Improving Adhesion in Interleaf Composites Using Plasma Processing

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SYNOPSIS

A novel radio frequency (RF) plasma processing technique, known as plasma induced polymerization (PIP), was used in a multistep plasma process to deposit a thin, uniform layer of viscoelastic material on Upilex-S high-temperature polyimide film in order to enhance adhesion between the film and the resin in carbon fiber interleaf composites using epoxy (Hercules 8551-7A) resin systems. In a three-phase study, the processing parameters of residence time, plasma power, plasma pressure, and monomer gas were varied to investigate adhesion improvement. Depositions were characterized using scanning electron microscopy and X-ray photoelectron spectroscopy (XPS) analysis. Compressive mode II strain energy release rate (G_{IIc}) was characterized by end-notched flexure testing to rank and predict the best RF process for a thermoplastic film interleaf composite structure using polyimide film. Adhesion was improved by as much as 140% over the adhesive performance of untreated Upilex-S using the epoxy resin system. However, adhesive performance was improved in the relatively low temperature (177°C) processing system, and this plasma deposition may not be stable at the higher processing temperatures needed for processing polyimide matrix systems such as PMR-15. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Recent studies have tried to incorporate the thermal properties of both polyimide and bismaleimide resins in advanced composite structures while overcoming their brittle nature. Schemes have been employed to improve their damage tolerance, such as resin formulation modification, through-thickness fibrous reinforcement, and interleaving.[1]

Interleaving appears to be the simplest approach to improving composite damage tolerance, because interleaving can be done using existing materials in a unique combination rather than creating newer, more exotic, and perhaps costlier materials.

There are three kinds of interleaving:

1. resin interleaving or duplexing;
2. thin film insertion with a thermoplastic film; and
3. fibrous, nonwoven mat insertion.

Since interleaf composites had their genesis in 1984, there have been several studies on resin interleaf systems.[2-6] Until recently there were only a few studies pertaining to thermoplastic film and mat interleaf systems.[1,7,8] The former system, which is the topic of this article, incorporates a thermoplastic film of prescribed thickness between plies of prepregged carbon fiber. This technique is particularly useful where composite systems are subject to high temperatures. Armstrong-Carroll and Donnellan[1] noted that high-temperature resin formulations of bismaleimide (BMI) are interleaved most effectively through the use of thin high-temperature thermoplastic films. The same authors also investigated interleaf films composites using PMR-15 prepreg resins.[2] The most significant challenge in using interleaf films is that bonding between the film and the adjacent prepreg is virtually nonexistent, because the thermoplastic films contain little or no chemical reactivity on the surface. Therefore, sufficient adhesive bonding between the thermoplastic film interleaving materials and the resin system forming the matrix must be achieved in order to assure damage tolerance of interleaved composite structures.

Without sufficient bonding between alternating plies and film, delamination will occur.

Adhesive strength is a function of bonding site density between the thermoplastic film and the resin. Because interleaved film materials have few or no active bonding sites, adequate bonding necessitates the creation of new bonding sites on the film surface. Radio frequency (RF) plasma processing is useful in this respect because it alters the surface chemistry of the substrate requiring modification while leaving the bulk properties of the modified material intact.

This article presents our work using RF plasma processing to lay down a thin, adherent, viscoelastic, and reactive interlayer material to provide a higher density of chemical bonding sites between a polyimide film (Upilex-S) and adjacent plies of prepregged carbon fiber (Hercules 8551-7A epoxy resin).

PLASMA PROCESSING

Plasma processing provides a way to enhance or create adhesion between two materials without changing bulk properties, because only the surface is modified. The thickness of the surface modification is usually on the order of angstroms to hundreds of nanometers. Plasma treatments can be used to modify or to add chemical bonding sites to the existing surface, thus providing a means to enhance adhesion of interleaf films to resins and allowing for a significant increase in toughness properties through interleaving. Reviews pertaining to plasma processing of polymers can be found elsewhere.[9-11]

Armstrong-Carroll and Donnellan[1] studied film-resin bonding of BMI interleaf composites through the use of plasma treatments and found that such processes allowed for a significant improvement in toughness. Further studies were conducted using Kapton and Upilex-S polyimide films with PMR-15 prepreg without plasma modification.[2] The Upilex-S film has greater modulus and strength than the Kapton film. For films with no plasma treatment, but identical composite curing conditions, the compressive mode II strain energy release rate, G_{IIc}, was 1736 ± 643 J/m^2 for the Kapton/PMR-15 system, but only 46 ± 15 J/m^2 for the Upilex/PMR-15 system.

Yang and Sung[12] used plasma induced polymerization on Kapton polyimide film to create strong bonding with rubbers. There is a significant difference between plasma induced polymerization (PIP) and conventional plasma polymerization (PP). In PP, the substrate is placed in the glowing plasma field, and the monomer gas is fragmented by the plasma and is subsequently deposited on the substrate where it reforms into a highly crosslinked network.[11] In PIP, the substrate is not placed directly in the plasma field, but is placed downstream from the plasma source. An inert gas, such as argon, is excited by the plasma and is convected toward the substrate. The polymerizable gas (butadiene, styrene, etc.) is mixed with the excited inert gas near the substrate and is subsequently excited to a level that initiates polymerization, but does not fragment the monomer to the same extent as in plasma polymerization. The deposited polymer is thought to be a lightly crosslinked or noncrosslinked linear polymer with significant viscoelastic properties. Yang and Sung used PIP processing with butadiene gas to produce a tough and adherent interface that bonded rubber to a Kapton film with sufficient strength that the film failed (not the interface) in a 180° peel test.

EXPERIMENTAL

Plasma Reactor

In this study, a Plasma Science 0500 reactor (Plasma Science, Santa Clara, CA) was modified by building a downstream delivery system consisting of a large flat steel plate with a hole to allow an external plasma jet to enter the reactor (see Fig. 1). Circumscribing this hole were eight small holes (1.5-mm diameter) that delivered the monomer gas into the argon stream just ahead of the target. Plasma in the external Pyrex glass tube was created by connecting a copper ring to the RF power source.[13,14]

A rotating disk target on a stand was built to allow a uniform distribution of the polymer deposition on the target film. This target stand was composed of a 28 cm × 2 mm circular aluminum disk. The position of the target was located such that the center of the PIP plasma jet contacted the rotating disk about 8 cm from the center of the disk. This arrangement created the most uniform coating on the target. The disk was attached to an insulated axle driven by a microprocessor-controlled stepping motor.

Plasma processing was done in three steps.[13] In the first step, the RF power was directed to the rotating aluminum disk, and the ground electrode was the steel plate providing monomer delivery. An argon plasma was established for 1 min between the disk and steel plate that etched the Upilex film mounted upon the rotating disk. This step removed
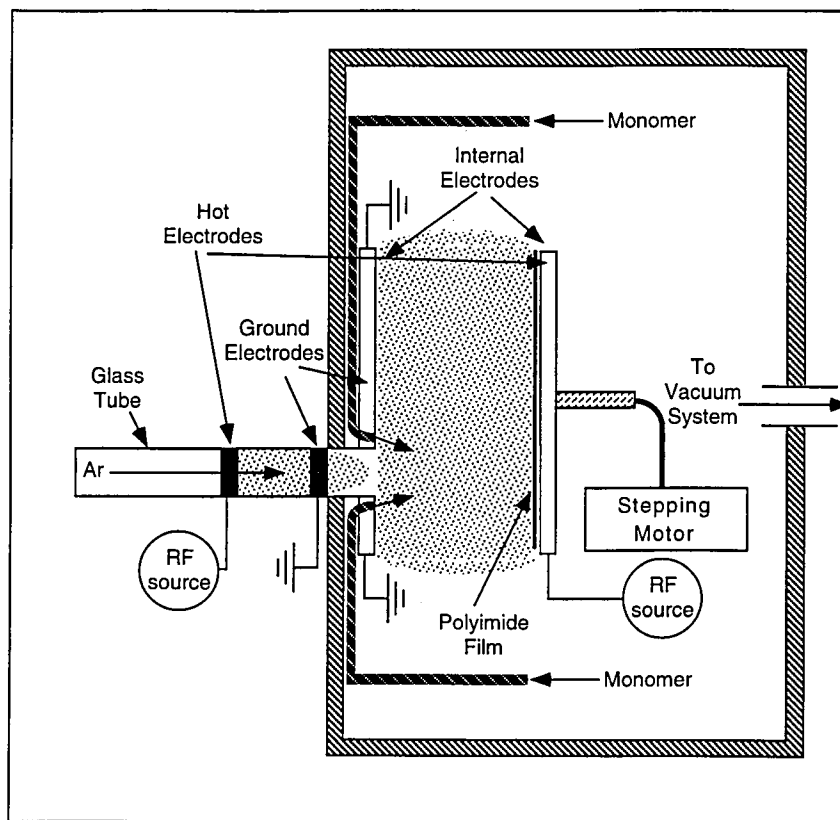
Figure 1 Schematic of the plasma polymerization reactor. Plasma can be generated either between the rotating disk and the reactor wall, or between the external electrodes around a Pyrex tube.

surface contaminants and activated the polymer surface for subsequent PIP processing. The second step employed PIP using the reactor's external electrode and argon as a carrier gas. The monomers were subjected to PIP for various processing times, plasma powers, and pressures. The third step employed the reactor's internal electrodes (as in step one) to do plasma processing or grafting of an amine-containing overlayer designed to react with adjacent epoxy groups upon autoclave curing of the complete interleaf composite laminate. Figure 2 depicts this multistep process. Following deposition on one side of the film, the Upilex was carefully removed, turned over, and replaced on the rotating disk, and an identical treatment was applied to the other side.

Materials

Upilex-S (Ube Industries Ltd., Japan) is based on biphenyl tetracarboxylate dianhydride and diamine and is produced by casting an imidized solution, with no accompanying dewatering reaction, so there are claimed to be fewer voids. A 0.025-mm thick film was used in these studies.

Hercules 8551-7A unidirectional tape was a gift from McDonnell–Douglas Corp. (St. Louis, MO).

Isoprene, allylamine, styrene, 1-3,diaminopropane, hexamethyldisiloxane (HMDS), and tetramethyldisiloxane (TMDS) were obtained from Aldrich Chemicals (Milwaukee, WI). Butadiene (99%) was obtained from Matheson Specialty Gas (Salt Lake City, UT). Ammonia (99.5%) was obtained from Thatcher Chemical Co (Salt Lake City, UT). Argon (99.9%) was supplied by Brigham Young University (Provo, UT).

The processing of the epoxy composites for end-notched flexure (ENF) testing was done according to the manufacturer's specifications in an autoclave at Brigham Young University. ENF testing was conducted using ASTM D30.02 Round Robin specifications to measure the compressive mode II strain energy release rate or G_{IIc}. The equation used is based upon classical beam theory[15] and is written as follows:
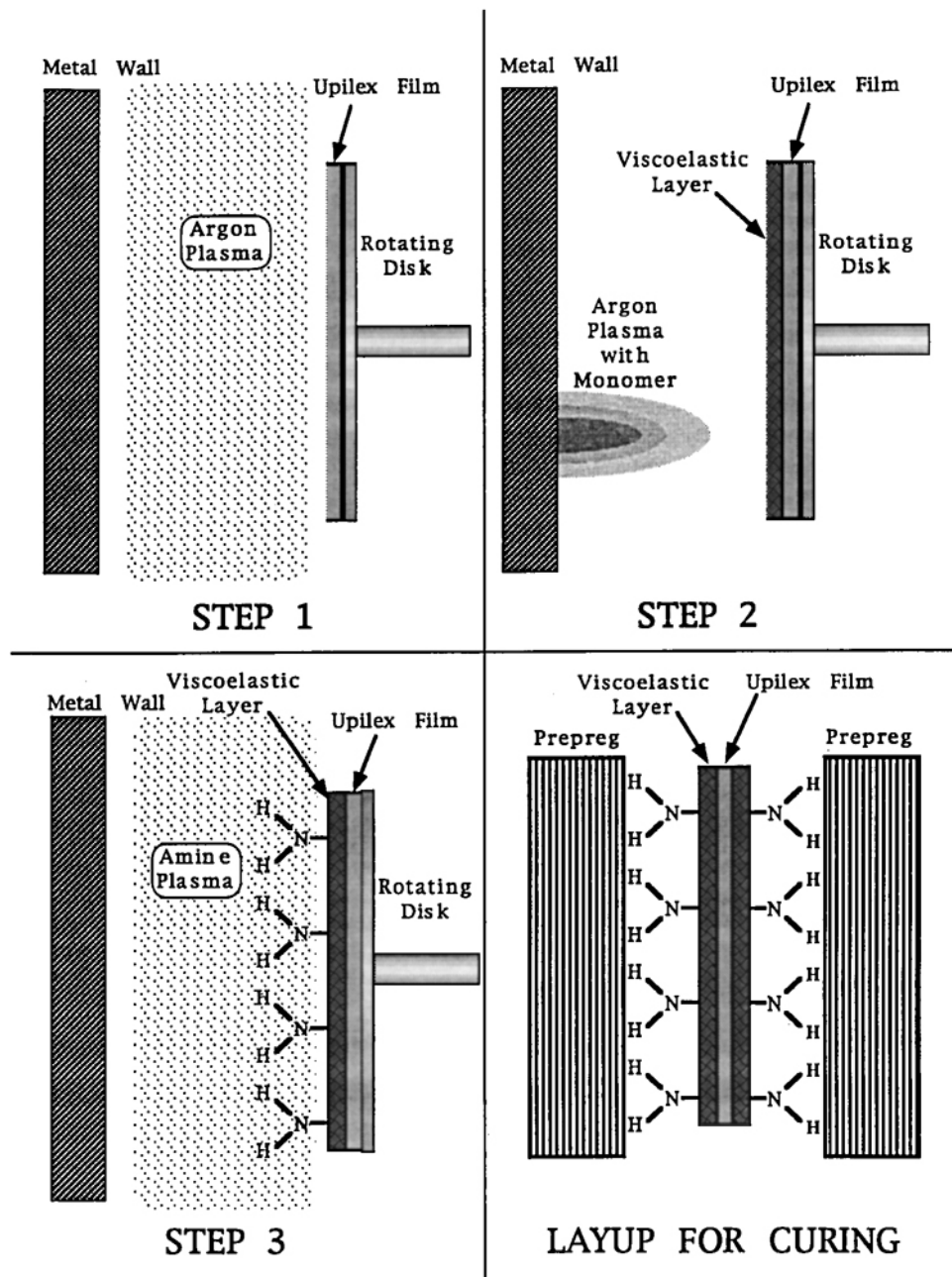
$$G_{IIc} = \frac{9P^2Ca^2}{2w(2L^3 + 2a^3)}$$

Figure 2 Plasma processing steps: 1. argon plasma activation; 2. plasma induced polymerization of a viscoelastic layer; 3. plasma deposition of an amine-containing overlayer. The film is then cocured with carbon fiber/epoxy prepreg.

where P is peak or critical load, C specimen compliance, w coupon width, a initial crack length, and L length between point of load application and pin support.

The surface morphology was examined by scanning electron microscopy (SEM) on a JEOL JSM 840a scanning electron microscope. A thin film microtensile tester was designed for use under the scanning electron microscope to qualitatively examine the processed polyimide films and to reveal any signs of cracking in the deposition when the films were subjected to tensile loads.

X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Hewlett–Packard 5950 XPS spectrometer at the University of Utah to determine

the atomic composition of the plasma processed amine layer. Water contact angles measurements and infrared spectroscopy of the processed film were measured and reported elsewhere.[13]

Experimental Design

A partial factorial design was employed to determine which monomers, plasma powers, and reactor pressures produced the highest values of G_{IIc}. The design was divided into three blocks, or "phases." A multidigit labeling nomenclature was used to identify the various processes. The first digit identifies the monomer used during PIP of the viscoelastic layer (I, isoprene; B, butadiene; S, styrene; A, allylamine). The second digit corresponded to the high and low RF power settings used during PIP ($H = 60$ W, $L = 30$ W). The third digit refers to the processing pressure during the PIP ($H = 365$ Pa, $M = 80$ Pa, and $L = 13$ Pa). The final digits identify the amine-containing gas or gasses used in the third processing step (A = allylamine, D = diaminopropane, N = NH_3).

Initial Argon Etch

A few miscellaneous experiments were conducted to examine any effect on G_{IIc} of the plasma power or process time during the initial argon etch. Samples were prepared with no initial Ar etch, 1 min of 60 W etch, and 10 min of 120 W etch. These etching steps were followed by a PIP step with isoprene monomer at 80 Pa and 60 W for 1 min, and then an allylamine deposition at 60 W and 80 Pa for 1 min.

Phase One Study

A parametric study was conducted to examine the effect of monomer used during the PIP and to examine the effect of plasma power while pressure was held constant at 80 Pa. High and low power settings were 60 W (for 1 min) and 30 W (for 10 min), respectively. The monomers used were isoprene, butadiene, allylamine, and styrene at flow rates of 0.13, 0.16, 0.15, and 0.06 standard liters per minute (SLM), respectively. The monomer that gave the best viscoelastic performance was selected for use in phase two of the study. In all of phase one, the initial argon etch was always kept at 60 W for 1 min at 80 Pa and 0.10 SLM, and the amine deposition (step 3) was done by plasma polymerization of allyamine at 60 W for 1 min at 80 Pa and 0.07 SLM.

Phase Two Study

In phase two, the monomers used in plasma deposition of the amine-containing overlayer were varied and the processing parameters during the PIP process were held constant at the following values: monomer = isoprene, RF power setting = 60 W, PIP process time = 1.0 min, pressure = 80 Pa, and flow rate = 0.13 SLM. During the amine deposition, the processing time, power, and pressure were also held constant at 1.0 min, 60 W, and 80 Pa, respectively. An unconstrained quadratic simplex experimental design[16] was used to investigate adhesive improvement through plasma deposition of mixtures of amine-containing monomers individually (0.20 SLM) or in equimolar flow ratios (0.10/0.10 or 0.07/0.07/0.07 SLM). Monomers used were allylamine (A), 1,3-diaminopropane (D), and ammonia (N). The pressure was always 80 Pa.

Phase Three Study

In this set of experiments, the pressure in the plasma reactor was varied during the PIP step to determine its influence upon the laminate G_{IIc} values. Pressures were set to 365, 80, or 13 Pa, and the monomers were butadiene or isoprene at 0.16 and 0.13 SLM, respectively. Power was held constant, and the amine deposition step was identical to the phase one experiments.

RESULTS

SEM

In most cases, SEM imaging revealed uniform and relatively featureless depositions on the Upilex film. In phase one, the PIP deposition of butadiene displayed submicron size waviness, but it was not determined whether these were microcracks or wrinkles. The PIP deposition of isoprene was smooth and uniform. When strained to about 10% in the microtensile tester, the PIP deposition of butadiene and isoprene showed no cracking or peeling. The PIP depositions of allylamine demonstrated poor adhesion by cracking and peeling off the Upilex film while clamped in the microtensile tester for 1 day under constant elongation. Also, the coating appeared to be thicker compared to other depositions. The PIP depositions of styrene were not visible, and the observed morphology was identical to that of the Upilex film, suggesting that this deposition was extremely thin or nonexistent.

Table I   XPS Data from Phase Two

Sample	C	N	O	C—C	C—N or C—O	N—C—O or C=O	O—C=O or N—C=O
IHMN	68	11	22	65	12	23	0
IHMD	69	7.3	24	62	12	26	0
IHMA	69	11	21	61	20	19	0
IHMND	70	9.8	20	73	4	23	0
IHMNA	69	11	20	59	23	17	0
IHMDA	62	9.7	28	36	37	27	0
IHMNDA	59	9.7	31	34	35	22	0
Upilex	82	5.6	12	89	0	0	11

All values are in percents.

XPS

The results of the XPS analysis for phase two samples are reported in Table I. Phases one and three samples all had a final coat of allylamine, and thus appear similar by XPS analysis, and are not reported in this table. These data indicate that the depositions were composed of only carbon, nitrogen, and oxygen (and hydrogen). There appeared to be no silicon or other contaminates. The oxygen in the samples probably came from atmospheric oxygen that reacted with residual free radicals after the films were removed from the plasma reactor. All of the plasma treatments increased the nitrogen content above that of the base Upilex-S film. In some cases, particularly process IHMNDA, the oxygen content was more than 25%, indicating that the surface was highly oxidized. The last four columns of Table I show the percentages of the carbon atoms in various oxidized forms. The IHMDA and IHMNDA depositions had very low aliphatic carbon content. Most of the samples had a moderate amount of carbonyl carbon or carbon bonded to both nitrogen and oxygen. The IHMNDA sample appeared to contain acid or amide species.

ENF Measurement of G_{IIc}

End-notched flexure (ENF) testing was conducted on each study phase. Scatter in reported results ranged from 7.5 to 36% of the mean. An analysis of variance (ANOVA) suggested that such scatter, while significant in some cases, still allowed for process ranking.

Studies on the effect of the initial Ar etch indicated that 1 min of 60 W Ar etch produced significantly ($p < 0.05$) higher G_{IIc} values than when there was no Ar etching step or when there was a 120 W etch for 10 min.

In phase one, the process ILMA (3565.9 J/m^2 ± 24.6%) produced the highest G_{IIc} value. The lowest value observed was that of untreated Upilex-S film (1508.7 J/m^2 ± 35.7%). All RF plasma processes yielded a 49.4% average improvement in G_{IIc}, ranging from 14 to 136%, over untreated Upilex-S film. The differences in G_{IIc} from process to process were not always significant. A graphical representation of all ENF response values is found in Figure 3. Mode II failure was always brittle. However, overall peak loading capacities were increased through the RF plasma processing technique.

The G_{IIc} values from the films produced in phase two are shown in Figure 4. Scatter, probably due to
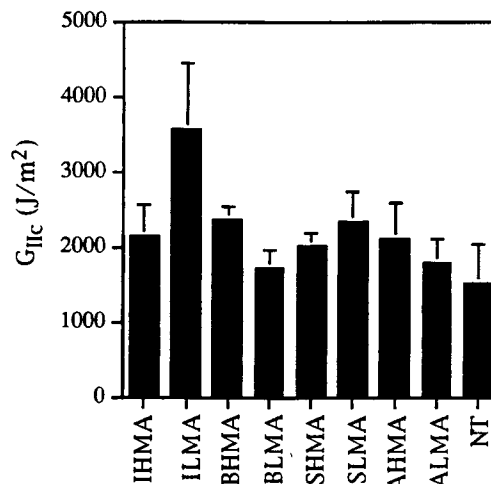

Figure 3 G_{IIc} values from ENF testing of phase one films interleaved with Hercules IM7/8551-7A epoxy resin prepreg. The monomer species and the plasma power were varied in this set. The error bars represent 1 standard deviation from the mean response. The nomenclature for each film treatment is described in the text. NT indicates that the film had no treatment.
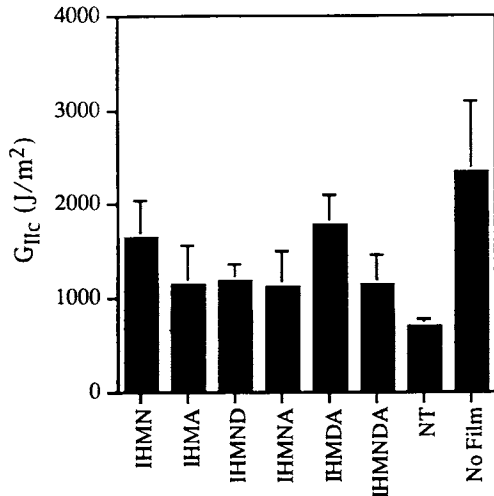
Figure 4 G_{IIc} values from ENF testing of phase two films interleaved with Hercules IM7/8551-7A epoxy resin prepreg. The composition of the amine overlayer was varied in this set. See text for nomenclature. No Film indicates that no polyimide film was interleaved in this composite.

inconsistencies in coupon geometry ranged from 12 (IHMND) to 38% (IHMA). Process IHMDA (1778 J/m^2 ± 18%) produced the highest G_{IIc} value. The lowest value observed was for the control laminate containing untreated Upilex-S film (694 J/m^2 ± 12%). An additional control of noninterleaved coupons (epoxy prepreg only) gave the highest overall G_{IIc} value (2331 J/m^2 ± 33%). All RF plasma processing yielded an average improvement of 92 ± 43%, ranging from a low of 63% (IHMA) to a high of 156% (IHMDA), compared to composites interleaved with untreated Upilex-S film. Again, mode II failure was brittle. However, peak load was dramatically improved.

The data from phase three, presented in Figure 5, show that for either isoprene or butadiene PIP, the G_{IIc} values increase as the processing pressure decreases. The IHLA had the highest G_{IIc} value (594 J/m^2 ± 21%), and the untreated film had the lowest G_{IIc} value (313 J/m^2 ± 7%) of the interleaf composites.

DISCUSSION

SEM

SEM confirmed that the PIP technique with isoprene, butadiene, and allylamine was successful in depositing a thin layer of material. The PIP depositions of butadiene and isoprene appeared to be both adherent and nonbrittle, because they did not crack

or peel under tensile strain. This suggests that the material may have some viscoelastic properties similar to lightly crosslinked rubber. The observations of Yang and Sung[12] also suggest that this plasma deposition technique produces a viscoelastic deposition. The brittleness of the allylamine PIP deposition eliminated it from further consideration as a candidate monomer for this application.

XPS

The most significant aspect of the XPS data was the presence of high amounts of oxygen in the depositions. None of the processing gases contained oxygen, indicating that the source of the oxygen was either leaks in the gas flow system or rapid quenching of residual radicals in the polymer by atmospheric oxygen after the samples were removed from the reactor. This latter possibility is a common and well-documented occurrence with plasma polymerized thin films.[9-11] The amount of oxygen appears to be a function of the treatment to deposit the amine-containing overlayer.

Of particular interest to the hypothesis of this work was the incorporation of significant amounts of nitrogen into the deposition that would react with the epoxy groups in the prepreg. Unfortunately the XPS analysis could not reveal whether this nitrogen was in the desired form of primary amines or reveal whether the nitrogen was accessible to react with
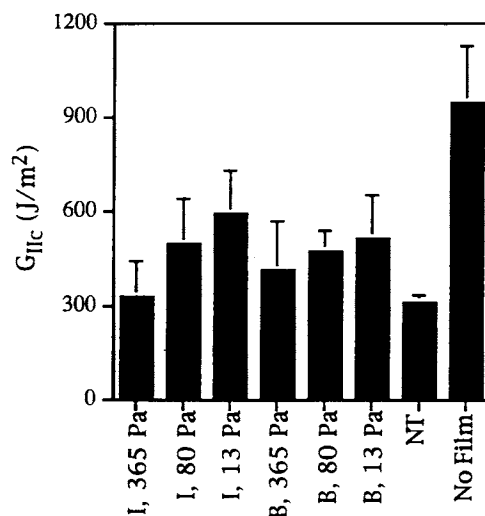

Figure 5 G_{IIc} values from ENF testing of phase three films interleaved with Hercules IM7/8551-7A epoxy resin prepreg. The pressure during the plasma induced polymerization was varied in this set. Isoprene was the monomer in the first three data, and butadiene was the monomer in the second three data.

the functional groups in epoxy resin. The increases in G_{IIc} values suggest that there is more bonding between this amine-containing layer and the epoxy than when the Upilex is not subjected to plasma processing. However, we found no significant correlation between nitrogen or oxygen content and the G_{IIc} values.

ENF Measurement of G_{IIc}

The ENF testing showed improvement in adhesive performance in the epoxy composites as high as 136% (process ILMA) over untreated Upilex-S films. None of the processes decreased the G_{IIc} values compared to untreated films processed in the same batch. We note that the absolute values of G_{IIc} for unprocessed films varied from batch to batch (phase to phase). This is attributed to aging of the prepreg and slight differences in autoclave processing. Therefore it is difficult to make comparisons between processes that were not run in the same phase. However it is probably safe to make relative comparisons within a phase.

The use of an initial Ar etch before PIP appears to enhance interlaminar shear strength as long as the etch is about 1 min. It is interesting that longer and more powerful etching processes decrease G_{IIc} values. It is possible that longer or more powerful etches create loosely bound ash on the surface, or weaken the cohesive strength of the polyimide film. In this research we have not established an optimum time or power for the etching step, but an optimum may exist. Other plasma processes have been shown to produce maximum strengths at intermediate process times.[17]

Data from the ENF testing within each phase was examined by ANOVA to determine which processing parameters produced significant changes in the ENF values. In phase one processes, the parameters of RF power and processing time produced a significant G_{IIc} response ($p < 0.01$). The monomer producing the best ENF response on phase one samples was isoprene. There was no significant difference resulting from PIP processing at 60 W for 1 min or processing at 30 W for 10 min.

In the ENF tests of the phase two epoxy composites, the ANOVA showed that the G_{IIc} values were not significantly different ($p > 0.05$) from each other, but they were significantly different ($p < 0.01$) from the control samples with untreated Upilex-S or with no film at all. This is interesting because the ANOVA of the phase one data showed that the nature of the viscoelastic layer was significant in determining the G_{IIc} values. These data suggest that

the composition and processing of the viscoelastic layer has more influence on the ENF values than the composition of the amine layer. Perhaps any of these amine-containing layers produced sufficient bonding to epoxy resin, such that the failure was related more to the PIP viscoelastic layer than to the PP amine-containing layer. Recall that the same amine overlayer (allylamine) was used in all of the phase one processes.

The phase three testing investigated the effect of processing pressure during the PIP step. An ANOVA analysis of the G_{IIc} values from composites with processed films shows that the 80 and 13 Pa pressures produce G_{IIc} values significantly higher than those produced at 365 Pa pressure, but they are not significantly different from each other. Similar trends with both monomers suggests that the 13 Pa pressure produces the highest G_{IIc}.

The data from all of these experiments indicate that plasma processing can improve the interlaminar shear strength between a polyimide film and the adjacent epoxy composite in an interleaf composite structure. The monomer and the pressure used in the PIP step appear to have more effect on interlaminar shear strength than do the plasma power in the PIP step or the monomer used in plasma deposition of the amine-containing overlayer. The use of a light Ar plasma etch prior to PIP appears to be significant in promoting shear strength.

The previous data were obtained using epoxybased composite systems in the interleaf composite. However, the most probable use of interleaf composites may be in applications using polyimide-based composite systems that are more brittle than epoxy systems, and that cannot easily be toughened through additives. Often the polyimide systems (e.g., bismaleimide or PMR-15) are processed at a much higher temperature than epoxy systems, and the plasma depositions may not be thermally stable at the higher temperatures. For example, butadiene and isoprene depositions on polyimide were subjected to a simulated PMR-15 cure (9 h at 316°C in an N_2 atmosphere) and a simulated epoxy cure (4 h at 179°C in an N_2 atmosphere). The XPS analyses of the films subjected to the 316°C treatment were identical to that of the bare polyimide film, suggesting that the plasma depositions had been removed from the surface; but the films exposed to 179°C had XPS spectra similar to the original PIP deposition. Better candidates for high temperature applications may be silicon-based polymers, which are stable up to 350°C.[18] When PIP deposition of TMDS and HMDS on Upilex were exposed to 9 h at 316°C in an N_2 atmosphere, no significant change

Table II Atomic Composition (%) of Siloxane Depositions by XPS Analysis

Description	C	O	N	Si
HHMHD (HMDS monomer)				
No heat treatment	53	31	6.4	9.1
Heat treatment	54	31	3.1	12
THMHD (TMDS monomer)				
No heat treatment	35	43	4.5	18
Heat treatment	37	40	1.9	21
HMDS monomer (theoretical)	67	11	0	22
TMDS monomer (theoretical)	57	14	0	29
PDMS silicone rubber (theoretical)	50	25	0	25

in their XPS analysis was observed (see Table II). Note also that the composition of the HMDS deposition was fairly similar to the theoretical composition of polydimethylsiloxane (PDMS).

CONCLUSIONS

RF plasma induced polymer depositions were successful in improving interlaminar shear strength between the Upilex-S polyimide film interleaf and an epoxy resin prepreg system. Isoprene appears to be the best monomer to use in the PIP process at either 30 W for 10 min or 60 W power for 1 min. Low pressure (13 Pa) during the PIP step also appears to increase interlaminar shear strength. Analysis of the ENF testing data indicated that the values of G_{IIc} were influenced more by the monomer chemistry used in the PIP viscoelastic layer than by the monomer chemistry used to form the amine-containing layer. The argon plasma etch preceding the PIP step is helpful in increasing G_{IIc} but should be kept to about 1-min exposure.

Although the PIP depositions of isoprene and butadiene may be suitable for use in epoxy-based composite systems, they may not be adequate for systems requiring higher processing temperatures, such as PMR-15 systems. For such high temperature systems, the use of plasma polymerized siloxanes deserves further investigation.

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