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Styrene-Terminated Polysulfone Oligomers as Matrix Material for Graphite Reinforced Composites—An Initial Study

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STYRENE-TERMINATED POLYSULFONE OLIGOMERS AS MATRIX MATERIAL FOR GRAPHITE REINFORCED COMPOSITES - AN INITIAL STUDY

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SUMMARY

Styrene-terminated polysulfone oligomers are part of an oligomeric class of compounds with end groups capable of thermal polymerization. These materials can be used as matrices for graphite reinforced composites. This report summarizes our initial evaluation of styrene-terminated polysulfone oligomer based composites in terms of fabrication methods, and mechanical and environmental properties. In addition the report also provides a description and evaluation of the NASA/Industry Fellowship Program for Technology Transfer.

INTRODUCTION

NASA/Industry Fellowship for Technology Transfer

The NASA/Industry Fellowship Program was set up by NASA to enhance the transfer of aerospace-related technology to industry. The program provides for the assignment of industry personnel to work at the NASA Lewis Research Center on a part-time basis for an initial period of 1 yr.

In the context of the above general statement the program that NASA and the BF Goodrich Company agreed upon was focused on the study of BF Goodrich proprietary resins as matrix materials for advanced structural composites containing graphite fibers as reinforcement.

Project definition. - The general aim of the NASA/Industry Fellowship program will be to explore the applicability of reactive oligomers, with varying structure and reactive end groups, as a matrix material for advanced composites. Examples of reactive oligomers are bismaleimides, PMR 15, and styrene-terminated sulfones and aryl ethers. Additional matrix materials may include thermoplastics such as polyimides. The fiber material to be incorporated in such a composite will mainly be graphite fibers. An integral part of the program will be understanding and developing composite test methods as well as establishing structure/property relationships.

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*NASA/Industry Fellow.

The program will be divided into three stages. The first will be the preparation of good quality composite samples. The collaboration with NASA Lewis should be invaluable at this stage. Once the composite samples have been prepared, the second stage will involve testing of the mechanical, thermal, and environmental properties. During both these stages we will be making use of NASA's know-how, manufacturing facility, and test equipment. Mechanical properties to be evaluated will include tensile, flexural, impact strength, and fatigue resistance. The role of matrix, fiber, fiber/matrix adhesion, and the effect of thermal stresses during the fabrication stage will be examined in order to best be able to appropriately modify the composite properties. The thermal and environmental properties of the composite will involve determining the effect of the fiber and any incorporated additive.

The program will also involve participation in NASA's ongoing research in the area of composites.

The NASA Lewis Mentor is Dr. Tito T. Serafini

Project status. - To date the project has concentrated on the processing and properties of styrene-terminated polysulfone oligomers as matrix material for graphite reinforced composites. The results are summarized in this report. In addition, a parallel study of the curing chemistry of PMR-15 was also undertaken. The results of this study are summarized in a recently submitted publication.[1]

Total time spent at NASA during the fellowship year has been 45 days.

Additional program elements. - As an integral part of this program, NASA Lewis personnel visited the BF Goodrich Research Center in Brecksville to present talks and help in the evaluation of composite related technology. Simultaneously the Industry Fellow is exposed to technology outside the immediate group where the research is being carried out via NASA internal presentations and technical reports.

Program evaluation. - The NASA/Industry Fellowship for Technology Transfer is an excellent vehicle for efficient transfer of technology developed by NASA to private industry. The results of such a program are both immediate and long term.

In the case of the program as outlined in the project definition section the immediate benefits encompassed transfer of knowledge of composite processing and property evaluations in terms of hands-on experience and equipment. The knowledge gained has proved invaluable in helping set up a composite research facilities at the BF Goodrich Research Center in Brecksville. Long term, the benefits of the program translate into future contacts and informational exchange. Such activities will permit continued transfer of technology from NASA to BF Goodrich.

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[1] Dana Garcia and Tito T. Serafini "FT-IR of PMR-15 Polyimides," J. Polym. Sci. Polym. Phys. Ed., submitted

Technical Introduction

In recent years, (refs. 1 and 2) the synthesis, curing mechanism and kinetics, as well as the properties of a number of oligomers end-capped by groups capable of thermally induced polymerization, have been investigated as a means to achieve polymers with improved high service temperature and solvent resistance.

A class of compounds falling in this category are acetylene-terminated arylsulfone oligomers (refs. 1 to 15). The advantage of these compounds, over the high molecular weight, linear polysulfone resin, lie in their easier processing (ref. 1) and improved solvent resistance (ref. 14). Nevertheless, a number of problems still plague these systems. They include network structures dependent on the cure pathway, (refs. 9 and 11) as well as the required high temperature (ref. 15) and long cure cycles necessary to achieve complete exhaustion of all reactive groups. In spite of these problems, these materials have received significant attention (refs. 3 to 15) as potential matrix material for fiber reinforced composite applications.

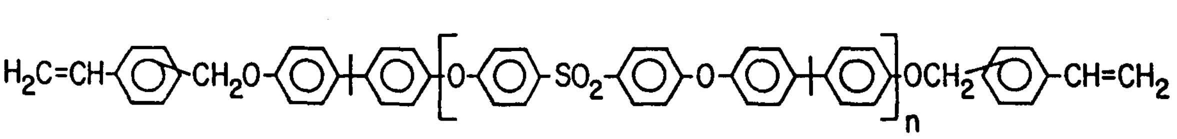
An alternative approach to thermally crosslinkable polysulfone oligomers is to replace the acetylene groups with styrene groups. In a previous publication (ref. 16) we have already outlined our studies on the curing kinetics and properties of these materials.

This report summarized our results on graphite reinforced composites containing styrene-terminated oligomers as the matrix material. The focus of the work was to determine the processing parameters and evaluate the properties of the resulting composite.

EXPERIMENTAL

Materials

<u>Resin</u>. - The resin used is an oligomer of polysulfone with thermally reactive styrene end groups. The general structure of the oligomer is shown below.



The details of the synthesis and properties of these oligomers as well as the resulting crosslinked resin can be found in reference 5.

<u>Graphite fiber reinforcement</u>. - The graphite fiber used in this investigation is a PAN (Poly-acrylonitrile) based high strength fiber marketed by the Celanese Company under the name of Celion 6000. The typical fiber properties are shown in table I.

<u>Prepregging solvents</u>. - Four solvents were employed to dissolve the oligomers. They are shown in table II.

Composite Fabrication

Unidirectional prepreg plies were obtained in the following manner: Dry Celion 6000 graphite fibers were wound onto a 15 in. diameter by 18 in. long cylindrical mandrel covered with a silicone coated release paper. The fibers were wound at a spacing of 12 turns/in. The resin was applied from solution and evenly distributed over the entire mandrel surface. The concentration of resin in solution was of the order of 30 percent and the amount of resin used was calculated to roughly produce a 60 vol % fiber laminate. The prepreg was allowed to dry on the mandrel until most of the solvent evaporated. Further drying was done in a vacuum oven at temperatures from 23 to 50 °C. Cut samples were stored in N_2 purged bag in vacuum desiccators.

All composite laminate test samples were made by compression molding in matched metal die molds. Typical laminate processing parameters are listed in table III.

Composite Characterization

Resin content. - The resin content for all composite samples was determined via two methods: Acid Digestion and Density. Three determinations were done for each composition.

Acid Digestion

Approximately 0.25 g of composite sample was weighed in 100 mL beaker and 50 mL concentrated sulfuric acid added. The mixture was heated on a hot plate to 100 to 120 °C with frequent stirring. The mixture became black in color. After approximately 4.5 hr the mixture was cooled to 60 to 70 °C and 2 mL of 30 percent H_2O_2 was added. The mixture was then reheated to 110 to 120 °C for an additional hour. At the end of this period the solution was colorless and white fumes were slowly evolving. The cooled mixture was filtered and the fibers washed several times with distilled water until a neutral pH was obtained. The washed fibers were dried at 175 °C in an air circulating oven and subsequently weighed. Three specimens were analyzed from each composite sample in this fashion. Control runs containing only Celion 6000 graphite fibers were simultaneously run to determine if this treatment had any effect on the fibers. None was observed. The volume fraction of fibers was calculated according to equation 1.

$$V_{ff} = \frac{\rho_f W_{ff}}{\rho_f W_{ff} + \rho_r W_{fr}} \tag{1}$$

where

V_{ff} volume fraction of fibers
W_{ff} weight fraction of fibers
W_{fr} weight fraction of resin
ρ_f density of fiber
ρ_r density of resin

Density

The density of the composite samples was determined according to ASTM D792-66. The volume fraction of fibers was calculated according to equation (2).

$$V_{ff} = \frac{(\rho - V_{fr}\rho_r)}{\rho_f} \tag{2}$$

Where ρ = the density of the composite; all other terms are the same as for equation (1).

Void Content

The void content is determined using equation 3.

$$V_v = 1 - \frac{\dfrac{W_f}{\rho_f} + \dfrac{W_c - W_f}{\rho_r}}{\dfrac{W_c}{\rho}} \tag{3}$$

where

V_v volume fraction of voids
W_f fiber weight
W_c composite weight

Glass transition temperature (Tg). - The Tg of the resin in the composite was determined by DSC on a Perkin Elmer DSC-7. A survey of all available methods to determine Tgs was made. The DSC was determined as being the most reliable, fastest, and accurate method: All runs were performed at a scan rate of 40 °C/min.

Thermal expansion coefficient. - The thermal expansion coefficient in both the parallel and perpendicular fiber direction were determined on a DuPont Thermal Analyzer.

The thermal expansion coefficient was calculated over the linear portion of the curve below the Tg.

Thermal stability. - The amount of weight loss as a function of temperature was determined using a Cahn TGA. The method was mostly employed to determine the amount of moisture absorbed by the sample and residual amounts of solvent.

Dynamic mechanical properties. - The dynamic mechanical properties of the composite samples were determined on a Rheometrics 770 RMS at a frequency of 10 rad/sec over a 450 °C range (-150 to 300 °C). The sample configuration was that of a torsional strip with dimensions of 2.0 by 0.50 by 0.06 in.

Flexural and short beam shear testing. - The bending modulus and flexural strength were determined in a three point bend test fixture according to ASTM D790-71. The span was set at either 2.0 or 2.1 in. The other sample dimensions were 0.25 by 0.06 in. In the case of elevated temperature measurements the samples were equilibrated at the desired temperature for 10 min. This procedure was not followed in the case of humidity aged samples where the testing was conducted with minimal temperature equilibration in order to prevent sample dry out.

The short beam shear test is designed to measure the interlaminar shear strength of the composite (σILS). σILS is calculated according to equation (4).

$$\sigma \mathrm{ILS} = \frac{3P}{4bh} \tag{4}$$

where P is the load; h the depth and b the width of the sample.

The test is run according to ASTM D2344-76 in a three point bending configuration for a span to depth ratio of 4:1. The above calculation applies to samples which have failed in shear. The short beam shear results to be presented in the next section will specify the type of failure. If the sample did not fail in shear the data will be reported in terms of the maximum strength (σ) achieved through the linear portion of the stress/strain curve.

Elevated temperature measurements were run after equilibrating the sample at the desired temperature for 10 min. Similar to the flexural runs humidity aged samples were testing with only minimal temperature equilibration to prevent sample dryout.

In all cases three samples were tested at each temperature.

Tensile testing. - The tensile tests were performed according to ASTM D3039-76. The sample dimensions were 10 by 0.5 by 0.035 in. The test length was 6 in. with fiberglass reinforced end tabs bonded in place. The strains were measured by mean of four strain gauges bonded two to each side.

During the course of the experiments we observed that final specimen fracture did not occur in the test region as desired but was initiated near the tabs and proceeded via delamination in the longitudinal direction. As a result the final composite strength values are probably under-estimated.

Four samples were tested via this procedure.

Drop weight impact testing. - The drop weight impact testing was carried out using a Dynatup Falling Weight Impact Tester (ref. 7). The test provides the applied load and energy absorption as a function of time and specimen deflection during impact. The impactor was 0.5 in. diameter cylinder with a spherical end and weighted 179 lb. The impactor is fitted with strain gauges which measure the load during the time of the run. The impacting energy is varied by changing the height from which the impactor is dropped and its weight.

The composite samples had dimensions of 4 by 4 in. by approximately 0.1 in. and were 15 plies in a 0/90° fiber orientation sequence. The impactor was dropped from a height of 1 ft. and achieved a velocity of approximately 8 ft/sec. Detailed of the instrumental set-up and calculations can be found in reference 7. Five samples of identical composition were impacted.

Following impact the samples were examined by C-scanning to determine the extent of damage. The damage area was determined by planimetry integration of the C-scanning photographs.

10° Off-axis tensile testing. - The 10° off axis tensile test is designed to measure the shear properties of the composite (ref. 7). Unidirection composite samples with the fibers oriented at 10° to the axis of the applied load are tested using a standard tensile set-up. The samples have dimensions of 0.5 by 8.0 by 0.12 in. and consist of approximately 15 to 18 plies. The ends are reinforced with fiberglass tabs and 60° strain gauge rosettes are bonded to each side of the specimen. The test results are presented in terms of the initial modulus and the strength.

Compression testing. - The compression specimen is a unidirectional composite sample with dimensions of 4.86 by 0.25 by 0.125 in. The specimen ends are reinforced with fiberglass tabs and two strain gauges are mounted on each side. The compression fixture is the one designed by the Illinois Institute of Technology Research Institute (IITRI). Details of the testing procedure are found in reference 20.

Humidity conditioning. - Composite samples were conditioned at 90 percent RH in the presence of a supersaturated solution of lead nitrate. In all cases the conditioning was done for a period of 30 days. Equilibrium was reached after 18 days. Sample testing was done immediately after removal from the conditioning chamber. Conditioning was also done by immersing the samples in distilled H_2O at 71 °C (160 °F) for a period of 30 days.

Other methods. - Scanning and transmission electron microscopy were utilized to examine the composite samples for evidence of voids and fiber/matrix adhesion.

RESULTS AND DISCUSSION

Effect of Prepregging Solvent

The four solvents employed to dissolve the oligomer samples for the prepregging step are shown in table II. The effect of each of these solvents on the quality of the prepreg and the final properties of the laminate are now going to be discussed.

Chloroform. - Prepregs made from chloroform solutions yielded extremely poor quality laminates exhibiting evidence for significant resin degradation. It is speculated that at the cure temperature (200 °C) residual solvent, still present, yields chlorine radicals (ref. 21) which promote severe degradation of both the oligomer and the cured resin.

Dimethylsulfoxide (DMSO). - Prepregs made from dimethylsulfoxide solution exhibited precipitation of the oligomer on the graphite fibers during the drying process. The oligomer powder easily flaked off the fibers making uniform resin distribution control rather difficult. Furthermore it was not possible to remove all of the DMSO from the prepreg during the drying and laminate fabrication step. As a result the trapped DMSO plasticized the cross-linked polysulfone oligomer resulting in a laminate exhibiting a lower Tg (150 °C) than expected (180 °C).

N-Methylpyrolidone (NMP). - Prepregs made from NMP solutions exhibited adequate tack and were easily processible into excellent quality laminates with no evidence of any voids. The typical laminate processing parameters are shown in table III(a). The mechanical properties of these laminates are discussed in the next section. The only drawback of using NMP as a solvent is its plasticizing effect on the cured resin in a similar manner to that observed for laminates prepared using DMSO solutions.

Methylene chloride. - Prepregs made from CH_2Cl_2 solutions were easily processible into excellent quality laminates with no evidence of any voids. The laminate processing parameters are those shown in table III(b). The mechanical properties of these laminates are discussed in a subsequent section. In contrast to the prepregs obtained from NMP solutions, no depression of the composite Tg is observed in this case. This is a direct result of the ease of CH_2Cl_2 removal on drying.. Furthermore no matrix degradation is observed as was seen in the case of $CHCl_3$ solution prepregs (ref. 21). To date CH_2Cl_2 is the solvent of choice for solution prepregging of these oligomers.

Properties of NMP Solution Laminate

All properties discussed in this section relate strictly to unidirectional composite laminates.

Glass transition temperature. - The glass transition temperature (Tg) of laminates prepared by consolidation of prepreg impregnated with styrene-terminated polysulfone oligomer solutions in NMP, shows the strong plasticization effect of the residual solvent. A Tg decrease of 35 °C is observed as compared with the expected value of 180 °C from neat resin property values (ref. 5). This decrease in Tg is still present after prolonged post-curing at 200 °C. The effect is illustrated in table IV. It is important to mention that the amounts on NMP left in the laminate are of the order of 0.5 percent as determined by TGA analysis. Additional drying of the prepreg at temperatures below onset of crosslinking (150 °C) does not remove all of the trapped solvent.

One additional method employed with some degree of success was to thoroughly wash the prepreg in water for 48 hr. This process results in an increase in Tg (table IV) but also makes the prepreg very boardy and more difficult to process.

The problem is of course most acute for thicker laminates.

Volume fraction of resin. - The composites were targeted to have roughly a 40 percent volume fraction of resin. Experimental results yielded a resin volume fraction of 42.6 percent. Electron micrographs in the direction perpendicular to the fibers reveals no evidence for the presence of voids. A typical electron micrographs is shown in figure 1.

Void content: According to equation 3 a maximum void content of 2 percent was determined for all NMP prepreged composites.

Moisture conditioning. - The maximum water uptake for the composite laminates, following exposure to 98 percent RH, is 0.3 percent. Based on neat resin data (refs. 1 and 2) this value is roughly twice what we had expected. It is very likely that the additional amount of water absorbed is due to the presence of residual NMP, which is known to be extremely soluble in water. An uptake of the order of 0.3 percent will result according to the equation of Kelly (ref. 18) in a 50 °C (90 °F) drop in Tg. The decrease in mechanical pro- perties of the laminate, discussed in the next section, are in agreement with this prediction.

One point of interest to be mentioned is the critical need to perform all testing of conditioned samples at elevated temperatures as fast as possible to prevent sample dry out. DSC and Rheometrics DMA runs although performed at as fast as possible a scan rate within the instrumental limitations failed to detect the magnitude of the Tg drop. An example of typical DMA run for a dry and conditioned sample is shown if figure 2.

Flexural and short beam shear properties. - The flexural and short beam shear results are shown in tables V and VI, respectively. The Tg of the laminate sample is also given as samples subjected to the prepreg washing step were also tested. The short beam shear results (table VI) show that the failure mode is thermoplastic for the high temperature runs. As a result the data is presented in terms of maximum strength over the linear portion of the stress/strain curve.

Tensile properties. - The tensile properties of the laminates are shown in table VII. Electron Microscopy of the fracture surface (fig. 3) indicated excellent fiber/matrix adhesion. The tensile data is in fair agreement to the calculated values based on percent fiber volume fraction and the tensile properties of the graphite fibers (table I).

Linear expansion coefficient. - The linear expansion coefficients parallel and perpendicular to the fiber direction are shown in table VIII.

Properties of CH_2Cl_2 Solution Laminates

Glass transition temperature. - The glass transition temperature (Tg) of laminates prepared by compression molding of the prepreg was determined to be 177 to 187 °C by DSC. These results indicate that no plasticization of the resin by residual solvent (CH_2Cl_2) had occurred. These results were also confirmed by DMA and TMA.

Volume fraction of resin. - The volume fraction of fiber for each composite laminate was obtained as described in the experimental section, and will be given along with the mechanical properties of the test specimen where appropriate.

Void content: According to equation (3), in the experimental section a maximum void content of 2 percent was calculated for all fabricated composite samples.

Electron micrograph of typical methylene chloride prepregged composite sample is shown in figure 4. Via this method no evidence of voids was observed.

Moisture content. - The maximum water uptake for the composite laminates, following immersion in H_2O at 160 °F, was determined to be 0.25 percent. This value is still higher than would be predicted from the neat resin properties and the resin volume fraction. One has to nevertheless remember that accurate weight measurements are difficult for such small water uptake values. As before water uptake manifests itself via a plasticization effect and is accompanied by a drop in mechanical properties at elevated temperatures (see tables IX and X).

Flexural and short beam shear properties. - The flexural and short beam shear results are shown in tables IX and X, respectively. As with previous data, if the failure mode for the short beam shear testing is not a shear type the results are presented in terms of the maximum strength over the linear portion of the stress/strain curve. All samples had a unidirectional stacking sequence.

The data in tables IX and X illustrates the high degree of property retention at high temperatures and after exposure to moisture. The improvement in properties is due to the higher Tg of the composite as a result of minimal plasticization by CH_2Cl_2 and thus is illustrative of the true material properties.

Linear expansion coefficient. - The linear expansion coefficient parallel and perpendicular to the fiber direction are shown in table XI.

Dynamic mechanical properties. - The stored shear modulus (G') and tan δ curves are shown in figure 5. The two major relaxations are at the Tg (α relaxation) and at -100 °C. The latter has been attributed (ref. 16) to relaxations involving the phenylsulfone group in the matrix material. All samples testes were unidirectional.

Thermal and thermooxidative stability. - TGA scans for typical composite samples in N_2 and air are shown in figure 6. The composite samples exhibit improved thermal and thermooxidative stability as compared to the neat resin where the onset of thermal degradation is at approximately 325 °C for N_2 and air scans. The latter conditions did show a significantly faster weight loss above 400 °C.

Drop weight impact. - The composite samples subjected to the drop weight impacted test exhibited complete impactor penetration. Typical load-time, energy-time, load-deflection and energy deflection curves are shown in figure 7. In general the sample appears to sustain most of the damage after the maximum load is attained. Photographs of a typical impacted sample are shown in figure 8. From the curves in figure 7 one can see that two-thirds of the total energy is absorbed by elastic deformation of the test plate up to the maximum loading laminate. Little or no apparent physical damage occurred within the laminate. This is indicative of a good impact resistant composite material. No damage other than the penetrator indentation is observed on the impacted surface. The backside shows, besides the impactor hole, delamination within the laminate.

The data calculated based on the curves shown in figure 7 is presented in table XII.

Intralaminar shear. - The results of the 10° off-axis tensile testing characterizing the shear properties of the composite are shown in table XIII. While the measured shear moduli show very little scatter, the measured shear strengths do exhibit a signification amount of scatter. Scanning electron microscopic examination of the fracture surfaces indicate that fracture occurred in the elastic position of the stress-strain curve. A photograph of a fracture surface is shown in figure 9. There are no shear lips which indicate matrix ductile failure. The lack of smooth fiber surfaces indicate that there is a very good matrix-fiber surface bond at the interface. The load-strain traces, recorded during the testing, are linear up to the point of failure for the specimens that were tested. This confirms the conclusions drawn from the SEM pictures. The electron micrographs also showed evidence for cracks within the matrix a possible explanation for the low strength values.

Compressive properties. - The compressive properties are given in table XIV. The compressive properties appear to reflect the composite shear properties. The modulus is constant at a value close to the value calculated from the standard rule of mixtures, assuming the matrix modulus is negligible in comparison to that of the fiber. The measured strengths are variable with a maximum measured value of 93 ksi. This is about half of what is expected for a sound composite (ref. 19). Microscopic examination cross sections of the material give no indications of cracking or excessive porosity. The matrix-fiber bond appears to be strong enough force the failure to occur in the matrix. These results are not consistent with the results of the flexural tests, where all the observed failures were due to flexural failure and not compressive failure. Also, the shear properties are not consistent with the impact behavior of the composite material, which indicate good shear properties of the material. These discrepancies are unexplainable.

COMPARISON WITH COMMERCIAL COMPOSITES

Table XV illustrates a comparison between the properties of STO's and STO/graphite composites with the available properties of commercial composites.

Selection of the data shown in table XV was based on resin matrices with similar Tg's to the STO's and composite employing graphite fibers of similar characteristics to Celion 6000. All materials falling into this category are epoxy based.

The data in general illustrates that the composite properties of STO's are similar to those of commercially available epoxies. The distinctive point of STO based composites is the significantly better retention of properties after exposure to hot/wet environments.

It is thus reasonable to say that composites based on styrene-terminated reactive oligomers could find applications in the same areas where today graphite reinforced epoxy composites are utilized.

CONCLUSIONS

The study presented in this report indicates that styrene-terminated polysulfone oligomers can be employed as matrix material for graphite reinforced composites.

For solvent impregnation techniques CH_2Cl_2 is the solvent of choice due to its easy removal during the prepreg drying and consolidation steps. It neither degrades the fibers and matrix as $CHCL_3$ does nor does it plasticize the matrix as was observed with DMSO and NMP. Good quality composite samples can be obtained with less than 2 percent void content if the appropriate cure schedule is employed to permit adequate resin flow prior to curing. Nevertheless the unmodified resin does not yield a prepreg with tack and drape characteristics. To achieve these features the resin formulation requires further modifications.

The mechanical properties of composites based on styrene-terminated oligomers are generally comparable to those of 177 °C (350 °F) cure epoxy composites. The former exhibit significantly better retention of mechanical properties after exposure to hot/wet environment.

Some inconsistency was found in the measured properties. The low compression strengths that were measured should be reflected in compressive failures in the flexural tests. This was not the cause. The low shear strengths measured by the ten degree off-axis tests were not reflected in the impact test results since initiation of failure did not occur prior to the attainment of maximum loading of the impact specimen. While flaws within the matrix could be a possible reason, the lack of agreement cannot be explained.

In conclusion graphite reinforced composites based on styrene-terminated polysulfone oligomers could find applications in some of the same areas where epoxy systems are presently employed and which require improved hot/wet property retention.

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TABLE I. - CELION 6000 GRAPHITE FIBER PROPERTIES

Modulus, msi	34.6±0.2
Tensile strength, ksi	523±14
Elongation, percent	1.52±0.04
Density, g/cm^3	1.77

TABLE II. - SOLVENTS USE FOR COMPOSITE PREPREGGING

	Boiling point, °C	P, g/cm^3
Methylene chloride (CH_2Cl_2)	40	1.335
Chloroform ($CHCL_3$)	61.2	1.492
Dimetryl sulfoxide [$(CH_3)_2SO$] (DMSO)	189	1.101
N-Methylpyrolidone (NMP)	202	1.033

TABLE III. - LAMINATE PROCESSING PARAMETERS

(a) For NMP Derived Laminates

Temperature		Time, hr	Pressure, psi
°C	°F		
130	266	1	1000
180	356	1	1000
200	392	2	1000
200	392	16	----

(b) For CH_2Cl_2 Derived Laminates

Temperature		Time, hr	Pressure, psi
°C	°F		
85	185	1	750
150	302	0.5	750
180	356	1	750
200	392	2	750
200	392	16	---

TABLE IV. - Tg AS A FUNCTION OF POST-CURING TIME AT 200 °C (392 °F) FOR NMP DERIVED LAMINATES

Post curing time, hr	Tg	
	°C	°F
16	145	293
72	145	293
104	152	306
228	176	349
Washed prepreg		
16	165	329

TABLE V. - FLEXURAL PROPERTIES FOR NMP DERIVED LAMINATES

Test temperature		Tg laminate		Orientation to fiber direction	Strength, ksi	Modulus, msi
°C	°F	°C	°F			
25	77 dry	145	293	0°	235±5	17.2±.65
	wet[a]	~100	212		214±18	16.0±.66
	dry	160	320		235±5	17.2±.65
82	180 dry	145	293	0°	195±6	15.8±.5
	wet[a]	~100	212		181±11	16.0±.3
121	250 dry	145	293	0°	127±21	15.2±.6
	wet[a]	~100			63±13	7.8±1.6
	dry	160	320		174±21	15.9±1
136	277 dry	160	320	0°	132±12	13.9±1.5
25	77 dry	145	293	90°	7.2±4	1.2±.1

[a]30 days at 98 percent RH, 77 °F

TABLE VI. - SHORT BEAM SHEAR FOR NMP DERIVED LAMINATES

Test temperature		Tg laminate		α,[a] psi	σILS,[b] psi	Failure type
°C	°F	°C	°F			
25	77 dry	145	293	--------	11317±719	Shear
121	250 dry			9576±536		Thermoplastic
	wet	~100	212	4710±497		Thermoplastic

[a]σ Maximum strength over the linear portion of the stress/strain curve.

[b]σILS Interlaminar shear strength.

TABLE VII. - TENSILE PROPERTIES FOR NMP DERIVED LAMINATES

Test temperature			
°C	°F		
25	77	Tensile strength (σ) ksi	282±30
		Tensile modulus (E) msi	22.5±2.5
		Tensile strain	1.26±.18
		Poisson's ratio (γ)	.314

TABLE VIII. - LINEAR EXPANISON COEFFICIENT (α) FOR NMP DERIVED LAMINATES

Direction with respect to fibers	α (K^{-1})
90°	30.3x10^{-6}
0°	~0

TABLE IX. - FLEXURAL PROPERTIES FOR METHYLENE CHLORIDE DERIVED LAMINATES

Test temperature			Tg laminate,		Strength, ksi	Modulus, msi	Fiber volume fraction, percent
°C	°F		°C	°F			
25	77	dry	177	350	275±18	17.8±3	53
		wet[a]			330±24	20.8±1.4	
82	180	dry	177	350	294±24	18.6±2	53
		wet[a]			278±10	18.5±.5	
121	250	dry	177	350	243±11	18.4±2	53
		wet[a]			278±10	18.5±1.5	
149	300	dry	177	350	227±20	17.9±1	53
		wet[a]			133±3	13.5±1	

[a] 30 Days immersion in H_2O at 71 °C (160 °F).

TABLE X. - SHORT BEAM SHEAR FOR METHYLENE CHLORIDE DERIVED LAMINATES

Test temperature		Tg laminate	σ,[a] psi	σ[b]ILS, psi	Failure type	Fiber volume fraction, percent
°C	°F					
25	77 dry	177 (350)	15933±2780	11972±2132	Shear	52
	wet[c]		15764±635	----------	thermoplastic	
82	180 dry	177 (350)	13843±1464	10383±1100	Shear	52
	wet[c]	177 (350)	12926±730	----------	thermoplastic	
121	250 dry	177 (350)	12292±728	9218±546	Shear	52
	wet[c]		11503±340	----------	thermoplastic	
149	300 dry	177 (350)	9707±120	----------	Thermoplastic	--
	wet[c]		7519±85	----------	Thermoplastic	--

[a] σ Maximum strength over the linear portion of the stress/strain curve.
[b] σILS Interlaminar shear strength.
[c] 30 days immersion is H_2O at 71 °C (160 °F).

TABLE XI. - LINEAR EXPANSION COEFFICIENT (α)
FOR METHYLENE CHLORIDE DERIVED LAMINATES

Direction with respect to fibers	α (°K^{-1})
90°	$27\times10^{-6}\pm2\times10^{-6}$
0°	~0

TABLE XII. - RESULTS FOR DROP WEIGHT IMPACTED METHYLENE CHLORIDE DERIVED COMPOSITES[a]

Sample thickness	Impact energy, ft • lb	Maximum load, lb	Energy at maximum load, ft • lb	Maximum energy, ft • lb	Deflection at maximum load, in.	Deflection at maximum energy, in.	Energy of penetration,[b] ft • lb
0.106±.004	172±1.4	1653±117	31.0±1.4	38±4.6	0.397±.10	0.803±0.05	7.0±3.2

[a] Fiber volume fraction = 0.52.
[b] Energy of penetration = Maximum energy - energy at maximum load.

TABLE XIII. - INTRALIMANAR SHEAR PROPERTIES OF METHYLENE CHLORIDE DERIVED COMPOSITES

Test temperature		Strength, ksi	Modulus, msi	Max strain	Fiber volume fraction, percent
°C	°F				
25	77	4.93±1.19	0.71±0.02	0.0059±0.0012	55

TABLE XIV. - COMPRESSIVE PROPERTIES OF METHYLENE CHLORIDE DERIVED COMPOSITES

Test temperature		Strength, ksi	Modulus, msi	Strain	Poisson's ratio	Fiber volume fraction, percent
°C	°F					
25	77	79.6±10.7	19.0±0.70	0.0042±0.0010	0.44	55

TABLE XV. - COMPARATIVE PROPERTIES OF STO COMPOSITES WITH COMMERCIAL PRODUCTS

Property	Test temp. °F	Tactix 696 Dow epoxy	XU-71788.00 Dow epoxy	Epon 9450 Shell epoxy	E707A US Polymeric epoxy	8551-7 Hercules epoxy	2220-1 Hercules epoxy	R6376 Ciba-Geigy epoxy	STO BFG sulfone
Resin									
Flexural/Tensile									
Strength, ksi	RT	22/13.3	22/14.3	7.1/3.4					5/5.95
	180 dry	18/----	16.5/--						-/5.10
	180 wet	16.5/--	15.2/--						
Modulus, ksi	RT	520/465	500/420	231/208					
	180 dry	475/---	450/---						374/220
	180 wet	480/---	430/---						-/225
Tg, °F dry		338	302	302			375		356
wet		302	275						
G_{IC}, J/m^2		550	600	138		1000	256		100-1800
Percent, H_2O abs		1.25	1.40						0.32
Composites									
Tensile, 0-deg									
Strength, ksi	RT		290	283	273	315	224	390	282
	250						225	361	
	350				240				
Modulus, msi	RT		17.7	19	20	18.5	16.4	19.7	22.5
	250						16.5	21.3	
	350				22				

TABLE XV. - Continued.

Property	Test temp. °F	Tactix 696 Dow epoxy	XU-71788.00 Dow epoxy	Epon 9450 Shell epoxy	E707A US Polymeric epoxy	8551-7 Hercules epoxy	2220-1 Hercules epoxy	R6376 Ciba-Geigy epoxy	STO BFG sulfone
Tensile 90-deg									
Strength, ksi	RT		8.5	5.1	9		5.6	12.7	
	250 dry						4.3	8.0	
	250 wet						2.0		
Modulus, msi	RT		1.25	1.2	1.3		1.2	1.38	
	250 dry						.96	1.13	
	250 wet						.71		
Flexural 0-deg									
Strength, ksi	RT dry		300	231	292	266	233	282	275
	180 dry		255			220		234	294
	180 wet		156			150		222	364
	250 dry						174	205	243
	250 wet						130		278
	300 dry								227
	300 wet								133
	350 dry				181				---
Modulus, msi	RT dry		16.7	16	18	18.6	13.8	19.8	17.8
	180 dry		16.6				18.4	20.5	18.6
	180 wet		14.7					20.8	19.2
	250 dry						13.6	18.5	18.4
	250 wet						13.6		18.5
	300 dry								17.9
	300 wet								13.5
	350 dry				18				----
Flexural 90-deg									
Strength, ksi	RT		19.6						7.2
	180 dry		13.9						
	180 wet		11.6						
	250 dry								
	250 wet								
Modulus (msi)	RT		1.66						1.2
	180 dry		1.0						
	280 wet		1.0						
	250 dry								
	250 wet								

TABLE XV. - Concluded.

Property	Test temp. °F	Tactix 696 Dow epoxy	XU-71788.00 Dow epoxy	Epon 9450 Shell epoxy	E707A US Polymeric epoxy	8551-7 Hercules epoxy	2220-1 Hercules epoxy	R6376 Ciba-Geigy epoxy	STO BFG sulfone
Short Beam Shear	RT		13	12	17	16	14.4	19.3	12.0
	180 dry		----			12.7		13.9	10.4
	180 wet		7.5			12.0		9.7	----
	250 dry					9.9	8.3	1.2	9.2
	250 wet					7.5		7.5	----
	300 dry								
	300 wet								
	350 dry				11				
G_{IC}in • lb/in^2			6.55				1.7		
Compression 0-deg									
Strength, ksi	RT		180	184	205	244		228	79.6
	180 dry					203			
	180 wet					174		204	
Modulus, msi	RT				17	19.2			19.0
	180 dry					19.8			
	180 wet					19.2			
Post impact compression, ksi 1500 lb impact						53			
10° Off axis tensile Strength, ksi	RT								4.93
Modulus, msi	RT								0.71
Drop weight impact Maximum load, lb	RT								1653
Maximum energy, ft • lb	RT								38
Maximum deflection, in.	RT								.803

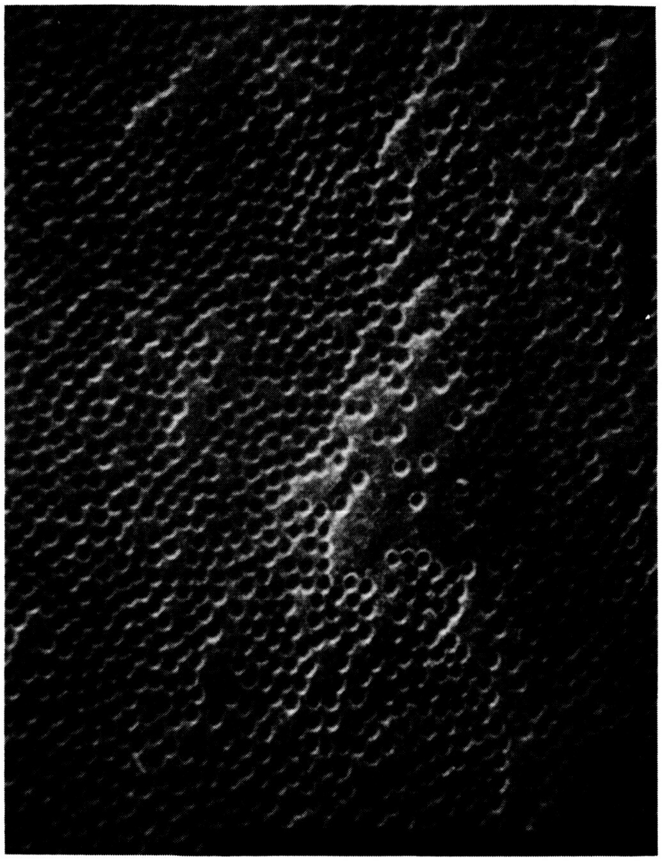

FIGURE 1. - ELECTRON MICROGRAPH FOR A TYPICAL COMPOSITE NMP DERIVED SAMPLE, PERPENDICULAR TO THE FIBER DIRECTION. (300X MAGNIFICATION)

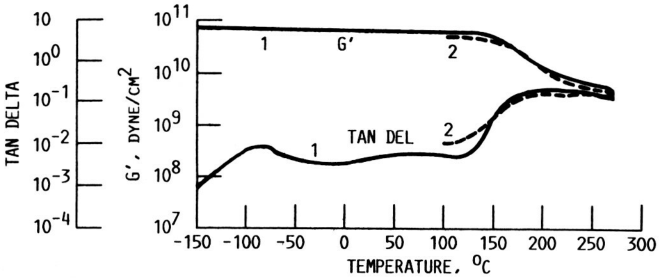

FIGURE 2. - STORED SHEAR MODULUS (G') AND TAN δ FOR DRY (CURVE 1) AND WET (CURVE 2) NMP DERIVED COMPOSITE SAMPLES AS A FUNCTION OF TEMPERATURE AT 10 RAD/SEC.

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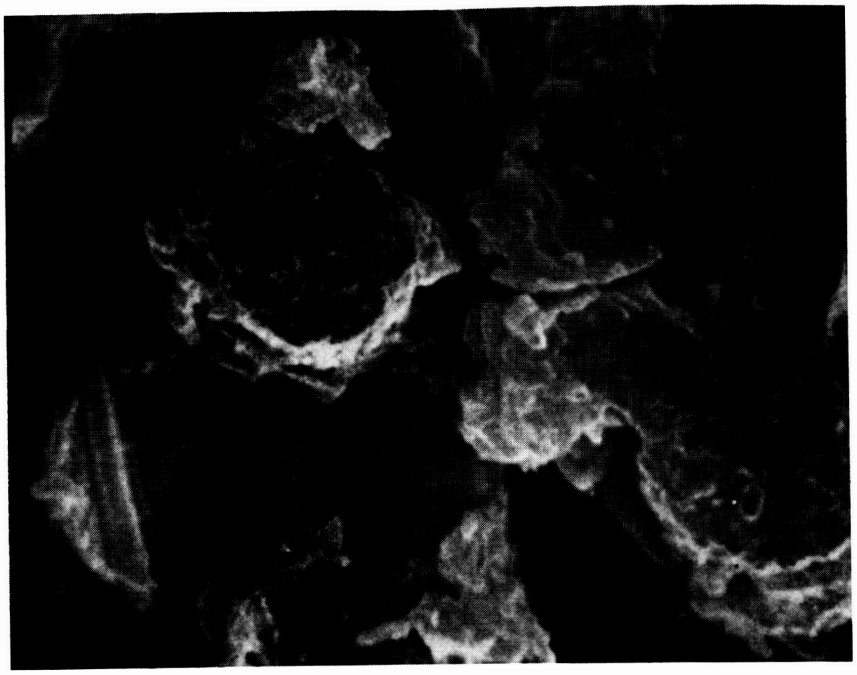
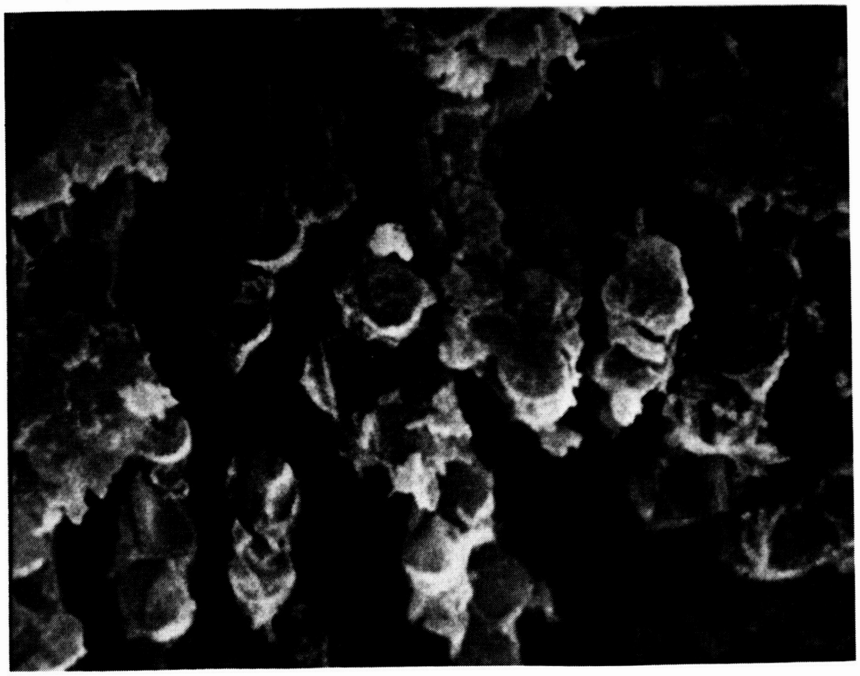


(A) AT 1000X MAGNIFICATION.



(B) AT 3000X MAGNIFICATION.

FIGURE 3. - ELECTRON MICROGRAPH FOR THE FRACTURE SURFACE OF A TYPICAL TESTED TENSILE SPECIMEN.

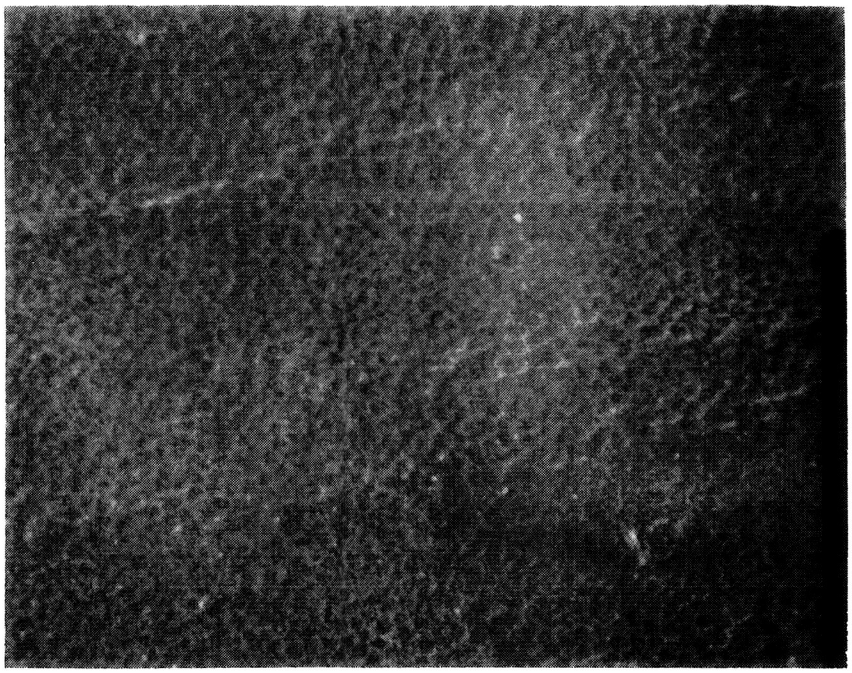


FIGURE 4. - ELECTRON MICROGRAPH FOR A TYPICAL METHYLENE CHLORIDE DERIVED COMPOSITE SAMPLE PERPENDICULAR TO THE FIBER DIRECTION. (300X MAGNIFICATION)

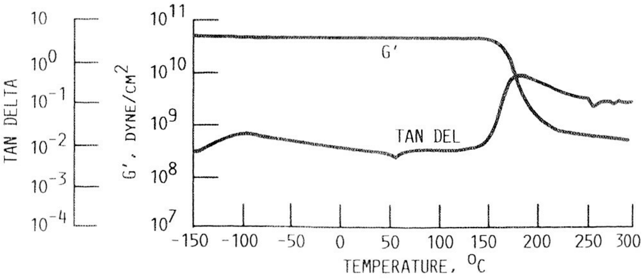


FIGURE 5. - STORED SHEAR MODULUS (G') AND TAN δ FOR METHYLENE CHLORIDE DERIVED COMPOSITE SAMPLE AS A FUNCTION OF TEMPERATURE AT 10 RAD/SEC.

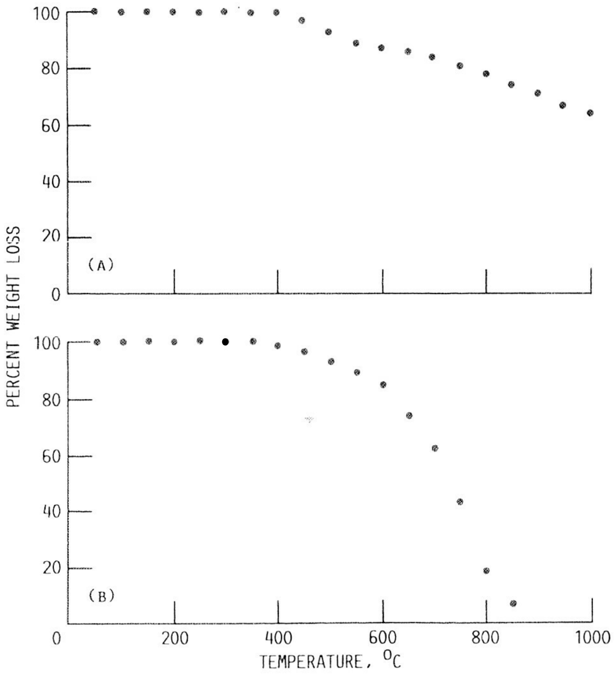


FIGURE 6. - TGA OF METHYLENE CHLORIDE DERIVED COMPOSITE SAMPLES IN N_2 (FIG. 6(A)) AND AIR (FIG. 6(B)); SCAN RATE 10 °C/MIN.

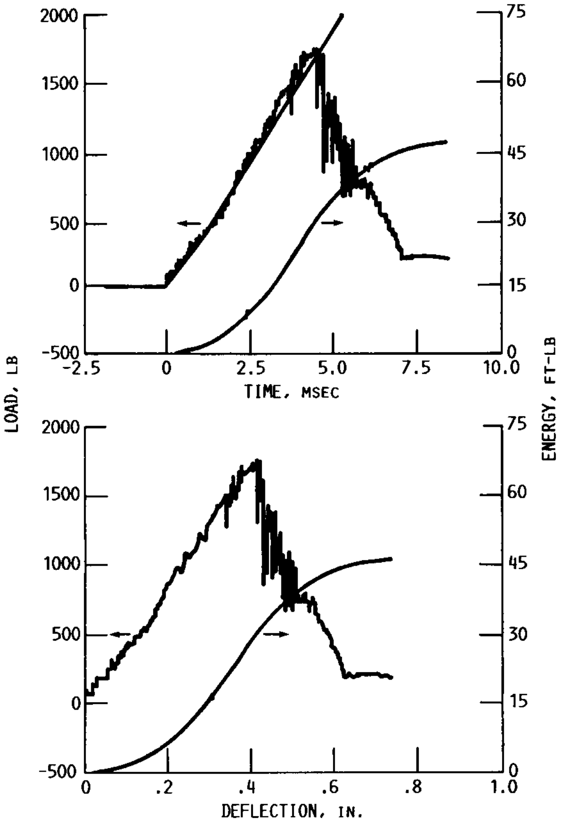
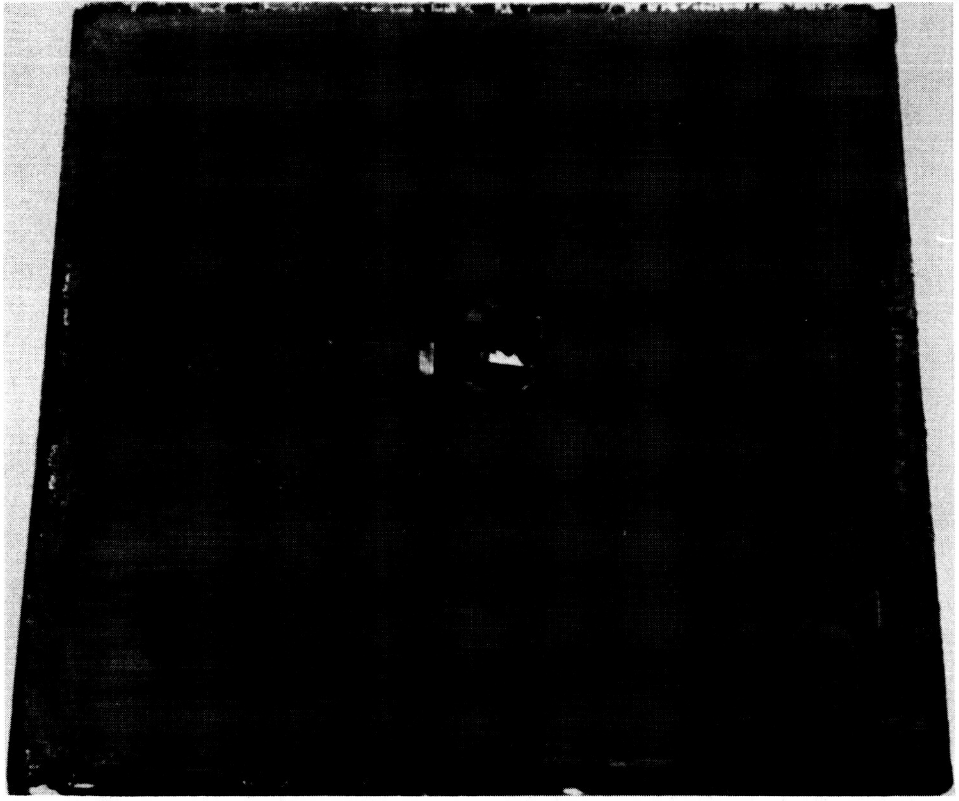
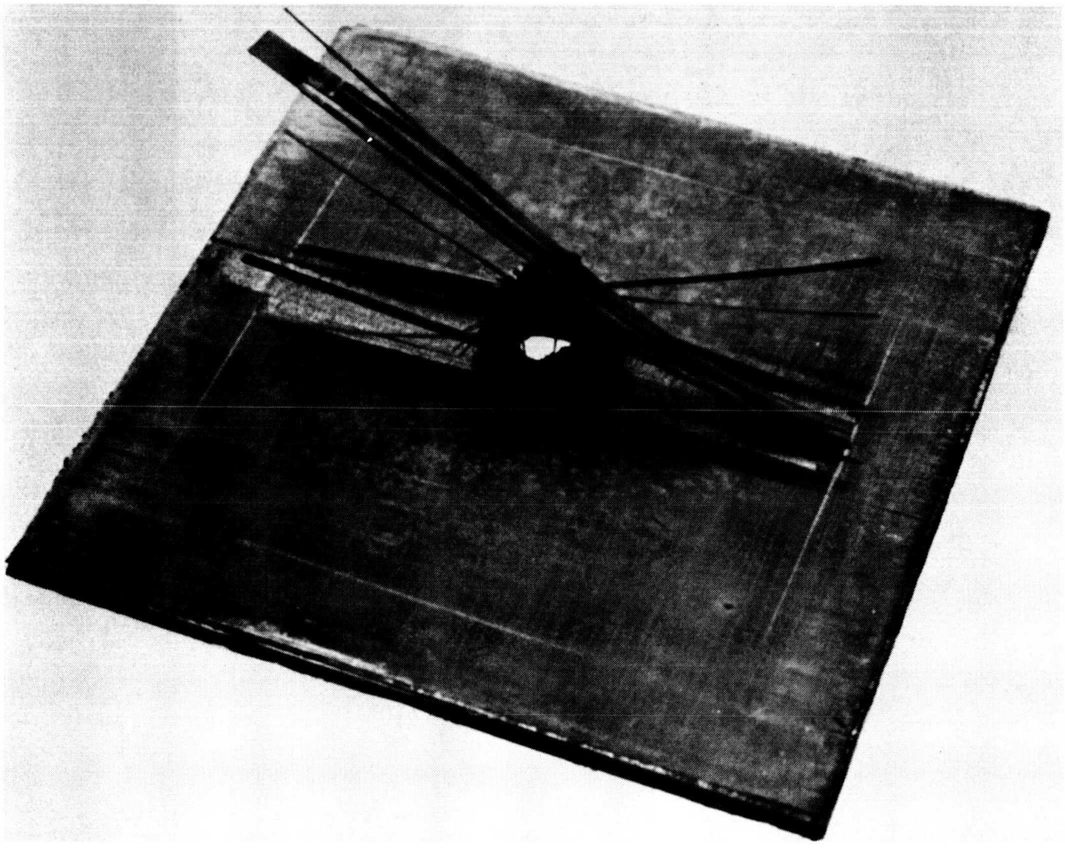


FIGURE 7. - TYPICAL LOAD VERSUS TIME; ENERGY VERSUS TIME; LOAD VERSUS DEFLECTION; AND ENERGY VERSUS DEFLECTION CURVES FOR DROP WEIGHT IMPACTED METHYLENE-CHLORIDE DERIVED COMPOSITES.



(A) IMPACTED SIDE.



(B) BACKSIDE.

FIGURE 8. - PHOTOGRAPHS OF DROP WEIGHT IMPACTED COMPOSITE SAMPLE.

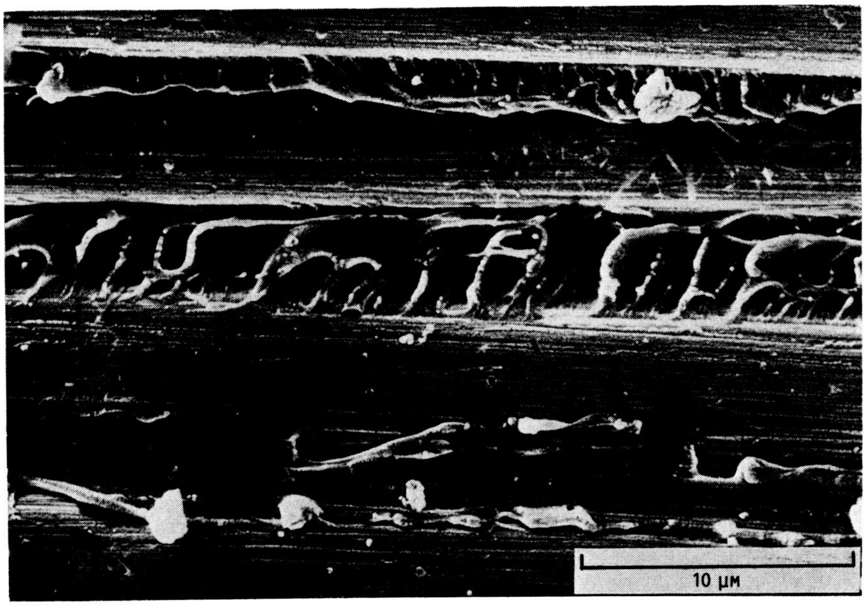


FIGURE 9. - PHOTOGRAPH OF THE FRACTURE SURFACE OF A 10° OFF-AXIS TENSILE SPECIMEN.

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15. Supplementary Notes

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16. Abstract

Styrene-terminated polysulfone oligomers are part of an oligomeric class of compounds with end groups capable of thermal polymerization. These materials can be used as matrices for graphite reinforced composites. This report summarizes our initial evaluation of styrene-terminated polysulfone oligomer based composites in terms of fabrication methods, and mechanical and environmental properties. In addition the report also provides a description and evaluation of the NASA/Industry Fellowship Program for Technology Transfer.

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