with this backbone, we prepared the high molecular weight linear polymer using conventional methods. This polymer is soluble in p-chlorophenol. Surprisingly, the polymer was insoluble in the same solvent after 30 minutes of heating to 350°C without added catalyst in a nitrogen atmosphere. It does not appear that the observed insolubility is the result of crystallization. This result was certainly unexpected for a semi-commercial thermoplastic intended for injection molding applications. Such molding processes must be conducted at temperatures higher than the crystalline melting point of the polymer (340°C). A possible explanation is that the crosslinking reaction is the result of trace impurities in the sample we prepared. We have unfortunately not been able to obtain a sample of the polymer from Idemitsu to test this theory. However, a recent patent[20] claimed that aryl nitriles incorporated in poly(ether imides) tend to undergo crosslinking reactions at temperatures as low as 110°C.

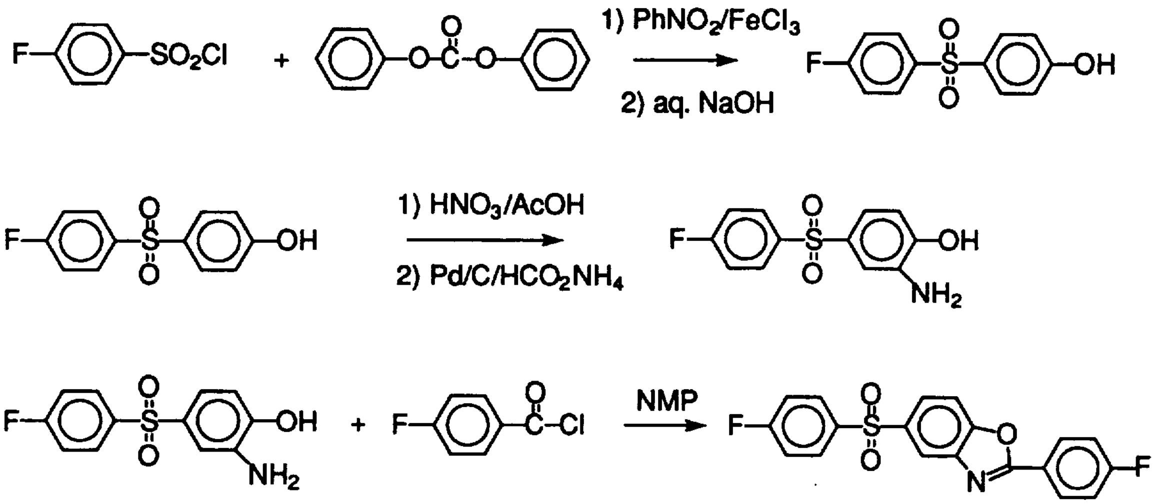
5.2.5. Poly(ether sulfone benzoxazoles) and the Corresponding Cyclooligomers.

Two benzoxazole containing polymers were chosen for inclusion in this program. We have had some experience from IR & D work with the preparation of related polymers using displacement chemistry, and have found that the mechanical properties are quite good. Each of these backbones were submitted to our polymer modelling group for property prediction. The results from the computer program were not as favorable as we expected with regard to T_g (AABB: 181°C, AB: 197°C) and tensile modulus (AABB: 392 ksi, AB: 425 ksi). This program had never been applied to benzoxazole containing polymers, and we therefore decided to be optimistic and proceed.





Our first order of business was to prepare the linear polymers, determine the properties, and decide whether these backbones would be suitable. The monomer synthesis is outlined below. The AB monomer was prepared in a similar fashion, with the exception that the p-fluorobenzoyl chloride used in the last step was replaced with p-methoxybenzoyl chloride, and the methoxy group was converted to a hydroxyl group with HBr.



After numerous attempts, a high molecular weight (η_{inh} 0.40 dL/g) sample of the AABB poly(ether benzoxazole) (shown in Figure 20 above) was prepared. The key to success was rigorous monomer purification and use of the "Kricheldorf" method in which the diol was converted to a silyl ether. A tough, clear, void free film was compression molded at 310°C from this polymer. A microtensile bar machined from the film was tested along with similar specimens of Ultem®. The properties from 4 specimens are as follows: tensile modulus 429±10 ksi, elongation 11±2%, tensile at yield 13.3±0.2 ksi, T_g 210°C. The corresponding properties for Ultem® were (502±4 ksi, elongation 8%, tensile at yield 15.5 ksi.

After our experience with the poly(ether nitriles) we also examined the thermal stability of the polymer. The powder isolated by precipitation is stable for 30 minutes at 300°C, but becomes insoluble after 30 minutes at 350°C. The compression molded film was mostly soluble after 30 minutes at 350°C. The AB polymer was prepared using a similar procedure. The polymer did not flow at temperatures as high as 400°C during compression molding. Although the reasons for this are unclear, this polymer was abandoned.

We felt that the AABB polymer properties were sufficiently promising to proceed with the synthesis of the corresponding cyclooligomers as shown in the figure below. We used our standard procedure of slow addition of the monomers to a hot suspension of K_2CO_3 in NMP. The isolated mixture of cyclooligomers appears to be amorphous, showing a broad T_g from 200-230°C in the DSC scan. HPLC trace of the product is shown in Figure 5.3. Initial experiments to polymerize these cyclooligomers were not been successful due to incomplete reaction or crosslinking. As we developed plans to investigate these problems further, viscosity determinations on the ether sulfone cyclooligomers indicated that they were more viscous than we had hoped. Further work on the ring-opening polymerization was abandoned in favor of synthesizing sufficient cyclooligomer for parallel plate rheometry. The results are discussed in the following section.

5.2.6. Melt Viscosity. As we developed a process which gave multigram quantities of amorphous mixtures of the ether sulfone cyclooligomers, they were examined by parallel plate rheometry. Data for several different batches of ether sulfone cyclooligomers are shown in Figure 5.4. The differences in viscosity correlates reasonably well with the M_w as measured by GPC: batch 1: 2550, batch 2: 4040, batch 3: 4000, batch 4: 3900, batch 5: 3530. This data indicates that the best sample does not meet our viscosity goal of 1000 cP (10 P) at 300°C, which we have chosen as an upper temperature limit for processing. Note that these cyclooligomers are substantially less viscous than commercial poly(ether sulfone) (ICI Victrex® 3600 and 5200), which exhibit complex viscosities ranging from about 100,000 to 500,000 P at 300°C at the identical shear rate. Another difference is that the cyclooligomers are Newtonian fluids (viscosity independant of shear rate), whereas the linear polymer viscosity drops with increasing shear.

The graph in Figure 5.5 compares the melt viscosity of three cyclooligomer samples (cPES: cyclo(ether sulfone) M_w 2550, cPESB: cyclo(ether sulfone benzoxazole) M_w 1860, and cPC: cyclocarbonate) M_w 1370. The cyclocarbonate sample was prepared using a method identical to that described by Brunelle, et al[21]. The data shown in the above graph were fitted to a Williams-Landel-Ferry (WLF) type equation[22]. The results of this fit are the lines between the points in the graph. The WLF equation (a simplified version is shown below) usually works quite well in describing the temperature dependence of rheological properties of glasses (both polymeric and non-polymeric) above Tg. In this formula $\eta^*(T)$ is the complex viscosity at a given temperature T, η^*_0 is the complex viscosity at a reference temperature T_0, and c_0^1 and c_0^2 are fit parameters. The value T_0, which roughly corresponds to a calculated glass transition temperature, was also adjusted for an optimum fit.

$$\eta^*(T) \approx \eta_0^* \cdot \exp\left\{\frac{-c_1^0(T-T_0)}{c_2^0+T-T_0}\right\}$$

Briefly, this formula suggests that the viscosity of a fluid is a function of the difference between the given temperature and the glass transition temperature. With this in mind, the data in Figure 5.6 was replotted with a horizontal axis which represents temperature above the T_g of the polymer.(cPC: 150°C; cPES: 230°C; cPESB: 210°C). The carbonate cyclooligomers reach 1000 cP (10 P) at ~250°C ($T-T_g=100$°C). The temperature above Tg at which the cPES and cPESB samples achieve the same viscosity is only slightly higher (cPES: 125°C, cPESB: 140°C). These curves are quite similar, especially given the differences in M_w of the samples. If this line of reasoning is correct, one can conclude that our target viscosity will be achievable at a temperature of about 140°C above the T_g of the cyclooligomers, which is similar to the T_g of the polymer. The combination of a minimum T_g of 200°C and a maximum processing temperature of 300°C will be difficult to achieve. The tendency for the smallest cyclooligomers to crystallize from the melt makes it difficult to lower the M_w of the mixture substantially in order to circumvent this problem. One possibility still open is to prepare a relatively low T_g cyclooligomer which ring-opens to a crystalline polymer. This might make it possible to achieve a high composite use temperature. The poly(ether nitrile) is an example, which unfortunately didn't succeed for other reasons.

5.3. CONCLUSION

We have gathered compelling evidence that it may not be possible to use poly(aryl ether) cyclooligomers as resins for the fabrication of high performance composite part using an RTM fabrication technique. The low melt viscosity required demands that the resin be of very low molecular weight. The lowest molecular weight cyclooligomers of all of the backbones we have synthesized have extremely high melting temperatures and a strong tendency to crystallize from a molten mixture. This crystallinity problem sets a lower limit on the molecular weight of a mixture which melts at a useful temperature. Still, we can't rule out the possibility that a low melting, low viscosity cyclooligomer exists. Discovery of such a cyclooligomer would be the result of a trial and error effort, as it is presently impossible to predict the melting points of organic materials with useful accuracy. A complicating factor is the tendency of some of the cyclooligomers to crosslink during ring-opening polymerization.

During the course of this investigation we have demonstrated the synthesis of a high molecular weight poly(ether imide) from commercially available starting materials with surprisingly good mechanical properties. Also, we have uncovered a new method for the preparation of poly(aryl ether) block copolymers which may have utility.

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5.5. EXPERIMENTAL

General Information. NMR spectra were obtained on a Varian VXR-300 spectrometer. Differential scanning calorimetry (DSC) was performed using a DuPont Model 2910 DSC equipped with a model 2100 controller using a nitrogen atmosphere. Glass transition temperatures (Tg's) were measured at the inflection points. Chemicals were purchased from Aldrich Chemical Co. unless otherwise noted. Solvents, N-methyl-2-pyrrolidinone (NMP), N,N-dimethylacetamide (DMAC), N,N-dimethylformamide (DMF) and tetrahydrofuran (THF), were purchased from Fisher Scientific. Gel permeation chromatography was performed on a Hewlett-Packard model 1090 liquid chromatograph equipped with a Polymer Laboratories PLgel 5μm Mixed-D (400K) 300 x 7.5 mm column using; 80% CH_2Cl_2 / 20% NMP (v/v) eluent; flow rate = 1.00 mL/min; detection via diode array detector, main signal at $\lambda = 265$ nm (bandwidth 4 nm) referenced to 550 nm (bandwidth 100 nm). The molecular weights reported are relative to narrow polystyrene standards for the poly(ether imide) and poly(ether nitrile) samples. For the others, molecular weights relative to polycarbonate were obtained via the following procedure. First, the column was calibrated with narrow molecular weight polystyrene standards ($526 \leq M_p \leq 8.5 \times 10^6$). Since these standards include both the void and exclusion limits of the column, a stepwise calibration curve was used to best cover the entire range, to pick up the curvature at the ends of the calibration curve, without introducing spurious curvature (e.g., from a polynomial fit) into the central linear region of the calibration curve. This polystyrene-based calibration curve was then transformed using a broad polycarbonate standard (Lexan® 101-112-38FW: $M_n = 12000$, $M_w = 30000$, $M_z = 45600$).

Preparation of 4-fluoro-N-(3-hydroxyphenyl)phthalimide. A mixture of 4-fluorophthalic anhydride (16.61 g, 0.10 mole, from Occidental Chemical Corp.), m-aminophenol (10.91 g, 0.01 mole) and glacial acetic acid (150 mL) was heated to reflux under a nitrogen atmosphere. A precipitate formed initially which soon dissolved. After 16 hours of reflux the solution was allowed to cool. A precipitate formed which was filtered and washed twice with water (100 mL), and three times with CH_2Cl_2 (100mL). The white crystalline solid was then dried in a vacuum oven at 150°C overnight (23.51 g, mp 236-238°C, 90.1% yield).

Preparation of 4-fluoro-N-(3-trimethylsiloxyphenyl)phthalimide. A mixture of 4-fluoro-N-(3-hydroxyphenyl)phthalimide (10.0 g, 39 mmoles) and 1,1,1,3,3,3-hexamethyldisilazane (23 g, 140 mmoles) was heated to reflux for 20 hours while the system was continuously purged with nitrogen. A white precipitate formed from the yellow solution on cooling. The excess silylating agent was removed using an evaporator, and the remaining solid was purified by bulb to bulb distillation (150°C at 0.1 mm Hg, 11.84 g, 92% yield, mp 101-102°C).

Polymerization of 4-fluoro-N-(3-trimethylsiloxyphenyl)phthalimide. A 300 mL resin kettle was charged with 4-fluoro-N-(3-trimethylsiloxyphenyl)phthalimide (47.7 g, 140 mmoles), 4-fluorophenyl phenyl sulfone (393.2 mg, 1.7 mmole), diphenyl sulfone (13.4 g) and 25 mL of chlorobenzene. The mechanically stirred mixture was heated under a continuous nitrogen purge to 330°C. The chlorobenzene was distilled into a receiver flask, which removed traces of water. A very small amount of cesium fluoride (~3 mg) was then added to the reactor. Immediately after addition of the catalyst, Me_3SiF rapidly distilled from the solution. The solution was stirred for 15 minutes, and then the reactor was removed from the heating bath. The polymer was dissolved in 500 mL of DMAC, filtered and precipitated into 2 L of methanol in a blender. The precipitate was filtered, washed with 1 L of methanol, and dried in a vacuum oven at 150°C for 16 hrs (31g, 91% yield). The mechanical data was determined using microtensile bars cut from a film (0.035" thick) which was compression molded from the product polymer at 330°C.

T_g: 208°C (20°C/min)
η_{inh}: 0.66 dL/g at 0.5 g/dL in m-cresol at 25°C
Tensile Modulus: 548±11 ksi

Polymerization of 4-fluoro-N-(3-trimethylsiloxyphenyl)phthalimide with no end-cap. A 300 mL resin kettle was charged with 4-fluoro-N-(3-trimethylsiloxyphenyl)phthalimide (36.9 g, 110 mmoles) and 25 mL of chlorobenzene. The mechanically stirred mixture was heated under a continuous nitrogen purge to 310°C. After the chlorobenzene distillate was collected, a very small amount of cesium fluoride (~3 mg) was added to the reactor. Immediately after addition of the catalyst, a liquid rapidly distilled from the solution. The reactor was then heated to 330°C. After 5 min. the solution was too viscous to stir, and the reactor was removed from the heating bath.

η_{inh} = 0.84 dL/g, 0.5 g/dL in m-cresol at 25°C

Attempt to polymerize of 4-fluoro-N-(3-hydroxyphenyl)phthalimide. A mixture of 4-fluoro-N-(3-hydroxyphenyl)phthalimide (5.00 g, 19.4 mmoles) and potassium t-butoxide (2.24 g, 20.0 mmoles) was placed into a reaction vessel with 30 ml of benzene. The reaction mix was stirred for 2 hours under a nitrogen atmosphere. Dry DMF (40 mL) was added and the reactor was heated to 80 °C for 4 hours. The heat was then removed and stirring was continued for an additional 16 hours. The product solution was poured into 500 mL methanol. A precipitate did not form, indicating that the product has very low molecular weight.

Attempt to polymerize 4-nitro-N-(3-hydroxyphenyl)phthalimide. A 100 mL single necked flask equipped with a magnetic stirrer, reflux condensor, and nitrogen inlet was charged with sodium methoxide (3.488 g, 25 wt%, 16.1 mmole), 4-nitro-N-(3-hydroxyphenyl)phthalimide (4.432g, 15.6 mmole), and 27 mL of benzene. After stirring at room temperature for 90 minutes, DMF (35 mL, dried over 4Å molecular sieves) was added. The reaction was then heated to 80°C for 3 1/2 hours. A red solution was present throughout this procedure. The heat was removed and the reaction was stirred for an additional 16 hours. An aliquot (~1 mL) was removed which was added to ~5 mL MeOH. No precipitate was observed. The product solution was concentrated to ~15 mL using an evaporator, and the viscous solution was poured in 150 mL MeOH. The dark precipitate which formed was filtered and dried in a vacuum at 130°C overnight (310 mg, 8.4% yield). This solid was dissolved in 3 mL hot DMF and reprecipitated into ~50 mL MeOH. A very small amount of a low molecular weight solid (66 mg, inherent viscosity 0.07 dL/g at 0.5 g/dL in m-cresol at 25°C) was isolated after filtration and drying in a vacuum oven at 130°C. A low dispersity (1.33 M_w/M_n) was measured by gel permeation chromatography in 80/20 CH_2Cl_2/NMP. This measurement also confirmed the low Mw of the product (M_w = 2170, narrow polystyrene standards used).

Preparation of the sodium salt of 4-fluoro-N-(3-hydroxyphenyl)phthalimide. A sample of the phenol derivative (4-fluoro-N-(3-hydroxyphenyl)phthalimide, 10.0 g, 39.0 mmole) was dissolved in 400 mL THF with stirring. Sodium hydride (984 mg, 41.0 mmole) was then added over a period of 5 minutes. A gas evolved and the solution changed from colorless to orange.

Preparation of ether imide cyclooligomers. DMAc (400 mL, dried with 3A molecular sieves) and benzene (50 mL) in a 1L flask was heated to 130° C under a continuous flow of nitrogen. The benzene distillate was collected in a Dean-Stark trap. Once the distillation of benzene ceased, the sodium salt of 4-fluoro-N-(3-hydroxyphenyl)phthalimide (10.89 g, 39.0 mmole) in THF solution was added using a constant rate addition funnel over a 24 hour period (16.7 mL/hr). During the addition the THF distilled over into the Dean-Stark trap, and a precipitate formed. After the addition was completed, the reaction mixture was heated at 140°C for an additional 96 hours. The reaction mixture was then allowed to cool to room temperature and filtered. The filtrate was evaporated to give a yellow solid, which was slurried with 300 mL methylene chloride and filtered. The insoluble portion was washed three times with 100 mL water to remove NaF, and then dried in a vacuum oven at 130°C for 65 hours. The resulting material was identified as the cyclooligomer with 4 repeat units (1.62 g, 17.5% yield). The filtrate was washed with 200 mL of water, 150 mL of 1M NaOH, and again with 200 mL of water. The methylene chloride was removed using a rotary evaporator and the resulting solid was dried in a vacuum oven at 130°C for 65 hours. This fraction (3.58 g, 38.7%) consisted primarily of the cyclooligomer with 3 repeat units along with small amounts of higher molecular weight cyclooligomers and traces of linear polymer. The insoluble portion from the methylene chloride wash was dried in a vacuum oven at 130°C for 65 hours. This fraction (2.15 g, 23.3%) contained predominantly high molecular weight cyclooligomers. The total recovery was 79.5%.

<u>Scale-up of the sodium salt of 4-fluoro-N-(3-hydroxyphenyl)phthalimide</u>. The monomer 4-fluoro-N-(3-hydroxyphenyl)phthalimide (25.00 g, 97.0 mmole) was dissolved in 1 L DMAC with stirring. Sodium hydride (2.38 g, 99.0 mmole) was then added over a period of 5 minutes. A gas slowly evolved and the solution changed from colorless to orange.

<u>Scale-up of cyclization of the sodium salt of 4-fluoro-N-(3-hydroxyphenyl)phthalimide</u>. The above cyclization was conducted using 27.1 g monomer in 500 mL DMAC at 130°C. After similar addition and isolation procedures, the following product fractions were obtained: 8.2 g (35.7%) methylene chloride soluble portion, 4.7 g (20.4%) methylene chloride insoluble portion, and 2.8 g (12.2%) of cyclooligomer with 4 repeat units.

<u>Polymerization of a mixture of ether imide and ether sulfone cyclooooligomers</u>. Cyclooligomers of poly(ether imide) (211 mg) and poly(ether sulfone) (210 mg) were dissolved in 5 mL of DMAC. Cesium fluoride (61.5 mg) dissolved in ~1 mL methanol was added to the cyclooligomer mixture. The solvents were removed under reduced pressure at 130°C. This solid was purged with N_2 and heated to 325°C for 30 min. The resultant clear brown pellet was a reasonably high molecular weight polymer as evidenced by an η_{inh} of 0.47 dl/g (0.28 g/dL in NMP at 25.0°C) and GPC measurements (M_n 8970; M_w 28050 relative to narrow polystyrene standards).

Polymerization of a mixture of ether imide and ether sulfone cyclooligomers. Cyclooligomers of poly(ether imide) (1.0 g) and poly(ether sulfone) (1.0 g) were dissolved in 10 mL of DMAC. Cesium fluoride (6.5 mg) dissolved in ~1 mL methanol was added to the cylooligomer mixture. The solvents were removed under reduced pressure at 130°C, and the remaining solid was dried under vacuum at 200°C for 16 hours. This solid was purged with N_2 and heated to 325°C for 30 min. The resulting polymer was compression molded at 330°C into a thick (30 mil) film. This film had many voids and was slightly brittle. An η_{inh} of 0.54 dL/g (0.5 g/dL in NMP at 22.8°C) was determined.

Aminolysis of copoly(ether sulfone-ether imide). The copolymer from above (750 mg), methyl amine (50 mL, 40% in H_2O) and benzene (10 mL) were added to a 100 mL flask. The mixture was allowed to stir under nitrogen at room temperature for 7 days. The volatiles were removed under reduced pressure and the remaining solid dried under vacuum for 2 hrs at 100°C. The ether imide block was calculated to be 3.9 repeat units long by ^1H NMR analysis of the residue.

Synthesis of ether nitrile cyclooligomers. A 1 L three-necked flask equipped with a Dean-Stark trap and condensor, a thermometer, a nitrogen inlet, and magnetic stirring was charged with 400 mL NMP, 150 mL of toluene, and 3.45 g (0.025 mole) potassium carbonate. After the solvents were heated to reflux (166°C pot temperature), two separate 0.40 M solutions of the monomers (resorcinol and 2,6-difluorobenzenenitrile) in NMP were added simultaneously using a syringe pump. The addition continued (rate 15 mL/hour) until 50 mL of both solutions were added. During an additional hour of reflux the pot temperature was raised to 200°C by draining toluene from the Dean-Stark trap. The reaction mixture was poured into 1 L water which was then neutralized with aqueous 1M HCl. The precipitate was filtered, washed with methanol, and treated with boiling chloroform. A pure cyclic oligomer with a DP of 4 (0.592 g, mp 397°C, mass spectrum: 836 m/e, elemental analysis: found C 74.41, H 3.41, N 6.58, calculated C 74.64, H 3.37, N 6.70) precipitated from the chloroform solution on cooling. Slow evaporation of the mother liquor afforded a second crop of crystals (0.21 g) which was a pure cyclic oligomer with a DP of 3 (mp 451°C, mass spectrum: 627 m/e, elemental analysis: found C 74.71, H 3.41, N 6.75, calculated C 74.64, H 3.37, N 6.70).

Preparation of 4-fluorophenyl 4-hydroxy-3-aminophenyl sulfone. A 2 L magnetically stirred flask was charged with $FPhSO_2PhOH$ (80.0 g, 0.317 mol) and 640 mL acetic acid and warmed to 75°C. Concentrated nitric acid (70%, density 1.42 g/mL, 30.4 mL, 0.48 mol) was added, and the reaction turned brown and warmed to 79°C. After heating an additional 45 minutes the heat was turned off. Crystals formed as the contents cooled, which were filtered and washed with 400 mL water. Crystals which formed in the filtrate were filtered. The combined crystals were washed several times with water, and dried in a vacuum oven at 50°C overnight to give 83.65 g (89% yield) yellow crystals. A portion of this intermediate nitro compound (80.0 g, 0.269 mol), ammonium formate (180 g, 2.86 mol), and 1250 mL 100% ethanol were added to a 2 L flask to form a suspension. Upon adding the catalyst (10% Pd/C, 7.2 g) gas evolved immediately. The reaction was then refluxed for 3 hours. After cooling the solids were removed by filtration and the filtrate was concentrated to ~600 mL and added to 1200 mL water. The tan solid which precipitated was filtered. Additional product was obtained by partially evaporating the filtrate. This solid was purified by redissolving it in 800 mL of a mixture of methanol and ethanol, and precipitating it into 2 L water. After filtering the solid and placing it in a vacuum oven (50°C) for 16 hours, 59.87 g product was obtained. An additional 7.45 g (94% total yield) was obtained from the original filtrate.

Preparation of AA benzoxazole monomer. A magnetically stirred 1 L three necked flask equipped with a Dean-Stark trap was charged with 4-fluorophenyl 4-hydroxy-3-aminophenyl sulfone (66.5 g, 0.249 mol), 500 mL NMP, 4-fluorobenzoyl chloride (47.3 g, 0.299 mol), and 50 mL benzene. The reaction was refluxed (pot temperature 155°C) for 5 hours, allowed to cool and poured into 1.2 L water. The acidic mixture was neutralized first with sodium carbonate and then with KOH. The solid was filtered and added to 600 mL chloroform. The chloroform suspension was heated to reflux, treated with $MgSO_4$, and filtered while still hot. Several different solvent combinations were tried to recrystallize the solid obtained from evaporation of the filtrate. The best combination was chloroform/methanol followed by passing a chloroform solution through a silica gel column (23.44 g in 240 mL hot chloroform passed through 95 g silica gel, elute with chloroform). This purification was performed in batches to give a total of 77.29 g (84% yield) light yellow solid.

Preparation of AABB ether sulfone benzoxazole cyclooligomers. A 250 mL three-neck round-bottom flask equipped with a thermometer, a Dean-Stark trap, a nitrogen inlet, a magnetic stirrer, and a heating mantle was charged with 70 mL NMP, 40 mL toluene, and K_2CO_3 (0.358 g, 2.59 mmole). The oxygen in the mixture was purged by alternately evacuating and venting the contents to nitrogen. The mixture was then brought to reflux for 30 minutes, and the final temperature was controlled at 175°C by adjusting the amount of toluene. To this well-stirred mixture a solution of 2-(4-fluorophenyl)-5-(4-fluorophenylsulfonyl)benzoxazole (0.8509 g, 2.291 mmole) and resorcinol (0.2542 g, 99% purity, 2.286 mmole) in 30 mL NMP was added slowly using a syringe pump at the rate of 20 mL/hr. The temperature was raised to 187°C after 1 hour by removal of 4 mL distillate. After the addition was completed, heating was continued for 3.5 hour. The reaction mixture was filtered and evaporated. The residue was dissolved in a minimal amount of THF, to which $CHCl_3$ was added until a large amount of greyish dark solid appeared. The mixture was then filtered and evaporated, giving a brown viscous residue. A small amount of THF was added to the residue and a fine yellow solid formed on standing. The solid was then collected by filtration and washed with MeOH. A white powder (68.7 mg) was obtained after drying in air. The filtrate was evaporated to a solid which was washed with THF. A second crop of white fine solid (148.3 mg) was collected similarly. The total yield was 21.5%. This product was identified by mass spectrometry as the cyclooligomer with 2 repeat units.

Rheological measurements. Cyclic samples had to be pre-melted in a vacuum oven to make good viscosity measurements. Samples were melted and devolatilized on Teflon sheets in a vacuum oven, at about 225°C (cPC) or 300°C (cPES and cPESB), for 30 min to 2 hr, until bubbling ceased. This procedure also helped remove any residual solvent or moisture. Use of non-pre-melted cyclic samples led to air trapped in the melt, resulting in unreliable data; such foams had lower viscosity, and greater elasticity, than well-fused cyclic samples. Compression molding of cyclics into disks was unsuccessful, due to the lack of mechanical integrity and brittleness of the molded disks. Dynamic mechanical measurements were performed on a Rheometrics RDS-IIE equipped with a force rebalance transducer (2000 g-cm full scale) and Recap III software package. Test geometry was parallel plate, using disposable aluminum fixtures: a 31.8 mm I.D. cup on the bottom, needed to contain low viscosity samples; and a 25.0 mm O.D. plate on the top. Tests were run under nitrogen, with temperature monitored by the tool thermocouple (pressed against a hole in the bottom cup). Typical sample size was 0.8-1.0 g, with gap set 0.7-0.8 mm. Most tests were started about 10-20°C above T_g. Frequency-temperature sweeps involved 5°C temperature steps with 4 min soak time, with frequency range $0.1 \leq \omega \leq 100$ rad/s. Strain was varied with T and ω, to try to maintain torque high enough for meaningful results. Despite this, torques were often quite low, especially at higher temperatures, leading to data scatter. A more rapid testing procedure, using constant ramp rate (2°C/min) at a single frequency ($\omega = 10$ rad/s), was used to collect most of the data in this report. The auto-strain adjust feature was used for these ramped temperature tests, starting at a strain of $\approx 1\%$ and increasing to 30% during the test. Relatively noise-free data could be obtained down to about 10 P, but below this viscosity, the torque measurements became scattered (torque < 0.1 g-cm).

5.6. TABLES AND FIGURES

Table 5.1. Mechanical Properties of Block Copolymer

	PEI/PES Copolymer	Ultem®
Tg	222°C	215°C
Inherent Viscosity	0.28 dL/g	0.38 dL/g
Tensile Modulus	478 ksi	487 ksi
Yield Strength	14.3 ksi	15.2 ksi
Elongation	5%	14%

Figure 5.1. HPLC of Ether Sulfone Cyclooligomers from AB Monomer

(The cyclic trimer appears at 6 minutes, the tetramer at 7.3, the pentamer at 8.5, and so on. The peak at 4 minutes is an internal standard)

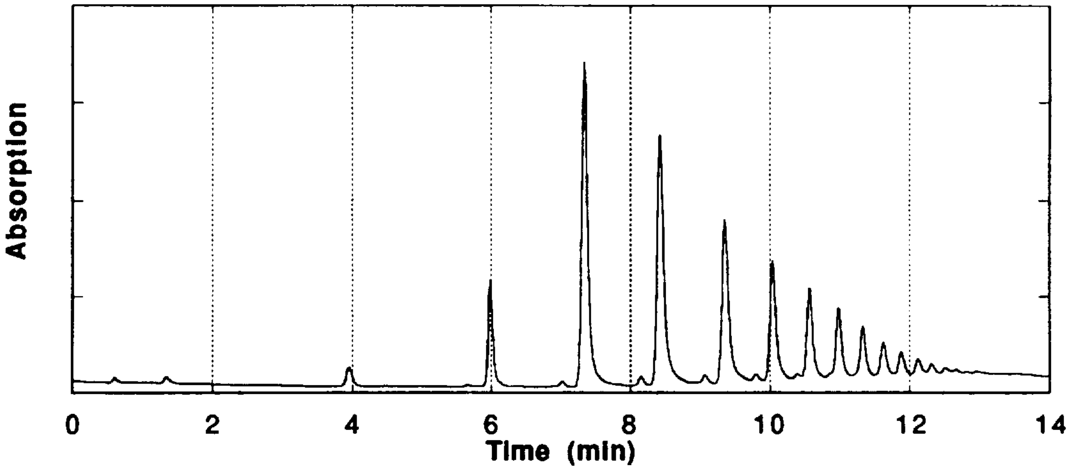


Figure 5.2. HPLC of Ether Nitrile Cyclooligomers

(The largest peak is the cyclooligomer with 3 repeating units)

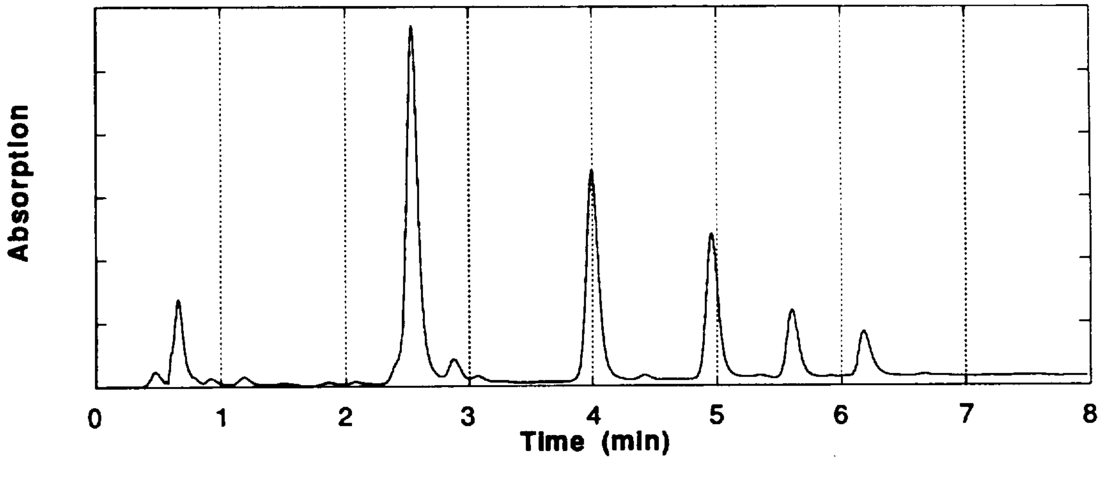


Figure 5.3. HPLC of AABB Ether Sulfone Benzoxazole Cyclooligomers

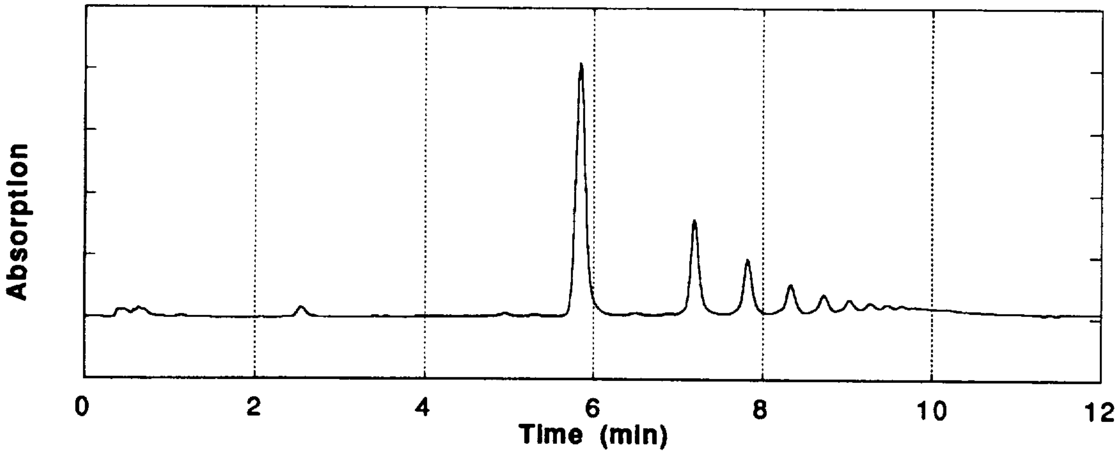


Figure 5.4. Parallel Plate Rheometry of Ether Sulfone Cyclcooligomers

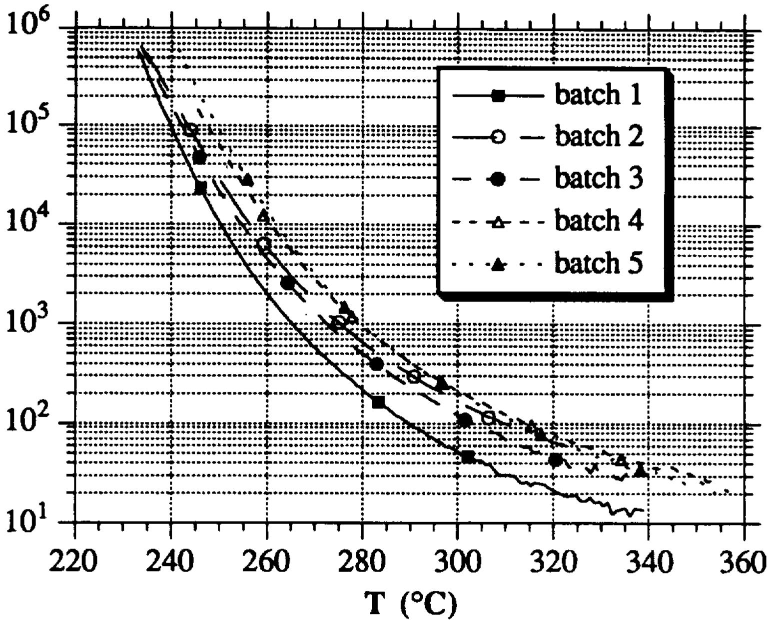


Figure 5.5. Complex Viscosity *vs* Temperature

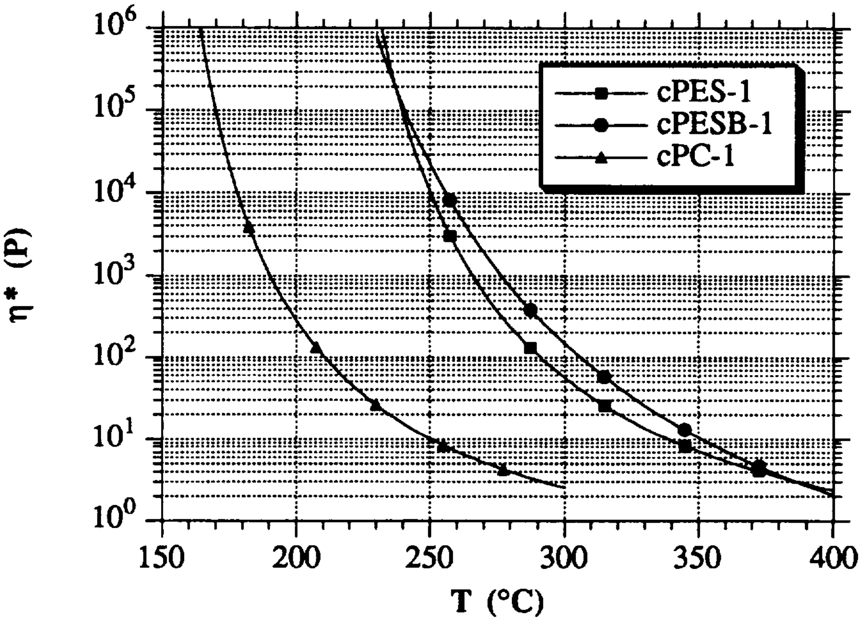
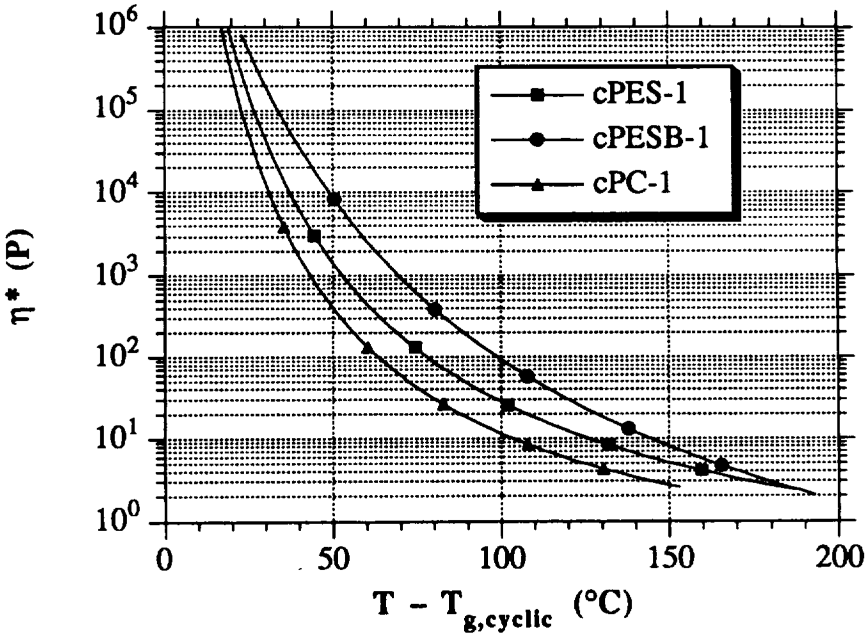


Figure 5.6. Complex Viscosity *vs* Temperature Above T_g



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13. ABSTRACT *(Maximum 200 words)*

The objective of the contract is the development of matrix resins with improved processability and properties for composites for primarily aircraft structures. To this end, several resins/systems have been identified for subsonic and supersonic applications. For subsonic aircraft, a series of epoxy resins suitable for RTM and powder prepreg has been shown to give composites with about 40 ksi compressive strength after impact (CAI) and 200°F/wet mechanical performance. For supersonic applications, a thermoplastic-toughened cyanate prepreg system has demonstrated excellent resistance to heat aging at 360°F for 4000 hours, 40 ksi CAI and useful mechanical properties at ≥310°F. An AB-BCB-maleimide resin has been identified as a leading candidate for HSCT. Composite panels fabricated by RTM show CAI of ~50 ksi, 350°F/wet performance and excellent retention of mechanical properties after aging at 400°F for 4000 hours.

14. SUBJECT TERMS
RTM, epoxy, cyanate, benzocyclobutene, AB-benzocyclobutene-maleimide, crosslinkable epoxy thermoplastic, toughening by thermoplastics, cyclooligomers.

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