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Graphite Fiber Surface Treatment to Improve Char Retention and Increase Fiber Clumping

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SUMMARY

Carbon and graphite fiber composite structures contain electrically conductive fibers which can be released into the environment by a fire and/or explosion. The fibers are potentially hazardous to some types of electrical equipment. Because of their small size, the fibers can be readily transported by atmospheric currents over relatively long distances. Techniques to reduce the degree of transport will decrease risks. One method to help contain the fibers to a relatively small area is to cause them to agglomerate into bundles during a fire. These bundles will settle out of the atmosphere more readily, limiting the area of contamination.

The use of high-char resins is one approach to producing larger bundles. However, the resin systems that currently provide the best composite mechanical properties are the epoxies, and these have low char yields. The high-char-yield resins generally are more difficult to handle than epoxies in composite fabrication and don't usually provide an optimum-strength structure.

An approach which does not appear to have received consideration is the modification of the carbon fiber surface and sizing to provide a system which will form fiber-to-fiber "bridges" when exposed to the heat of a fire and will then char to hold the fibers in larger bundles. The objective of this exploratory research and development program was to determine the feasibility of treating carbon or graphite fiber surfaces with char-forming monomers or polymers or of modifying the sizing used on the fibers to improve the char retention and/or increase fiber clumping when a graphite fiber-epoxy composite laminate is burned.

Three general approaches were evaluated as sizing modifications for commercially available carbon fiber. One used low molecular weight potential char-formers modified by adding epoxide functionality to enhance fiber to char-former adhesion. The second utilized the same approach except that the char-forming moiety was a copolymer expected to provide a high char yield. The third approach used a char-forming polymer dispersed in the fiber sizing composition. All showed evidence of reducing the fiber transport in a fire by causing fiber agglomeration. Resin-to-fiber adhesion could be maintained by incorporating difunctional epoxies in the sizing system.

Abbreviations Used:

GEPCP - Glycidyl ether of pentachlorophenol

AGE/HCCPD - allyl glycidyl ether adduct of hexachlorocyclopentadiene

GEsVCl - glycidyl ester of vinyl chloride/vinyl acetate/acrylic acid
terpolymer

GEVCl/VAc/VAl - glycidyl ether of vinyl chloride/vinyl acetate/vinyl
alcohol terpolymer

DMF - dimethyl formamide

ECH - epichlorohydrin

AGE - allyl glycidyl ether

SBS - short beam shear

PVC - polyvinyl chloride

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INTRODUCTION

Carbon or graphite fiber, as made, is relatively nonreactive at the fiber surface. As a consequence, adhesion in composite structures is poor and many structural properties suffer unless the fiber surface is pretreated to bond to the matrix resins. Most carbon and graphite fibers on the market today are so treated, usually to provide reactivity with, and bonding to, epoxy resins. These surface-treated fibers are available in differing degrees of surface reactivity; typically, more than sufficient bonding sites are available to assure that structural failure will occur within the resin matrix and not at the matrix-to-fiber surface.

The fact that the fiber surfaces are epoxy-reactive was used to modify the surface to provide "islands" of potential char-forming groups. These islands were varied in character and quantity in an attempt to provide an epoxy composite in which the filaments were held together at these "island" sites after exposure to the char-forming temperatures of a fire. While the typical epoxy resin will decompose within the fire and allow many of the carbon fibers to escape as single filaments, the char-forming groups should hold many filaments together, and are expected to increase the fall-rate of the fiber (clumps) and, thus, decrease the area over which the fiber is spread, reducing the potential hazard.

APPROACHES

A schematic representation of the method of providing char bridges during a fire while maintaining good resin-to-fiber adhesion in the laminate prior to the fire is shown in Figure 1.

Three general approaches were studied. One used low molecular weight compounds that are potential char-formers; these were reacted to form glycidyl ethers. The surface treated fiber surface was modified with a solution containing different ratios of a diepoxide and the char-former epoxy. It was anticipated that high ratios of the diepoxide would result in a predominantly epoxy-terminated surface with relatively few char-forming groups, while high ratios of char-former epoxy would provide a predominantly char-group surface. The ratio of epoxy to char-forming surface necessary to provide a suitable combination of good adhesion and good char-agglomeration was determined experimentally during the course of this program.

The second approach was similar to the first, except that the char-forming groups were prepared by epoxidizing (grafting) polymers with known char-forming capabilities to form glycidyl ethers or esters. The polymer approach has the potential advantage over the lower molecular weight approach of providing a local high viscosity melt zone during heating in a fire. In the event that the surface-to-modifier bond is broken or volatilized, the polymer melt could wet the filament locally. As the epoxy resin binder is volatilized and the polymer goes through the tar-stages leading to char, the tar groups should fuse together, char, and provide the char bridges. As in the first approach, the ratio of diepoxide to epoxy-char former provides different ratios in the modified fiber surface.

The third approach utilized a char-forming polymer finely dispersed within an epoxy resin and the carbon fiber was sized with this dispersion. This approach planned to incorporate the best modified surfaces from the first and second approaches to enhance the probability of forming char bridges. Difficulties were experienced in obtaining an evenly-coated sizing throughout the fiber bundle, so the combination system including the first and second approaches was not evaluated on small scale.

None of the techniques would be practical unless the composite made from the sized fiber retains its mechanical properties. Sufficient bonding between the matrix resin and the fiber surface requires that sufficient epoxide groups are available from either the diepoxide in the sizing or from the epoxide groups in the epoxy char former, or that the reactive fiber surface is available to the matrix during polymerization. To assure that sufficient surface reactive groups were present, a commercial type of carbon fiber (Hercules Type AS4) was used which has an abundance of surface-reactive groups capable of bonding to epoxy resins. To determine resin-to-fiber adhesion, experimental and control samples of fiber were made into short beam shear test specimens and tested over a 4/1 span/depth ratio.

disabledEXPERIMENTAL SECTION

Char-former Modifiers

The modification of the surface-treated fiber follows the general reactions of an epoxy group with a carbon fiber surface carboxyl group (1):

FIBER SURFACE ⟩ COOH + CH_2-CH-CH_2-OR

↓

COOCH$_2$CHOH-CH$_2$-OR
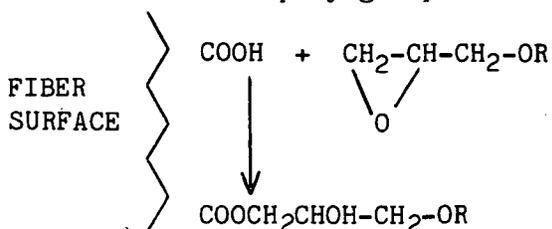
where R is either an epoxy functional group or a char-forming group. The concentration of char-forming groups on the surface is dependent on their relative concentration (compared to diepoxide) in the modifying solution. When R was an epoxy group, commercially available diepoxides such as the diglycidyl ether of bisphenol A were used. When R was a char-forming group, the epoxy group on the char-former entity was reacted with the fiber surface.

Glycidyl ethers and esters are simply prepared by reaction of epichlorohydrin (Shell Chemical Co.) with a hydroxyl compound in the presence of alkali or with a salt of a carboxylic acid.

CH_2-CH-CH_2Cl + ROH $\xrightarrow{NaOH}$ CH_2-CH-CH_2OR + NaCl

or

CH_2-CH-CH_2Cl + NaCOOR CH_2-CH-CH_2OCOOR + NaCl
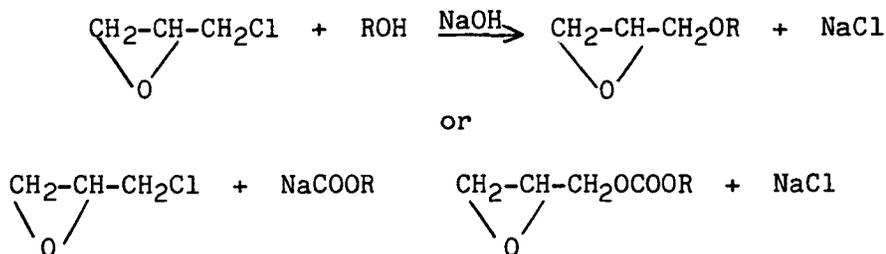
This type of reaction can be used directly to prepare compounds containing the epoxy group and a char-forming entity, either low molecular weight or polymeric.

Two low molecular weight modifiers were prepared for use as sizing agents for carbon fiber; the glycidyl ether of pentachlorophenol and the Diels-Alder adduct of hexachlorocyclopentadiene and allyl glycidyl ether (2).

The Glycidyl Ether of Pentachlorophenol
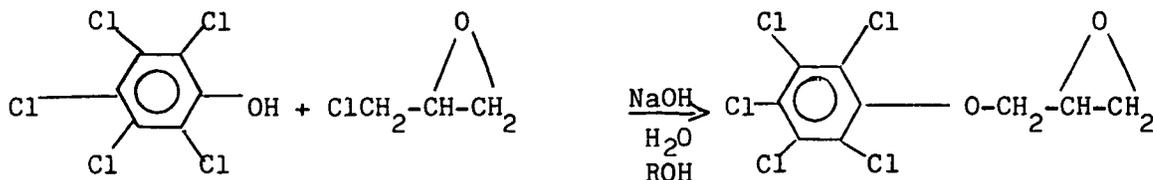
PCP	ECH	MW 322
MW 266	MW 92.5	Oxirane ox. 4.97% (calc)
m 188-191°C	B.115-117°C	
(Aldrich Cat.		
P-260-4)		

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was made from 26.6 g (0.1 mole) of PCP, 37 g (0.4 moles) ECH, and 20 ml
isopropyl alcohol which were charged to a 250 ml 3-necked flask fitted with
stirrer, heating mantle, thermometer, and reflux condenser. The solution
was heated to 75°C with stirring, 4.4 g NaOH (0.11 mole) as a 40% aqueous
solution was added dropwise over a 30 minute period. Stirring was continued
3 hrs. at 90-95°C (gentle reflux). Upon cooling, a copious precipitate
formed. One hundred ml water was added and the reaction mixture was
transferred to a Waring Blendor to break up large aggregates. The product
was collected on a medium porosity sintered glass funnel and washed with
water. The crude wet product was dissolved in 250 ml of isopropyl alcohol at
80°C and hot water (60°C) was added to incipient precipitation. The
recrystallized product upon cooling was isolated by filtration and dried 16
hrs at 70°C. The product weighed 27.7 g (86% yield) and had an oxirane
oxygen content of 4.9% (theory 4.97%) and a melting point of 113°C. The
compound when held in an open flame melted and was self-extinguishing. A
small amount of char remained on the tip of a spatula after heating to red
hot.

    The Diels Alder Adduct of hexachlorocyclopentadiene and allyl glycidyl
ether
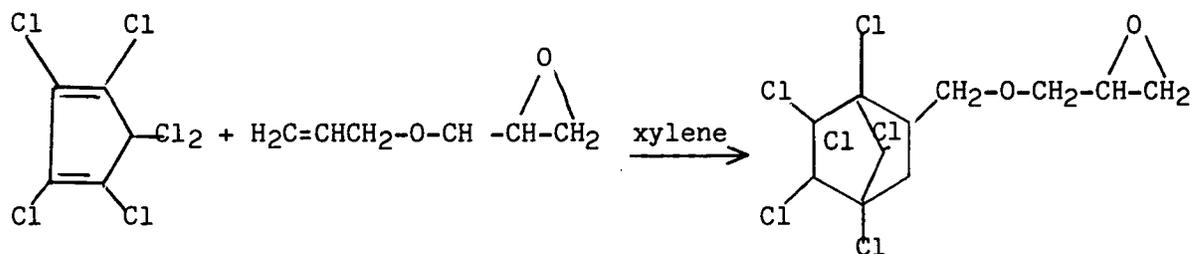
HCCP	AGE	MW 387
MN 273	(Alcolac, Inc.	4.13% Oxirane OX (Calc.)
(Aldrich Cat.	No. 701102)	
H-600-2)		

was made using a 500 ml round bottomed flask equipped with a reflux condenser
to which was added 136.5 g (0.5 mole) HCCP and 57 g (0.5 mole) of AGE and
125 ml xylene. The solution was refluxed at 152°C for 24 hours. A yellow
solution was obtained. Vacuum distillation removed xylene at 100 mm and
product distilled at 0.5 mm at 150-153°C. A pale yellow mobile liquid
weighed 150 g (79% yield) and contained 3.9% oxirane oxygen (94% pure).

    High molecular weight, or polymeric modifiers were prepared (3,4,5) by
selecting terpolymers containing vinyl chloride as the primary backbone. One
of the terpolymer groups was selected to be reactive with epichlorohydrin,
which resulted in conversion of the terpolymer to an epoxy-containing
terpolymer.

    The glycidyl ester of vinyl chloride/vinyl acetate/acrylic acid
terpolymer was prepared as follows:

$$
\begin{array}{c}
\text{polymer chain bearing} \\[-2pt]
\overset{\displaystyle O}{\underset{\displaystyle\parallel}{}}\!\!\text{C-OH},\ \ \text{O-C(=O)-CH}_3,\ \text{Cl-},\ \text{-Cl},\ \text{-Cl},\ \text{Cl-},\ \text{-O-C(=O)-CH}_3
\end{array}
\ +\ \text{CH}_2\text{Cl-CH-CH}_2\ \ (\text{epoxide})\ \xrightarrow{\ \text{NaOH}\ }\
\begin{array}{c}
\text{polymer chain bearing} \\[-2pt]
\text{-C(=O)-O-CH}_2\text{-CH-CH}_2\ (\text{epoxide}),\ \text{O-C(=O)-CH}_3,\ \text{Cl-},\ \text{-Cl},\ \text{-Cl},\ \text{-O-C(=O)-CH}_3
\end{array}
$$
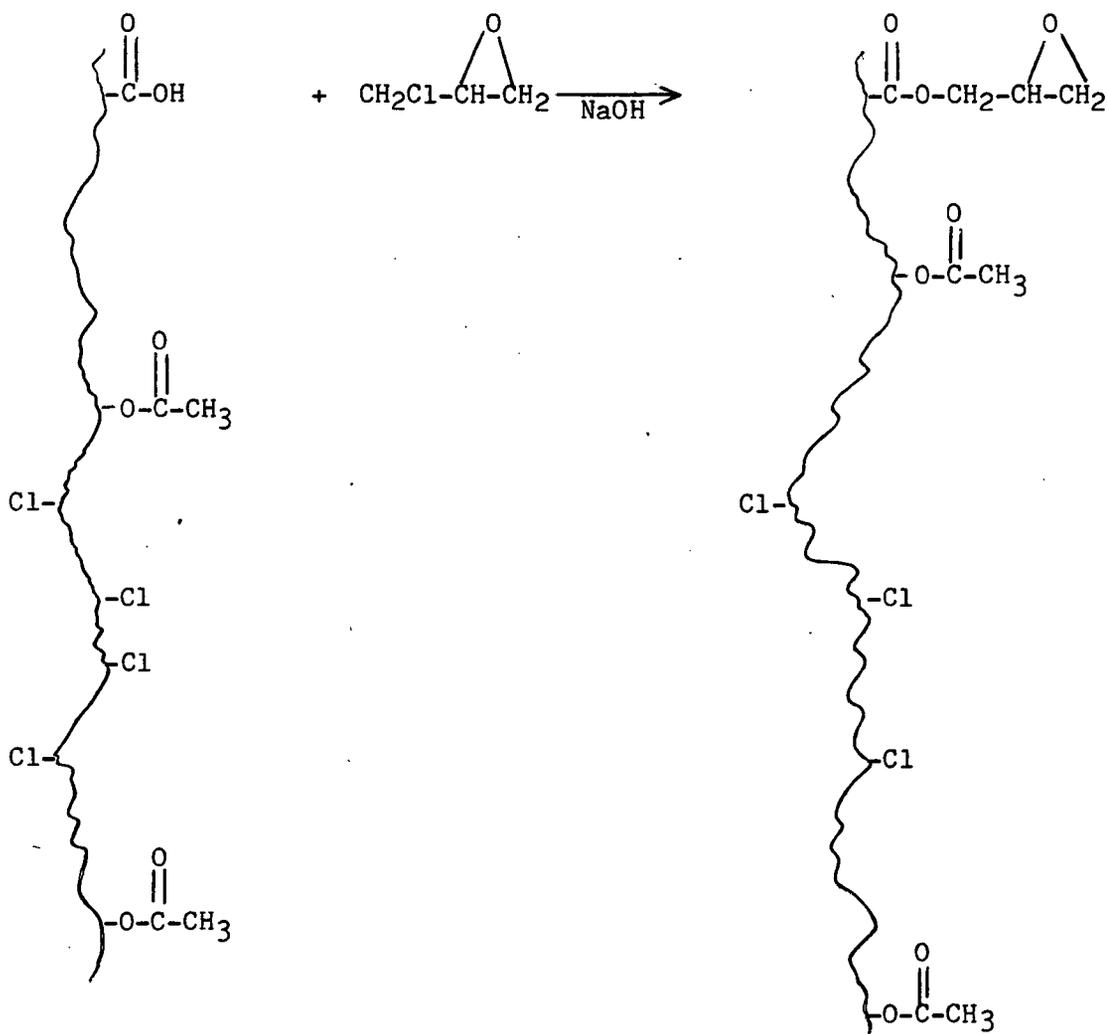
The starting material was a terpolymer containing 83 percent vinyl chloride, 13 percent vinyl acetate, and 1 percent acrylic acid (Aldrich Chem. Cat. 20,030-1). The remaining 3 percent in the composition is unknown. A 4 molar excess of epichlorohydrin was charged to a dimethylformamide solution of the terpolymer. A 10 percent excess over the stoichiometric amount of sodium hydroxide was added and the reaction carried out at 70-75°C for 4 hours. The product was isolated by precipitating in distilled water. Oxirane oxygen analysis was 0.33% (theory 0.35%). When removed from an open flame the compound was self-extinguishing. A small amount of char remained after heating to red heat.

During attempts to synthesize the glycidyl ether of vinyl chloride/-vinyl acetate/vinyl alcohol terpolymer (91/3/6) (Aldrich Chem. Cat. 18,290-0), it was noted that from 6 to 8 molar excess epichlorohydrin was necessary in the reaction to assure essentially complete conversion of hydroxyl functionality to the desired glycidyl ether. Dimethylformamide was satisfactory for the reaction solvent. The preparation proceeded as follows:

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$$\{-OH \quad + \quad Cl-C-\overset{O}{\overset{\triangle}{C}}-C \quad \longrightarrow \quad \{-O-C-C-\overset{OH}{\underset{|}{C}}-Cl \quad \xrightarrow{NaOH} \quad \{-O-C-\overset{O}{\overset{\triangle}{C}}-C$$

VC/VAc/VAl   ECH   Oxirane

           MW 92.5   Oxygen

                                                                2.1% (calc)
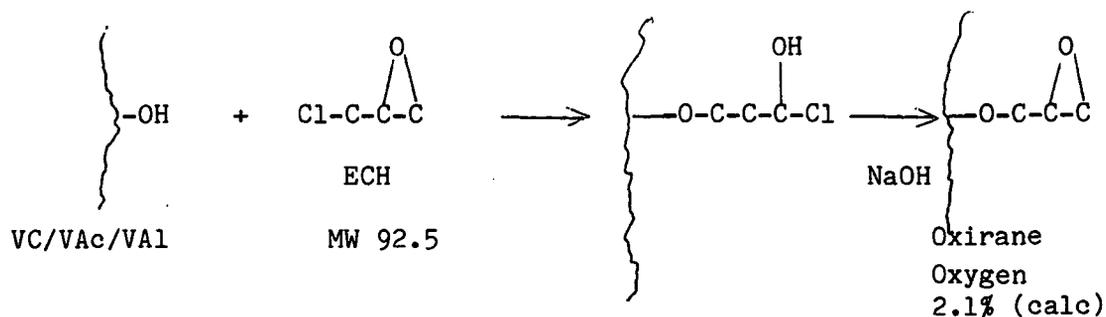
A 25 g quantity (0.034 equivalents) of VC/VAc/VAl was dissolved in 200 ml. DMF and heated with stirring with 25.2 g ECH (0.272 moles) to 90-95°. The ECH was 8 times molar equivalent based on the terpolymer. Heating was continued for 4 hours with stirring. The resulting solution was then treated with 1.48 g NaOH (0.037 moles) dissolved in 10 ml water. The base was added dropwise over a 30 minute period. Heating at 95°C was continued an additional 3 hours. The product was precipitated from 200 ml distilled water in a Waring blendor, filtered and dried. The following conversions were obtained:

| | Percent Conversion |
Molar Equivalent Epichlorohydrin	Based on Oxirane Oxygen
2	45.0
4	76.0
8	96.5

Sizing Application

Initially, sizings were prepared by making solutions of the diepoxide, char-former modifier, or combinations of these in methylene chloride. The concentration of sizing deposited on the fiber was controlled by the concentration of solids in the sizing solution. Fiber coating was by dip impregnation, followed by hot-air removal of the solvent. The time during the hot air heating and the ambient standing time after heating prior to fiber evaluation was relied on to react the size with the fiber surface.

The GEPCP crystallized during methylene chloride evaporation. This made surface reaction questionable. To obviate crystallization before reaction, the solvent was changed to a high boiling chlorinated hydrocarbon, perchloroethylene (boiling point 121°C). This assured that the size was in contact with the fiber surface at a temperature at least up to the boiling point of the solvent. Residence time during solvent evaporation and size setting was 6 minutes in 250°C air. This was assumed to be adequate to react the size with the fiber surface.

Chlorobenzene (boiling point 131°C) was used to apply AGE/HHCPP and GEs VCl, and dimethyl formamide (boiling point 152°C) was used to apply GEsVCl and GEVCl/VAc/VAl.

Attempts to use a dispersed polymer size were only partly successful. A quantity of the glycidyl ether of the vinyl chloride/vinyl acetate/vinyl alcohol terpolymer was micropulverized at liquid nitrogen temperature. This was necessary since at ambient temperature the product is flexible and tough

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and could not be finely ground. Three ratios of epoxidized terpolymer to Dow Epoxy Resin DER 330 were prepared in perclene. The epoxy component dissolved whereas the terpolymer char former remained suspended. A 2 percent total solids concentration was prepared.

Size Number	1	2	3
Parts perclene	100	100	100
Parts DER 330	1	1	0.67
Parts epoxidized terpolymer	1	0.67	1.33

Difficulty was experienced handling these sizes because of the suspended solids. Even size distribution could not be obtained, and the particles tended to float in the carrier liquid.

A very finely divided poly(vinyl chloride) (PVC) was obtained (Stauffer Chemical Co., type SLL-OH-1) and attempts made to disperse it in a sizing composition. The dispersion was not very stable, but the particles could be kept in suspension in methylene chloride by continuous stirring. This technique was used to apply sizings consisting of 50/50 PVC/Dow epoxy resin DER 330 and 66/34 PVC/330 to carbon fiber. Some difficulty was experienced with the fine fibers filtering out the larger PVC particles, but some particle coating was achieved within the bundle as evidenced by a dull, hazy coating on interior filaments. Spreading of the tow bundle during impregnation improved penetration of the solids but the outer surface of the bundle always appeared to pick up more of the particulate.

Laminate Preparation and Shear Testing

Sized fibers were dry-wound onto racks and vacuum-impregnated with a long working life epoxy resin system consisting of 100 parts by weight (pbw) of Dow DER 330 epoxy, 90 pbw Nadic[r] methyl anhydride, and 2 pbw N,N-benzyl dimethylamine. The schematic of the laminate preparation is shown in Figure 2. Fiber was checked for weight per unit length and density prior to sizing; these data were used to calculate the number of fibers required to achieve 62 volume percent in the mold. This number of fibers was wrapped onto a rack, the rack loaded into the mold cavity and the ends of the mold attached, the mold, fiber and rack degassed and excess resin added under vacuum, degassing was continued until no further air release was noted, the mold containing the resin-impregnated fiber rack was removed from vacuum, the mold closed in a press and pressure slowly applied to remove excess resin until the mold was closed to stops, and the mold heated via the press platen for 1 hour at 125°C followed by 4 hours at 165°C.

The same procedure was used for short beam shear samples, small unidirectional laminates, and large unidirectional laminates. Shear samples were cut from a 5 cm x 5 cm x 0.203 cm (2 inch by 2 inch by 0.080 inch) plate and measured 1.58 cm x 0.635 cm x 0.203 cm (0.625 inch long by 0.25 inch wide x 0.080 inch) thick using an 80 grit diamond wheel. Small laminates were molded slightly oversize and cut to 12.3 cm x 12.3 cm x 0.254 cm (4-7/8 inch by 4-7/8 inch by 0.100 width) thick. Large laminates were molded slightly oversize and cut to 30.5 cm x 30.5 cm x 0.254 cm (12 inch by 12 inch by 0.100 inch thick). Some difficulty was experienced with the large laminates

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cracking parallel to the longitudinal windings, about in the center of the laminates. This was found to be due to buckling of the undirectionally-reinforced plate due to thermal contraction of the mold on cooling from 165°C to ambient. This was eliminated by removing the laminate hot, well above the resin glass transition temperature.

Laminate Burn Tests

A small scale burning jig was devised to permit assessment of the sizings using sections cut from the short beam shear samples. This is illustrated in Figure 3. It consists of a laboratory forced-hot-air blower which supplied excess combustion air and the air velocity to carry fibers from the burned laminate. A Meeker burner was used as the combustion source. The specimen (0.14 cm x 0.2 cm x 1.59 cm; 0.055 x 0.080 x 0.625 inch) was cut from the edge of a SBS sample, parallel to the fiber direction, using a diamond saw. It was placed flat (1.59 cm x 0.2 cm; 0.625 x 0.080 face) on a 3 mm square mesh screen located 5 cm above the blower and burner. An inverted J-shaped Pyrex^r tube was used to cover the specimen and provide a chimney which carried the burned fibers to a collection screen of 1 mm square mesh. The combusted sample on the collection screen was examined to determine the character of the fiber bundle, whether it was composed of loose filaments or of tight bundles of filaments. Scanning electron micrographs were taken to determine the nature of the filaments on a small scale.

Larger unidirectional laminates were prepared for burn-assessment by NASA/Langley (Table 4).

DISCUSSION OF RESULTS

The general approach of this program was to randomly intersperse on carbon fiber surfaces char-forming epoxies and non-char-forming diepoxides in such a ratio that adhesion to the fiber would not be significantly reduced. The anticipation was that the char-formers would provide carbonaceous bridges at many points between individual filaments following a fire that consumes the epoxy resin. If such bridges could be achieved, much of the carbon fiber emitted from a fire should be in bridged bundles which will settle relatively rapidly out of the atmosphere.

Epoxidized low and high molecular weight compounds were prepared using highly chlorinated starting compounds. The starting materials were selected because they formed carbonaceous chars on combustion; they all retained this char-forming ability after epoxidation. Two low molecular weight char formers were made, the glycidyl ether of pentachlorophenol (GEPCP) and allyl glycidyl ether adduct of hexachlorocyclopentadiene (AGE/HHCPD). Both were soluble in chlorinated hydrocarbons such as methylene chloride, however, the GEPCP crystallized during solution evaporation such as would occur during sizing of a fiber. This made reaction of the epoxide with the carbon fiber surface questionable. The low boiling solvents were therefore replaced with high boiling solvents such as perclene or chlorobenzene.

Two polymeric char-forming epoxies were also synthesized. They were the glycidyl ester of the terpolymer of vinyl chloride, vinyl acetate, and acrylic acid (GEs VCl), and the glycidyl ether of the terpolymer of vinyl chloride, vinyl acetate, and vinyl alcohol (GEVCl/VAc/VAl). These could be applied as dilute solutions from chlorobenzene or dimethyl formamide.

An adhesion baseline was established using type AS4 surface treated fiber and a standard filament-winding epoxy resin consisting of 100 parts by weight (pbw) Dow DER 330, 90 pbw Nadic[r] methyl-anhydride, and 1.5 pbw N,N-benzyl dimethylamine. Relative adhesion on two sets of unidirectionally reinforced control laminates was determined by short beam shear strength to be 100.6 MPa (14,592 psi) and 103.8 MPa (15,048 psi) with variation coefficients (C_v) of 1.14% and 1.22%, respectively (Table 1). The excellent reproducibility of these controls eliminated a need for further control runs on the unsized fiber.

A second baseline was established using a sizing for the surface treated (Type AS4) fiber. Table 1 shows that the sized (with 0.28% Dow DER 330 epoxy) fiber adhesion as measured by short beam shear strength was statistically indistinguishable from the unsized, surface treated fiber at 102.5 MPa (14,869 psi) (C_v 1.55%) and 103.2 MPa (15,041 psi) (C_v 2.83%).

Sized fibers were made for preparation of laminates, for determination of adhesion, and for combustion screening. Sizings were initially applied from methylene chloride solution to surface treated Type AS4 carbon fiber using several ratios of a diglycidyl ether of bisphenol A (Dow DER 330) and the laboratory-prepared char-former glycidyl ether of pentachlorophenol (GEPCP). While adhesion (by short beam shear) was almost constant, extractability varied proportionately to the amount of DER 330 in the formulation (Table 2). It was found that the GEPCP had crystallized, and was fractionating out of the sizing solution as the solvent evaporated; it was suspected that reaction of the GEPCP did not occur with the fiber surface to any great degree since the crystals were not soluble in the DER 330. ESCA analysis of the sized surfaces (Table 3) implied that the GEPCP requires additional washing to remove the sodium chloride introduced as a contaminant during the glycidyl ether formation.

Sizings were also applied using the glycidyl ester of vinyl chloride/vinyl acetate/acrylic acid terpolymer with and without DER 330 using methylene chloride and chlorobenzene solutions, from GEPCP with and without DER 330 using perchloroethylene solution, and from the allyl glycidyl ether adduct of hexachlorocyclopentadiene (AGE/HCCPD) using perchloroethylene solution with and without DER 330. The purpose of the higher-boiling-point solvents was to avoid premature fractionation or crystallization of one component, and to allow sufficient contact time with the reactive fiber surface while the sizing was in a mobile, liquid phase to permit the oxirane group to couple to the fiber surface.

Sizes containing the glycidyl ether of the terpolymer of vinyl chloride/vinyl acetate/vinyl alcohol could not be applied from high boiling chlorinated solvents due to limited solubility of the polymer. Dimethylformamide was found to be a satisfactory high boiling point solvent for the epoxidized polymer and for the DER 330 epoxide and was used in all sizes containing this polymer.

Adhesion measurements on sized fibers, using short beam shear strength as the measurement technique, showed little effect of the epoxidized char-formers on adhesion at low size levels (Table 2). Incorporation of a diepoxide (DER 330) in small amounts into the size composition (25% of the size) resulted in short beam shear values statistically indistinguishable from the controls in all sizes except those containing GEs VCl. With this

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epoxidized polymer it was necessary to increase the diepoxide so that the size contained 75% diepoxide before adhesion equal to the control was achieved. The sized fiber was also rather stiff and difficult to handle and laminate. Laminates from this stiff fiber showed distinct"roping" of the fiber. This could be almost eliminated by "breaking" the fiber over stationary rods but only with some damage to the fiber. Fibers sized with GEsVCl from dimethyl formamide solution, even at high sizing levels, gave adhesion equal to the controls.

Increased size levels on the fiber reduced adhesion significantly in all cases but the DMF-applied GEsVCl. Incorporation of small amounts of DER 330 with the char-former sizes restored adhesion.

A simple technique was devised which permits burning of small, unidirectionally-reinforced short beam shear (SBS) samples and collection of the released filaments for examination (Figure 3). Several variations were required before soot-free released filaments were obtained. Initial burn-off of the epoxy resin produces an oxygen-starved flame around the SBS specimen which is the source of the soot. A forced-hot-air laboratory blower was used to provide excess combustion air and enough air velocity to carry filaments away from the specimen. A Meeker burner was used as the combustion source, combined with the blower. The specimen is placed on a wide-mesh screen with the blower and burner beneath the screen, pointed upward. An inverted J-shaped Pyrex tube is placed over the screen to direct the hot-gas and released-filaments up the J. The released filaments were collected at the short, open-end of the J on a small-mesh screen. The screen then served as the carrier for microscopic examination of the collected filaments.

Initial trials with this system used full-sized SBS specimens; these proved to be too large and generated too much soot. Use of thin slices of SBS sample, cut parallel to the fiber axis, provided filament collections which could be microscopically examined. Optical microscope examination indicated the presence of residue on many of the sized combusted samples; however, the resolution and depth of field of the optical microscope was insufficient to resolve the residue satisfactorily.

Scanning electron micrographs of burned slices from SBS specimens have not shown a clear, consistent distinction between treated and untreated fibers (Figures 4, 5, 6, 7, 8). Of the samples examined, the GEs VCl (Figures 6, 7) and GEVCl/VAc/VAl (Figure 8) sized fibers showed evidence of residual material on the burned fibers, but there was no clear evidence of char-bridging. Many fibers appear to be badly oxidized Figures 5, 7, 8); some have a honeycomb-type residual structure (Figure 5). This may be evidence of too much oxygen at the burning interface with the technique used. One interesting feature was the presence in some areas of many of the samples examined of whisker-like structures growing from the fiber surfaces (Figures 5,. 7), implying a highly-carbonaceous combustion environment.

Macrophotograhy appeared to be a more meaningful method of examining the burned fiber bundles. Generally, control samples (no char-former) produced a more disperse fiber collection than samples containing char-former. This is illustrated in Figures 9, 10, 11. More sophisticated methods are necessary, such as the techniques used by NASA, for assessment of the effects of the char-forming sizes.

One interesting phenomenon was observed in two burns of full size SBS samples. The sample was held in the flame long enough to burn off the resin during which the outer layers of fibers "fluffed" to form an insulating layer. The inner core of the sample continued to oxidize at a dull red color (est. 800-900°C) very slowly, even after the burner was removed, and for a considerable length of time - perhaps 5 minutes - before it was extinguished and examined. The hot-core ends had slowly eroded but left no ash or residue, similar to the way charcoal burns. This may offer a relatively innocuous method of disposing of laminate, i.e. not by forced air incineration, but by "charcoal" incineration.

Larger size unidirectional laminates were fabricated for NASA/Langley assessment of the fiber release characteristics of these sizing formulations. Four laminates each 12.3 cm (4-7/8 inch) square by 0.254 cm (0.100 inch) thick and one laminate 30.4 cm (12 inch) square by 0.25 cm (0.1 inch) thick were prepared from control fiber (Type AS4) and each of four sizing iterations for NASA testing, as shown in Table 4.

CONCLUSIONS

Epoxidized char-forming systems have been synthesized which will react with commercially available surface-treated carbon fiber. Fibers modified with these char-formers retained adhesion in a specific epoxy matrix resin. Small-scale combustion testing indicates that using these char-former-modified fibers in laminates will help to reduce the dispersement of fibers resulting from exposure to fire without sacrificing resin-to-fiber adhesion. Larger-scale testing is required to establish the degree of reduction of fiber dispersement due to fire.

REFERENCES

1. "Effects of Moisture on Chemical Interaction at a Polymer-Fiber Interface", Technical Report AFML-TR-77-214, Final Report, December 1977.

2. Beilstein's Handbuch der Organischen Chemie, Vierte Auflage, Drittes and Viertes Erganzungwerk, Die Literatur von 1930 bis 1959 unfassend., Vol. 17/2, Springer-Verlag, Berlin, New York, 1974, pp. 985-1016.

3. S. Evans and H. Marsh, "The Chemistry of Formation of Semi-Cokes from Aromatic Systems Using Mass Spectrometry - I. Carbonization of Single Substances and Mixtures Thereof", Carbon 9, 733-746 (1971).

4. F. H. Winslow, "Carbonization of Polymers", Am. Chem. Soc. Div. Org. Coat. Plast. Chem. Papers, 33 (1), 509-15 (1973).

5. 18-299-0; 20,038-0; and 10,039-9, Aldrich Catalog Handbook of Fine Chemicals, 1978, pp. 857-8.

6. "Kirk-Othmer Encyclopedia of Polymer Technology" Vol. 14, John Wiley, New York, 1971, pp. 573-5.

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Table 1 - Short Beam Shear Strength and
Incineration Response of Control Samples

X21476-Designation	Fiber Type	Number of Samples	Short Beam Shear Strength Average	Variation Coefficient	Incineration Remarks
62-1	AS4	12	103.8 MPa (15,048 psi)	1.22%	Breaks into individual filaments or small bundles
62-2	AS4	13	100.6 MPa (14,592 psi)	1.14%	Same
68-1	AS4 sized with 0.28% DER330	12	102.5 MPa (14,869 psi)	1.55%	Same
68-2	AS4 sized with 0.28% DER330	14	103.7 MPa (15,041 psi)	2.83%	Same
XA464-35	AU4	12	90.2 MPa (13,079 psi)	1.31%	Same

Fiber volume = 62%

Resin: 100 pbw DER330
90 pbw Nadic Methyl Anhydride
1.5 pbw N,N-benzyldimethylamine

Table 2 - Sizing Effect on Short Beam Shear Strength and Incineration Response

X21476- Designation	Sizing Composition	Short Beam Shear Strength MPa	(psi)	Cv (%)	Incineration Remarks
-69	0.1% GEPCP 0.1% DER330 MeCL$_2$	104.6	(15163)	2.30	Mostly Large Bundles
-70	0.05% GEPCP 0.15% DER330 MeCL$_2$	106.0	(15376)	1.62	Not Tested
-71	0.15% GEPCP 0.05% DER330 MeCL$_2$	101.7	(14749)	1.26	" " "
-72	0.1% GEPCP 0.1% DER330 0.0082 gm BDMA MeCL$_2$	104.0	(15078)	1.28	Not tested
-73-1	0.5% GEPCP MeCL$_2$	101.3	(14689)	1.63	Mostly large bundles
-74	0.2% VC/VAC MeCL$_2$	102.9	(14922)	1.51	Not tested
-75	0.5% GEPCP Perclene	99.6	(14435)	1.33	Mostly large bundles
-76	0.25% GEPCP 0.25% DER330 Perlene	106.2	(15404)	1.19	Not tested
-77	0.07% GEs VCL/VAC 0.13% DER330 Chlorobenzene	104.4	(15133)	0.73	Not tested

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Table 2 - Sizing Effect on Short Beam Shear Strength and Incineration Response - Continued

X21476-Designation	Sizing Composition	Short Beam Shear Strength MPa (psi)		Cv (%)	Incineration Remarks
X21476-78	0.2% GEs VCL Chlorobenzene	98.7	(14315)	1.17	Mostly large bundles
-79	0.1% GEs VCL VAC 0.1% DER330 Chlorobenzene	98.5	(14277)	1.13	Not tested
-80	0.13% GEs VCL VAC 0.07% DER330 Chlorobenzene	100.8	(14609)	1.30	Not tested
-81	0.5% AGE/HCCPD Perclene	99.5	(14421)	1.29	Mostly large bundles
-83	0.25% AGE/HCCPD 0.25% DER330 Perclene	104.4	(15139)	1.08	Not tested
-92	0.2% GEs VCL VAC DMF	105.1	(15234)	1.26	Not tested
-96	0.4% GEs VCL VAC Chlorobenzene	97.7	(14161)	1.44	Mostly Large Bundles
-98	0.4% GEs VCL VAC DMF	105.7	(15325)	1.59	Mostly Large Bundles
X22453-31	1.5% GEPCP Perclene	95.3	(13822)	1.51	Mostly Large Bundles
-32	1.5% AGE/HCCPD Chlorobenzene	100.1	(14509)	1.42	Mostly Large Bundles

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Table 2 - Sizing Effect on Short Beam Shear Strength and Incineration Response - Continued

X21476-Designation	Sizing Composition	Short Beam Shear Strength MPa	(psi)	Cv (%)	Incineration Remarks
X22453-33	1.0% AGE/HCCPD Perclene	100.1	(14509)	1.74	Came over in one piece
-34	1.5% GEs VCL DMF	104.1	(15098)	2.06	" " " "
-61	1.5% (75GEPCP/25 DER330) Perclene	104.8	(15194)	0.93	" " " "
-62	1.5% (75AGEHCCPD/25-330) Chlorobenzene	103.1	(14953)	1.00	" " " "
-63	1.5% (75 GEs VCL/25-330) DMF	105.8	(15345)	1.85	" " " "
XA464-49	1% PVC; 1% DER330 MeCL2	109.7	(15906)	1.00	Mostly one piece
-50	1% PVC; 0.5% DER330	111.9	(16219)	1.07	. " "

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Designation	Elements	Relative Atomic %					Size Composition	% Extractable
		C	O	N	Cl*	Na		
X22024-81-1		82.8	9.6	4.3	0.7	2.7	25/75 GEPCP/330	0.22%
-81-2		81.8	10.0	5.3	0.6	2.3	50/50 "	0.14%
-81-2		79.2	9.6	6.4	0.9	3.9	75/25 "	0.01%
-81-4		81.2	9.2	6.1	0.7	2.9	25/75 + BDMA	0.11%
-85-2		76.1	8.8	5.9	1.9	7.3	90/10	0.16%
-86-1		70.6	7.8	3.2	7.0	11.5	100% GEsVCl	0.52%

Note: Binding energies for Cl are consistent with reference data for aromatic ring chlorine (81 to 85) and vinyl chloride (86-1). Ref. Handbook of X-Ray Photoelectron Spectroscopy, Physical Electronic Div. of Perkin-Elmer.

Table 4 - Laminates Prepared for NASA Testing

Fiber Type	Sizing Composition	Designation of 4-7/8 inch Laminates	Designation of 12-inch Laminate
AS4	None (Control)	XA464-60, 61, 67, 69	XA464-85
AS4	1.5% AGE/HCCPD in perchloroethylene	XA464-63, 64, 65, 68	XA464-89
AS4	1.5% GE VCl/VA$_C$/VA1 in dimethylformamide	XA464-75, 76, 77, 78	XA464-90
AS4	1.5% GEPCP in perchloroethylene	XA464-71, 72, 73, 74	XA464-87
AS4	0.7% PVC (Stauffer Chem. Co.) type SLL-OH-1 0.7% GEPCP in methylene chloride	XA646-79, 80, 81, 82	XA464-86

Figure 1 - Anticipated Fiber Surface Modification and Char Formation

Figure 1 - Anticipated Fiber Surface Modification and Char Formation

VACUUM   DEGASSED
                RESIN

FIBER WRAPPED
ONTO RACK

RACK LOADED INTO
MOLD CAVITY

ADD MOLD
ENDS

IMPREGNATE
UNDER VACUUM

PRESS CURE

CUT & TEST

CLOSE MOLD
(ATMOSPHERIC PRESSURE)
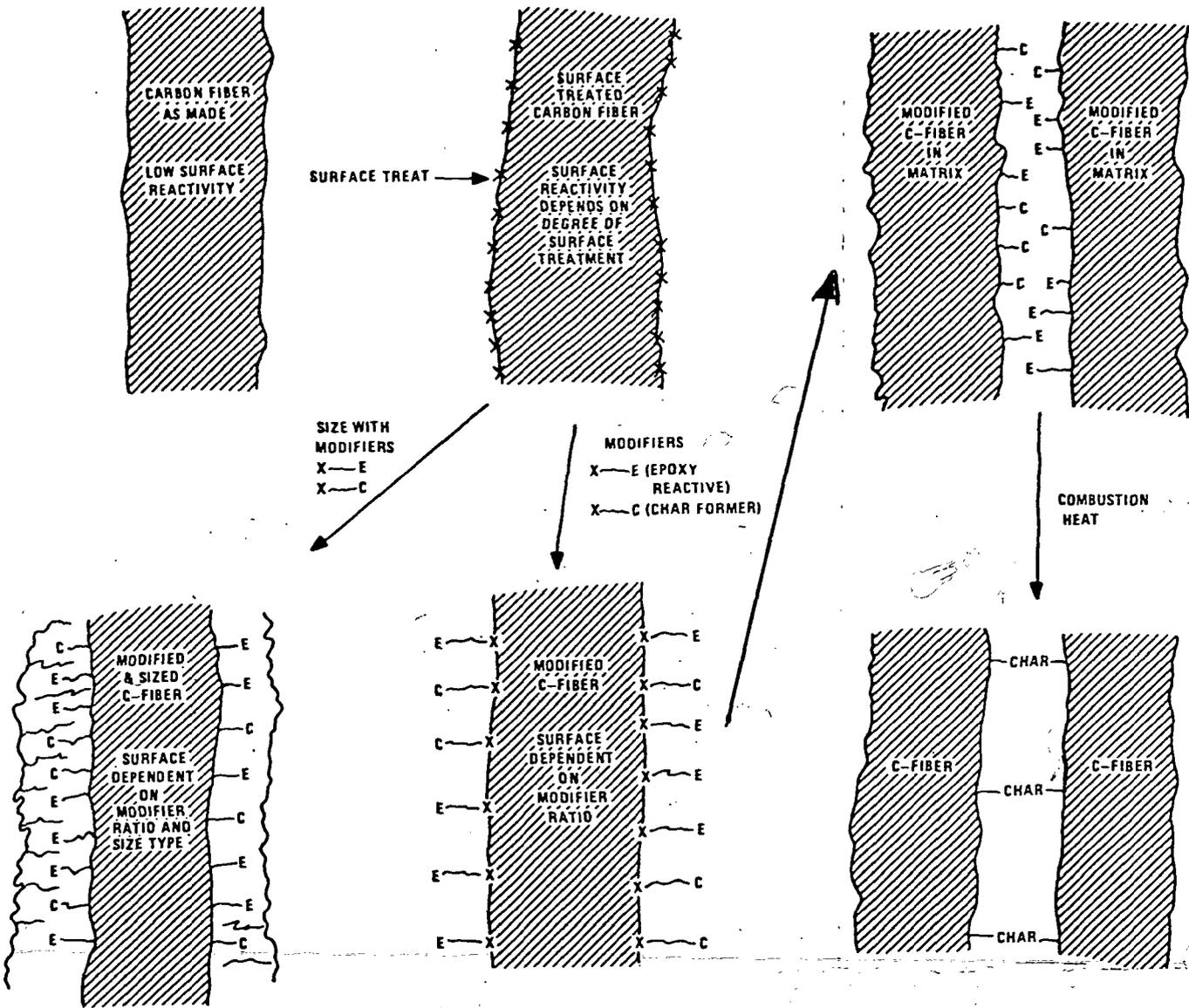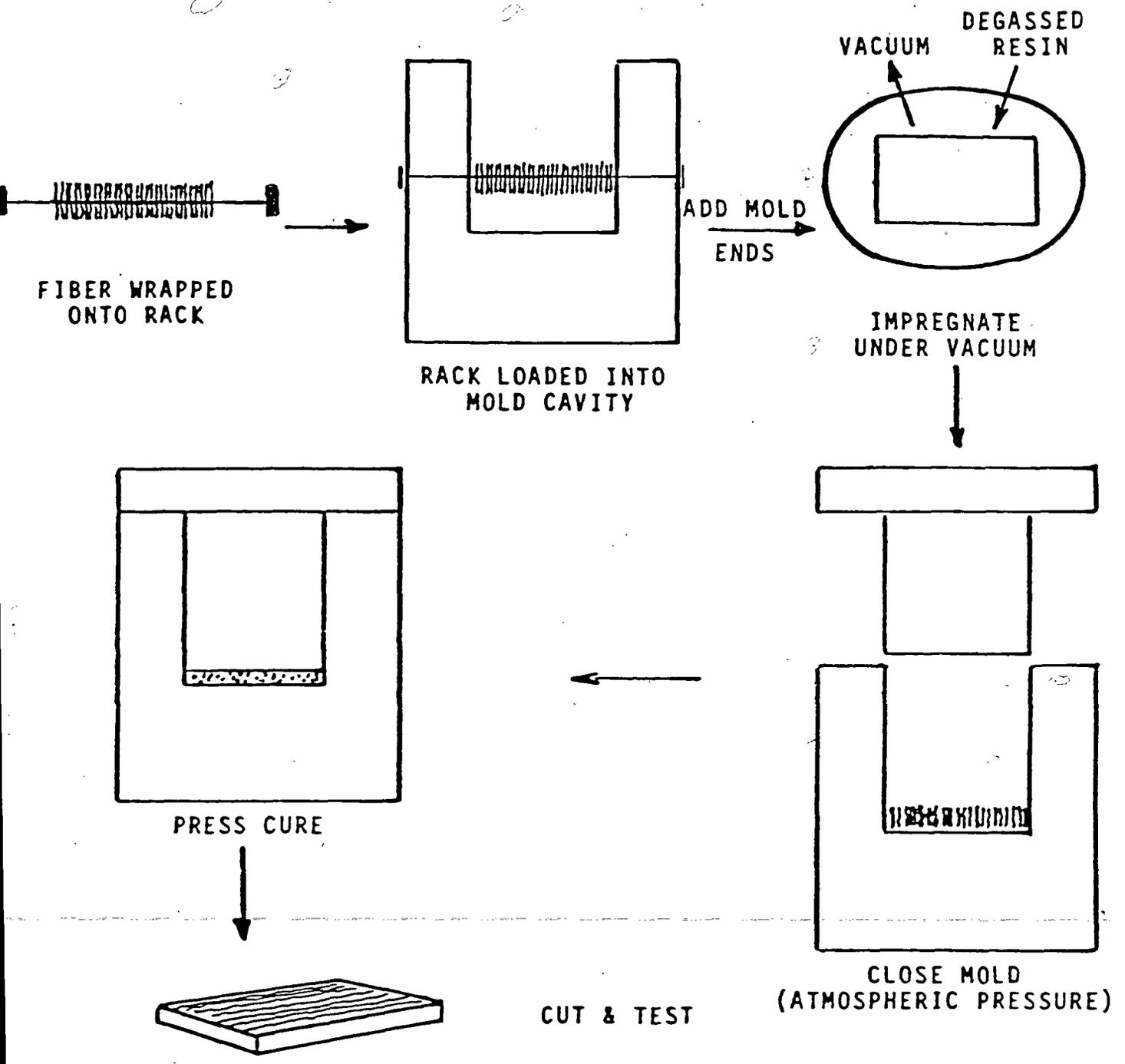
Figure 2 - Composite Laminate Preparation Method
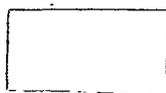
Figure 3 - Schematic of Sample Burning Jig

PYREX
INVERTED
"J"

COLLECTION
SCREEN

SAMPLE

LARGE MESH
SCREEN

HOT
AIR

MEEKER
BURNER

HOT
AIR
BLOWER

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA CR159357		

4. Title and Subtitle	5. Report Date
Graphite Fiber Surface Treatment to Improve Char Retention and Increase Fiber Clumping.	November 1980
	6. Performing Organization Code

7. Author(s)	8. Performing Organization Report No.
J. T. Paul, Jr. and W. E. Weldy	
	10. Work Unit No.

9. Performing Organization Name and Address	11. Contract or Grant No.
Hercules Incorporated Research Center Wilmington, Delaware 19899	NAS 1-15869
	13. Type of Report and Period Covered

12. Sponsoring Agency Name and Address	13. Type of Report and Period Covered
National Aeronautics and Space Administration Washington, D.C. 20546	Contractor Report
	14. Sponsoring Agency Code

15. Supplementary Notes

Langley technical monitor: Mr. Claude Pittman
Final Report

16. Abstract Composites containing carbon and graphite fibers can release fibers into the atmosphere during a fire. This release can potentially cause failure in some types of electrical equipment. Reduced fiber dispersion during and after combustion will reduce risks.

Epoxidized char-forming systems have been synthesized which will react with commercially available surface-treated carbon fiber. Fibers modified with these char-formers retained adhesion in a specific epoxy matrix resin. Small-scale combustion testing indicates that using these char-former-modified fibers in laminates will help to reduce the dispersement of fibers resulting from exposure to fire without sacrificing resin-to-fiber adhesion.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Carbon Fiber Surface Modification Laminate Fire Dispersion	Unclassified - Unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	29	

N-305   For sale by the National Technical Information Service, Springfield. Virginia 22161

7 photos

Figure 4 - SEM of Burned DER 330-Sized Sample Showing Typical Fiber Oxidation
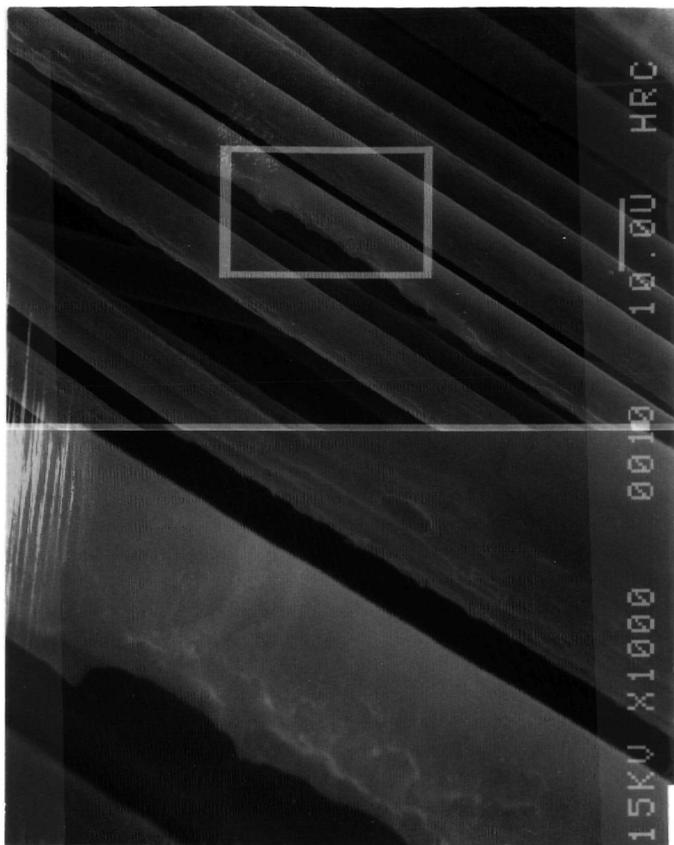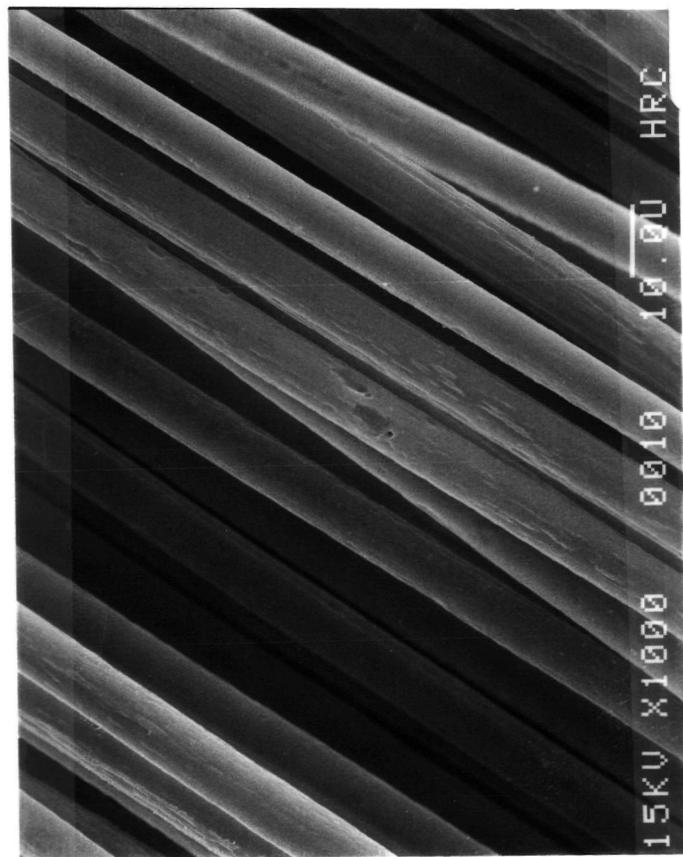

— 0.2% DER330/MeCl$_2$
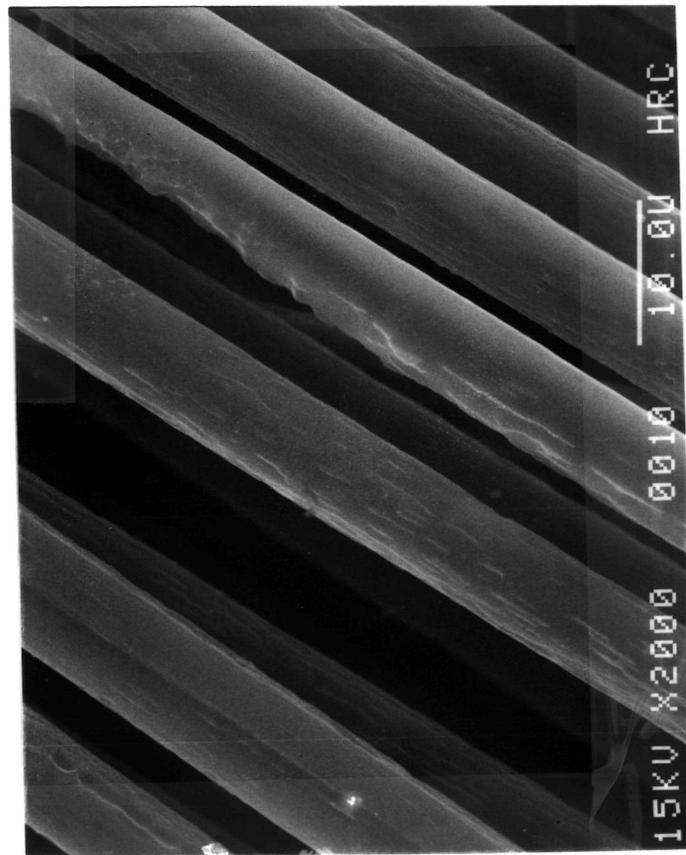
Figure 5 - SEM of Burned DER330 - Sized Sample Showing "Honeycomb" Structure and "Whiskers"
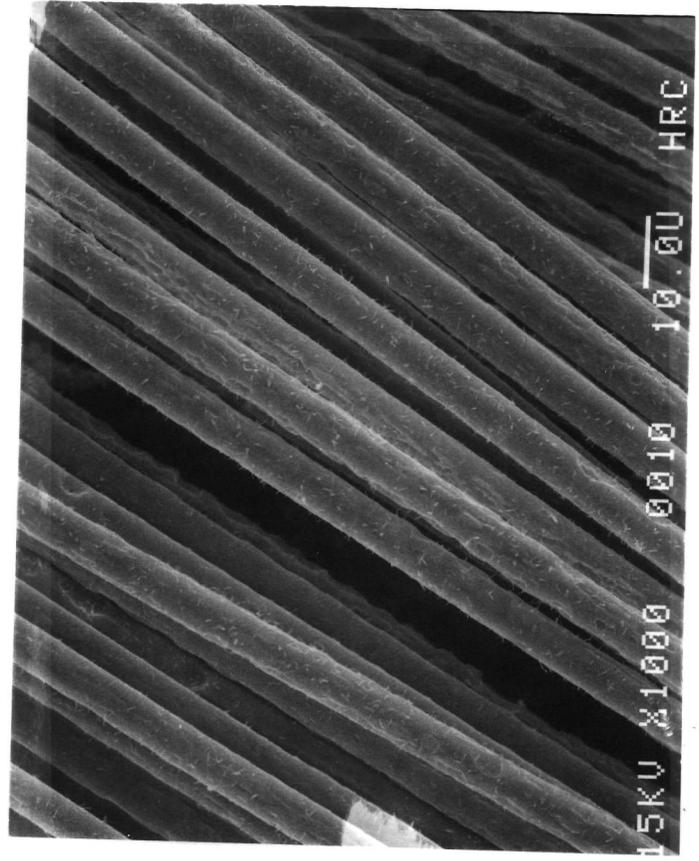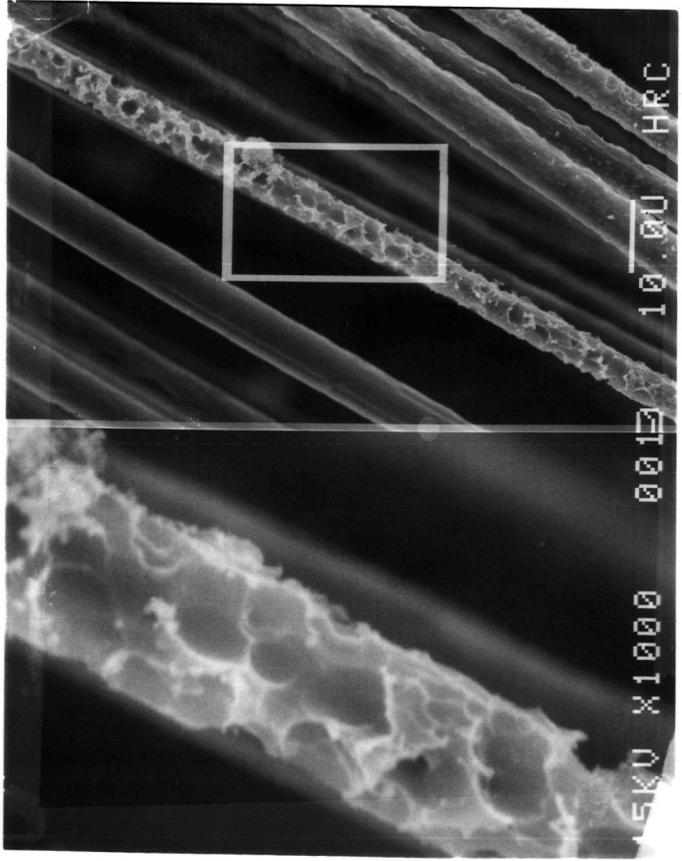
0.2% DER 330/MeCl₂
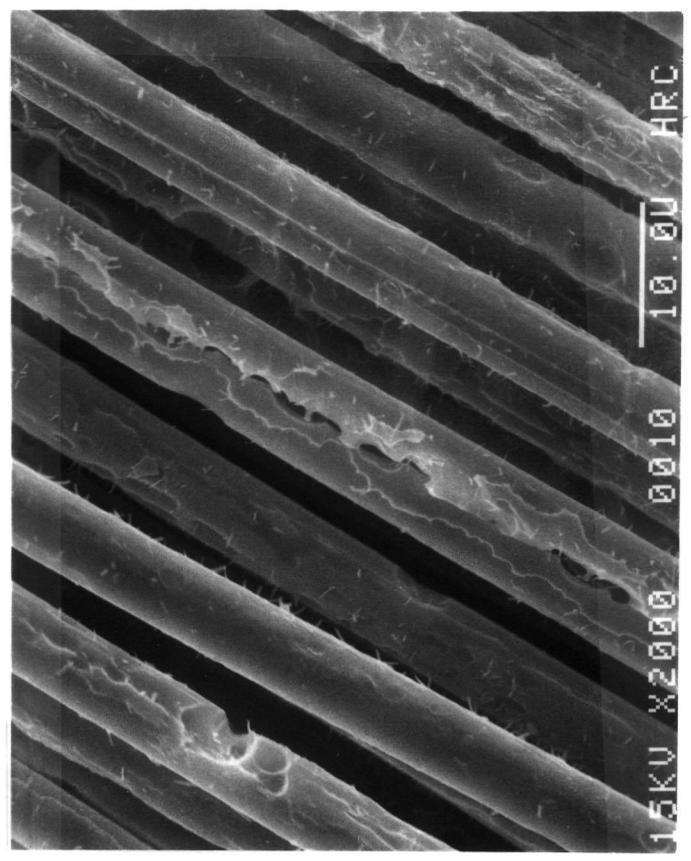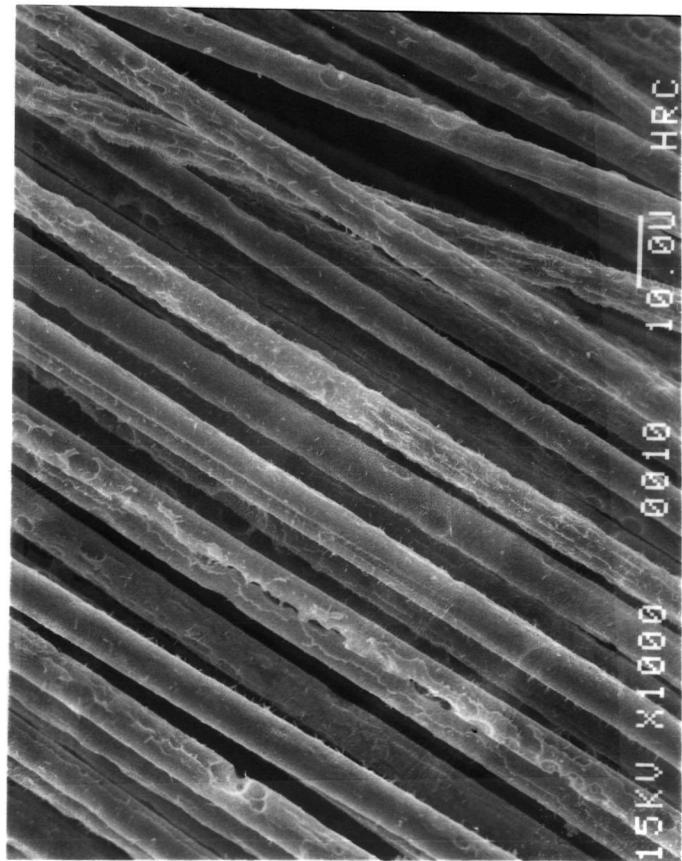
Figure 6 – SEM of Burned GEsVC1 – Sized Sample Showing Residue
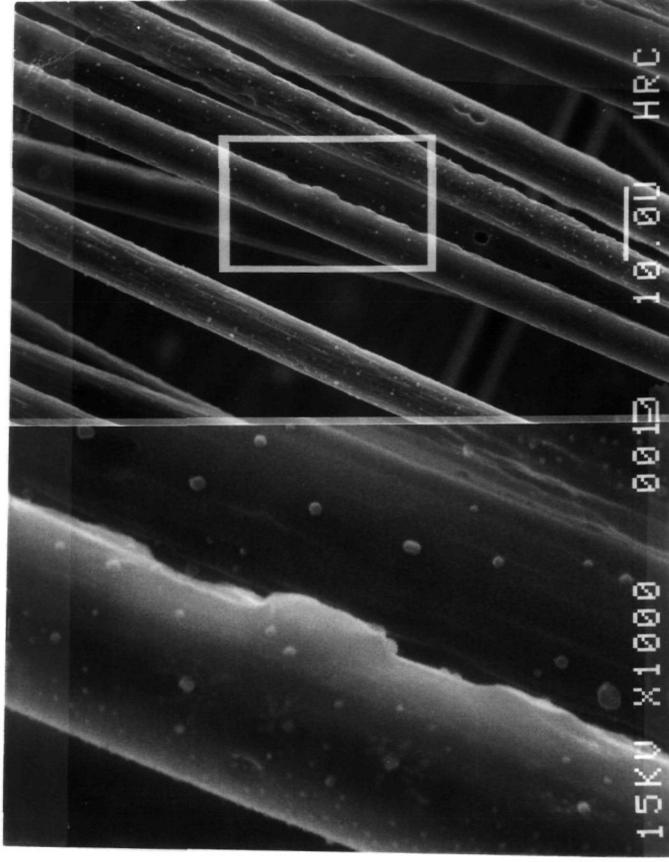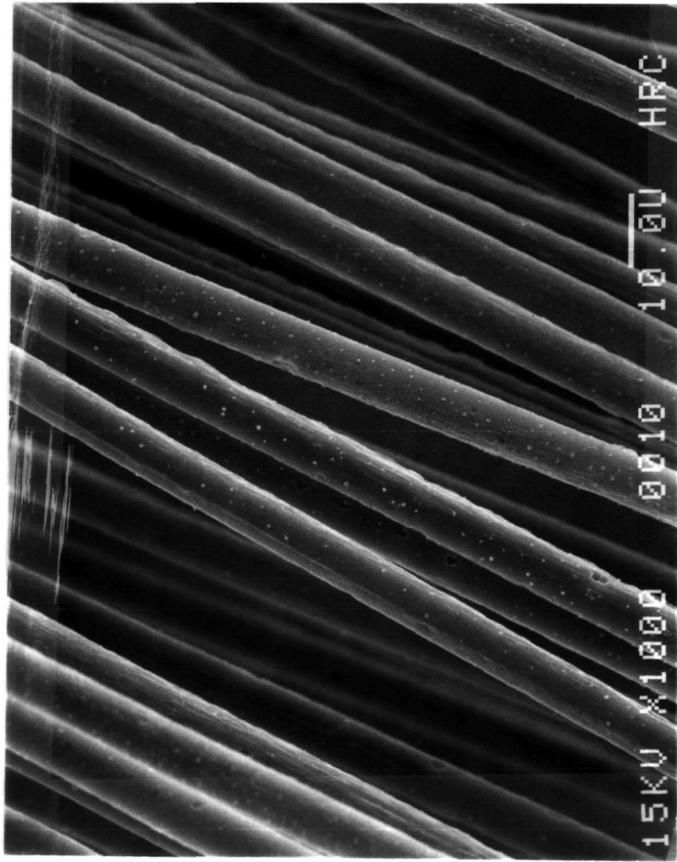
0.2% GEsVC1 in Chlorobenzene
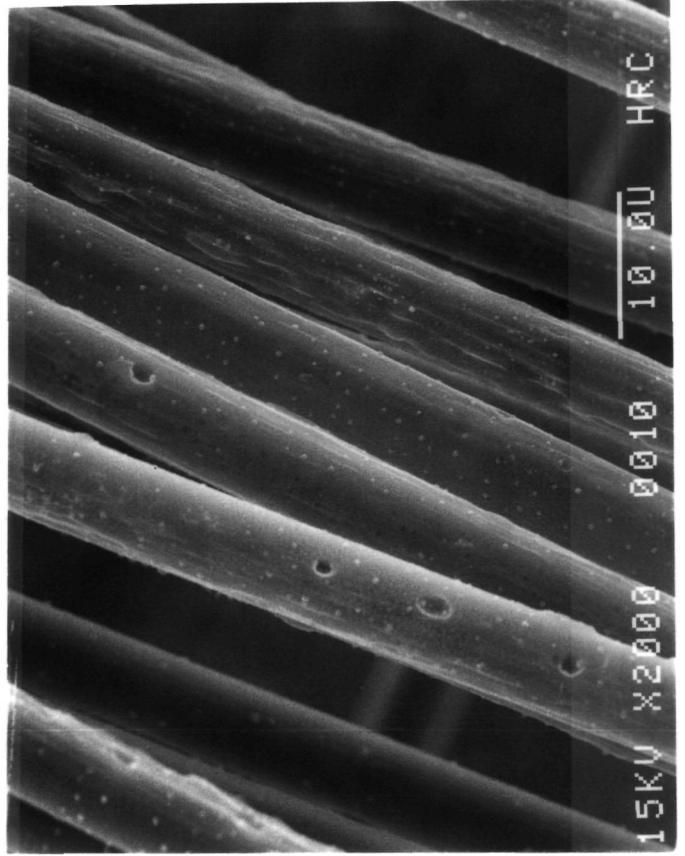
Figure 7 - SEM of Burned GEsVC1 - Sized Sample
Showing Fiber Oxidation, Residue, and Whiskers
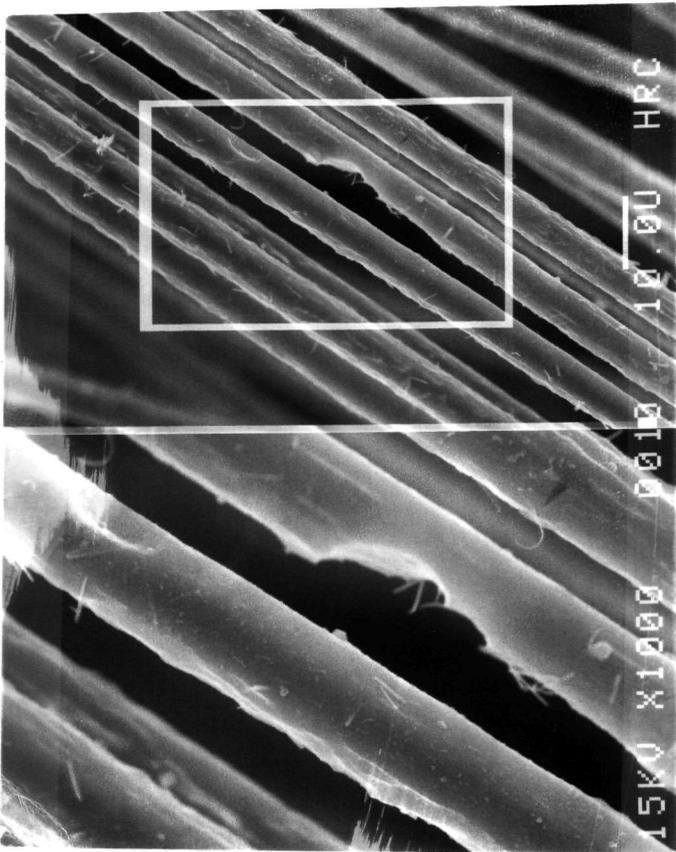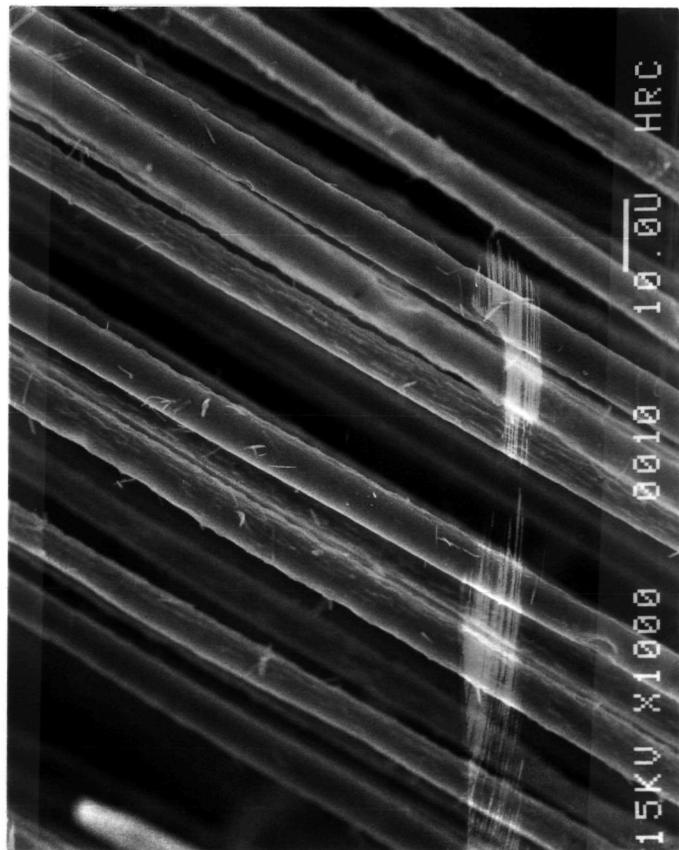
o.2% GEsVC1 in Chlorobenzene
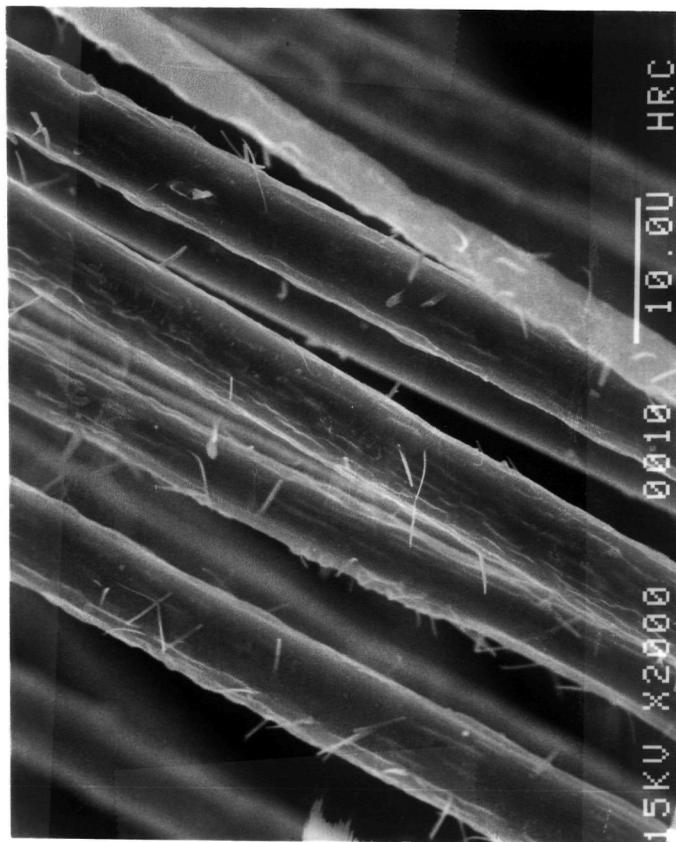
Figure 8 — SEM of Burned GEVC1/VAc/VA1 — Sized Samples Showing Residue
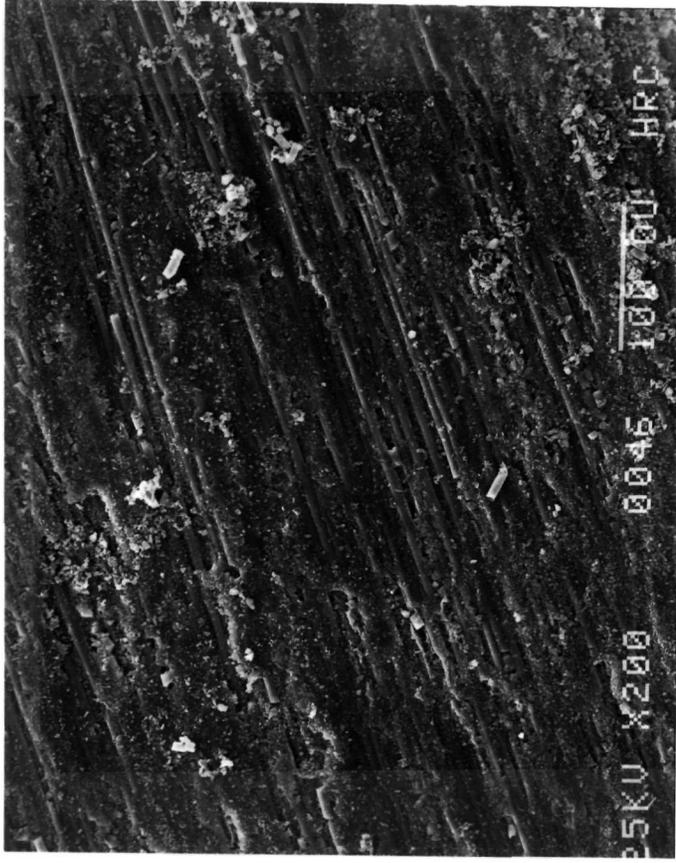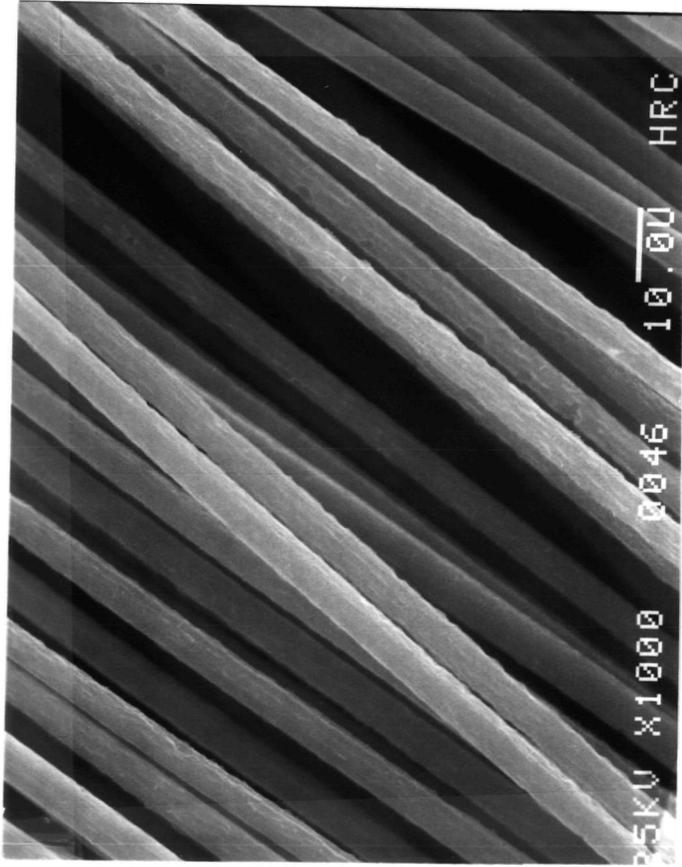
0.4% GEVC1/VAc/VA1 in DMF
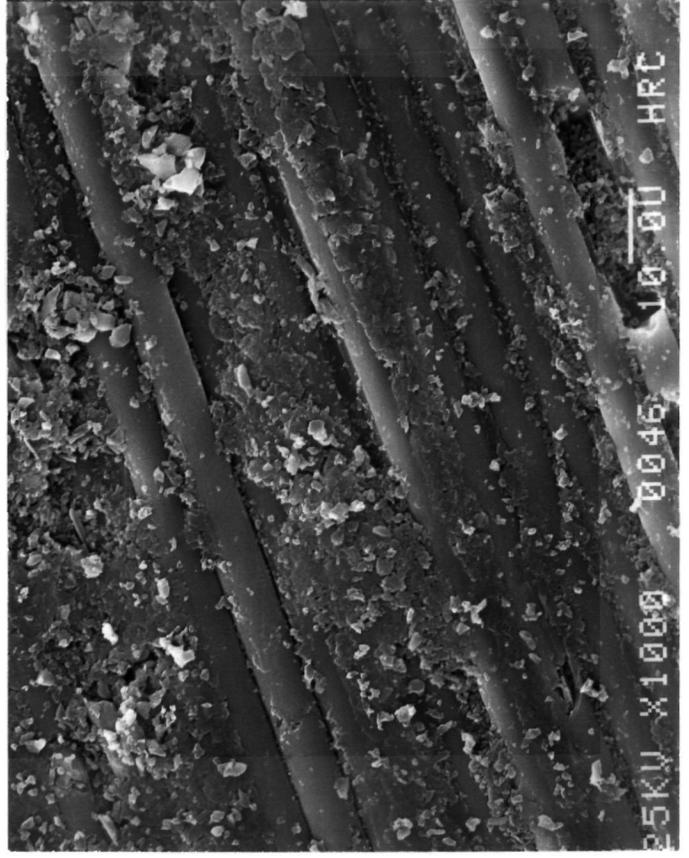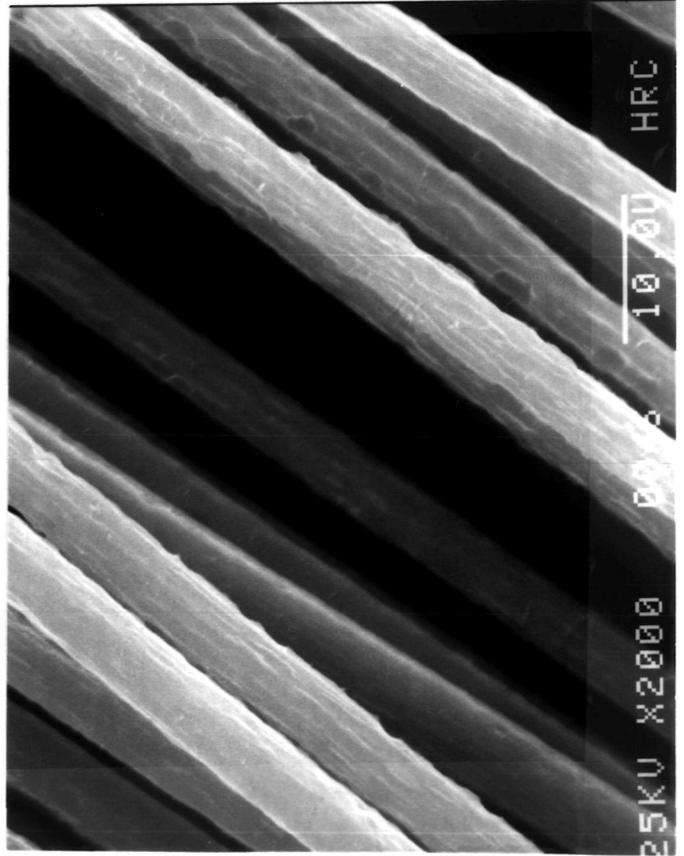
Figure 9 – Macrophotographs of Burned Fiber Bundles
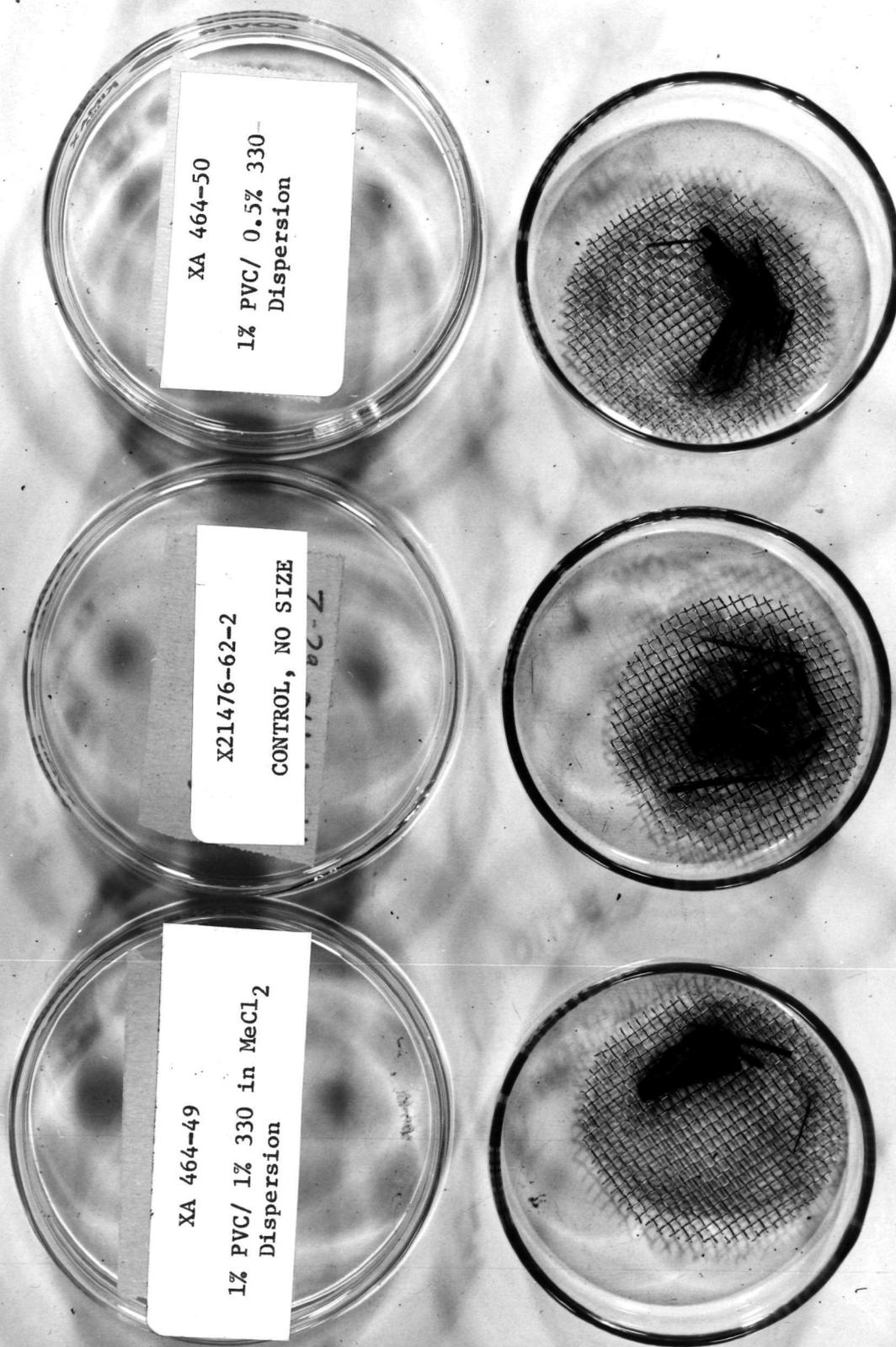
Figures 10 - Macrophotographs of Burned Fiber Bundles

S.S.

X22453-63

1.5%(75 GEsVC1/25 330) in Dimethyl formamide

CONTROL # 2

X21476-62-2 NO SIZE

X22453-61

1.5%(75 GEPCP/25 330) in PERCLENE

CONTROL #1

X21476-62-2 NO SIZE
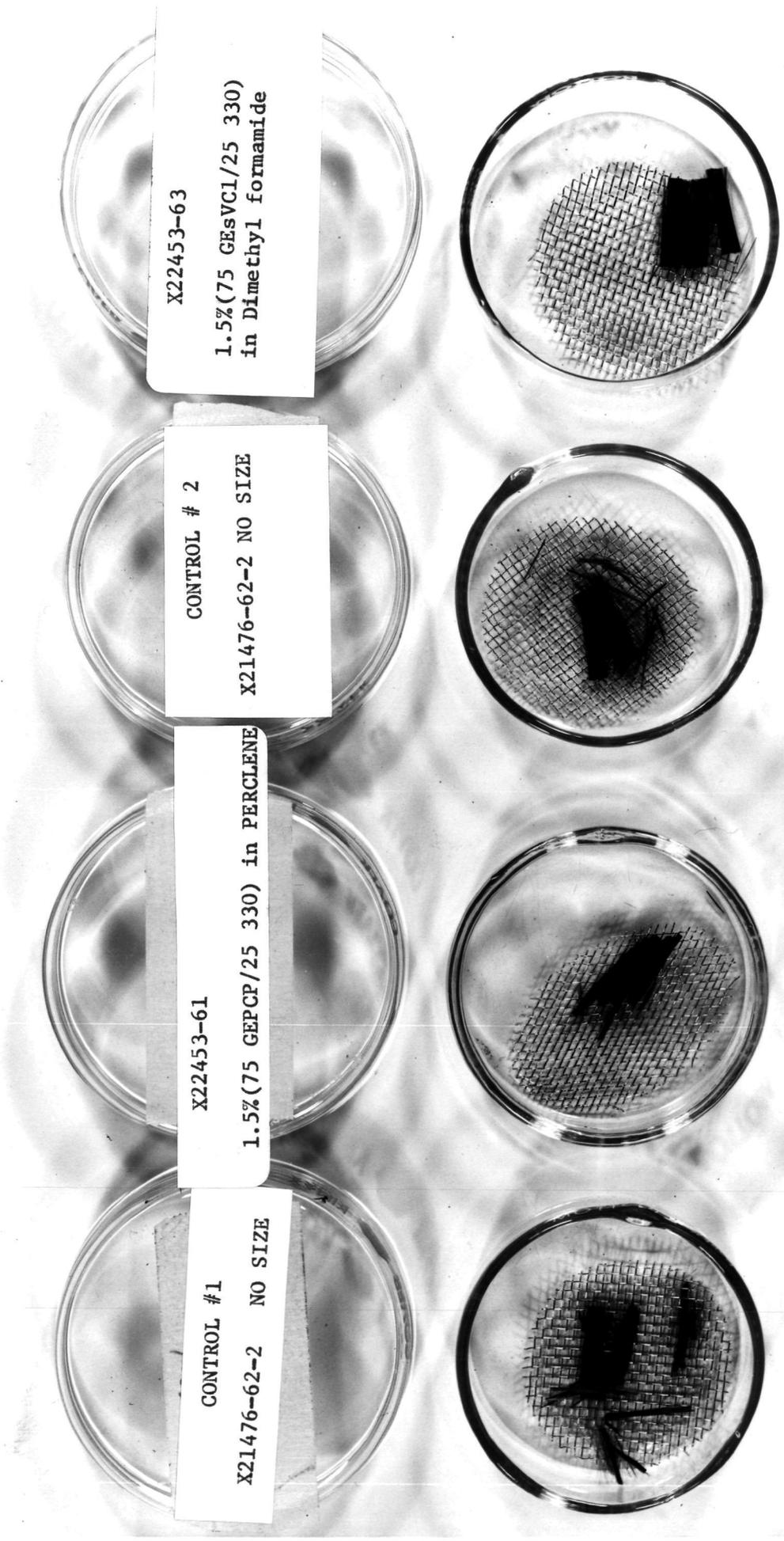
Figure 11 – Macrophotographs of Burned Fiber Bundles

The following labels appear in the photograph:

- X22453-34 — 1.5% Soln. GEsVCl in DMF
- X21476-62-2 — CONTROL, NO SIZE
- X22453-33 — 1.5% Soln. AGE/HCCPD
- X21476-62-2 — CONTROL, NO SIZE