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IMIDE MODIFIED EPOXY MATRIX RESINS

Final Report
Contract NAS3-23528

Prepared for
NASA-Lewis Research Center
Cleveland, Ohio 44135

by
D.A. Scola

March 1984

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for

National Aeronautics and Space Adminstration
Washington, D. C.   20546

Under Contract
NAS3-23528

DATE <u>March 1984</u>

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FOREWORD

This work was carried out under NASA contract NAS3-23528 and covers the period July 30, 1982 to January 1, 1984. Initial studies on imide modified epoxy matrix resins, were reported in NASA CR-165229, February 1, 1981 and in NASA CR-167942, February 27, 1982. Dr. Tito T. Serafini was the NASA Program Manager for the work carried out in the first phase of this program. Dr. Peter Delvigs was the Program Manager in the second phase of the program, and in the present study. Dr. Daniel A. Scola was the Program Manager and Principal Investigator for United Technologies Research Center.

Imide Modified Epoxy Matrix Resins

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Imide Modified Epoxy Matrix Resins

1.0 INTRODUCTION

This document constitutes the third phase of the final report on a twelve (12) month program to develop tough imide-modified epoxy (IME) resins cured by novel bisimide amine (BIA) hardeners, initially developed by investigators at NASA Lewis (Ref. 1, 2). The first phase of a ten (10) month program has already been reported (Ref. 3, 4). In this first phase of a ten (10) month program, the feasibility of using bisimide amines (BIA's) as curing agents for epoxy resins with improved moisture resistance, toughness and char yield over state-of-the-art epoxy resins and the control resin was demonstrated. Each BIA containing resin exhibited twice the char yield of the control resin 4,4'-(N,N'-tetraglycidyl)-methylene dianiline (MY720)/4,4'diaminodiphenylsulfone (4,4'-DDS) (40% char vs 20% char). The moisture absorption properties of these bisimide amine cured epoxies (IME's) were considerably less than those of state-of-the-art epoxies (0.5 wt% versus 2.0% after saturation at 87% RH at 82°C). The strain-to-failure of the MY720/4,4'-DDS control resin was improved 25% by replacement of 4,4'-DDS with 4,4'-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bis[N-4-(p-aminophenyl sulfonilylphenyl)phthalimide], (6F-4,4'-DDS) (MY720/6F-4,4'-DDS) (1.25% vs .99%).

In the second phase of this program, (Ref. 5, 6) additional studies were carried out to increase the toughness properties of the bisimide amine cured epoxies. A key intermediate, 4,4'-(hexafluoroisopropylidene)bis(phthalic anhydride) designated 6F dianhydride, is required for the synthesis of the bisimide amine curing agents. Because of the unavailability of a commercial source of 6F dianhydride, efforts were successfully directed toward the complete synthesis of the 6F dianhydride, in small quantities.

In this second phase, it was also demonstrated, using a 10° off-axis tensile test that three bisimide amine cured epoxies exhibited 1.5 to 2 times improvement in intralaminar shear strain-to-failure and significant improvements in tensile and intralaminar shear strengths relative to the control resin, MY720/3,3'-diaminodiphenylsulfone.

As an example, a composite consisting of Celion 6000 graphite fibers and the resin system MY720/4,4'[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bis[N-3-(m-aminophenyl sulfonilylphenyl)phthalimide], (6F-3,3'-DDS) (composite C-IME-9-2B), exhibited the following 10° off-axis properties: Tensile strength 433 MPa (62.8 psi), tensile modulus, 80 GPa (11.6 x 10^6 psi), intralaminar shear strength and strain-to-failure, 73.8 MPa (10.7 ksi) and 1.93% and calculated shear strain-to-failure in resin, 10.6%. For the control composite these values were 316 MPa (45.8 ksi), 84.8 GPa (12.3 x 10^6 psi), 54.0 MPa (7.84 ksi), 1.08% and 4.65%. In this study, replacement of 3,3'-DDS with 6F-3,3'-DDS improved the composite shear-strain-to-failure from 1.08% for the 3,3'-DDS system (MY720/3,3'-DDS) to 1.93% for the 6F-3,3'-DDS (MY720/6F-3,3'-DDS) system.

In the present program (third phase) the objectives were three fold: (1) to develop a synthetic procedure to produce 4,4'-(hexafluoroisopropylidene)bis(o-phthalic anhydride) in high yield (2) to utilize this intermediate in the synthesis of bisimide amines and (3) to develop bisimide amine cured epoxies with significantly improved toughness over state-of-the-art epoxy resin systems.

In meeting the objectives of item (3), studies were carried out to determine the effects of the epoxy resin composition and the cure cycle on the properties of the BIA cured resins and on 10°-off axis Celion 6000/IME epoxy composites. The resin system used in previous studies was 4,4'-(N,N'-tetraglycidyl-methylene-dianiline) (MY720). In the present studies, the effect of the cure cycle on MY720/IME resins was determined, and in addition the effect of an epoxy resin DER 383 and blend consisting of a DER383 with MY720 was investigated.

The program was divided into three tasks. In Task I, a method to optimize the synthesis of 4,4'-(hexafluoroisopropylidine)bis(phthalic anhydride), designated as 6F in a yield of at least 40% was investigated. In Task II, the synthesis of four bisimide amines and the synthesis and characterization of bisimide amine (BIA) cured epoxies were carried out. In this task, two epoxy oligomers were selected for evaluation with the BIA's. In Task III, 10° off-axis Celion 6000 graphite fiber bisimide amine cured epoxy composites were fabricated and characterized. Task IV was the reporting phase of the program, including monthly technical narratives, monthly financial reports and a final report.

1.1 Summary

This report describes the results of a twelve month program designed to develop tough imide modified epoxy (IME) resins cured by novel bisimide amine (BIA) hardeners. Initial studies of several bisimide amine cured epoxies have been reported by investigators at NASA Lewis. The state-of-the-art epoxy resin, MY720, was used as the epoxy in the former studies. In the present program state-of-the-art epoxies MY720 and DER383 were used. Four bisimide amines (BIA)

reported previously were evaluated in the present program. These were the BIA's derived from the 6F anhydride (4,4'-(hexafluoroisopropylidene)bis(phthalic anhydride) and the diamines 3,3'-diaminodiphenyl sulfone (3,3'-DDS), 4,4'-oxydianiline (4,4'-ODA), 4,4'methylene dianiline (4,4'MDA) and 1,12-dodecane diamine (1,12-DDA). A key intermediate, 4,4'-(hexafluoroisopropyline)bis (phthalic anhydride), designated 6F anhydride is required for the synthesis of the bisimide amines (BIA). Reaction parameters to synthesize a precursor to the 6F anhydride, namely 4,4'-(hexafluoroisopropylidene)bis(o-oxylene) (6FHC) in high yields was investigated. A novel catalyst, trifluoromethane sulfonic acid under autoclave conditions over a temperature range 150-225°C, using varying reactant and catalyst concentrations, was investigated. Although small scale runs yielded the 6FHC in 50 percent yield, efforts to translate these results to a larger scale synthesis gave the 6FHC in only 9 percent yield. The four bisimide amines mentioned above, were evaluated with epoxy resins DER383 and MY720 in efforts to improve the toughness properties of epoxy resin. The fracture toughness properties (K_{IC}) of the bisimide amine cured epoxy resins (IME's) was improved two-fold over the control systems and four-fold over the state-of-the-art Hercules 3501-6 epoxy resin. The studies also reveal that the IME's with the highest fracture toughness exhibited the lowest glass transition temperature (Tg). Consideration of both the Tg and fracture toughness K_{IC}, the best IME resins can be rated as follows: IME-40>IME-9-3B>IME-43>IME-45>IME-18-4>IME-42>IME-41>IME-47>IME-44>IME-46>IME-10-3B. The control resins can be rated as follows: C-15>C-4>C-3>C-1> Hercules 3501-6, all of which fall below the IME resins. The IME resins were also evaluated in 10° off-axis Celion 6000/IME epoxy resin composites. These tests also showed that several of the IME composites exhibited vastly superior 10° off-axis tensile strength, intralaminar shear strength and shear strain-to-failure over the control composites. For example, the composite C-IME-40-2 exhibited the following properties: tensile strength and modulus (70.1 ksi and 12.4×10^6 psi) and intralaminar shear strength and modulus (12.0 ksi and 1.08×10^6 psi) and intralaminar shear strain-to-failure (4.58%). For the control composites, these values were as follows: tensile strength and modulus (39-52 ksi and $\sim 13 \times 10^6$ psi), intralaminar shear strength and modulus (6.6-8.8 and 1×10^6 psi), and intralaminar shear strain-to-failure ~ 1.0 percent. With a few exceptions (IME-40 & 44), the resins with the highest fracture toughness values also exhibited the highest 10° off-axis tensile strength and shear strain-to-failure. The studies showed that the concept of using bisimide amine as curing agents to improve the toughness properties of epoxies is valid and has led to a two- to four-fold improvement in toughness properties of resins relative to the control resins and state-of-the-art epoxy, respectively.

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2.0 RESULTS AND DISCUSSION

2.1 Optimization of the Synthesis of
### 4,4'-(hexafluoroisopropylidene)bis(o-phthalic anhydride)

This is an important intermediate for various polymer applications (6F anhydride) which is not commercially available. The patent literature (Refs. 7, 8) reveals that the precursor compound 4,4'-(hexafluoroisopropylidene)bis(o-xylene) (6FHC) is synthesized commercially by reaction of o-xylene with hexafluoroacetone sesquihydrate in an autoclave using hydrogen fluoride as the Friedel-Crafts catalyst.
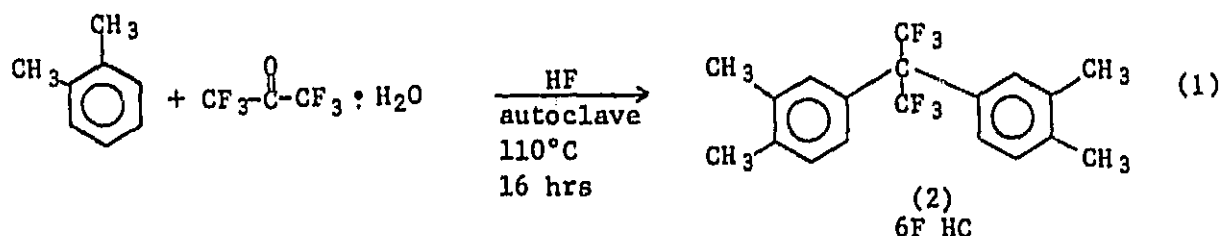
The properties of the product from this reaction were not disclosed but its isolation and oxidation to the 6F tetra acid and subsequent dehydration to the 6F anhydride were described (Refs. 7, 8).
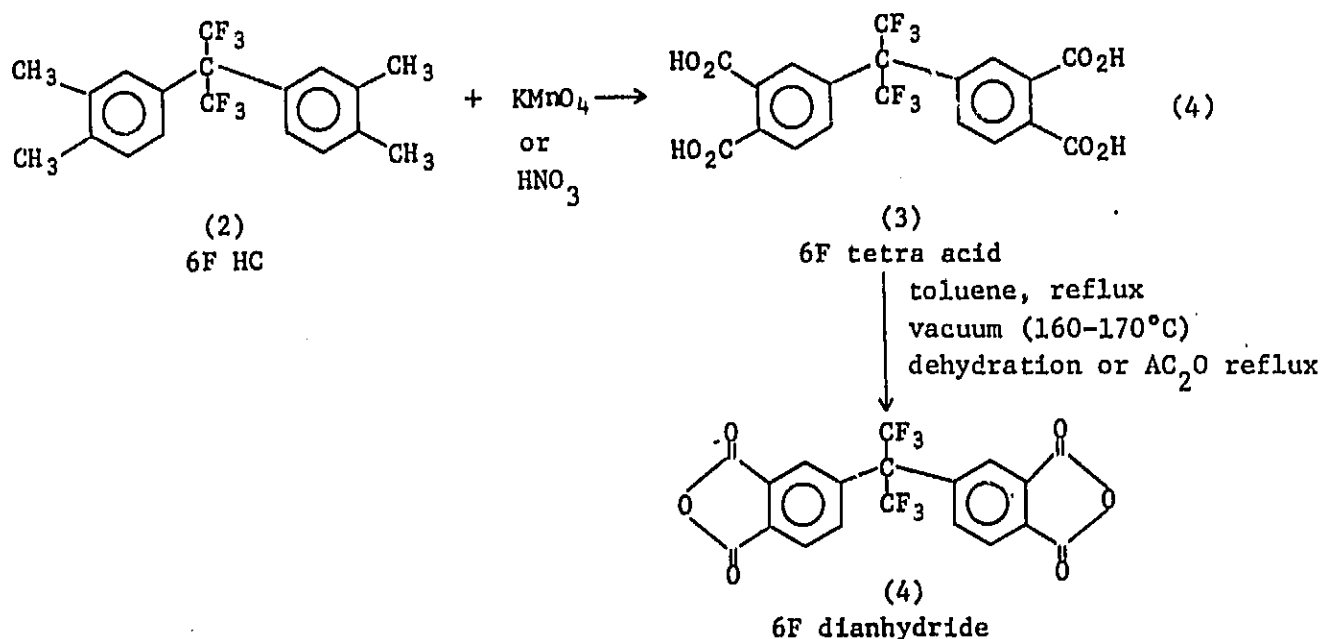
4
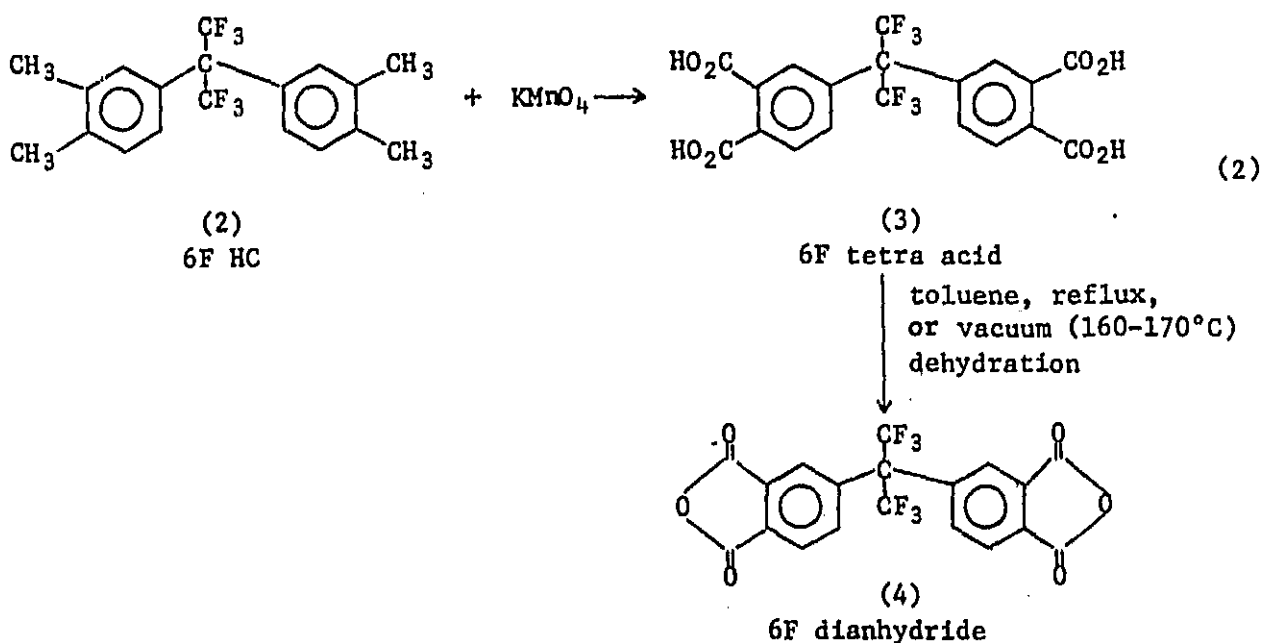
The yield of 6FHC was not defined, nor was the yield of pure 6F anhydride. In previous investigations under NASA contract (Ref. 5), a novel method was used to synthesize the 6FHC (2), the precursor to the 6F anhydride, but the major product was not 6FHC but the 6F alcohol (1), 53% vs 13%, as shown below

$$(3)$$

(1)
6F alcohol, 53%

(2)
6F HC, 13%
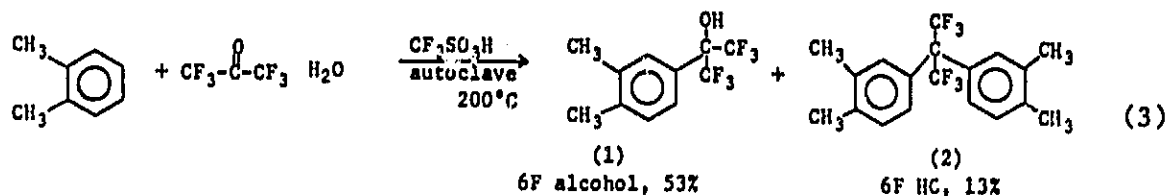
This involved the use of trifluoromethane sulfonic acid, a novel Friedel-Crafts catalyst. The catalyst has been shown to alkylate aromatics at atmospheric pressure (Ref. 9).

In this work, the 6F alcohol was isolated in considerably higher yield than the 6FHC by a factor of 4 (53%/13%). The 6FHC was then oxidized to the tetraacid (3)

$$(4)$$

(2)
6F HC

(3)
6F tetra acid

toluene, reflux
vacuum (160-170°C)
dehydration or AC_2O reflux

(4)
6F dianhydride

by potassium permanganate or nitric acid, (86% crude yield), followed by dehydration using acetic anhydride to produce the 6F anhydride (4) in 75% yield. The overall yield of 6F anhydride was 8.7%.

An exhaustive study of the reaction parameters to produce 6FHC was not performed, nor was any attempt made to convert the 6F alcohol to the 6FHC. The formation of 6F anhydride most likely is a two step process involving (1), and o-xylene, reaction (5) but this intermediate has never been isolated by other investigators.

$$(1) \qquad\qquad (2) \qquad\qquad\qquad (5)$$

6F alcohol   6F anhydride
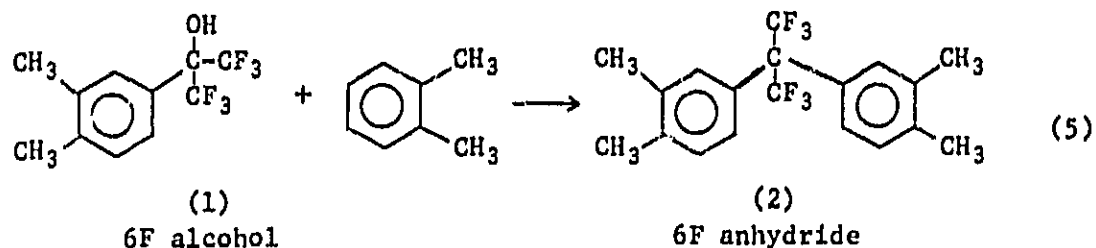
In the present investigation, a statistical experimental design, using the "Latin Square" approach was used in efforts to optimize the yield of the 6FHC. The conditions used in these experiments are listed in Table 1.

The approach used was to run the experiments in sealed tubes in small quantities under the conditions listed. The final conditions which caused separation of these components are listed as follows:

    Column μBondapak C_{18}, 4 mm ID x 30 cm length
    Flow rate: 2 ml/min (constant)
    Solvent system: (mobil phase): tetrahydrofuran (THF)/H_2O
    Detector: UV 254 at 2.0 AUFS
    Sample size: 10-20 μl
    Gradient: linear 45/55 to 70/30 (curve 06)

Time	Flow ml/min	% THF	% H_2O
initial	2.00	45	55
4.0	2.00	45	55
20.0	2.00	70	30
22.0	2.00	100	0
23.0	2.00	100	0
25.0	2.00	45	55

The reactants were placed in the glass tube at liquid nitrogen temperature, evacuated, and sealed under vacuum. They were then placed in an oil bath and maintained at a specific temperature for a certain time period. The tubes were then cooled to liquid nitrogen temperature, the upper portion of the glass tube was broken, and then the reaction products were isolated and analyzed by high

pressure liquid chromatography (HPLC), using the conditions described above. A standard HPLC analytical procedure using starting materials and products isolated from previous experiments (Ref. 5) was developed. Initially a linear gradient mobile phase consisting of tetrahydrofuran (THF)/water 50/50 to 80/20 was used to separate the components, o-xylene, 6F alcohol and 6F HC. However these conditions gave poor separation of o-xylene and 6F alcohol and o-xylene and 6F HC. Changing the conditions to 45/55 to 70/30, caused separation of these components.

Using the conditions described above, the retention times of three of the components of the reaction mixture could be defined when injected into the column as pure materials. O-xylene eluted in 10.20 minutes (Fig. 1), 6F alcohol eluted in 11.73 min (Fig. 2) and the 6FHC eluted in 17.16 minutes, (Fig. 3). The three components were then mixed, and the chromatogram (Fig. 4) of the mixture shows o-xylene eluting in 10.50 minutes, 6F alcohol eluting in 11.78 minutes and 6F HC eluting in 16.93 minutes. This demonstrated that these conditions were able to separate the components of the reaction mixture and therefore were used to establish the yield of products from reactions run under the statistically designed set of conditions listed in Table 1.

A chromatogram of product from run 6F-150-2 is shown in Fig. 5. The major components at 12.47 min and 17.53 minutes are 6F alcohol and 6FHC respectively. The o-xylene has been removed from the reaction mixture before HPLC analysis by careful evaporation at room temperature.

The unreacted hexafluoracetone sesquihydrate (HFA) and acid catalyst trifluoromethanesulfonic acid (TFS) are separated from the reaction mixture before analysis. For this reason and also because these components do not absorb in the ultraviolet (UV) region, they do not appear as component peaks in the chromatogram.

In determining the yield of major components of the reaction, the chromatogram was programmed to yield the area and area % of each component. No correction factors were used to convert the area percents to weight percent. The assumption was made that this would not change the ratios of the components to any great extent and would therefore have no effect on the conclusions derived from the data. An example of the data printout of the 6F-150-2 run is given in Table 2. In the tabulation of the data, other components that elute immediately before and after the 6F HC were considered isomers and other reaction products. These were combined and listed as other components in the final analysis. Using this technique, only small quantities of hexafluoroacetone, a very expensive starting material were required. This analytical procedure provided a basis on which to select the reaction conditions required to produce the 6F hydrocarbon in high yield on a large scale. A high yield of 6F HC would insure a high yield of 6F dianhydride.

Table 3 is a summary of the product yields based on the chromatographic separations. The data in Table 3 clearly suggest that at temperatures of 100°C and 150°C, the combined increases in the o-xylene and trifluoromethanesulfonic acid (TFS) concentrations caused a considerable improvement in the 6FHC yield, the desired product, from 1% using stoichiometric quantities of o-xylene and 2 ml TFS, to approximately 50% using 39.2 ml of o-xylene and 160 ml TFS. The reaction time does not appear to be an important variable at those temperatures. It is also apparent that at the higher temperatures 200°C and 225°C, at all concentrations of reactants, the tar yields increased, the yield of 6F alcohol decreased while the 6F HC yield was not effected appreciably. The highest yield of 6F alcohol (77%) was obtained with stoichiometric quantities of reactants of the lowest temperature (6F-100-1). Also, the conditions for run No. 6F-150-2 gave the best overall yield of 6FHC (63%), with only 11% yield of 6F alcohol and 26% yield of other components. These components consisted mostly of higher molecular weight fluorinated hydrocarbon materials. Reaction 6F-225-4 exploded. The quantities of reactants were cut by two-thirds, and the reaction was repeated. This reaction mixture also exploded. It was concluded that the large excesses of o-xylene and trifluoromethanesulfonic acids at this temperture reacted to form large quantities of gaseous materials which caused the explosions. This reactant ratio was not repeated a third time.

Based on these data, conditions for run 6F-150-2 was selected for large scale runs to produce 6FHC.

The reaction was run twice using the 6F-150-2 parameters on a 50g HFA scale, yielding the 6F alcohol in 23 and 22% yields, and the 6F HC in 8.6 and 9.4% yields.

The data in (Table 3) for the sealed tube reactions was analyzed by a variable weighted average method to further determine the best conditions for optimization of the 6FHC yield. In this method the yields of 6F alcohol, 6F HC and other components (Table 3) were assigned a weighted estimate of importance. Then, for a given variable, for example temperature, the weighted average was determined. This was also carried out for time and trifluoromethane sulfonic acid concentration. The data are summarized in Table 4. Inspection of the data reveals that for each weighted average assignment, the variable values resulting in the highest score are: temp. 150°C, time 10 hrs, trifluoromethane sulfonic acid concentration 4 ml. This suggests that the reaction conditions which should lead to the highest yield of 6FHC are: 150°C, 10 hrs, 4 ml TFS/4.0g HFA. These conditions were used in a large scale run. Therefore, the reaction was repeated on a 25g scale (HFA) yielding 6F alcohol and 6F HC in the highest yield obtained

thus far, 74.7% and 12.7% respectively. Analysis of the yield data suggested that the yield of 6FHC could be improved by running the reaction at lower temperatures (25 to 100°C) than those listed in Table 1 and for long reaction times, in the manner used to synthesize(5)   at UTRC (Ref. 10).

(5)
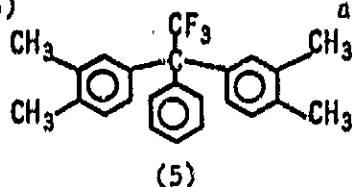
This product (5) was obtained in 76% yield at room temperature over a 72 hr period using o-xylene, α,α,α-trifluoroacetophenone (TFA) and TFS.

Therefore, two runs were made using the conditions used to synthesize compound (5): hexafluoroacetone sesquihydrate (25g, 0.1294 mole), o-xylene (400g, 3.77 mole), 12.5 ml trifluoromethanesulfonic acid, 4 days at room temperature. Workup of the reaction mixture gave 6F alcohol in 33% yield, and only 4.1g of hydrocarbon oil which contained only traces of the 6F HC. The reaction was repeated using 25 ml of trifluoromethanesulfonic (TFS) acid catalyst, instead of 12.5 ml. From this run, a much larger quantity of 6F alcohol (56% yield), and smaller quantity of hydrocarbon oil (2.0g) were isolated.

It is clear from the autoclave and ambient condition runs that formation of the 6F alcohol occurs readily. It is also apparent that reaction of the 6F alcohol with o-xylene to form the 6FHC is a difficult step and may require a stronger catalyst than TFS. The addition of another strong acid, such as conc. H_2SO_4 as a co-catalyst is worthy of investigation in this regard.

2.2   Synthesis of Bisimide Amines (BIA's)

Four bisimide amines were selected for evaluation in this program. These are as follows:

Bisimide Amines (BIA's)

9
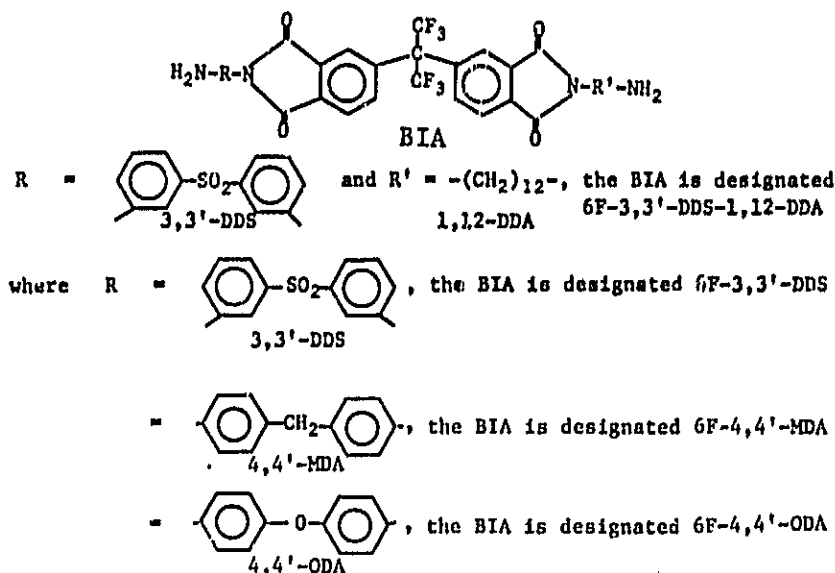
2.3 Evaluation of Bisimide Amines in Epoxy Resins

2.3.1 Initial Screening of Epoxy Resins

In the initial evaluation, the four bisimide amines were used as curing agents with two epoxy resin systems, namely Dow Chemical Epoxy Resin DER 383 and Shell epoxy/styrene resin 9102. The formulations of each resin are listed in Table 5. The components were mixed and cured at 150°C/1 hr + 200°C/2 hrs. Some of the systems resulted in a glassy homogeneous resin system, others were heterogeneous in nature with many void areas. The glass transition temperatures (Tg's) of each resin were determined by thermal mechanical analyses (TMA). The Tg's are listed in Table 5. It should be noted that four resin systems exhibit low Tg's; these are 383-1, 383-5, 9102-5 and 9102-6. Systems containing 9102 resin were ruled out because the 9102 resin contains approximately 50% styrene. This caused handleability problems and furthermore, resins containing 9102 were very brittle.

2.3.2 Selection of Epoxy Resins for Evaluation of Bisimide Amines as Curing Agents

The resin system DER 383 was further investigated to increase the Tg's by (1) changing the stoichiometric ratios of reactants and by addition of other components in the formulation, such as MY720 epoxy resin, a tetrafunctional epoxy, which leads to rigid epoxy resins. Therefore, the epoxy resins DER 383 OIC and MY720 were selected for further study. However, attempts to prepare void free DER 383 or MY720 containing resin systems by mixing the components and casting or by, heating the mixture in vacuum to 150°C, or higher, led to porous, sintered solids. Although some compositions were homogeneous, they contained many voids. Therefore, small specimens were fabricated by compression molding techniques for physical and thermal property characterization.

2.3.3 Synthesis and Characterization of Bisimide Amine (BIA) Cured Epoxy Resins

Table 6 lists the composition of the resins evaluated for molding into cured resin discs and used as a 70 wt% solution in tetrahydrofuran for impregnation of Celion 6000 graphite fibers.

2.3.3.1 Preparation of Homogeneous Bisimide Amine Epoxy (IME) Resin Molding Powers and Resin Impregnation Solution

Approximately 13g portions of powder for each IME resin system listed in Table 6 were prepared by concentration of a solution (50 wt%) of the resin components in tetrahydrofuran. The residual THF solvent was removed in vacuum

at 60°C for 2 hrs for all IME resins except for IME-18-4, -43, -41 and -40.
These were treated at room temperature in vacuum for times required (2 to 24 hrs)
to remove traces of solvent. For each IME system, a fine orange-to-red colored
powder was obtained. The resin powders were compression molded into resin discs.
Components of the resin were dissolved in tetrahydrofuran to yield approximately
a 70 wt% solution of the resin. This solution was used for impregnation of
Celion 6000 graphite fibers for tape and composite fabrication.

2.3.3.2 Fabrication of IME Resins Discs for Physical and Thermal Property Characterization

Resin discs (3.00 cm dia x 0.32 cm thick) of several of the IME resins
listed in Table 6 were fabricated by compression molding techniques by following
the gel point as the temperature approached 150°C in the mold. Details are given
in the experimental section. Two cure cycles were used as follows: cure cycle
#1 150°C/1 hr + 177°C/3 hrs (at ~6.89 MPa), cure cycle #2 150°C/1 hr + 177°C/2
hrs + 204°C/2 hrs (at ~6.89 MPa) + 204°C/22 hrs (postcure) no pressure.

2.3.3.3 Fabrication of Resin Discs for Fracture Toughness Tests

The same procedure used above was used to fabricate the fracture toughness
specimens. A 5.08 cm (2") diameter mold was used. Specimens were machined
according to ASTM E399-81 specification (Fig. 6) (Ref. 11). Approximately 18
grams of resin powder was used to fabricate discs with approximate thicknesses of
0.64 cm. The samples were tested at a loading rate of 0.0254 cm/min (0.01"/
min).

2.4 Resin Characterization

2.4.1 Density, Coefficient of Thermal Expansion and Cure Shrinkage

The density, coefficient of thermal expansion, and shrinkage due to cure of
each IME resin, the control resin and Hercules 3501-6 epoxy resin are listed in
Table 7. The control resins and 3501-6 cured by cycle #1 have densities in the
range 1.21-1.27 g/cc, as expected for a state-of-the-art epoxy resin. However,
the bisimide amine cured epoxy resins (IME's) exhibit higher densities due to the
presence of the hexafluoroisopropylidene group and ranged from 1.28 to 1.35
g/cc.

There is no significant effect of cure temperature on the density of the C-3
control and of three of the cured IME resins as shown by the values for the
control and for IME-9-3B, IME-10-3B, and IME-18-4 cured as indicated. The

coefficient of thermal expansion of the control resins fall in the range of 4.61 to 8.63 x 10^{-5} cm/cm/°C, while for the IME resins it ranged from 5.24 to 10.9 x 10^{-5} cm/cm/°C. There is no apparent effect of the cure cycle on the coefficient of thermal expansion of the control resin C-1 and IME resins IME-9-3B, IME-10-3B, and IME-18-4.

The percent shrinkage for most of the IME resins is much lower than the control resins from either cure cycle #1 or cure cycle #2. The higher temperature cure cycle caused a significant (50-65%) decrease in shrinkage of the IME-9-3B resin, and control resins C-1 and C-3 but had no effect on IME-10-3B.

2.4.2 Moisture Absorption

Moisture absorption characteristics of the control and IME resins cured by cycle #1 and #2 and a state-of-the-art epoxy resin Hercules 3501-6 (cure cycle #1) are listed in Table 8. For the exposure in water, absorption for the controls and many of the IME's are approximately equivalent. There are indications that the higher cure temperature (cycle #2) causes lower moisture absorption than the lower temperature cycle. Moisture absorption after the 72 hours water boil for IME's 18-4, -40, -41, -43, and -45 is considerably less than the control resins C-1, C-3, and C-4. IME resins -42, -44 and -46 absorb almost twice as much moisture as control resins C-4 and C-51. For two of the IME resins -9-3B, and 10-3B, the higher temperature cure cycle reduced moisture absorption by approximately 45 percent while for control C-3, it reduced absorption by 18 percent, and for control C-4, increased absorption by 21 percent, showing effects of mixed moisture behavior modes on cure cycle. The moisture absorption behavior of the control resins and IME resins after exposure to 95% relative humidity at 60°C for two weeks (equilibrium weight gain) are listed in Table 8. The control samples C-1 and C-3 and Hercules 3501-6, all of which contain MY720 epoxy resin absorb approximately 4.0 wt% moisture. The control sample C-3 which contains the epoxy resin DER383 absorbed only 1.94wt% moisture, while control sample C-51 which contains a 50:50 mixture of MY720/DER383 absorbed 2.66wt% moisture. These results suggest that the cured epoxy resins, which contain MY720 have a much greater capacity to absorb moisture than cured epoxy resins which contain DER383. Except for resins IME-44 and IME-46, the IME resins absorb less moisture than the control resins containing the same basic epoxy resin(s). Of particular note is the low moisture absorption behavior of resins IME-18-4, IME-41, IME-43, IME-45 and IME-47 relative to the control, (1.28 vs. 4.0; 1.38 vs 1.94; 1.12 vs 1.94; 1.62 vs 2.66; 1.70 vs 2.66). In general, the data reveal that several of the IME resins are more moisture resistant than the control resins and 3501-6, while others are either equivalent or less moisture resistant.

2.4.3 Resin Thermal Properties

2.4.3.1 DSC Analysis

The DSC thermograms are shown and Figs. , , and the data are tabulated in Table 8. The DSC endotherms of the resins show   adual absorption of energy to

a endotherm maximum point, and then as the resin is heated beyond this endotherm maximum it becomes exothermic. The maximum in the endotherm in each resin system approaches the glass transition temperature of the resin as defined by the thermomechanical analysis data. Beyond 300°C, the resin undergoes subsequent chemical reactions and finally decomposition.

2.4.3.2 Thermogravimetric (TGA) Analysis

The TGA curves for each resin are shown in Figs. 11-14. The weight percent loss of each resin at 300°C and 800°C in nitrogen based on this data is listed in Table 9. The weight loss at 300°C for most of the resins falls in the range 0 to 3%; but the weight retention (char yield) at 800°C experienced by the IME resin is approximately twice that of the control resins and one-and one-half times the state-of-the-art Hercules 3501-6 epoxy resin.

2.4.3.3 Thermomechanical (TMA) Analysis

The TMA curves for each resin are shown in Figs. 15-18, and the glass transition temperature of each cured control and IME resin from cure cycles #1 and #2 is shown in Table 9. It is apparent that the Tg of the control resin C-1 (MY720/3,3'-DDS) is considerably higher than the Tg of the control resin C-3(DER 383/3,3'-DDS), both cured according to cycle #1. It is also apparent that the tetraepoxide MY720 yields a more rigid structure than the diepoxide DER 383. Therefore, most of the DER 383 containing IME's exhibit low Tg's relative to the MY720 containing systems (IME's 9-3B, 10-3B, 18-4 versus IME's-40 through-47). The data also shows that BIA 6F-4,4'-ODA, 6F-3,3'-DDS-1,12-DDA or 6F-4,4'-MDA cured DER 383 yield IME resins with considerably lower Tg's than the 6F-3,3'-DDS cured DER 383. With the exception of IME-18-4, the higher temperature cure cycle (#2) also increased Tg's approximately 20°C higher than the lower temperature cure cycle (#1), showing effect of cure temperature on Tg.

2.4.4 Resin Fracture Toughness Properties

The fracture toughness tests were made according to ASTM-E399-81 (Ref. 11). The specimen specifications are listed in Fig. 19. The fracture toughness of these resin specimens was calculated from the expression (Ref. 11)

$$K_Q = (P_Q/BW^{1/2})f(a/W)$$

where

$$f(a/W) = (2+a/W)(0.76+4.8a/W-11.58(a/W)^2+\frac{11.43(a/W)^3-4.08(a/W)^4}{(1-a/W)^{3/2}}$$

where

P_Q = the load on the linear portion of the stress strain curve

B = specimen thickness

W = specimen width as defined in Fig. 6

a = crack length as defined in Fig. 6

If $P_{max}/P_Q \leq 1.10$, where P_{max} is the maximum load the specimen can sustain, then $K_Q = K_{IC}$ and the test is a valid fracture toughness test. K_{IC} is defined as the plain-strain _fracture_ _toughness_ or Mode I critical stress intensity factor. In the present tests, $P_Q = P_{max}$ then $P_{max}/P_Q = 1.0$ which satisfies the criteria for a valid K_{IC} test.

The fracture toughness K_{IC} is related to the critical strain energy release rate G_{IC} (Ref. 12) by the expression

$$G_{IC} = \frac{K_{IC}^2}{E}$$

where E = modulus.

In the present work, the modulus of each specimen was assumed to be 0.50×10^6 psi which is a typical value for these materials based on previous work (Ref. 5, 6). Therefore, in this case, the G_{IC} values reexpress the K_{IC} values in terms of an energy per unit area, and may or may not reflect the influence of this material property on the actual G_{IC} value. The use of an average modulus value normalizes the data and does not change the overall relative K_{IC} rating for each resin system. The results of the tests are listed in Table 10, in terms of toughness without the plastic zone which occurs on deformation and with the plastic zone in the calculations of K_{IC}. In general terms, it is noted that the rating of the toughness of each resin in terms of the K_{IC} value does not change whether or not the K_{IC} values without the plastic zone or with the plastic zone are used to rate the specimens. Resins with the highest or lowest K_{IC} value retain this position with or without the plastic zone. Therefore, the present discussion will focus on the K_{IC} values without use of the plastic zone in the K_{IC} calculation. The state-of-the-art Hercules 3501-6 epoxy and control resins C-1 and C-3 exhibited the lowest fracture toughness K_{IC} values, 260, 330 and 343 Pa $\sqrt{m}$ and G_{IC} values 18.7, 29.9 and 32.4 Joules/m^2

respectively, while control resins C-4 and C-51 exhibited K_{IC} values approximately twice the values for C-1 and C-3 showing the positive effect of the diglycidyl ether of bisphenol A (DGEBA), DER 383 on resin toughness. This is further illustrated by comparing IME-42 (DER 383/6F-3,3'-DDS-1,12-DDA) with IME-18-4 (MY720/6F3,3'-DDS-1,12-DDA) which have K_{IC} values of 893 Pa $\sqrt{m}$ and 463 Pa $\sqrt{m}$ respectively. The influence of bisimide amine curing agent on toughness is illustrated in the resin series containing the epoxy resin DER 383. The BIA's 6F-3,3'-DDS-1,12-DDA, 6F-ODA and 6F-MDA exhibit about equal influence in toughness. Comparison of toughness value for control resin C-4 (591 Pa $\sqrt{m}$) (DER 383/3,3'-DDS) with the value for IME-40 resin (DER 383/6F-3,3'-DDS) (630 Pa $\sqrt{m}$) suggests that the BIA 6F-3,3'-DDS has only a negligible influence on the toughness properties of DER 383.

The brittle nature of resins containing MY720 is illustrated in the control resin K_{IC} values and by comparing the K_{IC} value for IME-18-4 (MY720/6F-3,3'-DDS-1,12-DDA) with the K_{IC} value for IME-42(DER 383/6F-3,3'-DDS-1,12-DDA). IME-42 exhibits one and one-half the toughness as IME-18-4 (893 Pa $\sqrt{m}$ vs 597 Pa $\sqrt{m}$). Using the K_{IC} value (without plastic zone), the resins can be rated as follows:

IME-42>IME-41>IME-43>IME-47>IME-46>IME-44>IME-45>IME-40>IME-18-4 ≡ C-4>IME-9-3B> C-51>IME-10 3B>C-1 ≡ C-3> Hercules 3501-6

Comparison of the fracture toughness values in Table 10, with the corresponding glass transition temperature (Tg) (Table 7) for each resin system clearly shows a trend, namely the resins with high fracture toughness (K_{IC}) values have lower glass transition temperatures, (Tg) than resins with low fracture toughness values.

The fracture toughness values K_{IC} as a function of glass transition temperature are plotted in Fig. 19. With the exception of resins IME-44, IME-46 and control C-4, the data suggest that the fracture toughness increases as the glass transition temperature (Tg) of the resin decreases.

For aerospace applications, it is desirable to have a resin with a glass transition temperature (Tg) of 150°C or greater. In consideration of both the glass transition temperature (Tg) and fracture toughness properties, the resins can be rated as follows:

IME-40>IME-9-3B>IME-43>IME-45>IME-18-4>IME-42>IME-41>IME-47>IME-44>IME-46> C-51>IME-10-3B>C-4>C-3>C-1>3501-6

2.5 Characterization of IME Resins in Ten Degree
Off-Axis Celion 6000/IME Resin Composites

2.5.1 Fabrication of 10° Off-Axis Celion 6000/IME Composites

Prepregs were fabricated by drum winding epoxy sized Celion 6000 graphite fibers and brush application of a THF solution of the resin (26.1g) to the dried fiber tape (11.43 cm wide x 137 cm long), calculated to yield a composite with a fiber volume of 60 ± 2%. Details are given in the experimental section. The tape was cut and plies (5 ply, 14.0 cm x 25.4 cm x 0.139 cm) were stacked unidirectionally and processed by compression molding techniques. An open ended mold was used to follow the gelation point by probing the laminate as a function of time at specific temperatures. This procedure is required to produce void free compression molded composites. Of critical importance in the fabrication process is the time/temperature parameter for the application of pressure in the initial stages of gelation. Specific details given in the experimenal section. The composites were molded under pressure. Glass cloth/epoxy doublers (5.04 cm x 15.2 cm x 0.254 cm thick) were bonded to each end of the composite using FM-300K adhesive at an angle 10° to the fiber direction. The unidirectional composites were cut 10° to the fiber direction, to produce specimens 1.25 cm wide x 25.4 cm long x ~0.14 cm thick with 3.81 cm (1.5") doublers on each end (Ref. 13). The composition of each Celion 6000/IME composite is tabulated in Table 6.

2.5.2 Physical Properties of Celion 6000 Epoxy Resin Composites

2.5.2.1 Composition, Density, Ply Thickness and
Void Determination

The density, calculated resin and fiber volume percents, and composite ply thickness for the compression molded 5 ply composites (15.24 cm x 25.4 cm x 0.139 cm) are listed in Table 11. In this series the fiber and resin weight before processing were determined, and the final composite weight after removal of excess resin flash was determined to calculate a resin and fiber volume, assuming zero void content. The C-scan of each composite was carried out and each panel was found to be void free.

2.5.3 Tensile and Shear Properties of 10° Off-Axis Celion 6000/IME
Epoxy Resin Composites

The 10° off-axis test specimens and tests were made according to the procedure of Chamis and Sinclair (Ref. 13). This test has been recommended by the authors as a convenient test method for the intralaminar shear characterization of unidirectional composites. This test was selected as a method to evaluate the "relative toughness" characteristics of each system by comparing the

intralaminar shear properties and strain-to-failure of each composite system with the control composites and by comparing shear stress-strain curves for each composite with the control composite, and other state-of-the-art resin composite systems.

In a 10° off-axis tensile specimen, the fibers are aligned at an angle 10° to the uniaxial load direction. When the 10° off-axis specimen is subject to a uniaxial load, a biaxial stress state develops (Ref. 13). This biaxial-stress state consists of three stresses, longitudinal $\sigma_{\ell 11}$, transverse $\sigma_{\ell 22}$, and intralaminar shear $\sigma_{\ell 12}$ at the 10° plane. When the uniaxial composite is subject to its maximum load, the intralaminar shear stress $\sigma_{\ell 12}$ is the only one of these three stresses that is near its critical value and fracture therefore occurs at the 10° plane when $\sigma_{\ell 12}$ reaches this critical value. The symbol σ denotes stress; the subscript ℓ = ply (unidirectional composite) property; the subscripts 1 and 2 refer to an orthogonal right hand coordinate system, with 1 taken along the fiber direction and 2 along the load direction.

The shear stress in a ply with fibers oriented at a 10° angle from the load direction is given by the following equation (Chamis and Sinclair, Ref. 13):

$$\sigma_{\ell_{12}} = 0.171 \ \sigma_{cxx}$$

where σ_{cxx} is the uniaxial fracture strength of the 10° off-axis composite in the x-axis (load) direction. For each composite system, the shear strain-to-failure $\epsilon_{\ell 12}$, shear modulus $G_{\ell 12}$, and uniaxial tensile strength σ_{cxx} and modulus G_{cxx} were measured. The tensile and shear properties of Celion 6000/IME resin composites cured by cycle #1 are listed in Table 12. Comparison of the data for the control composite specimens with the IME composite data clearly shows that several of the IME composites exhibit superior tensile properties and intralaminar shear properties than the control systems. This is demonstrated by composites containing resins IME-9-3B, IME-18-4, IME-40-2, IME-42, IME-43-2, IME-46, and IME-44. The composite system C-IME-40-2 exhibited the best properties; tensile strength and modulus (70.1 ksi and 12.4 x 10^6 psi) and intralaminar shear strength and modulus (12.0 ksi and 1.08 x 10^6 psi) and intralaminar shear strain-to-failure of 4.58%. For the control composites these values were as follows: tensile strength and modulus (39-52 ksi and ~13 x 10^6 psi), intralaminar shear strength and modulus (6.6-8.8 ksi and 1 x 10^6 psi), and intralaminar shear strain-to-failure ~1.1%.

The effect of cure cycle on the tensile and shear properties of 10° off-axis composites for the control system and three of the IME systems are listed in Table 13. In general the higher temperature cure cycle generated composites with a significant improvement in the tensile and intralaminar shear strengths, but with no real significant changes in the tensile and shear modulus and intra-laminar shear-strain-to-failure. The one exception to this is composite C-IME-10-3B. The higher temperature cure caused a 50% improvement in the tensile shear strengths and a 100% improvement in the shear-strain-to-failure.

2.5.4 Shear Stress-Strain Properties of 10° Off-Axis Celion 6000/IME Composites

The shear stress-strain properties of each composite system was determined to compare the resins in each composite system and to rate the relative performance of each system as measured by the stress-strain curves.

The structural axes strains for the 10° off-axis specimens were obtained using a rectangular rosette of strain gages at 0°, 45° and 90°. The inter-laminar-shear strain along the 10° plane was obtained from the 0°, 45°. 90° rosette of strain gages using the expression

$$\varepsilon_{\ell 12} = -1.282 \ \varepsilon_{g1} + 1.879 \ \varepsilon_{g2} - 0.598 \ \varepsilon_{g3} \qquad (1)$$

where ε_{g1}, ε_{g2}, and ε_{g3} are the true gage strains for the 0°, 45° and 90° gages (ε = strain). For each gage, the strain is read directly from the tensile stress-strain curve. Using the 10° off-axis data, intralaminar-shear-stress-strain curves for each 10° off-axis composite were generated according to Chamis and Sinclair (Ref. 13).

For each load increment (1) the intralaminar shear strain from Eq. (1) was calculated; (2) the ply-intralaminar stress for each load was calculated using the expression

$$\sigma_{\ell 12} = 0.171 \ \sigma_{cxx} \qquad (2)$$

where $\sigma_{\ell 12}$ = intralaminar shear stress in the 10° direction to the applied
load, σ_{cxx} = uniaxial applied load in the 0° direction; (3) the calculated values
of $\sigma_{\ell 12}$ were plotted against the calculated values of $\varepsilon_{\ell 12}$ thereby generating
the intralaminar-shear-stress-strain curve. The initial ply-shear modulus was
determined from the slope of the initial tangent to the stress-strain curve. The
intralaminar-shear stress strain curve for each 10° off-axis composite listed in
Table 14 are shown in Figs. 20 through 23, and in composite figures 24a and 24b.
The shear stress-strain curve can be considered a measure of the relative "tough-
ness" of each system based on the total shear strength and shear-strain-to-fail-
ure. A relative rating of each system in terms of these properties can be made
since each composite contains a different IME resin but the same graphite fiber
material, Celion 6000 (epoxy size). Based on the shear stress-strain curves the
order of toughness of each composite system is as follows:

C-IME-40-2>-44>41-2>-42>-43-2>-46>-9-3B>-47>C-4>3501-6>-18-4>C-3≅-10-3B≅C-
51 ≅-45

2.5.5 Comparison of Resin Fracture Toughness and Tg with 10° Off-Axis Tensile Strength and % Shear-Strain-to-Failure Results

Table 14 compares the Tg's and fracture toughness K_{IC} of the IME resins
and tensile strength and % shear-strain-to-failure of the Celion 6000/IME compos-
ites. The toughness of the IME resins are listed in order of decreasing K_{IC}
values and in order of decreasing tensile strength and shear-strain-to-failure.

The IME resin with the lowest fracture toughness value K_{IC} is IME-10-3B;
the IME-10-3B composite containing this resin also exhibited low 10° off-axis
tensile strength and shear-strain-to-failure. An anomaly in the series is the
IME-40 system. This system exhibited a fairly low fracture toughness, but the
composite containing this resin exhibited the highest 10°-off axis tensile
strength and shear-strain-to-failure of all the composite systems examined. With
this exception, the resins and composites exhibited the same order of toughness
and 10° off-axis tensile strength and shear-strain-to-failure. This suggests
that there may be a correlation between the fracture toughness of the resin and
the 10° off-axis tensile strength and shear-strain-to-failure.

3.0 EXPERIMENTAL

3.1 Optimization of Yield of 4,4'-(hexafluoroisopropylidene)bis(o-xylene)

The reactions were carried out in glass sealed tubes (2.5cm diameter x 7.5cm long). Trifluoromethane sulfonic acid and o-xylene was added to the glass tube. It was cooled in a chloroform-dry ice mixture, then the hexafluoroacetone sesquihydrate was added. The tube was evacuated while cooling in the chloroform-dry ice mixture. The tubes were allowed to warm up to room temperature and placed in the oil bath and heated at the temperature indicated in Table 1.

3.2 Isolation of Reaction Products

After the tube was cooled to room temperature, the tube was further cooled in a chloroform-dry ice bath, and then the tube was opened. The contents were poured in water (100 ml) and the two phases were separated using a separatory funnel. The organic phase was washed with water until the water wash was neutral. The organic layer was dried over anhydrous calcium sulfate, gravity filtered, and then allowed to concentrate at room temperature to a volume containing only minor quantities of o-xylene. The brown yellow or amber residue was then analyzed by HPLC.

3.3 HPLC Analyses of Reaction Products

Waters Model ALC/GPC 244 chromatograph equipped with WIIP (Waters Intelligent Information Processes) modules (Model 720 Systems Controller) and Model 730 (data module), an automated M-710B WISP (Waters Intelligent Sample Processor), sample processor and a Model 450 UV/VIS tuneable spectrophotometer was used. The final conditions established to separate the o-xylene, the 6F alcohol and the 6FHC in the reaction mixture are listed as follows:

Column: µBondapak C_{18}, 4 mm ID x 30 cm length
Flow rate: 2 ml/min (constant)
Solvent system: (mobile phase): tetrahydrofuran (THF)/H_2O
Detector: UV 254 at 2.0 AUFS
Sample size: 10-20µl
Gradient: linear 45/55 to 70/30 (curve 06)

Time	Flow ml/min	% THF	% H_2O
initial	2.00	45	55
4.0	2.00	45	55
20.0	2.00	70	30
22.0	2.00	100	0
23.0	2.00	100	0
25.0	2.00	45	55

Using these conditions, o-xylene eluted in 10.20 min (Fig. 1), 6F alcohol eluted in 11.73 min (Fig. 2), and the 6FHC eluted in 17.13 min (Fig. 3). The chromatogram of the three component mixture (Fig. 4) shows o-xylene eluting in 10.50 min, 6F alcohol eluting in 11.78 min and the 6FHC eluting in 16.93 min. Clearly, these conditions are able to separate the components of the reaction mixture and were used to establish the yield of products from reactions run under a statistically designed set of conditions. A chromatogram of run 6F-150-2 is shown in Fig. 5.

3.4 Synthesis of Bisimide Amines (BIA's)

The synthesis, purification, and characterization of two of the four bisimide amine (BIA's) hardeners required for this program, are described below.

a. 4,4'-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bis[N-3-(m-aminophenyl sulfonilylphenyl)phthalimide],(6F-3,3'-DDS)

The synthetic reaction for this compound is depicted in the equation below.

3,3'-DDS 6F
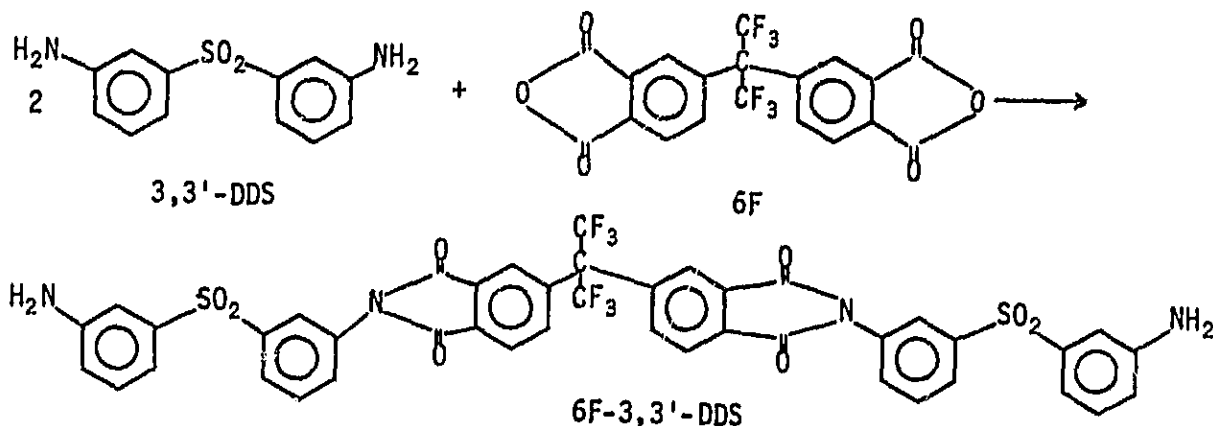
6F-3,3'-DDS

A solution of 113.6g (0.25 mole) of 6F in 250 ml NMP was added dropwise over a one-half hour period to a refluxing solution of 3,3'-DDS (124.2g, 0.5 mole) in 150 ml NMP. The reaction mixture was refluxed for an additional 2 hrs, cooled to room temperature, and poured, while stirring, in water (600g). The off-white solid was filtered and washed several times with distilled water. The solid was placed in 1000 ml water and the mixture was heated to 80°C for 1 hr. The hot slurry was blended in a Waring blender and filtered. Air drying yielded 248.4g of off-white powder. Vacuum drying at 100°C for 2 hrs yielded 211.1g of an off-white powder (93% yield). Reverse phase HPLC analysis of this compound using C_{18} Bondapak column showed the pressure of several components eluting between 33 to 45 min, but only a trace quantity of 3,3'-DDS eluting in 13.30 min. The DSC showed several endotherms, suggesting the presence of many components.

IR, cm^{-1}(dichloromethane solution) 3700, 3610 (S, -OH of CO$_2$H), 3080 (W, aromatic -CH), 3500, 3400 (S, amine N-H), 3240 (W, amine N-H), 1790 (m, imide C=O), 1730 (S, imide C=O), 1690 (S, -CO$_2$H), 1310 (S, sulfone O=S=C), 1250 (bs, sulfone O=S=O), 1150 (S, sulfone O=S=O), 1110 (m, sulfone O=S=O), 875 (W, 2 adj H's on aromatic ring), 855 (s, 1 lone H on aromatic ring).

Elemental Analysis:

Calc. for C$_{43}$H$_{26}$N$_4$F$_6$S$_2$O$_8$ (MW 904.8)
C, 57.08; H, 2.88; N, 6.20; F, 1261, S, 7.08
Found: C, 56.95; H, 2.96; N, 6.15; F, 12.54; S, 6.89.

The infrared and elemental analyses are consistent for the bisimide amine containing carboxylic and other impurities but these techniques cannot differentiate between bisimide amine and oligomers of the bisimide amines. HPLC and DSC reveal that this product contains many minor components with a major component, which is most likely the bisimide amine.

b. 4,4'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidine]-[N-3-(m-aminophenyl)sulfonilylphenyl)-N'-1-(12-aminododecenyl biphthalimide]. 6F-3,3'-DDS-1,12-DDA

The synthetic reaction for this compound is depicted in Eq. (2)

3,3'-DDS   1,12-DDA   6F

6F-3,3'-DDS-1,12-DDA
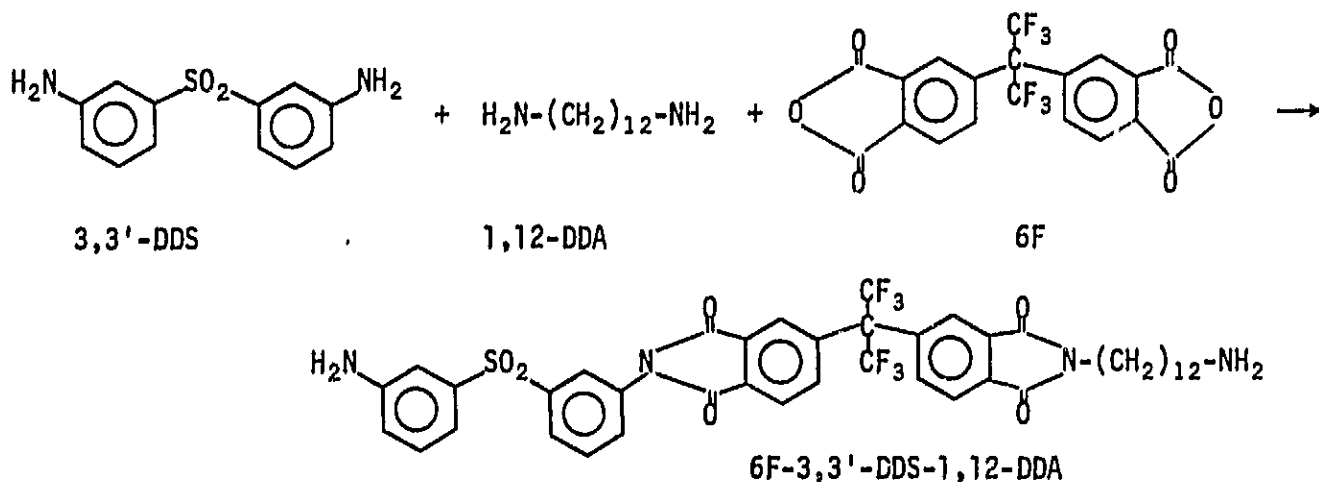
A solution of 6F (227.16g, 0.5 mole) in 600 ml NMP was added to a refluxing solution of 3,3'-DDS (31.06g, 0.125 mole) and 1,12-dodecanediamine (23.0g, 0.125 mole) in 200 ml NMP over a half-hour period. The reaction mixture was refluxed 2 hrs, cooled to room temperature, added to 800 ml of distilled water while stirring to yield a tan solid. This was filtered, washed with distilled water, purified in 2000 ml of hot water (80°C) by treating portions at a time in a Waring blender. The treated product was filtered, dried at 80°C for 3 hrs, then in vacuum at 50°C for 62 hrs to a yield tan solid (204.0g, 95% yield). Reverse phase HPLC analysis of this product using C_{18} Bondapak column revealed the presence of many components, with two major components eluting at 31.44 and 71.98 min dominating the mixture. A volatile component is eluted in 1.40 min. The DSC showed three major endotherms, up to 340°C.

IR, cm^{-1}(dichloromethane solution): 3700, 3610 (m, -OH of $-CO_2H$), 3480, 3410 (w, amine -N-H), 2940, 2870 (S, aliphatic CH_2), 1780 (m, imide C=O, 1730 (S, imide C=O, 1690 (m, $-CO_2H$), 1340, 1300 (m, sulfone O=S=O), 1150, 1100 (S, sulfone O=S=O), 855 (S, 2 adjacent H's on aromatic ring), 840 (m, 1 lone H on aromatic ring).

Elemental Analysis:

Calc'd for $C_{43}H_{42}N_4F_6O_6S$ (MW 856.8) bisimide amine
    C, 60.28; H, 4.94; N, 6.54; F, 13.30; S, 3.73
Calc'd for $C_{62}H_{44}N_4F_{12}SO_{16}$ polymer
    C, 58.86; H, 3.48; N, 4.44; F, 18.03; S, 2.53
Found: C, 55.60; H, 3.57; N, 3.76; F, 18.19; S, 1.89

This product appears to contain impurities of carboxylic acid and is polymeric in nature.

c. 4,4'-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bis[N-[-(p-aminophenyl)-p-tolyl]phthalimide], (6F-4,4'-MDA)

This compound was prepared according to the equation

MDA   6F

6F-4,4'-MDA
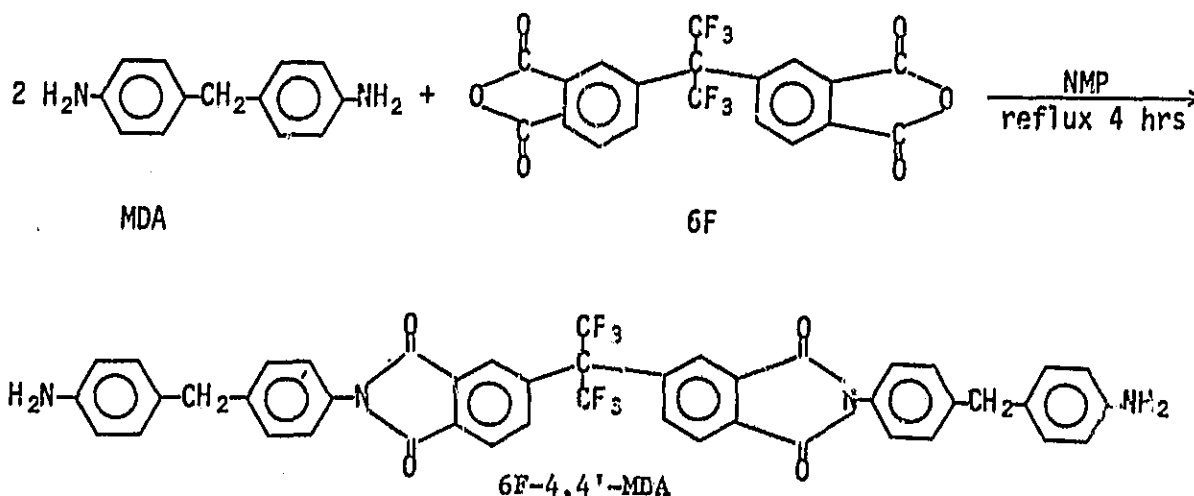
To a stirred solution of MDA (95.2g, 0.48 mole) in 350 ml of NMP, a solution of 6F (108g, 0.24 mole) in 350 ml of NMP was added over a 1/2 hour period. The reaction mixture was stirred and refluxed for 4 hrs. The solution was concentrated under vacuum (0.5 mm Hg) to half of its initial volume. Upon cooling to room temperature, the concentrated solution was poured into ice-water mixture. The brown solid material which precipitated was filtered and washed seven times with 100 ml distilled water. After drying in vacuum oven at 60°C overnight, this yielded crude brown product (192.4g, 99.6% yield). The crude product was dissolved in a minimum quantity of hot acetone. After cooling to room temperature, cold distilled water was added to the acetone solution. The precipitates were collected by suction filtration and washed several times with boiling distilled water until the filtrate appeared clear and colorless. Drying of the recrystallized product gave an analytical sample of 6F/MDA ('54.5g, 80% yield): IR (chloroform solution); 3485 (w, amine N-H), 3380 (m, amine N-H), 1780 (m, imide C=O), 1720 (s, imide C=O). NMR (CDCl$_3$); δ 3.2 (s, 2H methylene group), 3δ-42 (m, 4H, NH$_2$), 6.4-7.5 (m, 16H, aromatic H), 8.0 (s, 6H, aromatic H), signals at δ 1.3-2.9 are impurity peaks. Melting point 230°C as determined by DSC.

Elemental Analysis:

Calc. for C$_{45}$H$_{30}$N$_4$F$_6$O$_4$ (MW 804.7): C, 67.16; H, 3.73; N, 6.97; F, 14.18
Found: C, 66.50; H, 4.00; N, 7.09; F, 14.51.

d. 4,4'-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bis[N-[p-(p-aminophenyoxyphenyl)phthalimide](6F-4,4'-ODA)

This compound was prepared in accordance with the equation
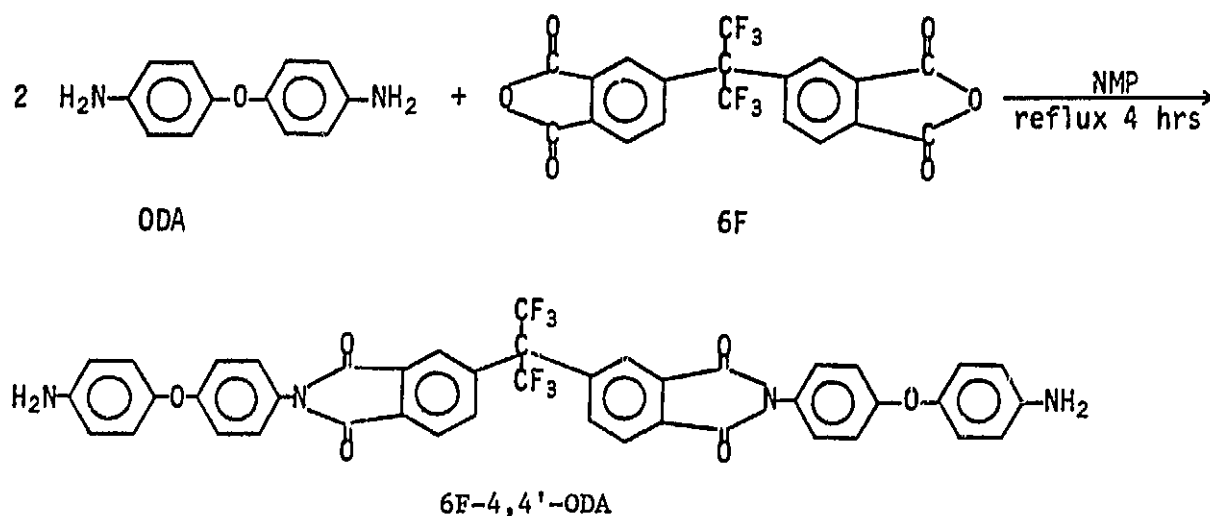
6F-4,4'-ODA

A solution of 4,4'-ODA (196.23g, 0.98 mole) in 400 ml of NMP was added to a 2000-ml four-necked round-bottom flask equipped with a stirrer, a reflux condenser, an addition funnel, and a thermometer. A solution of 6F (216.0g, 0.49 mole) in 600 ml of NMP was (dropwise) added over a 1 hr period to the ODA solution which was stirred and held at reflux. The progress of the reaction was followed by measuring the optical densities of the 6F anhydride band at 1840 cm^{-1} and the 6F/ODA imide band at 1720 cm^{-1}. The reaction was essentially complete in 4 hrs refluxing time. After 4 hrs, the reaction solution was concentrated under reduced pressure (2 mm Hg) to half of its original volume. Upon cooling to room temperature, the concentrated solution was poured into 1000 ml distilled water to precipitate yellowish products. The fine crystalline materials were suction filtered, washed with distilled water, and dried in a vacuum oven at 60°C overnight to give 388g (98% yield) of crude products. The crude products were recrystallized from acetone-water to afford 356.3g (90% yield) off-white recrystallized products. Final purification was accomplished by treating the solid with hot distilled water in a Waring blender followed by filtration, air drying and vacuum oven (100°C) drying for 2 hrs. The GPC chromatogram of the materials purified revealed two major peaks (99%) and traces of starting amine indicating a compound of good purity. The IR, NMR, DSC, and elemental analysis of the recrystallized products were determined and are presented as follows:

3480 (w, amine N-H), 3370 (m, amine N-H), 1780 (m, imide C=O), 1720 (S, imide C=O), 1220 (bs, ether C-O).

NMR (CDCl$_3$): δ 3.50 (bs, 4H, NH$_2$), 6.50-7.60 (m, 16H aromatic H), 7.8-8.2 (m, 6H, aromatic H). Note that the signals in the region of δ 2.20 to 3.00 are probably due to solvents and impurities.

DSC: Endotherms at 90, 165, 215, and 325°C.

Elemental Analysis:

Calc. for $C_{43}H_{26}N_4F_6O_6$, (MW 808.6):
　　　　C, 63.86; H, 3.22; N, 6.93; F, 14.11

Found: C, 64.27; H, 3.86; N, 6.69; F, 13.80

3.5 Synthesis and Characterization of Bisimide Amine (BIA) Cured Epoxy Resins

3.5.1 Preparation of Homogeneous Bisimide Amine Epoxy (IME) Resin Powders

Table 6 lists the composition of resin powders prepared for molding into cured resin discs and used in tetrahydrofuran solution (~70 wt%) for impregnation and fabrication of Celion 6000 graphite fiber tape and composites.

Approximately 13g portions of powder for each IME resin system listed in Table 6 were prepared by concentration of a solution (50 wt%) of the resin components in tetrahydrofuran. The residual THF solvent was removed in vacuum at 60°C for 2 hrs for all IME resins except for IME-18-4, -43, -41 and -40. These were treated at room temperature in vacuum for times required (2 to 24 hrs) to remove traces of solvent. For each IME system, a fine orange-to-red colored powder was obtained.

3.5.2 Fabrication of IME Resin Discs for Physical and Thermal Property Characterization

Resin discs (3.00cm diameter x 0.32cm thick) of several of the IME resins listed in Table 6 were fabricated by compression molding techniques by following the gel point as the temperature approached 150°C in the mold. Resin powder (5.0g for the 3cm diameter mold) was placed into the mold. The assembly was placed into a preheated press, a pressure of 6.89 MPa was applied to consolidate the powder. Pressure was released, and the specimen was then compression molded by applying pressure (6.89 MPa) at gelation (~150°C). The resin was cured using two cure cycles: Cycle #1 150°C/1 hr + 177°C/3 hrs (at 6.89 MPa), Cycle #2 150°C/1 hr + 177°C/2 hrs + 204°C/2 hrs at 6.89 MPa + 204°C/22 hrs (post cure) no pressure.

3.5.3 Fabrication of Resin Discs for Fracture Toughness Tests

The same procedure used above was used to fabricate the fracture toughness specimens. A 5.08cm (2") diameter mold was used. Specimens were machined according to ASTM E399-81 specification (Fig. 6 and Ref. 11). Approximately 18 grams of resin powder was used to fabricate discs with approximate thicknesses of 0.64cm. The samples were tested at a loading rate of 0.0254 cm/min (0.01"/min).

3.5.4 Physical Properties

Density was determined by measuring the volume of a symmetrical sample, and then determining the weight of the sample. The density was calculated as follows: density = weight in grams/volume (cc) = g/cc. The cure shrinkage of each resin system was determined as follows: % shrinkage = diameter of mold (RT) − diameter of resin spec (RT)/diameter of mold (RT). The coefficients of thermal expansion were determined on 0.64cm x 0.64cm x 0.64cm to 1.00cm length specimens (cut from the 2.54cm diameter disks) on the DuPont 1090-DMA thermal analysis unit in the expansion mode.

3.5.5 Thermal Properties

A DuPont 1090 thermoanalyzer equipped with a 943 thermomechanical analyzer (TMA) and a DuPont thermogravimetric analyzer (TGA) were used to determine the glass transition temperature (Tg) and weight losses in nitrogen as a function of

temperature of each resin specimen. The DSC behavior was also determined on a DuPont 1090 thermoanalyzer equipped with a DuPont differential scanning calorimeter (DSC).

The anaerobic char yield of each resin was determined in nitrogen by the TGA technique up to a temperature of 800°C.

3.5.6 Fracture Toughness Tests

The fracture toughness test was made according to ASTM procedure E399-81 (Ref. 11). The specimen configuration used is shown in Fig. 6. The specimens were tested at a loading rate of 0.0254cm/min (0.01"/min).

3.6 Fabrication and Characterization of Celion 6000/IME Resin Composites

3.6.1 Fabrication of Prepreg

Prepregs were fabricated by drum winding epoxy sized Celion 6000 graphite fibers and brush application of a THF solution of the resin (26.1g) to the dried fiber tape (11.43cm wide x 137cm long), calculated to yield a composite with a fiber volume of 60±2%. The prepreg tapes were air dried on the drum at room temperature, then vacuum dried at 60°C for 2 hrs to remove traces of THF, except prepregs containing IME-18-4, -40, -41 and -43. These were dried at room temperature in vacuum for 2 hrs, instead of 70°C to prevent advancement of the resin. The plies were stacked unidirectionally and processed by compression molding techniques, as described below. The composition of each Celion 6000/IME composite is tabulated in Table 6.

3.6.2 Compression Molding of Celion 6000/IME Composites

A series of 5 ply (14.0cm x 25.4cm x 0.139cm) Celion 6000/IME composites (Table 12) were fabricated by compression molding techniques for determination of 10° off-axis tensile properties of each system. An open ended mold was used to follow the gelation point by probing the laminate as a function of time at specific temperatures. This procedure is required to produce void free compression molded composites. Of critical importance in the fabrication process is the time/temperature parameter for the application of pressure in the initial stages of gelation. The composites were fabricated by placing the mold in a preheated press (150°C) at contact pressure. The mold is held at 150°C for about 1 hr or until gelation occurs, at which time pressure is applied to reach the stops which are required to yield a finished composite of 0.14cm thickness. The system is held at 150°C under pressure for 1 hr, then raised to 177°C and held at this temperature for 3 hrs under pressure (~3.45 MPa). Glass cloth/epoxy doublers (6.25cm x 15.2cm x 0.254cm thick) were bonded to each end of the composite at an angle of 10° to the fiber direction. The unidirectional

composites were cut 10° to the fiber direction, to produce specimens 1.25cm wide x 25.4cm long x ~0.14cm thick with approximately 3.81cm (1.5") doublers on each end, meeting the specifications published by Chamis and Sinclair (Ref. 13).

3.6.3 Composite Characterization Techniques

3.6.3.1 Physical Properties

The density of each composite was determined by dividing the weight of a symmetrical composite sample by its volume. For comparison purposes the density was also determined by the liquid displacement technique. The fiber and resin volume percents were calculated from a portion of a 10° off-axis specimen with the approximate dimensions 11.53cm x 1.27cm x 0.022cm assuming zero void content. The calculation was based on the number of strands of fiber (88) in a 11.43cm (4.5") wide ply of a 5 ply composite. The weight of Celion 6000 graphite per inch of strand

$$= 0.009994 \text{ g/in/strand}.$$

Composite weight $= 3.26829$

Composite dimensions $= 11.53\text{cm} \times 1.254\text{cm} \times 0.134\text{cm}$

Calculation: $\dfrac{88 \text{ strands}}{4.5 \text{ in ply}} \times 0.494 \text{ in} \times 5 \text{ plies} \times \dfrac{4.63 \text{ in}}{\text{strand}}$

$$\times 0.009994 \text{ g/in} = 2.24 \text{ g fiber}$$

Resin wt $= 3.2682 = 1.0282 \text{ g}$,

Fiber Vol. $= \dfrac{2.235}{1.76 \text{ g/cc}} = 1.270$ ⠀⠀⠀⠀ Resin Vol. $= \dfrac{1.0282 \text{ g}}{1.33 \text{ g/cc}} = 0.773$

Total Composite Vol. $= 1.270 + 0.773 = 2.043 \text{ cc}$

Vol. % Fiber $= 62.2$ ⠀⠀⠀⠀⠀⠀⠀ Vol. % Resin $= 37.8$

The C-scan of each composite was carried out and each panel was found to be void free.

3.6.3.2 Mechanical Properties

Ten Degrees Off-Axis Tensile Test - This test was carried out according to the procedure of Chamis and Sinclair (Ref. 13). A rectangular rosette (0°, 45°, 90°) of strain gages (type EA-06-062RB-120) was used. The load versus strain for each strain gage was recorded. The samples were loaded at a rate of 0.254 cm/min (0.1"/min).

3.6.4 Shear Stress-Strain Curves

The shear strain stress curves were generated by the procedure of Chamis and Sinclair (Ref. 13).

4.0 SUMMARY OF RESULTS

Studies to optimize the yield of the 6F hydrocarbon, (6FHC) 4,4'-(hexafluoroisopropylidene)bis(o-xylene) a precursor to 4,4'-hexafluoroisopropy-lidene(o-phthalic anhydride) from hexafluoroacetone sesquihydrate (HFA) and o-xylene using trifluoromethanesulfonic acid (TFS) catalyst utilizing a series of statistically designed experiments covering the parameters of temperature, reaction concentrations, and catalyst concentration were carried out. These investigations using small sealed glass tubes revealed that the reaction conditions, 150°C, excess o-xylene, HFA (4.0g), TFS (4.0ml), 36 hours gave maximum yield of 6FHC (50%) as determined by HPLC. However, efforts to translate these results to a larger scale synthesis gave the 6FHC in only 9% yield. The results suggest that the synthesis of 6FHC may require a stronger catalyst than TFS.

Four bisimide amines (BIA's) were synthesized and evaluated with epoxy resins DER 383 and MY720 in efforts to improve the toughness properties of epoxy resins. Homogeneous powders of the BIA's and epoxy resin have been prepared from evaporation of tetrahydrofuran solutions of the resin. Solid void free resin specimens were fabricated from these powders by compression molding techniques. The fracture toughness properties of the bisimide amine cured epoxy resins (IME's) was improved four-fold over the control systems and ten-fold over the state-of-the-art Hercules 3501-6 epoxy resin. The studies also reveal that the IME's with the highest fracture toughness exhibited the lowest glass transition temperature (Tg). Consideration of both the Tg and fracture toughness K_{IC}, the best IME resins can be rated as follows:

IME-40>IME-9-3B>IME-43>IME-45>IME-18-4>IME-42>IME-41>IME-47>IME-44>IME-46>IME-10-3B

The control resins can be rated as follows: C-51>C-4>C-3>C-1>Hercules 3501-6>, all of which fall below the IME resins.

The IME resins were also evaluated in 10° off-axis Celion 6000/IME epoxy resin composites. These tests also showed that several of the IME composites exhibited vastly superior 10° off-axis tensile strength, intralaminar shear strength and shear strain-to-failure over the control composites. This was also revealed in the stress-strain curves, suggesting superior "toughness" properties over the control composites. For example, the composite IME-40-2 exhibited the following properties: tensile strength and modulus 483.5 MPa and 85.5 GPa (70.1 ksi and 12.4 x 10^6 psi) and intralaminar shear strength and modulus 83.8 MPa and 7.44 GPa (12.0 ksi and 1.08 x 10^6 psi) and intralaminar shear strain-to-failure 4.58%. For the control composites these values

were as follows: tensile strength and modulus 269-359 MPa and ~ 89.7 GPa (39-52 ksi and ~13 x 10^6 psi), intralaminar shear strength and modulus 45.5 to 60.7 MPa and 6.89 GPa (6.6 to 8.8 ksi and 1 x 10^6 psi), and intralaminar shear strain-to-failure ~1.10%. With a few exceptions (IME-40 and 44), the resins with the highest fracture toughness values also exhibited the highest 10° off-axis tensile strength and shear strain-to-failure.

The studies showed that the concept of using bisimide amines as curing agents to improve the toughness properties of epoxies is valid and has led to a four-fold to a ten-fold improvement in toughness properties of resins relative to the control resins and state-of-the-art epoxy respectively.

4.1 Conclusions

Three general conclusions can be made:

1. A statistically designed experiment improved the yield of 6FHC, 4,4'-(hexafluoroisopropylidene)bis(o-xylene) to 50% when carried out in sealed tubes, but did not give an improved yield when scaled up.

2. DER 383 (diglycidylether of bisphenol A) epoxies and MY720 (4,4'(N,N'-tetraglycidyl)-methylene dianiline) epoxy resins cured with bisimide amines exhibited a four-fold increase in Mode I fracture toughness as measured by K_{IC}, compared to control epoxy resins.

3. Celion 6000 graphite fiber/bisimide amine-cured epoxy composites exhibited up to 25% increase in 10° off-axis tensile strength, up to 37% increase in interlaminar shear strength, and up to 300% increase in interlaminar shear strain-to-failure, compared to control composites.

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TABLE 1

REACTION OF HEXAFLUOROACETONE SESQUIHYDRATE WITH O-XYLENE WITH CF_3SO_3H CATALYST

Sealed Tube Reactions

Hexafluoroacetone (HFA) constant weight 4.0g (0.0207 mole)
o-xylene (X), ml   Each multiple of X is 4.9ml (4.3g, 0.0414 mole)
Trifluoromethane sulfonic
acid (TFS), ml

100°C	150°C	200°C	225°C
6F-100-1	6F-150-1	6F-200-1	6F-225-1
36 hrs	16 hrs	10 hrs	4 hrs
4.9 ml(X)	4.9 ml(X)	4.9 ml(X)	4.9 ml(X)
2.0 ml(TFS)	2.0 ml(TFS)	2.0 ml(TFS)	2.0 ml(TFS)
6F-100-2	6F-150-2	6F-200-2	6F-225-2
4 hrs	36 hrs	16 hrs	10 hrs
9.8 ml(X)	9.8 ml(X)	9.8 ml(X)	9.8 ml(X)
4.0 ml(TFS)	4.0 ml(TFS)	4.0 ml(TFS)	4.0 ml(TFS)
6F-100-3	6F-150-3	6F-200-3	6F-225-3
10 hrs	4 hrs	36 hrs	16 hrs
19.6 ml(X)	19.6 ml(X)	19.6 ml(X)	19.6 ml(X)
8.0 ml(TFS)	8.0 ml(TFS)	8.0 ml(TFS)	8.0 ml(TFS)
6F-100-4	6F-150-5	6F-200-4	6F-225-4
16 hrs	10 hrs	4 hrs	36 hrs
39.2 ml(X)	39.2 ml(X)	39.2 ml(X)	39.2 ml(X)
16 ml(TFS)	16 ml(TFS)	16 ml(TFS)	16 ml(TFS)

TABLE 2

HPLC ANALYSIS DATA FOR RUN NO. 6F-150-2

FEB. 12, 1983   11:24:12   CHART   0.50 CM/MIN
                                 RUN #87   CALC #0
COLUMN   SOLVENT   OPR ID: 5

EXTERNAL STANDARD QUANTITATION

PEAK #	AMOUNT	RT	EXP RT	AREA		RF
	15718.40000	12.47		15718518	L	0.000000E0
	1668.59000	15.28		1668600	L	0.000000E0
	14007.40000	16.76		14007550	F	0.000000E0
	87146.40000	17.53		87146970	F	0.000000E0
	8733.41000	18.73		8733460	F	0.000000E0
	11997.00000	19.21		11997160	HL	0.000000E0
TOTAL	139270.00000					

PEAK #	AMOUNT	RT	%
	15718.40000	12.47	11.28
	1668.59000	15.28	1.19
	14007.40000	16.76	10.05
	07146.40000	17.53	62.57
	0733.41000	18.73	6.27
	11997.00000	19.21	8.61
TOTAL	139270.00000		100.00

TABLE 3

PRODUCT YIELDS FROM REACTION OF HEXAFLUOROACETONE (HFA) AND O-XYLENE UNDER VARIOUS REACTION CONDITIONS
(HFA, 4.0g Constant)

Run No.	Temp °C	Time hrs	Conc. o-xylene (ml)	Conc. TFS (ml)	Percent (%)		
					6F alcohol	6F HC	Other Components
6F-100-1	100	36	4.9	2.0	77	1	22
6F-100-2	100	4	9.8	4.0	4.0	45	51
6F-100-3	100	10	19.6	8.0	5.2	36	59
6F-100-4	100	16	39.2	16	5.0	48	47
6F-150-1	150	16	4.9	2.0	60	9	31
6F-150-2	150	36	9.8	4.0	11	63	26
6F-150-3	150	4	19.6	8.0	1	40	59
6F-150-4	150	10	39.2	16.0	0	50	50
6F-200-1	200	10	4.9	2.0	22	19	59
6F-200-2	200	16	9.8	4.0	3.0	36	61
6F-200-3	200	36	19.6	8.0	1.4	19	80
6F-200-4	200	4	39.2	16.0	0	29	71
6F-225-2	225	10	9.8	4.0	8.1	45	47
6F-225-3	225	16	19.6	8.0	4.0	30	66
6F-225-4	225	36	39.2	16.0	– (exploded twice)		

TABLE 4

WEIGHTED AVERAGE METHOD OF DATA ANALYSIS

Weighted Average Assignments			Variable/Score					
			Temp°C/Score		Time hrs/Score		TFS Conc (ml)/Score	
6F alc	6F HC	Others						
0	1	0	100	130	4	114	2	29
			150	162	10	150	4	189
			200	103	16	123	8	125
			225	75	36	83	16	127
.2	1	0	100	148	4	115	2	61
			150	176	10	157	4	194
			200	108	16	137	8	127
			225	77	36	101	16	128
0.5	1	0	100	176	4	115	2	61
			150	198	10	157	4	194
			200	116	16	137	8	127
			225	81	36	101	16	128

TABLE 5

BISIMIDE AMINE CURED EPOXY RESINS
Initial Screening Studies

Formulation No.	Composition	Equivalent Weights	No. of Equivalents	Weight, g	Glass Transition Temp°C
C-4	383/3,3'-DDS	185/62.1	0.135/0.128	25/8.0	110
IME-40	383/6F-3,3'-DDS	185/226.2	0.034/0.032	6.3/7.25	160
IME-41	383/6F-4,4'-ODA	185/202.2	0.034/0.0346	6.3/7.42	120
IME-42	383/6F-3,3'-DDS-1,12 -DDA	185/214.2	0.034/0.030	6.3/6.5	100
IME-43	383/6F-4,4'-MDA	185/201.2	0.034/0.0303	6.3/6.1	140
9102-1	9102/3,3'-DDS	153/62.1	0.163/0.159	25/9.9	130
9102-2	9102/6F-3,3'-DDS	153/226.2	0.163/0.128	25/29.0	130
9102-3	9102/6F-3,3'-DDS	153/226.2	0.041/0.032	6.3/7.25	160
9102-4	9102/6F-4,4'-ODA	153/202.2	0.041/0.037	6.3/7.42	160
9102-5	9102/6F-3,3'-DDS-1,12 -DDA	153/214.2	0.04/0.032	6.3/0.032	60
9102-6	9102/6F-4,4'-MDA	153/201.2	0.04/0.030	6.3/6.1	90

cure cycle: 150°C/1 hr + 200°C/2 hrs

TABLE 6

COMPOSITION OF BISIMIDE AMINE EPOXY (IME) EPOXY RESINS
FOR RESIN[1] AND COMPOSITE SPECIMENS[2]

Resin No.	Composition	Equivalent Weights	Equivalents of Each Component	Component[4,5] Weights for Composites, g
Control C-1	MY720/4,4'-DDS	125/62.1	0.138/0.138	17/26/8.63
Control C-3	MY720/3,3'-DDS	125/62.1	0.138/0.138	17.26/8.63
Control C-4	DER 383/3,3'-DDS	185/62.1	0.106/0.101	19.62/6.28
Control C-51	DER 383/MY720/3,3'-DDS	185/125/62.1	0.061/0.061/ 0.116	11.3/7.62/7.2
Hercules 3501-6[3]	MY720/Cresol Novolac/ CY-179/4,4'-DDS/BF$_3$·MEA	---	---	---
IME-9-3B	MY720/6F-3,3'-DDS	125/226.2	0.074/0.074	9.29/16.8
IME-10-3B	MY720/6F-3,3'-DDS/ 3,3'-DDS	125/226.2/62.1	0.097/0.0508/ 0.048	12.14/11.5/3.0
IME-18-4	MY720/6F-3,3'-DDS-1, 12-DDA	125/214.2	0.0768/0.0796	9.60/16.48
IME-40	DER 383/6F-3,3'-DDS	185/226.2	0.0656/0.0617	12.14/13.96
IME-41	DER 383/6F-4,4'-ODA	185/202.2	0.069/0.0653	12.80/13.2
IME-42	DER 383/6F-3,3'-DDS-1, 12-DDA	185/214.2	0.0673/0.0637	12.45/13.65
IME-43	DER 383/6F-4,4'-MDA	185/201.2	0.0694/0.0659	12.84/13.26
IME-44	DER 383/MY720/6F -3,3'-DDS	185/125/226.2	0.0353/0.0353/ 0.06675	6.53/4.41/15.1
IME-45	DER 383/MY720/6F -4,4'-ODA	185/125/202.2	0.0378/0.0378/ 0.0712	6.99/4.72/14.4
IME-46	DER 383/MY720/6F -3,3'-DDS-1,12-DDA/ 3,3'-DDS	185/125/214.2/ 62.1	0.0359/0.0359/ 0.03398	6.65/4.49/ 7.28/2.11
IME-47	DER 383/MY720/6F- 4,4'-MDA	185/125/201.2	0.0378/0.0378/ 0.0707	7.00/4.73/14.3

[1,2] See experimental details of resin and composite fabrication.
[3] See Ref. 14.
[4] This is the resin weight for 137cm (54") long tape, but 127cm (50") used in fabricating the composite.
[5] Each composite contains about 42.8g fiber.

TABLE 7

SOME PHYSICAL AND THERMAL PROPERTIES OF CURED IME RESINS

Resin System	Density, g/cc		Coefficient of Thermal Expansion cm/cm/°C, $\alpha \times 10^5$		Shrinkage, %		Tg, °C	
	Cure Cycle # 1	Cure Cycle # 2	Cure Cycle # 1	Cure Cycle # 2	Cure Cycle # 1	Cure Cycle # 2	Cure Cycle # 1	Cure Cycle # 2
Control C-1	1.26	--	5.24	5.51	2.28	0.81	205	230
Control C-3	1.27	1.24	5.08	8.63	1.98	0.80	200	222
Control C-4	1.21	-	4.61	-	3.94	--	110	-
Control C-51	1.25	--	6.73	-	2.00	-	170	-
Hercules 3501-6	1.26	-	4.52	-	2.67	-	195	--
IME-9-3B	1.33	1.33	6.98	5.25	1.39	0.74	185	197
IME-10-3B	1.35	1.29	5.53	5.80	0.80	0.80	180	200
IME-18-4	1.29	1.32	6.45	7.38	0.96	-	150	150
IME-40	1.31	-	5.24	-	0.79	-	170	-
IME-41	1.29	-	6.62	-	0.48	-	110	-
IME-42	1.31	-	7.98	-	0.32	-	100	-
IME-43	1.28	-	9.45	-	0.64	-	140	-
IME-44	1.33	-	10.9	-	0.32	-	120	-
IME-45	1.30	-	8.35	-	0.48	-	150	-
IME-46	1.30	-	7.40	-	0.32	-	90	-
IME-47	1.33	-.	7.51	-	0.96	-	120	-

TABLE 8

MOISTURE ABSORPTION OF CURED IME RESINS

Resin System	After RT 24 hrs in Water, Wt%		After 72 hrs Water Boil, Wt%		After Saturation at 95% RH, 60°C wt%
	Cure Cycle # 1	Cure Cycle # 2	Cure Cycle # 1	Cure Cycle # 2	Cure Cycle # 1
Control C-1	0.38	0.39	3.3	4.0	3.74
Control C-3	0.28	0.20	3.9	3.2	4.10
Control C-4	0.05	-	3.0	-	1.94
Control C-51	0.28	-	2.7	-	2.67
Hercules 3501-6	0.40	-	5.04	-	4.35
IME-9-3B	0.39	0.22	4.1	2.2	2.73
IME-10-3B	0.20	0.24	4.1	2.6	2.77
IME-18-4	0.23	0.17	2.0	2.0	1.28
IME-40	0.29	-	2.4	-	2.03
IME-41	0.22	-	2.4	-	1.38
IME-42	0.43	-	3.9	-	2.45
IME-43	0.29	-	2.1	-	1.12
IME-44	0.42	--	6.1	-	3.04
IME-45	0.27	-	2.4	-	1.62
IME-46	0.22	-	5.2	-	3.45
IME-47	0.31	-	3.7	3.3	1.70

TABLE 9

THERMAL PROPERTIES OF CURED IME RESINS

Resin System	DSC Transitions, °C Cure Cycle #1 endothermic	exothermic	Tg, °C Cure Cycle #1	Cure Cycle #2	TGA, Wt% Loss 300°C Cure Cycle #1	Cure Cycle #2	% Char Yield TGA Method[1] Cure Cycle #1	Cure Cycle #2
Control C-1	170-220	255,300-360	205	203	0.5	0.5	18	20
Control C-3	160-210	240,300-360	200	222	0.2	0.5	14	20
Control C-4	110-220	250-360	110	-	0.2	-	16	-
Control C-51	170-185	240-400	170	-	0.2	-	18	-
Hercules 3501-6	180-200	250,280,360	195	-	0.2	1.0	25	15
IME-9-3B	170-240	280-350	185	197	3.0		35	38
IME-10-3B	195-240	270-350	180	200	2.0		33	37
IME-18-4	150-220	280,320-390	150	150	2.0		42	
IME-40	170-240	280-370	170	-	0.2		30	
IME-41	140-220	240-420	110	-	0.2		28	
IME-42	100-220	280-400	100	-	2.0		20	
IME-43	150-230	240-380	140	-	4.0		33	
IME-44	120-220	280-380	120	-	3.0		30	
IME-45	160-220	240-370	150	-	2.0		37	
IME-46	90-190	240-400	90		3.0		22	
IME-47	120-220	290,390-380	120	-	3.0		32	

[1] In nitrogen, % residue up to 800°C

TABLE 10

FRACTURE TOUGHNESS[1] OF IME AND CONTROL RESINS
USING THE COMPACT TENSION (CT) SPECIMEN (RT)

Resin System	Fracture Length, (a+w) (Includes Precut) Without Plastic Zone in.	mm	With Plastic Zone in.	mm	Without Plastic Zone K_{IC} $Pa\sqrt{m}$	G_{IC}^2 J/m^2	With Plastic Zone K_{IC} $Pa\sqrt{m}$	G_{IC}^2 J/m^2
Control C-1	0.186	3.96	0.326	8.28	330	29.9	464	59.2
Control C-3	0.156	3.96	0.182	4.62	343	32.4	370	37.8
Control C-4	0.146	3.71	0.172	4.37	591	96.3	640	113
Control C-51	0.167	4.24	0.220	5.59	541	80.5	625	108
Hercules 3501-6	0.192	4.88	0.227	5.77	260	18.7	286	22.5
IME-9-3B	0.171	4.34	0.185	4.69	581	93.1	605	101
IME-10-3B	0.185	4.70	0.230	5.84	480	63.5	542	80.9
IME-18-4	0.168	4.26	0.223	5.66	597	98.1	693	132
IME-40	0.175	4.44	0.240	6.09	630	109	725	14.5
IME-41	0.165	4.19	0.175	4.44	853	200	879	213
IME-42	0.184	4.67	0.277	7.04	893	220	1130	353
IME-43	0.192	4.88	0.229	5.82	800	176	881	214
IME-44	0.192	4.88	0.218	5.54	691	132	741	151
IME-45	0.157	3.99	0.207	5.26	634	111	733	140
IME-46	0.145	3.68	0.162	4.11	713	140	740	151
IME-47	0.159	4.04	0.185	4.70	788	171	851	199

[1]Tested at .0254 cm/min (0.01 in/min) cross-head speed
[2]A nominal modulus value of 3.46 GPa (0.5 x 10^6 psi) used for every specimen

TABLE 11

COMPOSITION DATA FOR 10°-OFF-AXIS CELION 6000/EPOXY RESIN
COMPOSITES (5 PLY COMPOSITES)[1]

Composite No.	Resin Composition	Density[2] g/cc	Calculated[3] Vol% Resin	Calculated[3] Vol% Fiber	Composite Ply Thickness mm/ply
Control C-1	MY720/4,4'-DDS	1.607	66	34	0.269
Control C-3	MY720/3,3'-DDS	1.588	64	36	0.269
Control C-4	DER 383/3,3'-DDS	1.637	66	33	0.251
Control C-51	DER 383/MY720/3,3'-DDS	1.573	63	37	0.271
Hercules 3501-6	MY720/Cresol Novolac/CY-179/4,4'-DDS/BF$_3$-MEA	1.630	67	33	0.256
C-IME-9-3B	MY720/6F-3,3'-DDS	1.611	62	38	0.269
C-IME-10-3B	MY720/6F-3,3'-DDS/3,3'-DDS	1.613	64	36	0.264
C-IME-18-4	MY720/6F-3,3'-DDS-1,12-DDA	1.594	57	43	0.278
C-IME-40-2	DER 383/6F-3,3'-DDS	1.613	64	36	0.264
C-IME-41-2	DER 383/6F-4,4'-ODA	1.590	61	39	0.279
C-IME-42	DER 383/6F-3,3'-DDS-1,12-DDA	1.578	58	42	0.295
C-IME-43-2	DER 383/6F-4,4'-MDA	1.610	66	34	0.251
C-IME-44	DER 383/MY720/6F-3,3'-DDS	1.481	59	41	0.299
C-IME-45	DER 383/MY720/6F-4,4'-ODA	1.562	54	46	0.315
C-IME-46	DER 383/MY720/6F-3,3'-DDS-1,12-DDA/3,3'-DDS	1.566	54	46	0.315
C-IME-47	DER 383/MY720/6F-4,4'-MDA	1.597	63	37	0.274

[1]See Ref. 14
[2]Calculated from weight of symmetrical sample divided by its volume
[3]See experimental section for calculations

TABLE 12

TENSILE PROPERTIES OF 10° OFF-AXIS CELION 6000/IME COMPOSITES

Composite No.	Composition	Tensile Properties				Intralaminar Shear Properties				Composite Intralaminar Shear Strain-to Failure, %
		Strength		Modulus		Strength		Modulus		
		ksi	MPa	10^6 psi	GPa	ksi	MPa	10^6 psi	GPa	
Control C-1	MY720/4,4'-DDS	39.6	273	14.2	97.9	6.77	46.7	0.853	5.88	0.70
Control C-3	MY720/3,3'-DDS	38.3	264	14.9	103	6.55	45.1	0.92	6.34	1.21
Control C-4	DER 383/3,3'-DDS	51.8	357	14.1	97.2	8.86	68.9	0.93	6.41	1.25
Control C-51	DER 383/MY720/ 3,3'-DDS	39.1	270	12.0	82.8	6.68	46.0	1.07	7.38	0.91
Hercules 3501-6	MY720/Cresol Novolac CY179/4,4'-DDS/ BF₃-MEA	50.1	346	14.0	96.6	8.71	60.1	0.84	5.79	0.93
C-IME-9-3B	MY720/6F-3,3'-DDS	52.6	363	12.2	84.1	8.99	62.0	1.15	7.93	1.73
C-IME-10-3B	MY720/6F-3,3-DDS/ 3,3'-DDS	41.2	284	13.1	90.3	7.05	48.6	1.15	7.93	0.89
C-IME-18-4	MY720/6F-3,3'-DDS- 1,12-DDA	41.3	285	12.9	88.9	7.07	48.7	1.18	8.14	2.15
C-IME-40-2	DER 383/6F-3,3'-DDS	70.1	483	12.4	85.5	12.0	82.8	1.08	7.45	.58
C-IME-41-2	DER 383/6F-4,4'-ODA	57.9	399	11.2	77.2	9.91	68.3	1.01	6.96	3.73
C-IME-42	DER 383/6F-3,3'-DDS- 1,12-DDA	49.9	344	9.54	65.8	8.43	58.1	0.86	5.93	4.82
C-IME-43-2	DER 383/6F-4,4'-MDA	48.3	333	12.6	86.9	8.27	57.0	1.05	7.24	3.57
C-IME-44	DER 383/MY720/6F- 3,3'-DDS	67.5	466	12.0	82.8	11.5	79.3	0.77	5.31	4.28
C-IME-45	DER 385/MY720/6F- 4,4'-ODA	35.1	242	8.86	61.1	6.00	41.4	0.715	4.93	1.13
C-IME-46	DER 383/MY720/6F- 3,3'-DDS-1,12-DDA/ 3,3'-DDS	45.7	315	10.3	71.0	6.55	45.2	0.904	6.23	4.32
C-IME-47	DER 383/MY720/6F- 4,4'-MDA	53.4	360	12.6	86.9	9.13	62.9	0.715	4.93	1.13

TABLE 13

EFFECT OF CURE CYCLE ON TENSILE PROPERTIES OF 10° OFF-AXIS CELION 6000/IME COMPOSITES

Composite No.	Cure Cycle	Tensile Properties				Intralaminar Shear Properties				Composite Intralaminar Shear Strain to Failure, %
		Strength		Modulus		Strength		Modulus		
		ksi	MPa	10^6 psi	GPa	ksi	MPa	10^6 psi	GPa	
Control C-3	150°C/1 hr+177°C/3 hrs	38.3	264	14.9	103	6.55	45.1	0.92	6.34	1.21
	150°C/1 hr+177°C/2 hrs + 204°C/24 hrs	45.8	316	12.3	84.8	7.84	54.1	1.13	7.79	1.08
C-IME-9-3B	150°C/1 hr+177°C/3 hrs	52.6	363	12.2	84.1	8.99	62.0	1.15	7.93	1.73
	150°C/1 hr+177°C/2 hrs + 204°C/24 hrs	62.8	433	11.6	80.0	10.7	73.8	1.09	7.52	1.93
C-IME-10-3B	150°C/1 hr+177°C/3 hrs	41.2	284	13.1	90.3	7.05	48.6	1.15	7.93	0.89
	150°C/1 hr+177°C/2 hrs + 204°C/24 hrs	65.8	454	12.3	84.8	11.2	77.2	1.05	7.24	1.79
C-IME-18-4	150°C/1 hr+177°C/3 hrs	41.3	285	12.9	88.9	7.07	48.7	1.18	8.14	2.15
	150°C/1 hr+177°C/2 hrs + 204°C/24 hrs	56.2	388	10.5	72.4	9.61	66.3	0.99	6.82	1.71

TABLE 14

COMPARISON OF RESIN FRACTURE TOUGHNESS AND Tg WITH
10° OFF-AXIS CELION 6000/RESIN COMPOSITES

Resin Fracture Toughness			Composite 10° Off-Axis Properties			
IME Resin No.	Tg, °C	K_{IC} Pa$\sqrt{m}$	IME Composite No.	Tensile Strength ksi	(MPa)	Shear-Strain-to Failure %
IME-42	100	893	C-IME-40	70.1	483	4.58
IME-41	110	853	C-IME-44	67.5	466	4.28
IME-43	140	800	C-IME-42	49.9	344	4.82
IME-47	120	788	C-IME-41	57.9	399	3.73
IME-46	90	713	C-IME-43	48.3	333	3.57
IME-44	120	691	C-IME-46	45.7	315	4.32
IME-45	150	634	C-IME-9-3B	52.6	363	1.73
IME-40	170	630	C-IME-18-4	41.3	285	2.15
IME-18-4	150	597	C-IME-47	53.4	368	1.13
IME-9-3B	185	581	C-IME-45	35.1	242	1.13
IME-10-3B	180	480	C-IME-10-3B	41.2	284	0.89

FIG. 1

HPLC CHROMATOGRAM OF o·XYLENE

TIME, min ⟶
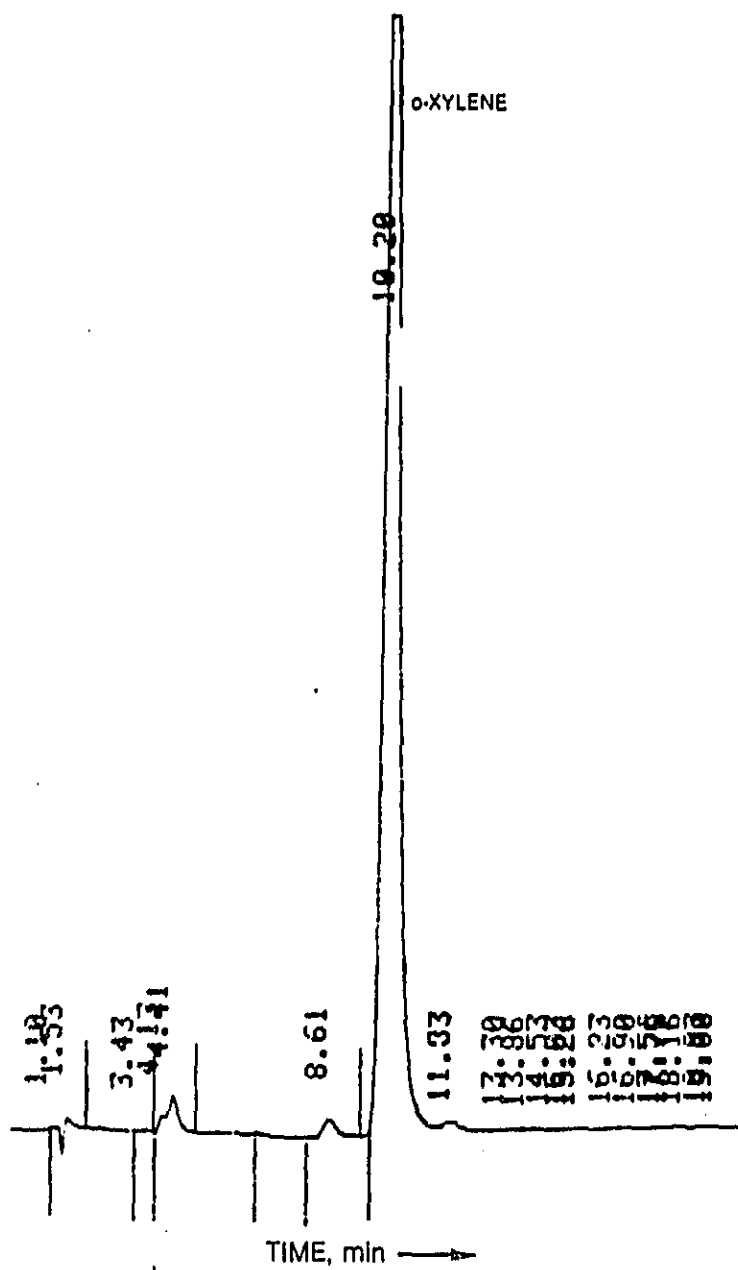
HPLC CHROMATOGRAM OF 1,1,1,3,3,3-HEXAFLUORO-2-(4-XYLYL)ISOPROPANOL (6F ALCOHOL)

TIME, min ⟶

FIG. 3
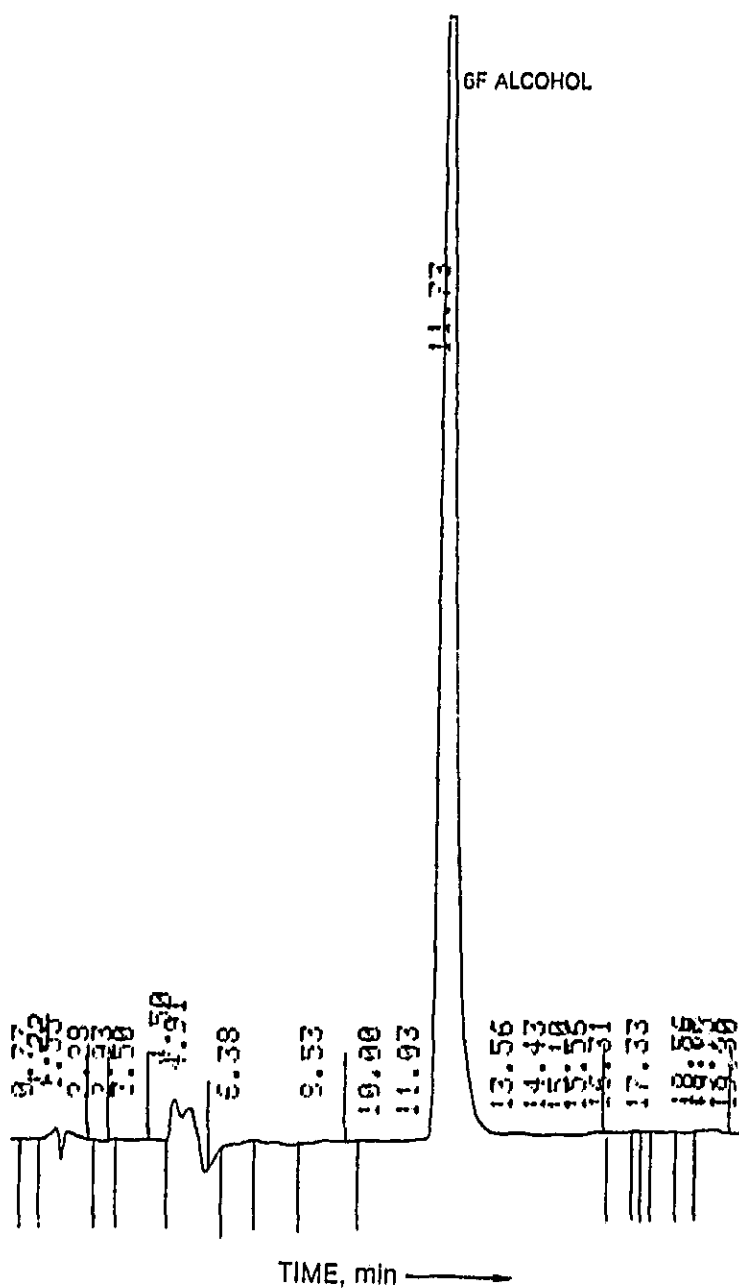
HPLC CHROMATOGRAM OF 4,4'-HEXAFLUOROISOPROPYLIDENE BIS(o-XYLENE)(6FHC)

6F HC HYDROCARBON

TIME, min ⟶
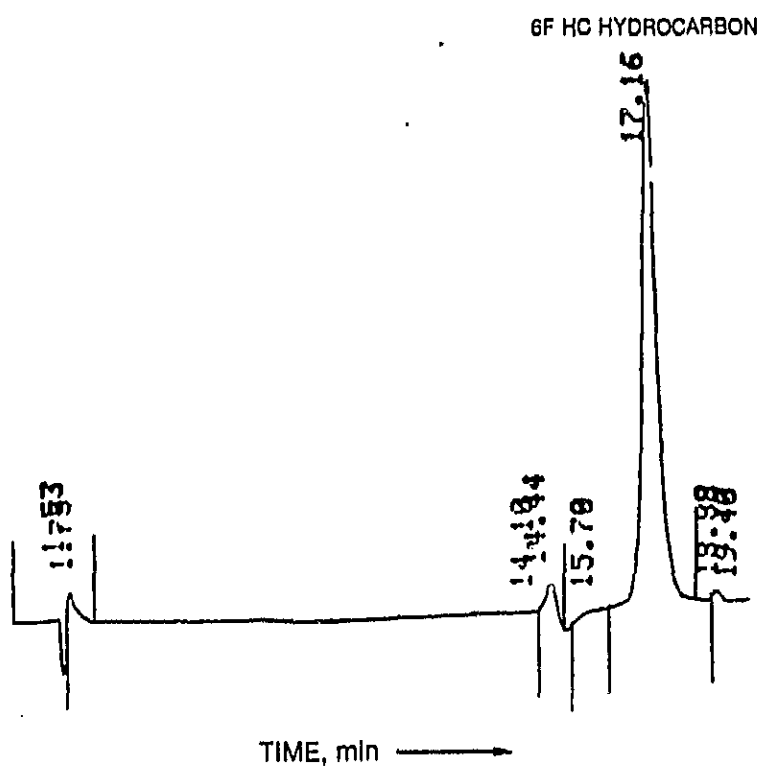
HPLC CHROMATOGRAM OF o-XYLENE, 6F ALCOHOL AND 6F HC MIXTURE

TIME, min ──────▶

FIG. 5
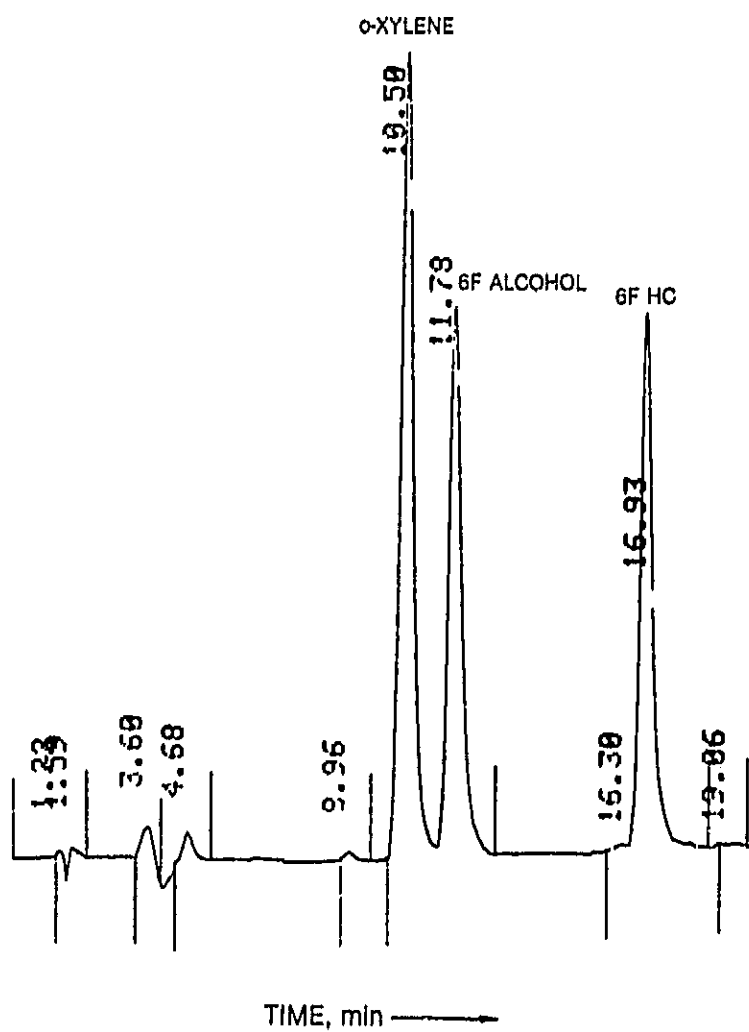
HPLC CHROMATOGRAM OF 6F-150-2 REACTION MIXTURE

TIME, min ⟶
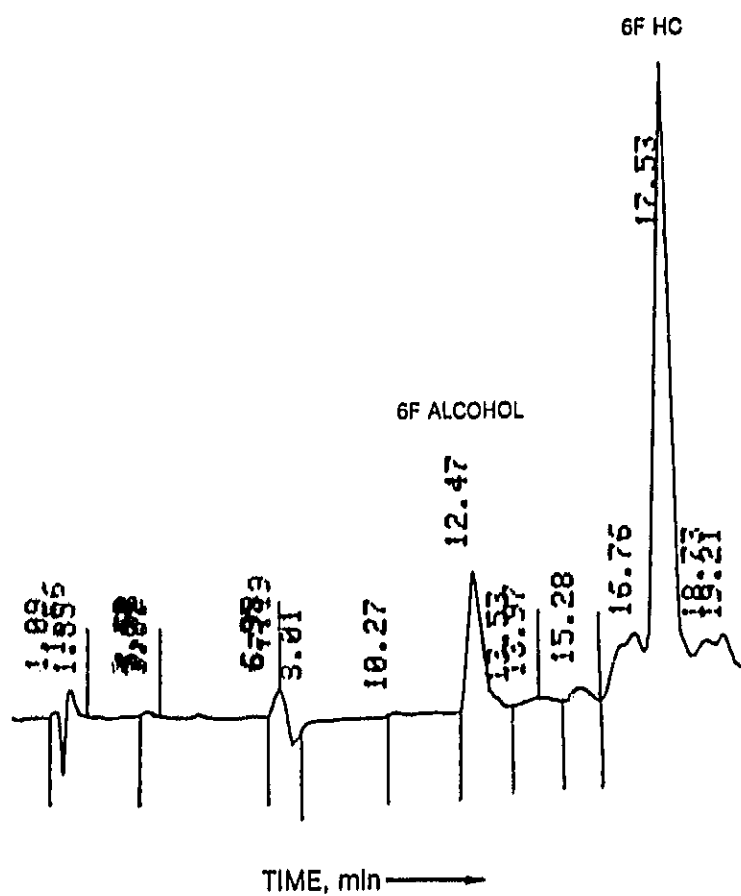
COMPACT TENSION SPECIMEN
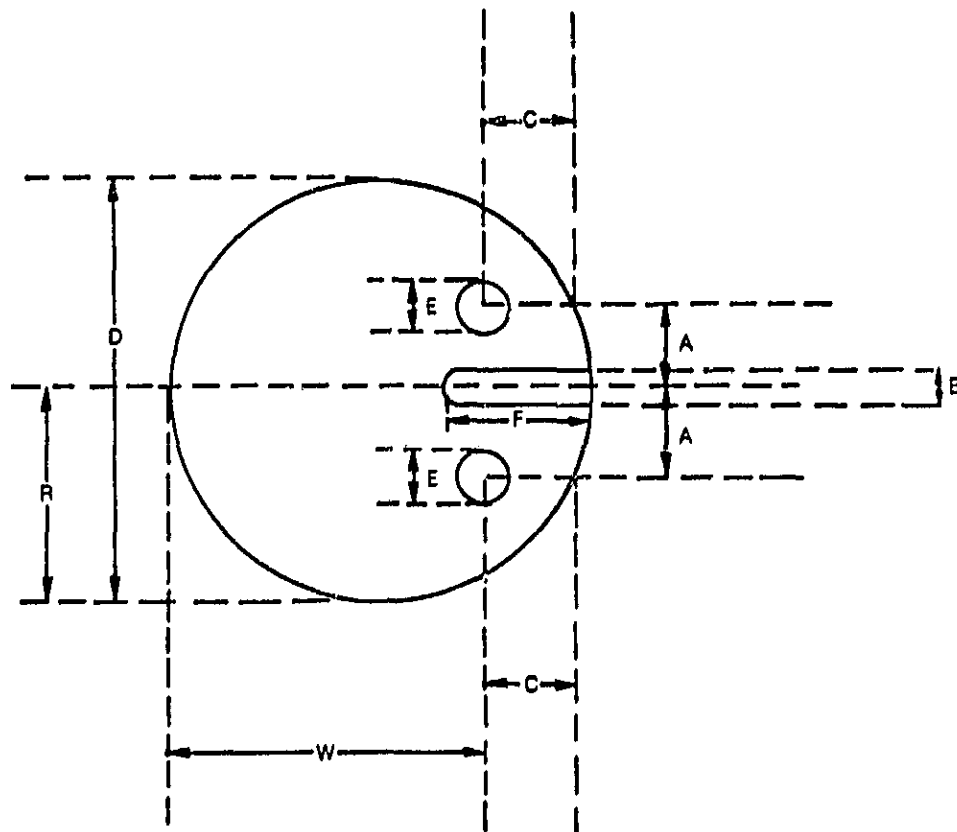
DIAMETER (D)	RADIUS (R)	W ($W = \frac{R}{0.675}$)	C (C = 0.275W)	A (A = 0.275W)	B	E	F (F = 1/9 D)
IN 2.00	1.000	1.48	0.41	0.41	0.125	0.25	0.66
cm 5.08	2.54	3.76	1.04	1.04	0.32	0.64	1.68

FIG. 7

DSC SCANS OF CURED EPOXY RESINS
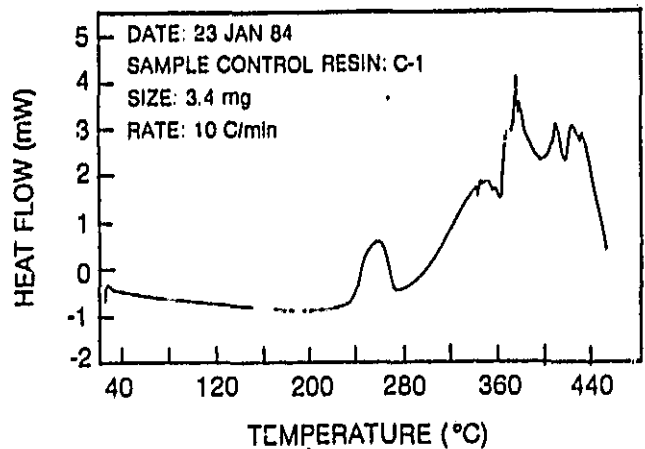
a) CONTROL RESIN C-1
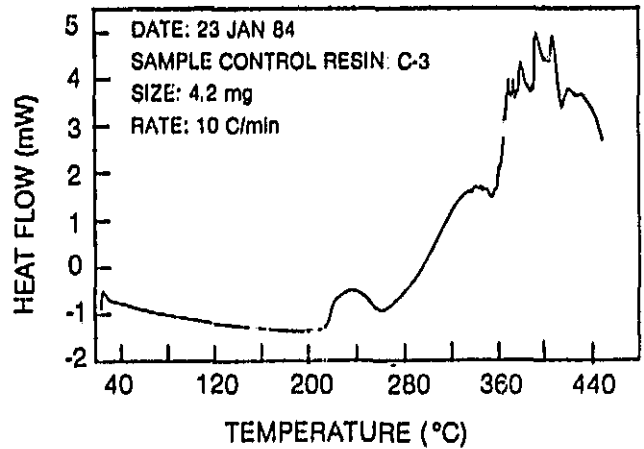
b) CONTROL RESIN C-3
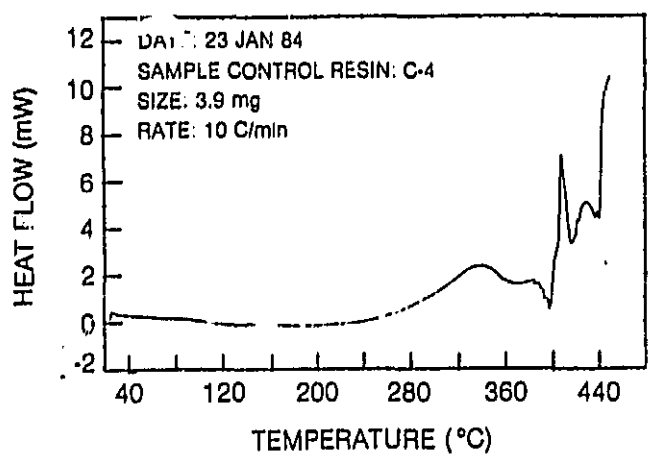
c) CONTROL RESIN C-4
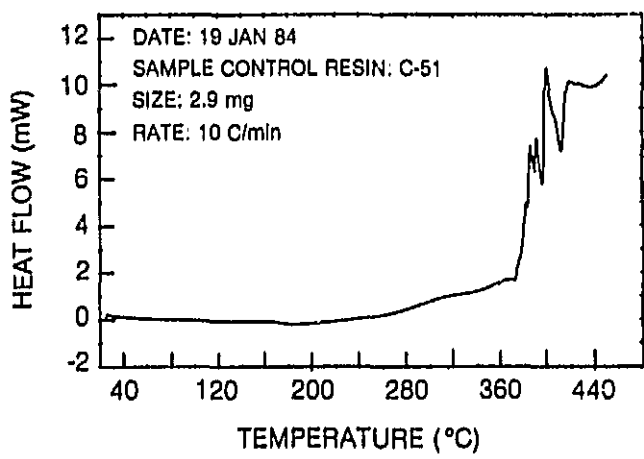
d) CONTROL RESIN C-51
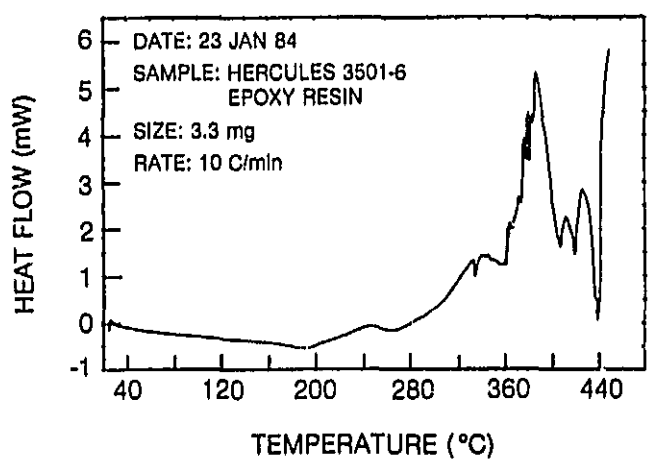
e) HERCULES 3501-6 EPOXY RESIN

DSC SCANS OF CURED IME RESINS
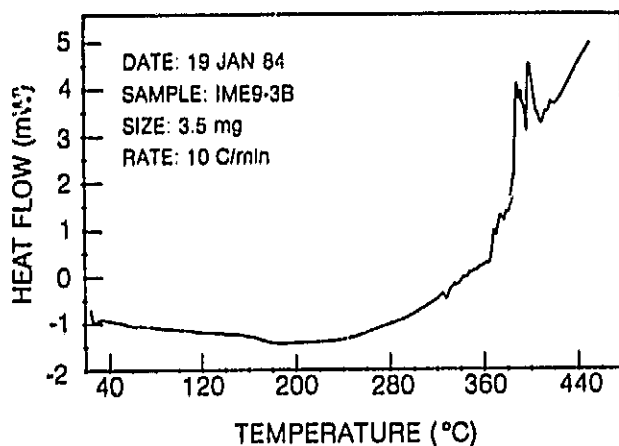
a) IME9-3B
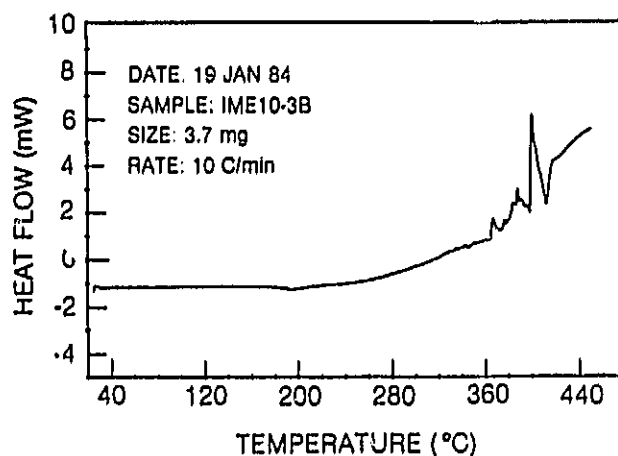
b) IME10-3B
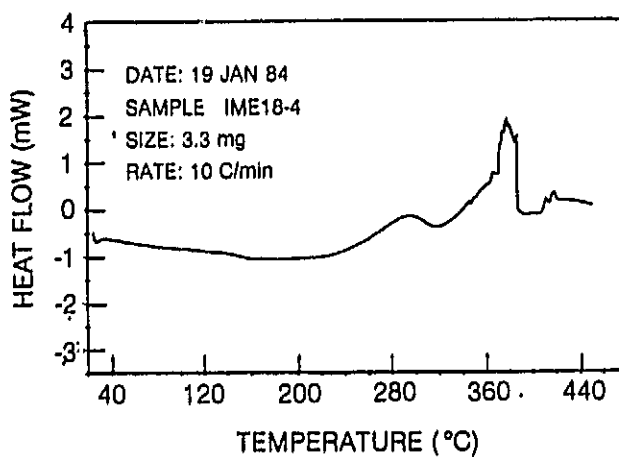
c) IME18-4
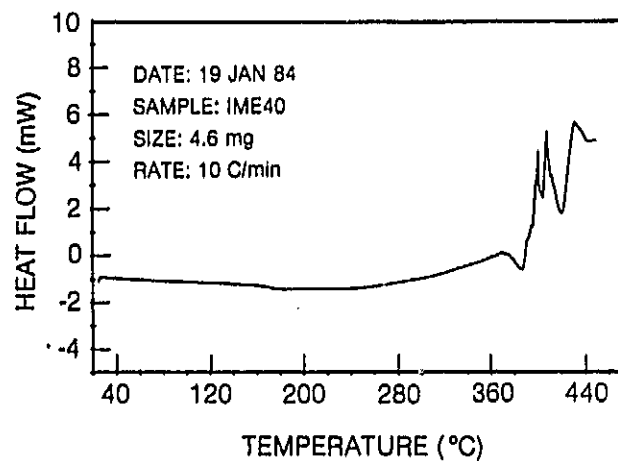
d) IME-40

DSC SCANS OF CURED IME RESINS

a) IME-41

b) IME-42

c) IME-43

d) IME-44

FIG. 10
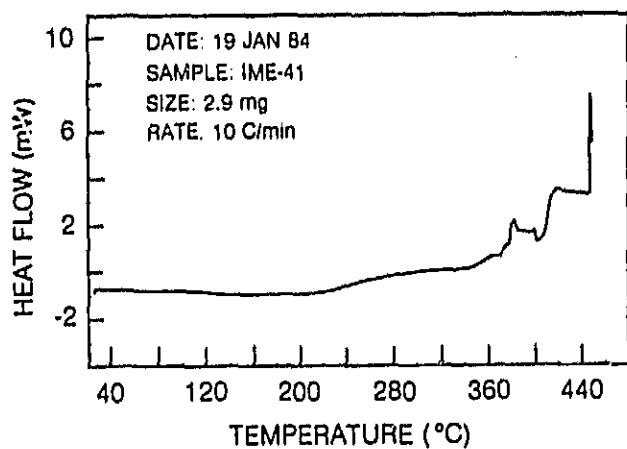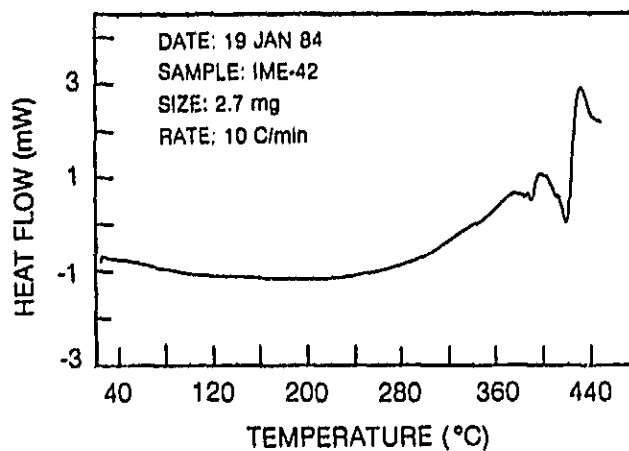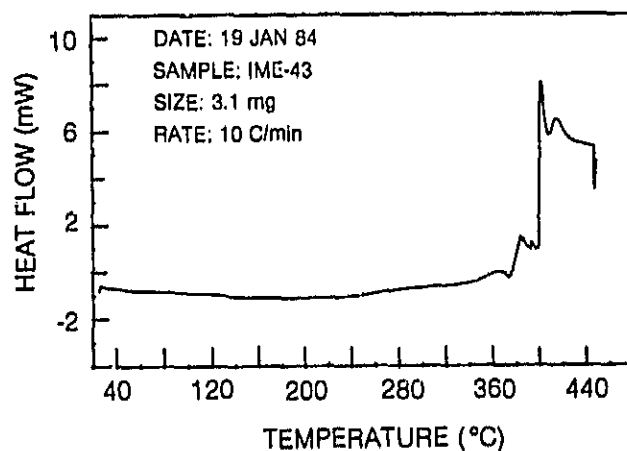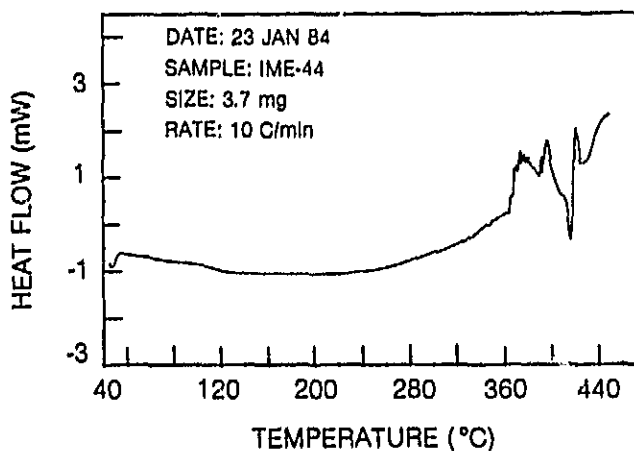
DSC SCANS OF CURED IME RESINS
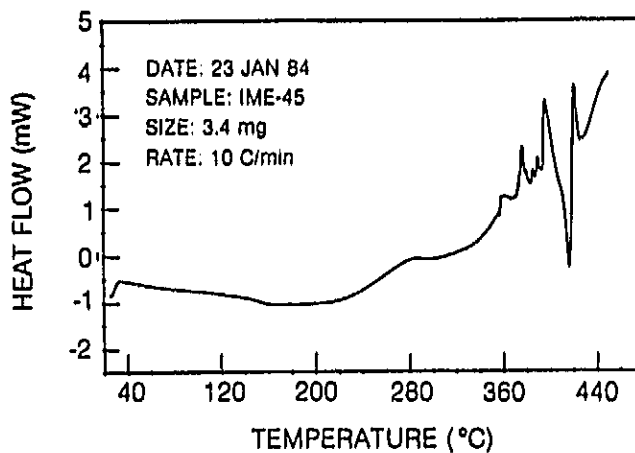
a) IME-45
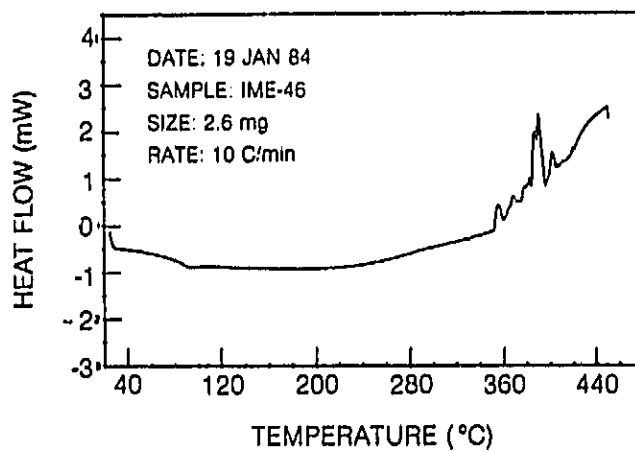
b) IME-46
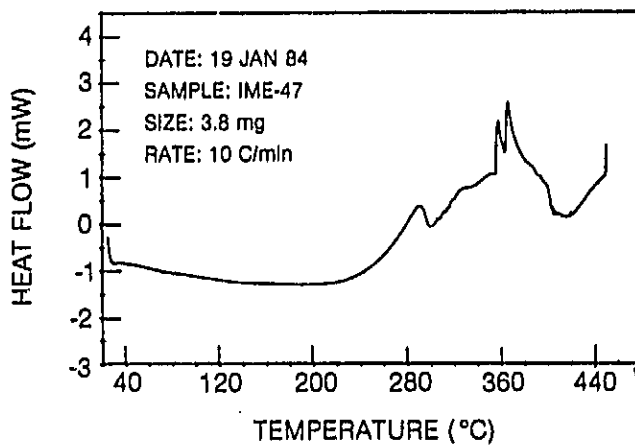
c) IME-47

THERMOGRAVIMETRIC ANALYSIS (TGA) OF CURED EPOXY RESINS

NITROGEN ATMOSPHERE
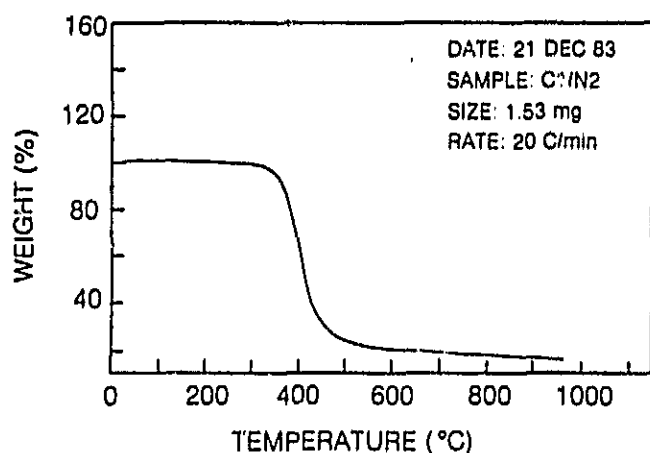
a) CONTROL C-1
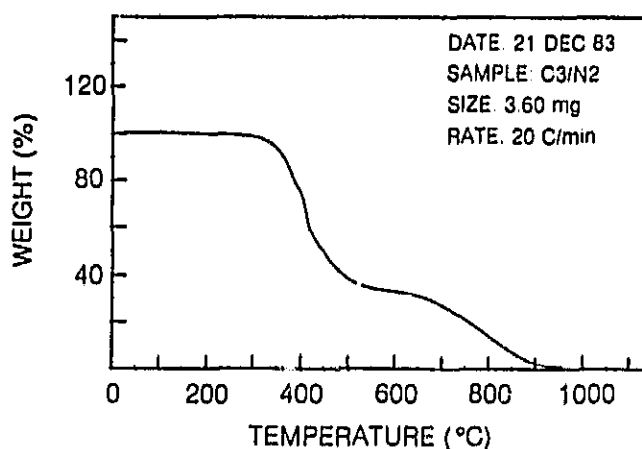
b) CONTROL C-3
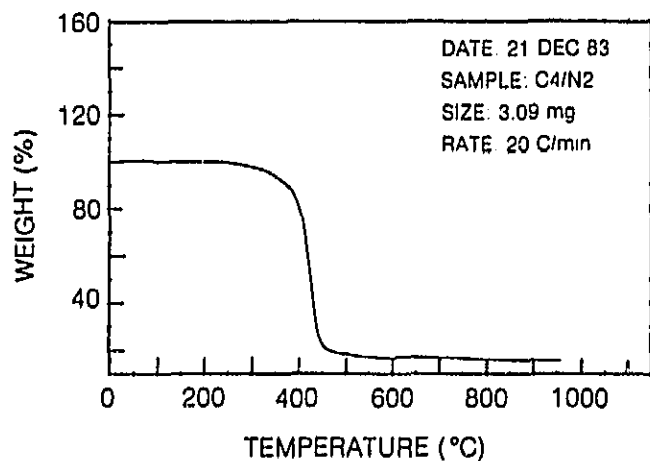
c) CONTROL C-4
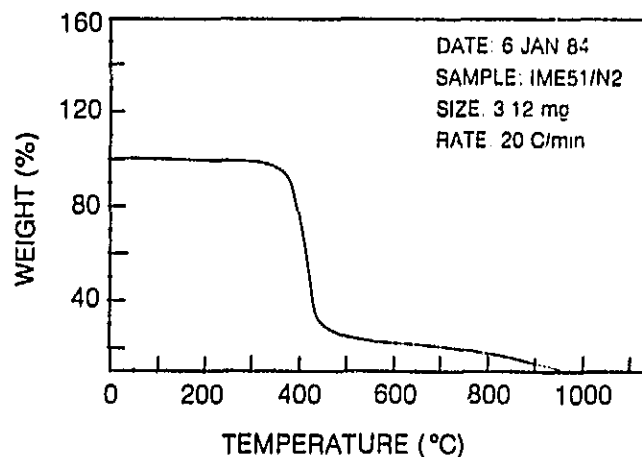
d) CONTROL C-51
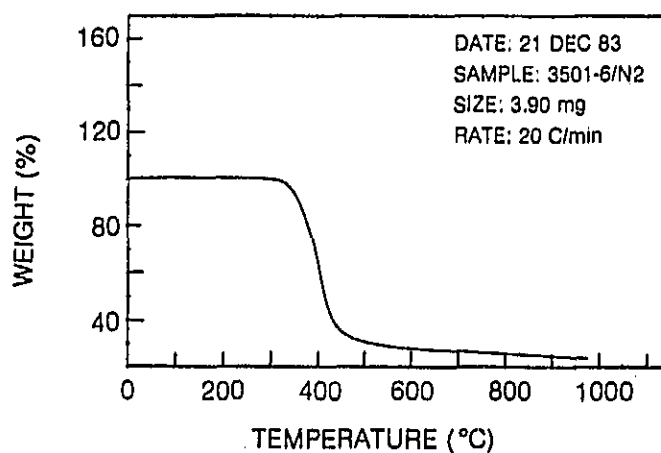
e) HERCULES 3501-6 EPOXY

FIG. 12

THERMOGRAVIMETRIC ANALYSIS (TGA) OF CURED IME RESINS

NITROGEN ATMOSPHERE

DATE: 3 JAN 84
SAMPLE: IME9-3B/N2
SIZE: 2.18 mg
RATE: 20 C/min

a) IME-9-3B

DATE: 23 DEC 83
SAMPLE: IME10-3B/N2
SIZE: 2.54 mg
RATE: 20 C/min

b) IME-10-3B

DATE: 9 JAN 84
SAMPLE: IME18-4/N2
SIZE: 1.66 mg
RATE: 20 C/min

c) IME-18-4

DATE: 3 JAN 84
SAMPLE: IME40/N2
SIZE: 1.18 mg
RATE: 20 C/min

d) IME-40

FIG. 13
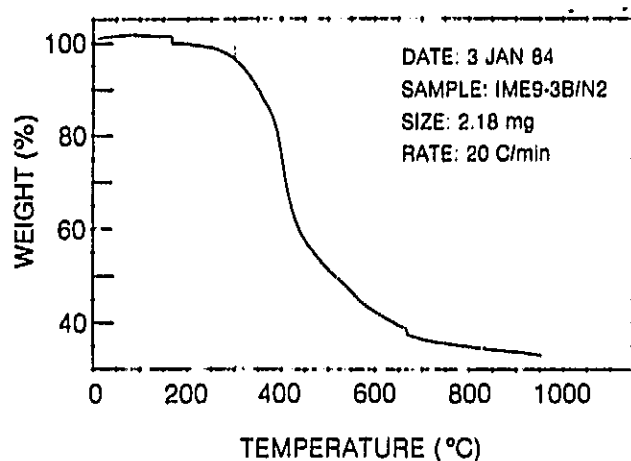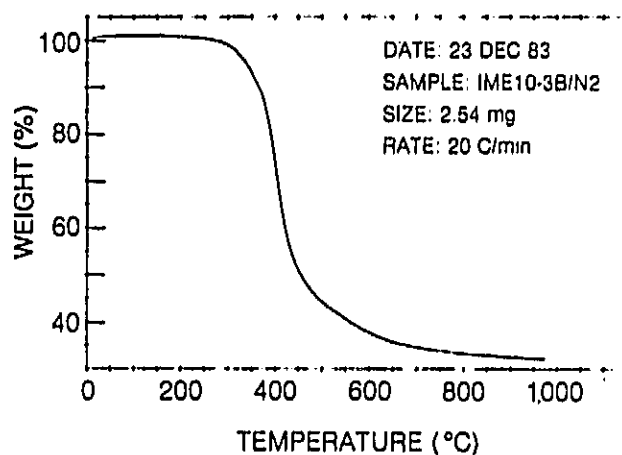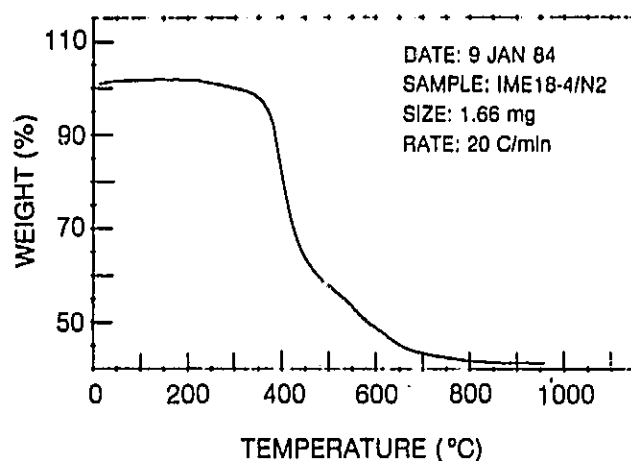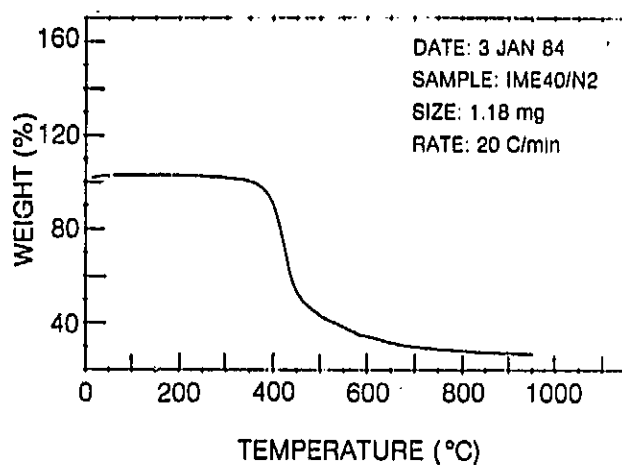
THERMOGRAVIMETRIC ANALYSIS (TGA) OF CURED IME RESINS

NITROGEN ATMOSPHERE

a) IME-41

b) IME-42
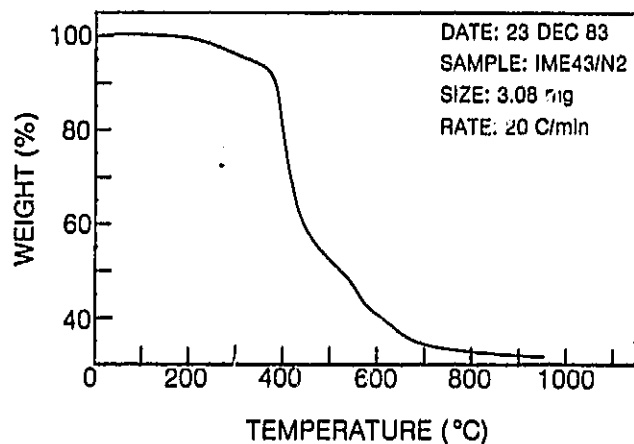
c) IME-43
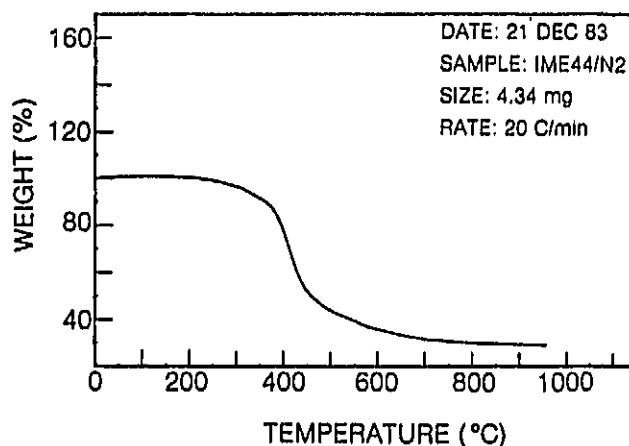
d) IME-44

THERMOGRAVIMETRIC ANALYSIS (TGA) OF CURED IME RESINS

NITROGEN ATMOSPHERE

a) IME-45

b) IME-46

c) IME-47

FIG. 15
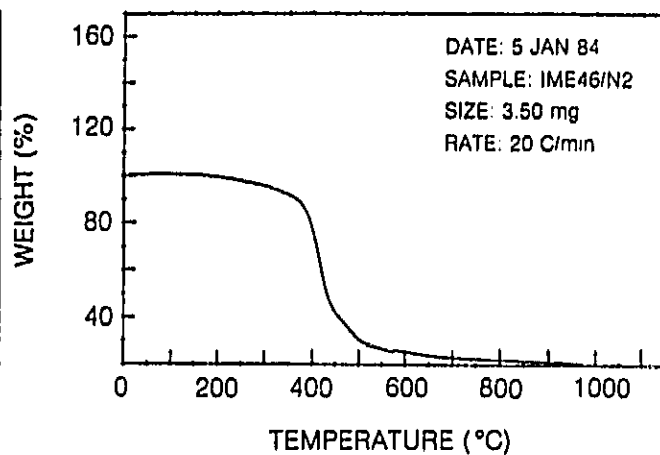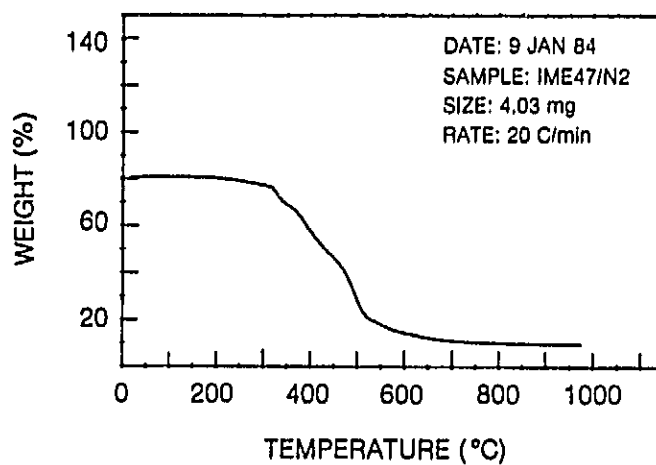
THERMOMECHANICAL ANALYSIS (TMA) OF CURED EPOXY RESINS

DATE: 23 NOV 83
SAMPLE: C1
SIZE: 6.10 mm
RATE: 5 C/min

a) CONTROL RESIN C-1

DATE: 23 NOV 83
SAMPLE: C3
SIZE: 3 73 mm
RATE: 5 C/min

b) CONTROL RESIN C-3

DATE: 2ᵗ NOV 83
SAMPLE: C4
SIZE: 5.88 mm
RATE: 5 C/min

c) CONTROL RESIN C-4

DATE: 11 NOV 83
SAMPLE: IME-51
SIZE: 2.05 mm
RATE: 5 C/min

d) CONTROL RESIN C-51

DATE: 26 NOV 83
SAMPLE: 3501-6
SIZE: 3.47 mg
RATE: 5 C/min

e) HERCULES 3501-6 EPOXY

FIG. 16

THERMOMECHANICAL ANALYSIS (TMA) OF CURED IME RESINS

a) IME-9-3B

b) IME-10-3B

c) IME-18-4

d) IME-40

THERMOMECHANICAL ANALYSIS (TMA) OF CURED IME RESINS

a) IME-41

b) IME-42

c) IME-43

d) IME-44

FIG. 18

THERMOMECHANICAL ANALYSIS (TMA) OF CURED IME RESINS

DATE: 11 NOV 83
SAMPLE: IME-45
SIZE: 2.76 mm
RATE: 5 C/min

a) IME-45

DATE: 11 NOV 83
SAMPLE: IME-46
SIZE: 3.10 mm
RATE: 5 C/min

b) IME-46

DATE: 11 NOV 83
SAMPLE: IME-47
SIZE: 3.24 mm
RATE: 5 C/min

c) IME-47

FRACTURE TOUGHNESS OF BISIMIDE AMINE CURED EPOXY
AND CONTROL EPOXY RESINS VS Tg

FIG. 20
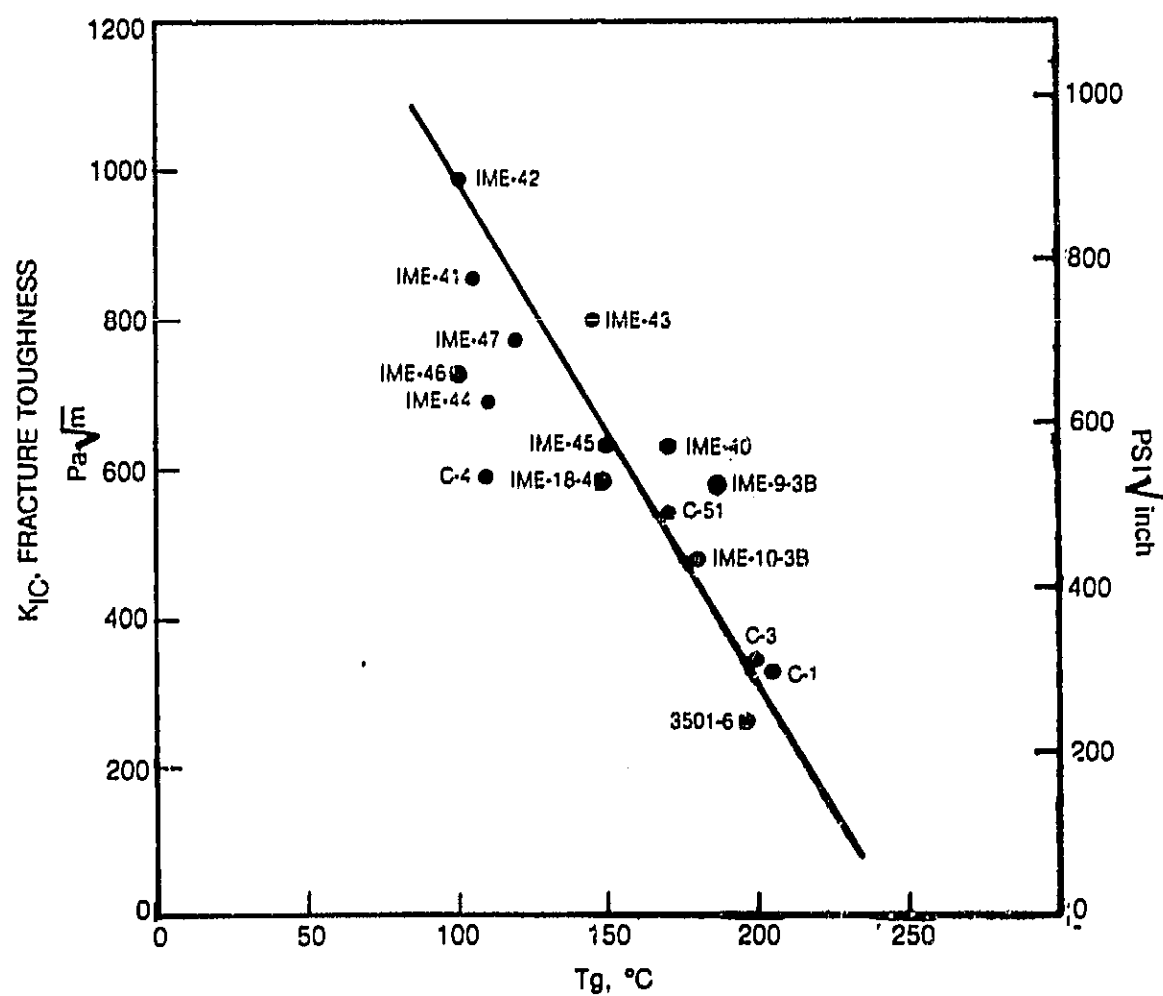
SHEAR STRESS-STRAIN CURVES OF 10°-OFF AXIS CELION 6000/EPOXY RESIN COMPOSITES
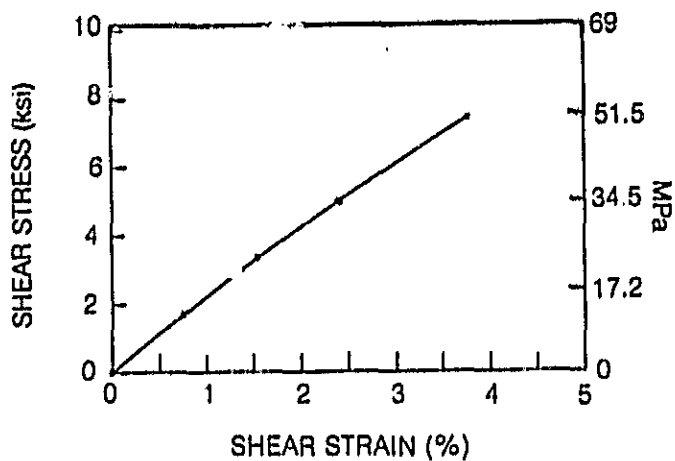
a) COMPOSITE C-1
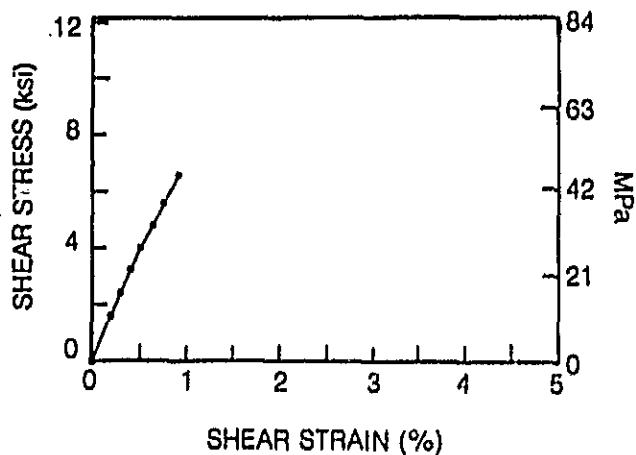
b) COMPOSITE C-3
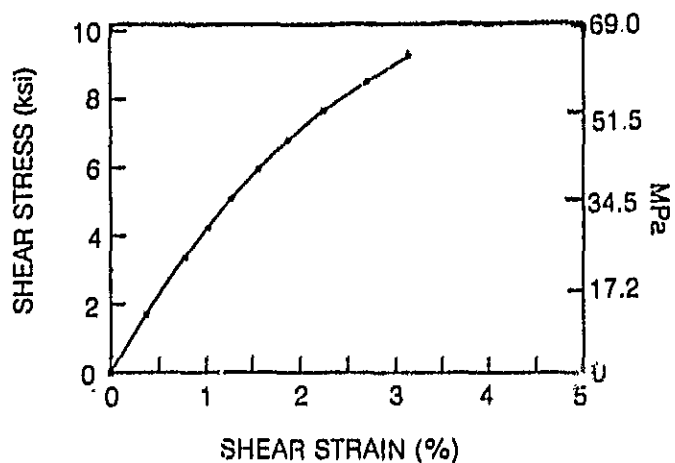
c) COMPOSITE C-4
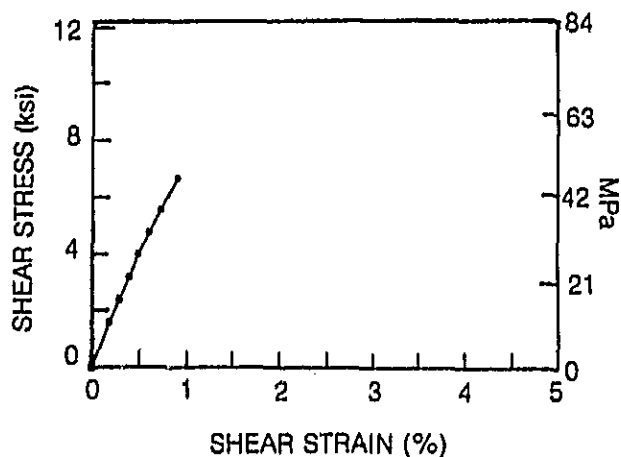
d) COMPOSITE C-51
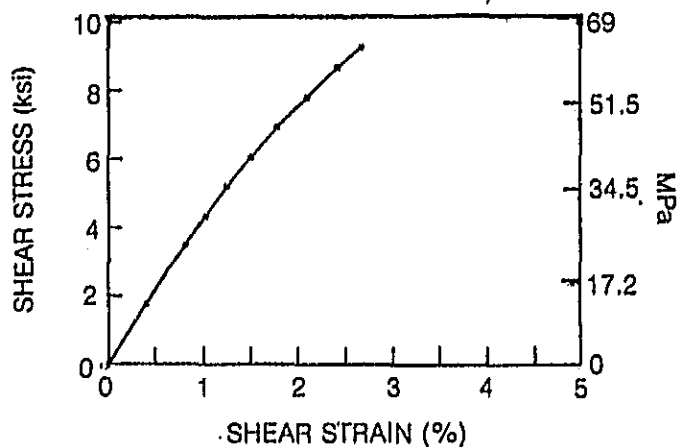
e) COMPOSITE 3501-6

FIG. 21

SHEAR STRESS-STRAIN CURVES OF 10°-OFF AXIS
CELION 6000/EPOXY RESIN COMPOSITES
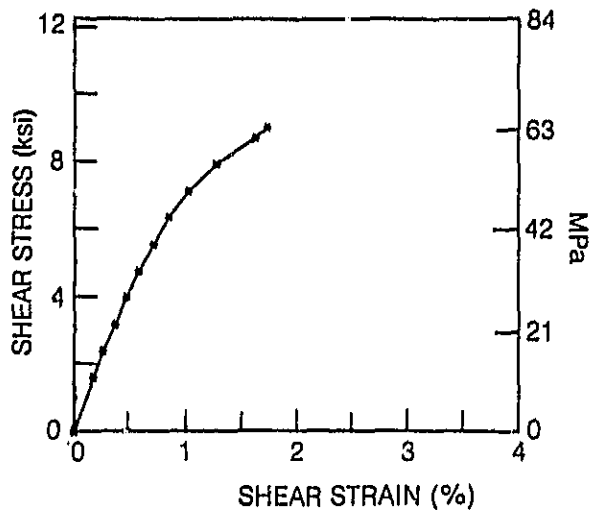
a) C-IME-9-3B
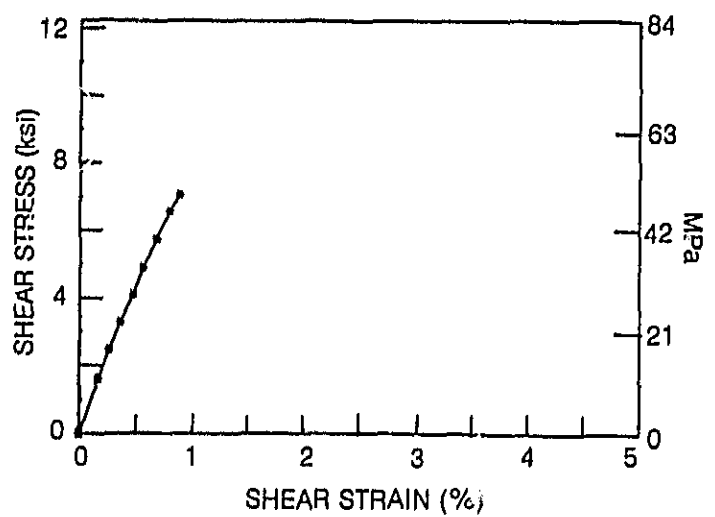
b) C-IME-10-3B
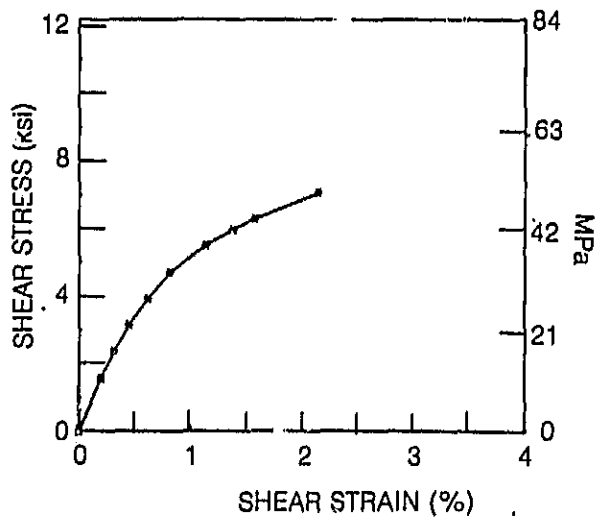
c) C-IME-18-4
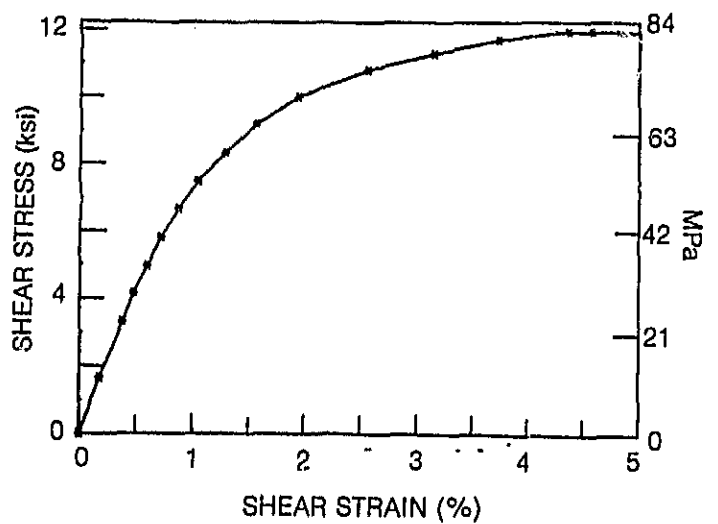
d) C-IME-40

SHEAR STRESS-STRAIN CURVES OF 10°-OFF AXIS CELION 6000/IME RESIN COMPOSITES
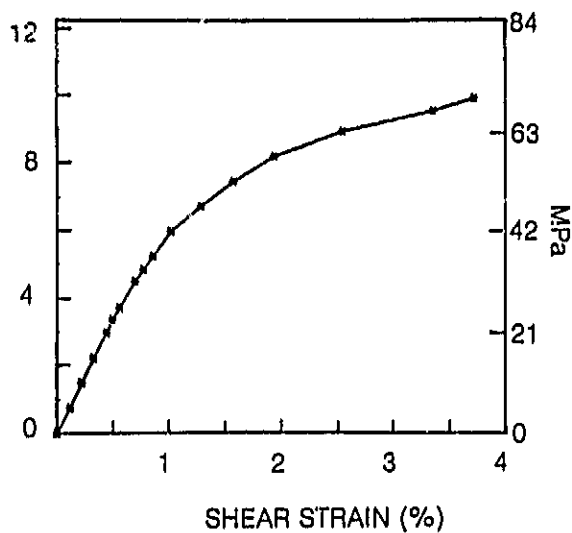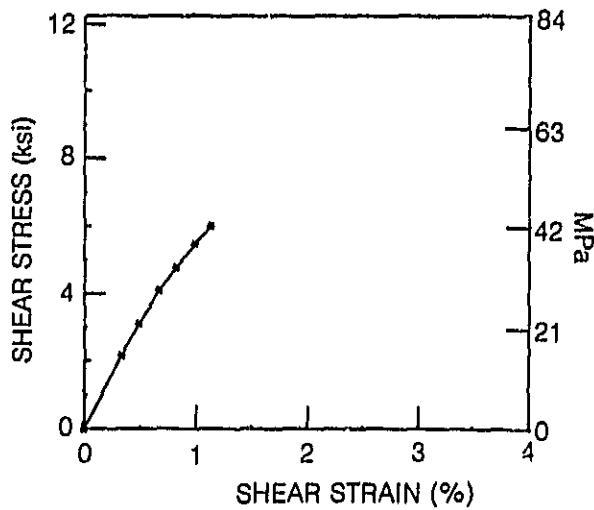

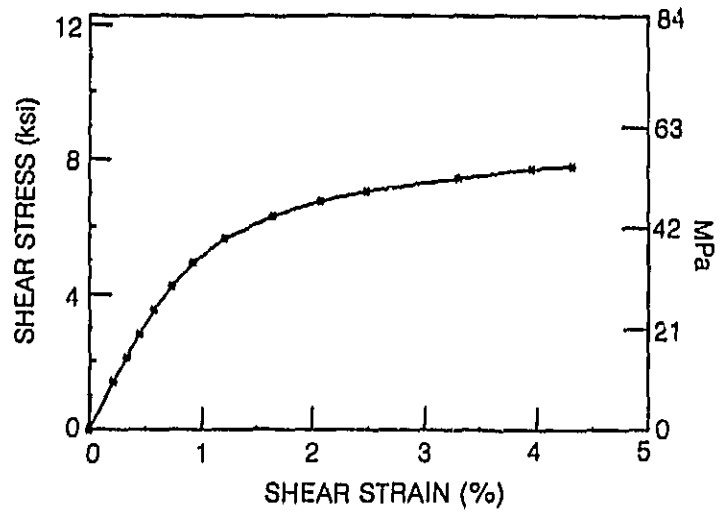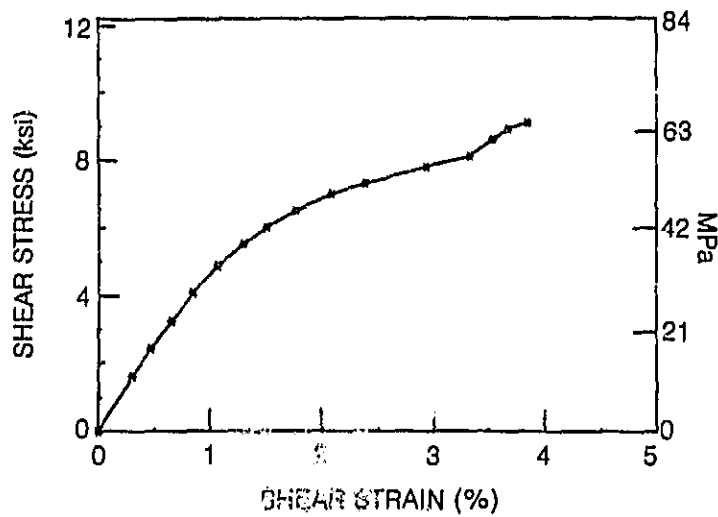a) C-IME-41-2
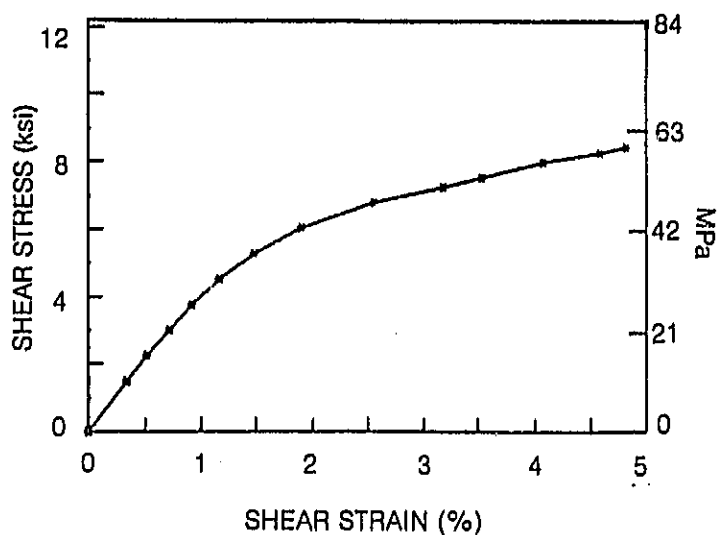
b) C-IME-42
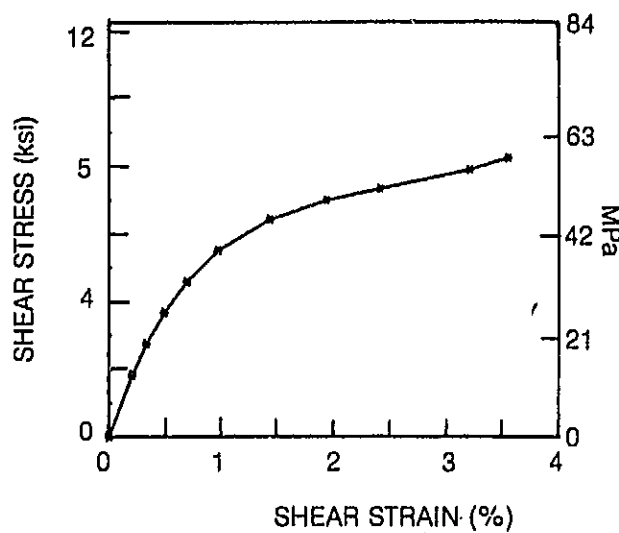
c) C-IME-43-2
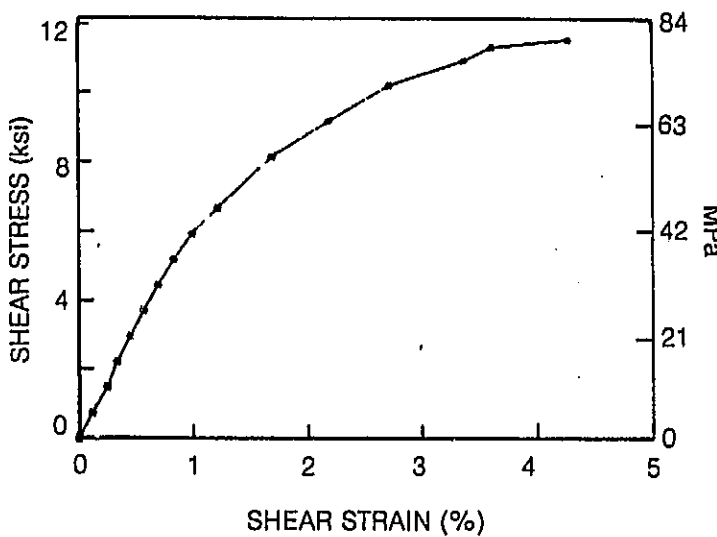
d) C-IME-44

FIG. 23

SHEAR STRESS-STRAIN CURVES OF 10°-OFF AXIS
CELION 6000/EPOXY RESIN COMPOSITES

a) C-IME-45

b) C-IME-46

c) C-IME-47

10° DEGREE OFF-AXIS TENSILE SHEAR STRESS-STRAIN CURVES FOR CELION 6000/IME COMPOSITES