PHYSICO-CHEMICAL CHARACTERISTICS OF HIGH PERFORMANCE POLYMER MODIFIED BY LOW AND ATMOSPHERIC PRESSURE PLASMA

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In this work, the effect of low pressure plasma and atmospheric-pressure plasma treatment on surface properties and adhesion characteristics of high performance polymer, Polyether Ether Ketone (PEEK) are investigated in terms of Fourier Transform Infrared Spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and Atomic Force Microscopy (AFM). The experimental results show that the PEEK surface treated by atmospheric pressure plasma lead to an increase in the polar component of the surface energy, resulting in improving the adhesion characteristics of the PEEK/Epoxy adhesive system. Also, the roughness of the treated surfaces is largely increased as confirmed by AFM observation. These results can be explained by the fact that the atmospheric pressure plasma treatment of PEEK surface yields several oxygen functionalities on hydrophobic surface, which play an important role in increasing the surface polarity, wettability, and the adhesion characteristics of the PEEK/Epoxy adhesive system.

УДК 544.55

INTRODUCTION

Presently, polymeric composites appear to be materials of choice for different types of high-end commercial applications in automotive and aerospace industries as these components can help to save nearly 60–80% in component weight by replacing steel components and 20–50% weight by replacing aluminium parts [1].

Polyether Ether Ketone (PEEK) (service temperature -250^{0}C to +300^{0}C, tensile strength: 120 MPa) is a high performance thermoplastic polymer which is gaining significant interest in aerospace and automotive industries. PEEK is lightweight high performance polymer that can successfully replace metals and other polymers due to its unique combination of outstanding wear performance, processing flexibility, and excellent chemical resistance. It offers significantly high thermal and chemical stability as well as mechanical properties [2].

A high performance polymer like PEEK is hydrophobic in nature like any other polymers resulting in poor adhesion characteristics and consequently, exhibits insufficient adhesive bond strength due to relatively low surface energy [3]. It is established that for successful application of polymeric composite materials to form structural parts, polymeric materials are adhesively bonded to form desired structures [4]. Therefore, in order to increase adhesion characteristics of polymer, surface modification of polymer is often carried out by low pressure plasma that essentially transforms hydrophobic surface to hydrophilic surface [5]. Structure of PEEK clearly reveals presence of an oxygen atom between two phenyl groups and therefore, chain scission occurs readily due to irradiation of electrons or ions [6–8]. Inagaki et al. [8] studied the effect of remote oxygen plasma on PEEK and observed that PEEK is susceptible to plasma actions, and as a result, the degradation of PEEK and the introduction of oxygen functionality occur simultaneously on the surfaces of PEEK films.

Based on these considerations, the surface of PEEK was modified by atmospheric pressure plasma for 30 and 60 seconds using a frequency of 60 Hz at a power of 600 W and by low pressure plasma using radio frequency (RF) Glow Discharge for 30, 60, 120, 240 and 480 seconds. The hydrophilicity of the PEEK surface after the plasma treatment was analyzed by using contact angle and surface energy measurements.

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Surface functionalization of the polymer for the basic and surface modified polymer has been carried out by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Topographical changes of the polymer surface after plasma treatment has been analyzed by Atomic Force Microscopy (AFM). Adhesive joints of PEEK to PEEK were prepared using high performance epoxy adhesive and lap shear tensile tests were performed to measure the increase in adhesion characteristics of PEEK. Fractured surfaces of adhesive joint of PEEK were analyzed under scanning electron microscope (SEM) to investigate the failure modes of bonded joints.

EXPERIMENTAL MATERIALS

In this investigation, PEEK sheets for service temperature ranging from -250°C to + 300°C, tensile strength of 140 MPa and density of 1.3 gm/cm^3 (as reported by the manufacturer, Victrex, Lancashire, UK) was used as substrate material. The ultra-high-temperature-resistant epoxy adhesive, DURALCO 4703 (service temperature ranging from -260°C to + 370°C), supplied by Cotronics Corp., Brooklyn, NY was used to join the polymer sheets. Two test liquids, deionized water and formamide of known polar and dispersion components of surface tension were used to determine the polar and dispersion components of surface energies of PEEK through measurement of their contact angle by the sessile drop method.

ATMOSPHERIC PRESSURE PLASMA AND LOW PRESSURE PLASMA TREATMENT AND SURFACE ENERGY MEASUREMENT

Atmospheric pressure plasma was used to modify the surface of PEEK by using TIGRES Plasma-BLASTER MEF equipment which operates at a power of 600 W and 60 Hz frequency. A controlled electrical discharge – but no arc – is ignited between a pencil electrode and a metallic, grounded nozzle. The produced potential-free plasma is directed towards the polymer surface by an air flow as shown in fig. 1. 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 seconds was maintained.

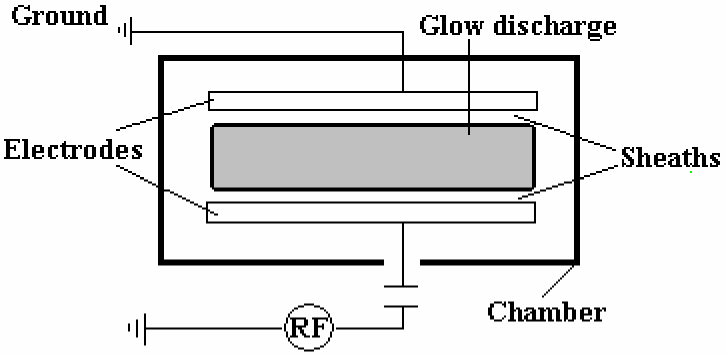


Fig. 1. Schematic diagram of atmospheric pressure plasma jet

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 as shown in fig. 2. The electrodes are capacitively coupled to a RF power generator that operates at a fixed frequency of 13.56 MHz and a power of 100 W. 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 seconds.

Contact angles 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 [5]

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

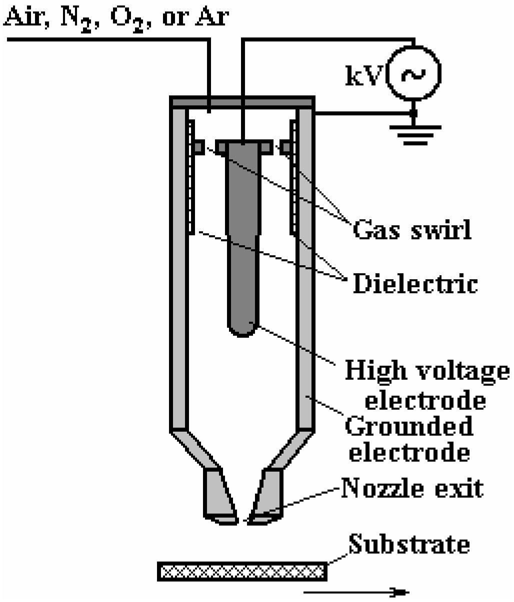


Fig. 2. Schematic diagram of RF low pressure plasma

Firstly, the contact angle of de-ionized water θ was measured on the PEEK surface. Therefore in this equation θ is the measured contact angle of de-ionized 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. Secondly, 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 equation (2):

$$\gamma_S = \gamma^{D}_{S} + \gamma^{P}_{S}. \tag{2}$$

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) OF PEEK

FTIR analysis of the untreated PEEK was performed on IR Prestige Shimadzu, Japan using ATR mode. The Polymeric samples were analyzed at 4 cm^{-1} resolution and 10 scans were performed between 4000–400 cm^{-1}.

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) FOR CHEMICAL ANALYSIS

The XPS analysis of the unmodified and modified PEEK was carried out in an ultra-high vacuum chamber (PHI1257) with a base pressure of 4×10^{-10} Torr. The XPS spectrometer was equipped with a high-resolution hemispherical electron energy analyzer (279.4 mm diameter) with 25 meV resolution, and a dual anode Mg/Al Kα x-ray source. The source used for this study was the Al (Kα) x-ray excitation of energy 1486.6 eV with pass energy 100eVfor survey scan and 40eV for core level spectra of each element. All binding energies (BE) were calibrated by the BE (284.6 eV) of C1s, which gave BE values within an accuracy of 0.1 eV.

ATOMIC FORCE MICROSCOPY (AFM) FOR TOPOGRAPHICAL ANALYSIS

AFM-measurements were performed with a commercial AFM (easyScan, Nanosurf AG, Switzerland). In dynamic and phase contrast mode a cantilever (NanoProbe NCRC) having a spring constant

k_{tip} = 48 N/m, resonance frequency f_{res} = 190 kHz, and a tip radius r_{tip} < 10 nm was applied. All measurements were carried out under controlled atmosphere (T = 295 K, relative humidity RH = 40%).

ADHESIVE JOINT PREPARATION AND TENSILE LAP SHEAR TESTING

Rectangular specimens, having dimensions length x width x thickness: 150x25x3 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 hours. Three types of PEEK joints were prepared and tested. Untreated PEEK joint with 25 mm overlap length. Atmospheric plasma treated PEEK joint with 25 mm overlap length and 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 tested and the mean value is reported in the results. All tests were performed at room temperature of 25^0C and at 50% humidity.

FRACTOGRAPHY AND MICROSCOPIC STUDIES OF THE FRACTURED JOINTS

Typical features of the fractured surfaces of the unmodified and modified PEEK surfaces were photographed and analysis of the fractured surfaces was done using SEM.

RESULT AND DISCUSSSION

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) ANALYSIS

Structure of Poly Ether Ether Ketone is shown in fig. 3. Fig. 4 shows the infrared spectrum of PEEK. The main groups of PEEK molecule are benzene, ketone and aromatic ether bond. The wavenumbers of carbon-hydrogen (=C-H in the Benzene ring) extension vibration are 3030 and 3070 cm^{-1}, the aromatic ring (C=C) are 1500 cm^{-1} and 1600 cm^{-1}, and C-H out-of-plane bending substitution patterns is seen below 900 cm^{-1}.The wavenumbers of ketone (C=O) is at 1660 $cm^{-1}$and aromatic ether bond (C-O-C) are present at 1050 cm^{-1} and 1220 cm^{-1}. The wave numbers ranging from 1200–1000 cm^{-1} correspond to CO, alcohol and ether stretches. Thus, the FTIR analysis confirms the structure of Poly Ether Ether Ketone as shown in fig. 3.

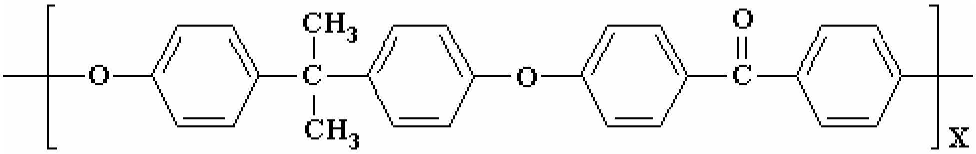


Fig. 3. Structure of PEEK

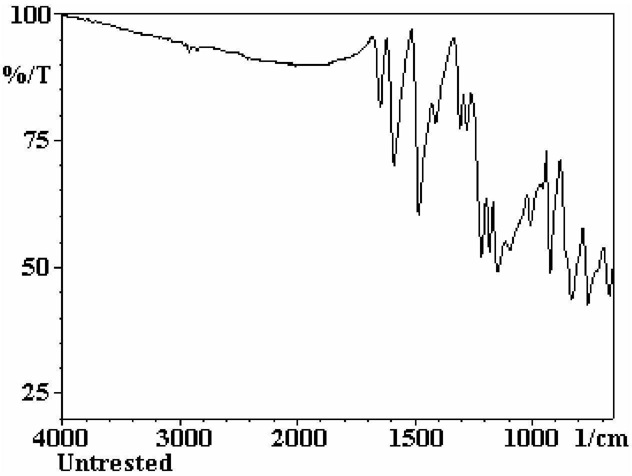


Fig. 4. FTIR of Untreated PEEK

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) ANALYSIS

The XPS analysis of PEEK was carried out for the untreated polymer surface and those treated with low pressure plasma and atmospheric pressure plasma. Survey scan spectra of the untreated, low pressure plasma and atmospheric pressure plasma treated PEEK is shown in figs. 5–7 respectively. The figures clearly show that C1s peak and O1s peak are the major components. The intensity of O1s peak although increases with the low pressure plasma treatment as seen in fig. 6, but shows a considerable increase after the atmospheric pressure plasma treatment as evident from fig. 7. These results suggest that oxygen was incorporated on the surface of PEEK after the plasma treatment. This observation is further strengthened by the percentage composition of the elements as listed in Table 1. The atomic concentration of C1s and O1s of the untreated PEEK were 86.63% and 10.70% respectively. After the low pressure plasma treatment, C1s component decreased to 81.92% and O1s component increased to 15.08% and with the atmospheric pressure plasma treatment, C1s component further decreased to 76.78% while O1s component shows a remarkable increase to 21.13%. Therefore, low pressure plasma and atmospheric pressure plasma essentially increase the oxygen/carbon (O/C) ratio because of incorporation of oxygen functionalities on the polymer surface. Along with carbon and oxygen, there are traces of nitrogen too in the sample which shows a slight increase after low pressure plasma treatment as the plasma treatment was carried out in air.

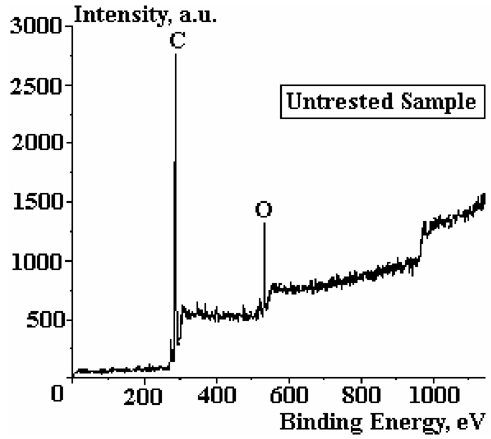


Fig. 5. Survey Scan spectra of untreated PEEK

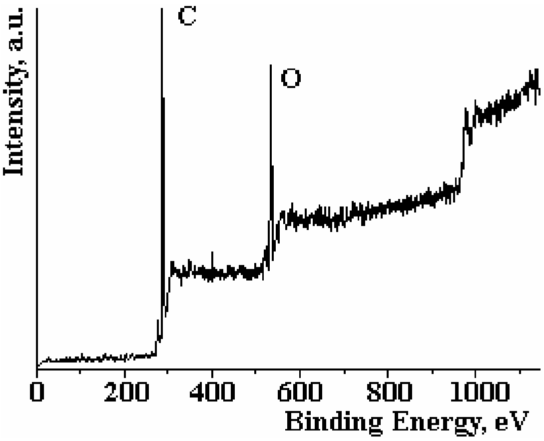


Fig. 6. Survey Scan spectra of Low Pressure Plasma (LPP) treated PEEK

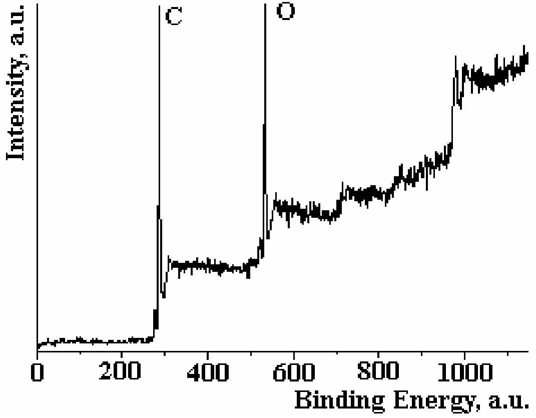
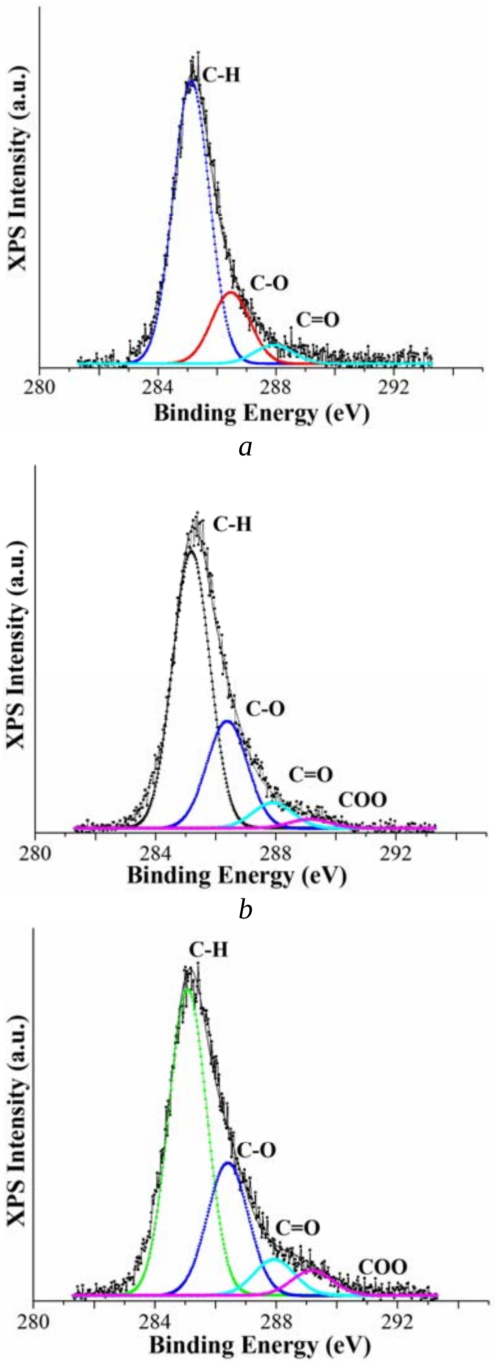


Fig. 7. Survey Scan spectra of Atmospheric Pressure Plasma (APP) treated PEEK

Table 1. Percentage Contribution of Elements in the Sample

Elements	Untreated PEEK	Low-pressure plasma treated PEEK	Atmospheric-pressure plasma treated PEEK
% Carbon	86.63	81.92	76.78
% Oxygen	10.70	15.08	21.13
% Nitrogen	2.67	3.0	2.09

Figure 8,*a* shows the spectra of untreated PEEK. It can be deconvoluted into three main components: 285.0 eV (CH groups), 286.5 eV (C-O groups), and 287.9 eV (C=O groups). The relative concentrations of the CH, the C-O, and the C=O components for the Untreated PEEK film are 75, 19.2, and 5.2%, respectively. These results show a close agreement with the theoretical values (74.1, 20.7, and 5.1% for the CH, the C-O, and the C=O groups, respectively). Figure 8,*b* shows the spectra of low pressure plasma treated PEEK which can be deconvoluted into four components: 285.0 eV (CH group), 286.5 eV (C-O group), and 287.9 eV (C=O group), and a new peak at 289.0 eV (CO-O group). The low pressure plasma treated PEEK possesses higher concentrations of the C-O as well as C=O group than the original PEEK film as seen in Table 2. The C1s peaks of atmospheric pressure plasma treated PEEK can also be deconvoluted into four components: 285.0 eV (CH group), 286.5 eV (C-O group), and 287.9 eV (C=O group), and 289.0 eV (CO-O group) (as shown in fig. 8,*c*), but with a higher concentrations of all the three functional groups, C-O, C=O and CO-O as is evident from Table 2.



a

b

c

Fig. 8. XPS C 1s spectra: (a) Untreated PEEK; (b) Low pressure plasma treated PEEK; (c) Atmospheric pressure plasma treated PEEK

Table 2. Percentage contribution of each component

	C-H	CO	C=O	COO
Untreated PEEK	75	19.8	5.2	–
Low-pressure plasma treated PEEK	64.2	27.0	6.5	2.3
Atmospheric-pressure plasma treated PEEK	59.6	27.6	7.6	5.2

Plasma treatment in air generates several oxygen and nitrogen functionalities on the surface. The XPS spectra of PEEK exposed to ion beam radiation [9] clearly reveals the generation of new peak at 289.0 eV which corresponds to the formation of CO-O group resulting from plasma oxidation. More highly oxidized carbon increases with an increase in the O/C ratio. Initially the oxygen adds preferentially to specific carbon atoms resulting in formation of C=O bonds. Once the C=O bonds are formed, oxygen gets attached to such oxidized carbon atoms which leads to the formation of O-C=O species [10]. Qureshi et al. [11] have studied the effect of nitrogen plasma on the surface of polycarbonate and have observed that the intensity of C-C / C-H bonds reduced with the increased intensity of C-O/C=O bonds after plasma treatment. The change in surface chemistry of a polymer surface due to plasma treatment has been investigated in detail by several researchers [12, 13] and their observation supports the findings of present investigation. Inagaki et al. [8] studied PEEK surfaces modified by using remote oxygen plasma and observed that degradation products were formed on the PEEK surface by the oxygen plasma treatment. The formation of new groups on the surface of PEEK after plasma treatment is attributed to the depletion of hydrocarbon in the benzene ring and uptake of oxygen by polymer surface leading to the formation of C-O-C (or C-OH), C=O and O-C=O groups while the stability of the carbonylic component and the ether-like bond is due to the high radiation resistance of linkages stabilized by two contiguous benzene rings [14, 15].

EFFECT OF OXYGEN/CARBON RATIO ON SURFACE ENERGY

Surface energy and its polar and dispersion components of PEEK polymer was calculated using contact angle measurements. It is observed from Table 3 that surface modification of polymer by atmospheric pressure plasma; results in significant increase in surface energy when compared to the surface energy of low pressure plasma treated and untreated PEEK. There is a substantial increase in the polar component of surface energy after atmospheric pressure plasma treatment; however, there is no appreciable change in the dispersion component of surface energy. The increase in polar component of surface energy results in an increase in O/C ratio as shown in Table 4. A similar observation has been made by Pandiyaraj et al. [16] and Pelagade et al. [17] with polymers like PET and polycarbonate respectively. The increase in polar component of surface energy is attributed to the incorporation of oxygen functional groups on the polymer surface. The ratio of oxygen to carbon concentration increases as a result of increase of the oxygen component after plasma treatment [18, 19]. The effect of O/C ratio on surface energy of polymer is shown in fig. 9 which clearly reveals that, with the increase in O/C ratio, the polar component of surface energy increases that adds to the total surface energy of the polymer and thus makes the surface hydrophilic.

Table 3. Surface energy values on the surface of PEEK

Name	Treatment time	γ_S^P mJ/m^2	γ_S^D mJ/m^2	γ_S mJ/m^2
Basic PEEK	0 sec	4.31	46.83	51.14
Low pressure plasma treated PEEK	30 sec	24	29	53
	60 sec	30	26.2	56.2
	120 sec	40	25.54	65.54
	240 sec	34	23	57
	480 sec	31	20	51
Atmospheric pressure plasma treated PEEK	30 sec	56	17.44	73.44
	60 sec	52	16	68

Table 4. O/C ratio and surface energies on unmodified, low-pressure plasma treated and atmospheric-pressure plasma-treated PEEK

Poly Ether Ether Ketone (PEEK)	O/C ratio	γ_S^P mJ /m^2	γ_S^D mJ /m^2	γ_S mJ /m^2
Untreated	0.12	4.31	46.83	51.14
Low-pressure plasma treated	0.18	40	25.54	65.54
Atmospheric –pressure plasma treated	0.27	56.79	16.65	73.44

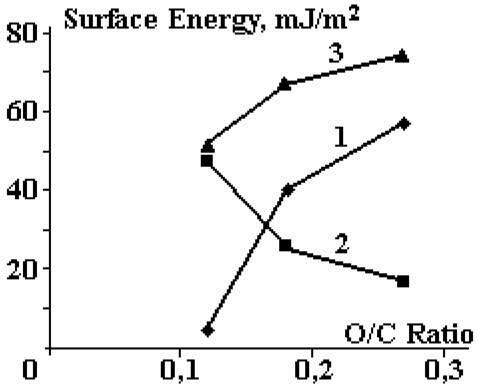


Fig. 9. Effect of O/C ratio on surface energy of PEEK. 1 – polar component; 2 – dispersion component; 3 – total Surface Energy

The presence of polar groups on the polymer surface bridge the forces of physical adsorption and chemical adsorption where covalent bond is the primary force responsible for adhesion. Thus, when the polymers are modified by different treatment methods, the formation of polar groups on the polymeric surface, results in the formation of covalent bond with the adhesive. This covalent bond plays a significant role to produce adhesive bonds which are even stronger than the cohesive strength of polymeric materials as is clear from the following equation

$$W_A \infty \gamma_S. \quad (3)$$

The increase in surface energy of the polymer surface results in better adhesion of the substrate with the adhesive.

ATOMIC FORCE MICROSCOPY (AFM) ANALYSIS

The change in morphology of PEEK surface was investigated by AFM analysis. Fig. 10,*a* shows the surface of the untreated PEEK which is relatively smooth. After the low pressure plasma treatment, the surface of the PEEK showed a rough morphology as shown in fig. 10,*b* and after atmospheric pressure plasma treatment there is further increase in surface roughness as evident from fig. 10,*c*. These changes result in the distortion of few molecular layers (approx.10 nm) at or near the surface of the polymer due to the bombardment of plasma particles leading to the formation of micro-dents, which increases the surface roughness and the effective surface area [10]. This apparent increase in the surface roughness results in improvement of wettability and bonding strength.

Gisbert et al. [20] used low pressure glow discharge plasma with different gases (O_2 and N_2) to increase wettability in different polymer films such as low density polyethylene and polyurethane in order to obtain laminates with polyethylene foams for uses in automotive industry. It was found that changes in surface topography (change of surface roughness) have a positive effect on surface wettability together with surface activation.

The present investigation demonstrates that, when PEEK is modified by atmospheric pressure plasma, a relatively rougher morphology is observed on the surface as compared to the low pressure plasma. Park et al. [21] have studied the effect of atmospheric pressure plasma on polyimide surface and they have observed that the roughness of the film surfaces is largely increased by the plasma effect which is similar to the present investigation. Tang et al. [22] studied the effects of radio frequency (RF), atmospheric pressure plasma (APP), and low pressure plasma (LPP) treatment on the surface morphology of poly (methyl methacrylate) (PMMA) plate. Their observation under atomic force microscopy revealed that atmospheric pressure plasma treatment on PMMA creates more surface roughness on the surface of the polymer. It was also observed that, the atmospheric pressure plasma treatment on PMMA raised the surface temperature up to a certain extent that exceeds the glass transition temperature (T_g) of PMMA, where as in the case of low pressure plasma, the increase in surface temperature is relatively much lower and below the T_g of the polymer [22].

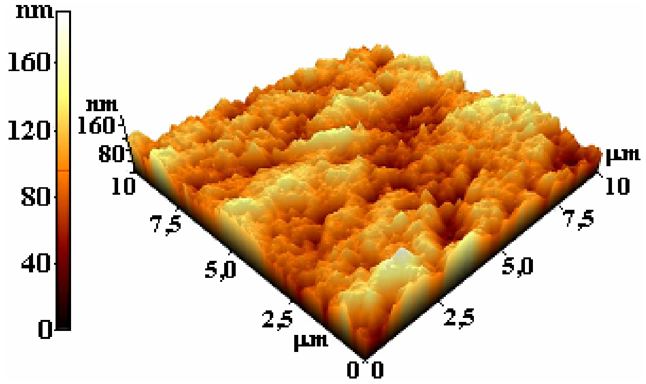


Fig. 10,a. AFM of untreated PEEK

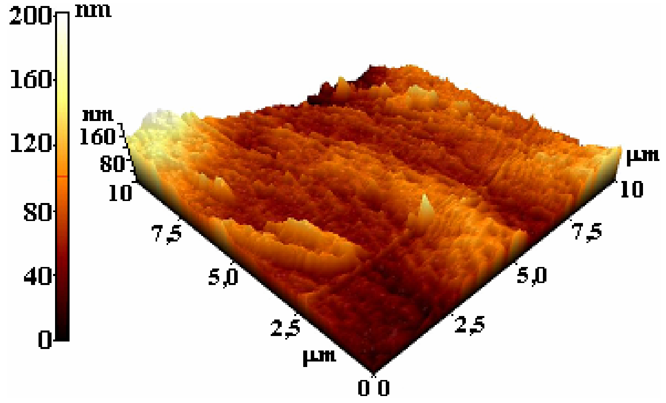


Fig. 10,b. AFM of low pressure plasma treated PEEK

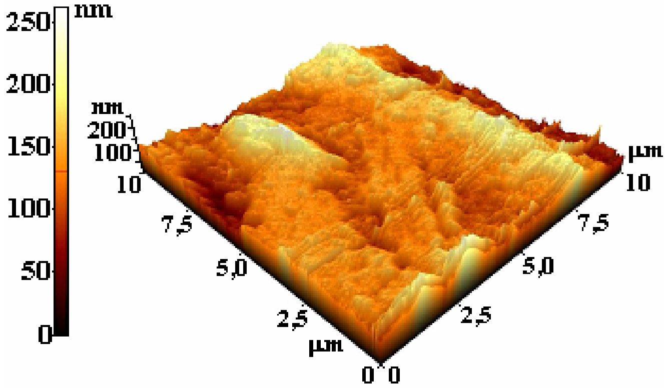


Fig. 10,c. AFM of atmospheric pressure plasma treated PEEK

EFFECT OF SURFACE ENERGY ON THE LAP SHEAR TENSILE PROPERTIES OF ADHESIVE BONDED POLYMER JOINT

Earlier investigation [23] reveals that surface energy of PEEK when exposed to low pressure plasma for 120 sec attains to the maximum up to 65.54 mJ/m^2 and when exposed to atmospheric pressure plasma for 30 sec attains its maximum value up to 73.44 mJ/m^2. Therefore, in this investigation, lap shear tensile strength is correlated to the maximum values of surface energy obtained from low pressure plasma and atmospheric pressure plasmas and shown in fig. 11. It is observed that the joint strength increases from 0.5 MPa to 4.00 MPa when the PEEK surface is exposed to low pressure plasma for 120 sec and shows a substantial increase to 8.00 MPa after exposure to atmospheric pressure plasma for 30 sec resulting in considerable improvement in the adhesion properties of PEEK. Therefore, from this investigation one can clearly conclude that with the increase in surface energy of the polymer surface, the lap shear tensile strength also increases which supports the fundamentals of adhesion.

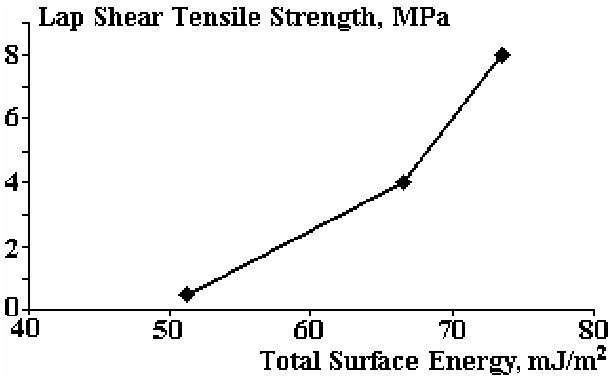
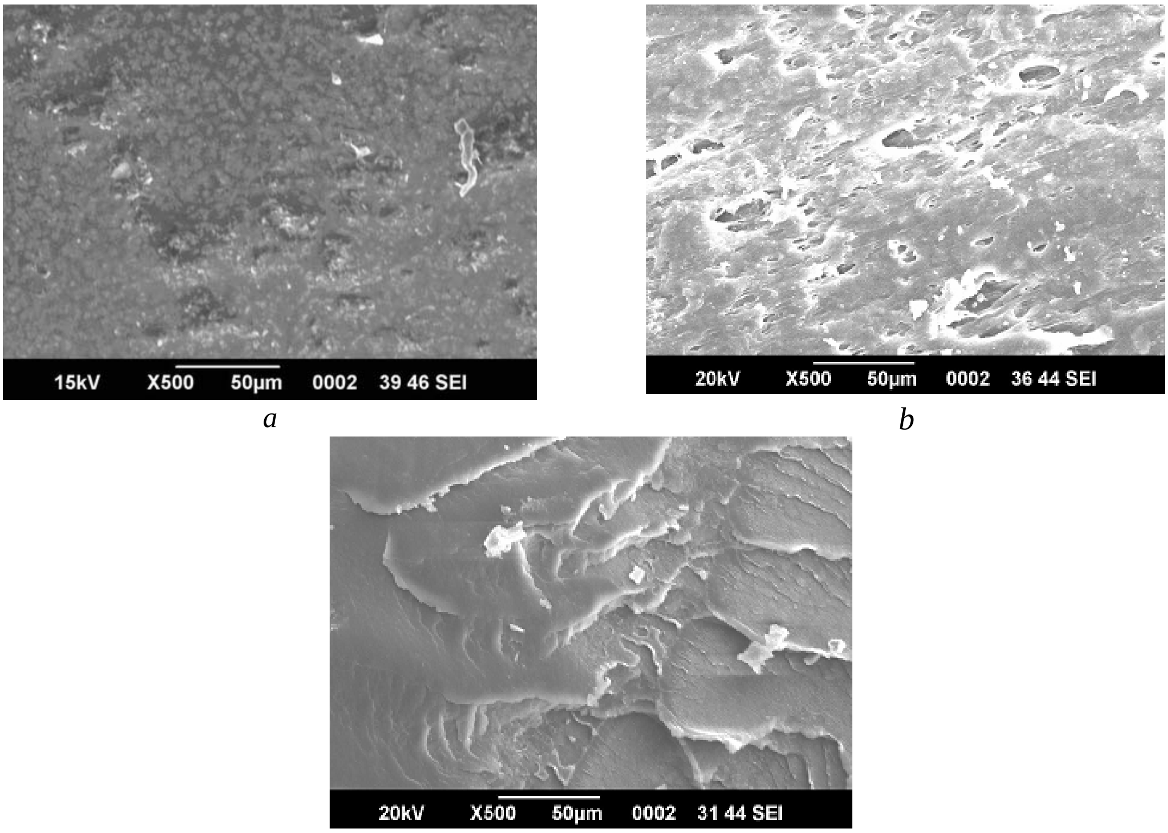


Fig. 11. Effect of Surface Energy on Lap Shear Tensile Strength



a

b

c

Fig. 12. SEM micrograph of (a) untreated PEEK; (b) low pressure plasma treated PEEK; (c) atmospheric pressure plasma treated PEEK

The increase in surface energy of polymer is usually correlated with the adhesive bonded joint strength and it is important to note that in number of cases atmospheric pressure plasma is more capable than low pressure plasma [23]. In this context Hobson et al. [24] have revealed that when PBI surface has been modified under an electron beam, the IR (ATR) spectroscopy shows generation of CO2H 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 and it could be possible that atmospheric pressure plasma also plays similar role. Bhowmik et al have revealed that higher incorporation of oxygen functionalities have been obtained, when polypropylene surface is exposed to DC glow discharge under stainless steel electrode followed by nickel and copper electrodes as evident from XPS studies and these oxygen functionalities have been transformed into various polar functional groups and which has been attributed to increase in surface energy of the polymer leading to increase in adhesion [25]. Tyczkowski et al. [26] have investigated low-pressure plasma generated in a typical parallel plate reactor and atmospheric pressure plasma produced by a plasma needle to modify the surface of poly(styrene–butadiene–styrene) (SBS) elastomers. It has been found that such plasma treatments drastically improve the strength of adhesive-bonded joints between the SBS surfaces and polyurethane adhesives; however, the plasma needle operation under atmospheric pressure plasma has turned out to be more effective.

FRACTOGRAPHIC ANALYSIS

SEM images of the fractured surfaces of untreated, low pressure plasma treated and atmospheric pressure plasma treated PEEK after the lap shear test are shown in figs. 12,*a,b,c* respectively. Images for all the samples have been obtained at a resolution of 500 μm. The joint with the unmodified PEEK fails essentially from the adhesive to PEEK interface as evident from fig. 12,*a*. It indicates poor interfacial interaction occurred between the two polymer surfaces with the adhesive during the bonding process. 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 as shown in fig. 12,*b* resulting in increase in adhesion properties of PEEK . 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 as seen in fig. 12,*c*. The tensile failure in case of atmospheric pressure plasma treated PEEK clearly justifies why there is an increase of the joint strength up to 15 times with respect to unmodified PEEK. Also, 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.

CONCLUSIONS

The present investigation has led to the following conclusions:

Atmospheric plasma treatment has a remarkable effect on the surface energies of PEEK as compared to low pressure plasma treatment resulting in hydrophilic properties of the polymer.

XPS analysis show a remarkable increase in the percentage contribution of oxygen as well as O1s peak after the atmospheric pressure plasma treatment resulting in significant increase in surface energy.

AFM analysis shows that the surface roughening increases after atmospheric pressure plasma treatment which contributes to the increase in adhesive strength.

The adhesive joint strength of the PEEK increases about 15 times when the surface is modified by atmospheric pressure plasma.

The locus of failure shifts from the adhesive-substrate interface to within adhesive or substrate material after atmospheric pressure plasma treatment.

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Реферат

Рассматривается влияние на свойства поверхности и адгезионные характеристики эффективного полимера полиэфир-эфир кетона (PEEK) – при обработке плазмой низкого или атмосферного давления с использованием инфракрасной спектроскопии с фурье-преобразованием; рентгеновской фотоэлектронной спектроскопии; сканирующей атомно-силовой микроскопии. В результате экспериментов выяснилось, что при обработке плазмой атмосферного давления поверхности полимера (PEEK) возрастает полярная компонента поверхностной энергии, что приводит к улучшению сцепляемости системы склеивания PEEK/ эпоксидная смола. Кроме того, обработанная поверхность становится более шероховатой, что подтверждается сканирующей атомно-силовой микроскопией. Полученные результаты можно объяснить тем, что обработка плазмой атмосферного давления поверхности PEEK приводит к различным функциональным возможностям кислорода на гидрофобной поверхности, что играет важную роль в повышении полярности поверхности, ее смачиваемости и сцепляемости системы склеивания PEEK/ эпоксидная смола.