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PROCESSING AND PROPERTIES OF POLY(p-PHENYLENE BENZOBISTHIAZOLE/ BISBENZOCYCLOBUTENE MOLECULAR COMPOSITES

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An approach to realize the reinforcement of a thermoset system at the molecular level by rigid-rod polymers was investigated. A mixture of bisbenzocyclobutene-terminated imide oligomers constitutes the thermosetting component, and the rigid-rod polymer utilized in the present study was poly(p-phenylene benzothiazole).

The cure chemistry of the thermoset materials is based upon the ability of benzocyclobutene functions to homopolymerize under the influence of heat. Thermal properties, as well as film processing and mechanical properties of PBT/BCB thermoset composites, are presented.

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SECTION I
INTRODUCTION

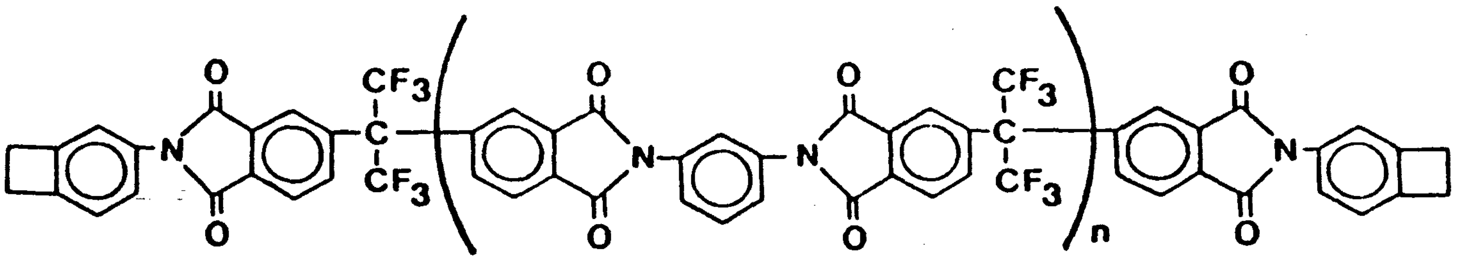
Rigid-rod molecular composite is a new material concept [1] developed by the Air Force Materials Laboratory. It consists of two polymers with vastly dissimilar conformation; a high modulus, high strength rigid-rod polymer dispersed in a host matrix of flexible coil polymer. The rigid-rod polymers, being of high aspect ratio, act as the reinforcing elements similar to that of a chopped fiber composite, but with the reinforcement taking place at the molecular level.

Research into this new type of material has focused on using poly(p-phenylene benzobisthiazole) (PBT) as the reinforcing rigid-rod polymer because of its superior mechanical properties and thermal stability. Heat treated PBT fiber was reported to have a tensile modulus of 330 GPa and a strength of 3 GPa [2]. However, PBT degrades before it melts, therefore processing of molecular composite has to be carried out in a solution state with acid as the solvent, such as methane sulfonic acid (MSA). Not many flexible coil polymers can be dissolved or are stable in MSA, thus limiting the choice of matrix polymers. Molecular composites based on PBT and poly-2,5(6) benzimidazole (ABPBI) [3] had been fabricated into fibers and thin films, which showed improved mechanical properties. The moduli obtained were as high as those predicted from a volume fraction rule-of-mixtures with a full translation of the fiber modulus into the composites. However, ABPBI does not have a glass transition temperature, and its molecular composites were difficult to thermally consolidate into thicker specimens. To overcome this, thermoplastic matrices such as nylons and polyether ether ketone [4,5] were used so that the molecular composite films could be laminated. Using a thermoset matrix was another goal in the molecular composite technology. Because of the acid solvent, conventional thermoset resins such as bismaleimides, acetylene terminated oligomers and epoxies are not stable in the acid medium and therefore cannot be used as a host matrix for molecular composites.

Recently, a new class of bisbenzocyclobutene (BCB) terminated thermoset materials was synthesised in this laboratory [6]. This thermoset has a strained 4-membered ring which undergoes electrocyclic ring opening upon heating to generate an extremely reactive diene. It can react with a dienophile to afford a Diels-Alder adduct or react with itself to form a linear or crosslinked polymer [7]. It was further found that the BCB thermoset is soluble and its 4-membered ring is quite stable in MSA. Such discovery in our synthesis laboratory is important since it offers for the first time a thermoset matrix that can be processed in an acid medium into rigid-rod molecular composites. This paper discusses their processing and properties.

SECTION II
EXPERIMENTAL METHODS

Chemical structure of the BCB oligomer is shown in Figure 1. Previously, we reported the synthesis of the BCB oligomer in acetic acid/toluene [6]. We had later found that a higher yield could be achieved by using dimethylacetamide (DMAc) as the solvent. Detailed procedure is provided as follows: 100 g (0.225 mol) of 2,2-bis(4-phthalic anhydrido)hexafluoropropane (6FDA) was placed in a one-liter round-bottomed flask. About 400 ml of dry DMAc was added to attain complete dissolution. Meta-phenylenediamine (12.0 g, 0.111 mol, freshly purified by vacuum-distillation) was subsequently added in one portion. The resultant amber solution was stirred at room temperature under N_2 overnight. To the amic acid solution was added freshly prepared 4-aminobenzocyclobutene (30.0 g, 0.252 mol) and the resulting dark amber solution was stirred at 45°C under nitrogen for another 20 hours. Finally, the benzocyclobutene-endcapped amic acid was imidized by a mixture of acetic anhydride (88 ml) and pyridine (70 ml). The final dark reaction mixture was stirred at 45°C for still another 20 hours. Then, the reaction mixture was allowed to cool to room temperature and poured into 2700 ml of cold, 1 NHCl solution. The precipitated crude product was stirred at room temperature for about an hour and then collected by suction-filtration. It was washed with copious amounts of H_2O, followed by air-drying (with suction) overnight. The off-white crude product was extracted with 800 ml of methylene chloride and the residual water was separated by a separatory



n = 0,1,2,3,....

n	WT%
0	23.2
1	20.6
2	16.7
3	12.1
4	8.8
5	6.5
6 AND HIGHER	12.1

Figure 1. Chemical Structure of BCB Oligomer and Its Composition Determined by Size Exclusion Chromatography.

funnel. The dark CH_2Cl_2 extract was dried over $MgSO_4$ and then filtered through a filter system consisting of a layer of Celite, followed by a layer of silica gel (about 150 g) and a layer of sand in a 600-ml-capacity, coarse-porosity, fritted filter funnel. The filter system was initially saturated with hexane. Elution with CH_2Cl_2 was continued until the filtrate was almost colorless. (The silica gel became light brown.) The filtrate collected was then subjected to rotary evaporation to afford yellow product, which was subsequently dried in a vacuum oven (~90°-100°C) for 24 hours. Yield: 120 g (95 percent, based on m-phenylenediamine). Their composition was obtained from size exclusion chromatography. More than 70 percent of the oligomers are made up of repeating units of less than three.

The PBT polymer with $[\eta] = 21.4$ dl/g was supplied by SRI International. PBT/BCB solutions with 30 to 70 percent PBT content by weight were prepared in a freshly distilled MSA at 2-3 wt. percent concentration under a dried nitrogen atmosphere. Homogenous PBT solutions were first prepared from distilled MSA. Just prior to processing, freshly prepared BCB oligomer solution was added and mixed for 3 hrs. Vacuum was applied to deaerate the solution. The mixed PBT/BCB solution was then transferred to an extrusion cell and further deaerated. Continuous thin film, 10 - 20 μm thick, was made by extruding the solution through a coat hanger die onto a rotating drum into cold distilled water of <10°C to coagulate the film. The details of film processed this way was previously described [8]. The coagulated film was washed to remove the residual acid and wound onto a hexagonal drum to build up the film thickness. Each side of the hexagonal drum had a clamp to hold the wound wet film together. Torque of 125 lbs. was applied to the clamp and the films were dried in a vacuum oven at 90°C for 48 hrs. After drying, a coherent stacked film about 0.5 mm thick was obtained.

Rectangular tensile test specimens, 0.5 inch x 3 inch, were prepared by curing the films in a compression mold under a pressure of 2,000 psi and at 260°C for 25 minutes. Tensile properties were tested with a MTS tester using a strain gage mounted on the flat face of the samples.

Thermal properties on Du Pont/Omnitherm and the kinetics of curing on Perkin-Elmer Differential Scanning Calorimeter (DSC) II were determined.

SECTION III
RESULTS AND DISCUSSION

Several BCB oligomers with various backbones have been synthesized in this laboratory [6]. A particular BCB was chosen for this study due to its superior thermal oxidative properties when compared to others in the series. Under isothermal thermo-oxidative aging, it loses 12 percent in weight at 343°C and 24 percent at 371°C, while others in the series can lose up to 50 percent in weight [6]. Figure 2 shows the DSC scan of the oligomer. It has a glass transition temperature of 153°C. Curing begins at 226°C with a maxima in the exotherm at 257°C. The exothermic heat of reaction is 133±24 kJ/kg.

Since PBT can only be processed from acid solution, a ternary solution of rigid-rod and flexible coil polymers had to be prepared. A homogenous solution can only be formed at low concentration. Above a critical concentration, aggregation of the rods occurs forming a biphasic solution and processing from such solution will result in poor reinforcement. The ternary solution at below the critical concentration is rapidly coagulated into thin film with water in such a way that the rod/coil mixture is "frozen" to overcome the unfavorable thermodynamic driving force for phase separation. This is the basis used in processing molecular composites [9].

The critical concentration (C_{crit}) of the PBT/BCB system was first determined experimentally by diluting a solution with known concentration until stir opalescence disappeared, and no biphasic domains were observed in an optical microscope. The critical

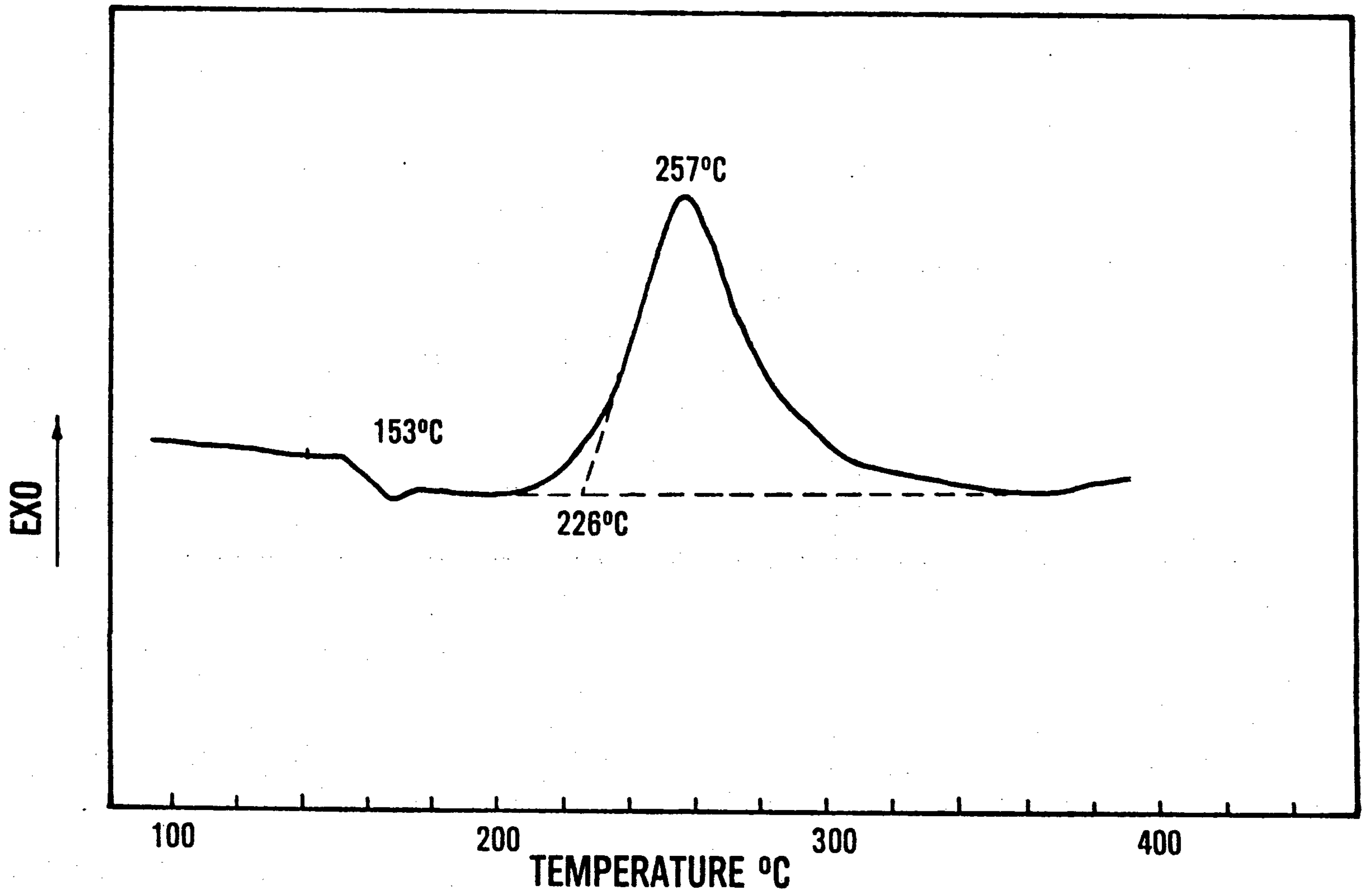


Figure 2. DSC Scan of BCB Oligomer, Heating Rate: 10°C/min.

concentrations measured are shown in Figure 3. It increases from 3 percent to 14 percent as the rod content is reduced from 90 to 30 wt. percent. C_{crit} of this system at low rod content is much higher than those previously observed in a solution of PBT/ABPBI which is about 6 percent [9]. In Figure 3, C_{crit} based on Flory's theory [10] for an athermal solution of a rod/coil ternary system, using various axial ratios and contour lengths of PBT and BCB oligomers were also plotted for comparison. Reasonable agreement between theory and experiment is obtained at high rod contents. However, at low rod contents, the experimental C_{crit} deviates strongly from theory. This is because over 70 percent of the BCB oligomer is made up of repeating units less than three. The hydrodynamic size of the low molecular weight BCB oligomer approaches that of a solvent when compared to a much larger flexible coil polymer. As far as the rod was concerned, the presence of the oligomers did not significantly alter its partition function. The rod treats the oligomers as similar to a solvent. In fact, from the experimental C_{crit} of PBT/BCB solution, a biphasic solution is formed when the rod content in the ternary solution exceeds 3-4 percent. This is similar to what would be observed in a binary solution of PBT/MSA.

To process PBT/BCB solution into thin films, special precautions had to be taken. BCB oligomers were added to the PBT solution prior to processing and the coagulation bath was kept cold, at <10°C. Although the 4-membered ring of BCB oligomer is quite stable in acid, prolonged exposure, especially if moisture is

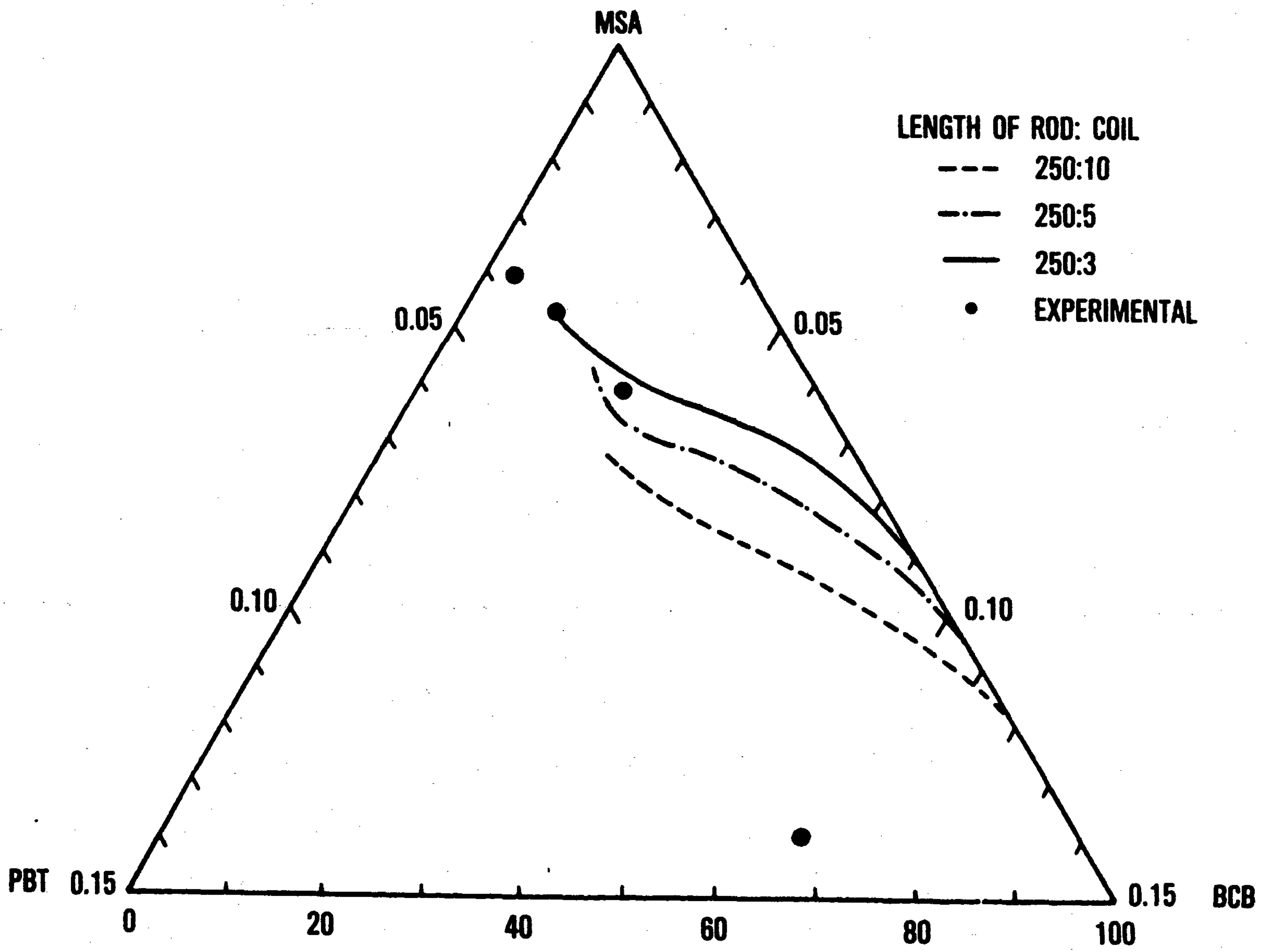


Figure 3. Ternary Phase Diagram of PBT/BCB in Methane Sulfonic Acid. ● experimental; solid and broken lines are calculated with different length ratios of rod and coil polymers.

present, can hydrolyze the BCB imide backbone. This was determined in the initial processing runs of PBT/BCB fibers in which PBT and BCB were dissolved in MSA together. Because of the difficulty in dissolving PBT completely, the solution was mixed for a week and coagulated in a water bath at room temperature. It was found that fibers prepared under these conditions showed a reduction in the cure exothermic heat of reaction as evidenced by a DSC scan, Table 1. At low BCB content, the exotherm was almost completely lost and was not sufficiently distinct from the base line. Two possible events were thought to have happened. Either the 4-membered ring opened during processing, or the small BCB oligomers precipitated faster than PBT and leached out during coagulation, which resulted in the loss of material. Both will cause a reduction in the ΔH. Since the BCB molecular structure contains fluorine atoms, elemental analysis of fluorine content in the processed fiber was carried out. Table 1 shows the experimentally measured and calculated fluorine contents, which agree well within experimental error. Thus, there is no loss of BCB oligomers.

TABLE 1

ELEMENTAL ANALYSIS OF FLUORINE CONTENT AND THE HEAT OF REACTION ON PBT/BCB AFTER COAGULATION

	F(percent)		ΔH(kJ/kg)	
PBT/BCB	CALD.	EXPT.	CALD.	EXPT.
0/100	19.0	18.6		132.2
30/70	13.0	12.5	113.9	58.6
50/50	9.3	7.9	81.2	-
90/10	1.9	1.9	16.3	-

This opens the question of whether the 4-membered ring is stable in MSA. Under strong oxidizing conditions, e.g. in nitric acid, benzocyclobutene can be oxidized, ensued by subsequent rupture of the 4-membered ring. However, MSA is a non-oxidizing acid and is unlikely to attack the 4-membered ring. A further evidence that the ring was still present after processing was that the fibers which showed no exotherm in the DSC scan can still be cured, with an increase in tensile strength and elongation at break [11]. Furthermore, the cured fiber swelled in MSA while the as-spun fiber dissolved completely. It is likely that the acid has little effect on the 4-membered ring.

Hydrolysis, if any, probably occurred on the imide backbone. This was investigated by dissolving the BCB oligomer in MSA for various amounts of time, from 1 hr. to 7 days. The precipitate in water was collected and examined with liquid chromatography (LC), using a silica gel column with THF as solvent. In a 3.5 hr. sample, the precipitate showed a totally different chromatogram compared to the original BCB sample. Several absorption peaks appeared in the polar regions. The longer BCB was in MSA, the stronger is the absorption peak, Figure 4. The high polarity observed in LC was due to the hydrolysis of the imide backbone into the highly polar amic acid. It was further found that during the precipitation of the BCB oligomer, the exothermic heat evolved from the mixing of acid and water could cause local rise in temperature which promote further hydrolysis. The hydrolyzed imide backbone is likely to be the cause of the reduction in curing heat of reaction in the DSC scan because in the solid

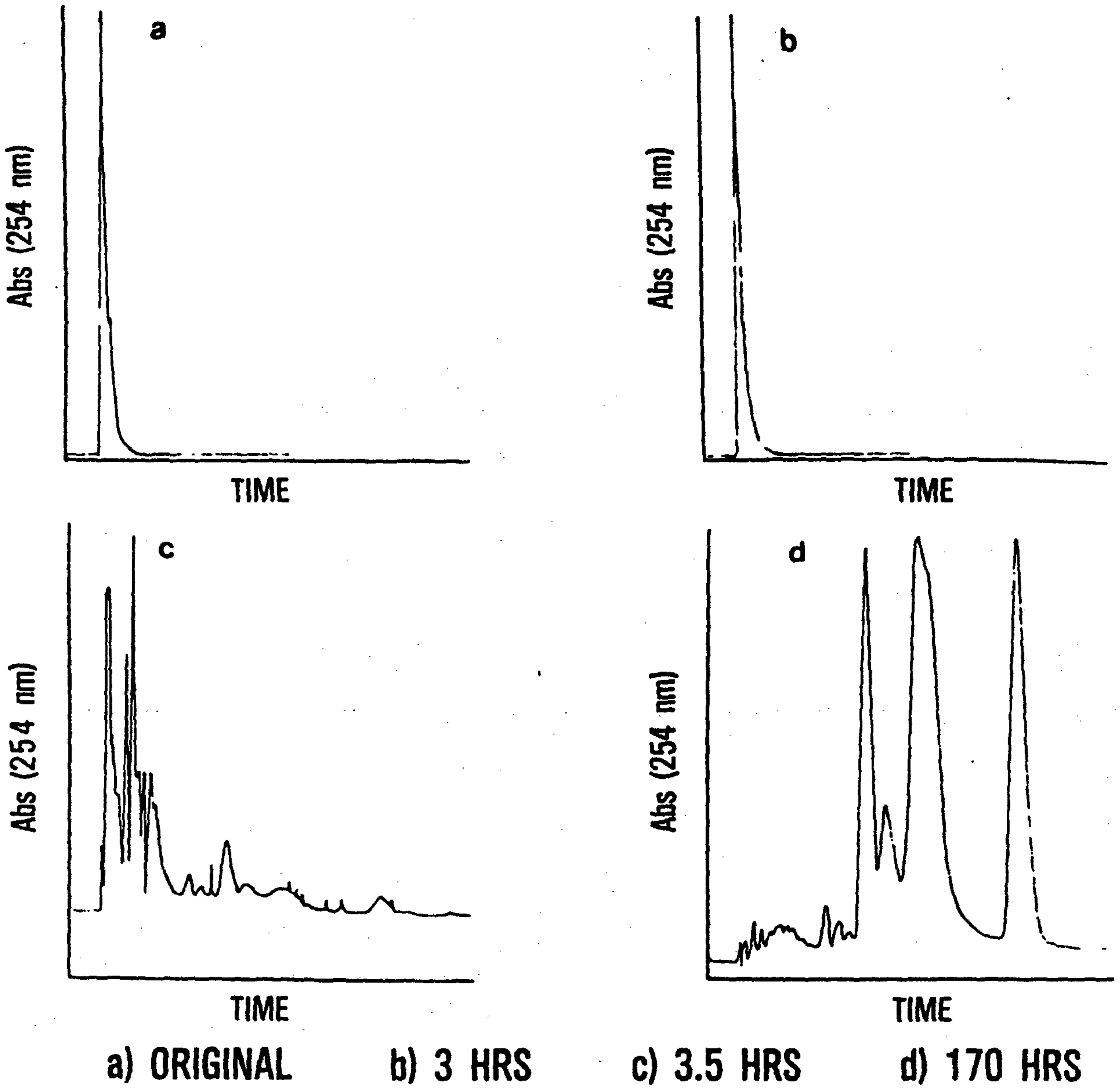


Figure 4. Chromatograms of BCB Oligomers (a) Not Subjected to MSA, and Subjected to MSA for (b) 3.5 hrs and (c) 170 hrs.

state, polyamic acid can convert back to imide on heating. This conversion was reported to occur over a wide range of temperature from 200 to 300°C [12], and the reaction was endothermic with an enthalpy of 34 kJ/mole for the amic acid group [13]. The endothermic conversion caused a reduction in the cure exotherm which also occurred in the same temperature range. If the imide groups in the BCB oligomers were fully hydrolyzed to amic acid, based on the oligomer composition, it was calculated that the conversion of amic acid back to imide in the solid state would produce an endothermic heat of reaction of 118 kJ/kg. This is 11.3 percent less than the 133 kJ/kg cure exotherm. It is likely that the observed reduction of BCB exotherm was due to the opposite endothermic effect of converting back the hydrolyzed imide.

Figure 4(b) shows that if the precipitation of BCB solution was kept <10°C, hydrolysis could be avoided. Also by mixing the BCB solution only prior to processing and maintaining a cold coagulation bath, hydrolysis of the BCB oligomers was minimized. Table 2 shows the ΔH of PBT/BCB processed this way. They compared nearly the same as those calculated based on the weight fraction of BCB, indicating that hydrolysis was brought under control.

The kinetics of curing of the processed PBT/BCB films were studied using DSC to obtain the reaction window for the curing conditions. This was done by following the conversion as a function of heating rates [14]. The conversion was then replotted as a function of both time and temperature. A typical reaction window plot is shown in Figure 5. It shows the time and temperature

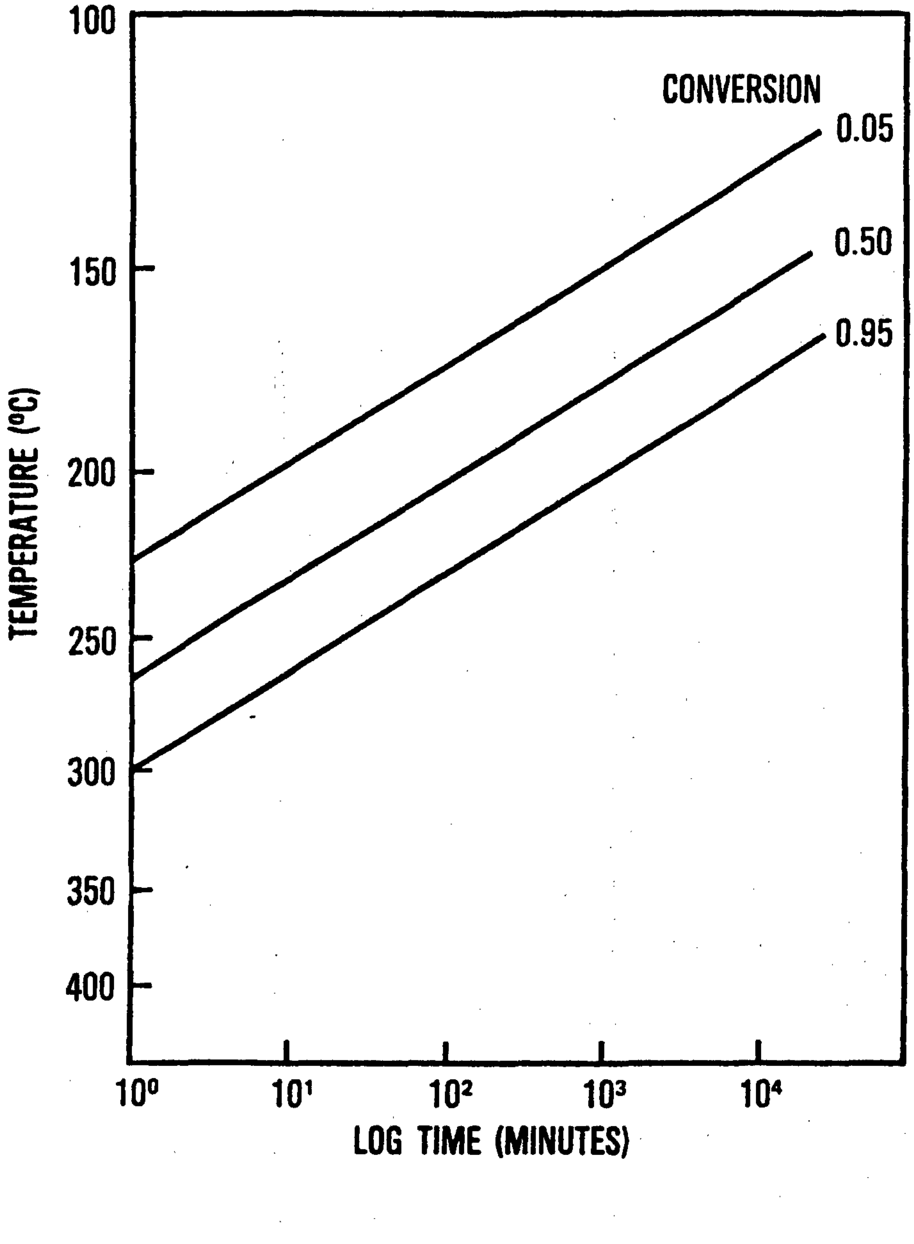


Figure 5. Reaction Window of a 30/70 PBT/BCB Composite Showing the Time-Temperature Relationship to Achieve Various Degree of Cure.

TABLE 2

THE ACTIVATION ENERGIES, ORDER OF CURING AND HEAT OF REACTION DETERMINED BY DSC

PBT/BCB	Activation Energy (kJ/mole)	Order	ΔH(kJ/kg)	ΔH(kJ/kg)
20/80	180.0	2.2	120.6	107.2
30/70	159.7	1.6	85.8	93.8
40/60	195.7	2.4	93.8	80.4
50/50	154.0	1.5	58.2	67.0
70/30	186.4	1.9	32.2	40.2

required to achieve various degree of curing. From the plots, both the activation energy and the order of curing reaction were obtained and are shown in Table 2. The activation energy varies from 154.0 to 195.7 kJ/mole and the order of reaction varies from 1.5 to 2.4. Both did not show any trend correlating to the BCB contents. Curing conditions were chosen such that 95 percent cure was achieved. It appears that changing the rod content did not appreciably change the curing conditions.

Table 3 shows the tensile properties of the cured PBT/BCB films. The neat BCB oligomer which was compression molded showed typical resin properties with a tensile modulus of 3.22 GPa, strength of 71.4 MPa, and an elongation at break of 2.3 percent [15]. With 30 wt. percent PBT, there is a significant improvement in the modulus of the BCB oligomer matrix to 11.55 GPa, a four times increase. The strength improvement was marginal at 89.6 MPa. When compared to molecular composites with other host matrices, such as ABPBI, the properties of the present system were much lower indicating a poorer reinforcement efficiency. This was due to a significant degree of phase separation

TABLE 3

TENSILE PROPERTIES OF PBT/BCB FILMS

PBT/BCB	MODULUS	TENSILE STRENGTH (GPa)	Eb percent (MPa)
30/70	11.6	89.6	0.86
50/50	14.5	127.4	1.35
70/30	18.0	259.0	-

encountered during processing, to be discussed later. When the rod content was increased, the modulus increased correspondingly. However, at 70 wt. percent PBT, the modulus increased only to 18.0 GPa. Compared to 30 wt. percent PBT, even though the rod content was more than double, the improvement in modulus did not commensurate. However, the tensile strength was improved to 273 MPa as a result of more load bearing PBT.

From morphological studies, the poor reinforcement with BCB oligomer as a matrix was attributed to phase separation. Scanning electron microscopy of the surface of an uncured 30/70 PBT/BCB film fractured under liquid nitrogen showed spherical domains 100 - 200 nm in size, Figure 6. Such domains resulted from phase separation during coagulation. One criteria in making a homogenous molecular composite film is that the coil molecules must entangle the rigid-rod such that they are prevented from separating during rapid coagulation. In order to have the entanglements, the flexible coil must be of high molecular weight. The BCB oligomeric system, being of low molecular weight and with 70 percent of it as monomer, dimer and trimer, was not long enough to provide the entanglements needed. Although they form a homogenous solution, they readily phase separate when the

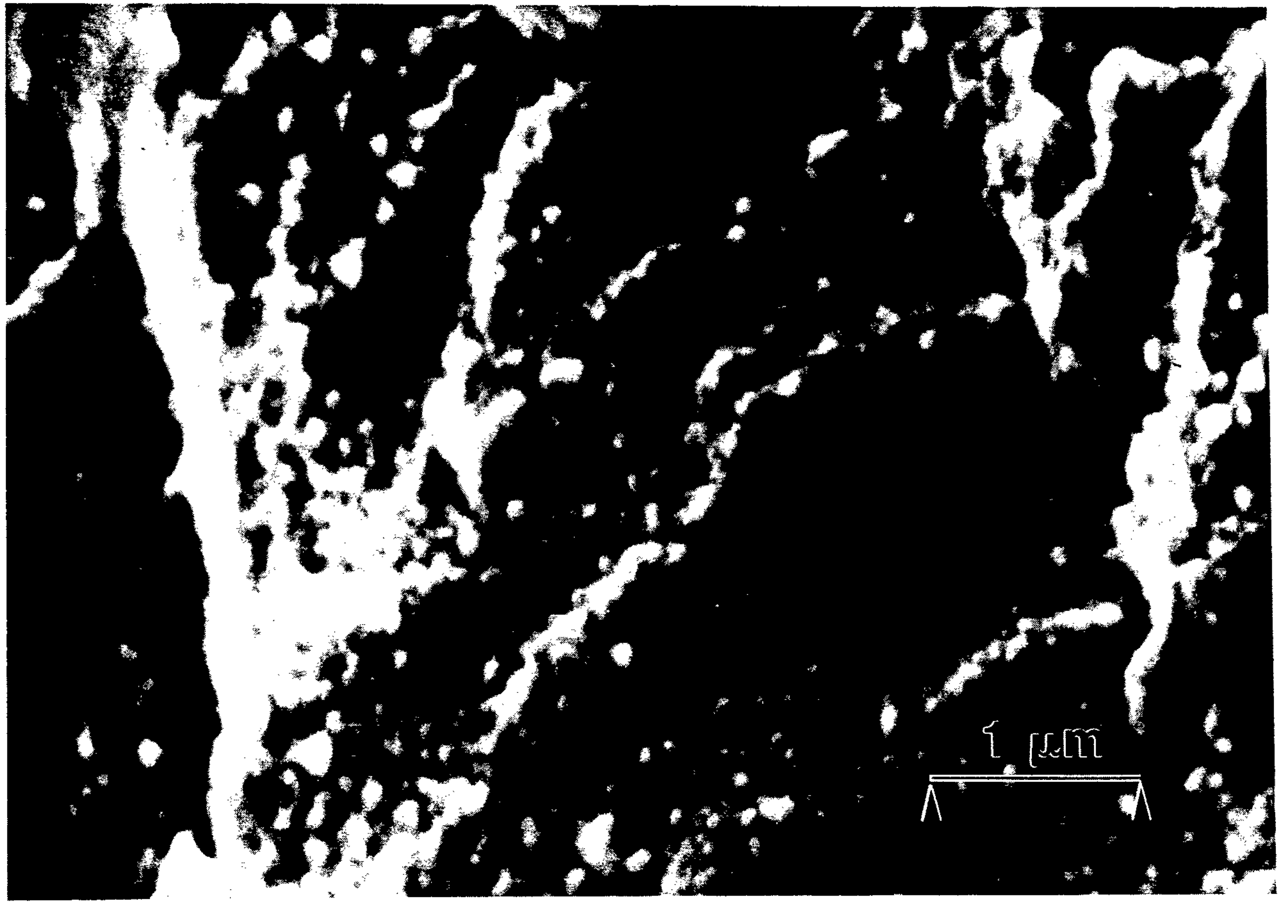


Figure 6. Scanning Electron Micrograph of a Fracture Surface of 30/70 PBT/BCB Composite Film Before Curing Showing the Phase Separated Domains.

solubility is changed during the coagulation, resulting in phase separated domains.

Once the domains were formed, they do not grow in size when heated to the curing temperature at 260°C. This is a feature different from other rigid-rod molecular composites using thermoplastic as matrix, e.g. PBT/Nylon 66 which undergoes thermally induced phase separation and growth of domains into μm size [16]. Either the phase separation temperature is higher than the cure temperature or the formation of a cross-linked BCB network and the resulting increased viscosity during cure inhibits molecular mobility. This would prevent further separation for domains to increase in size in the coarsening process. With such morphology, PBT/BCB oligomers do not form a molecular composite as defined by the level of molecular dispersion, even though there was some degree of reinforcement in modulus. However, the efficiency of modulus reinforcement was not as good as other rigid-rod molecular composites previously reported [3]. The deleterious effect of phase separation was reflected by the poor tensile strength.

Although the concept of making thermoset rigid-rod molecular composites was not successful with the present oligomers, BCB offered the first opportunity of using a thermoset resin in a molecular composite, and it also showed that curing of the matrix can prevent subsequent phase separation during thermal consolidation. Future effort will be directed at synthesizing BCB thermoset systems with higher molecular weight and with acid stable backbones.

SECTION IV
CONCLUSIONS

The concept of rigid-rod molecular composites was pursued using a new class of bisbenzocyclobutene-terminated resins. Because of the instability of the BCB imide backbone, careful processing conditions had to be used to avoid hydrolysis. The critical concentration for the PBT/BCB/MSA ternary solution varies from 3 to 14 wt. percent depending on the rod content. Thermal and mechanical properties of PBT/BCB films were studied. There was an improvement in the BCB resin tensile modulus with PBT, however, the increase was not as high as in other PBT/flexible coil molecular composites previously studied. The tensile strength was very poor. The poor reinforcement was due to phase separation during coagulation with domain sizes of 100 - 200 nm.

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