

Experimental Investigation into the Effect of Adhesion Properties of PEEK Modified by Atmospheric Pressure Plasma and Low Pressure Plasma

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ABSTRACT: High performance polymer, Polyether Ether Ketone (PEEK) (service temperature -250°C to $+300^{\circ}\text{C}$, tensile strength: 120 MPa) is gaining significant interest in aerospace and automotive industries. In this investigation, attention is given to understand adhesion properties of PEEK, when surface of the PEEK is modified by two different plasma processes (i) atmospheric pressure plasma and (ii) low pressure plasma under DC Glow Discharge. The PEEK sheets are fabricated by ultra high temperature resistant epoxy adhesive (DURALCO 4703, service temperature -260°C to $+350^{\circ}\text{C}$). The surface of the PEEK is modified through atmospheric pressure plasma with 30 and 60 s of exposure and low pressure plasma with 30, 60, 120, 240, and 480 s of exposure. It is observed that polar component of surface energy leading to total surface energy of the polymer increases significantly when exposed to atmospheric pressure plasma. In the case of low pressure plasma, polar

component of surface energy leading to total surface energy of the polymer increases with time of exposure up to 120 s and thereafter, it deteriorates with increasing time of exposure. The fractured surface of the adhesively bonded PEEK is examined under SEM. It is observed that unmodified PEEK fails essentially from the adhesive to PEEK interface resulting in low adhesive bond strength. In the case of surface modified PEEK under atmospheric pressure plasma, the failure is entirely from the PEEK and essentially tensile failure at the end of the overlap resulting in significant increase in adhesive bond strength. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 173–179, 2010

Key words: polyether ether ketone (PEEK); epoxy adhesive (DURALCO 4703); low pressure plasma; atmospheric pressure plasma; SEM; adhesive bond strength

INTRODUCTION

Various industrial sectors like automotive, aviation, space etc. is constantly striving for high strength light weight materials. These materials are often fabricated by adhesive bonding to form desired structural components. Adhesive bonding is advantageous than other ways of joining especially riveting.^{1–3} Riveting of components results in stress concentration and reduces the overall load capacity of the structure.⁴ Adhesive bonds are more effective in assembling composite structures than other mechanical joining methods, as they provide more uni-

form stress distribution, lower stress concentration and better fatigue life and corrosion resistance.⁵ Adhesive joint can distribute the applied load over the entire bonded area and is suitable for joining dissimilar materials with low manufacturing cost.⁶ The use of adhesive bonding for high performance application is still challenging due to low thermal and mechanical properties of adhesives. However, due to the development of high performance adhesives the limitations in terms of thermal and mechanical properties have overcome considerably.^{7,8}

It is established that for successful application of polymeric composite materials to form structural parts using adhesive bonding, they need to have special surface properties like hydrophilicity.⁹ Recent advances in the use of polymers and the resulting need for hydrophilic surfaces for adequate adhesion has fueled the development of the plasma surface modification industry.¹⁰ Low-pressure plasma methods have been investigated, but they are difficult to apply on a industrial scale as they require vacuum and consume considerable amounts of energy. Moreover, these treatments can only be carried out in a batch mode, which increases the overall treatment time. New methods based on atmospheric plasma

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treatments seem to be quite attractive for the industry. These treatments have the advantage of being applicable online without need for vacuum.¹¹ They also improve surface wettability by increasing the hydrophilic nature of the film surface. Some of the advantages resulting from this improved hydrophilic behavior of the material are better biocompatibility and much better adhesive properties because of an increase in the surface activity of the polymer.^{12–15}

Poly(etheretherketone) (PEEK) is high-temperature-resistant semicrystalline thermoplastic. It possesses an outstanding thermal stability with melting temperatures above 280°C. It offers the highest thermal and chemical stability and good mechanical properties.¹⁶

The main purpose of surface preparation is to improve the adhesion properties to such an extent that the interface failure from adhesive to polymer does not take place.

On the basis of these considerations, surface modification of polymer is carried out by atmospheric pressure plasma for 30 and 60 s using a frequency of 60 Hz at a power of 600 W and by low pressure plasma using RF Glow Discharge for 30, 60, 120, 240, and 480 s. The surface energy of untreated, atmospheric pressure plasma and low pressure plasma treated PEEK are calculated using contact angle measurement method. Adhesive joints of PEEK to PEEK are prepared using high performance epoxy adhesive. Lap shear test is carried out of adhesive bonded joints prepared with and without surface modified PEEK. Finally, fractured surfaces are analyzed under scanning electron microscope (SEM) to investigate the failure modes of bonded joints.

EXPERIMENTAL

Materials

In this investigation, high temperature resistant epoxy adhesive, DURALCO 4703, Supplied by Cotronics Corp., Brooklyn, NY was used. The service temperature of this epoxy adhesive is ranging from –260°C to +370°C and cohesive strength is 24 MPa. The adhesive was prepared by using 100 parts of resin and 22 parts of curing agent as instructed by manufacturer. The curing time for this adhesive is 4 h at 120°C. Before application of adhesive to the substrate material, it was kept under vacuum for 20 min at room temperature to remove any air bubbles. PEEK sheet was used as substrate materials. Two test liquids, deionized water and formamide of known polar and dispersion components of surface energy were used to determine the polar and dispersion components of surface energies of substrate materials through measurement of contact angle by the sessile drop method. The polar and dispersion

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

Liquid	γ_{LV}^P (mN/m)	γ_{LV}^D (mN/m)	γ_{LV} (mN/m)
Deionized water	50.2	22.0	72.2
Formamide	18.6	39.6	58.2

components of surface tensions of deionised water and formamide are listed in Table I.

Atmospheric pressure plasma and low pressure plasma treatment

Atmospheric pressure plasma treatment was carried out to modify the surface of polymeric materials by using TIGRES Plasma-BLASTER MEF equipment. It operates at 600 W and 60 Hz frequency. During plasma treatment, the treatment distance of polymer surface from nozzle head of plasma equipment was 5 mm and air was used as processing gas with a total flow rate of 51 L/min at a pressure of 4.5 bars. In this investigation, time of exposure of 30 and 60 s was maintained.

Low-pressure plasma under RF glow discharge was also used for surface modification of the PEEK. 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 PEEK 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 at this pressure, the RF power supply was switched on to ignite the RF glow discharge. In this investigation, the surface of the polymer was modified under 30, 60, 120, 240, and 480 s.

Before performing the plasma treatment, the polymeric samples were first cleaned by acetone using ultrasonic cleaning in order to remove contamination on the polymeric surface. Thereafter, the specimens were heated under vacuum for 4 h to dry. The specimens were then placed under the atmospheric pressure plasma and low pressure plasma separately and treated with plasma using air.

Contact angle measurement and surface energy estimation

Contact angle of untreated and treated PEEK sheets using test liquids were measured by Modular “CAM 200– Optical contact angle and surface tension meter” followed by estimation of surface energy of untreated, atmospheric pressure plasma and low

pressure plasma treated polymers using deionized water and formamide as test liquids. The surface energy and the polar and dispersion components of PEEK polymer was calculated using the following equation.¹⁰

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

First, the contact angle of deionised water θ was measured on the PEEK surface. Therefore, in this equation, θ is the measured contact angle of deionised water where surface tension of deionized water γ_{LV} and its two components, the polar γ_{LV}^P and the dispersion γ_{LV}^D are known and the two unknowns are γ_S^P and γ_S^D for the solid PEEK surface. Second, the contact angle of formamide θ was measured on the PEEK surface and consequently θ is the measured contact angle of formamide where surface tension of formamide γ_{LV} and its two components, the polar γ_{LV}^P and the dispersion γ_{LV}^D are known and the two unknowns are γ_S^P and γ_S^D for the solid PEEK surface. Thereby solving these two equations, the unknowns γ_S^P and γ_S^D of the PEEK were calculated.

Finally, the total surface energy γ_S was estimated by eq. (2):

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

Adhesive joint preparation and tensile lap shear testing

Rectangular specimens, having dimensions length \times width \times thickness: $150 \times 25 \times 3 \text{ mm}^3$ were used for tensile lap shear testing. The specimens were bonded to perform single tensile lap shear tests. Prior to the preparation of an adhesive bonded joint, degassing of the adhesive was carried out under a pressure of 1 Pa for 10 min. The tensile lap shear specimens were prepared by applying high temperature resistant epoxy adhesive. Any excessive adhesive present at the interface was expelled by mechanical pressing of the joint, which resulted in a joint having an adhesive of uniform thickness about 0.20 mm. Pressure was applied to the lap joint during the curing cycle by two binder clips. The bonded specimens were cured at 120°C for 4 h. Three types of PEEK joints were prepared and tested (i) Untreated PEEK joint with 25 mm overlap length, (ii) Atmospheric plasma treated PEEK joint with 25 mm overlap length, and (iii) Low pressure plasma treated PEEK joint with 25 mm overlap length. Lap Shear testing was carried out using computer-controlled testing machine, ZWICK 2010, under a load cell of 50 kN. The specimens were loaded in tension at a test speed of 5 mm/min. Five specimens were

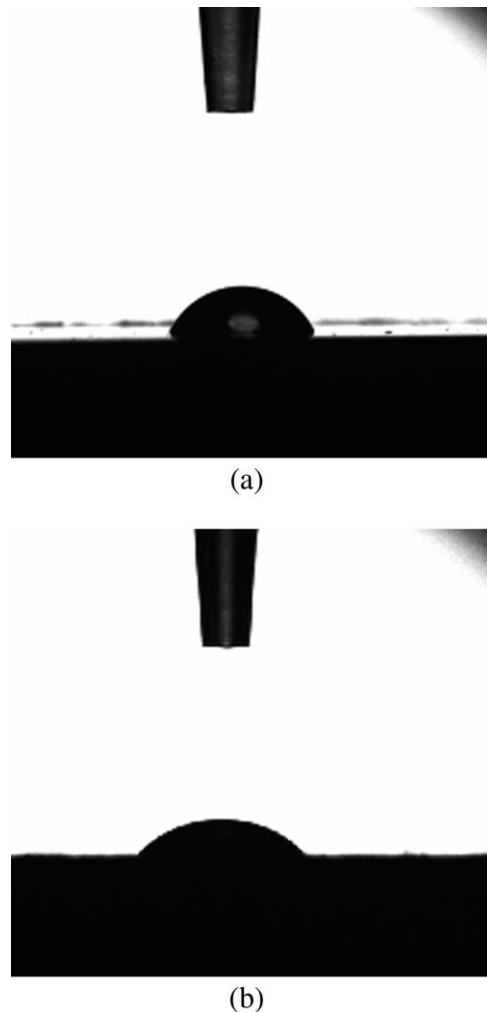


Figure 1 (a) Contact angle on unmodified PEEK sheet—water as medium: 69.65 deg. (b) Contact angle on unmodified PEEK sheet—formamide as medium: 49.11 deg.

tested and the mean value is reported in the results. All tests were performed at room temperature of 25°C and at 50% humidity.

RESULTS

Surface modification of PEEK by atmospheric pressure plasma and low pressure plasma and estimation of surface energy

Surface energy and its polar and dispersion components of PEEK polymer was calculated using contact angle measurements. The contact angles on the surfaces of untreated, atmospheric pressure plasma treated and low pressure plasma treated PEEK are shown in Figures 1(a,b), 2(a,b), and 3(a,b) and the values are listed in Table II. The figures reveal that the contact angle is more on untreated PEEK, decreases with treatment with low pressure plasma and further decreases with atmospheric pressure plasma. It is observed that surface modification of

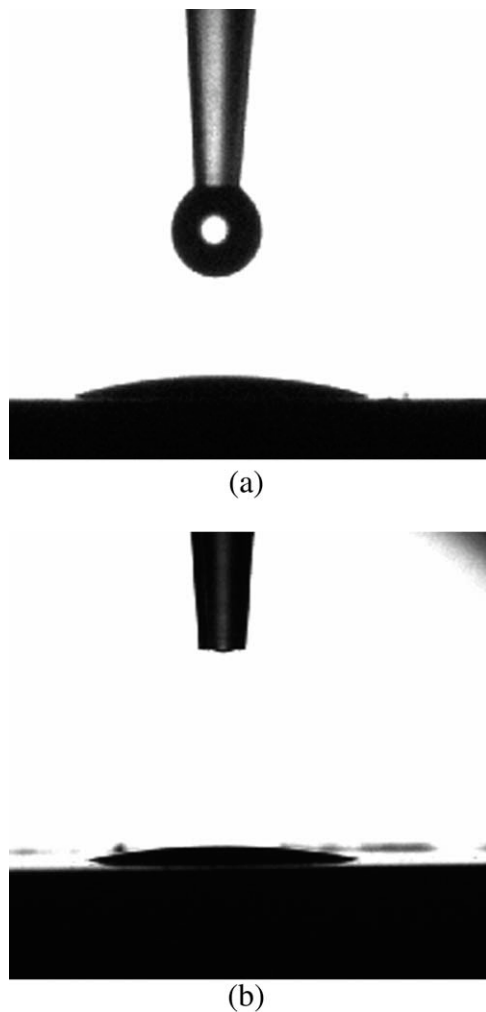


Figure 2 (a) Contact angle on atmospheric pressure plasma treated PEEK sheet for 30 sec—water as medium: 13.27 deg. (b) Contact angle on atmospheric pressure plasma treated PEEK sheet for 30 sec—formamide as medium: 12.99 deg.

polymer by atmospheric pressure plasma, results in significant increase in surface energy when compared to the surface energy of untreated polymers as shown in Figure 4. In the case of low pressure plasma treated PEEK; it is observed that polar component of surface energy leading to total surface energy of PEEK increases up to 120 s of exposure, thereafter it decreases with increasing exposure time as shown in Figure 5. It is also interesting to observe that atmospheric pressure plasma is more effective

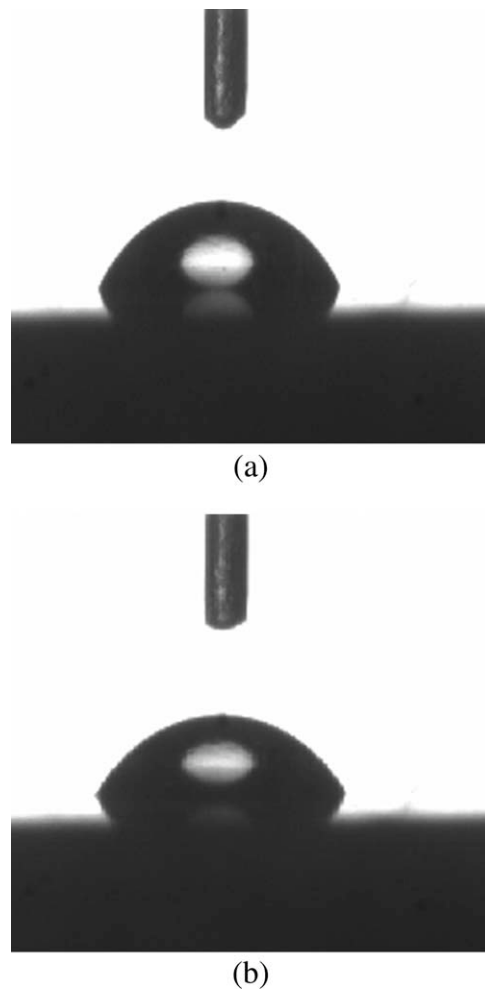


Figure 3 (a) Contact angle on low pressure plasma treated PEEK sheet for 30 sec—water as medium: 40.0 deg. (b) Contact angle on low pressure plasma treated PEEK sheet for 30 sec—formamide as medium: 34.2 deg.

in comparison to low pressure plasma in terms of improvement of surface energy of the PEEK.

Lap shear tensile properties of adhesive-bonded polymer joints

Lap shear tensile strength of atmospheric pressure plasma and low pressure plasma treated PEEK to adhesive bonded joint is shown in Figure 6. The figure demonstrates the comparison of lap shear tensile strength of PEEK bonded joint before and after the plasma treatments with an overlap length of 25 mm.

TABLE II
Contact Angle Measurement Values on PEEK Sheets

Sl#	Time (in sec)	Untreated		Low pressure plasma treated		Atmospheric pressure plasma treated	
		Water	Formamide	Water	Formamide	Water	Formamide
1	0	69.65	49.11	—	—	—	—
2	30	—	—	40.0	34.2	13.27	12.99

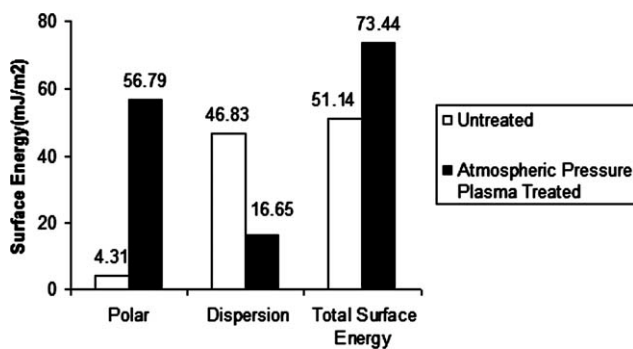


Figure 4 Comparison of surface energy of untreated and atmospheric pressure plasma treated PEEK.

The figure reveals that the lap shear tensile strength of adhesive joint increases from 0.5 MPa to a maximum of 8.00 MPa resulting in considerable improvement in the adhesion properties of PEEK after atmospheric pressure plasma treatment. However, low pressure plasma treatment results in the improvement of adhesive bond strength up to 4.00 MPa.

Failure modes of adhesive bonded joints of PEEK

It is interesting to observe that unmodified PEEK fails essentially from the adhesive to PEEK interface as shown in Figure 7 resulting in low adhesive bond strength. However, in the case of surface modified PEEK under atmospheric pressure plasma, the failure is entirely from the PEEK and essentially tensile failure at the end of the overlap resulting in significant increase in adhesive bond strength as shown in Figure 8 (a,b). Apparently, this type of failure is not so common for polymer bond; however, it is possible that as PEEK is essentially a high strength polymer with low toughness properties, therefore, instead of shear failure, the mode of failure is tensile. However, in the case of low pressure plasma treated PEEK, the failure of adhesive bonded joint is primarily cohesive from the adhesive and partly from interface of adhesive to PEEK resulting in rela-

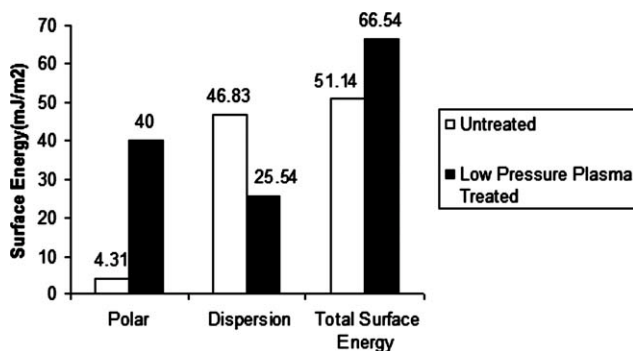


Figure 5 Comparison of surface energy of untreated and low pressure plasma treated PEEK.

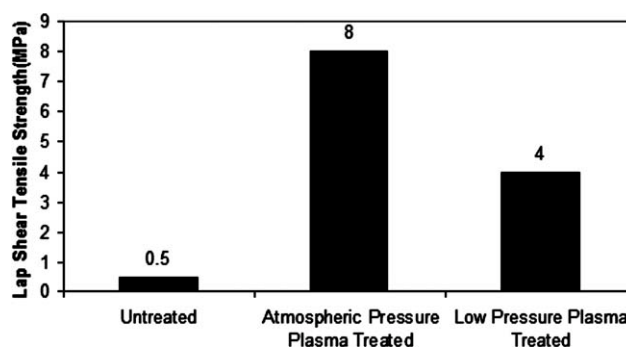


Figure 6 Lap shear tensile strength of untreated, atmospheric pressure plasma, and low pressure plasma treated PEEK.

tively low adhesive bond strength in comparison to atmospheric plasma treated PEEK.

DISCUSSION

This investigation is carried out to justify the effect of atmospheric plasma treatment and low pressure plasma treatment on the surface energy of PEEK leading to adhesion characteristics of PEEK. High performance polymers like PEEK very often do not possess the desired surface properties in terms of strong adhesive bonding. They are hydrophobic in nature, and in general exhibits insufficient adhesive bond strength due to relatively low surface energy.² Therefore, to improve the surface energy of polymers, surfaces of PEEK, are modified by atmospheric pressure plasma and low pressure plasma treatment. The surface treatment creates hydrophilic properties which results in increased adhesion. The improvement in adhesion properties is attributed due to the formation of polar groups on the polymer surfaces.⁹ It is reported that surface modification

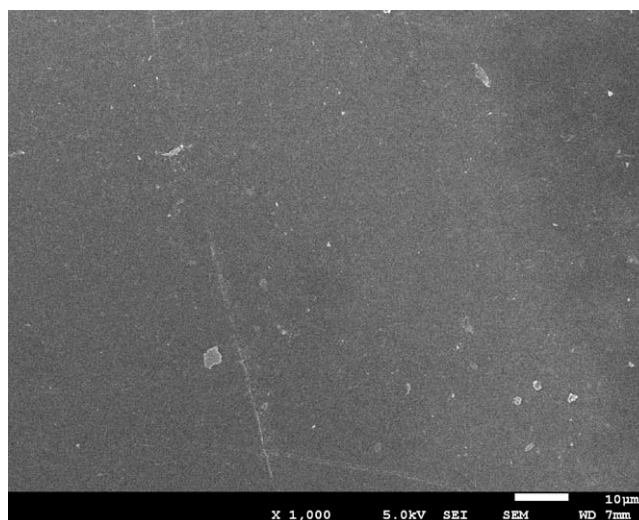


Figure 7 SEM micrograph of fractured surface of untreated PEEK.

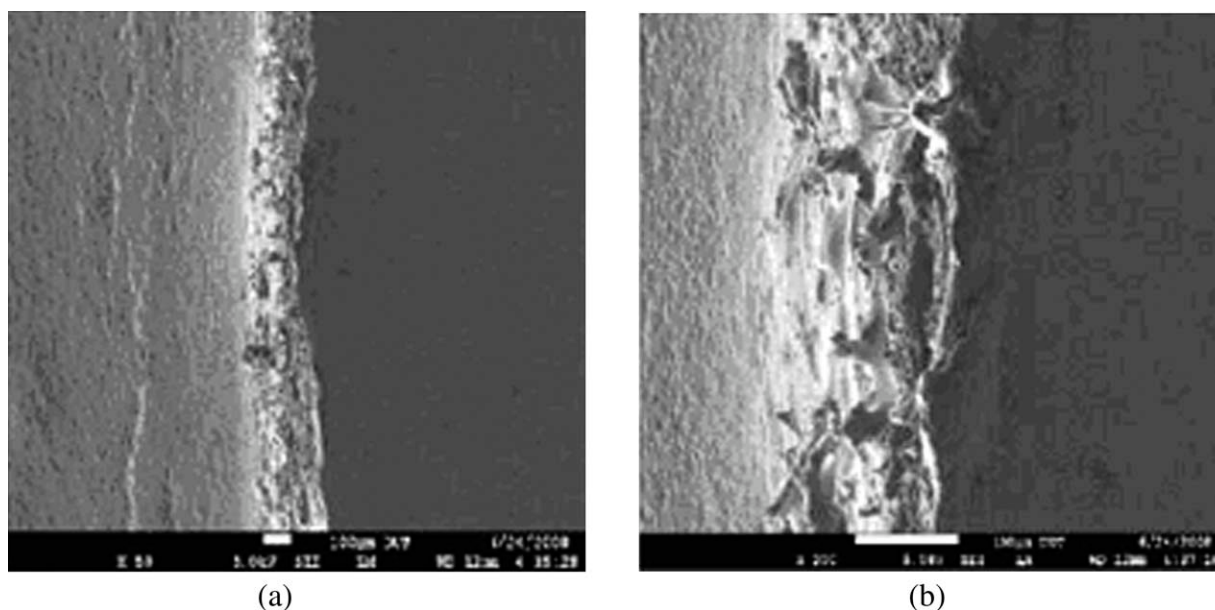


Figure 8 (a) SEM micrograph of fractured surface of plasma treated PEEK at $\times 50$ magnification. (b) SEM micrograph of fractured surface of plasma treated PEEK at $\times 200$ magnification.

under plasma treatment is confined to top several hundred angstrom and bulk properties of the material remain the same.⁶

In this context, the present investigation also supports this statement that there is considerable improvement in surface energy of the polymer especially under atmospheric pressure plasma treatment as shown in Figure 4. The polar component of surface energy of the polymers are mainly responsible for such increase in the surface energy of the PEEK due to the formation of the polar functional groups on the surface of the PEEK resulting in better adhesion characteristics.⁶ The increase in surface energy of polymer is usually correlated with the adhesive bonded joint strength as discussed in the previous paragraph, and it is important to note that atmospheric pressure plasma is more capable than low pressure plasma. However, it is unclear why atmospheric pressure plasma is more capable than low pressure plasma. Therefore, this could be concluded that transformation of physicochemical characteristics of polymer is governed by charged ionized particles of plasma and atmospheric pressure plasma may generate more ionized particles and which opens a new direction of research in terms of adhesion properties of polymer under plasma treatment.

Rachel et al. has revealed that the improvement in adhesion properties of polymer is due to the formation of some chemical bonds on the material surfaces.¹⁷ Plasma treatment oxidizes the surface of the polymer to such an extent that the adhesive can permeate the roughness of the thin oxidized layer.¹⁴ Bowditch and Shaw have revealed that when oxygen gas was used to modify polymer surfaces, it

resulted in the most effective way to introduce the hydrophilicity to a polymer surface.¹ It has been emphasized that the desired gas react with a wide range of polymers to produce various functional groups, including C—O, C=O, and O—C—O at the surface.

Although the increase in surface energy is usually correlated with the adhesive bonded joint strength as discussed in the previous paragraphs, however, a recent study carried out by coinvestigators of the study¹⁸ reveals that the lap shear strength of PEEK increases with the decrease in overlap length and it is very interesting to note that even after the overlap length of merely 6.25 mm, failure from PEEK takes place instead from adhesive as such. Therefore, to justify the toughness and stiffness effect, the investigation was also carried out with polymers of high stiffness and toughness properties such as carbon fibers and glass fibers reinforced polyphenylene sulfide (PPS) and tested under lap shear configuration.¹⁷ It has been clearly justified when polymers with high stiffness and toughness were used; failure was essentially from the adhesive and not from the polymer as such. Therefore, it is necessary to use polymers of high stiffness and toughness properties for fabricating high performance polymeric adhesive bonding.

Adhesive bonded joints in general fail by variety of failure modes. The most common failure modes are (a) interfacial failure (b) cohesive failure in the adhesive or in the adherend and (c) adherend failure.⁹ The failure mode depends on the materials, surface preparation techniques; adhesive, and proper joint preparation as discussed in previous

paragraphs. After atmospheric pressure plasma treatment on PEEK, scanning electron microscope analysis clearly demonstrates that failure of adhesive joint is either cohesively from the substrate or at times cohesively from the adhesive. Therefore, this can be concluded that after atmospheric pressure plasma treatment, locus of failure transformed from the adhesive-substrate interface to within substrate or adhesive. Therefore, this investigation concludes with a high note that application of plasma treatment especially atmospheric pressure plasma treatment is a very effective method to promoting strong adhesion properties of PEEK.

CONCLUSION

This study has led to the following conclusions.

- a. Atmospheric plasma treatment has a remarkable effect on the surface energies of PEEK
- b. Formation of functional groups after plasma treatment improved the adhesion properties of substrate surfaces which ultimately increase the adhesive bonded joint strength
- c. Atmospheric pressure plasma treatment results in the shift of locus of failure from the adhesive-substrate interface to within adhesive or substrate material

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