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# " MICRO AND MACRO APPROACHES TO TOUGH POLYMERS FOR COMPOSITES"

Progress Report
September 25, 1986 through September 25, 1987
By

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# ABSTRACT

The present report summarizes the progress to date on the development of techniques to toughen continuous thermoplastic composites. Our work, using the approach of toughening the polycarbonate composite matrix with rubber particles, has focused on determining the differences between DCB samples molded "in-house" and those molded by NASA. Specifically, an effort is made to account for the differences in fracture toughness observed between the various specimens. In addition, preliminary results of tensile dilatometry tests are described; these tests suggest that processes leading to increased volume and enhanced shear banding are occurring within the rubber toughened system.

We also report on the results of our efforts using another approach - the preparation of random block copolycarbonates. The synthetic route to these species has been modified so that higher molecular weights of these materials can be obtained. In addition, an attempt is being made to determine the exact block length or the number of functional groups in the oligomers since this procedure also should lead to high molecular weight materials. Dynamic mechanical analysis of the copolymer prepared so far ($-[-B_5-T_5-]_n-$) indicates that the scale of cooperative molecular motion of the BPA polycarbonate at sub-Tg temperatures is larger than five monomer units.

Finally, given NASA's more recent interests in developing tough fiber composites for high temperature applications, our efforts to find a suitable rubber-toughener for a thermoset system (bismaleimides) are also mentioned. Included in this section is a description of the various tougheners we intend to use or are currently using.

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## INTRODUCTION

The initial objective of the project supported by NASA research grant (NAG-1-607) was to develop a technique to toughen a thermoplastic resin. The objective of the project has remained the same from its conception in 1985. However, NASA recently redirected its interests to developing tough continuous fiber composites for higher temperature applications than current thermoplastics permit. As a result, the matrix material has been changed from a thermoplastic to a thermoset (BMI). Because thermoplastic systems still hold some interest, and the BMI material supplied by NASA in Kilogram quantities has not yet arrived, work is continuing simultaneously on three fronts. This progress report will present the work completed to date on toughening thermoplastics for continuous fiber composites, and on our efforts to synthesize copolycarbonates, BMI's, and tougheners.

## THERMOPLASTIC SYSTEMS

We are investigating two approaches to toughening high strength continuous fiber thermoplastic composites. First, a polycarbonate matrix will be toughened using rubber particles with a diameter much smaller than the interfibrillar spacing (< 1 micron). We propose that by using such small rubber particles, the cavitation induced shear banding mechanism will operate in the small spacing between the fibers. The shear band growth will increase the plastic zone perhaps beyond the interfibrillar spacing, thereby improving the impact resistance of the composite.

Our second approach will be to synthesize random block copolycarbonates. We expect these materials to behave on a macroscopic scale as a one phase system, but microscopically on the level of segmental motion as two phases. The aim is to produce a copolymer with a high $T_g$ that possesses low temperature ductility. Such a material would be an ideal candidate for toughening.

Progress toward these objectives is summarized below:

APPROACH 1: Rubber Toughening of Polycarbonate Composites

A brief review of our results during the period of our last report (September 1985 to September 1986) would be appropriate at this time.

Polycarbonate (Lexan 141 from General Electric Co.) was compounded with rubber particles from Rohm & Haas (KM330 and KM653). The amount of rubber particles used varied in 5% increments over the range of 5 to 15 wt%.

Disk shaped compact tension specimens 2 inches (50.8 mm) in diameter and 0.5 inches (12.7 mm) thick were produced by injection molding. The ASTM standard test (E399) was used to determine the plane strain fracture toughness, $K_{IC}$. A $K_{IC}$ value of 2.75 Ksi-in$^{1/2}$ (3.02 MN/m$^{3/2}$) for 100 % polycarbonate was recorded (at a 10 in./sec. displacement rate [25.4 mm/sec.]). Rubber toughened polycarbonate samples containing 5 wt% KM653 and KM330 were tested at displacement rates up to 30 in./sec. (762 mm/sec.). All fractures were ductile, therefore, a valid $K_{IC}$ value could not be obtained. Although the toughness could not be quantified by a $K_{IC}$ measurement, the results did indicate substantial toughening. We concluded at this point that the J-integral technique should be employed to determine the fracture toughness of the rubber toughened matrices.

Three pounds of each material containing 10 wt% rubber were made into pre-pregs by NASA-Langley. These pre-pregs were in turn molded into double cantilever beam (DCB) specimens to determine their Mode I interlaminar fracture toughness $G_{IC}$. Problems arose with molding the DCB specimens, adhering the test grip fixture to the DCB specimens, and excessive fiber bridging across the fracture surface. These problems prevented the determination of a representative $G_{IC}$ value. Solutions to these problems had to be discovered to complete the testing of the DCB specimens.

## CURRENT WORK

### DCB Cantilever Beam Tests

DCB specimens were molded from the pre-pregs supplied by NASA. The interlaminar fracture toughness ($G_{IC}$) for the composites were determined using the method described in NASA publication 1092. According to this publication the DCB specimens should be 9 inches (229 mm) long and 1.5 inches (38.1 mm) wide. Due to size constraints placed upon us by our compression molder and limitations on the quantity of material, our specimen dimensions were 6 inches (152.4 mm) long and 1 inch (25.4 mm) wide. We investigated whether or not variances in the width of the sample influenced the $G_{IC}$ value by testing a specimen that was 1.5 inches (38.1 mm) wide and 1.0 inch (25.4 mm) wide. The resulting $G_{IC}$ values were nearly identical (Table I). Therefore, a 1 inch (25.4 mm) wide, 6 inch (152.4 mm) long specimen was used throughout our DCB tests.

The fracture surface of the DCB specimens were littered with deep grooves created by coarse fiber bridging/bundling. Excessive fiber bundling occurred primarily for two reasons: First, our current molding equipment is rather old and does not provide adequate control of molding pressure. High molding pressure may enhance intermeshing of fiber layers. An attempt was made to reduce this effect by molding the above samples using a two step process. First, two halves of a DCB specimen were individually molded at a molding pressure of 300 psi. The two halves were then sandwiched together with two layers of aluminum foil (1.5 inches long [38.1 mm]) placed on one end in between the two layers to act as a starter crack. This assembly was returned to the compression molder where it was reheated and molded into a DCB specimen. The molding pressure used during the second step was reduced to 250 psi in order to reduce the intermeshing of fibers across the midplane of the specimen. Using this process we found that the fibers were skewed approximately 10 degrees from the crack propagation direction in a plane parallel to the crack plane. Misalignment of the fibers could result in the deviation of the crack front out of the plane creating multiple crack fronts during testing. Subsequent test results also indicate an increase in fiber bridging.

Table I: DCB Test Results (samples molded at U of M)

| Sample I. D. | Material | Width (inches) | Thickness (inches) | $G_{IC}$* $KJ/M^2$ |
|---|---|---|---|---|
| Sample_1 | PC + 10 wt% KM653<br>1.70<br>+ AS4 fiber | | 1.0 | 0.145 |
| DCB0003 | PC + 10 wt% KM330<br>+ AS4 fiber | 1.0 | 0.145 | 1.20 |
| Sample_2 | PC + 10 wt% KM330<br>+ AS4 fiber | 1.5 | 0.146 | 1.24 |

* $G_{IC}$ values are based on area calculations.

A displacement rate of 0.5 in./min (12.7 mm/min.) was used for all tests.

The $G_{IC}$ values recorded in Table I must therefore be considered as an over estimate of the true interlaminar fracture toughness. This is a result of the additional energy expended in fiber pullout and breakage as well as an underestimate of the crack extension area used for calculating the toughness.

However, the tests did show that the voiding process used to toughen the neat resin was still operating within the interfibrillar spacing in the composite. This is shown by comparing SEM photos taken of the fracture surface of a compact tension specimen (toughened neat resin) to that of a DCB specimen (Figures 1 and 2). In both cases, voiding is observed. SEM analysis indicated an unsatisfactory adhesion in the composite between the toughened resin and the carbon fibers. This has been a common problem for composites with thermoplastic matrices. The significance of poor adhesion will be discussed in greater detail at a later time.

Because of the encouraging results of the earlier tests, additional material was compounded and sent to NASA to be made into pre-pregs and molded into 6 inch square (152.4 mm square) plaques. These plaques were then sectioned into DCB specimens with typical dimensions of 1 inch (25.4 mm) wide, 5.75 inches (146.1 mm) long and 0.128 inches (3.25 mm) thick. Each specimen had a layer of Kapton film molded into the midplane of the specimen to act as a starter crack. Two DCB specimens each of the following materials were tested using a displacement rate of 0.5 in./min. (12.7 mm/min.):

1) PC + AS4 fibers (no rubber particles added, used as a control).
2) PC + 10 wt% KM330 + AS4 fibers.
3) PC + 10 wt% KM653 + AS4 fibers.

A typical force/deflection diagram recorded during testing is illustrated in Figure 3. The results of the DCB test are presented in Table II.

The data in Table II raises two questions: 1) Why are the results of the toughened material significantly lower than results found when testing samples molded at the University of Michigan? (Table I) 2) Why is the interlaminar fracture toughness of the

FIGURE 1

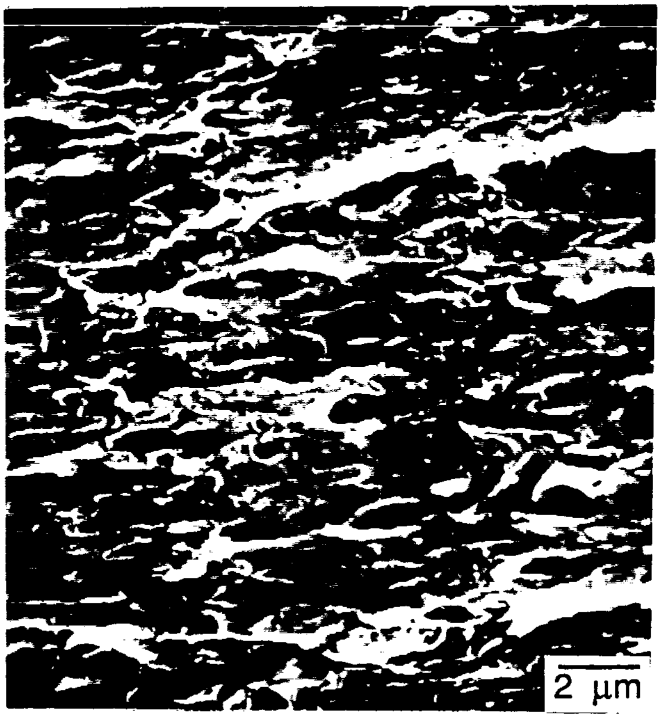

Fig. 1. SEM micrograph of the fracture surface of a disk shaped compact tension specimen. (PC + 5 wt% KM653) Photograph indicates that voiding and tearing are processes which occur during fracture of the rubber toughened material. Extension rate was 10 in./sec. (25.4 cm/sec.).

Figure 2

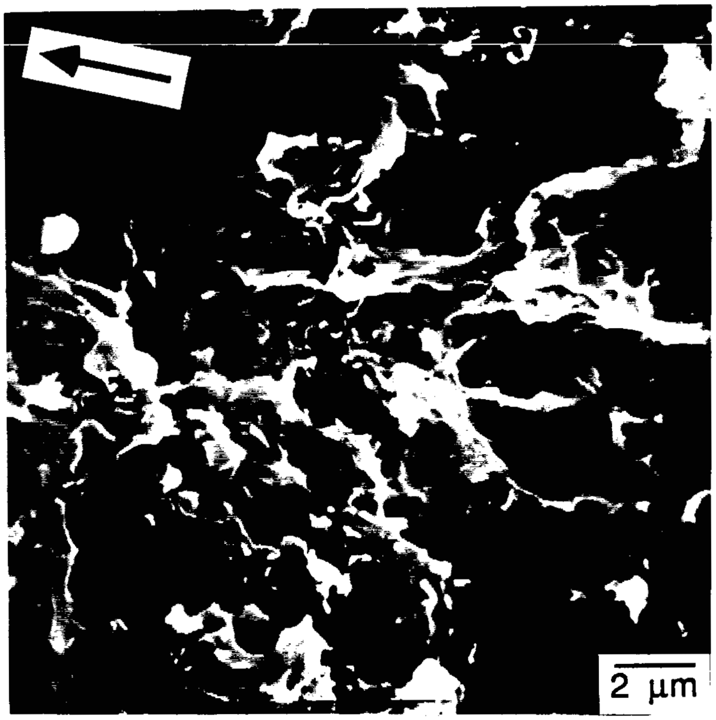

Fig. 2. SEM photograph of the fracture surface of the DCB specimen "Sample-5". This picture shows that voiding may still occur within the interfibrillar spacing. Extension rate was 0.5 in./min. (12.7 mm/min.). (Sample was molded at U of M.)

Figure 3

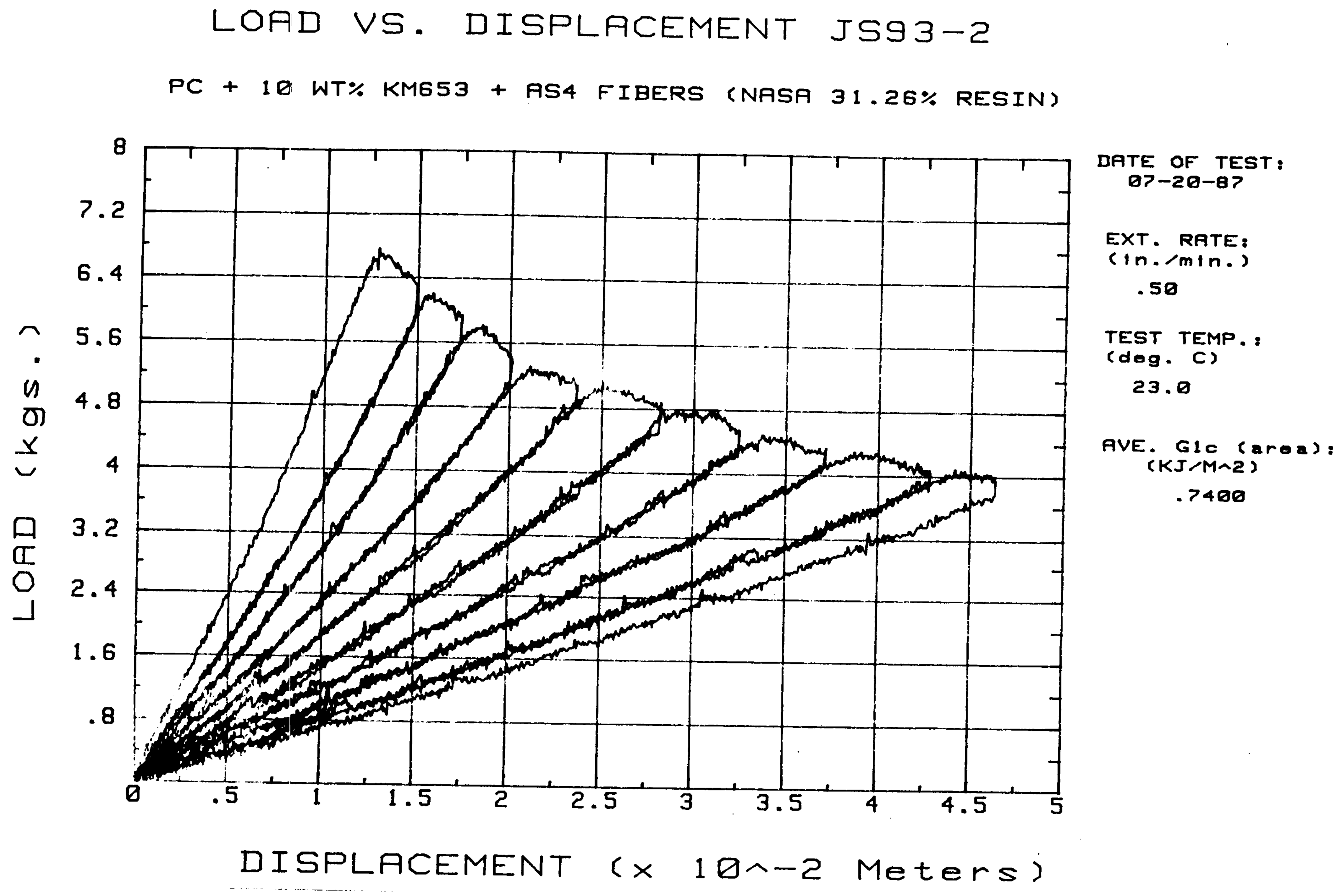

Fig. 3. A typical load deflection diagram recorded during a DCB test. The mode I interlaminar fracture toughness was calculated by the area method.

control material superior to that of the toughened systems?

Table II: DCB Test Results (samples molded by NASA)

| I. D. | % Resin | Material (method) | $G_{IC}$ (KJ/m$^2$)<br>Area | Modified Beam | Compliance |
|---|---|---|---|---|---|
| JS120-1 | 37.1 | PC + AS4 Fibers (control) | 1.15 | 1.51 | 0.94 |
| -2 | | | 1.20 | 1.54 | 0.96 |
| | | Average | 1.18 | 1.53 | 0.95 |
| JS104-1 | 34.73 | PC + 10 wt% KM330 + AS4 fibers | 0.86 | 0.76 | 0.69 |
| -2 | | | 0.75 | 0.61 | 0.65 |
| | | Average | 0.81 | 0.69 | 0.67 |
| JS93-1 | 31.26 | PC + 10 wt% KM653 + AS4 fibers | 0.76 | 0.87 | 0.62 |
| -2 | | | 0.74 | 0.88 | 0.62 |
| | | Average | 0.75 | 0.88 | 0.62 |

Note: The tests were conducted at room temperature using a displacement rate of 0.5 in./min. (12.7 mm/min.).

During the inspection of the fracture surface using an optical microscope, we found that the fracture surface of the NASA molded DCB specimens was quite different from the U of M molded samples. The NASA specimens showed very little coarse fiber bundling. Fiber bridging did occur, however, it consisted mainly of individual fibers. The fiber alignment of the NASA specimens was much closer to unidirectional and was parallel to the plane of crack propagation. These features are shown in Figures 4 and 5. These observations are consistent with a lower interlaminar fracture toughness being recorded for the NASA molded DCB specimens. An additional influence that has not been quantified is the difference in percent resin between the two series of DCB specimens. The original pre-pregs received from

# Figure 4

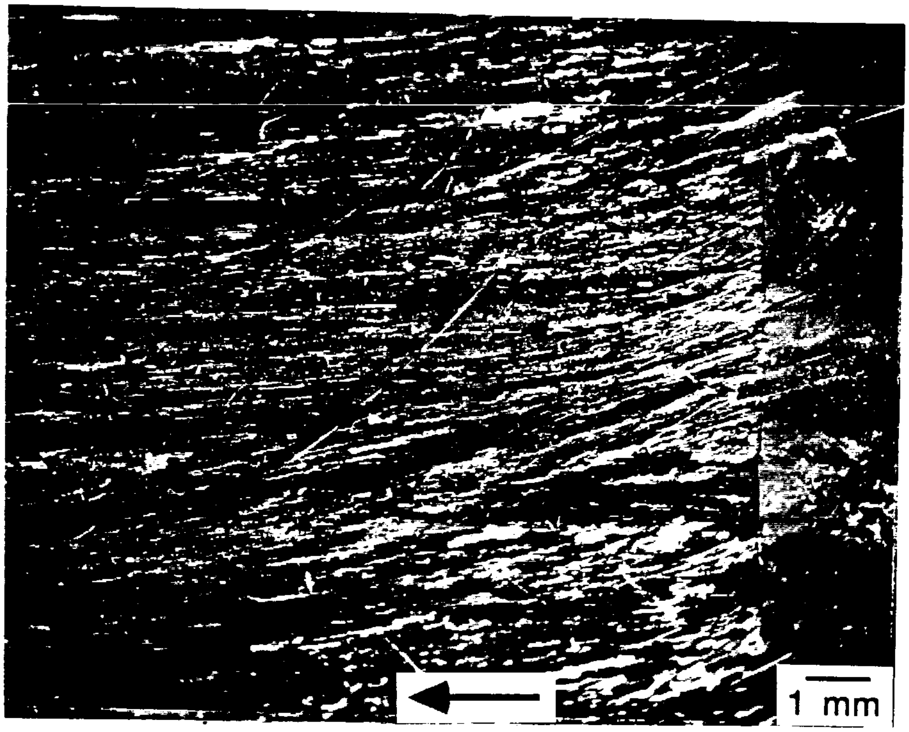

Fig. 4. Optical micrograph of the fracture surface of a rubber toughened DCB specimen molded at U of M. (Material: PC + 10 wt.% KM653 + AS4 fibers). Fibers are not parallel to the crack propagation direction. Arrow indicates the direction of crack propagation. Coarse grooves in the fracture surface are a result of fiber bundling. Extension rate was 0.5 in./min. (12.7 mm/min.).

Figure 5

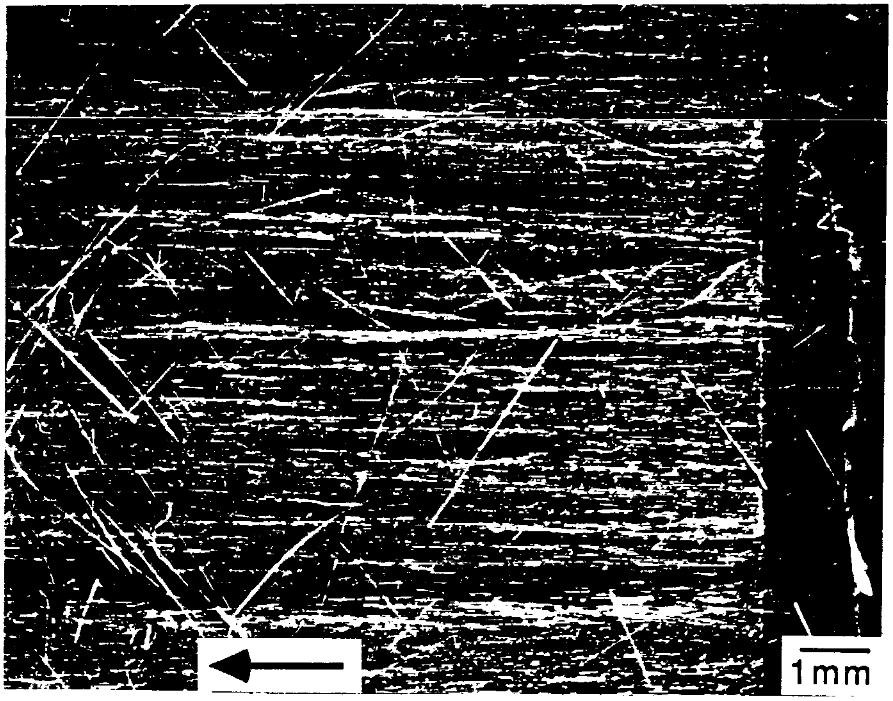

Fig. 5. Optical micrograph of the fracture surface of DCB specimen JS93-2 molded by NASA. (PC + 10 wt% KM653 + AS4 fibers) Fibers are parallel to the direction of crack propagation. The magnitude of fiber bridging/ bundeling is less than that observed in Figure 4. Extension rate was 0.5 in./min. (12.7 mm/min.).

NASA, which were used to mold the U of M samples, had a heavier resin coating on one side of the pre-preg than the other. This could result in an increase of resin in the final composite which would influence the fracture toughness significantly.

The DCB tests showed that the NASA-molded control samples had a greater toughness than the toughened composites. These results occur because of the differences in fiber/matrix adhesion in the two systems. A SEM photograph of the fracture surface of each of the three materials tested are shown in Figures 6 thru 14. By comparison it is clear that the control resin's adherence to the fiber is better than that of the two rubber toughened systems. Voiding does occur in the pure polycarbonate matrix composite (Figures 6 and 7) but on a more reduced scale (in terms of the number of voids) as compared to the rubber toughened composites (Figures 9 thru 14). Since fewer voids are formed, the voids grow larger in size. This results in the large dimple texture on the fracture surface of the control DCB specimen.

Very small voids (0.1 to 0.4 um dia.) are visible in the rubber toughened systems but only near the fiber matrix interface. This is a direct consequence of the poor matrix/fiber adhesion. During loading the voids first form to relieve the bulk strain energy, however, before the shear bands have a chance to grow the fiber/matrix interface fails. Thereafter, the fibers simply pull free from the matrix while the crack front moves through the specimen. Failure of the interface prematurely terminates the growth of voids and in turn retards the formation of shear bands. The end result is a lower interlaminar fracture toughness. Therefore, adhesion of the matrix to the fibers must be improved in order to appreciate the full potential of the rubber toughened matrix on a composite's fracture toughness.

In order to improve the fiber/matrix adhesion, the cause of interfacial failure must be identified. The only known difference between the control and toughened composites are the rubber

Figure 6

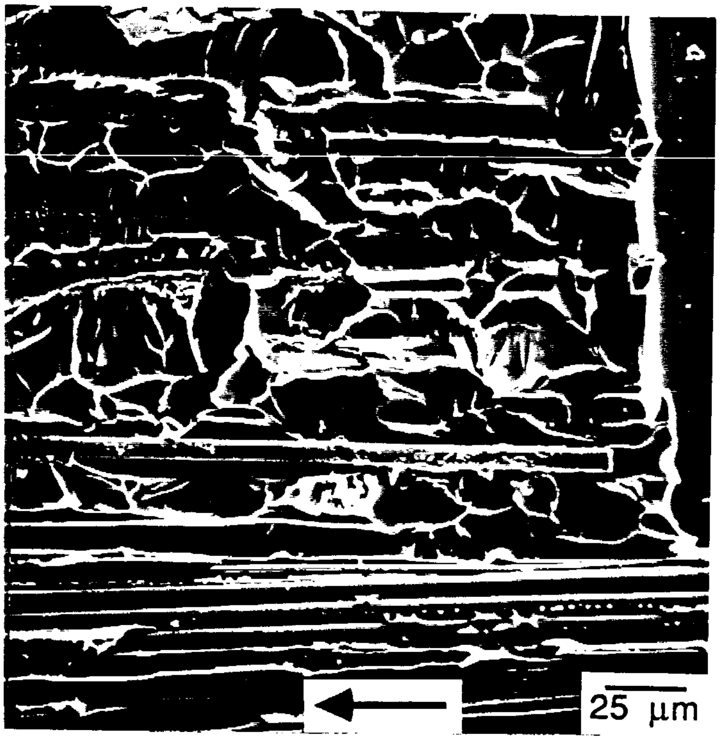

Fig. 6. Sem photograph of the fracture surface of the DCB specimen JS120-2 (control). Large pockets of deformed material on the fracture surface are a result of voids which have grown very large during fracture.

Figure 7

Fig. 7. Same area as in fig. 6 but at a greater magnification. Voids which form during fracture grow very large.

Figure 8

Fig. 8. SEM photomicrograph of the fracture surface of the DCB specimen JS120-2 (control). Excellent adhesion of the resin to the fibers is apparent.

Figure 9

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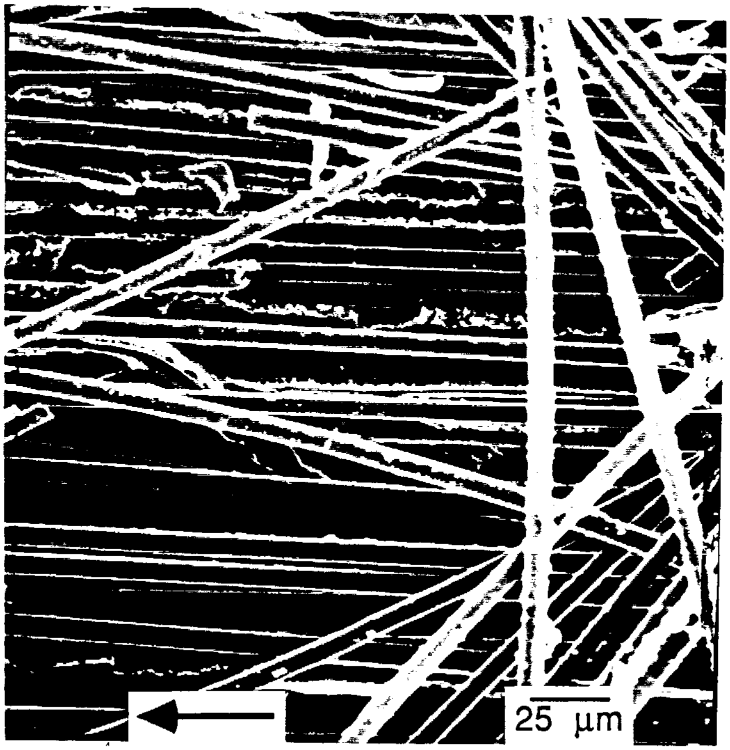

Fig. 9. SEM photomicrograph of the DCB specimen JS104-2. The resin has been almost completely removed from the fibers during fracture.

Figure 10

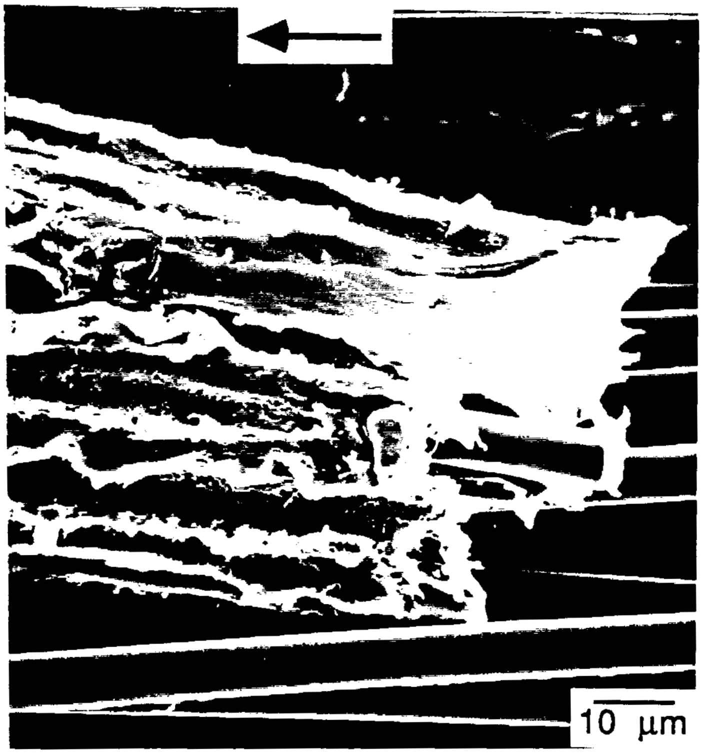

Fig. 10. SEM photomicrograph of specimen JS104-2. Voids do form during fracture, however, they do not grow very large. Again, the resin adherence to the fibers is poor.

Figure 11

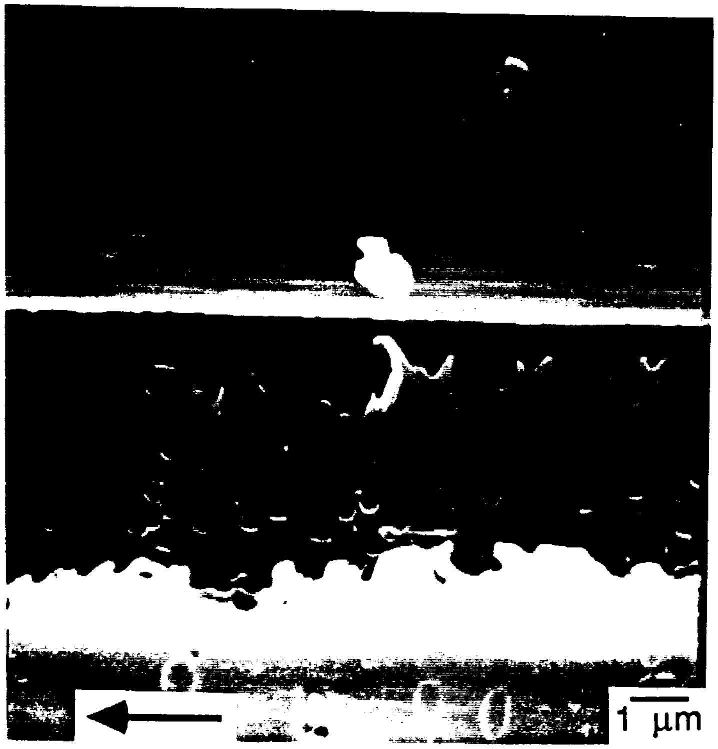

Fig. 11. SEM photomicrograph of specimen JS104-2. The resin has pulled free from the fiber during fracture. Voiding does occur, but they are unable to grow very large due to the interface failure.

Figure 12

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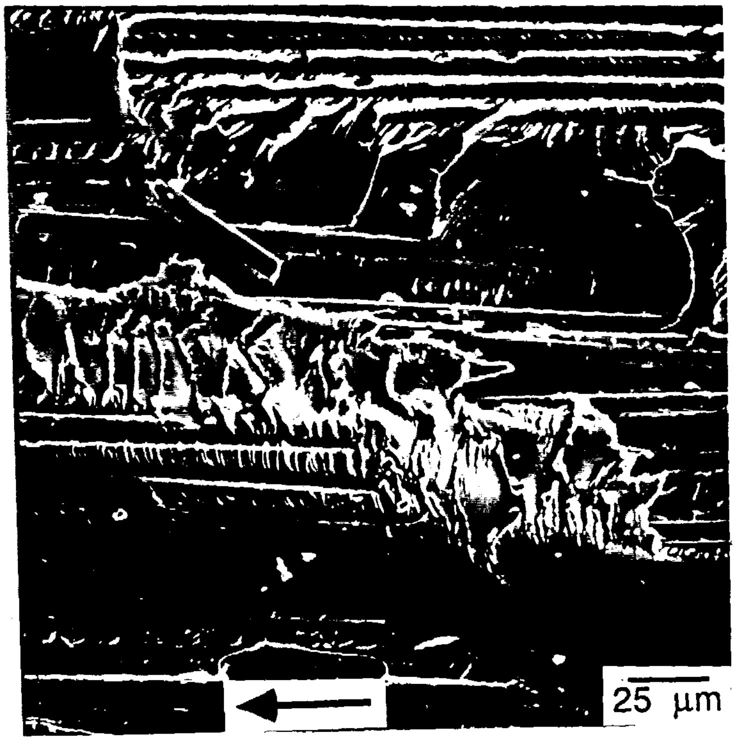

Fig. 12. SEM photomicrograph of the fracture surface of specimen JS93-2. It is clear that fibers along the fracture plane were pulled completely out of the specimen during fracture.

Figure 13

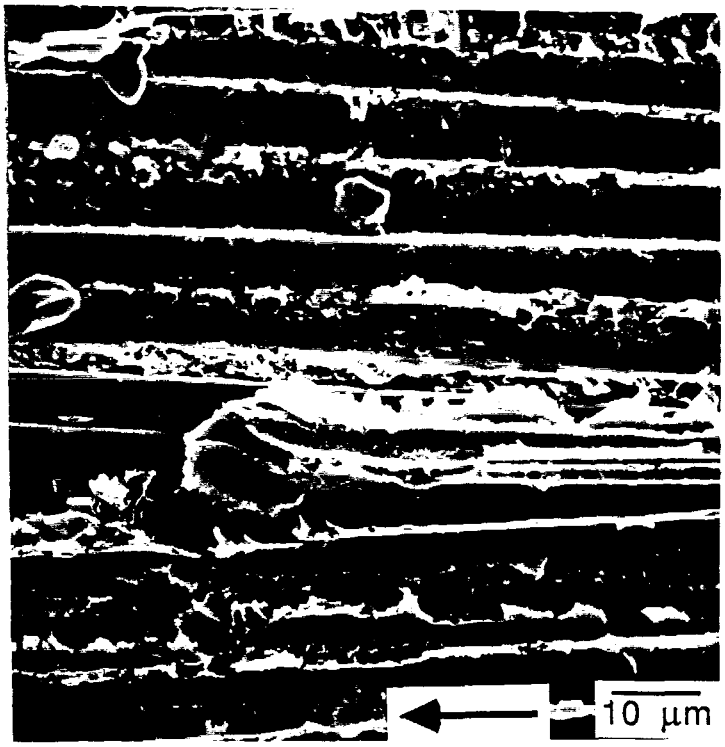

Fig. 13. SEM photomicrograph of DCB specimen JS93-2. This photograph demonstrates that the fibers pulled free of the matrix. during fracture and although, many voids are initiated they remain very small.

Figure 14

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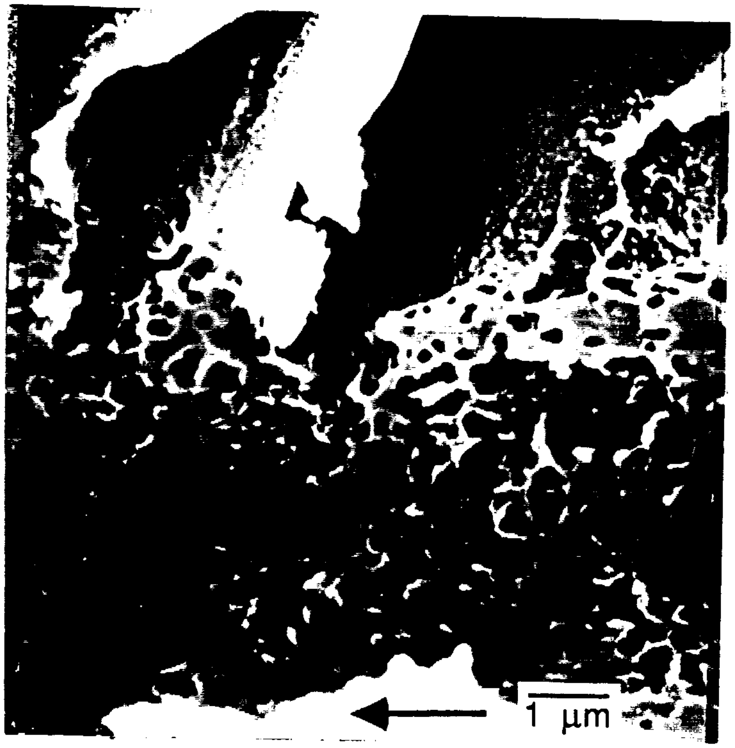

Fig. 14. SEM photomicrograph of the fracture surface of the DCB specimen JS93-2. This is a high magnification view of an area where a fiber has pulled free of the matrix. Very small voids form during fracture but only within the volume of material near the resin/fiber interface.

particles. We speculate that the rubber particles are preferentially collecting along the fiber surface (this could be a result of the processing technique used to produce the pre-pregs.). Little to no bonding would be expected between the core/ shell rubber particles and the fibers. Therefore, the fiber/matrix interface has been weakened by the presence of the rubber particles along the fiber surface. Methods used to determine the cause of interfacial failure will be discussed under the section titled future work.

## Tensile Dilatometry

Tensile dilatometry work began in early September, 1987. It is a method used to gain insight regarding what deformation mechanisms, such as voiding or shear banding, are operating during fracture. It also allows a determination of whether or not a particular mechanism has been enhanced or retarded.

Injection molded ASTM D638 type I tensile specimens were used for dilatometry testing. The tests were performed with a computer aided servo-hydraulic testing machine under constant displacement rate control. Analysis of the dilatometry work is incomplete due to poor statistics from an insufficient number of tests. Initial indications however do indicate that within the rubber toughened systems processes are occurring which increase volume and enhance shear banding (Figures 15 and 16). Differences between the two rubber toughened systems are apparent. The KM653 system indicates shear banding is enhanced but only at low strain rates. Polycarbonate with KM330 as a toughener indicates an increase in volume presumably due to voiding; however, there was no indication of shear band enhancement. Again, it must be emphasized that these are only our initial test results. Additional dilatometry work to increase our data base along with supporting scanning electron and optical microscopy must be completed to verify the deformation mechanisms.

Figure 15

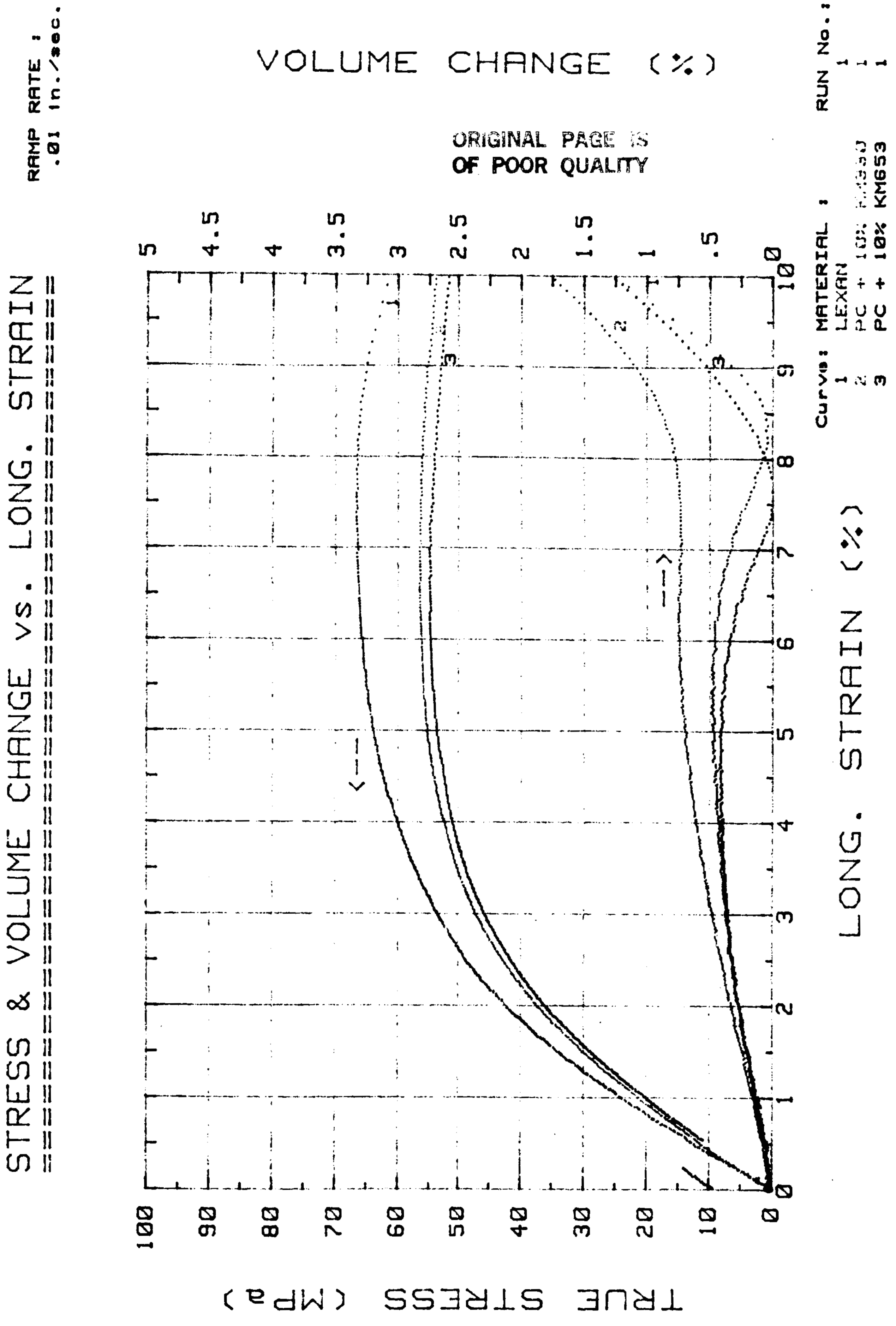

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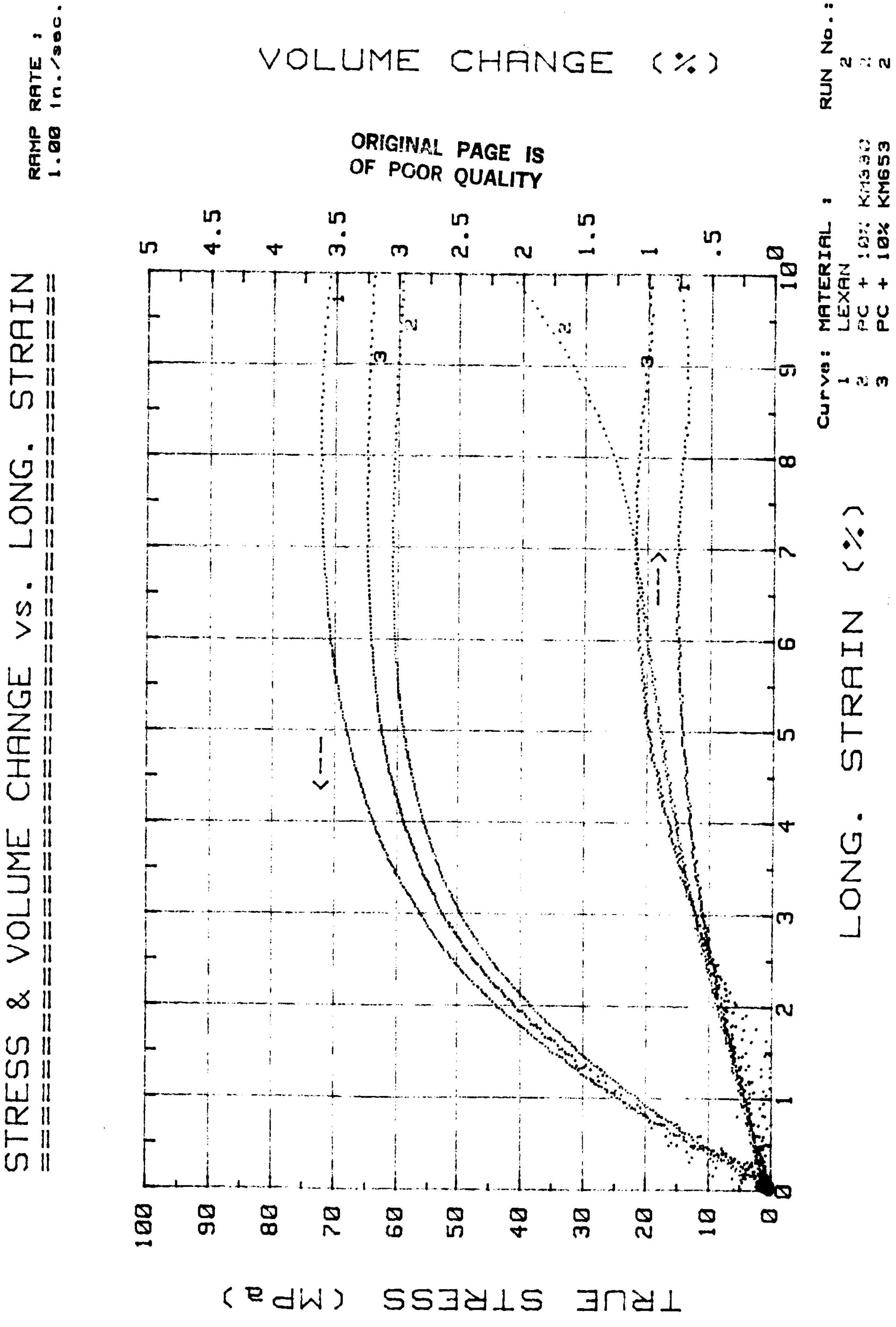
Figure 16


STRESS & VOLUME CHANGE vs. LONG. STRAIN
RAMP RATE :
1.00 in./sec.
VOLUME CHANGE (%)
5
4.5
4
3.5
3
2.5
2
1.5
1
.5
0
TRUE STRESS (MPa)
100
90
80
70
60
50
40
30
20
10
0
LONG. STRAIN (%)
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1 LEXAN 2
2 PC + 10% KM330 2
3 PC + 10% KM653 2

## FUTURE WORK

1) J-integral tests will be performed to determine the neat resin and the rubber toughened resins Mode I plane strain fracture toughness. These tests will be performed using a 3-point bend technique described by ASTM E813. The computer program used to control the servo-hydraulic testing machine has been completed. Various notch tip radii will be tested to investigate notch sensitivity. An appropriate notching method has yet to be determined.

2) The cause of the fiber/matrix interfacial failure observed during testing of the DCB specimens will be investigated. Our approach will be two fold:

   a) The rubber toughened material will be mixed with 50:50 solution of methylene chloride and Chloroform (solvent used to produce the pre-pregs). Our concern is with whether or not we see separation occur. The rubber particles may come out of solution and float to the surface. If this does occur during the production of the pre-pregs, it could result in a high concentration of rubber particles along the fiber surfaces which would produce a weak interface. If the speculations above are found to be true, a change in the type of solvent used to produce the pre-pregs may be in order.

   b) Plasma etching will be used to determine the distribution of the rubber particles throughout the DCB specimens. This technique may enhance the demarcation between the rubber particles and the matrix which will allow observations to be made using the SEM. Initially, sections taken perpendicular to the fiber direction will be used for this work.

3) Once the adhesion problems are resolved, additional DCB tests will be performed to determine a more accurate value of the Mode I interlaminar fracture toughness ($G_{IC}$) of the rubber toughened resins.

   If a solution to these problems cannot be found, other techniques to determine the interlaminar fracture toughness may have to be investigated. One technique may be an adhesive joint test. This test attempts to predict a composite's Mode I interlaminar fracture toughness from the measured adhesive joint fracture toughness. However, to date a direct relationship between the two fracture toughness values has not been established.

4) Tensile dilatometry work will continue. A larger data base must be developed in order to interpret these test results accurately.

5) Scanning electron and optical microscopy of fracture specimens will be performed to verify the deformation mechanisms indicated by the tensile dilatometry tests.

## APPROACH 2: Copolycarbonates

The goal of this approach is to develop a candidate material for toughening by copolymerization. Incorporation of a second rigid block species would impart a high glass transition to the copolymer without a loss of ductility which would exist by virtue of the first block species. For a polymer to have these desirable properties, it must have two distinct secondary relaxation peaks, one sufficiently below ambient temperature. In addition it should have only one glass transition temperature in order not to suffer phase separation. We have proposed that this requirement be met by controlling block length of the two polymers, which, for the present study, are bisphenol-A (BPA) carbonate and tetramethyl bisphenol-A (TMBPA) carbonate.

In our previous report, a synthetic route to alternating multi-block copolycarbonate was described. In summary, a copolymer of BPA and TMBPA carbonate was synthesized by the reaction of hydroxyl-terminated BPA oligicarbonate with bischloroformate terminated TMBPA oligomer. Oligocarbonates were prepared by non-stoichiometric condensation of BPA or TMBPA with the corresponding bischloroformates which had been derived from their phenols by reaction with excess phogene. The essential characterization of the monomers and their derivatives was carried out.

## CURRENT WORK

### (1) Synthesis

The synthesis and characterization of the multi-block copolymers has continued. In addition, the synthetic route has been somewhat modified. The bischloroformate of BPA oligocarbonate instead of the TMBPA block was prepared and condensed with the hydroxyl-terminated TMBPA oligocarbonate. This change was made in order to enhance the solubility, and thus the reactivity, of the TMBPA species which has substituents on the ring near the reaction site. The revised reaction scheme is shown in Fig. 17. With this modification, block copolymers with alternating sequences of BPA and TMBPA carbonate blocks were successfully prepared.

As in conventional copolycondensation, high molecular weight copolymer formation is favored by an equimolar balance of two block species. For this reason a knowledge of the exact block length or the number of functional groups in the reactant oligomers is necessary. The number of functional groups in the bischloroformate oligomer was determined with good accuracy and reproducibility using the Volhard titration of chlorine. The results of this determination agree well with those observed by NMR and elemental analysis. For hydroxyl-terminated oligomers, however, analysis techniques including end-group titration, NMR, and elemental analysis were found not to be accurate enough to allow the predetermination of optimum feed ratios in the copolycondensation reaction. Other techniques such as spectrophotometry and vapor phase osmometry are being developed.
Therefore, at the present stage of study, the polymers prepared by the condensation of two block species with poorly characterized lengths, and, thus, with inexact equimolar concentration of functional groups, suffer from low molecular weight as judged by intrinsic viscosity measurement.

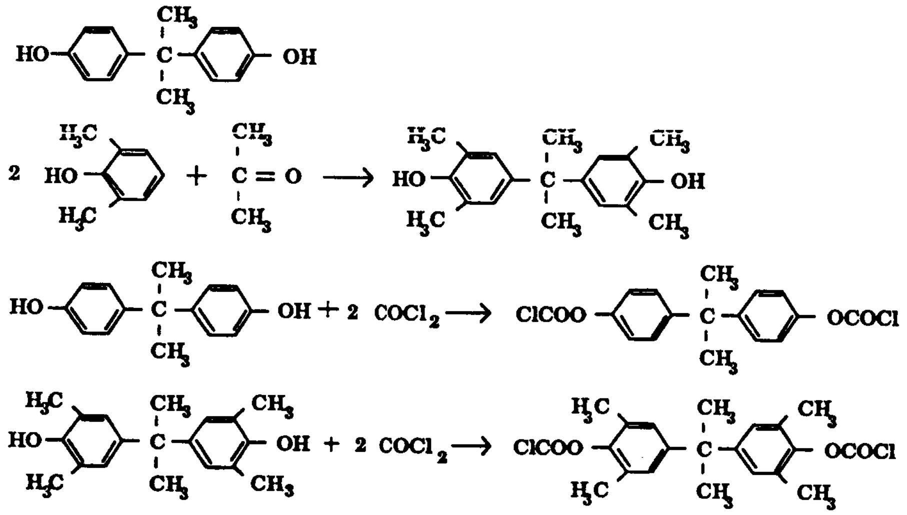
(2) Mechanical Characterization

To produce the proposed copolymer with regulated block lengths, it is necessary to elucidate the scale of molecular motion at sub-Tg temperature by finding the block length where two distinct secondary relaxation peaks emerge.

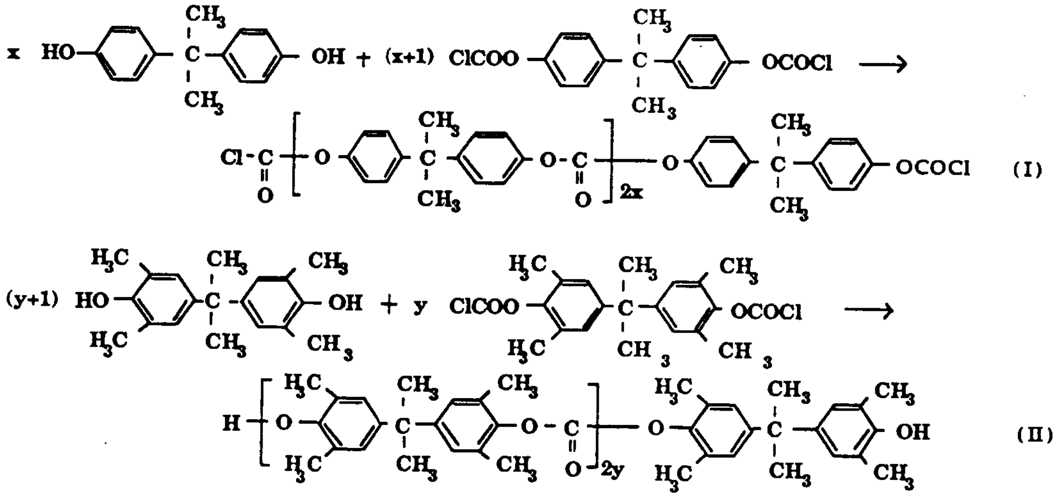
Figure 17

## SCHEME FOR SYNTHESIS OF COPOLYCARBONATE

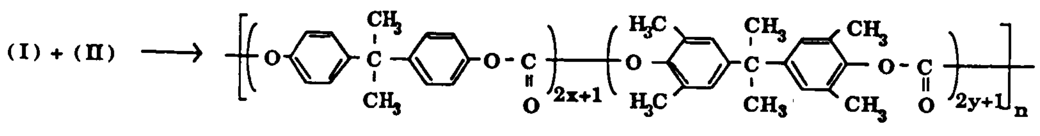
### 1. Monomers



### 2. Oligomers



### 3. Block Copolymer



A dynamic mechanical analysis was carried out on the polymer which has alternating sequences of five units of BPA and TMBPA carbonates, i.e., $-[-B_5-T_5-]_n-$. The result is shown in Fig. 18. As shown in the spectrum, only one secondary peak was found at a temperature (25°C at 11 Hz) intermediate between secondary relaxation temperatures of the two homopolymers, -90°C and 70°C, at 10 Hz. This result shows that the scale of cooperative molecular motion of the BPA polycarbonate at sub-Tg temperature is larger than five monomer units. To determine the exact length of motion, dynamic mechanical tests for a series of copolymers with systematically changing block length is required. As mentioned before, however, the other polymers with various block lengths suffer from low molecular weight, and can hardly be casted into film specimens with the necessary strength for testing.

On the other hand, these results have already caused us to revise our research plans regarding the bismaleimides. If cooperative motion of polycarbonate involves more than five units, then the BMI's must have even more units between the end groups to have enhanced toughenability. This change in strategy is reflected in our BMI synthesis, which is described in a separate section.

## FUTURE WORK

(1) Development of more dependable techniques for analysing hydroxyl terminated oligomers will be continued. There is a spectrophotometric technique for detecting hydroxyl groups which appears dependable and refinement of this technique is currently being performed. Vapor phase osmometry for both types of oligomers will also be carried out to confirm the analysis data obtained by other techniques.

(2) If analyses of oligomers turn out not to be dependable, alternative methods, which requires more laborious efforts and yet is more promising for producing high molecular weight copolymer will be

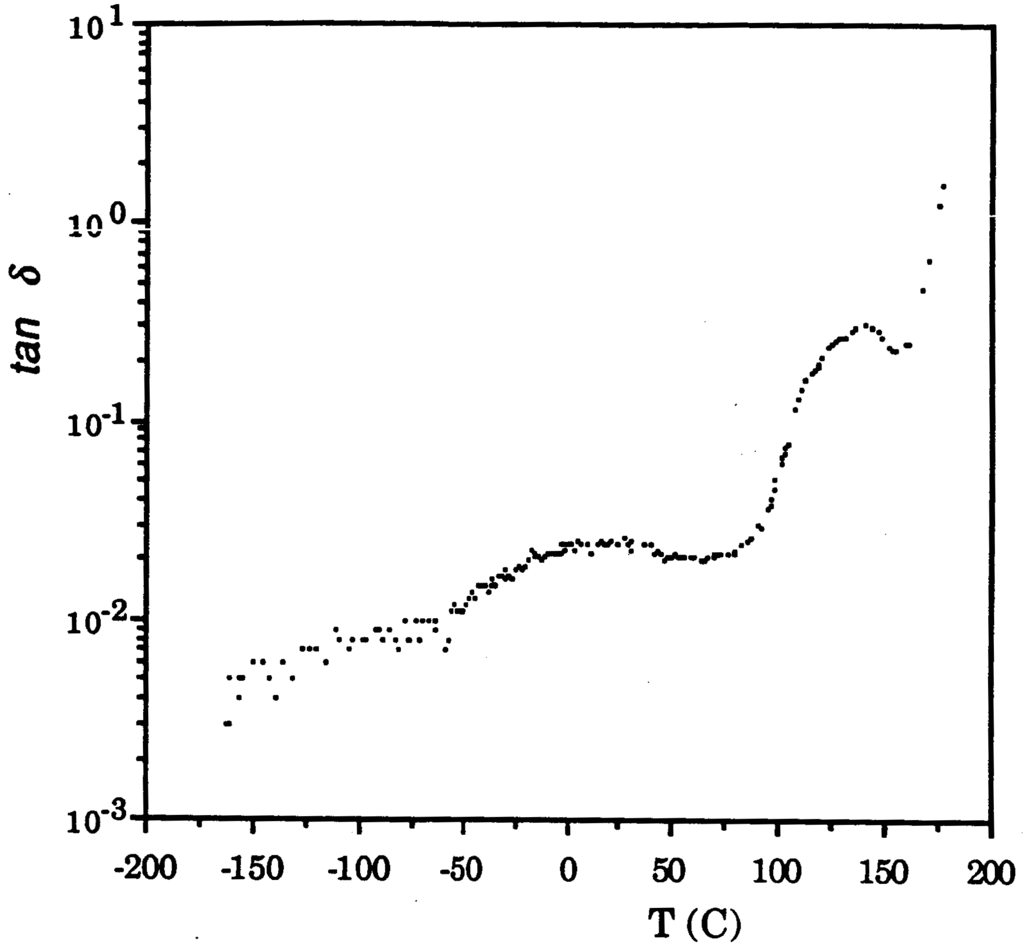


Fig. 18. Dynamic mechanical spectrum of the copolymer, $-[-B_5-T_5-]_n--$, at 11 Hz.

explored. This effort will include a series of small scale copolycondensations with constant total weight and various coreactant weight ratios. The relative viscosities of each batch will then be measured to determine the optimum ratio needed to obtain high molecular weight, which should give high viscosity. Since, at the ratio giving highest molecular weight there must be an equal number of end groups present and the number of bischloroformate groups can readily be determined prior to these experiments, the block length of hydroxyl-terminated oligomer can also be determined.

(3) After a series of block copolymers with systematically varying block lengths is prepared, dynamic mechanical analyses will be performed for these specimens to find the critical length of molecular motion of polycarbonate at sub-Tg temperature.

## THERMOPLASTIC SYSTEMS - Toughened Bismaleimides

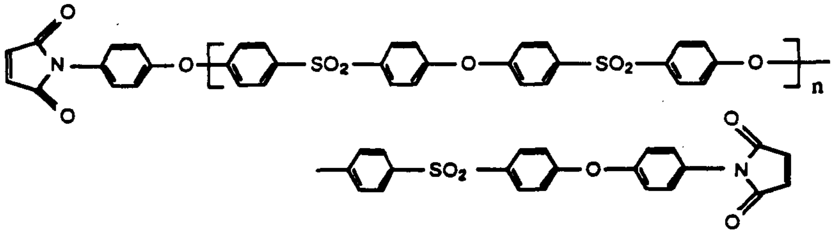
What follows is a report of our initial results concerning the toughening of bismaleimide thermosets. The work so far has been directed towards the synthesis of the matrix materials (polysulfone-bismaleimides) as well as the preparation of specific toughening systems. Therefore, in this preliminary report, we will describe only the synthesis and characterization of these materials.

## MATRIX MATERIALS

To date, compounds **I, II, III**, and **IV** have been synthesized using methods described previously in the literature.[1,2] These materials with the exception of **III** and **IV**, are identical to those obtained from NASA in mid-July. Compounds **III** and **IV** also were prepared since there is some evidence that, in thermosets, toughening can be enhanced by increasing the molecular weight between crosslinks ($M_c$).[3] The specific details of the synthesis of these materials are shown in Schemes 1 and 2. The method of Kwiatkowski and coworkers[2] is quite suitable for the preparation of the polysulfone diamines. Nevertheless, the large-scale preparation of these species is made somewhat difficult by a tedious and time-consuming filtration step that is required upon precipitating the product in water. Current efforts are focused on the possibility of using another solvent to precipitate the diamine; another solvent may allow this material to be filtered more easily.

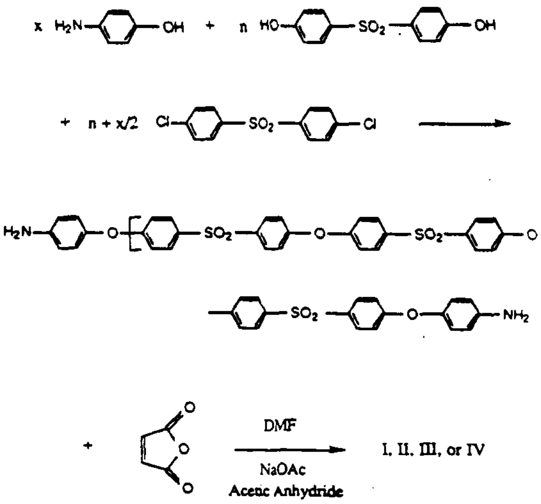
The classical "Searle" synthesis, outlined in Schemes 1 and 2, generally results in low yields of bismaleimide. The poor yields generally have been attributed to side reactions. In response to these problems, we have begun an investigation of other synthetic routes to these materials; one involving the reaction of an amic acid with ketene is of particular interest. On a previous occasion, this process resulted in higher yields of bismaleimide.[4] This reaction sequence is depicted in Scheme 3. At this early stage, we have not been able to determine whether this method results in higher yields of the desired product.

It should be noted that thermal imidization of aroamtic diamines requires the use of temperatures in the range of 180-200°C. Unfortunately, temperatures such as these results in some isomerization of the amic acid to a fumaric group.[5] As illustrated in Scheme 4, this undesirable side reaction might account for some of the low yields observed in the preparation of the bismaleimides.

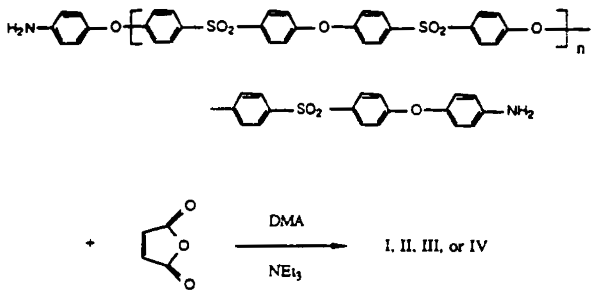


**I**: n = 1; **II**: n = 3; **III**: n = 6; **IV**: n = 9

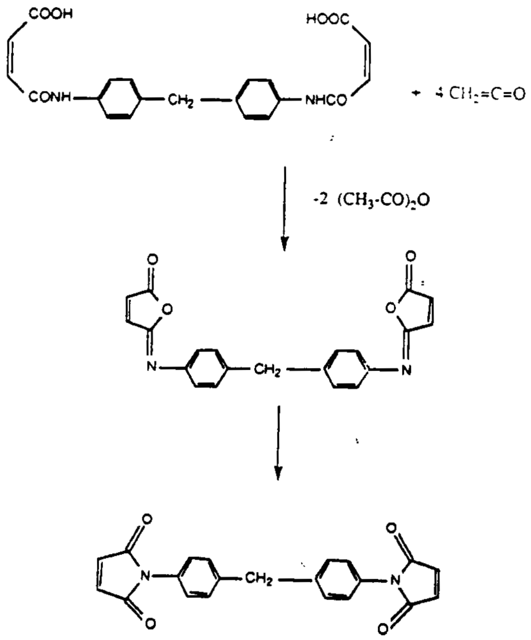
Scheme 1
Synthesis of bismaleimides from diamines according to reference 1



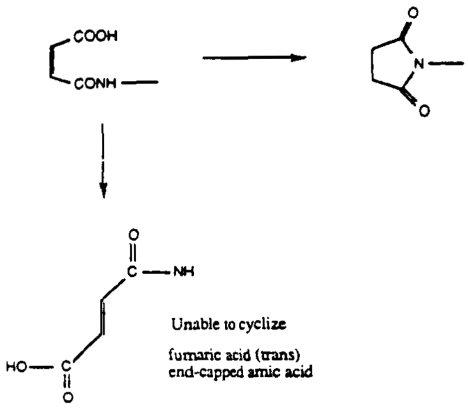
## Scheme 2
## Synthesis of bismaleimides according to reference 2



## Scheme 3
## Alternate route to bismaleimides[4]

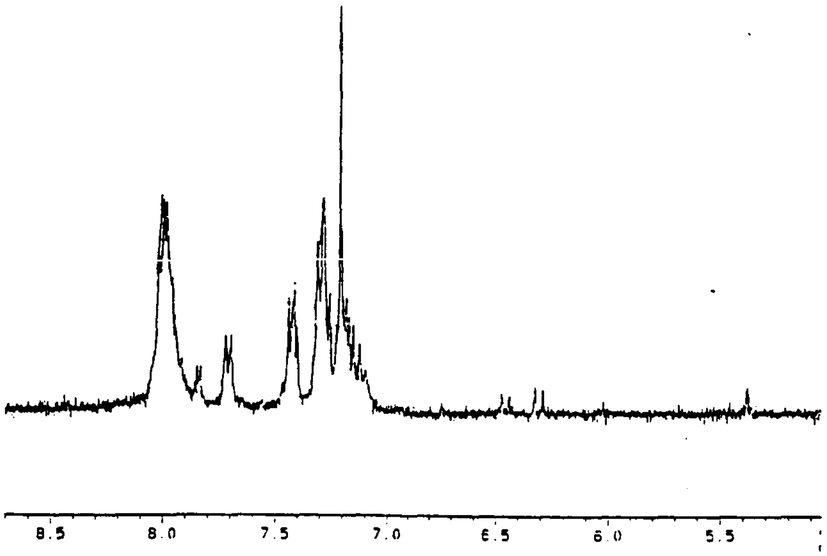


Scheme 4
Formation of a fumaric group in the preparation of bismaleimides[5]



In addition, attempts are being made to fully characterize these materials. Infrared spectroscopy, as well as proton and carbon-13 nuclear magnetic resonance (NMR) spectroscopies are being used for this purpose. In fact, we are using proton NMR spectroscopy to determine the molecular weight of the polysulfone diamines. This procedure is an alternative to the titration method employed by Pratsil, Inc. to evaluate the molecular weight of these species. As shown in Figure 19, the determination of molecular weight using proton NMR spectroscopy requires that the resonances corresponding to the protons of the amino end-groups (6.63 and 6.82 ppm) be integrated relative to the resonances corresponding to the aromatic protons of the other groups of the chain. In addition, this particular spectroscopic technique provides some indication of the purities of the diamines.

Figure 19
$^1$H NMR Spectrum of a bismaleimide, molecular weight: 900 g/mole (spectrum obtained in dimethylsulfoxide-$d_6$)



## MATERIALS FOR INCLUSION INTO THE MATRIX

### A. Core/Shell Systems

Several core/shell systems are being investigated simultaneously for inclusion into the bismaleimide matrix. Potential constituents of these core/shell system are evaluated on the basis of the compatibility of the shell material with the matrix or the ability of the shell material to undergo a reaction with the matrix. Each of these events should lead to good adhesion between the matrix and the rubber particles. In addition, good adhesion between the shell and the core materials is also desirable. A specific example of a reaction that promotes good adhesion between the matrix and the shell material, a Michael reaction between the bismaleimide and an amine or some other nucleophlic group can be exploited. Unfortunately, most potential Michael reactors cannot be prepared using emulsion polymerization techniques - techniques which are required for the preparation of core/shell materials. Therefore, we are limited in terms of the constituents for these core/shell systems.

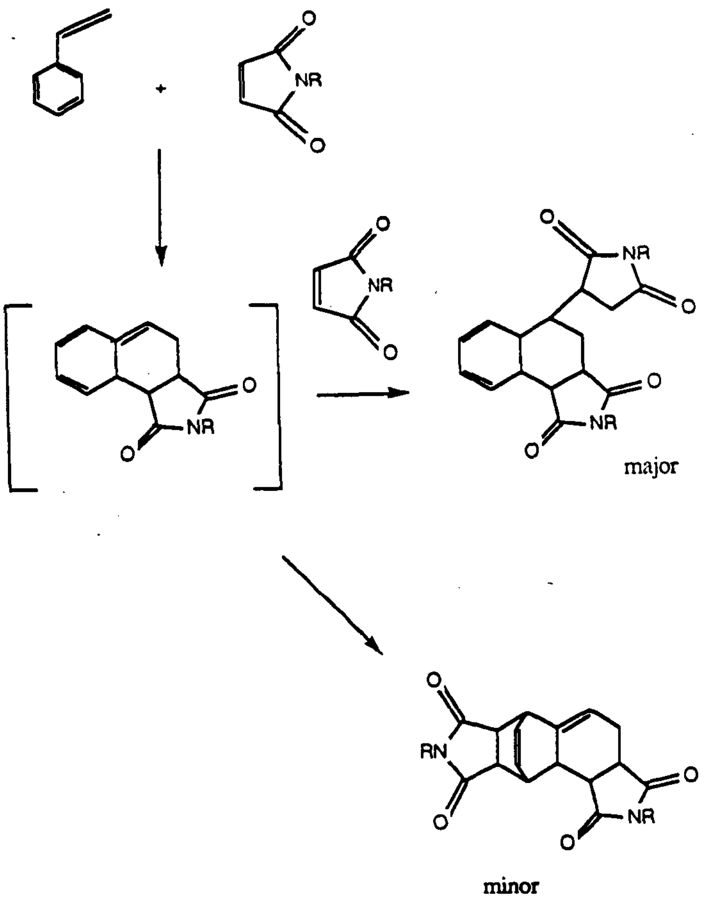
One of the core/shell systems we have been investigating consists of polystyrene as the core material and the polymer of *p*-vinylanisole as the shell material. In short, we are attempting to use the polarity of the methoxy group of the *p*-vinylanisole to promote compatibility between the bismaleimide matrix and the shell. In addition, the shell material can be copolymerized with styrene, the core monomer. There are numerous parameters that can be varied in the preparation of these core/shell systems (polymerization temperature, stirring speed, etc.); only a few of these have been examined thus far. For example, the effect on the resulting core/shell system of varying the amount of seed latex vs. the amount of monomer for the shell has been examined; a low concentration of monomer appears to produce some polystyrene particles which are insufficiently coated with poly (*p*-vinylanisole).

The method used to characterize these core/shell materials involves treating the particles with solvent and observing the constituents of fractions collected over a period of time, using proton and carbon-13 NMR spectroscopies. For the polystyrene-poly (*p*-vinylanisole) system, the initial toluene fractions show evidence of poly (*p*-vinylanisole) (a peak at 3.85 ppm in the $^1$H NMR spectrum is observed) while successive fractions show increasing amounts of polystyrene. Unfortunately, this particular method is insensitive to the presence of copolymers of styrene and *p*-vinylanisole. In order to detect these species, we have employed techniques of thin-layer chromatography (TLC): the copolymer has a different $R_f$ value than either homopolymer and, therefore, appears as a third spot on the TLC plate.

Other core/shell systems that are being investigated include polystyrene/polyacryl-amide, polystyrene/polyacrylonitrile, and polystyrene/polybutylacrylate. Again, there is some difficulty in finding a core/shell system that allows for a reaction to occur between the shell material and the matrix. Along these lines, we also are exploring the possibility of a core/shell system consisting of polystyrene and divinylbenzene. If divinylbenzene emerges as the shell material (the reaction would have to be carried out in the presence of polymerization inhibitors), a reaction can be promoted between the unsaturated divinylbenzene moiety and the bismaleimide (Scheme 5). It has been well-documented that toughening of bismaleimides by styrene occurs by virtue of reactions of this type.[6] For the most part, however, shell materials that are able to promote reactions with the matrix are not polymerizable by emulsion techniques.

Scheme 5

Diels-Alder addition of styrene to bismaleimides

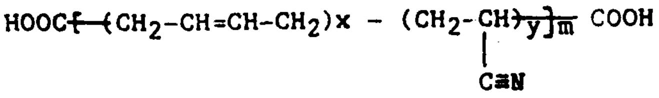


## B. Rubber Tougheners

In contrast to the core/shell systems, we much less limited in terms of tougheners of an additive type for the bismaleimide resins. In fact, a number of useful systems are commercially available. Listed below are the systems we are currently investigating; in each case, we have proposed how the particular additive will be able to promote toughening in the bismaleimides. Where appropriate, the synthetic routes to the additives are noted.

### 1. Carboxyl-terminated butadiene-acrylonitrile copolymer (Hycar® 1300X13 CTBN polymer) -

This carboxyl-terminated liquid copolymer, the general structure of which is indicated below (V), was received from The BF Goodrich Company. For Hycar® 1300X13, m is approximately 7 and the amount of bound acrylonitrile is 26%.[7] There is some evidence in the literature[8] which suggests that toughening of bismaleimide resins can be achieved using carboxy-terminated elastomers, however, the nature of the specific reaction that occurs between the bismaleimide moiety and the carboxyl group (if one exists) is still a point of controversy. Along these lines, we have examined a model system - that of 1,1'-(methylene di-4,1-phenylene) bismaleimide and Hycar® 1300X13 - to determine if a reaction takes place between the bismaleimide moiety and the carboxylic acid group. We are using carbon-13 NMR spectroscopy in this investigation since infrared spectroscopy provides very little information due to overlapping of certain critical bands in the spectrum.

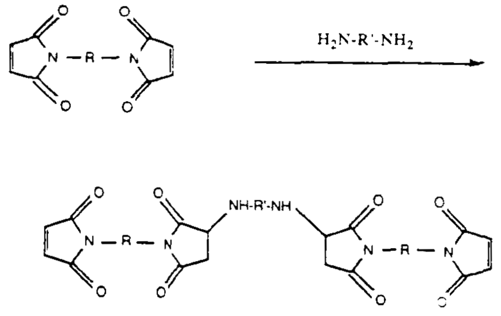


$$HOOC\{(CH_2-CH=CH-CH_2)_x-(CH_2-\underset{\displaystyle C\equiv N}{\underset{|}{CH}})_y\}_m COOH$$

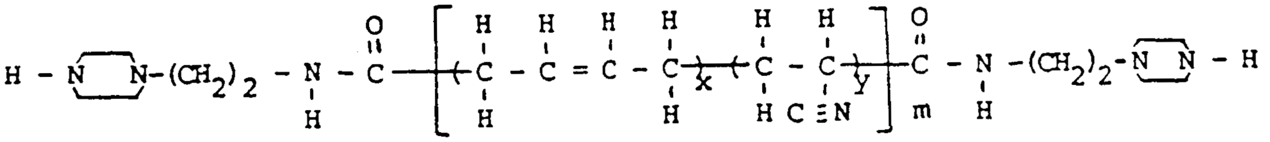
V

2. Amine-terminated butadiene-acrylonitrile copolymer (Hycar® 1300X16 ATBN polymer) -
As indicated in Scheme 6, the amine end-groups of this liquid copolymer serve to copolymerize with the bismaleimide matrix in a Michael reaction.

Scheme 6
Michael reaction between amine end-groups and bismaleimides



There are a number of commercial resins that exploit the reaction between bismaleimides and aromatic diprimary amines. Most often, the bismaleimide is used in excess and the reaction is performed in the melt to give low molecular weight, crosslinkable prepolymers.[9] The use of a secondary amine system alleviates the possibility of further reaction occurring during the curing process, between the remaining secondary amine and the bismaleimide. Again, this material was given to us by The BF Goodrich Company. As indicated in the structure shown below (VI), Hycar® 1300X16 is a copolymer of butadiene and acrylonitile where m=10 (approximately) and the amount of bound acrylonitrile is 16%.[10]

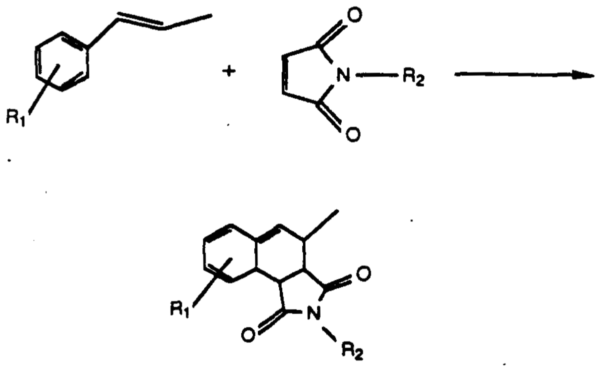

VI

## 3. Diallyl Systems

### a. *o,o'* -Diallylbisphenol A (Matrimid 5292B)

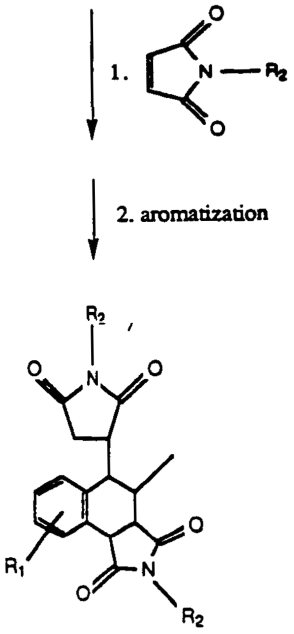
The Ciba-Geigy Plastics R&D Laboratories have generously supplied us with this material. In fact, these laboratories use this material in their two-component bismaleimide resin XU 292. The "A" component of this resin consists of 4,4'-bismaleimidodiphenylmethane (VII), while the "B" part is *o,o'* -diallylbisphenol A (VIII).[11,12] It is anticipated that the chemistry taking place on cure is essentially that outlined in Scheme 7. As indicated in the scheme, the copolymerization consists of effectively two reactions - an "Ene" reaction, followed by a

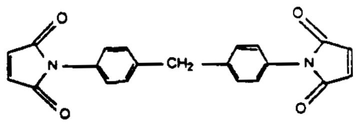
Scheme 7
Copolymerization of bismaleimides with propenyl-terminated arylene ether
compounds
Diels-Alder reaction

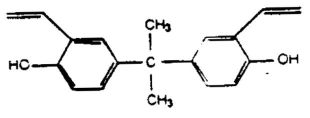


Scheme 7, continued

Ene reaction




VII

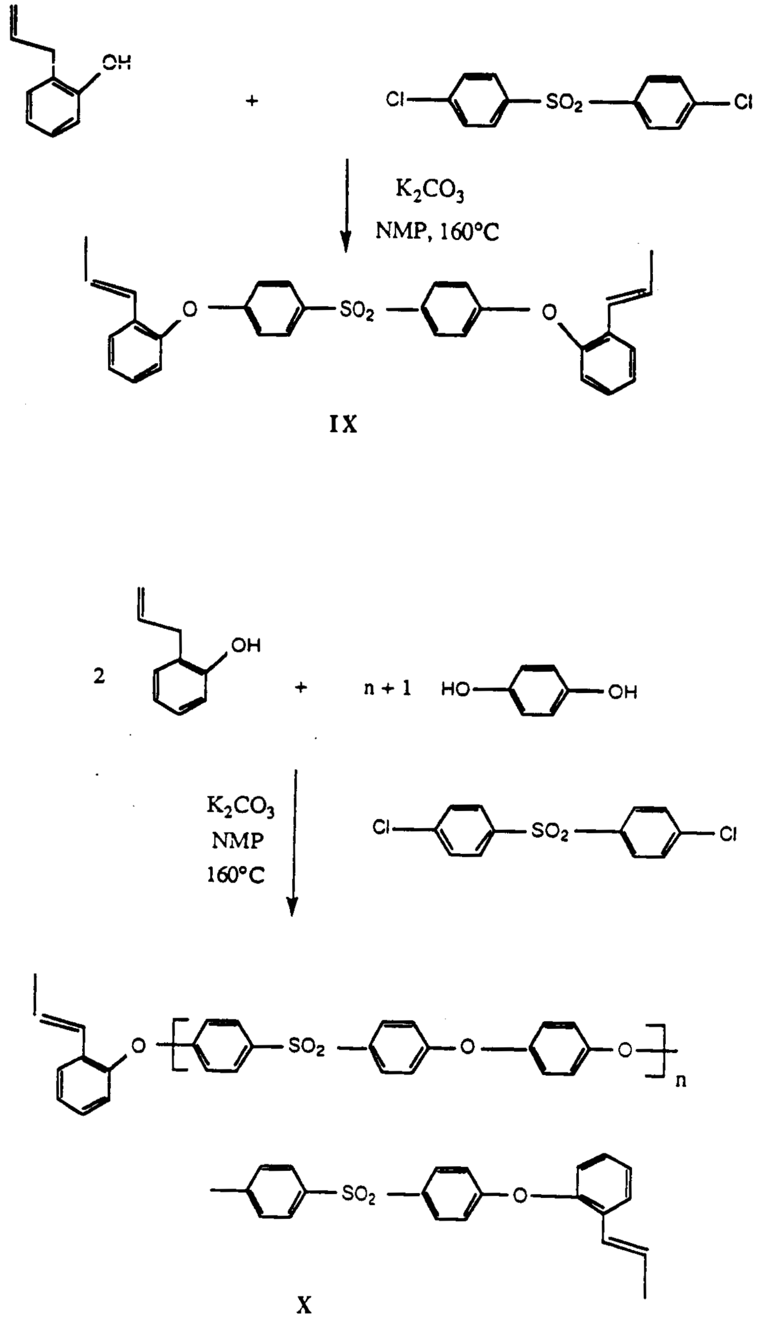

VIII

"Diels-Alder" reaction. We anticipate that the Matrimid 5292B material will undergo a similar reaction with the polysulfone-bismaleimide system.

b. Allyl-(propenyl)-terminated arylene-ether-sulfones

Another series of compounds we are examining for the purpose of exploiting such reactions as those outlined in Scheme 7 consists of allyl-(propenyl)-terminated arylene-ether-sulfones. This particular system has been used as a toughening modifier for other bismaleimide resins.[13,14] The preparation of these compounds of varying molecular weight (**IX** and **X**) is outlined in Scheme 8. The copolymerization takes place between 150-200°C. It is hoped that this system will provide for improved adhesion between the matrix and the rubber particle due to a better match in polarity between the two phases; it is anticipated that Matrimid 5292B might not provide as much adhesion due to the difference in polarity between the modifier and the matrix.

Scheme 8
Preparation of allyl-(propenyl)-terminated arylene-ether-sulfones

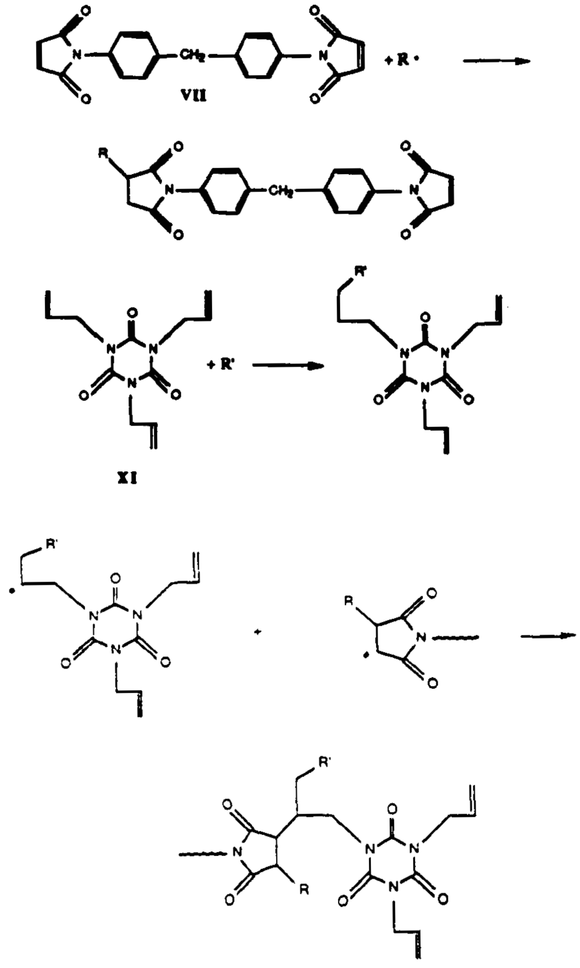


4. Triallyl Systems - Triallyl isocyanurate

Triallyisocyanurate (XI) was described previously as an effective toughener of a bismaleimide-graphite prepreg (VII).[15] In fact, Hexcel's F-178 resin is based on this resin. The reactions outlined in Scheme 7 that occur when a diallyl toughener is added to a bismaleimide presumably occur when a triallyl toughener is added instead. Nash and coworkers[15] have proposed another reaction that could promote additional compatibility between the triallyl material and the bismaleimide matrix: it is possible that during cure, free radical polymerization of the olefinic bonds occurs. This reaction is indicated in Scheme 9.

Scheme 9

Free radical reaction between bismaleimides and triallyl isocyanurate

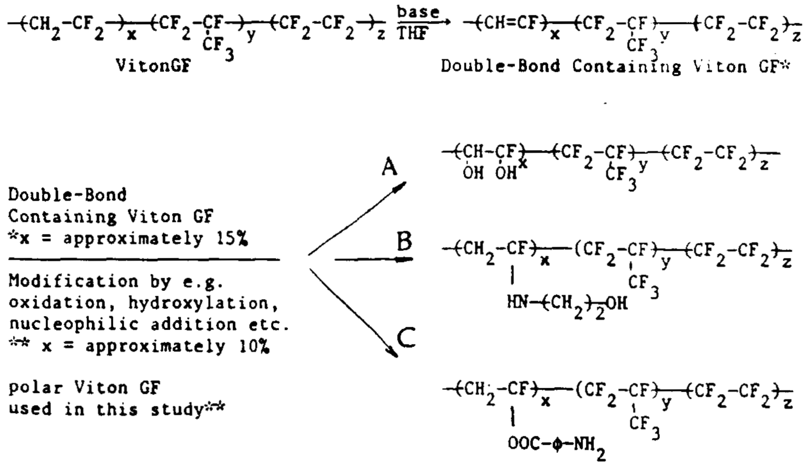


## 5. Fluoroelastomers

We also are considering the toughening of the bismaleimide matrices with fluorocarbon elastomers. These elastomers have been used in the toughening of rather unique bismaleimide systems.[16] More specifically, Du Pont's Viton® GF (XII) was selected for the purpose of controlling the formation of the rubbery phase in the matrix. It was believed that chemical modification of the Viton® GF, i.e., the introduction of more polar groups (Scheme 10) would lead to compatibility with the matrix through various intermolecular interactions. These interactions would then be disrupted at the high temperatures of cure thereby leading to separation of the rubbery phase. Carefully controlling the postcure conditions (time and temperature) would allow the morphology of the blends and, in turn, some of the physical-mechanical properties to be controlled. Again, these concepts, applied to a specific bismaleimide system, were met with limited success. Nevertheless, the chemical composition of the bismaleimide system used in these studies is significantly different from that of the polysulfone-bismaleimide system we are using. We anticipate that the resin-rubber compatibility will be improved in the latter system. At this point, however, we do not have a ready supply of Viton® GF.

Scheme 10

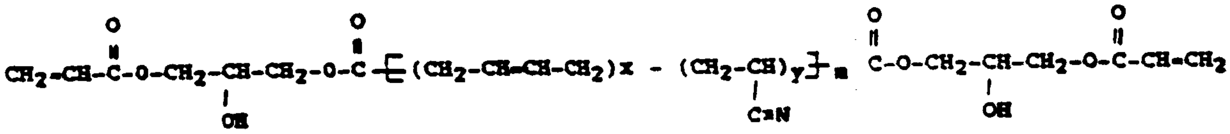
Chemical modification of Viton® GF[16]



6. Vinyl terminated resin modifiers

a. Vinyl terminated butadiene-acrylonitrile copolymer (Hycar® 1300X22)-

This vinyl terminated liquid copolymer is a product of The BF Goodrich Company. It consists of a butadiene and acrylonitrile random copolymer with carboxylic acid moieties at each terminus.[17] This material is represented structurally as **XIII** where m=10 (approximately) and the amount of bound acrylonitrile is on the order of 16%. It has been postulated[18] that vinyl terminated aromatic compounds copolymerize with bismaleimides in a free radical mechanism.

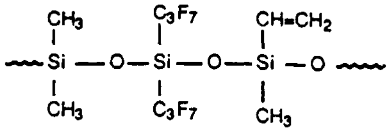


$CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}\underset{OH}{\underset{|}{CH}}{-}CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}[(CH_2{-}CH{=}CH{-}CH_2)_x - (CH_2{-}\underset{C\equiv N}{\underset{|}{CH}})_y]_m\ \overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}\underset{OH}{\underset{|}{CH}}{-}CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH{=}CH_2$

XIII

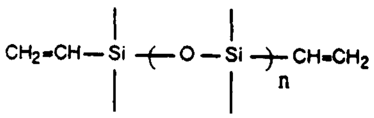
b. Siloxane-based vinyl terminated compounds

Silastic® E RTV (XIV) and Sylgard® 184 (XV), both silicone rubber products of the Dow Corning Corporation, are being examined as tougheners for the polysulfone-bismaleimide matrix. Their characteristically low Tg's, high flexibility, and good thermal and oxidative stability of these siloxane materials have made these appropriate toughners for epoxy resins.[19] In addition, the presence of siloxane groups should influence the friction and wear behavior of the modified resins. Friction and wear are known to be functions of surface energy, fatigue, and toughness.[20] Again, a free radical reaction will allow the vinyl end-groups of Sylgard® 184, or the vinyl side group in the case of Silastic® E RTV, to copolymerize with the bismaleimide matrix.



$\sim\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{Si}}}}{-}O{-}\underset{C_3F_7}{\underset{|}{\overset{C_3F_7}{\overset{|}{Si}}}}{-}O{-}\underset{CH_3}{\underset{|}{\overset{CH{=}CH_2}{\overset{|}{Si}}}}{-}O\sim$

XIV



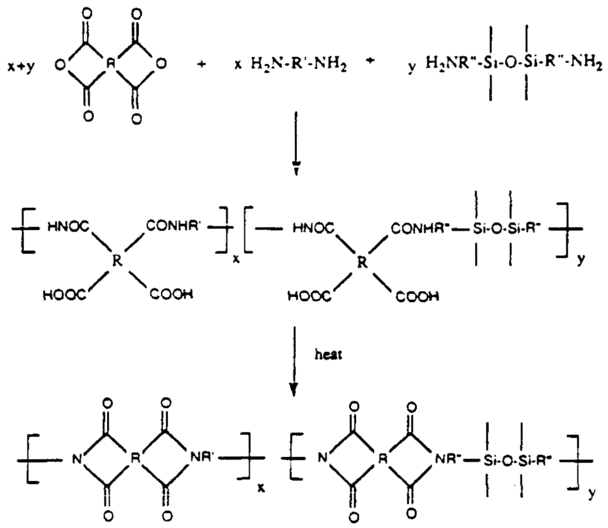
$CH_2{=}CH{-}\underset{|}{\overset{|}{Si}}{-}({-}O{-}\underset{|}{\overset{|}{Si}}{-})_n{-}CH{=}CH_2$

XV

### 7. Polyimide-polysiloxane tougheners

Recently, it was suggested to us that it would be worthwhile to examine a system which takes advantage of the compatibility that naturally exists between polyimides and the specific polyimide system of polysulfone-bismaleimide. In addition, it was suggested that the processibility of the polyimide toughener could be improved by the incorporation of flexible segments that are copolymerized with the rigid imide polymer. Bis (aminoalkyl) siloxanes, for example, could copolymerize with a polyimide and serve as a suitable source of flexibility in the system such that processing could be made easier. This processibility, however, is obtained at the expense of other physical properties such as heat distortion, thermal stability, hardness and modulus. On the other hand, impact resistance is improved. A system such as that desribed above has been reported in the literature.[21] In this particular study, it appeared that the most desirable properties of the silicone additives were preserved while the best features of a completely aromatic polyimide were maintained. The preparation of this system involves the use of a dianhydride with molar quantities of an organic diamines and/or aromatic aminofunctional polysiloxanes (Scheme 11).[21] The presence of an aminofunctional siloxane allows this reaction to be performed in a variety of solvents including chlorinated solvents, hydrocarbon solvents, and glyme solvents. These solvents, in contrast to the dipolar aprotic solvents typically used in the preparation of polyimides, can be easily removed, thereby precluding the formation of voids during cure. In addition, the siloxane diamine can be modified by equilibration reactions.[21] Therefore, with polyimide-polysiloxane systems, tougheners possesing a wide varity of properties would be possible.

Scheme 11
Preparation of a polyimide-polysiloxane toughener



We are currently seeking a supplier for the materials described above.

## CURING REACTIONS

Our most recent efforts have focused on the curing of the modified matrices noted above. For the most part, we are carrying out these studies using the curing scheduals reported in the literature for similar or identical tougheners which have been employed to toughen other bismaleimide matrices. In addition, we are studying the effect of slight variations in certain parameters of the curing reactions, namely time and temperature, on the ultimate properties of the system.

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