

# Modification of High-Performance Polymer Composite through High-Energy Radiation and Low-Pressure Plasma for Aerospace and Space Applications

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**ABSTRACT:** In this investigation, attempts are made to modify a high-performance polymer such as polybenzimidazole (PBI) (service temperature ranges from  $-260^{\circ}\text{C}$  to  $+400^{\circ}\text{C}$ ) through high-energy radiation and low-pressure plasma to prepare composite with the same polymer. The PBI composites are prepared using an ultrahigh temperature resistant epoxy adhesive to join the two polymer sheets. The service temperature of this adhesive ranges from  $-260^{\circ}\text{C}$  to  $+370^{\circ}\text{C}$ , and in addition, this adhesive has excellent resistance to most acids, alkalis, solvents, corrosive agents, radiation, and fire, making it extremely useful for aerospace and space applications. Prior to preparing the composite, the surface of the PBI is ultrasonically cleaned by acetone followed by its modification through high-energy radiation for 6 h in the pool of a SLOWPOKE-2 (safe low power critical experiment) nuclear reactor, which produces a mixed field of thermal and epithermal neutrons, energetic electrons, and protons, and  $\gamma$ -rays, with a dose rate of 37 kGy/h and low-pressure plasma through 13.56 MHz RF glow discharge for 120 s at 100 W of power using nitrogen as process gas, to essentially increase the surface energy of the polymer, leading to substantial improvement of its adhesion characteristics. Prior to joining, the polymer surfaces are characterized by estimating surface energy and electron spectroscopy for chemical analysis (ESCA). To determine the joint strength, tensile lap shear tests are performed according to ASTM D 5868-95 standard. Another set of experiments is carried out by exposing the low-pressure plasma-modified polymer

joint under the SLOWPOKE-2 nuclear for 6 h. Considerable increase in the joint strength is observed, when the polymer surface is modified by either high-energy radiation or low-pressure plasma. There is further significant increase in joint strength, when the polymer surface is first modified by low-pressure plasma followed by exposing the joint under high-energy radiation. To simulate with spatial conditions, the joints are exposed to cryogenic ( $-196^{\circ}\text{C}$ ) and high temperatures ( $+300^{\circ}\text{C}$ ) for 100 h. Then, tensile lap shear tests are carried out to determine the effects of these environments on the joint strength. It is observed that when these polymeric joints are exposed to these climatic conditions, the joints could retain their strength of about 95% of that of joints tested under ambient conditions. Finally, to understand the behavior of ultrahigh temperature resistant epoxy adhesive bonding of PBI, the fractured surfaces of the joints are examined by scanning electron microscope. It is observed that there is considerable interfacial failure in the case of unmodified polymer-to-polymer joint whereas surface-modified polymer essentially fails cohesively within the adhesive. Therefore, this high-performance polymer composite could be highly useful for structural applications in space and aerospace. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1959–1967, 2006

**Key words:** adhesion; composites; high performance polymers; plasma polymerization and radiation

## INTRODUCTION

Reinforced polymer laminates have many attributes that are highly desirable properties for applications in aerospace and spacecraft structures because of their high strength-to-weight and stiffness-to-weight ratios. Equally well known is their typically poor stability under elevated temperatures and cryogenic environments.<sup>1</sup> Nevertheless, polymers with much improved

resistance to both high and cryogenic temperatures have been developed and are playing an important role in many advanced engineering applications, especially in the aerospace and space technology.<sup>2,3</sup>

Presently, neither rockets nor satellites or aerospace applications are possible without polymers and polymeric composites. However, the use of polymeric materials in primary structures of a spacecraft and aircraft is limited by the high temperatures encountered during launch, e.g., combustion gases, aerodynamic heating, and ultra violet and high-energy radiations.<sup>4,5</sup> Often in the fabrication processes, polymer sheets are joined by adhesives to form polymeric composites. The acceptance of adhesives as a high-performance engineering material has grown steadily in the last

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few decades.<sup>5,6</sup> Adhesives contribute highly to structural integrity, ease of manufacturing, enhanced performance, improved safety, and cost and time savings. The reasons for this are numerous and include the continuity of the adhesive bond. Therefore, upon loading, there is a more uniform distribution of stresses over the bonded area.<sup>6</sup>

To solve the problems mentioned above, it is necessary to use such high temperature resistant polymeric sheets such as polybenzimidazole (PBI) sheets, which also have excellent cryogenic properties (service temperature ranges from  $-260^{\circ}\text{C}$  to  $+400^{\circ}\text{C}$ ) as well as high stability in the radiation environments. This polymer can therefore be highly useful as a structural composite material in aerospace and spacecraft.<sup>2</sup> The composite can be prepared by employing recently developed ultrahigh temperature resistant epoxy adhesive (DURALCO 4703, service temperature ranges from  $-260^{\circ}\text{C}$  to  $+370^{\circ}\text{C}$ ), as this adhesive retains its cohesive properties even when exposed to cryogenic atmosphere. However, the high-performance polymer, like other polymers, is hydrophobic in nature and in general exhibits insufficient adhesive bond strength due to relatively low surface energy. It is therefore necessary to modify the surface of the polymer to make sure that the polymer surface becomes hydrophilic by increasing its surface energy and to improve adhesive bond strength.<sup>7</sup>

Different modification methods are employed to modify the polymer surfaces, such as chemical, thermal, mechanical, and electrical treatments through low-pressure plasma. Glow discharge under low-pressure plasma is a popular technique, which results in better uniformity in the surface modification of the polymers.<sup>8-10</sup> The present trend of research reveals that modification of polymers through high-energy radiation could also be beneficial in the context of polymeric composite.<sup>11,12</sup> In this regard, the surface of PBI sheet is modified by high-energy radiation for 6 h in the pool of a SLOWPOKE-2 nuclear reactor, which produces a mixed field of thermal and epithermal neutrons, energetic electrons and protons, and  $\gamma$ -rays, with a dose rate of  $37\text{ kGy/h}$ <sup>12</sup> and low-pressure plasma using a  $13.56\text{ MHz}$  RF Glow Discharge for 120 s at  $100\text{ W}$  of power<sup>13</sup> using nitrogen as process gas, to essentially increase the surface energy of the polymer, leading to substantial improvement of its adhesion characteristics. The surface-modified PBI sheet under high-energy radiation and low-pressure plasma are characterized by surface energy measurements and by electron spectroscopy for chemical analysis (ESCA) and joined by the ultrahigh temperature epoxy adhesive. Another set of experiments is carried out on those polymers, modified by low-pressure plasma, joined by the adhesive and subsequently exposed to high-energy radiation for 6 h in the pool of a SLOWPOKE-2 nuclear reactor to understand the be-

**TABLE 1**  
Polar, Dispersion and Total Surface Tension  
of the Test Liquids

Liquid	$\gamma_{LV}^P$ (mN/m)	$\gamma_D^{LV}$ (mN/m)	$\gamma_{LV}$ (mN/m)
Deionized water	50.2	22.0	72.2
Formamide	18.6	39.6	58.2

havior of the adhesive under the high-energy radiation environment. Lap shear tensile tests of all these joints are carried out to determine the joint strength. To simulate other spatial conditions, the joints are exposed to cryogenic ( $-196^{\circ}\text{C}$ ) and high temperature ( $+300^{\circ}\text{C}$ ) environments for 100 h. Then, tensile lap shear tests are carried out to determine the effects of these environments on the joint strength. Failure modes of the joints are investigated using the scanning electron microscope (SEM) and typical features are analyzed and correlated with the joint strength.

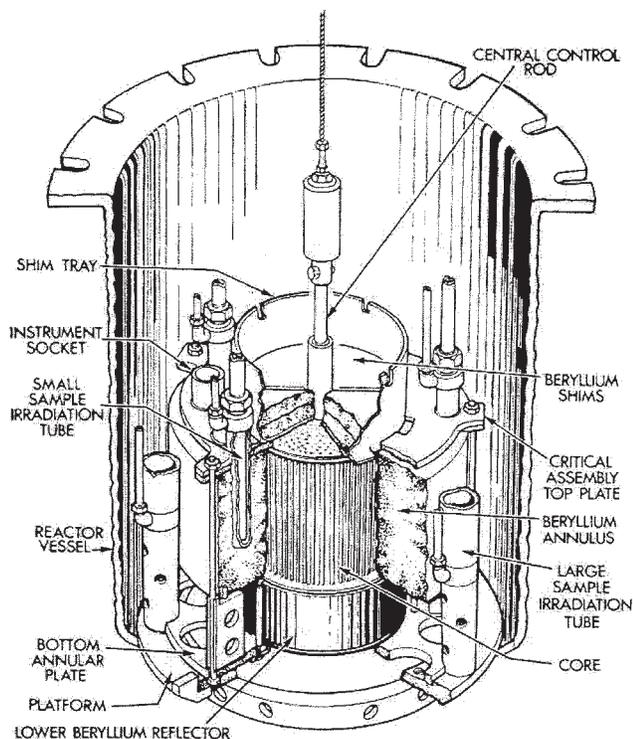
## EXPERIMENTAL

### Materials

In this investigation, PBI sheets of service temperature ranging from  $-260^{\circ}\text{C}$  to  $+400^{\circ}\text{C}$ , tensile strength of  $160\text{ MPa}$ , and density of  $1.3\text{ g/cc}$ , as reported by the manufacturer (Boedeker Plastics) were used. Recently developed ultrahigh temperature resistant epoxy adhesive, DURALCO 4703, manufactured by Cotronics Corp., Brooklyn, NY of service temperature ranging from  $-260^{\circ}\text{C}$  to  $+370^{\circ}\text{C}$  and cohesive strength of  $24\text{ MPa}$ , was used to join the polymer sheets. The mixing ratio of resin to hardener, curing temperature, and time of this adhesive are:  $1:0.22$ ,  $25^{\circ}\text{C}$ , and  $24\text{ h}$ , respectively. Two test liquids, such as deionized water and formamide of known polar and dispersion components of surface tension, were used to evaluate the polar and dispersion components of surface energies of PBI through measurement of their contact angle by the sessile drop method.<sup>14-16</sup> The temperature during the measurement was  $20^{\circ}\text{C}$ . The known components of surface tension of liquids are given in Table I.

### SLOWPOKE-2 nuclear reactor

Surface modification of PBI was carried out through exposure to high-energy radiation for 6 h in the pool of a SLOWPOKE-2 nuclear reactor. The dose rate at the irradiation site is  $37\text{ kGy/h}$ , when the reactor is at steady state half power operation of  $10\text{ kW}$  (thermal).<sup>12</sup> At this site, the radiation components contributing to this dose rate are a combination of 1% neutron, 3% proton, 9% gamma, and 87% electron radiation.<sup>12</sup> The sample holder used for the irradiation was an aluminum sector-shaped box designed to fit snugly against the reactor vessel. The



**Figure 1** Schematic diagram of SLOWPOKE-2 nuclear reactor.

holder could accommodate 10 samples, which were all well covered by a waterproof tape to avoid all contact with water in the reactor pool. The sample holder was held in position in the reactor pool by a positioning device called the elevator, designed to position and maintain samples at a repeatable irradiation site at mid-reactor plane and against the reactor vessel. The schematic diagram of the SLOWPOKE-2 nuclear reactor is shown in Figure 1.

### Low-pressure plasma setup

A schematic diagram of the low-pressure plasma i.e., RF glow discharge set up, used for surface modification of the PBI sheet is shown in Figure 2. The set up consists of a 220 mm high and 225 mm diameter closed glass chamber. Through an inlet, air or other desired gases are introduced into the glass chamber. The glass chamber is fitted with a pressure gauge and a vacuum system. The electrodes are capacitively coupled to a RF power generator that operates at a fixed frequency of 13.56 MHz. The PBI sheet, ultrasonically cleaned by acetone, was kept in the chamber. The chamber was evacuated by a rotary pump up to a base pressure of  $10^{-2}$  Torr (1.31 Pa), and then nitrogen gas was introduced into the system and a steady pressure of 100 Pa was maintained. At this pressure, the RF power supply was switched on to ignite the RF glow discharge. In this investigation, the surface of the poly-

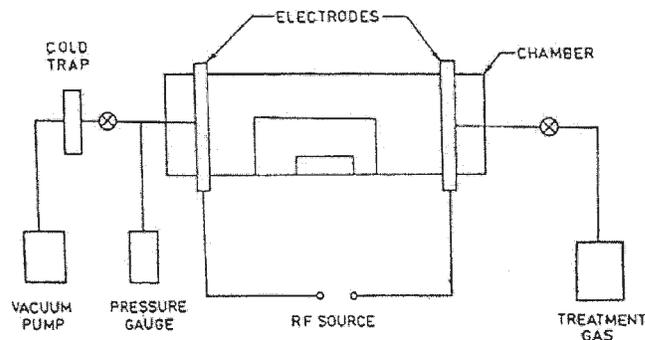
mer was modified under 120 s of exposure under 100 W of power.<sup>13</sup>

### Estimation of surface energy

Contact angles of deionized water and formamide on the unexposed PBI sheets and those PBI surfaces modified by exposure under high-energy radiation and low-pressure plasma through RF glow discharge were measured by the sessile drop technique. The geometry of the sessile drop was studied at a magnification of  $\times 12.8$  under an optical stereo zoom microscope having a crosshead glass graticule fitted with an eyepiece. Vertical and horizontal reference lines of the graticule were positioned at the corner of the drop and rotated to make the vertical line tangent to the drop. The extent of the rotation angle was measured using a goniometer of  $\pm 1^\circ$  accuracy. The surface energy was estimated by using the following equation<sup>16</sup>:

$$(1 + \cos\theta)\gamma_{LV} = 2(\gamma_S^D \gamma_{LV}^D)^{1/2} + 2(\gamma_S^P \gamma_{LV}^P)^{1/2} \quad (1)$$

on the unmodified PBI sheet and those PBI sheet exposed to high-energy radiation and low-pressure plasma. First, the contact angle of deionized water  $\theta$  was measured on the PBI surface. Therefore, in this equation,  $\theta$  is the measured contact angle of deionized water where the surface tension of deionized water  $\gamma_{LV}$  and its two components, the polar  $\gamma_{LV}^P$  and the dispersion  $\gamma_{LV}^D$ , are known and the two unknowns are  $\gamma_S^P$  and  $\gamma_S^D$  for the solid PBI surface. Second, the contact angle of formamide  $\theta$  was measured on the PBI surface and consequently  $\theta$  is the measured contact angle of formamide where surface tension of formamide  $\gamma_{LV}$  and its two components such as polar  $\gamma_{LV}^P$  and dispersion  $\gamma_{LV}^D$  are known and the two unknowns are  $\gamma_S^P$  and  $\gamma_S^D$  for the solid PBI surface. Thereby, solving these two equations, the unknowns  $\gamma_S^P$  and  $\gamma_S^D$  of the PBI were calculated. Finally, total surface energy  $\gamma_S$  has been estimated by adding  $\gamma_S^P$  and  $\gamma_S^D$  as given in eq. (2).



**Figure 2** Schematic diagram of the RF glow discharge system used.

$$\gamma_s = \gamma_s^D + \gamma_s^P \quad (2)$$

### Electron spectroscopy for chemical analysis

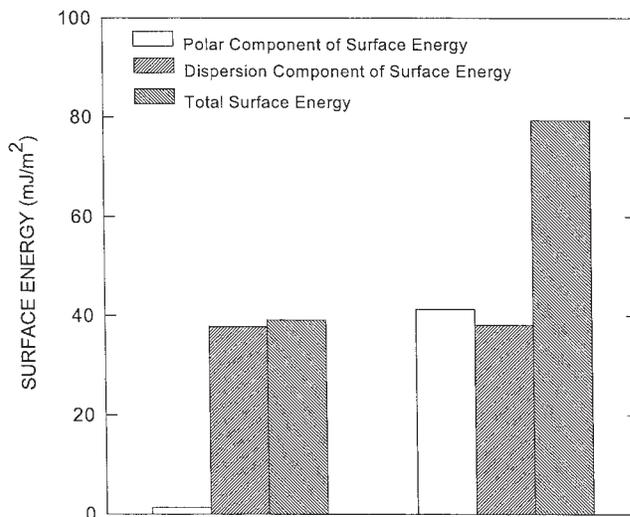
The ESCA of the polymer surface was carried out on the unmodified polymer as well as on modified polymer surfaces. The ESCA was carried out using an SSLSSX-100 X-ray photoelectron spectrometer at Ecole Polytechnique, Canada, by using monochromatized AlK $\alpha$  X-ray source, operated at a power of 200 W. The binding energy reference for the carbons of the C—C and C—H peak was set at 285.0 eV and that of C—O and C—F peaks were at 535.0 and 680.0 eV, respectively. The base pressure in the sample chamber during analysis was  $2 \times 10^{-10}$  Pa. Survey spectra were obtained using a pass energy of 58.7 eV and during the analysis, the electron take-off angle was set at 45° and the acquisition time was 6 min.

### Adhesive joint preparation

Prior to the preparation of an adhesive joint, degassing of the adhesive was carried out under a pressure of 1 Pa for 10 min. Polymer sheets of 6 mm thick were used for the preparation of the polymer-to-polymer adhesive joint to ensure that the possibility of failure of the lap joint from either polymer was remote. The lap shear tensile specimens were prepared using the polymer sheets of dimensions 110 mm  $\times$  25 mm  $\times$  6 mm, by applying high temperature resistant epoxy adhesive at an overlap length of 25 mm, according to the ASTM D 5868–95 standard and any excess adhesive present at the interface was expelled by mechanical pressing of the joint, which resulted in a joint having an adhesive of thickness of about 0.2 mm. Four types of PBI joints were prepared (i) unmodified PBI, (ii) PBI surface modified by high-energy radiation for 6 h, (iii) PBI surface modified by low-pressure plasma, and (iv) PBI surface modified by low-pressure plasma followed by exposing the joint under high-energy radiation for 6 h. Tensile lap shear test was carried out using an Instron Universal Testing Machine under a load cell of 10 kN at a test speed of 5 mm/min. For each set of conditions, seven joints are tested and the mean value is reported in the result along with the standard deviation.

### Durability test

To simulate spatial conditions, the joints were exposed to cryogenic ( $-196^\circ\text{C}$ ) and high temperature ( $+300^\circ\text{C}$ ) for 100 h, and then tensile lap shear tests were carried out. In this case, the type-IV joints are used and compared with the strength of the joint when tested under ambient conditions.



**Figure 3** Polar, dispersion, and total surface energy of PBI when the polymer surface is modified by high-energy radiation.

### Fractography

The fractured surfaces of the adhesive joints were examined under SEM. Typical features of the fractured surfaces were photographed.

## RESULTS

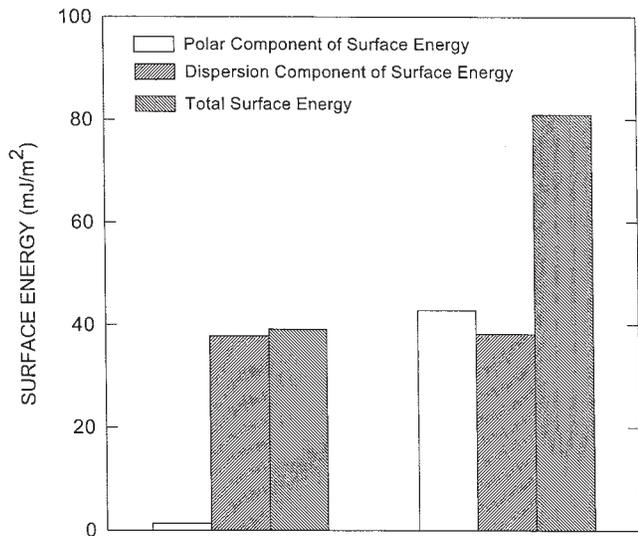
### Surface modification of polymer under high-energy radiation and low-pressure plasma and wettability

When the PBI surface is modified by high-energy radiation, a significant increase in polar component of surface energy is observed as shown in Figure 3. The figure shows that the dispersion component of surface energy remains almost same even with the exposure under high-energy radiation. Therefore, due to the increase in the polar component in surface energy, a considerable increase in total surface energy of PBI is also observed as shown in Figure 3.

A similar trend has also been observed in the case of PBI surface modified under low-pressure plasma through RF glow discharge under nitrogen atmosphere. There is a considerable increase in polar component of surface energy of PBI as shown in Figure 4; however, the dispersion component of surface energy does not increase as shown in Figure 4. Therefore, in this case also, because of the increase in the polar component in surface energy of the polymer the total surface energy of the polymer increases as shown in Figure 4.

### ESCA studies on the polymer surface

The ESCA studies of PBI have been carried out for the unexposed surface and those exposed to high-energy



**Figure 4** Polar, dispersion, and total surface energy of PBI when the polymer surface is modified by low-pressure plasma.

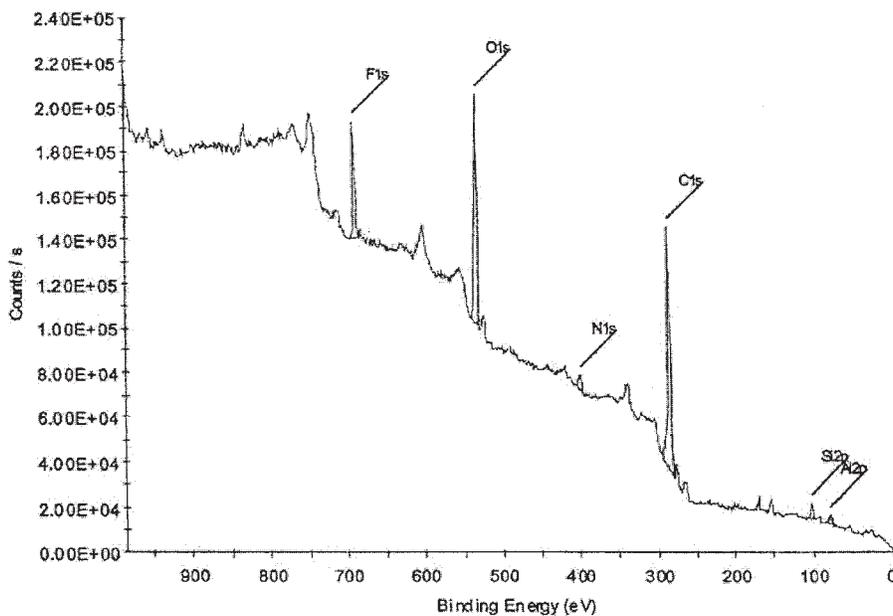
radiation and low-pressure plasma through RF glow discharge under nitrogen atmosphere. Widescan spectra of the unexposed PBI shows the C 1s peak, O 1s peak, and a significant concentration of F 1s peak as shown in Figure 5. However, the PBI surfaces exposed to high-energy radiation and low-pressure plasma show significant decrease in F 1s peak, and a small increase in N 1s peak although C 1s peak and O 1s peak are similar as evident from in Figures 6 and 7 respectively.

**Lap shear tensile properties of the polymer-polymer adhesive joint**

Figure 8 shows the lap shear tensile properties of adhesive joints of PBI-PBI when the polymer surface has been modified by high-energy radiation, low-pressure plasma and those polymer joints subsequently exposed to high-energy radiation modified by low-pressure plasma. The figure reveals that the adhesive joint strength of the unexposed PBI to PBI is 1 MPa and this increases to 13 MPa when the PBI surface is either modified under high-energy radiation or low-pressure plasma. Therefore, the exposure of the polymer to high-energy radiation or low-pressure plasma thus results in an improvement of joint strength by a factor of 13. Further, it is observed that there is a considerable increase in joint strength even up to 20 MPa when the PBI surface is modified by low-pressure plasma and subsequently the joint is exposed to high-energy radiation as shown in Figure 8. The standard deviation of lap shear tensile strength is  $\pm 0.2$  MPa. The joint with the unexposed polymer sheet failed at the interface between the adhesive and polymer as shown in Figure 9. Therefore, in this case, the surface of the polymer is clearly visible through SEM. But in the other three cases the joint fails cohesively within the adhesive, and therefore, the features are different as evident from SEM images as shown in Figures 10-12.

**Durability of the polymer joint under aerospace and space environments**

When the joints were exposed to cryogenic ( $-196^{\circ}\text{C}$ ) and high temperatures ( $+300^{\circ}\text{C}$ ) for 100 h, the joints



**Figure 5** ESCA widescan spectra of unexposed PBI surface.

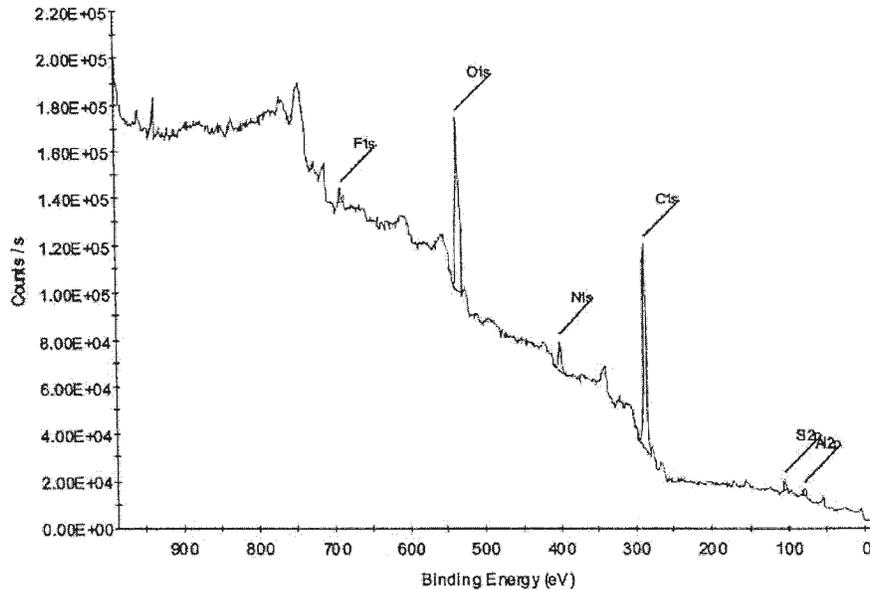


Figure 6 ESCA wide-scan spectra of PBI surface modified by high-energy radiation.

could retain the joint strength of about 95% of the strength of joint tested under ambient condition as shown in Figure 13.

## DISCUSSION

This study examined high-performance polymer composite, i.e., composite of PBI through adhesive bonding, in the context of its structural applications for aerospace and space. However, like any other polymers, the high-performance polymer also shows hydrophobic characteristics leading to low surface energy resulting in weak adhesion.<sup>2</sup> Therefore, to ease fabrication, it is necessary to modify the surface of this polymer so as to make it hydrophilic, resulting in high joint strength when fabricated for structural applications. Exposure to high-energy radiation and low-pressure plasma results in crosslinking in chain scis-

sion and formation of polar groups on the polymer surface, leading to increase in the surface energy of the polymer.<sup>1,3,9,10,12,13</sup> The wide-scan spectra of ESCA shows a relatively high nitrogen peak and significantly low fluorine peak when the PBI is exposed either to high-energy radiation or low-pressure plasma through RF glow discharge at 100 W for 120 s under nitrogen atmosphere as evident from the Figures 5–7. Therefore, the exposure of the polymer under high-energy radiation and low-pressure plasma

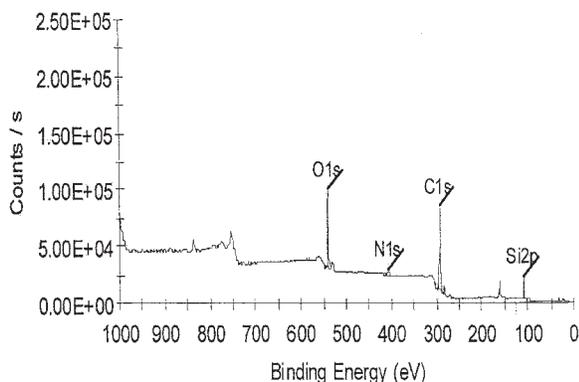


Figure 7 ESCA wide-scan spectra of PBI surface modified by low-pressure plasma.

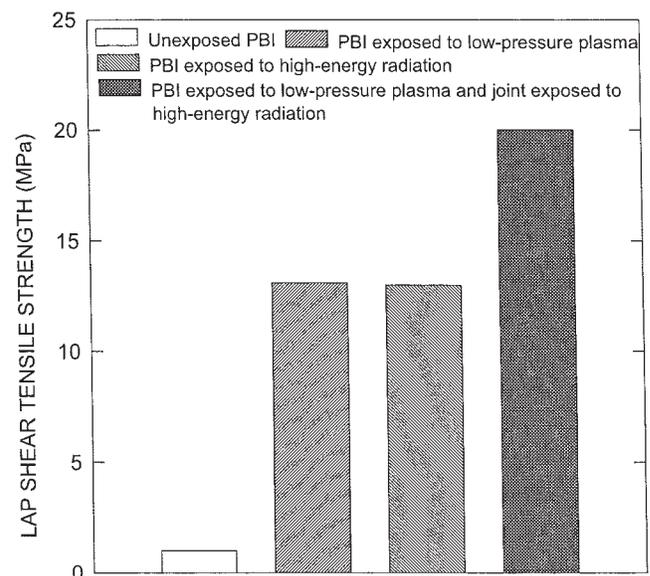
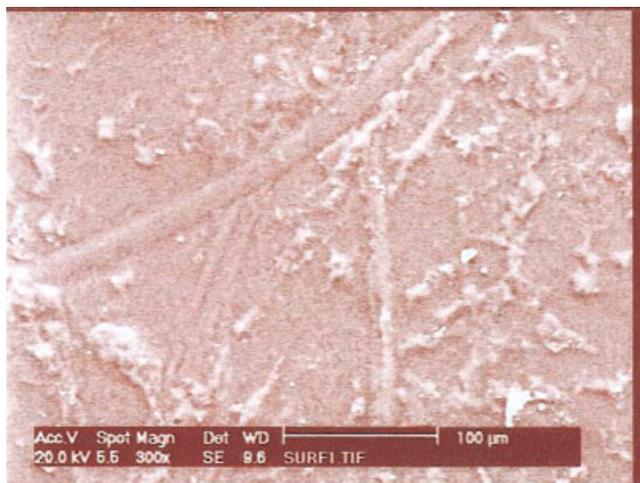


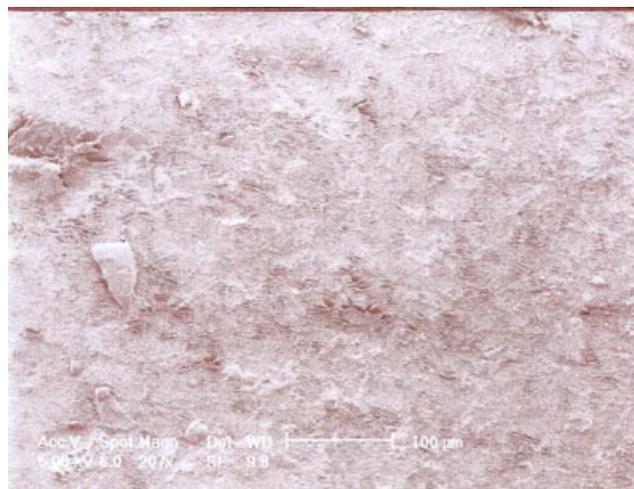
Figure 8 Lap shear tensile strength of adhesive joint of PBI when PBI surface is exposed to low-pressure plasma, high-energy radiation, and PBI surface first exposed to low-pressure plasma and joint exposed to high-energy radiation.



**Figure 9** Scanning electron micrograph showing fractured surface of the adhesive joint of unexposed PBI (magnification  $\times 300$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

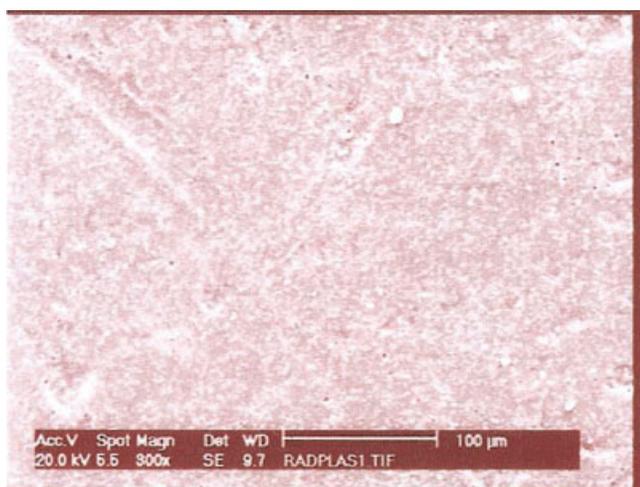
has essentially made the polymer significantly hydrophilic by reducing the fluorine groups, and consequently, there is a significant increase in surface energy as evident from Figures 3 and 4. The increase in surface energy of the polymer results in significant improvement of the adhesion characteristics of the polymer as evident from Figure 8.

The ESCA studies related to surface modification of polymer shows that when the polymer surface is exposed to low-pressure plasma under glow discharge, there is a considerable incorporation of polar functional groups on the polymer surfaces.<sup>17</sup> The ESCA spectra of exposed polyolefin<sup>1</sup> clearly reveals the gen-



**Figure 11** Scanning electron micrograph showing fractured surface of the adhesive joint when PBI surface is modified by low-pressure plasma (magnification  $\times 300$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

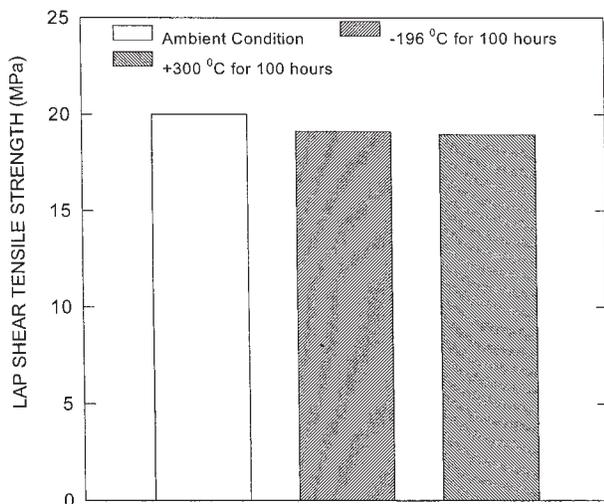
eration of new peaks resulting from plasma oxidation, namely C2 at 286.5 eV due to C—O groups (hydroxyl, ether, or epoxide), C3 at 288.0 eV due to C=O or O—C—O (carbonyl or double ether), and C3 at 289.4 eV due to O=C—OH or O=C—O—C. Honek et al.<sup>11</sup> have revealed that irradiation of polyolefin through electron beam and  $\gamma$ -rays have essentially introduced oxygen-containing groups into molecular chains of polyolefin, resulting in increasing adhesion with polar fillers. It has been reported that when the PBI surface has been modified by the exposure under an electron



**Figure 10** Scanning electron micrograph showing fractured surface of the adhesive joint when PBI surface is modified by high-energy radiation (magnification  $\times 300$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 12** Scanning electron micrograph showing fractured surface of the adhesive joint when PBI surface is modified by low-pressure plasma and the joint is exposed to high-energy radiation (magnification  $\times 300$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 13** Durability of the best PBI joint under ambient, cryogenic ( $-196^{\circ}\text{C}$  for 100 h), and elevated temperature ( $+300^{\circ}\text{C}$  for 100 h) conditions.

beam, the IR (ATR) spectroscopy revealed the generation of  $\text{CO}_2\text{H}$  units at the site of the polymer backbone and the concurrent loss of fluorine groups ( $-\text{OCF}_2-\text{C}(\text{CF}_3)-\text{F}-$ ) $_n-\text{OCF}_2\text{CF}_2-\text{SO}_3\text{H}$  into the side chain, leading to significant increase in hydrophilic properties of the polymer.<sup>18</sup> Similarly, the present investigation clearly indicates that the adhesive joint strength of unexposed PBI to PBI is relatively very low, resulting in interracial failure from the polymer to adhesive and increases significantly up to the order of 13 under the surface modification of PBI either through high-energy radiation or low-pressure plasma, resulting in cohesive failure from the adhesive, and in this context, both processes offer similar chemistry.

An earlier investigation carried out on high-energy radiation on polymeric composite reveals that there is a considerable influence on the mechanical strength of the polymeric composite when exposed to high-energy radiation,<sup>19</sup> because the exposure under high-energy radiation promotes crosslinking essentially affecting the overall behavior and mechanical properties of the polymer. However, with the longer exposure at high-energy radiation, mechanical properties of adhesive joint degrades because of chain scissions within the adhesive.<sup>12</sup> A similar observation has been reported by Xu et al.<sup>20</sup> and Berejka and Eberle<sup>21</sup> on electron beam irradiation on polyolefin and polymeric composite and it states that with the lower dose rate, mechanical properties of polymer increase; however, with the higher dose rate of electron beam, there is chain scission of polymer, resulting in deterioration of mechanical properties of the polymer. Therefore, in this investigation, the joints are essentially exposed to high-energy radiation for those polymer surfaces modified by low-pressure plasma so as to promote

crosslinking within the adhesive by high-energy radiation, and as surface modified polymer essentially fails cohesively within the adhesive, it is a clear justification to increase the joint strength even 20 times with respect to unmodified PBI as shown in Figure 8. However, when these polymeric joints are exposed to climatic conditions such as elevated as well as cryogenic temperature related to aerospace and space conditions, the joints could retain the joint strength of about 95% of strength of the joint tested under ambient conditions. This could be due to generation of residual stress along the interface, leading to minor decrease in the joint strength within a reasonable limit. Strauss<sup>2</sup> has also revealed the similar observation and stated that when PBI laminates are exposed to elevated temperature there is a little degradation in joint strength. Therefore, the adhesive bonding of PBI by high temperature resistant epoxy adhesive could be highly useful for structural applications in aerospace and space as a high-performance polymeric composite.

## CONCLUSIONS

The present investigation has led to the following conclusions:

1. When the PBI sheet is exposed to high-energy radiation for 6 h or low-pressure plasma under RF glow discharge at 100 W for 120 s using nitrogen as process gas, the polar component of surface energy and total surface energy of the polymer increase significantly.
2. Studies under ESCA confirm a sharp decrease in fluorine peak and a small increase in nitrogen peak, resulting in an increase in hydrophilic properties of the polymer.
3. The adhesive joint strength of the PBI increases about 13 times when the polymer surface is modified by either high-energy radiation or low-pressure plasma. Failure of tensile lap shear joints of unexposed PBI joined by adhesive is essentially through the interface of the polymer to adhesive. For the surface-modified polymer, the failure of the joint is essentially cohesive within the adhesive.
4. When the polymer surface is modified by low-pressure plasma and the joints are irradiated for 6 h in the pool of SLOWPOKE-2 nuclear reactor, the joint strength increases drastically about 20 times.
5. When the joints are exposed to cryogenic as well as elevated temperature for 100 h the joints could retain about 95% of their strength in comparison to the joint tested under ambient conditions.

### RECOMMENDATIONS

1. The polymer surface can also be modified by other desired gases in low-pressure plasma and a comparative study could be made for this treatment.
2. The joints can be exposed under high-energy radiation for longer duration even up to 60 h to see the effect of longer duration of exposure on the joint strength.

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### References

1. Liston, E. M.; Martinu, L.; Wertheimer, M. R. *J Adhes Sci Technol* 1993, 7, 1077.
2. Strauss, E. L. *Polym Eng Sci* 2004, 6, 24.
3. Akovali, G.; Rzaev, Z. M. O.; Mamedov, D. H. *J Appl Polym Sci* 1995, 58, 645.
4. Shaw, S. J.; Tod, D. A. *Mater World* 1994, 2, 523.
5. Boeing-Puget Sound. Environmentally complaint sol-gel surface treatments for metal bonding; The Boeing Company: St. Louis, MO.
6. Leahy, W.; Baron, V.; Buggy, M.; Young, T.; Mas, A.; Schue, F. *J Adhes* 2001, 77, 215.
7. Bhowmik, S.; Ghosh, P. K.; Ray, S.; Barthwal, S. K. *J Adhes Sci Technol* 1998, 12, 1181.
8. Behnisch, J.; Hollander, A.; Zimmermann, H. *J Appl Polym Sci* 1993, 49, 117.
9. Bhowmik, S.; Ghosh, P. K.; Ray, S. *J Appl Polym Sci* 2001, 80, 1140.
10. Dalet, P.; Papon, E.; Villenave, J. J. *J Adhes Sci Technol* 1999, 13, 857.
11. Honek, T.; Hausnerova, B.; Saha, B.; Xu, X. *Plast Rubber Compos* 2004, 33, 275.
12. Bonin, H. W.; Bui, V. T.; Pak, H.; Poirer, H.; Harris, H. *J Appl Polym Sci* 1998, 67, 37.
13. Bhowmik, S.; Chaki, T. K.; Ray, S.; Hoffmaan, F.; Dorn, L. J. *Metall Mater Trans A* 2004, 35, 865.
14. Friedrich, I. F.; Rohrer, P.; Saur, W.; Gross, Th.; Lippitz, A.; Unger, W. *J Surf Coat Technol* 1993, 59, 371.
15. Gavrilov, N.; Yakusheva, D.; Kondyurin, A. *J Appl Polym Sci* 1998, 69, 1071.
16. Comyn, J. *Int J Adhes Adhes* 1992, 12, 145.
17. Suzuki, M.; Kishida, A.; Iwata, H.; Ikada, Y. *Macromolecules* 1986, 19, 1804.
18. Hobson, L. J.; Oozu, H.; Yamaguchi, M.; Hayase, S. *J Electrochem Soc* 2001. First presented at the 4th International Symposium for New Materials for Electrochemical Systems, Montreal, July 9–13, 2001.
19. Page, D. J. Y. S.; Bonin, H. W.; Bui, V. T.; Bates, P. J. *J Appl Polym Sci* 2002, 86, 2713.
20. Xu, W.; Pengbo, L.; Hengbo, L.; Xu, X. *J Appl Polym Sci* 2000, 78, 243.
21. Berejka, A. J.; Eberle, C. *Radiat Phys Chem* 2002, 63, 551.