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Structure-Processing-Property Relationships at the Fiber-Matrix Interface in Electron-Beam Cured Composite Materials

Christopher J. Janke
Engineering Technology Division
Oak Ridge National Laboratory

November 1998

OAK RIDGE NATIONAL LABORATORY

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Prepared by the
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-8048

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EXECUTIVE SUMMARY

The objective of this project was to characterize the properties of the resin and the fiber-resin interface in electron beam cured materials by evaluating several structural and processing parameters. The Oak Ridge National Laboratory (ORNL) has recently determined that the interlaminar shear strength properties of electron beam cured composites were 19 - 28% lower than for autoclave cured composites. Low interlaminar shear strength is widely acknowledged as the key barrier to the successful acceptance and implementation of electron beam cured composites in industry.

In this project we found that simple resin modification and process improvements are unlikely to substantially improve the interlaminar shear strength properties of electron beam cured composites. However, sizings and coatings were shown to improve these properties and there appears to be significant potential for further improvement. In this work we determined that the application of epoxy-based, electron beam compatible sizings or coatings onto surface-treated, unsized carbon fibers improved the composite interlaminar shear strength by as much as 55% compared to composites fabricated from surface-treated, unsized carbon fibers and 11% compared to composites made from surface-treated, GP sized carbon fibers.

This work has identified many promising pathways for increasing the interlaminar shear strength of electron beam cured composites. As a result of these promising developments we have recently submitted a U.S. Department of Energy-Energy Research (DOE-ER) sponsored Laboratory Technical Research-Cooperative Research and Development Agreement (LTR-CRADA) proposal entitled, "Interfacial Properties of Electron Beam Cured Composites", to continue this work. If funded, ORNL will lead a 3-year, $2.6 million effort involving eight industrial partners, NASA-Langley, and the U.S. Air Force. The principal objective of this CRADA is to significantly improve the interfacial properties of carbon-fiber-reinforced composites beyond the current state-of-the art electron beam cured composites for use in several DOE, DoD, and industrial applications. In addition, several papers from this Laboratory Director's Research and Development (LDRD) project will be submitted to the Society for the Advancement of Materials and Process Engineering for oral presentations and publications.

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1. OBJECTIVE

The objective of this LDRD project was to characterize the properties of the matrix and the fiber-matrix interface in electron beam cured materials by evaluating several structural and processing parameters.

The recently completed DOE sponsored CRADA on "Electron Beam Curing of Polymer Matrix Composites" determined that the interlaminar shear strength is about 19 – 28% lower in electron beam cured composites versus thermally cured composites. Low interlaminar shear strength is widely acknowledged as a key barrier to the industrial acceptance and implementation of electron beam cured composites. Funding from the LDRD program was provided at the direction of ORNL Associate Director R. G. Gilliland to characterize the technical issues and assess technical and programmatic resources required to overcome these challenges.

There are significant advantages to be gained in electron beam processing of composite materials if the fiber-matrix interphase properties, particularly fiber-matrix adhesion, can be improved to the level attainable in thermally processed composite materials. There are strong indications that the interactions that take place between a carbon fiber surface and a polymeric matrix under electron beam curing conditions may influence the chemistry and dynamics of interphase formation to produce a lower level of adhesion than is achievable in thermally cured systems. This unfavorable interaction may be the cause for the mechanical properties of the resulting composites to be lower than some thermally cured composites.

The primary objective of this project is to evaluate several structural and processing variables which may affect the properties of the fiber-matrix interface. These variables include: initiator concentration; cure dose; dose per pass; carbon fiber type; carbon fiber surface treatment; carbon fiber sizings; as well as various epoxy coatings; and various epoxy coating thicknesses applied onto carbon fibers. It is hoped that by studying how the structure and processing parameters affect the fiber-matrix properties of electron beam cured composites one can improve the interfacial properties.

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2. TECHNICAL BACKGROUND

Electron beam curing is a nonthermal curing method that uses radiation from an energetic electron beam to effect polymerization and crosslinking reactions in radiation sensitive polymers. The advantages over conventional curing methods are lower cost and improved performance resulting from significantly shorter and simpler cure cycles; reduced energy consumption; lower residual thermal stresses; reduced volatile toxic by-products; simpler, less expensive tooling; and improved resin stability.

For the past three years, ORNL's Engineering Technology Division (ETD) has led a CRADA to better understand and utilize electron beam curing for polymer matrix composite materials. The primary objective was to develop new and/or modify existing electron beam curable resin systems for use in aerospace composite structures. ETD developed new electron beam curable epoxy resins with properties far surpassing the previous benchmarks and established ORNL as a world leader in electron beam curable materials development. The developers of these resin systems were recognized with a 1997 R&D 100 Award. Patent applications on these materials have been filed and issued, and three licenses have been granted. Licensees' marketing forecasts projected hundreds of millions of dollars in sales by the year 2000.

There is much yet to be learned about electron beam curable composites, specifically identifying the primary mechanisms or structures that produce the observed engineering properties. At this time, the most pressing need is to understand the properties that are dominated by the fiber-matrix interface. The determination of chemical/morphological structures at the fiber-matrix interface, with correlation to engineering properties and processing parameters, is expected to yield new insight into the nature of these materials. Generating this information will be the first step in removing a major barrier to industrial acceptance of these materials, and may stimulate the invention of new or improved electron beam curable composites.

ORNL research on electron beam cured carbon fiber/epoxy composites has documented that interface dependent properties such as composite shear strength are about 19 - 28% lower than those of thermally cured composites of similar formulations [1,2,3,4,5,6,7]. Similar observations have been made in composite systems involving carbon fibers and vinyl ester matrices cured through a free radical mechanism[8]. In addition, it has been shown in earlier work that

nonconventional curing methods such as microwave processing can produce unexpected changes in fiber-matrix adhesion because of preferential energy absorption by the carbon fiber[9]. The result of these interactions can be a reduction in adhesion or a change in the locus of failure from interfacial to matrix dominated.

Epoxy resins used in producing composites are all of the general chemical structure shown in Figure 1, although the number of epoxy groups may exceed two. The R group of the general structure shown in Figure 1 is usually composed of multiple repeating units of the fundamental resin building block. Figure 2 demonstrates the use of repeating units in the diglycidyl ether of bisphenol A (DGEBPA) derived epoxy resin. Within this and similar resins, the epoxides are the reactive functionality which allows for cross-linking and resin curing.

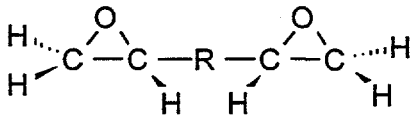


Figure 1. General epoxy resin structure.

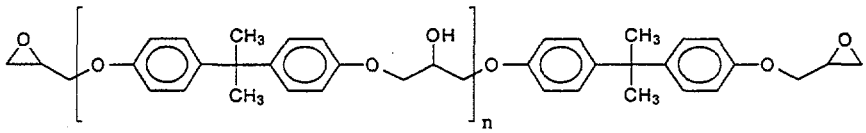


Figure 2. Diglycidyl ether of bisphenol A epoxy. Unlabeled atoms are carbon; all hydrogen atoms are suppressed, except on -OH and CH_3 groups.

Traditional thermal curing of epoxy resins normally proceeds via one of three chemical reaction schemes. These include the amine/epoxide reaction, anhydride/epoxide reaction and Lewis acid-catalyzed epoxide homopolymerization. The amine and anhydride reactions utilize chemical entities (hardeners or cross-linking agents) that will react with epoxides to chemically link the resin components. Additional chemical structures, resident within the amine or anhydride, are introduced into the structure of the cured epoxy. The stoichiometry of the amine (or anhydride) and epoxy resin reaction is dictated by the number of reactive functional groups within each component. In the Lewis acid-catalyzed epoxide homopolymerization, the epoxide groups react to chemically link resin components, thus leading to cured material. The polymerization is induced by the addition of small (non-stoichiometric) amounts of catalysts.

ORNL has recently demonstrated that diaryliodonium and triarylsulfonium salts (cationic initiators) will promote rapid and efficient electron beam induced curing of epoxy resins[7]. Electron beam curable cationic epoxy resin systems do not require a chemical hardener, as do thermally curable epoxies. The exact mechanism of the electron beam induced curing is not known, although a mechanism has been proposed. The proposed mechanism[10], shown in Figure 3, is initiated by the ionization of the epoxide by impinging electrons (reaction A). The radical cation deprotonates (reaction B) and the resulting radical isomerizes (reaction C) to a resonance stabilized structure. The isomerization in reaction C is accompanied by the relief of approximately 112 kJ mol^{-1} of strain energy in the epoxide. The radical can reduce the initiator (reaction D), resulting in a carbocation which can induce polymerization of the epoxide (reaction E). The initiator, diphenyliodonium hexafluoroantimonate in Figure 3, is also proposed to be reduced by solvated electrons generated from the electron beam irradiation (reaction F), eventually leading to a strong protic acid which also polymerizes the epoxide (reaction G).

There is a strong possibility that a chemical interaction is occurring between the carbon fiber surface and the reacting resin under electron beam processing conditions. Successful commercial surface chemical treatments of the carbon fiber etch away the native fiber surface until a structurally sound surface is available. At the same time, the surface concentration of polar chemical groups is increased and the surface microtopography is altered[11]. Surface analysis of intermediate modulus carbon fibers by X-ray Photoelectron Spectroscopy (XPS) has shown that the chemical species added are primarily oxygen (carboxylic acid, carbonyl and phenol) and nitrogen (amino) containing species[12]. Trace elemental ions such as sodium, potassium, sulfur and silicon are also found on the surface but usually in concentrations of 1% or less[13]. In some cases alkali elemental ions (e.g. sodium) in high concentrations ~3% have been shown to be detrimental to composite interfacial durability in high temperature oxygen and high moisture environments[14].

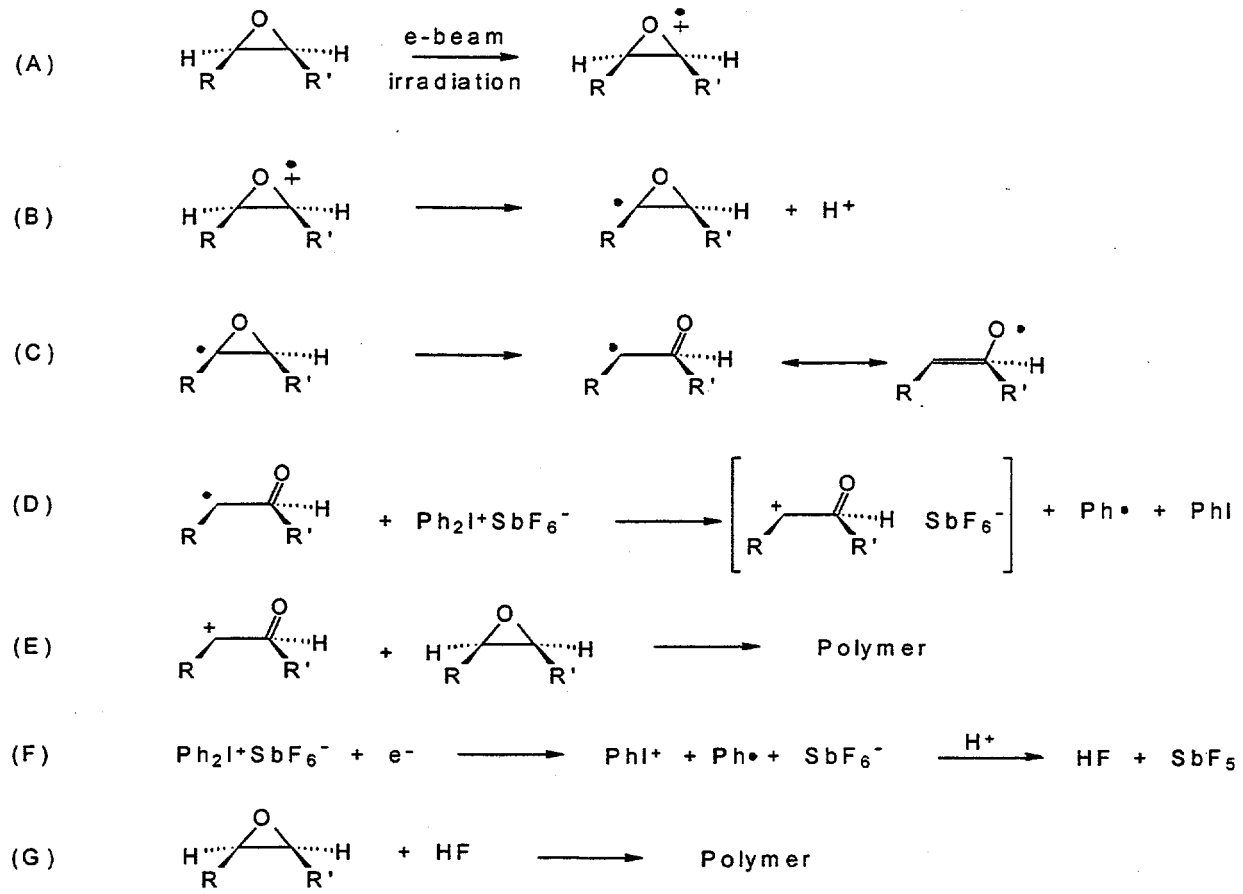


Figure 3. Proposed electron beam induced epoxy homo-polymerization mechanism in the presence of diphenyliodonium hexafluoroantimonate.

During thermal curing, chemical bonding has been found to take place between the epoxy and amine groups of the resin system and the oxygen and nitrogen species present on the fiber surface. The amine group is more reactive than the epoxy. It has been shown that as little as 3% chemical bonding accounts for a 25% increase in interfacial shear strength. The chemical groups increase the thermodynamic surface free energy and hence increase the thermodynamic wettability. Topographical variations with a depth of 5-15 nm and a periodicity of 100 nm are produced on the surface as a result of surface treatment. The increase in surface topography can account for a 25% increase in interfacial shear strength independent of the enhancement as a result of chemical bonding[15].

It is quite probable that there are interactions between the reactive species generated during electron beam curing that have a deleterious effect on the typical physical and chemical interactions that take place at the fiber-matrix interface. For example, in microwave processing[16]

it has been shown that microwave radiation is selectively absorbed by conductive carbon fibers causing reaction and cure to take place at the fiber-matrix interface before curing in the bulk resin[17]. The microwave environment actually causes the carbon fiber surface to exceed the local matrix temperature by as much as 100°C. This has resulted in a 25% increase in adhesion. In the case of carbon fibers and a free radical polymerized vinyl ester matrix, it has been shown that the carbon fiber surface strongly adsorbs the free radical initiators (e.g. cobalt naphthanate). This causes a depletion of these initiators in the matrix within 50 nm of the carbon fiber surface resulting in a lower crosslinked network and hence lower modulus in the interphase. Previous work has shown that the adhesion is dependent on the shear modulus of the matrix[18] in the fiber-matrix interphase region so that this type of phenomena can result in lower fiber-matrix adhesion[19].

It is conceivable that some or all of these mechanisms could be operating at the carbon fiber/epoxy interface under electron beam processing conditions, causing the observed reduction in adhesion. Active nitrogen is a base in the Lewis sense and all the initiators are acids in the Lewis sense. Hence active nitrogen might neutralize the initiators. Similarly, strong anions (Cl^-, Br^-, OH^-) or anionic surfactants will have the same effect on the initiators used in the electron beam curing of epoxy resins. Protons in acids like HPF_6 might be replaced by alkaline materials since these materials are higher in the emf series[20]. Conventional commercial carbon fiber surface treatments are the result of electrolytic anodization of the carbon fiber surface in solutions containing ammonium bicarbonate which produce concentrations of amino type nitrogens on the carbon fiber surface to 5-6%. Alkali ions also have been shown to be present on the carbon fiber surface to the 1-2% level as well[21].

Most carbon fibers are sold after being surface-treated and then coated with a fiber sizing. The application of a thin layer of matrix compatible sizing (~100 nm) to the fiber surface has been shown to have little effect unless the sizing interaction with the matrix creates an interphase with significantly different properties than the bulk matrix[22,23]. Based on fundamental studies with epoxies where the mechanical properties of the interphase were systematically varied while the surface topography and chemistry remained constant, a higher interphase modulus has been shown to be responsible for higher levels of adhesion while a lower modulus interphase lowers the adhesion levels[24]. If the sizing composition is fundamentally the same as the matrix, little

difference will be noted. However, the use of a sizing and/or a coupling agent specifically engineered to mitigate deleterious electron beam processing effects would be a logical solution for improving fiber-matrix adhesion under electron beam processing. Indeed, a difunctional coupling agent has been developed for use with carbon fibers and acrylic matrix composites which relies on the chemical coupling of the isocyanate end group to the carbon fiber surface with the surface hydroxyl group of the fiber and chemical reaction to the acrylic matrix through the unsaturation in the other difunctional coupling agent end group[25].

Fundamental information about these molecular level events which are taking place at the fiber-matrix interphase is not available. It is important to be able to identify and elucidate these mechanisms if the proper interphase is to be designed for the carbon fiber/epoxy composite systems.

3. RESEARCH TASKS

The fiber-matrix interface characterization studies elucidating the structure, processing, and property relationships of electron beam cured cationic epoxy neat resin systems and carbon fiber reinforced composites were conducted by evaluating several structural and electron beam processing parameters. The structural and processing variables which were evaluated in this project include:

1. **Initiator Concentration:** The initiator concentrations for the electron beam curable and thermally curable cationic epoxy resin formulations were 1.0, 1.5, 2.0, 2.5, and 3.0 phr;

2. **Total Electron Beam Cure Dose:** The total electron beam cure doses for curing the cationic epoxy resin formulations were 80, 100, 120, 140, and 160 kGy;

3. **Electron Beam Dose Per Pass:** The electron beam dose per pass was varied among 5, 10, or 20 kGy/pass for curing the electron beam curable cationic epoxy resin formulations;

4. **Carbon Fiber Type:** The types of carbon fibers that were evaluated for the electron beam cured composites included AU4, AS4, IM6, and IM7;

5. **Carbon Fiber Surface Treatment:** The carbon fiber surface treatments that were evaluated ranged from those having no surface treatment to those that underwent significant electrolytic oxidation;

6. **Carbon Fiber Sizings:** The carbon fiber sizings which were used included unsized carbon fiber, GP sized carbon fiber, and C sized carbon fiber;

7. **Epoxy Coatings on Surface-treated and Unsized Carbon Fibers:** The types of epoxy coating materials that were coated onto surface-treated and unsized carbon fibers ranged from high melting point solid epoxy resins to low viscosity epoxies and;

8. **Epoxy Coating Thickness on Carbon Fibers:** The thickness of the epoxy coating materials that were coated onto the surface-treated and unsized carbon were varied by using different

concentrations of epoxy resin solutions ranging from 1% to 10% epoxy (epoxy coating formulations were dissolved in acetone or methyl ethyl ketone).

The effects of these structural and processing parameters on the mechanical and thermal properties of electron beam cured materials were investigated by using several characterization methods including: dynamic mechanical analysis for evaluating changes in glass transition temperature (T_g) and moduli; Iosipescu shear testing for evaluating changes in the shear strength, shear strain, and shear modulus; fiber-matrix interfacial shear strength testing to determine the degree of bonding that exists between carbon fibers and the matrix and; composite interlaminar shear strength testing in which, the carbon fibers were previously coated with one of several different epoxy resin formulations.

3.1. Task 1 - Dynamic Mechanical Analysis Results on Electron Beam Cured and Thermal Cured Cationic Epoxy Neat Resin Systems

3.1.1. Experimental

Several neat resin plaques having nominal dimensions of 5 in. by 8 in. by 0.125 in. were produced by dissolving a specific amount (1.0, 1.5, 2.0, 2.5, and 3.0 phr) of cationic initiator (4-octyloxyphenyl) phenyliodonium hexafluoroantimonate (OPPI), into Dow Tactix 123 epoxy resin, pouring said composition into FEP spray released 6 in. x 9 in. metal molds, followed by electron beam curing at a dose per pass of 5 kGy or 20 kGy to a total electron beam dose of 80, 100, or 140 kGy (see Table 1).

Subsequent to electron beam or thermal cure, the plaques were removed from their molds and machined into Dynamic Mechanical Analysis (DMA) specimens. The DMA tests were used to determine the T_g and flexural modulus values for the electron beam cured and thermally cured specimens. The thermally cured neat resin samples were produced by using the above described materials and molds. These plaques were cured using a conventional thermal cure procedure which included 250°F for 1 hour, then 350°F for 3 hours.

Table 1. Neat Resin Plaques for DMA Specimens. Effects of Initiator Conc., Dose, and Dose/Pass on Resin and Fiber/Matrix Interfacial Properties.

Material: Dow Tactix 123 Epoxy/OPPI Initiator

OPPI Initiator Conc. (Phr)	Dose per Pass: 5 kGy			Dose per pass: 20 kGy			Thermal
	Dose kGy 80	Dose kGy 100	Dose kGy 140	Dose kGy 80	Dose kGy 100	Dose kGy 140	250°F, 1hr. 350°F, 3hr.
1	x	x	x	x	x	x	x
1.5	x	x	x	x	x	x	x
2	x	x	x	x	x	x	x
2.5	x	x	x	x	x	x	x
3	x	x	x	x	x	x	x

3.1.2. Results

The resultant DMA curves for the electron beam cured and thermally cured cationic epoxy neat resin specimens are shown in Figures 4-7. Conclusions resulting from comparing and contrasting the various different electron beam and thermally cured specimens relative to their DMA results include:

1. For the electron beam cured specimens the T_gs, as determined by the peak in the loss modulus values (or by the peak tan delta values), generally increase as the initiator concentration decreases from 3 phr to 1 phr. The peak tan delta T_g values range from about 185°C for an initiator concentration of 3 phr to 210°C for an initiator concentration of 1 phr. However, even though the T_gs are greater for the electron beam cured materials having an initiator concentration of 1 or 1.5, these materials are not as completely cured as those above an initiator concentration of 1.5 phr because of the presence of beta transitions (which generally signify incomplete curing of the polymer) which appear around 100°-150°C in the tan delta curves. Therefore, concentrations above 1.5 phr should be used for achieving a full cure of the material.

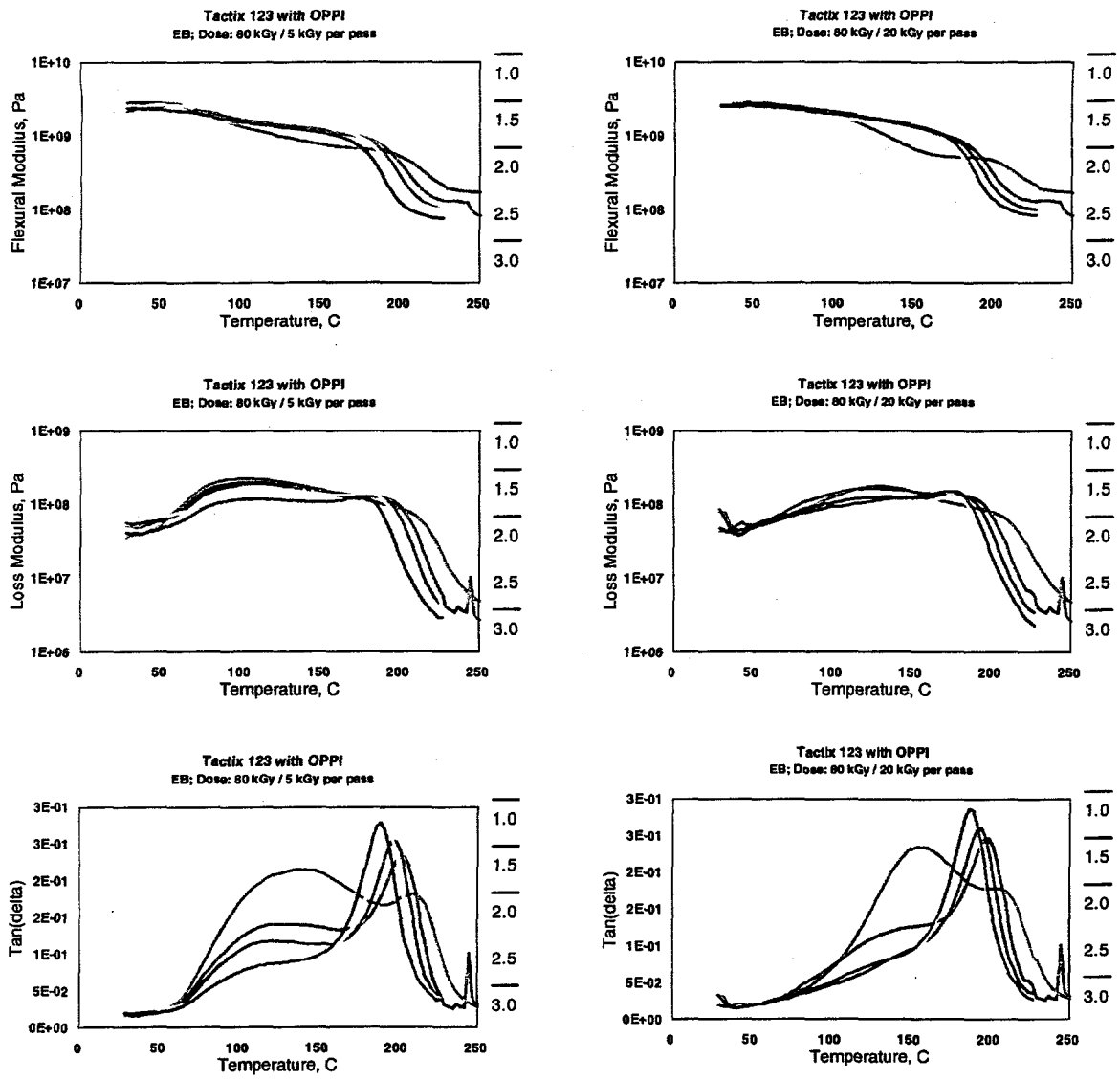


Figure 4. DMA Plots on electron beam cured Tactix 123 with various concentrations of OPPI. Total Dose = 80 kGy; Dose/Pass = 5 or 20 kGy.

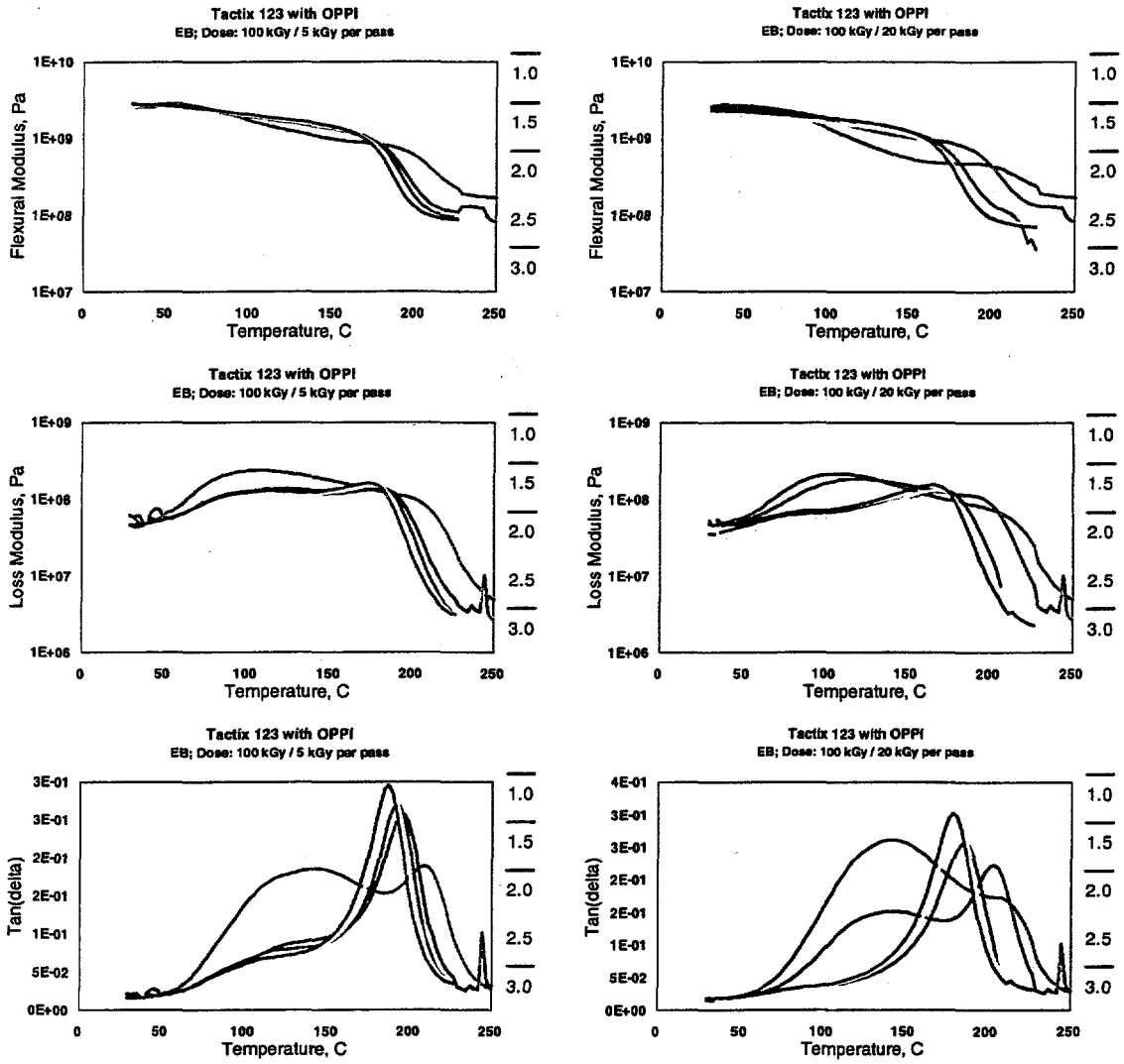


Figure 5. DMA Plots on electron beam cured Tactix 123 with various concentrations of OPPI. Total Dose = 100 kGy; Dose/Pass = 5 or 20 kGy.

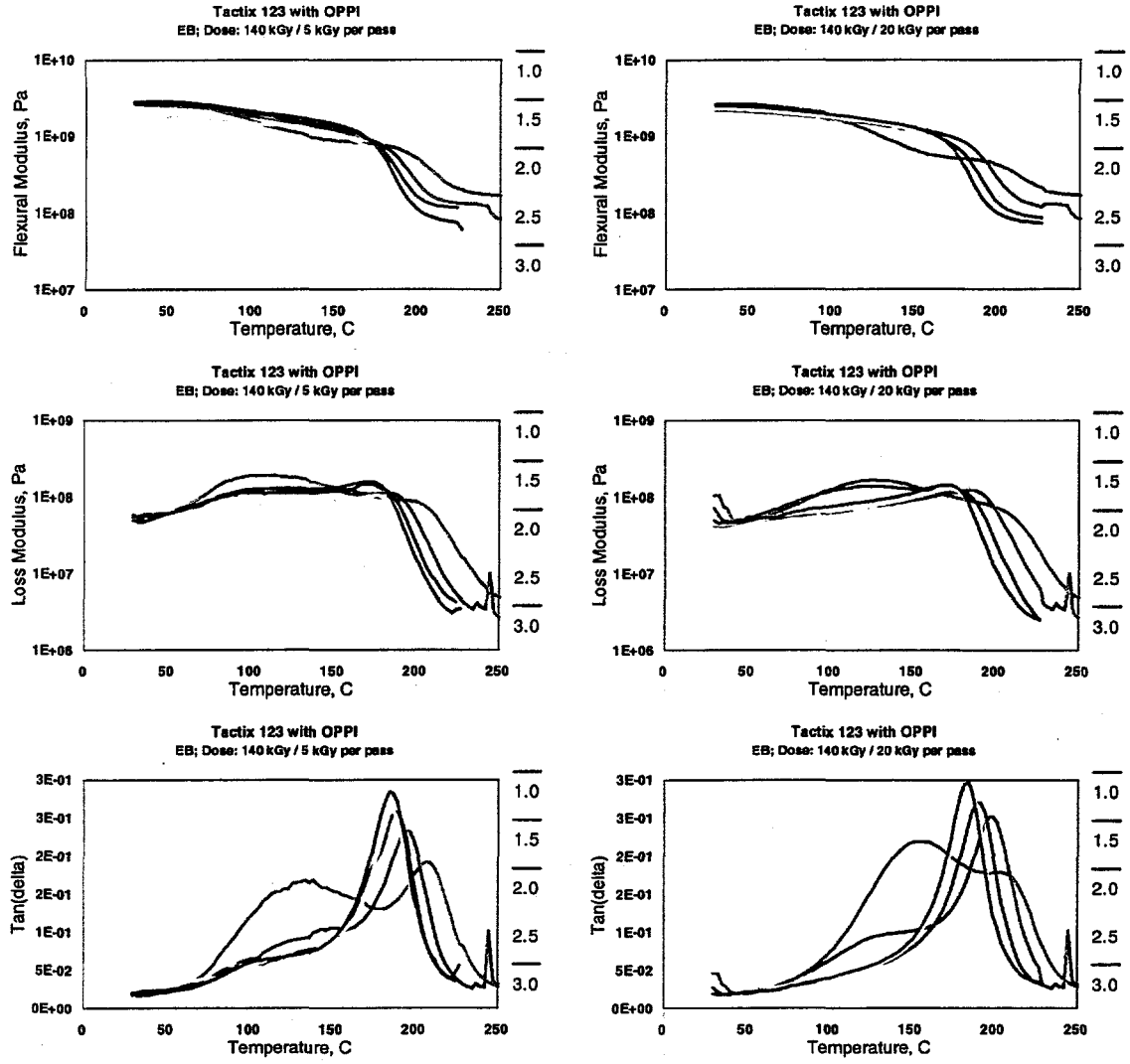


Figure 6. DMA Plots on electron beam cured Tactix 123 with various concentrations of OPPI. Total Dose = 140 kGy; Dose/Pass = 5 or 20 kGy.

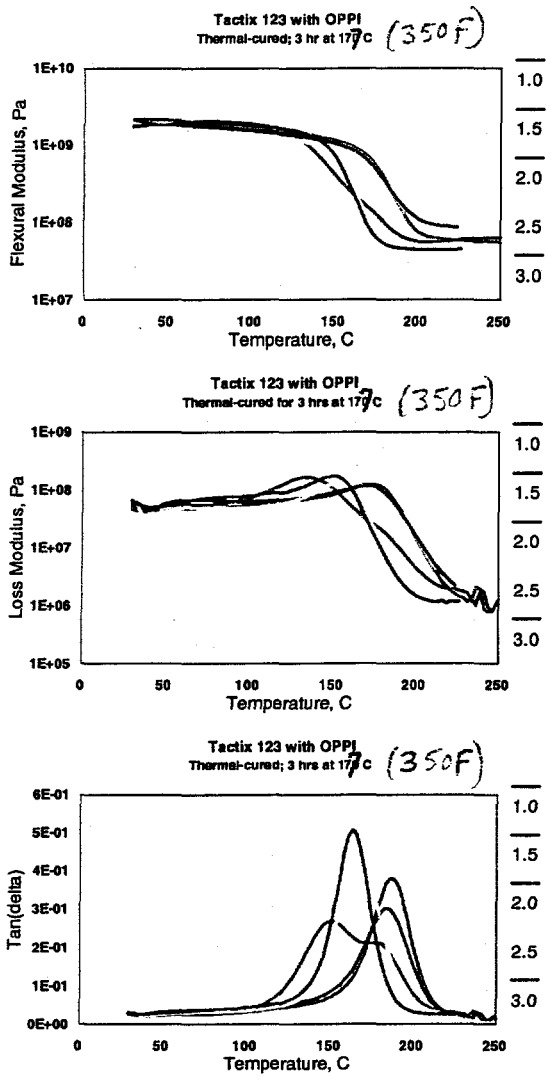


Figure 7. DMA Plots on thermal cured Tactix 123 with various concentration of OPPI.

2. For the thermally cured specimens the T_gs determined by the peak in the loss modulus values (or by the peak tan delta values) generally increase as the initiator concentration decreases from 3 phr to 1 phr. The peak tan delta T_g values range from about 165°C for an initiator concentration of 3 phr to 195°C for an initiator concentration of 1.5 phr. However, the presence of a beta transition in the tan delta curve for the 1 phr initiator concentration material signifies incomplete cure for this polymer and therefore it is not the ideal initiator concentration for fully curing the polymer.

3. The T_gs determined by the peak in the loss modulus values (or by the peak tan delta values) are generally higher by about 20°C, for a given initiator concentration, for the electron beam cured specimens compared to the thermal cured specimens.

4. The presence of beta transitions (which can signify incomplete cure of the polymer) in the electron beam cured materials generally disappear above an initiator concentration of 1.5 phr, a total dose of 80 kGy, and a dose/pass of 5 kGy.

5. There appears to be more efficient electron beam curing taking place at higher doses per pass (20 kGy vs. 5 kGy). This difference, though, becomes less noticeable at higher initiator concentrations and higher total cure doses.

3.2. Task 2 - Iosipescu Shear Results on Electron Beam Cured Cationic Epoxy Neat Resin Systems

3.2.1. Experimental

Previous work on thermally cured composites has shown that the fiber-matrix adhesion properties can be improved by increasing the shear modulus of the matrix in the fiber-matrix interphase region.

As for the DMA testing discussed earlier, three variables were selected for evaluating the effects on the shear properties of electron beam cured resins including: 1). varying the epoxy resin formulation initiator concentration from 1 to 3 phr; 2). varying the total electron beam cure dose from 80 to 100 to 140 kGy and; 3). varying the electron beam dose/pass from 5 kGy/pass to 20 kGy/pass.

Several electron beam cured neat resin plaques were prepared in the same fashion as the DMA specimens discussed earlier. After cure, the plaques were removed from their molds and machined into Iosipescu shear specimens. The specimens were then measured and strain gaged (EA-06-062TV-350 - Measurements Group, Inc.), and tested in accordance with ASTM D5379, - "Shear Properties of Composite Materials by the V-Notched Beam Method", for determining shear strength, shear modulus, and strain-to-failure properties.

3.2.2. Results

Iosipescu shear results on the electron beam cured neat resin samples are tabulated and plotted in Table 2 and Figures 8-10. As seen in Figure 8, the shear modulus values were, in most cases, invariant with respect to the formulation and electron beam processing variables that were evaluated (initiator concentration, total electron beam dose delivered, and the electron beam dose per pass). Therefore, simple resin modifications and process improvements are unlikely to substantially improve the interlaminar shear strength properties of electron beam cured composites. On the other hand, the data for the maximum shear strain and the shear strength shown in Figures 9 and 10 indicates a fair amount of scatter within data sets and appears to be somewhat dependant on the material formulation and on the electron beam processing conditions. The data indicates that both the shear strain and shear strength values are at a maximum for neat resin specimens having an initiator concentration of 1 phr and cured at 100 kGy at either 5 or 20 kGy/pass and for specimens having an initiator concentration of 3 phr and cured at 80 kGy at either 5 or 20 kGy/pass. These values reached a maximum of 61000 microstrain and about 8200 psi shear strength. The strain and strength data for the other sets of specimens was generally below about 20000 microstrain and about 4000 psi, respectively.

3.3. Task 3 - Interfacial Shear Strength Results on Electron Beam Cured Composites (Via Interfacial Testing System Method)

3.3.1. Experimental

Characterizing the structure-processing-property relationships at the fiber-matrix interface in electron beam cured composites was conducted by evaluating the interfacial shear strength (IFSS) of electron beam cured, carbon fiber reinforced composites using the Interfacial

Table 2. Neat Resin Iosipescu Results.

Note: The Electron Beam Cured Resins, Tactix 123/OPPI, were processed on the AECL 10 MeV, 1 kW Electron Beam Accelerator.

PI Conc./TI. Dose/Dose per pass/Spec. #	Shear Modulus (MSI)	Maximum Shear Strain (με)	Maximum Shear Strength (psi)
1/80/5/1	0.2164	14230	3023
1/80/5/2	0.228	6604	1385
1/80/5/3	0.2005	16452	3085
1/80/20/1	0.2024	30710	5493
1/80/20/2	0.1752	29617	5008
1/80/20/3	0.1676	19646	3394
1/100/5/1	0.1948	30083	5340
1/100/5/2	0.2584	24675	5046
1/100/5/3	0.2357	38469	6862
1/100/20/1	0.1956	47131	7370
1/100/20/2	0.1909	33334	5663
1/100/20/3	0.1927	6714	1342
1/140/20/1	0.1818	19135	3228
1/140/20/2	0.198	11069	2057
1/140/20/3	0.1979	13733	2578
1/140/5/1	0.1906	3464	764
1/140/5/2	0.1995	19052	3607
1/140/5/3	0.2008	12759	2431
3/80/5/1	0.4176	27424	8196
3/80/5/2	0.2306	38434	6968
3/80/5/3	0.1549	21852	3681
3/80/20/1	0.153	60974	7520
3/80/20/2	0.1701	43083	6588
3/80/20/3	0.2148	38466	6336
3/100/5/1	0.2213	11169	2380
3/100/5/2	0.1955	20831	3834
3/100/5/3	0.1751	19093	3345
3/100/20/1	0.1789	21864	3710
3/100/20/2	0.1908	19777	3667
3/100/20/3	0.2011	23521	4006
3/140/5/1	0.1921	12755	2351
3/140/5/2	0.1999	19409	3684
3/140/20/1	0.1835	31523	5170
3/140/20/2	0.1988	15234	2731
3/140/20/3	0.1745	12910	2324

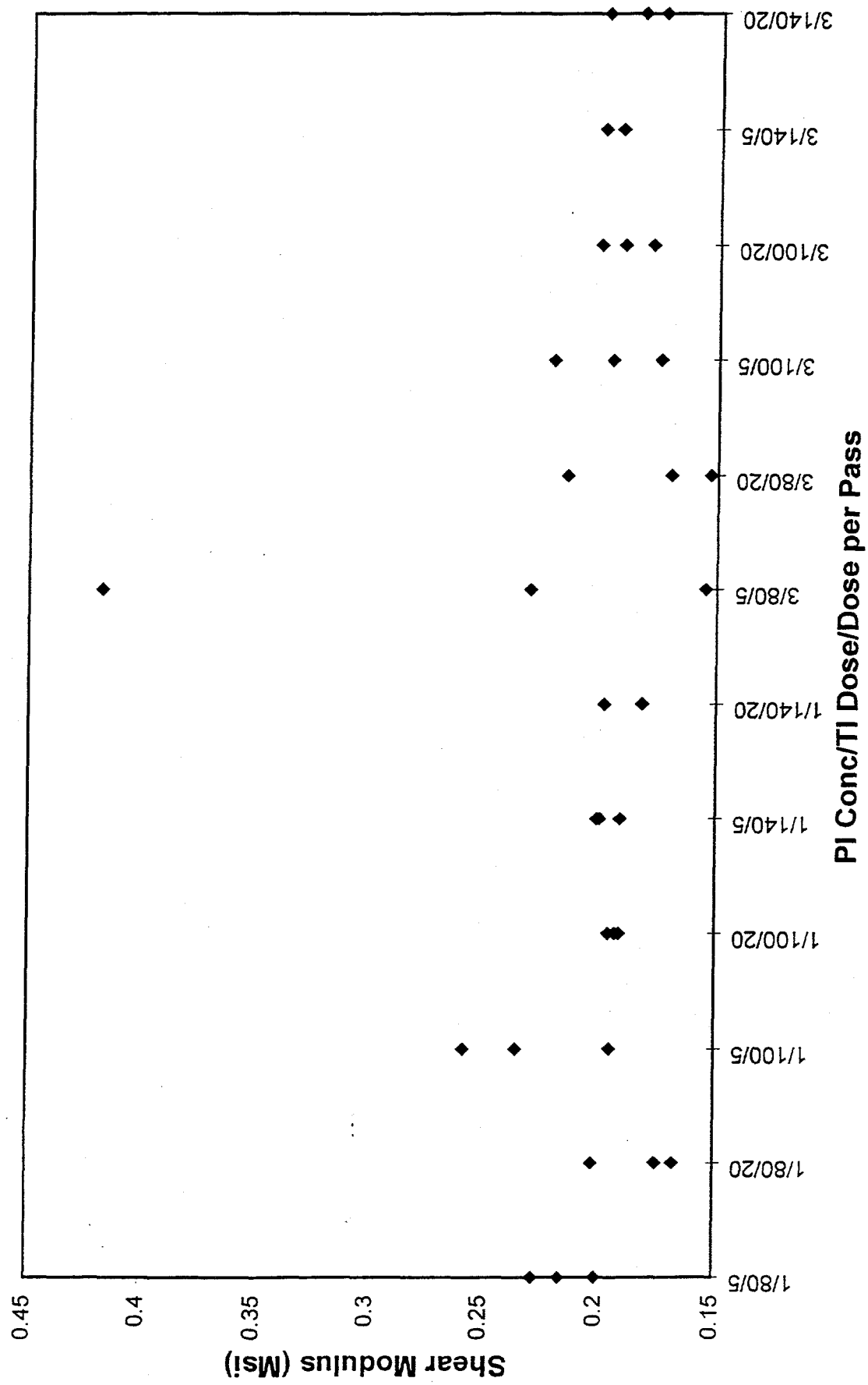


Figure 8. Iosipescu Shear Modulus Results on Electron Beam Cured Neat Resins (Tactix 123/OPPI); Factors Considered Include: Initiator Concentration, Total Electron Beam Dose and Dose Per Pass.

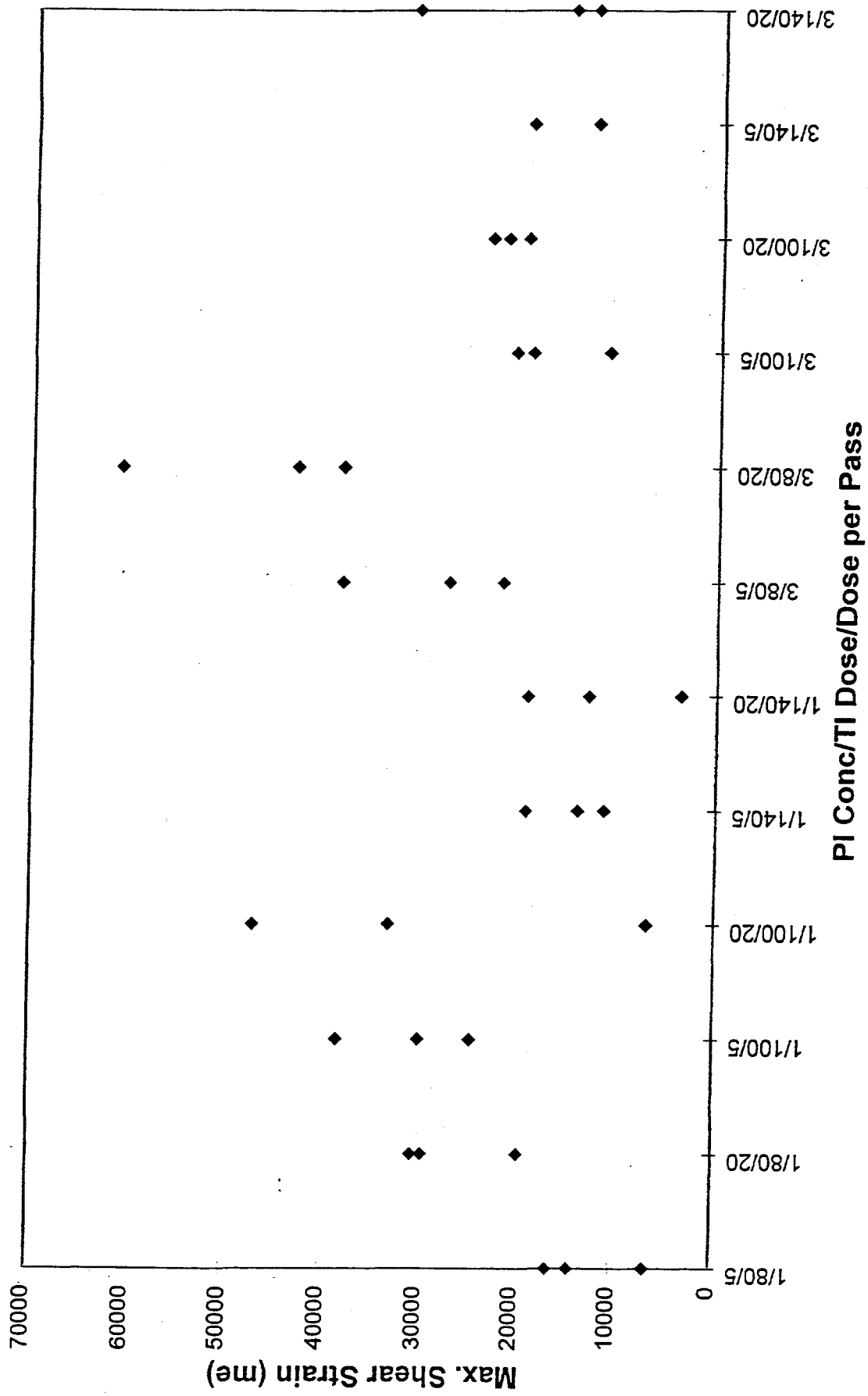


Figure 9. Iosipescu Maximum Shear Strain Results on Electron Beam Cured Neat Resins (Tactix 123/OPPI); Factors Considered Include: Initiator Concentration, Total Electron Beam Dose and Dose Per Pass.

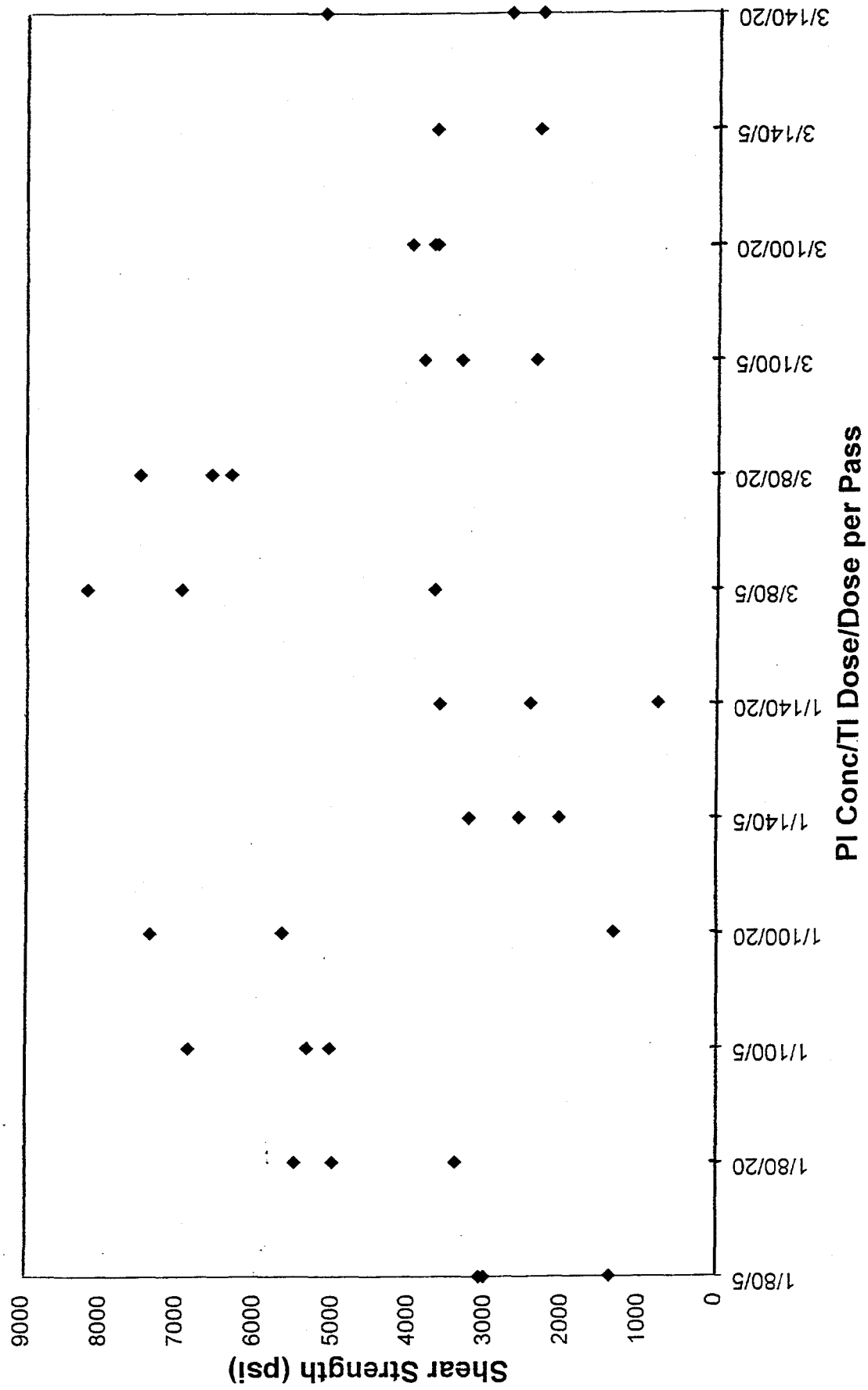


Figure 10. Iosipescu Shear Strength Results on Electron Beam Cured Neat Resins (Tactix 123/OPPI); Factors Considered Include: Initiator Concentration, Total Electron Beam Dose and Dose Per Pass.

Testing System Measurement (ITS) Method[18]. The ITS method, which uses microindentation provides valuable information on the degree of bonding that exists between the carbon fibers and the electron beam cured epoxy matrix. The ITS measurements were performed at Michigan State University under the direction of Dr. Larry Drzal.

Several kinds of Hercules carbon fibers were used in the ITS evaluation studies including:

1. AU4 - As processed carbon fiber without any surface treatment;

2. AS4 - Same carbon fiber as AU4 with electrolytic oxidation to remove the original surface and to add surface chemical groups;

3. AS4C - Same carbon fiber as AU4 but with electrolytic oxidation to remove the original surface and to add surface chemical groups. The fiber has also been coated (sized) with a thin layer of Dow D.E.R. 330 epoxy resin having a coating thickness of about 1000-2000 angstroms (100-200 nm). Nominal size content is 0.3% for 12K and 1.0% for 3K and 6K fibers.

4. IM6-0% - IM6 carbon fibers undergo a higher degree of elongation during processing and generally have a slightly higher modulus and tensile strength compared to AU or AS fibers. The IM6-0% is the as processed fiber without any surface treatment and is similar to AU4 in its surface condition;

5. IM6-100% - Is the same IM6 carbon fiber with electrolytic oxidation to remove the original surface and to add surface chemical groups (is similar to AS4);

6. IM6-600% - Is the same IM6 carbon fiber with electrolytic oxidation to remove the original surface and to add surface chemical groups but to six times the level of the IM6 - 100% fiber. This has the effect of increasing the surface chemical groups as well as the fiber surface roughness.

Specimens for testing on the ITS were cast in bars 3 in. long by 0.5 in. wide. Sections of carbon fiber tow (AU-4, AS-4, IM6-100% and IM6-600%) were cut to length and placed in the rectangular shaped cavities of a silicone mold. Tactix 123 with variable amounts of OPPI from 1 to 5 phr was poured around the fibers to fill the mold cavity and exposed to 100 kGy (10 passes of 10 kGy each). The composite samples were cut into 0.5 in. segments using a water-cooled diamond saw. Four segments from the center were mounted in phenolic ring-forms with a room-temperature processed epoxy and allowed to harden overnight. A Struers Abramin Polisher was used in the grinding and pre-polish stages with Silicon Carbide papers under the conditions shown in Table 3.

Table 3. Sample Polishing Schedule.

Grit	Time (min:sec)
320	0:45
600	2:00
1200	3:00
2400	4:00
4000	4:00

Final polish used a rotating lap with a low-nap cloth and 1 micron Al_2O_3 in water. The specimens were polished for 1 minute, rinsed and polished again for 1 minute. Specimens with 3 phr and 5 phr OPPI produced acceptable finishes, the specimen with 1 phr OPPI exhibited an unacceptable amount of matrix removal. The specimen with 1 phr OPPI was reworked at 4000 grit and polished with the Al_2O_3 for 45 seconds, this produced a finish acceptable for testing.

Thermal Post Treatment of 1 phr OPPI Sample. After testing on the ITS, the sample mount containing the AS-4 in Tactix 123 with 1 phr OPPI was sectioned to remove the carbon fiber/epoxy composite sections. The sample was then thermally treated in a forced convection oven at 225°C for 30 minutes (5°C ramp rate). The carbon fiber/epoxy composite sections were remounted and polished using the same schedule in **Table 3** and two 1 minute cycles on the rotating lap polisher which produced an acceptable finish.

ITS Procedure. Testing was carried out using the following microindentation (ITS) settings:

Tip:	5 micron diameter diamond indentor
Step Rate:	9.1 steps/second
Debond Criteria:	90° to 120°
Sample Size:	10 fibers tested

The procedure consists of mounting the ring containing the carbon fiber/electron beam processed epoxy composites sections on an x-y stage of the ITS microscope. The sample is examined for fibers that are surrounded by nearest neighbors between 0.5 and 2 microns from the selected fiber edge. The indentor is placed in contact with the fiber and the stage is moved in the z direction perpendicular to the fiber end. The load is monitored continuously and periodically the fiber is unloaded and the sample examined under the microscope for evidence of debonding. When a debond of between 90 and 120 degrees is detected, the load is recorded as the debond load which is used for calculating the interfacial shear stress. This ITS test has advantages over the single fiber fragmentation tests since the matrix is not loaded in tension and will not fail under these loading conditions. However, events taking place below the surface can not be observed and the debonding at the surface is used as the indicator of interfacial failure.

3.3.2. Results

Measured values for the shear modulus of the matrix and literature values of the tensile modulus of the fiber were used for the computations to reduce the debond load to interfacial shear strength. DMA scans (Figures 11-14) of neat rectangular bars of Tactix 123 containing 1 phr, 3 phr or 5 phr OPPI processed under 100kGy were conducted in order to determine the matrix mechanical properties. Values for the storage modulus (E') were obtained for temperatures between 42°C and 45°C from the DMA scans. Table 4 is a listing of the shear moduli of the Tactix 123 with various amounts of OPPI calculated using a Poison's Ratio of 0.35. It should be noted that while the Tactix 123 with 3 phr and 5 phr gave similar results for the shear modulus, the Tactix 123 with 1 phr produced a material with significantly higher modulus (65%). Modulated differential scanning calorimetry (DSC) scans (Figures 15-19) on these specimens showed that the Tactix 123 with 1 phr OPPI was not fully processed after 100 kGy exposure. When this sample was given a 225°C postcure, the shear modulus decreased to slightly less (16%) than the value obtained with the Tactix containing either 3 phr or 5 phr.

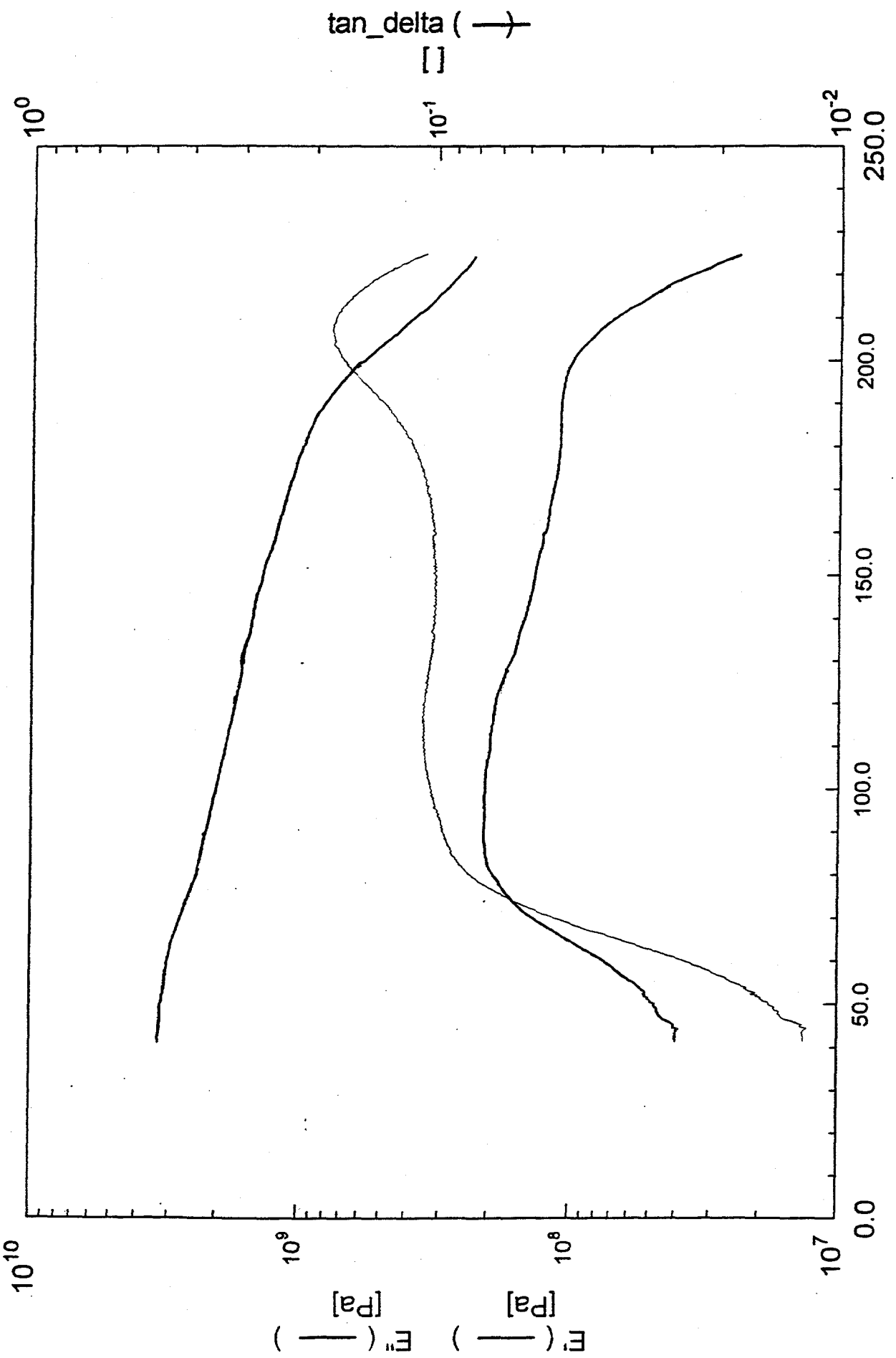


Figure 11. DMA Plot on Tactix 123/1 phr OPPI.

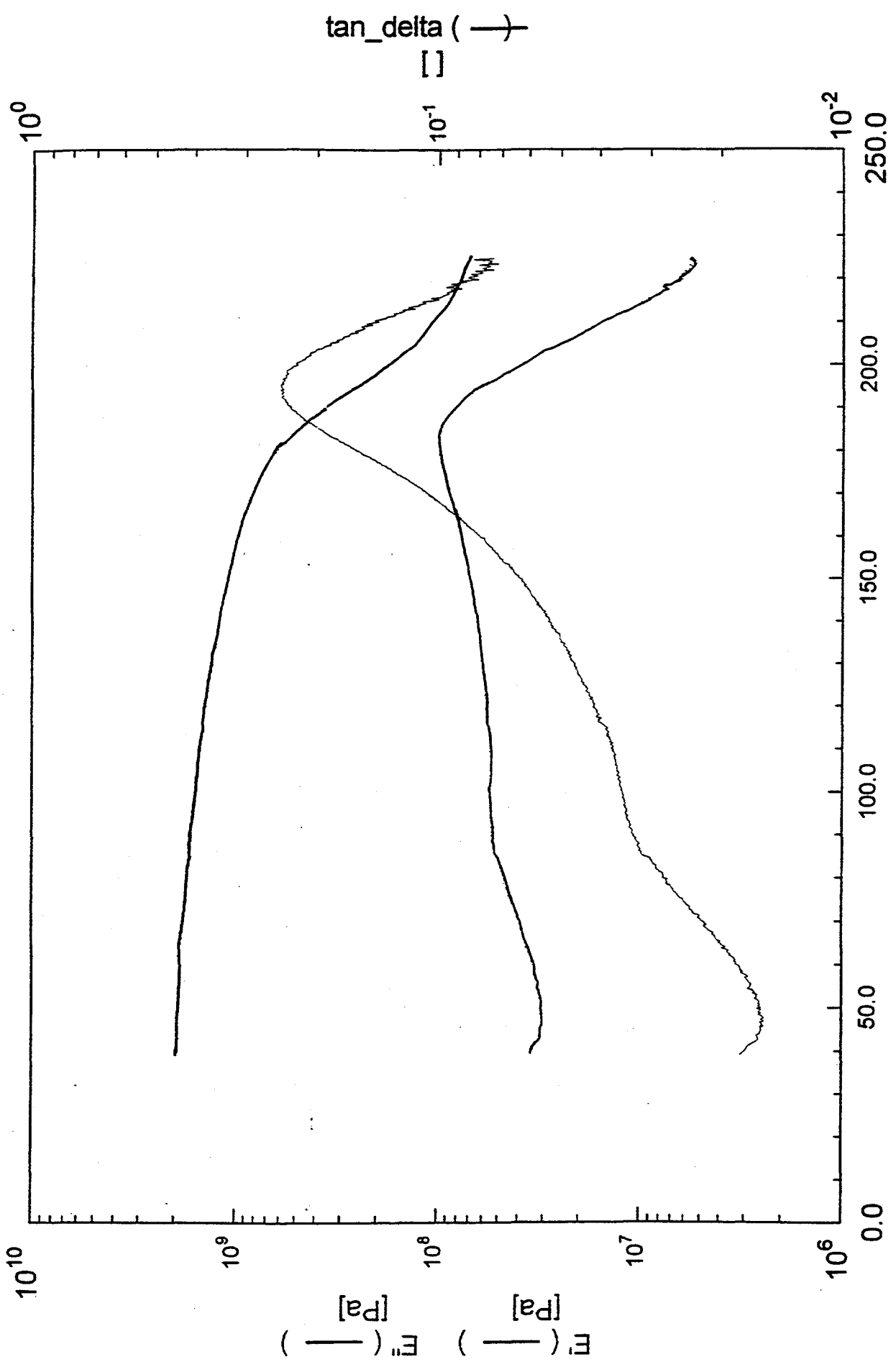


Figure 12. DMA Plot on Tactix 123/3 phr OPPI.

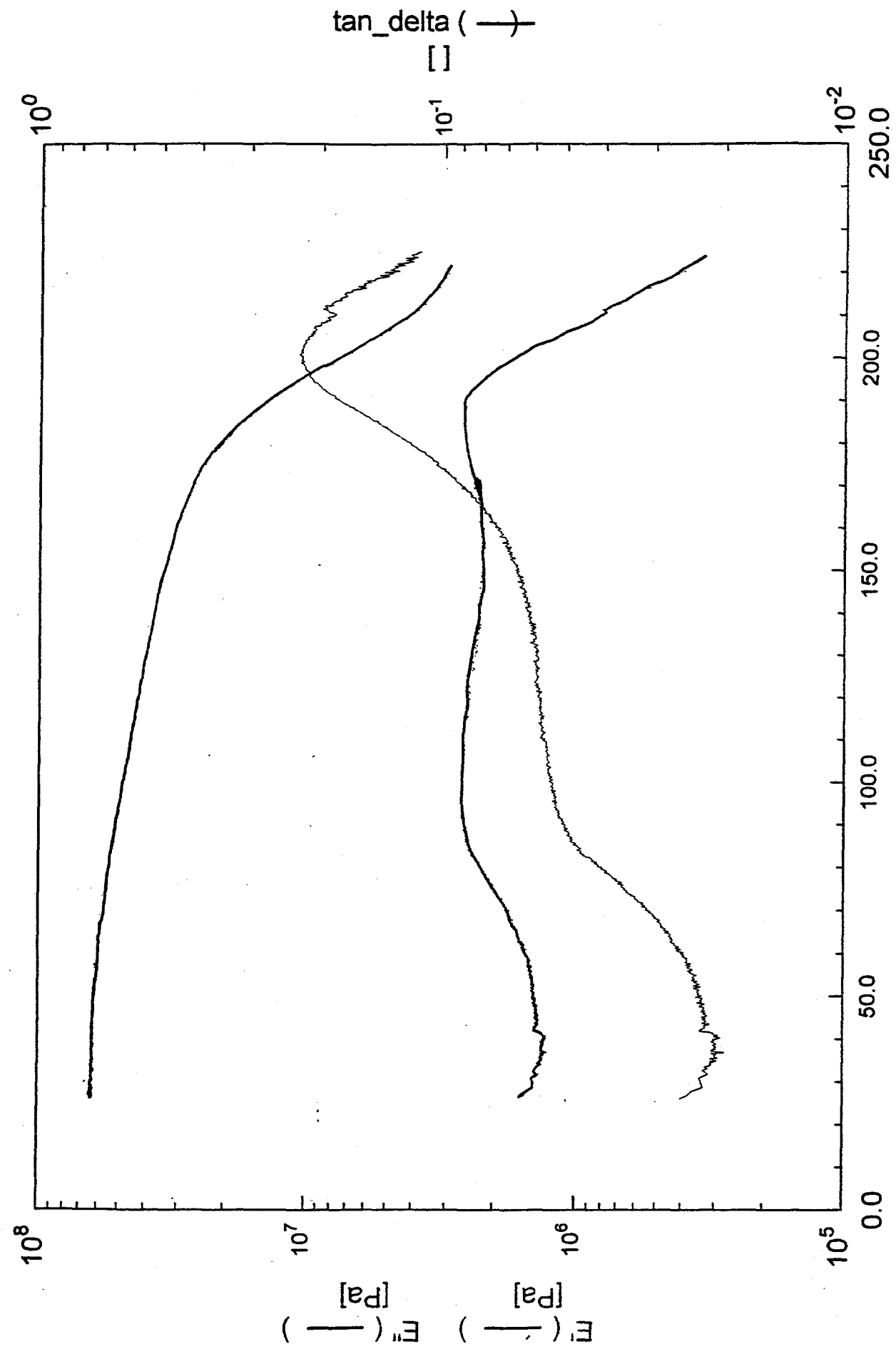


Figure 13. DMA Plot on Tactix 123/5 phr OPPI.

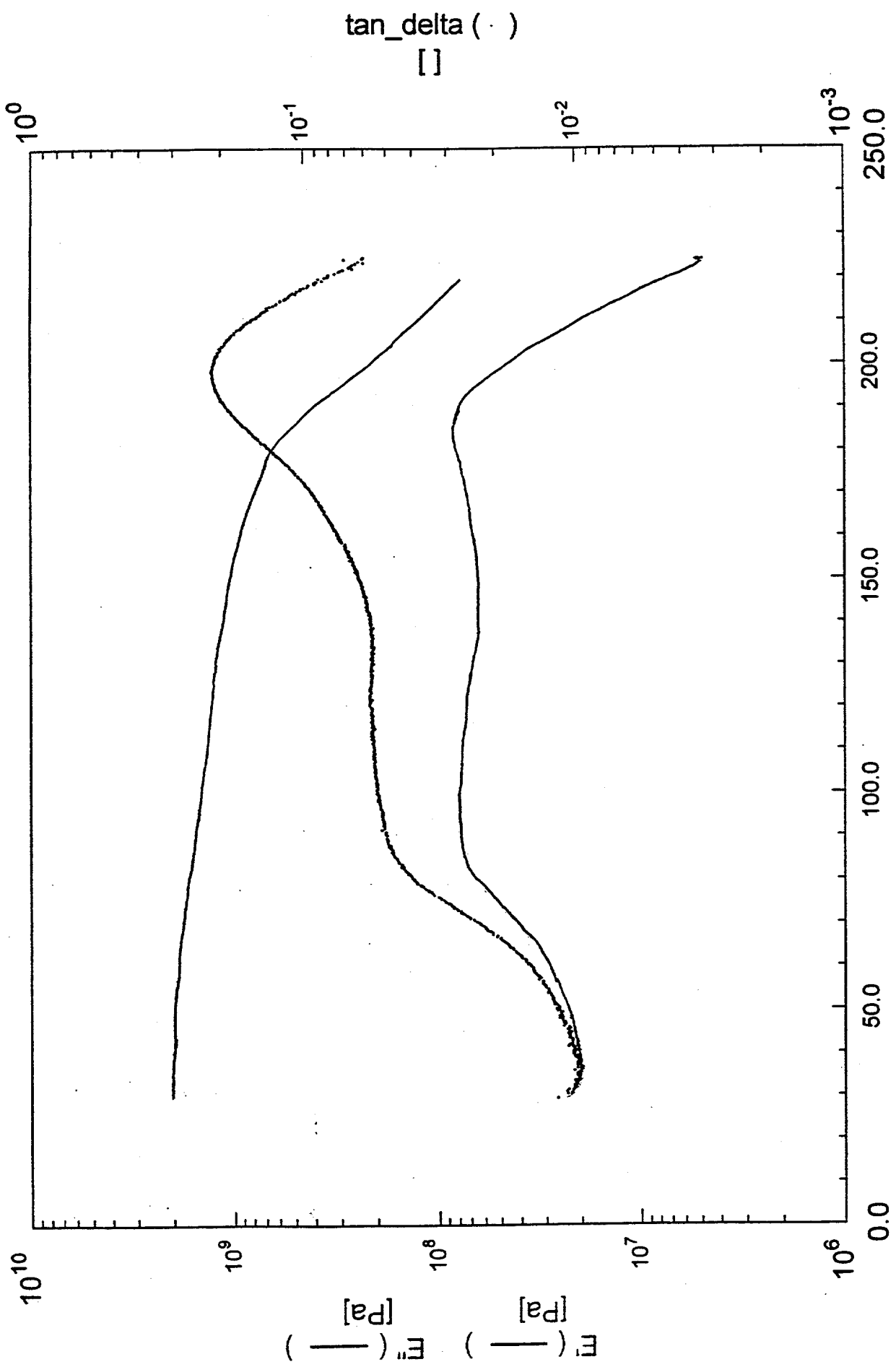


Figure 14. DMA Plot on Tactix 123/5 phr OPPI (2nd run).

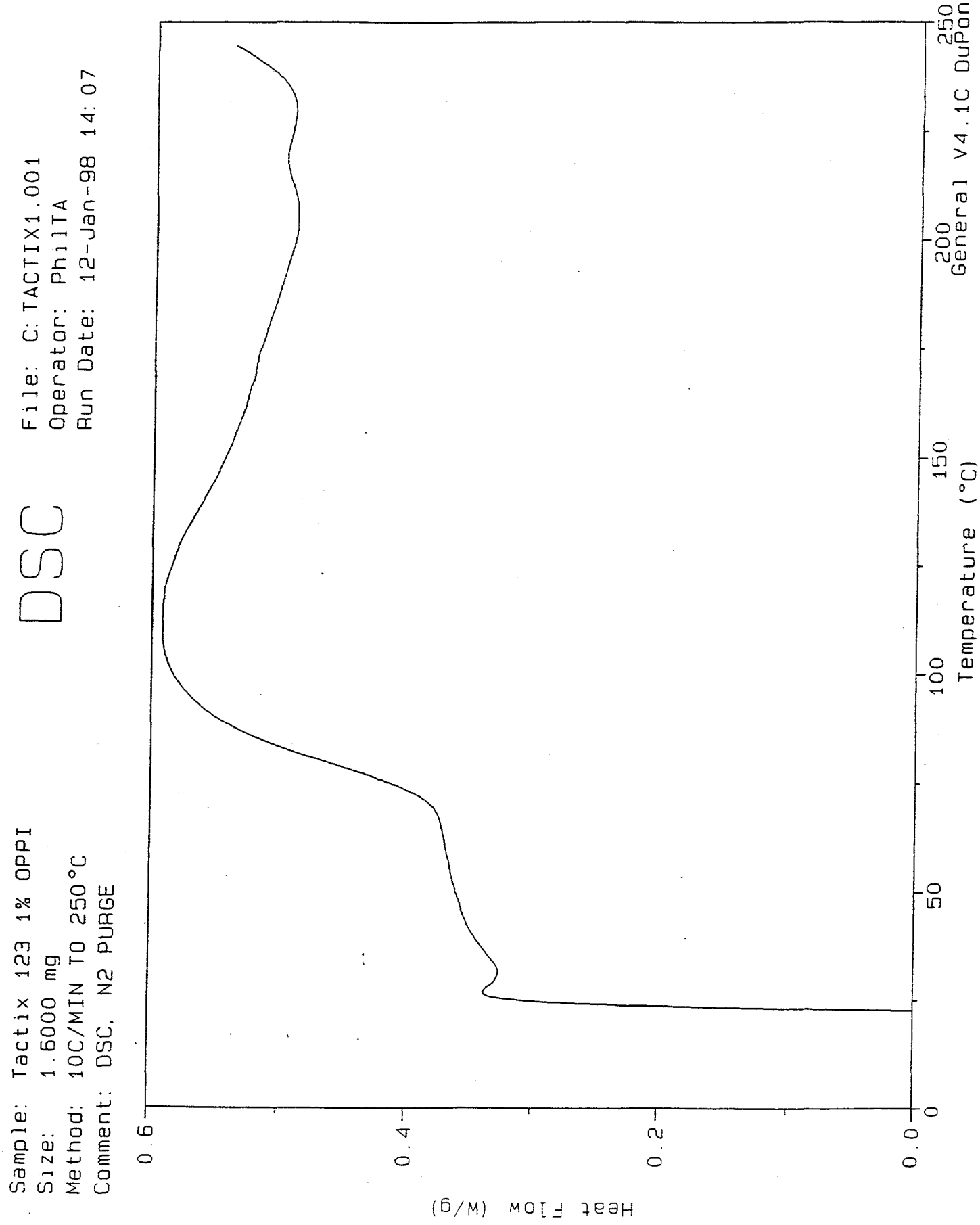


Figure 15. DSC Plot on Tactix 123/1 phr OPPI.

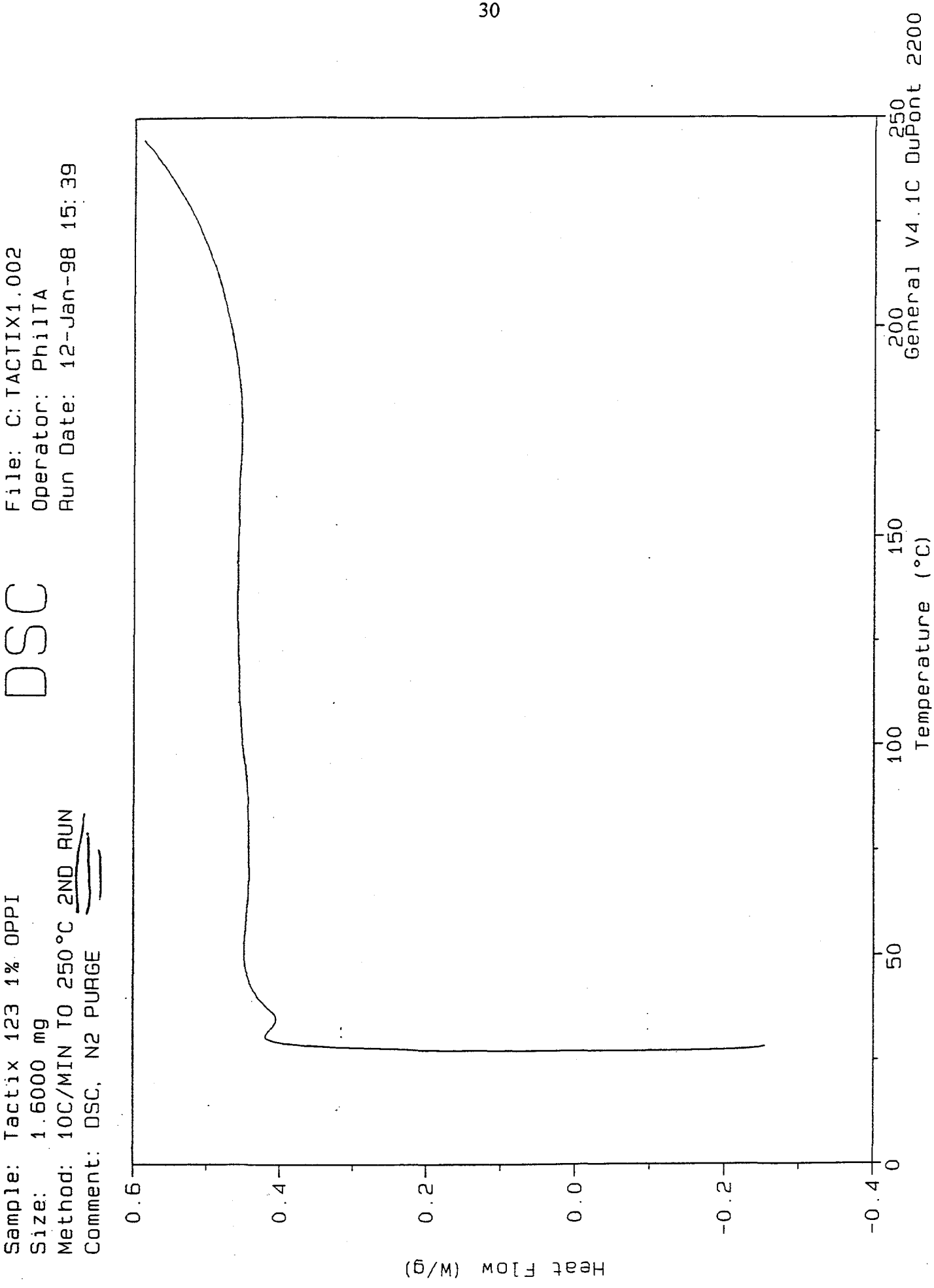


Figure 16. DSC Plot on Tactix 123/1 phr OPPI (2nd run).

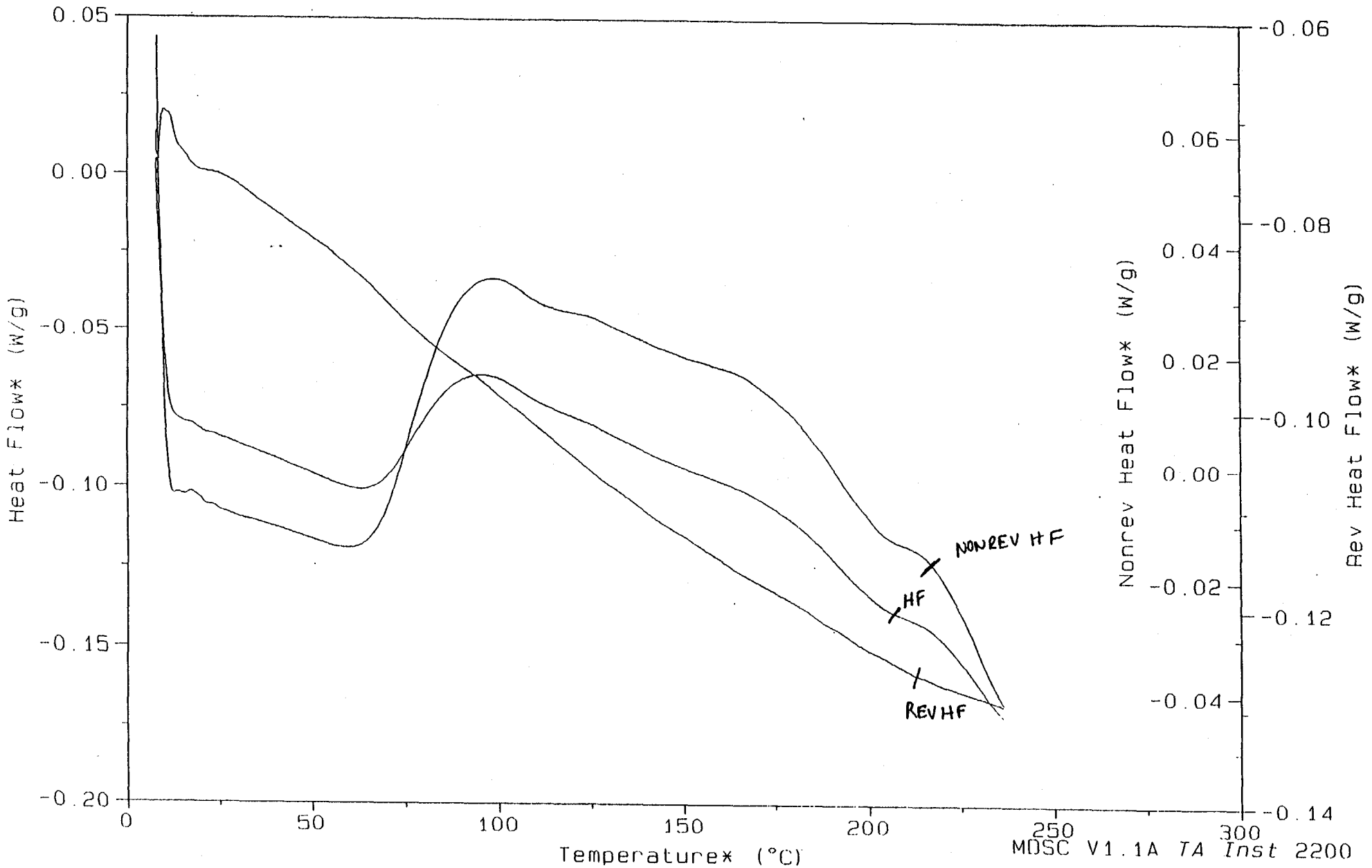


Figure 17. DSC Plot on Tactix 123/1 phr OPPI (MOD).

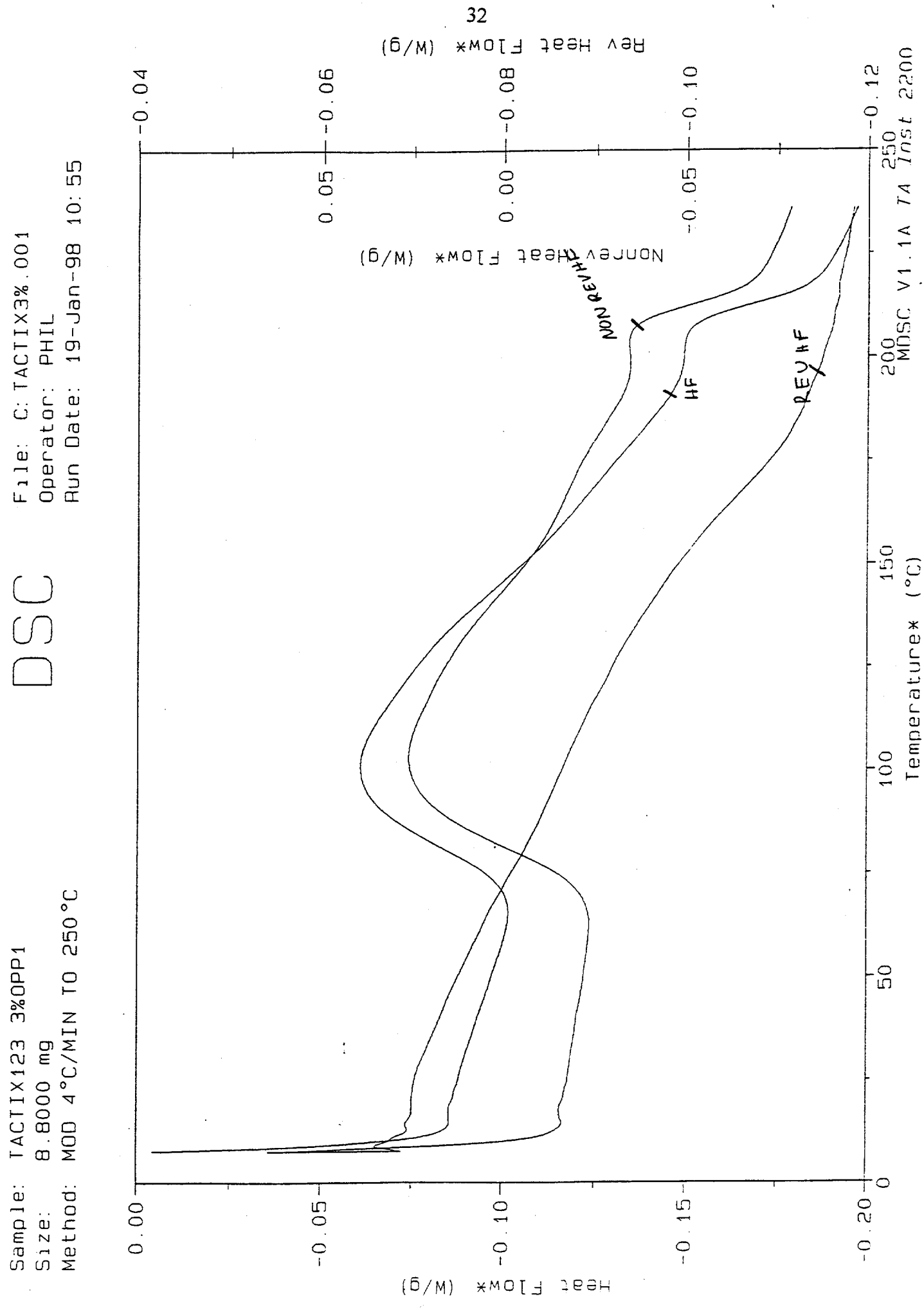


Figure 18. DSC Plot on Tactix 123/3 phr OPPI.

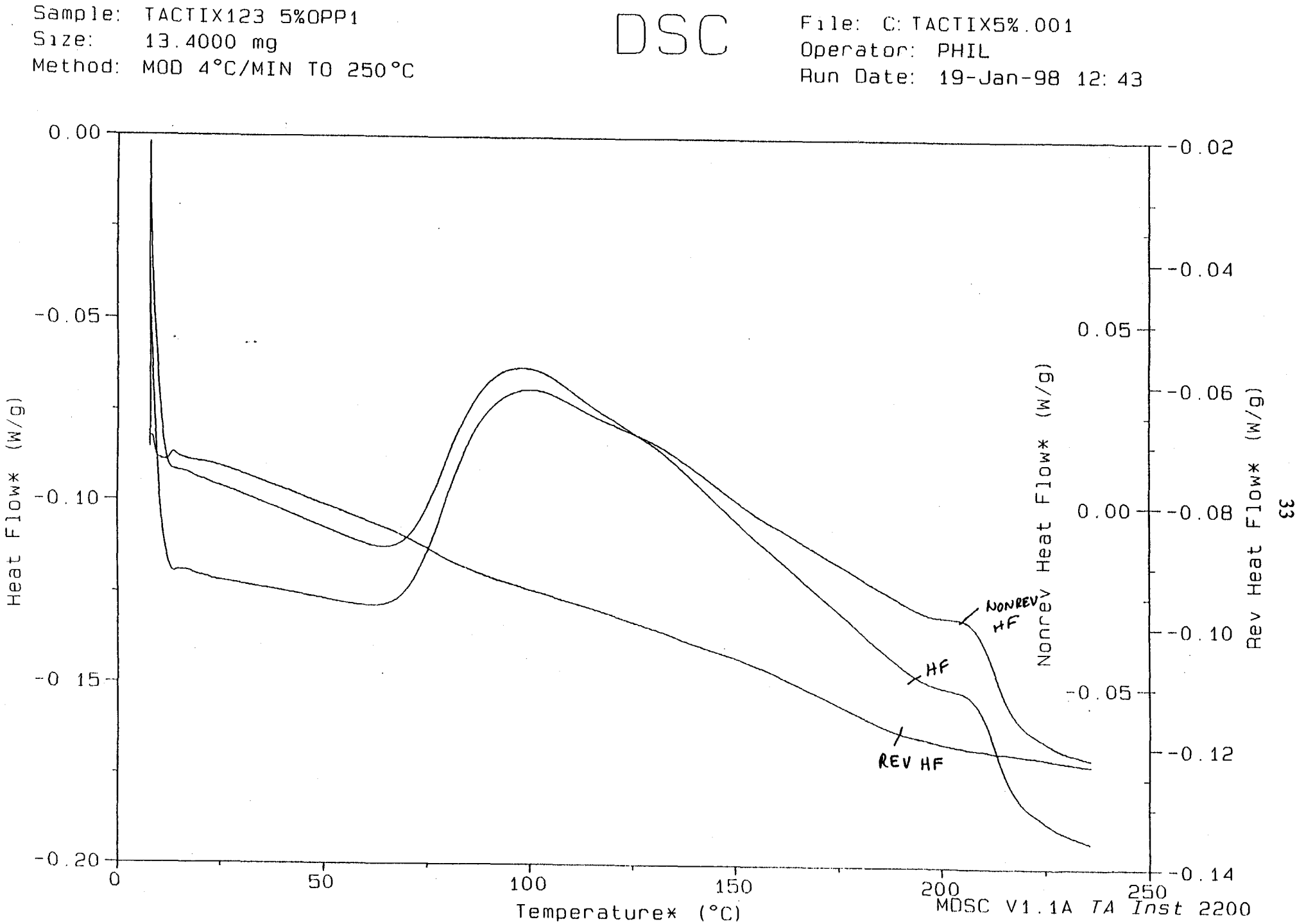


Figure 19. DSC Plot on Tactix 123/5 phr OPPI.

Table 4. Shear Moduli of Electron Beam Processed Epoxy.

phr OPPI	Shear Modulus (psi)
1 phr	177,000
1 phr + 225°C postcure	90,000
3 phr	105,000
5 phr	109,000

The carbon fiber moduli were obtained from Hercules product data for the A4 and IM-6 series of fibers (32,000,000 and 40,000,000 psi, respectively).

The results of the ITS measurements of adhesion between carbon fiber and electron beam processed Tactix 123 containing various amounts of OPPI initiator are listed in Table 5 and plotted in Figures 20 and 21.

Table 5. Carbon Fiber/Tactix 123 Adhesion ---ITS Results.

Carbon Fiber	*Parts per Hundred OPPI*	*Average IFSS (psi)*	*Standard Deviation (psi)*
IM-6 (0%)	3 phr	1000	200
IM-6 (100%)	3 phr	3100	400
IM-6 (600%)	3 phr	3000	400
AU-4	3 phr	2600	500
AS-4	3 phr	4100	500
AS-4	5 phr	4600	600
AS-4	1 phr	6500	800
AS-4	1 phr + 225°C postcure	4000	300

Figure 20 clearly shows the variation in interfacial shear strength (adhesion) that results from the specific interactions taking place between each of the carbon fiber surfaces and the Tactix 123 with 3 phr OPPI processed under 100kGy conditions. The IM6-0% carbon fiber shows the lowest value of adhesion to this matrix. In comparison the IM6-100% and IM6-600% carbon fibers have substantially greater (~200%) adhesion to the same matrix. Likewise, the AU4 carbon fiber exhibits a low value of adhesion but after surface treatment the AS4 carbon fiber adhesion to the Tactix 123 with 3 phr OPPI again increases substantially (~60%). It is also worth noting that the AS4 carbon fiber has greater interfacial shear strength than the IM6-100% carbon fiber by about 30%. Similar results are seen in direct comparisons of AS4 and IM6-100% with the thermally processed epoxy Epon 828/meta-phenylene diamine (mPDA) system.

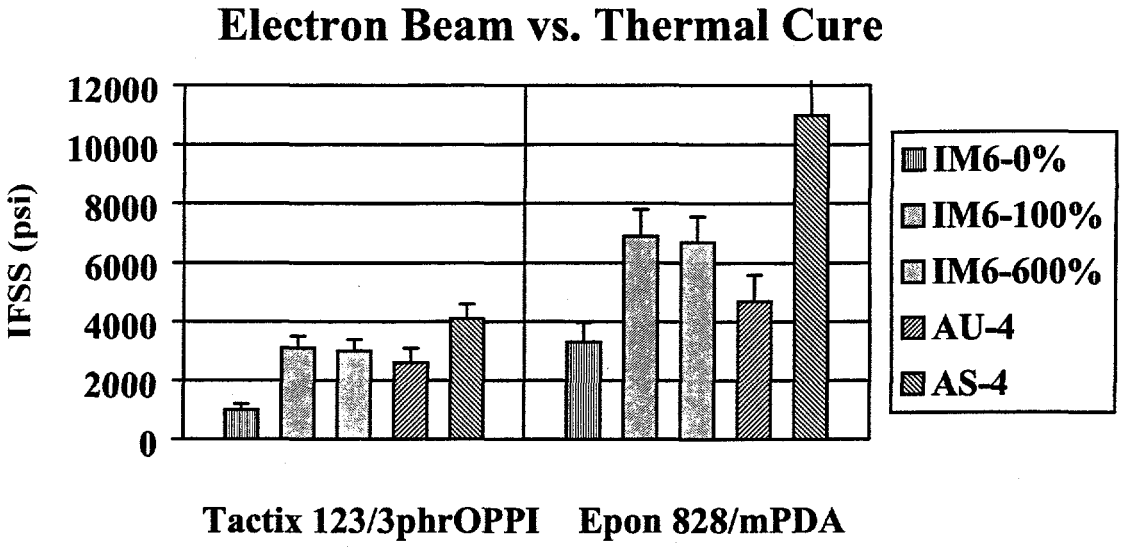


Figure 20. Interfacial Shear Strength (IFSS) of A4 and IM6 Carbon Fibers in Tactix 123 with 3phr OPPI Processed at 10kGy/100kGy or in Epon 828 with 14.5 phr mPDA processed at 75°C/125°C.

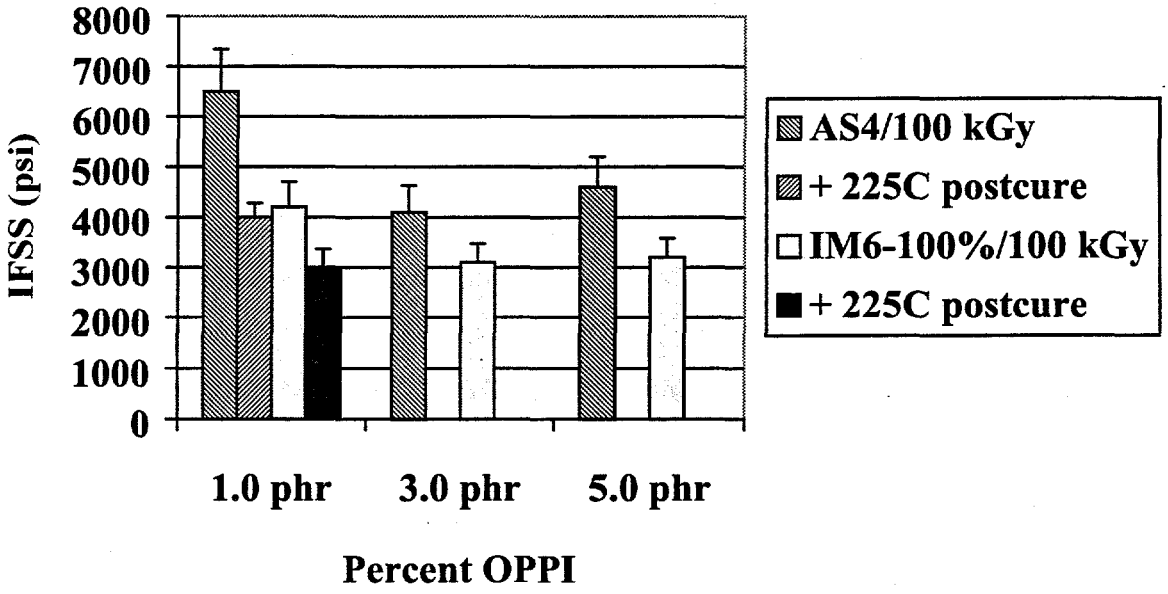


Figure 21. IFSS of AS4 and IM6 Carbon Fiber to Tactix 123 with Varying Amounts of OPPI Processed at 10kGy/100kGy.

The IFSS for thermally processed systems is 200% to 300% greater than for the electron beam cured systems for the same fibers.

Figure 21 is a plot of the interfacial shear strength (adhesion) between AS4 and IM6-100% carbon fiber and the Tactix 123 epoxy resin that has been formulated with different amounts of OPPI initiator. Note that in all cases the AS4 shows greater interfacial shear strength than the IM6-100% carbon fiber. Within experimental scatter, adding additional initiator over the normal amount, i.e. 5 phr vs. 3 phr, does not appear to affect the interfacial shear strength for either the AS4 or IM6-100% fiber. However, when less than the normal amount, i.e. 1 phr vs. 3 phr, is used, the interfacial shear strength (adhesion) for both AS4 and IM6-100% carbon fibers are substantially greater by about 60% for AS4 and 40% for IM6-100%. Recall that the shear modulus of the 100kGy electron beam processed Tactix 123 with 1 phr of OPPI was about 65% greater than the 3 phr or 5 phr systems as well. After postcuring the 1 phr Tactix composite, the interfacial shear strength drops down to a level equivalent to the 3 phr Tactix system for both AS4 and IM6-100% fibers and this corresponds to a decrease in modulus of the same magnitude.

Although the comparison between electron beam processed Tactix 123 and thermally processed, amine cured epoxy, gives a direct comparison with conventionally processed epoxy, it is not exactly the same since there is a high probability that the amine curing agent can chemically interact with the carbon fiber surface. Therefore, it was decided to generate a 2nd set of *"reference"* carbon fiber/epoxy fiber specimens. In this case, the Tactix 123 system with 3 phr of OPPI were prepared, thermally processed, and their interfacial strengths measured via ITS testing. Sections of tow were placed in DMA silicone mold cavities, which were then filled with the epoxy resin. The resin was prepared by heating a measured quantity of epoxy to 50°C, then adding sufficient OPPI to yield a concentration of 3 phr. The resin was reheated and mixed well to dissolve the OPPI. The resin was degassed before filling the mold cavities and poured slowly into one end of the cavity to infiltrated the tow. The thermal cure schedule included heating to 170°C for 3 hours with a temperature ramp of 10°C per min. The model composite specimens were cut, potted and polished following the protocol and schedules previously established. The polished sections displayed acceptable fiber distribution and a low void content. Ten fibers were tested for each condition. The shear modulus of the Tactix123 with 3 phr OPPI was calculated to be 157 ksi. The thermally processed T123 with 3 phr OPPI has a flexural modulus of 424 ksi (2.92 Gpa) at 0.1% strain, and the Poisson's ratio was assumed to be 0.35. The ITS values

obtained for these specimens are tabulated in Table 6 and plotted in Figure 22 along with the previous ITS data shown in Figure 20.

Table 6. ITS Results for Carbon Fibers in Thermally Processed Tactix123 with 3phr OPPI.

Condition	Average IFSS (psi)	Standard Deviation (psi)
IM-6 (0%)	3000	500
IM-6 (100%)	5400	700
IM-6 (600%)	5600	800
AU-4	4500	700
AS-4	6900	600

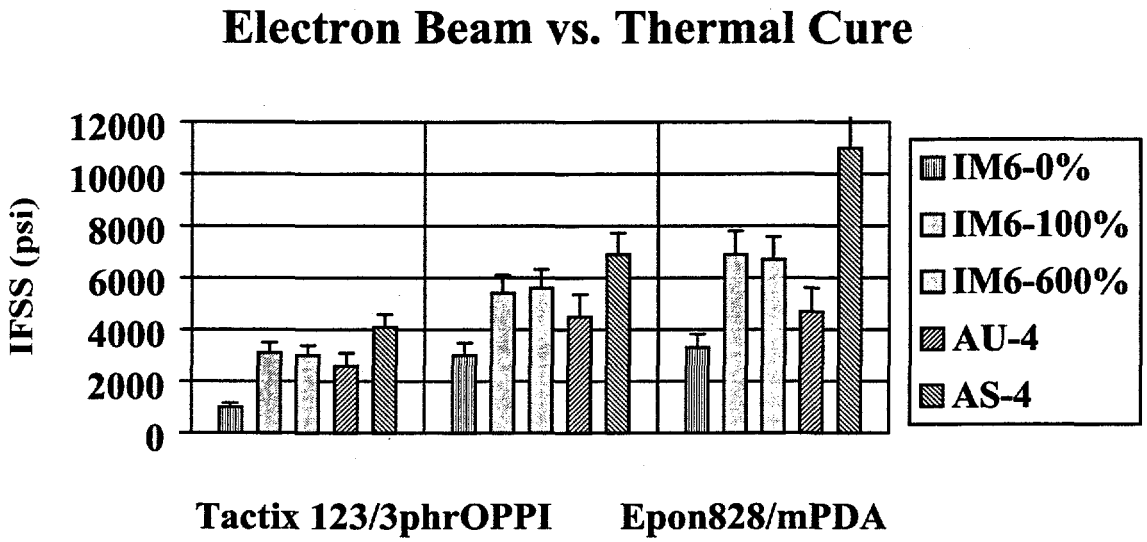


Figure 22. IFSS of A4 and IM6 Carbon Fibers in: i) Tactix 123 with 3phr OPPI Processed at 10kGy/100kGy; ii) Tactix 123 with 3 phr OPPI Processed at 170°C; and iii) Epon 828 with 14.5 phr mPDA Processed at 75°C/125°C.

It is clear that the electron beam processed samples have lower interfacial shear strength than the thermally processed samples with the same Tactix 123 with 3 phr OPPI. Furthermore, the thermally processed amine cured epoxy still has a significantly higher level of interfacial shear strength.

A second group of electron beam cured carbon fiber epoxy specimens were prepared. The specimens consisted of tows of AS4 and AS4C carbon fibers in polypropylene sample tubes that had been filled with Tactix 123 containing varying concentrations of OPPI initiator. The tubes were placed in an oven at 140°F for 30 minutes and 95°F for 12 hours, then electron beam curing was performed at a dose per pass of either 5 kGy or 20 kGy to an electron beam total dose of 100, 120, or 160 kGy. The tows were located next to the inner surface of the sample tubes, allowing the most aligned section of the tow to be located visually to be used for testing. The tubes were oriented to place the tow perpendicular to the direction of cutting and were then sectioned using a water-cooled diamond cut-off saw. Samples were polished using the same sample polishing procedure described earlier. Mechanical properties of the matrix were taken from the DMA data shown in Table 7.

Table 7. Flexural Moduli of Tactix 123 Cured with 3 phr OPPI at varying Passes and Doses, Strain 0.1%.

Pass (kGy)	Dose (kGy)	Flexural Modulus (ksi)
5	80	435
5	100	455
5	140	453
20	80	345
20	100	418
20	140	421

Nine conditions were tested, eight of which had the concentration of OPPI fixed at 3 phr, a dose per pass of 5 or 20 kGy and a total electron beam cure dose of 100, 120 or 160 kGy. Since the dose values at which the DMA and ITS specimens were processed did not completely overlap, the DMA values of the modulus at 100 and 140 kGy were averaged and used in calculating the ITS results for doses of 100, 120 and 160 kGy. Assuming a Poisson's Ratio of 0.35, the calculated shear moduli are listed below in Table 8.

Table 8. Calculated Shear Moduli of Tactix 123 Cured with 3 phr OPPI at varying Passes and Doses, Strain 0.1%.

Pass (kGy)	Dose (kGy)	Shear Modulus (ksi)
5	100, 120, 160	168
20	100, 120, 160	155

For the one sample not covered by these values, (1 phr OPPI, Pass: 5, Dose: 100), the supplied flexural modulus (0.1% strain) was 480 ksi (3.31 Gpa). Converted, this yields a shear modulus of 178 ksi. Ten fibers were tested at each condition. It was noted that the polished cross-section of the sample tubes was discolored in all cases where the carbon fibers touched or came near the wall of the tube. The effect ranged from a change to a milky/cloudy appearance to an opaque white containing fractures; in contrast, the portion of the tubes not near carbon fibers remained clear.

Table 9 contains the results of the ITS measurements for AS4 fibers at various total doses and dose rates. It is apparent that the interfacial shear strength between the AS4 carbon fiber and the electron beam cured Tactix 123 with 3 phr OPPI is sensitive to both the dose per pass as well as the total dose.

Table 9. ITS Results for AS-4 Carbon Fibers in Tactix 123 Cured with 3phr OPPI at varying Passes and Doses.

Fiber	phr OPPI	Pass (kGy)	Dose (kGy)	Average IFSS (psi)	Standard Deviation (psi)
AS-4	3	5	100	5200	900
AS-4	3	5	120	5700	500
AS-4	3	5	160	5100	800
AS-4	3	10	100	4100	500
AS-4	3	20	100	3000	500
AS-4	3	20	120	4400	800
AS-4	3	20	160	5000	400

Figure 23 contains the same data of Table 9 plotted as a function of both dose per pass and total dose. Reducing the dose per pass while keeping the total dose fixed at 100 kGy increases the IFSS from 3000 to 5200 psi. Increasing the dose per pass to 20 kGy reduces the IFSS. The same observation can be made at 120 kGy total dose. At a total dose of 160 kGy, the adhesion appears to be insensitive to dose per pass. This difference can not be explained by a change in matrix modulus since, independent experiments have shown that the matrix modulus does not change significantly once the total dose rate is greater than 100 kGy. However, since DMA results have demonstrated that composites do not completely cure until about 150 kGy, the tweaking of these process variables (dose and dose per pass) to effect an increase in the interfacial properties is not a viable option for electron beam processing.

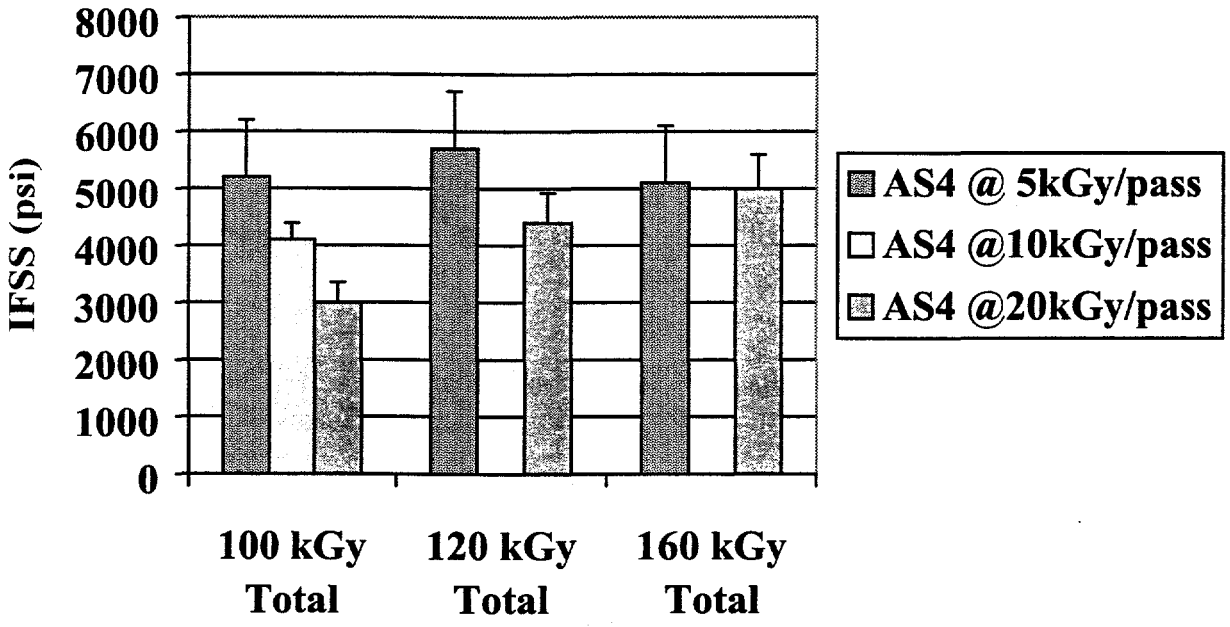


Figure 23. IFSS of AS4 Carbon Fiber to Tactix 123 with 3 phr OPPI Processed at Various Rates and Total Dose

AS4 carbon fiber with an epoxy compatible sizing was also evaluated under electron beam conditions. This carbon fiber is designated as AS4C. ITS composite samples using Tactix 123 with 3 phr as well as 1 phr were processed at a total dose of 100 kGy but at dose per pass of 5 and 20 kGy. Table 10 contains these results. The IFSS values for these epoxy sized fibers were significantly greater (at least 20%) than for the same carbon fiber without the epoxy sizing

and under the same total dose and dose per pass. Figure 24 is a replot of the data in Figure 23 but with the AS4C results added.

Table 10. ITS Results for AS4C Carbon fibers in Tactix 123 Cured with 3phr OPPI at varying Passes and Doses.

Fiber	phr OPPI	Pass (kGy)	Dose (kGy)	Average IFSS (psi)	Standard Deviation (psi)
AS4C	1	5	100	6500	600
AS4C	3	5	100	6600	500
AS4C	3	20	100	6800	1000

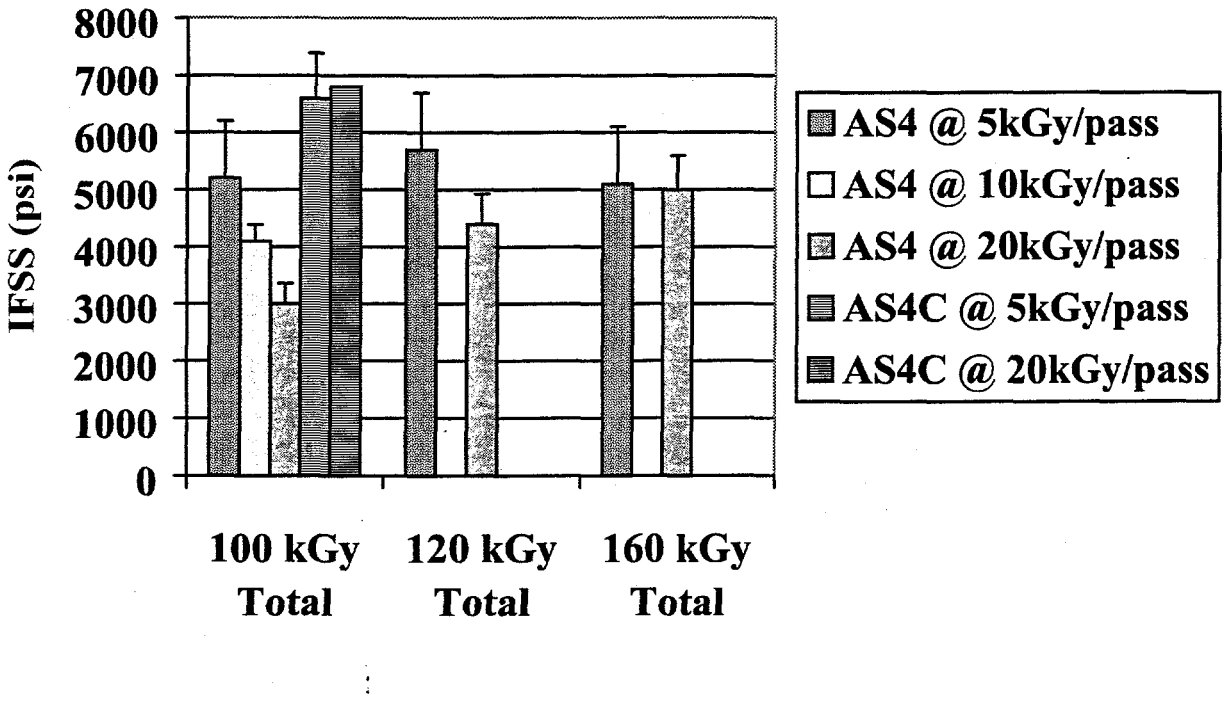


Figure 24. IFSS of AS4 and AS4C Carbon Fiber to Tactix 123 with 3 phr OPPI Processed at Various Rates and Total Dose.

3.4. Task 4 - Effects of Epoxy Coated Carbon Fibers on the Interlaminar Shear Strength of Carbon Fiber Reinforced Composites

3.4.1. Experimental

Due to the favorable ITS findings, we undertook an investigation to evaluate the effects of epoxy coated carbon fibers on the interlaminar shear strength of electron beam cured, filament wound composites. The carbon fiber coating trials were conducted on conventional surface-treated, unsized, IM7-12K carbon fibers at Adherent Technologies Inc. in Albuquerque, New Mexico using their fiber coating line and tube furnace.

Four epoxy resins (having different melting points and epoxide equivalent weights) and one cationic initiator were selected for coating the carbon fibers. The epoxy coating resin materials and the intiator that was used included: Shell Epon 1001F Epoxy; Shell Epon 1007F Epoxy; Dow D.E.N. 439 Epoxy; Shell Epon 826 Epoxy; and Sartomer CD1012 Initiator. These epoxy resin systems were dissolved in either acetone or MEK and were chosen based on their excellent resin solubility and fiber wettability characteristics and their fast evaporation rates. Several concentrations of the epoxy resins and the initiator were evaluated in our trials which resulted in a variety of coating thicknesses onto the fibers. Calculations for a few coating thicknesses and coating weights for IM7 and AS4 carbon fibers are tabulated in Table 11. The procedure for coating the carbon fibers included unspooling the carbon fiber tow using a tensioned roller, dipping the fibers into a resin bath, evaporating the solvent from the fiber tow by passing them through the heated tube furnace, then respooling the fiber onto a cardboard tube.

The IM7 coated carbon fibers were then used for filament winding a series of 6 in. diameter, 0.125 in. thick, 4-5 in. wide composite cylinders. The electron beam curable filament winding resin used for the majority of these cylinders was ERL-2258 with 3 phr OPPI initiator. In addition to the above cylinders, two control cylinders were also fabricated in this effort, including one which used conventionally surface-treated, uncoated, and unsized IM7 carbon fiber, and one fabricated with conventionally surface-treated, uncoated, and GP Sized IM7 carbon fiber. Both control cylinders were made using ERL-2258 with 3 phr OPPI initiator as the filament winding resin.

Table 11. IM7 and AS4 Carbon Fiber Coating Calculations.

IM7 diameter (cm)	5.00E-04	AS4 diameter (cm)	8.00E-04
IM7 radius (cm)	2.50E-04	AS4 radius (cm)	0.0004
pi	3.141593	pi	3.141593
IM7 volume (cm^3) = pi*r^2*h	1.9635E-07	AS4 volume (cm^3) = pi*r^2*h	5.0265E-07
IM7 density (g/cm^3)	1.77	AS4 density (g/cm^3)	1.79
IM7 wt. (g) = IM7 density * IM7 vol.	3.4754E-07	AS4 wt. (g) = AS4 density * AS4 vol.	8.9975E-07
For Coating Thickness of 1000A (100nm, 0.1micron, or 1e-05cm)		**For Coating Thickness of 1000A (100nm, 0.1micron, or 1e-05cm)**	
IM7 dia. + coating dia. (cm)	5.20E-04	AS4 dia. + coating dia. (cm)	8.20E-04
IM7C radius (cm)	2.60E-04	AS4C radius (cm)	0.00041
pi	3.141593	pi	3.141593
IM7C volume (cm^3) = pi*r^2*h	2.1237E-07	AS4C volume (cm^3) = pi*r^2*h	5.281E-07
Coating vol. (cm^3) = IM7C vol. - IM7 vol.	1.6022E-08	Coating vol. (cm^3) = AS4C vol. - AS4 vol.	2.5447E-08
Coating density (g/cm^3)	1.2	Coating density (g/cm^3)	1.2
Coating wt. (g) = coating vol.*coating den.	1.9227E-08	Coating wt. (g) = coating vol.*coating den.	3.0536E-08
% coating wt. = coating wt./IM7 wt. *100	5.53220339	% coating wt. = coating wt./AS4 wt. *100	3.39385475
For Coating Thickness of 2000A (200 nm, 0.2micron, or 2e-05cm)		**For Coating Thickness of 2000A (200 nm, 0.2micron, or 2e-05cm)**	
IM7 dia. + coating dia. (cm)	5.40E-04	AS4 dia. + coating dia. (cm)	8.40E-04
IM7C radius (cm)	0.00027	AS4C radius (cm)	0.00042
pi	3.141593	pi	3.141593
IM7C volume (cm^3) = pi*r^2*h	2.2902E-07	AS4C volume (cm^3) = pi*r^2*h	5.5418E-07
Coating vol. (cm^3) = IM7C vol. - IM7 vol.	3.2673E-08	Coating vol. (cm^3) = AS4C vol. - AS4 vol.	5.1522E-08
Coating density (g/cm^3)	1.2	Coating density (g/cm^3)	1.2
Coating wt. (g) = coating vol.*coating den.	3.9207E-08	Coating wt. (g) = coating vol.*coating den.	6.1827E-08
% coating wt. = coating wt./IM7 wt. *100	11.2813559	% coating wt. = coating wt./AS4 wt. *100	6.87150838
For Coating Thickness of 1500A (150 nm, 0.15micron, or 15e-06cm)		**For Coating Thickness of 1500A (150 nm, 0.15micron, or 15e-06cm)**	
IM7 dia. + coating dia. (cm)	5.30E-04	AS4 dia. + coating dia. (cm)	8.30E-04
IM7C radius (cm)	0.000265	AS4C radius (cm)	0.000415
pi	3.141593	pi	3.141593
IM7C volume (cm^3) = pi*r^2*h	2.2062E-07	AS4C volume (cm^3) = pi*r^2*h	5.4106E-07
Coating vol. (cm^3) = IM7C vol. - IM7 vol.	2.4269E-08	Coating vol. (cm^3) = AS4C vol. - AS4 vol.	3.8406E-08
Coating density (g/cm^3)	1.2	Coating density (g/cm^3)	1.2
Coating wt. (g) = coating vol.*coating den.	2.9123E-08	Coating wt. (g) = coating vol.*coating den.	4.6087E-08
% coating wt. = coating wt./IM7 wt. *100	8.37966102	% coating wt. = coating wt./AS4 wt. *100	5.1222067

Another technology which has shown great promise in increasing the interfacial shear properties of composites was also evaluated. The Utility Development Corporation has recently demonstrated that the interlaminar shear strength of thermally cured composites can be increased by >25% by using epoxy resins which have been formulated with ceramic whiskers. This technology was combined with our electron beam curable epoxy resin technology and its effectiveness was evaluated by determining their composite interlaminar shear properties. Identically sized cylinders as described above using IM7 GP-sized carbon fibers were used to filament wind cylinders composed of a resin system consisting of 85% Tactix 123 with 3 phr OPPI initiator and 15% of the ceramic whiskers. This particular resin system was blended by the Utility Development Corporation using their dispersion technology. Wet filament winding of this formulation was very difficult. Due to the extreme abrasiveness of the ceramic particles we experienced a large number of fiber breaks during processing. Although we were able to fabricate a cylinder using this resin system, we do not consider this a viable material for future use in filament winding. On the other hand, formulations incorporating these types of ceramic particles may be workable for producing hot melt, unidirectional prepreg. A control cylinder using Tactix 123 with 3 phr OPPI initiator as the filament winding resin was also produced in order to compare and contrast with the ceramic whisker formulation.

After fabrication of the filament wound cylinders, they were shipped to Acsion Industries in Pinawa, Manitoba Canada and electron beam cured on a 10 MeV, 1 kW electron beam accelerator. During the electron beam curing cycle, which involved 9 passes at about 17 kGy per pass for a total dose of 150 kGy, the cylinders were individually rotated and conveyed fore and aft in a direction that was perpendicular to the length of the scan horn. Subsequent to cure, the cylinders were shipped back to Oak Ridge and carefully machined into short-beam-shear specimens and tested in interlaminar shear per ASTM D 2344.

3.4.2. Results

Table 12 details the material and process parameters that were used to yield the interlaminar shear strength properties of several different electron beam cured, IM7 filament

Table 12. Effects of Epoxy Coated Carbon Fibers on the Interlaminar Shear Strength of Electron Beam Cured, Filament Wound Cylinders.

Carbon Fiber (IM7-12K) Epoxy Coating Trials						Filament Winding Trials				Electron Beam Curing	Results
Mandrel, FW Sample, and Coated Fiber ID	Fiber Type	Epoxy Coating Material	Soln. Conc. (Phr Epoxy in Acetone or MEK)	Coated Fiber Drying Speed (ft/min)	Temp. of Tube Furnace (C)	Electron Beam Curable Filament Winding Resin	No. of FW Passes (approx. final t = 0.125")	Pot/Mandrel Temp.	Order of Filament Winding Trials (1-26)	Electron Beam Curing Dose (9 passes; 17 kGy per pass)	ASTM D 2344 Short Beam Shear Strength (psi)
EB2A-980721C	IM7-12K Unsized	Epon 1001F	1	35	165	ERL 2258 w/ 3 phr OPPI	25	RT/RT	1 (New Resin Bath)	150 kGy	9991
EB2B-980722E	IM7-12K Unsized	Epon 1001F	2.25	35	180	ERL 2258 w/ 3 phr OPPI	22	RT/RT	2	150 kGy	10428
EB2C-980722A	IM7-12K Unsized	Epon 1001F	3.5	35	180	ERL 2258 w/ 3 phr OPPI	21	RT/RT	3	150 kGy	9886
EB2D-980722D	IM7-12K Unsized	Epon 1001F	6	35	180	ERL 2258 w/ 3 phr OPPI	21	RT/RT	4	150 kGy	9764
EB2E-980723B	IM7-12K Unsized	Epon 1001F	10	35	180	ERL 2258 w/ 3 phr OPPI	20	RT/RT	5 (Resin Bath Changed After Run)	150 kGy	11169
EB4C-980727A	IM7-12K Unsized	Epon 1001F w/ 1 phr CD1012	1	35	180	ERL 2258 w/ 3 phr OPPI	22	RT/RT	9	150 kGy	10784
EB4D-980727B	IM7-12K Unsized	Epon 1001F w/ 3 phr CD1012	1	35	180	ERL 2258 w/ 3 phr OPPI	22	RT/RT	10	150 kGy	13457
EB4E-980728A	IM7-12K Unsized	Epon 1001F w/ 1 phr CD1012	6	35	180	ERL 2258 w/ 3 phr OPPI	21	RT/RT	11	150 kGy	11288
EB4F-980728B	IM7-12K Unsized	Epon 1001F w/ 3 phr CD1012	6	35	180	ERL 2258 w/ 3 phr OPPI	21	RT/RT	12 (Resin Bath Changed After Run)	150 kGy	11305
EB4B-980723A	IM7-12K Unsized	Epon 1007F	1	35	180	ERL 2258 w/ 3 phr OPPI	22	RT/RT	8 (New Resin Bath)	150 kGy	10244
EB1E-980729A	IM7-12K Unsized	Epon 1007F	6	35	180	ERL 2258 w/ 3 phr OPPI	22	RT/RT	17	150 kGy	10320

Notes: MEK was used to dissolve Epon 1007F and DEN 439; Acetone was used to dissolve Epon 1001F and Epon 826. FW Parameters: tension = 12 lbs.; compaction = 10 lbs./roller, tl. = 20 lbs.; resin scraping performed on each pass w/ plastic cup .

Table 12. Effects of Epoxy Coated Carbon Fibers on the Interlaminar Shear Strength of Electron Beam Cured, Filament Wound Cylinders.

Carbon Fiber (IM7-12K) Epoxy Coating Trials						Filament Winding Trials				Electron Beam Curing	Results
Coated Fiber ID	Fiber Type	Epoxy Coating Material	Soln. Conc. (Phr Epoxy in Acetone or MEK)	Coated Fiber Drying Speed (ft/min)	Temp. of Tube Furnace (C)	Electron Beam Curable Filament Winding Resin	No. of FW Passes (approx. final t = 0.125")	Pot/Mandrel Temp.	Order of Filament Winding Trials (1-26)	Eelectron Beam Curing Dose (9 passes; 17 kGy per pass)	ASTM D 2344 Short Beam Shear Strength (psi)
EB1D-980729B	IM7-12K Unsized	Epon 1007F w/ 1 phr CD1012	1	30	195	ERL 2258 w/ 3 phr OPPI	21	RT/RT	16 (New Resin Bath)	150 kGy	10377
EB1F-980730A	IM7-12K Unsized	Epon 1007F w/ 1 phr CD1012	6	30	195	ERL 2258 w/ 3 phr OPPI	20	RT/RT	18	150 kGy	8721
EB3A-980730B	IM7-12K Unsized	Epon 1007F w/ 3 phr CD1012	6	30	195	ERL 2258 w/ 3 phr OPPI	20	RT/RT	19 (Resin Bath Changed After Run)	150 kGy	8098
EB1A-980730C	IM7-12K Unsized	DEN 439	1	30	195	ERL 2258 w/ 3 phr OPPI	22	RT/RT	13 (New Resin Bath)	150 kGy	11016
EB1B-980803C	IM7-12K Unsized	DEN 439	6	30	195	ERL 2258 w/ 3 phr OPPI	22	RT/RT	14	150 kGy	9625
EB1C-980803B	IM7-12K Unsized	DEN 439 w/ 3 phr CD1012	6	30	200	ERL 2258 w/ 3 phr OPPI	22	RT/RT	15 (Resin Bath Changed After Run)	150 kGy	9285
EB3B-980731A	IM7-12K Unsized	Epon 826	1	35	185	ERL 2258 w/ 3 phr OPPI	22	RT/RT	20 (New Resin Bath)	150 kGy	10834
EB3E-980804A	IM7-12K Unsized	Epon 826	6	35	185	ERL 2258 w/ 3 phr OPPI	22	RT/RT	23	150 kGy	10165
EB3C-980731B	IM7-12K Unsized	Epon 826 w/ 1 phr CD1012	1	35	185	ERL 2258 w/ 3 phr OPPI	22	RT/RT	21	150 kGy	11242
EB3D-980731C	IM7-12K Unsized	Epon 826 w/ 3 phr CD1012	1	35	185	ERL 2258 w/ 3 phr OPPI	22	RT/RT	22	150 kGy	10015
EB3F-980803A	IM7-12K Unsized	Epon 826 w/ 3 phr CD1012	6	35	185	ERL 2258 w/ 3 phr OPPI	22	RT/RT	24 (Resin Bath Changed After Run)	150 kGy	9677

Notes: MEK was used to dissolve Epon 1007F and DEN 439; Acetone was used to dissolve Epon 1001F and Epon 826. FW Parameters: tension = 12 lbs.; compaction = 10 lbs./roller, tl. = 20 lbs.; resin scraping performed on each pass w/ plastic cup .

Table 12. Effects of Epoxy Coated Carbon Fibers on the Interlaminar Shear Strength of Electron Beam Cured, Filament Wound Cylinders.

Carbon Fiber (IM7-12K) Epoxy Coating Trials						Filament Winding Trials				Electron Beam Curing	Results
Coated Fiber ID	Fiber Type	Epoxy Coating Material	Soln. Conc. (Phr Epoxy in Acetone or MEK)	Coated Fiber Drying Speed (ft/min)	Temp. of Tube Furnace (C)	Electron Beam Curable Filament Winding Resin	No. of FW Passes (approx. final t = 0.125")	Pot/Mandrel Temp.	Order of Filament Winding Trials (1-26)	Electron Beam Curing Dose (9 passes; 17 kGy per pass)	ASTM D 2344 Short Beam Shear Strength (psi)
EB2F-83A	IM7-12K Unsized	None	NA	NA	NA	ERL 2258 w/ 3 phr OPPI	21	RT/RT	6 (New Resin Bath)	150 kGy	8708
EB4A-83B	IM7-12K GP (lot #D1234-6D)	None	NA	NA	NA	ERL 2258 w/ 3 phr OPPI	22	RT/RT	7 (Resin Bath Changed After Run)	150 kGy	12118
EB6A-07A	IM7-12K GP (lot #D1234-6D)	None	NA	NA	NA	Tactix 123/3 phr OPPI	20	200F/RT	25 (New Resin Bath - Resin Bath Changed After Run)	150 kGy	10597
EB6B-807B	IM7-12K GP (lot #D1234-6D)	None	NA	NA	NA	Tactix 123 (85%)/UDC Particles (15%)/3 phr OPPI based on T123 wt.	20 (0.188 inches thick)	220F/Heated wIR heater and hot guns	26 (New Resin Bath)	150 kGy	9427

Notes: MEK was used to dissolve Epon 1007F and DEN 439; Acetone was used to dissolve Epon 1001F and Epon 826. FW Parameters: tension = 12 lbs.; compaction = 10 lbs./roller, tl. = 20 lbs.; resin scraping performed on each pass w/ plastic cup .

wound composites. The ILSS data comparing the surface-treated-unsized (EB2F) specimens versus the surface-treated-conventional GP sized (EB4A) specimens versus the surface-treated-EB4D coated composite specimens averaged 8708, 12118, and 13457 psi, respectively. For the EB4D (Epon 1001F with 3 phr CD1012) coated composite specimens, these values translate into a 55% improvement in ILSS relative to the surface-treated, unsized specimens (EB2F), and an 11% improvement in ILSS relative to the surface-treated-conventional GP sized (EB4A) specimens. This improvement is very encouraging since the epoxy coatings which were used to coat the IM7 carbon fibers were performed on surface-treated, unsized fibers which were several months old. It is theorized that, with age, the functional groups formed as a result of the original fiber surface treatment on the unsized fibers lose a large percentage of their surface functionality. As a result of this aging process one would suspect that these fibers would not have bonded nearly as well as fibers that are coated immediately after the fiber surface treatment process. On future work this hypothesis will be evaluated and determined whether it is possible to improve the ILSS beyond the level of our initial promising attempts in this project. Figures 25-28 are scanning electron micrographs (SEM) of surface-treated and unsized IM7 carbon fibers that were coated with one of the epoxy coating materials evaluated in this study. These particular fibers were coated out of an acetone solution containing about 10% by weight Epon 1001F. Subsequent to coating the fiber, the acetone was evaporated off the fiber using a furnace temperature of 120°C.

With the exception of one epoxy coating formulation all of the other 22 formulations that were applied to the aged, surface-treated, and unsized IM7 fibers had ILSS properties significantly greater than the conventional surface-treated-unsized specimens (EB2F). This finding supports the argument for further developing sizing or coating strategies that can potentially improve the fiber-matrix interphase properties and adhesion.

In Figure 29 there does not appear to be a relationship between the epoxy concentration of a given epoxy coating resin, in this case Epon 1001F with no initiator, and its effect on the ILSS of electron beam cured composites. In Figures 30-32 the maximum ILSS for the lower melting and lower weight per epoxide Epon 1001F coatings is improved by using a greater amount of initiator (3 phr versus 1 phr) and a lower epoxy coating concentration (1% versus 6%). On the other hand, for compositions involving the higher melting and higher weight per epoxide Epon 1007F formulations, or the higher melting, epoxy novolac DEN 439 materials, or

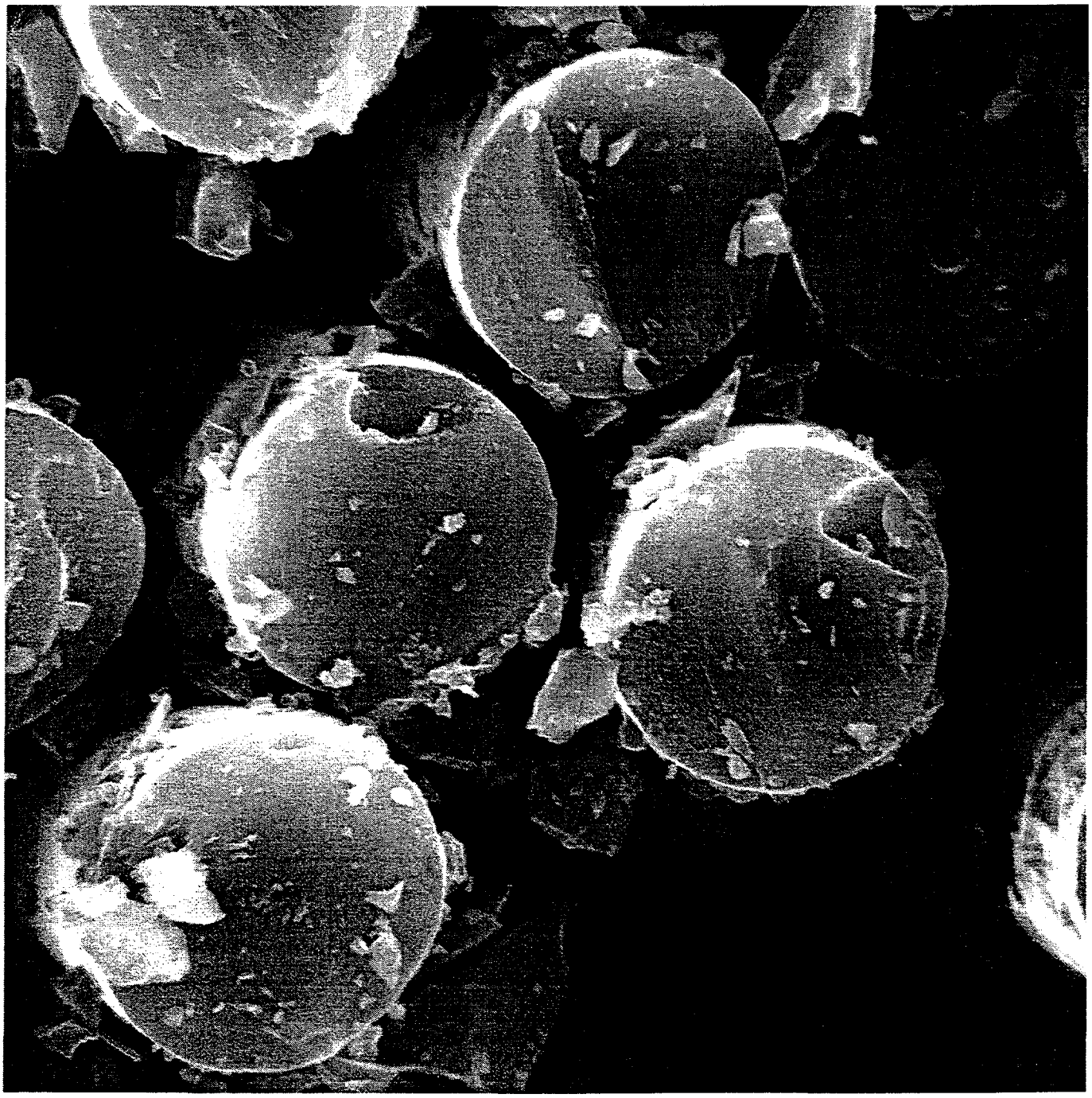


Figure 25. SEM of epoxy coated IM7 Carbon Fibers (6000X). The coating was applied onto the fiber out of a 10% Epon 1001F solution.

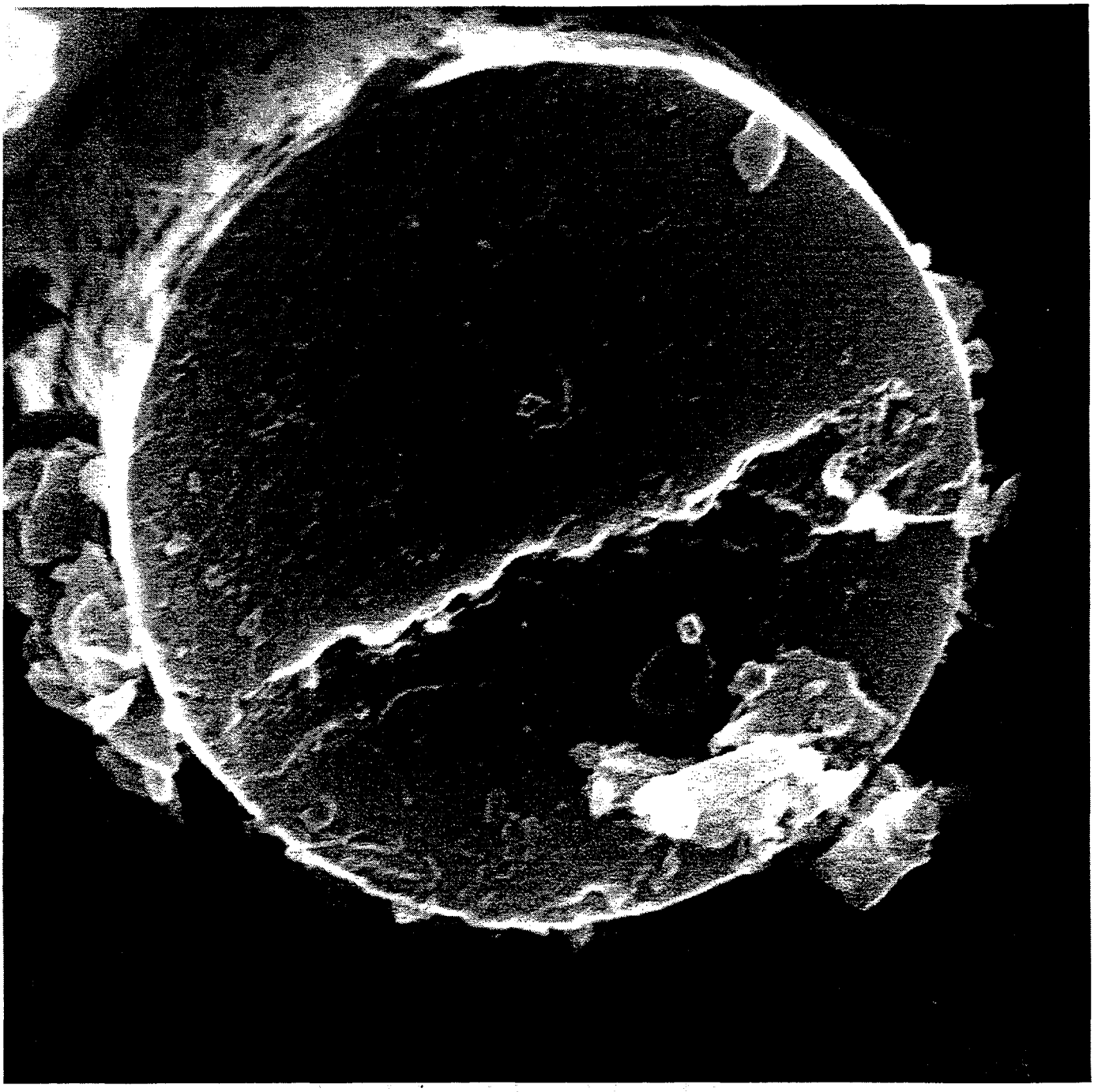


Figure 26. SEM of epoxy coated IM7 Carbon Fiber (15,000K).

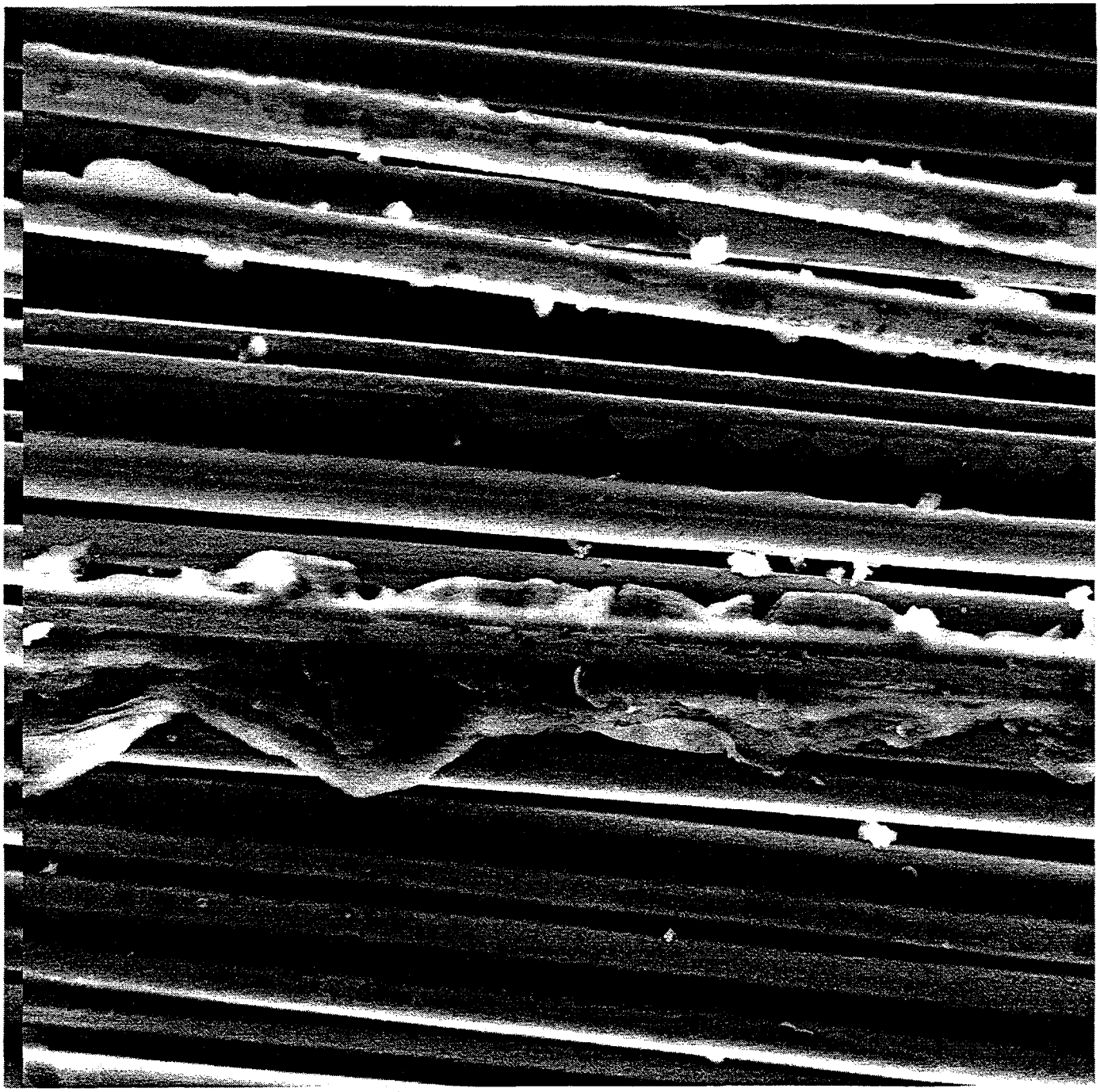


Figure 27. SEM of epoxy coated IM7 Carbon fibers (1000X).

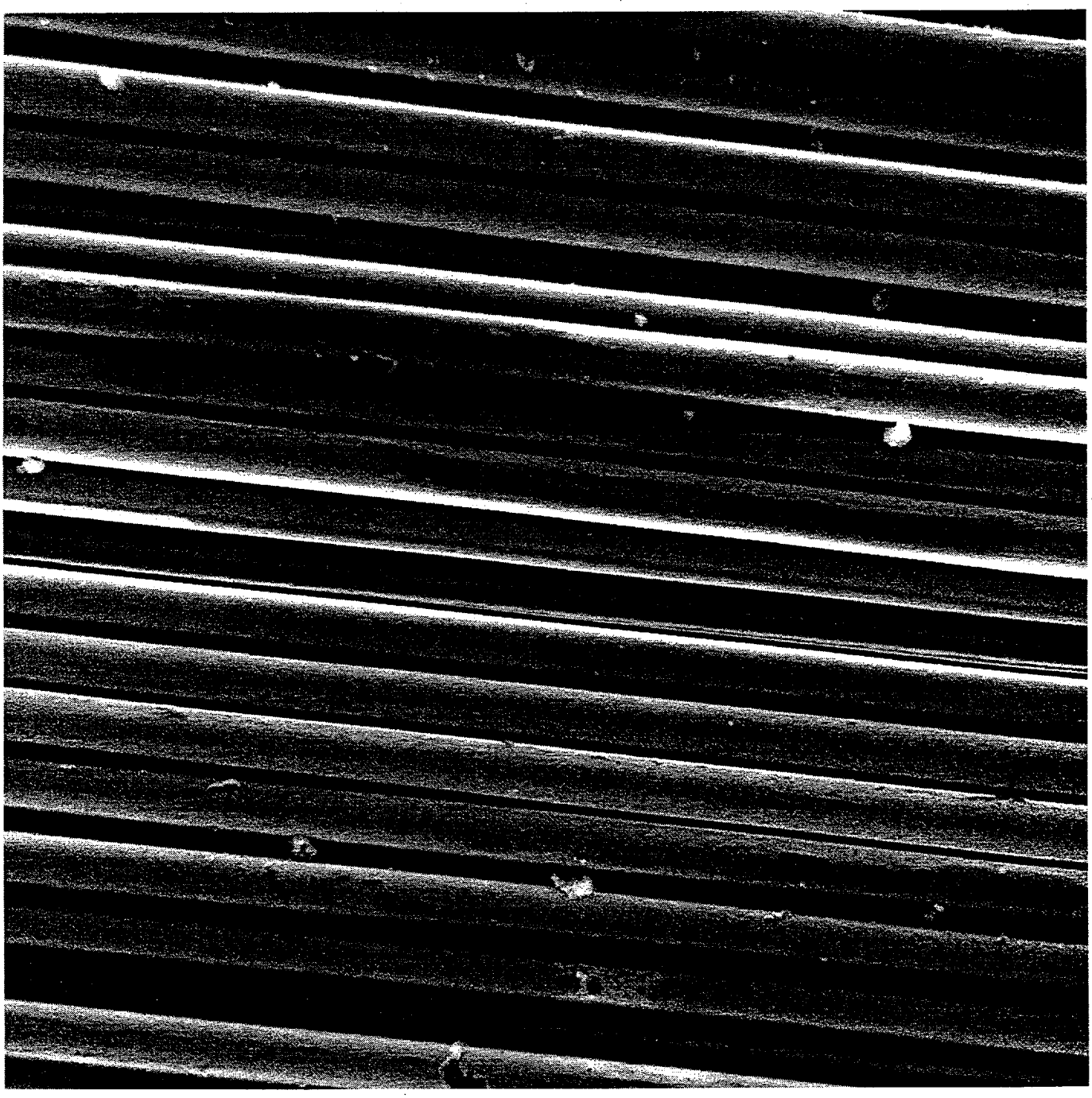
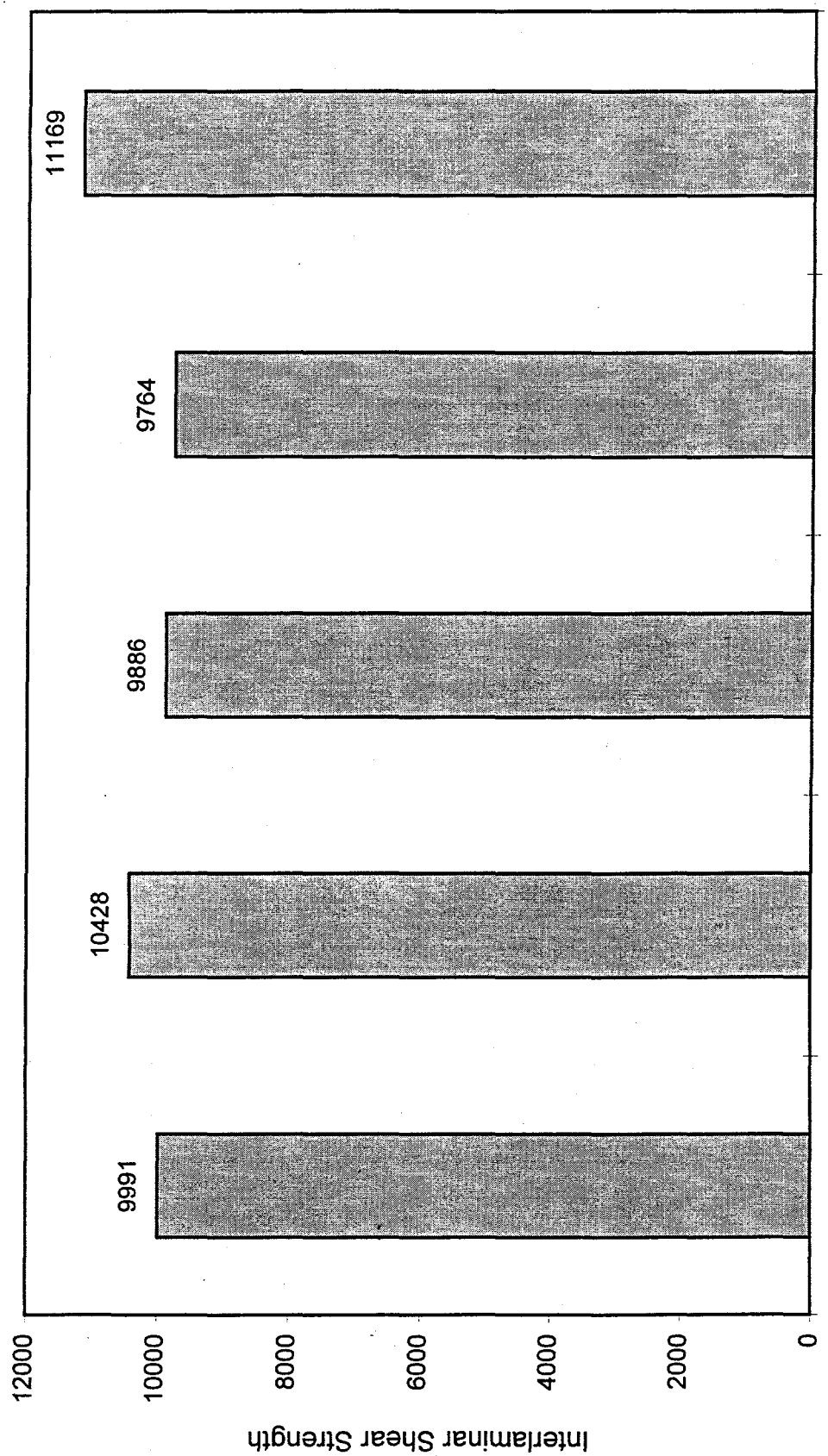
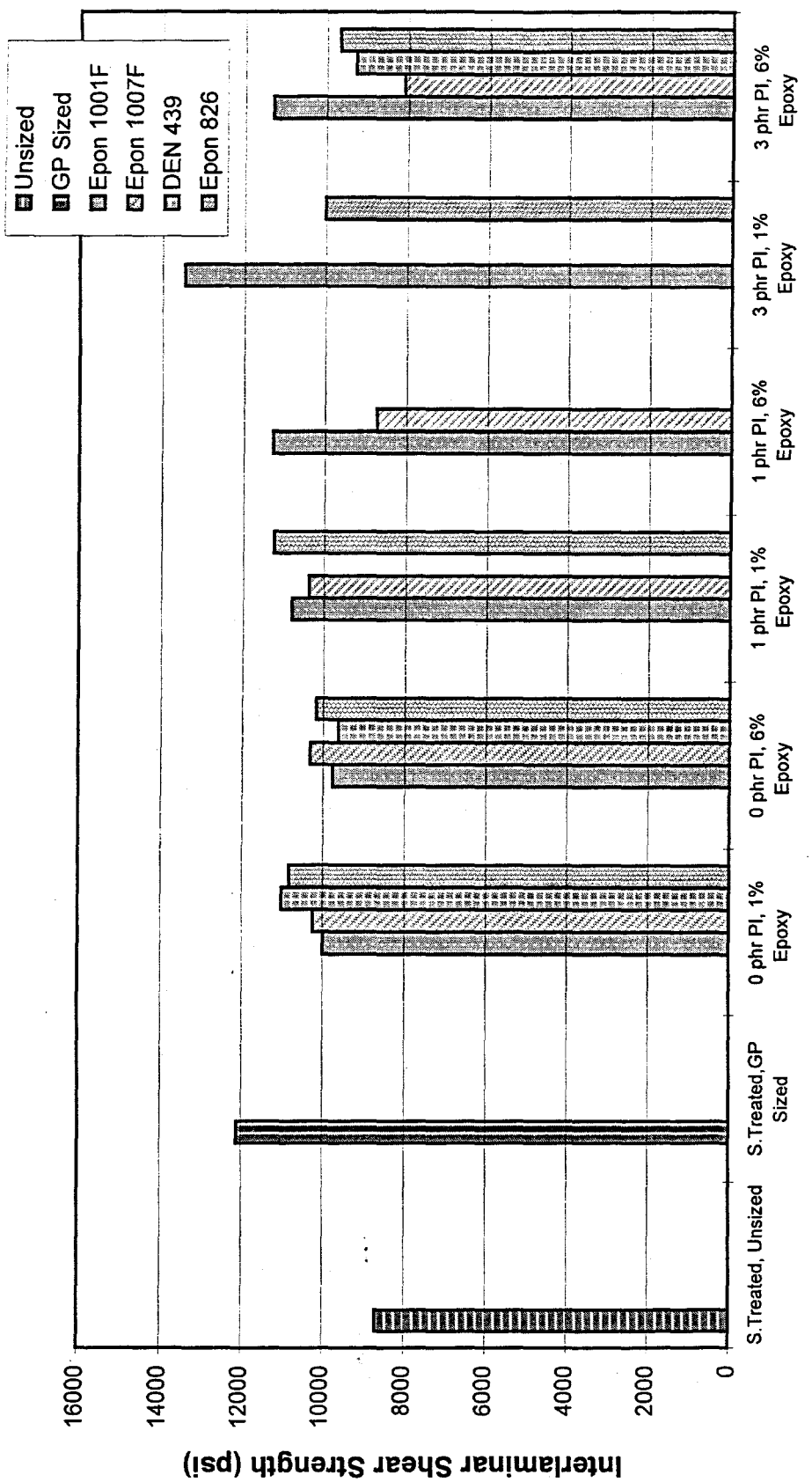


Figure 28. SEM of epoxy coated IM7 Carbon Fibers (1000X).



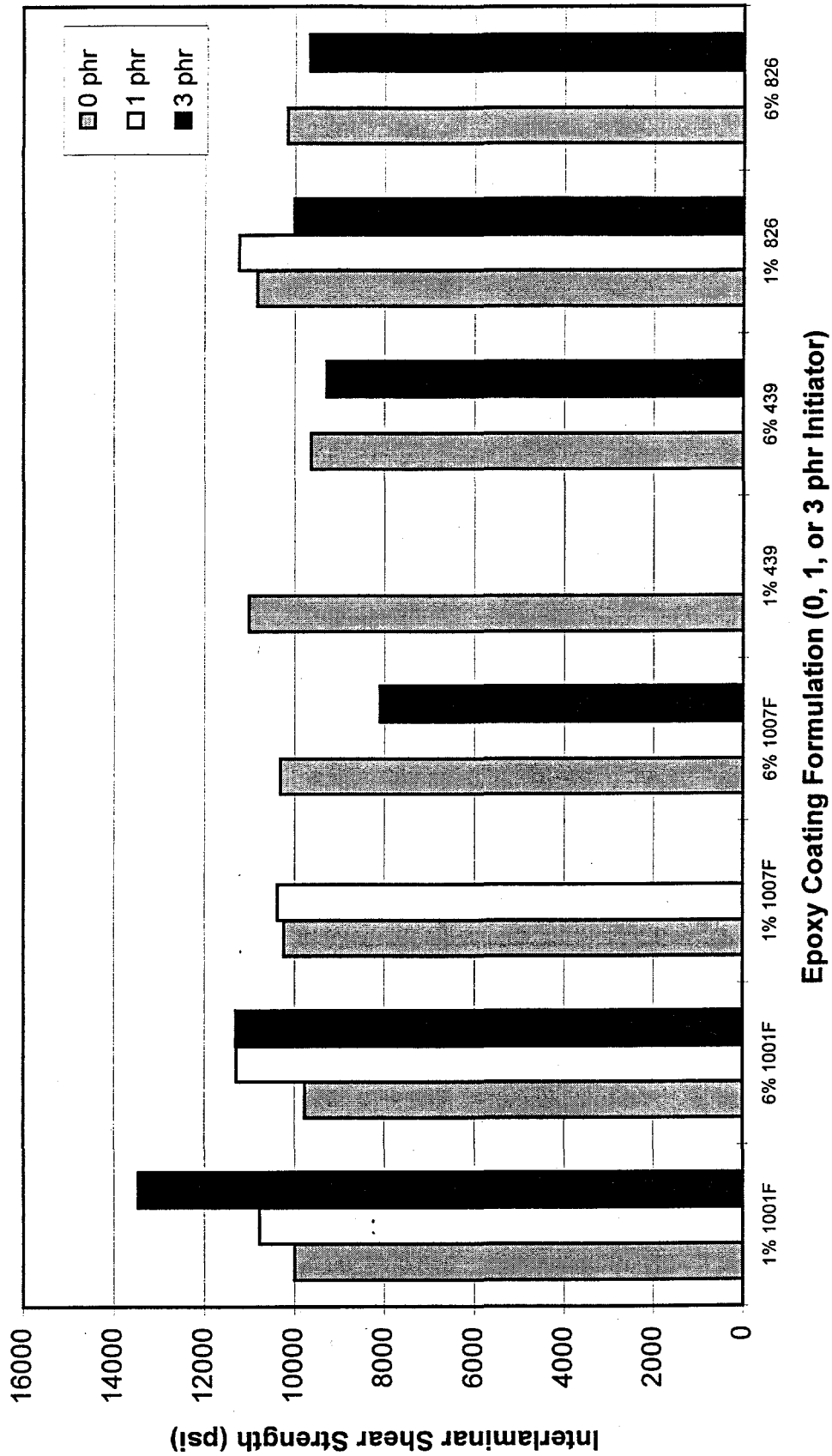
Note: The epoxy coatings were applied onto conventionally surface treated and unsized IM7 fibers out of an epoxy solution. Subsequent to solvent evaporation the fiber was filament wound at RT using ERL 2258/3phr OPPI and electron beam cured at 150 kGy.

Figure 29. Effects of Epoxy Coated IM7 Carbon Fibers on the Interlaminar Shear Strength of Electron Beam Cured, Filament Wound Composites.



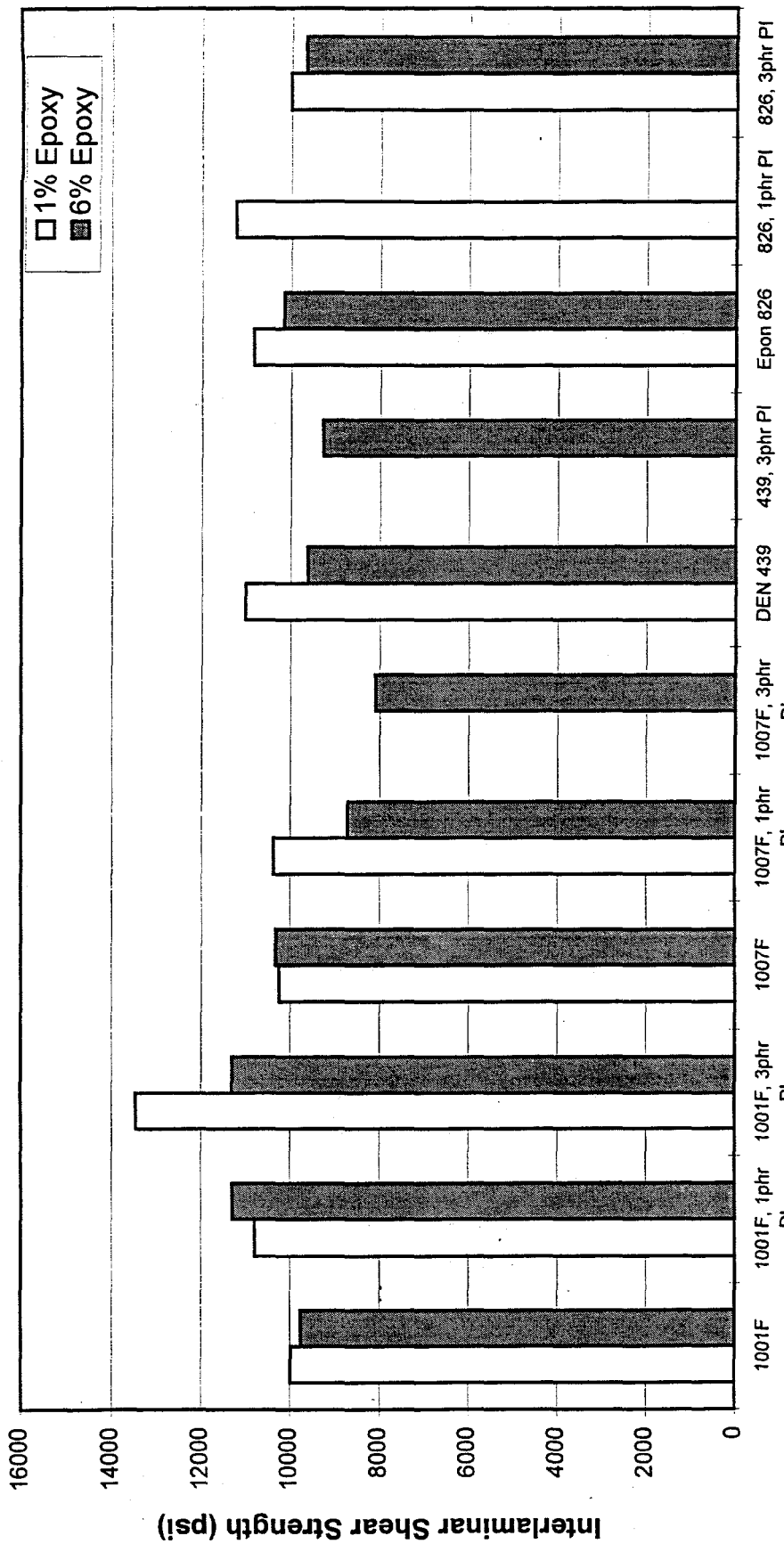
Note: On all but the first two columns (Controls) the epoxy coatings were applied to surface treated, unsized fibers out of an epoxy solvent. After solvent evaporation the fiber was filament wound at RT w/ERL 2258/3 phr OPPI and electron beam cured at 150 kGy.

Figure 30. Effects of Epoxy Coated IM7 Carbon Fibers on the Interlaminar Shear Strength of Electron Beam Cured, Filament Wound Composites



Note: The epoxy coatings were applied onto conventionally surface treated and unsized IM7 fibers out of an epoxy solution. Subsequent to solvent evaporation the fiber was filament wound at RT using ERL 2258/3 phr OPPI and electron beam cured at 150 kGy.

Figure 31. Effects of Epoxy Coated IM7 Carbon Fibers on the Interlaminar Shear Strength of Electron Beam Cured, Filament Wound Composites



Note: The epoxy coatings were applied onto conventionally surface treated and unsized IM7 fibers out of an epoxy solution. Subsequent to solvent evaporation the fiber was filament wound at RT using ERL 2258/3 phr OPPI and electron beam cured at 150 kGy.

Figure 32. Effects of Epoxy Coated IM7 Carbon Fibers on the Interlaminar Shear Strength of Electron Beam Cured, Filament Wound Composites.

the low viscosity, difunctional epoxy Epon 826 formulations, the trends for optimizing the ILSS are favored by using lesser amounts of initiator or no initiator (0 phr or 1 phr versus 3 phr) in combination with lower epoxy concentrations (1% versus 6%).

Due to the problems that we experienced in wet filament winding with the formulations incorporating the ceramic particles it was not surprising that the ILSS properties for these specimens were low. In future work we may reevaluate these materials by attempting to make unidirectional prepreg and fabricate laminates via hand lay-up.

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4. CONCLUSIONS

1. T_g values for electron beam and thermally cured Tactix 123 epoxy resins are optimum for formulations having initiator concentrations >1.5 phr.

2. For a given initiator concentration (1-3 phr) the T_g values for electron beam cured Tactix 123 epoxies are generally higher by about 20°C versus thermally cured Tactix 123 epoxies.

3. Incomplete cure for Tactix 123 epoxies is indicated at initiator concentrations below 1.5 phr and doses ≤ 140 kGy. Complete cure for Tactix 123 epoxies is indicated at initiator concentrations above 1.5 phr initiator, 80 kGy dose, and 5 kGy/pass.

4. Data on electron beam cured, Tactix 123 epoxy neat resins indicates that while shear strain and shear strength are somewhat dependent on initiator concentration and cure dosage, the shear modulus is not greatly affected by these parameters. This indicates that the most simple formulation and process changes are not likely to generate substantial improvement in the interfacial properties.

5. Surface-treated and unsized AS4 carbon fibers have higher adhesion to the electron beam processed epoxy (Taxtix 123 with OPPI) than surface-treated and unsized IM6 carbon fibers. Based on results from other published studies, a similar relationship would hold true for IM7 carbon fibers versus AS4.

6. The differences in adhesion with fiber surface treatment (i.e. untreated versus surface-treated) for electron beam processed composites are similar to those observed for thermally processed epoxy composites. Surface-treated fibers produce higher adhesion than untreated fibers.

7. The adhesion of the electron beam processed epoxy (Tactix 123 with 3 phr OPPI) to the same carbon fibers was generally lower than measured for similar epoxies processed thermally and much lower than epoxies cured with aromatic amines.

8. Significantly higher adhesion (~60%) was measured for surface-treated and unsized AS4 carbon fibers and the Tactix 123 epoxy with 1 phr OPPI versus Tactix 123 epoxy with 3 phr

OPPI. This was a result of the resin being incompletely processed with this lower amount of initiator. Postcuring at 225°C completed the cure and reduced the modulus and the adhesion to the same level as obtained with Tactix 123 having 3 phr and 5 phr OPPI.

9. The observation that adhesion of carbon fiber to Tactix 123 with 1 phr OPPI can be 60% greater than that attained for other formulations and the lower amount of epoxy chemisorbed to the carbon fiber surface under electron beam conditions indicates that sizing strategies can potentially be developed to improve the fiber-matrix interphase properties and adhesion.

10. Preliminary interfacial shear strength measurements of electron beam cured Tactix 123 with 3 phr OPPI combined with a surface-treated and epoxy sized AS4C fiber (from Hercules) gave superior results compared to surface-treated and unsized AS4 fiber. IFSS values were at least 25% greater for the AS4C fiber versus the AS4 fiber. This value of IFSS was still 60% of the value attainable in a thermally processed, amine cured epoxy.

11. One epoxy based coating applied onto aged, surface-treated and unsized IM7 carbon fibers improved the composite ILSS of electron beam cured composites by 11% versus composites made with surface-treated and GP sized IM7 carbon fibers (GP size is the current IM7 fiber sizing material applied by Hercules).

12. Several epoxy-based coatings that were applied to aged, surface-treated, and unsized IM7 fibers exhibited up to 55% greater ILSS versus composites made with surface-treated and unsized IM7 fibers.

13. We believe that the composite ILSS can be improved beyond these initial values by applying these types of epoxy based coatings or sizings (with or without initiator) to carbon fibers immediately following the fiber surface treatment.

The results of this effort firmly suggests that the fiber-resin interface is probably the source of the deficient shear properties for electron beam-curable cationic epoxy, carbon fiber reinforced composites.

5. FOLLOW-ON FUNDING

As a result of the promising developments from this LDRD effort, a proposal entitled, "Interfacial Properties of Electron Beam Cured Composites", is currently being considered for funding by the DOE-ER sponsored LTR-CRADA program to continue this work. If the project is funded, ORNL will lead a 3-year, $2.6 million dollar effort involving eight industrial partners, NASA-Langley, and the U.S. Air Force. The partners are providing cash contributions to ORNL equal to over half of DOE's total contribution ($400K from partners versus $750K from DOE) and the total partner funding (in-kind plus funds-in) exceeds a 2:1 match to DOE funding. The principal objective of this proposal is to significantly improve the interfacial properties of carbon fiber reinforced composites beyond current state-of-the-art electron beam cured composites for use in several DOE, DoD, and industrial applications.

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6. ACKNOWLEDGEMENTS

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7. REFERENCES

1. C. J. Janke, R. E. Norris, K. Yarborough, S. J. Havens, V. J. Lopata, "Critical Parameters for Electron Beam Curing of Cationic Epoxies and Property Comparison of Electron Beam Cured Cationic Epoxies Versus Thermal Cured Resins And Composites," 42nd International SAMPE Symposium, Anaheim, CA, 42, 477 (1997).

2. C. J. Janke, "Properties of Electron Beam Cured vs. Autoclave Cured Composites and Adhesives," Proc. 2nd Electron Beam Curing of Composites Workshop, Oak Ridge, TN, Sept. 10-11, 1997.

3. C. J. Janke, J. D. Farmer, V. J. Lopata, "The Electron Beam Cure of Fiberglass/Epoxy Prepregs," 29th International SAMPE Technical Conference, Orlando, FL, (1997) - In Printing.

4. C. J. Janke, S. J. Havens, V. J. Lopata, and M. Chung, "Electron Curing of Epoxy Resins: Initiator and Concentration Effects on Curing Dose and Rheological Properties," 28th International SAMPE Technical Conference, Seattle, WA, 28, 901 (1996).

5. C. J. Janke, "Materials Development," Proc. 1st Electron Beam Curing of Composites Workshop, Oak Ridge, TN, Sept. 18-19, 1996.

6. C. J. Janke, S. J. Havens, G. F. Dorsey, V. J. Lopata; "Toughened Epoxy Resins Cured by Electron Beam Radiation," 28th International SAMPE Technical Conference, Seattle, WA, 28, 877 (1996).

7. C. J. Janke, S. J. Havens, G. F. Dorsey, V. J. Lopata, "Electron Beam Curing of Epoxy Resins by Cationic Polymerization," 41st International SAMPE Symposium, Anaheim, CA, 41, 196 (1996).

8. L. T. Drzal, "Final Report: Adhesion of Carbon Fibers to Vinyl Ester Matrices," NSF State/Industry University Cooperative Research Center on Low-Cost, High-Speed Polymer Composite Processing, 1997.

9. R. Agrawal and L. T. Drzal, "Effects of Microwave Processing on Fiber-Matrix Adhesion in Composites," J. Adhesion, 29, pp. 63-79 (1989).

10. J. V. Crivello, M. Fan, and D. Bi, Journal of Applied Polymer Science, 44, 9-16 (1992).

11. L. T. Drzal and G. Hammer, "Graphite Fiber Surface Analysis Through XPS and Polar/Dispersion Free Energy Analysis," App., Surf. Sci., 4, 340-355 (1980).

12. L. T. Drzal, N. Sugiura and D. Hook, "The Role of Chemical Bonding and Surface Topography in Adhesion Between Carbon Fibers and Epoxy Matrices," Composite Interfaces 4, pp. 337-354 (1997).

13. L. T. Drzal, "The Surface Composition and Energetics of Type A Graphite Fibers," Carbon 15, 129-138 (1997).

14. K. J. Hook, R. K. Agrawal, and L. T. Drzal, "Effects of Microwave Processing on Fiber-Matrix Adhesion. II. Enhanced Chemical Bonding of Epoxy to Carbon Fibers," J. Adhesion, 32, p. 157-170 (1990).

15. L. T. Drzal, N. Sugiura and D. Hook, "Effect of Interfacial Chemical Bonding and Surface Topography on Adhesion in Carbon Fiber/Epoxy Composites," Proceedings of the 10th Annual Meeting of the American Society for Composites (1994).

16. R. Agrawal and L. T. Drzal, "Effects of Microwave Processing on Fiber-Matrix Adhesion in Composites," J. Adhesion, 29, pp. 63-79 (1989).

17. K. J. Hook, R. K. Agrawal, and L. T. Drzal; "Effects of Microwave Processing on Fiber-Matrix Adhesion. II. Enhanced Chemical Bonding of Epoxy to Carbon Fibers," J. Adhesion, 32, pp. 157-170 (1990).

18. V. Rao and L. T. Drzal, "The Dependence of Interfacial Shear Strength on Matrix and Interphase Properties," Polymer Composites, 12, pp. 48-56 (1991).

19. L. T. Drzal, "Final Report: Adhesion of Carbon Fibers to Vinyl Ester Matrices," NSF State/Industry University Cooperative Research Center on Low-Cost, High-Speed Polymer Composite Processing, 1997.

20. S. P. Pappas, UV Curing: Science and Technology, Technology Marketing Corporation, Stamford, CT, 1978 (Chapters 1, 2, 6-9).

21. L. T. Drzal, "The Surface Composition and Energetics of Type A Graphite Fibers," Carbon, 15, 129-138 (1977).

22. L. T. Drzal, M. Rich, M. Koenig, and P. Lloye, "Adhesion of Graphite Fibers to Epoxy Matrices. II. The Effect of Fiber Finish," J. Adhesion, 16, 133-152, (1983).

23. B.K. Larson and L.T. Drzal, "Glass Fiber Sizing-Matrix Interphase Formation in Liquid Composite Molding: Effects on Fiber-Matrix Adhesion and Mechanical Properties," Composites, 25, No. 7, pp. 711-721 (1994).

24. V. Rao and L. T. Drzal, "Interphase Mechanical Property Effects on Fiber-Matrix Adhesion in Composite Materials," American Society for Composites, Proceedings of the 4th Technical Meeting (1989).

25. Y. Thomas, J. R. Parisi, B. Boutevin, D. Beziers, E. Chataignier and G. Desarmot, "Improvement of Fiber/matrix Bonding in Carbon-acrylic Composites by Electron Irradiation: Concept of Difunctional Coupling Agent," Comp. Aci. Tech. 52, pp. 299-307.

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