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Plasma Surface Treatment In Composites Manufacturing

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Introduction

A plasma is a partially or fully ionized gas containing electrons, ions, and neutral atoms or molecules, also called the fourth state of matter (Eliezer, 1989). The technology of plasma processing of materials impacts and is of vital importance to several of the largest manufacturing industries in the world. Foremost among these industries is the electronics industry, in which plasma-based processes such as plasma etching and plasma-enhanced chemical vapor deposition are indispensable for the manufacturing of very large-scale integrated microelectronic circuits. Plasma thermal spray coatings, plasma welding and cutting are the critical processes in the aerospace, automotive, steel, biomedical, and toxic waste management industries (Kalpakjian, 1995). This pervasive use of plasma in modern technology is a result of its ability to excite gas atoms and molecules into transient and nonequilibrium conditions with very high gas temperatures and densities. Plasma can thereby alter the normal pathways through which chemical systems evolve from one stable state to another and can thus enable production of novel materials.

In composite manufacturing industries, carbon fibers, one of the most important reinforcements with excellent mechanical properties, can be produced from various precursors by a series of thermal processes such as oxidation, carbonization and graphitization. But the efficient translation of these outstanding mechanical proper-

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ties into usable structure form such as composite has not been achieved. The carbon fiber composites have poor interlaminar shear strength which can be attributed to weak adhesion between the carbon fiber surface and the resin matrix (Donnet and Bansal, 1984). Several surface treatment methods have been developed to improve the fiber-matrix interfacial bonding, they can be divided into two groups - oxidative and non-oxidative. The major method is the liquid-phase oxidative treatment which is done by drawing the fibers through a bath of some oxidizing agents such as nitric acid, potassium permanganate, or sodium hypochlorite, or through an acidic or alkaline electrolytic bath. Non-oxidative treatments are of three different types: whiskerization, pyrolytic surface coating, and polymer grafting (Strong, 1989). These treatments are often quite complicated. For example, when fibers are treated in concentrated nitric acid, the equipment used must have good corrosion resistance and the acid absorbed onto the fibers must be properly removed. The waste of acid solution also needs to be treated properly to avoid polluting the environment.

Purposes

In this study, gas plasma was applied to carbon fiber surfaces. The primary goal of this research was to explore the capability and the limitations of utilizing the plasma reaction techniques for modifying the interfacial adhesion in composites. A second goal was to determine and correlate the changes in physical and chemical states of the carbon fiber surface due to plasma treatments and the resultant fibers and composite properties.

Methodology

Materials

The increasing demand for higher temperature matrix resins motivated us to choose a two-component bismaleimide system as the matrix material. A two-component bismaleimide (BMI) resin (CIBA-GEIGY, Matrimidä 5292) was used as the matrix material. The two components are 4, 4' Bismaleimido-diphenylmethane (component A) and 0,0'-Diallyl Bisphenol A (component B). The ratio of A to B is 113/85 parts by weight, as recommended by the manufacturer (CIBA-GEIGY, 1985). PAN-based untreated and unsized high-strength carbon fiber tows (Hercules, AU4-12K) were used for the study.

Plasma Treatments

Carbon fiber tows were carefully wrapped around a stainless steel frame having inside dimensions of 7.62cm x 10.16cm x 0.1cm. The fiber strands along the frame were placed inside the chamber of a plasma reactor (Tegal Corporation, PLASMOD). The reactor consists of an RF generator (13.5 MHz), a matching network, a pyrex glass reaction chamber, and other accessories. The oxygen and ammonia gases were introduced into the reactor through the mass flow meters respectively according to the conditions shown in the Table 1.

Composite Preparation

Upon completion of the plasma treating process, the fiber-wrapped frame was removed from the reaction chamber. The tows which were laid parallel to each other on the steel frame were impregnated with a well mixed BMI resin to produce a small prepreg layer. Four prepreg layers for each treatment time were stacked into a

Gases used	Oxygen	Ammonia
Chamber pressure	53.3 Pa (0.374 torr)	25.7 Pa (0.18 torr)
Flow rate of gas	40 sccm*	35 sccm
Plasma power	50 Watts	50 Watts
Treatment time (min.)	1,3,5,10,20	1,3,5,10,20

* sccm = standard cubic centimeter per minute.

Table 1. Various Operation Conditions of Oxygen and Ammonia Plasmas

mold, and compression molded under a contact pressure with the temperature ramped from room temperature to 177 °C at a rate of 3 °C/min. The mold was subsequently held at 177 °C for 10-15 minutes first under a light contact pressure, then a pressure of 0.69 MPa for 1 hour. The mold was then cooled to room temperature under this pressure. The demolded laminate was post-cured in an air circulating oven at 200 °C for 2 hrs, then at 250 °C for 6 hrs. The fiber volume fraction of this composite measured by a photomicrographic method is about 0.67.

Mechanical Testing

Each laminate fabricated was machined into three transverse tensile specimens with the dimensions of 10cm x 2cm x 0.1cm. Aluminum alloy end tabs were glued on both ends of each specimen to facilitate gripping. A transverse tensile test was conducted to assess the relative interfacial adhesion strength in composites. At least 10 filaments from each treatment sample were removed from both the treated and untreated carbon tows. The two ends of each filament were carefully glued between two small pieces of plastic plates by a super glue. They were tested in tension to determine if and when plasma treatments would become harmful to the fiber strength.

Surface Characterizations

Adhesion between an adhesive and a solid substrate can be achieved by three main mechanisms; a) mechanical keying or interlocking, b) molecular forces and dipole interactions, and c) chemical bonding. All mechanisms can occur at the interface either alone or in combination to produce the necessary bond. The physical and chemical properties of carbon fibers play a major role in determining the degree of

adhesion between the fiber and the resin. Several surface characterization techniques were applied to provide the needed information. The surface texture of fibers, before and after plasma treatments, were examined by using a scanning electron microscope (SEM). An X-ray photoelectron spectroscopy (XPS) analysis (Kratos, model XSAM 800) was also conducted to study the surface compositions of various treated carbon fibers and to calculate the elemental surface concentrations from the corrected XPS peak area. The chemical states of the surface atoms of carbon fibers was determined using non-linear-least-squares-curve fitting program with a Gaussian/Lorentzian production function (Proctor and Sherwood, 1982). The surface energy of the carbon fibers was

determined by measuring the contact angles of a variety of liquids according to the method proposed by Kaelble, Dynes, and Cirlin (1974). The surface energies of solids and liquids are considered to be the sum of separate dispersive (London-d) and polar (Keesom-p) components. The method measures the surface energies due to dispersive and polar contributions. The rule of thumb is the higher the surface energy of the substrate, e.g., the fibers, the better of its wettability by the resin.

Results and Discussion

Figure 1 shows the transverse tensile test results for the composites with various treatment times of the oxygen and the ammonia plasmas. For oxygen plasma treatments, the transverse tensile strength increases gradu-

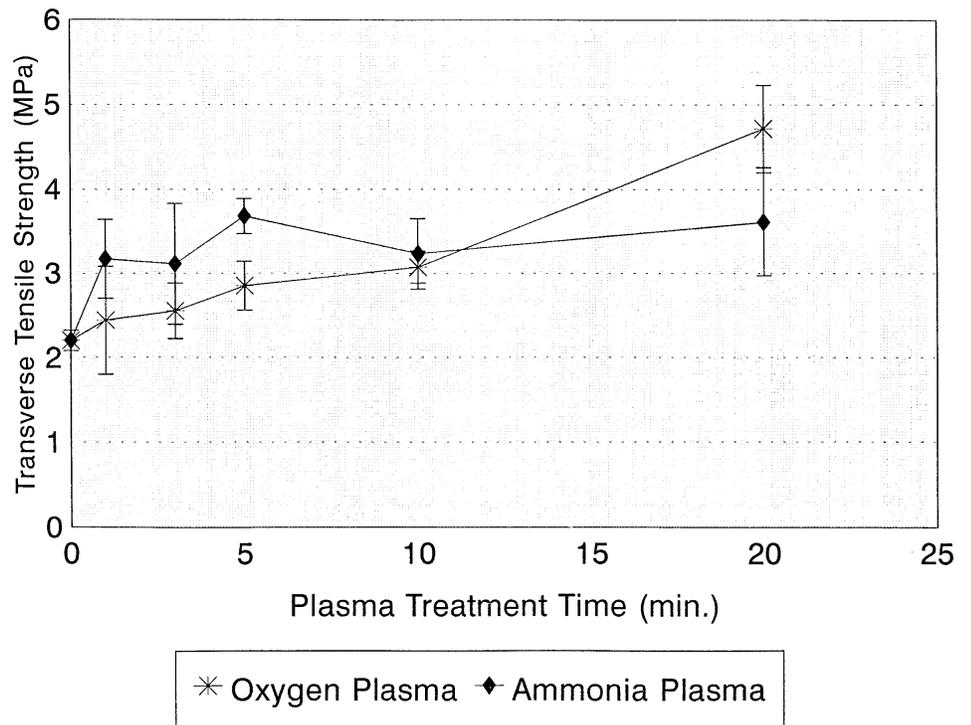


Figure 1. The Results of Transverse Tensile Tests

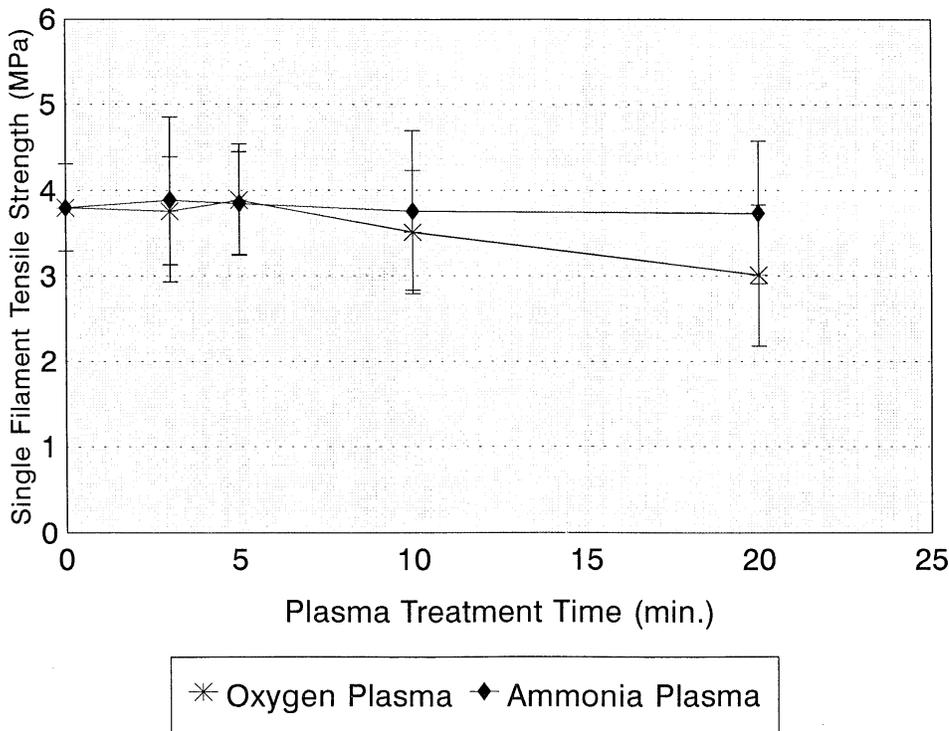


Figure 2. The Results of Single Filament Tensile Tests

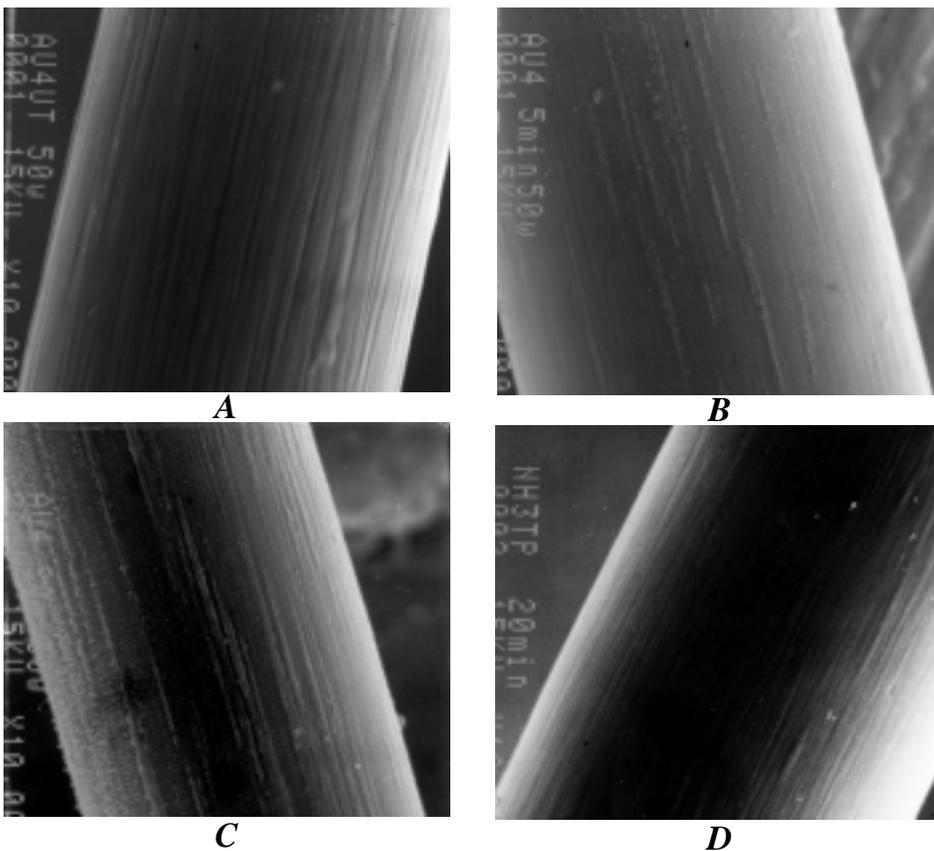


Figure 3. SEM micrographs showing surfaces of carbon fibers. Graphs of A, B, and C are for 0 minute, 5 minute, and 20 minute oxygen plasma treated ones. Graph D is for 20 minute ammonia plasma treated.

ally from 2.20 MPa (untreated) to 4.71 MPa (20 minute treated). For ammonia plasma treatments, it increases to 3.61 MPa (20 minute treatment). Both plasmas appear to show the positive effects in enhancing the interfacial adhesion between the carbon fibers and the BMI resin. The effects of the plasma treatments on fiber strength are shown in Figure 2. It indicates that the average tensile strength of fibers was degraded from 3.8 GPa (untreated) to 3.01 GPa (20 minute treatment) for the oxygen plasma treatments. The reduction extent in fiber strength (3.74 GPa at 20 minutes of treatment) for the ammonia treatments appears to be much less than that of the oxygen plasma.

The SEM photographs shown in Figure 3 provide some clues about the properties of fibers and composites. The gradual increase of surface roughness on oxygen-treated fibers promotes more mechanical keying which enhances the interfacial bonding between the fibers and the resin. Removing a weak boundary layer initially present on the fiber surface is also believed to play a positive role during the early stage of plasma treatments as described in the study of Drzal, Rich, and Lloyd (1982). Nevertheless, since a plasma consists of various highly energetic species, exposure of fibers to the plasmas for an extended period of time could produce a negative effect on fiber strength.

For ammonia plasma treatments, there is no sign of surface roughening on fibers up to 20 minutes at the given conditions shown in Figure 3(d). Mechanical keying is not a factor in increasing the interfacial adhesion. Other adhesion mechanisms play the major roles. The detrimental effect on fiber strength is minute for ammonia plasma treatments. Between the two plasmas techniques, the ammonia plasma system is seen to be the better one in enhancing interfacial bonding without producing an undesirable reduction in fiber strength.

The surface energies for the dispersive and polar components, and the totals are summarized in Figures 4 and 5. For both techniques, the results indicate that the polar component and

total energy are increased steeply within the early 5-minute period, and then they level off to a saturation state. There are much fewer changes to the dispersive component. The reason for the decreasing polar part after the 10-minute treatment is due to the increasing surface roughness which causes a calculation deviation from Kaelble's method that assumes the substrate surface is smooth. The increase in wettability of the resin to the fibers due to the enhancement of fiber surface energy accounts for the increase of interfacial adhesion for both treatments, yet it is believed that wettability plays a heavier role in the ammonia treatment.

From the results of the XPS analysis, a semi-quantitative comparison of relative atomic concentration of oxygen and carbon on the fiber surface for the oxygen treatments is shown in Table 2. Apparently, the oxygen concentration on the surface of fibers has been increased by oxygen plasma treatment from 10.47% of the untreated to 27.53% of the 20 minute treated case. The curve-fitting spectra of the C1s peaks for the untreated and the 20-minute treated fibers are shown in Tables 3 and 4, these indicate a significant increase in carboxylic acid and/or ester groups by oxygen plasma treatment. Similar observations were made by Sun, Hu, and Wu et al. (1989), who treated carbon fibers by oxygen plasmas. In general, oxygen plasma treatment increases the oxygen content and the polarity of the fiber surface.

For ammonia plasma, because of the absence of available references and possible overlapping of oxide peaks and nitrogen-containing peaks in fitting of the C1s peak, no attempt was made to do curve fitting of C1s and N1s peaks in XPS analysis. Only atomic ratios are calculated. The surface nitrogen and oxygen contents increase from 0% and 10.47% (the untreated) to 6.43% and 22.14% (20 minute treated) respectively. The increase in oxygen content may be due to the impurities of ammonia gas used, leakage of the plasma system, etc. Recent studies of the plasma decomposition of ammonia suggest that $\cdot\text{NH}_2$ is the most likely species available for recombination with

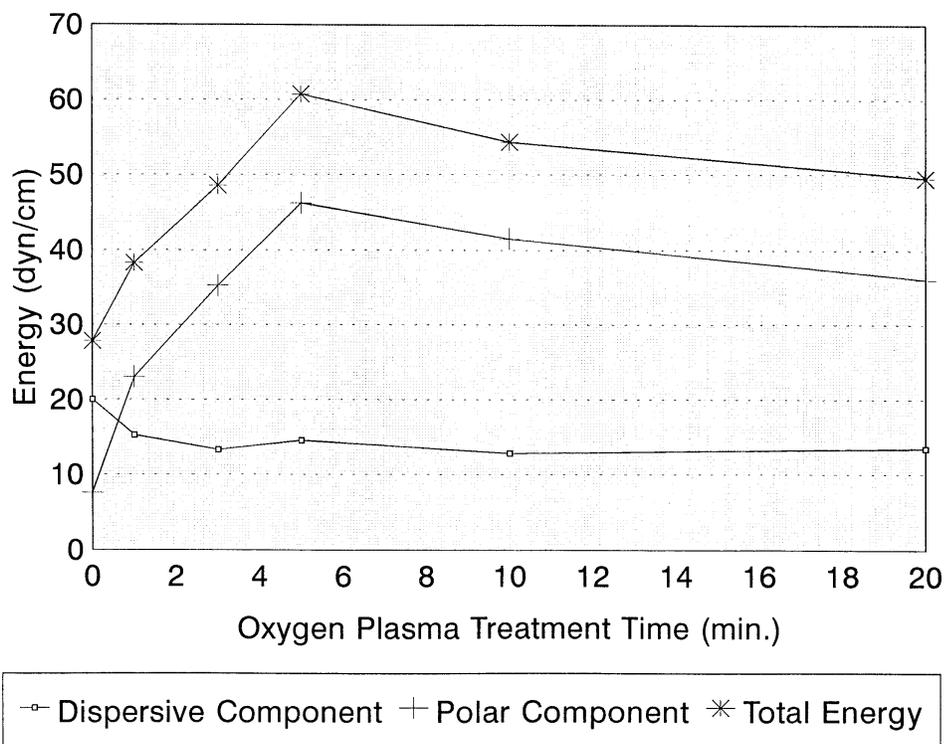


Figure 4. The Surface Energies of Carbon Fibers Treated by Oxygen Plasma.

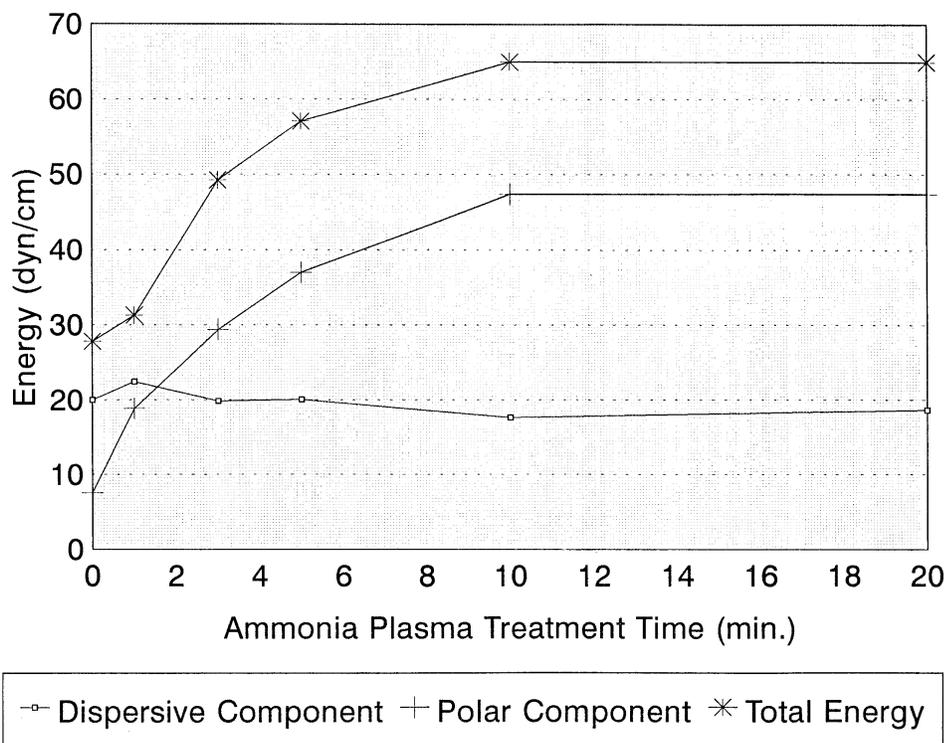


Figure 5. The Surface energies of Carbon Fibers Treated by Ammonia plasma.

Treatment Time (min.)	0	1	3	5	10	20
O1s	10.47	20.22	20.27	22.27	23.27	27.53
C1s	89.53	79.78	79.73	77.23	76.73	72.47

Table 2. XPS Atomic Conc.(%) of Carbon Fibers Treated by Oxygen Plasma at Various Periods

Peak Position (eV)	Relative Area Ratio	Chemical Shift (eV)	Possible Functional Groups
284.53	1.00	0.00	Graphite
286.40	0.29	1.87	-C-OH and/or C=O and/or Quinone
288.60	0.07	4.07	Carboxylic Acid and/or Ester
290.60	0.01	6.07	-CO ₃ type or Plasmon

* Relative area ratio = (area of peak_i) / (area of peak_{284.50})

Table 3. Curve Fitting Results and Relative Areas for C1s Spectrum of the Untreated Carbon Fibers.

Peak Position (eV)	Relative Area Ratio*	Chemical Shift (eV)	Possible Functional Groups
284.50	1.00	0.00	Graphite
286.60	0.26	2.10	-C-OH and/or O and/or Quinone
288.60	0.16	4.10	Carboxylic Acid and/or Ester
290.60	0.04	6.10	-CO ₃ type or Plasmon

* Relative area ratio = (area of peak_i) / (area of peak_{284.50})

Table 4. Curve Fitting Results and Relative Areas for C1s Spectrum of the Carbon Fibers Treated by Oxygen Plasma for 20 minutes.

surface radicals (Allred, Merrill, & Roylance, 1983; d'Agostino & Cramarossa, et al, 1981; Captelli & Molinari, 1980). It is speculated that useful functional groups such as -NH₂ might have been deposited to the carbon fiber surface to promote chemical bonding (primary or hydrogen) between the fiber and matrix resin.

Conclusions

The present study has led to the following conclusions:

1. The oxygen and the ammonia plasma treatments appear to have a positive effect in improving the interfacial adhesion between carbon fibers and BMI.
2. Ammonia plasma seems to be the better plasma system in enhancing the interfacial adhesion between carbon fibers

- and BMI resin without producing an undesirable reduction in the fiber strength.
3. Oxygen plasma shows a greater etching effect on the carbon fiber surface than ammonia.
4. Various adhesion mechanisms can be promoted by plasma treatments. Each mechanism works to a different extent in a different plasma environment. For oxygen plasma, the improved level of mechanical keying, the increased surface wettability, and chemical bonding are the mechanisms in improving carbon fiber-BMI adhesion. For ammonia plasma, chemical bonding between amine groups and bismaleimide and enhanced surface energy are the two important factors in

controlling interfacial adhesion in the carbon fiber/BMI composites.

Future Plan

More samples with various treatment conditions will be prepared and tested to statistically investigate the optimum conditions of the two plasmas in enhancing the interfacial bonding between the BMI resin and the carbon fibers. Still, more studies on vacuum technology for continuous process, plasma reactor design, and process conditions etc. are needed to realize the advantages of plasma on fiber surface treatment in composites manufacturing.

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