

Energy dispersive spectroscopy study of surface modified PEEK

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Received: 6 Dec 2010, Revised: 12 Jan 2011 and Accepted: 16 Jan 2011

ABSTRACT

PEEK (polyether etherketone) polymer, is increasingly used in many industrial applications as a replacement for metal components. In this investigation, attention is given to understand the chemical changes that have been introduced on the surface of PEEK, when surface of the PEEK is modified by low pressure plasma under RF (radio frequency) glow discharge. The contact angle measurements show that the contact angle decreases after the plasma treatment which results in the increase in surface energy. This paper also discusses the common surface characterisation technique like Energy Dispersive Spectroscopy (EDS) analysis to determine the chemical changes that have been introduced on the surface. Copyright © 2011 VBRI press.

Keywords: PEEK; surface modification; RF glow discharge; EDS analysis.



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Introduction

The amazing properties of polymers and polymeric composite materials are frequently replacing metallic materials in many applications and are being extensively used in a variety of engineering industries not just for their ease in manufacturing and low unit cost, but also for their potentially excellent tribological performance in engineered forms [1].

Polymeric composite materials with their excellent mechanical, thermal, cryogenic and dynamic properties have found their numerous applications in the automotive, aircraft, and aerospace industries. Thermoplastic polymers can be remelted and remoulded; and hence can be reshaped as compared to thermosets. Therefore, they can be recycled which makes their use more preferable. High performance engineering thermoplastics, used in more demanding applications in Automotive industry include polyphenylene sulfide (PPS), polyether etherketone (PEEK), polyetherimide (PEI) and several formulations of polyamide, commonly called Nylon.

Advanced polymeric composites which are high performance materials consisting of a polymer matrix resin reinforced with fibers such as carbon, graphite, aramid, boron or S-glass have their market in aerospace. Commercial aircrafts such as Boeing 757 and 767 contain

less than 5% advanced composites by wt. while military aircraft like GA-18A contain 10-20%.

PEEK polymer (service temperature -250 to 300 °C) is lightweight and offers excellent mechanical performance at high temperatures. It can successfully replace metals and other polymers due to its unique combination of outstanding wear performance, processing flexibility, and excellent chemical resistance, including all automotive and aerospace industry. The different properties of PEEK are discussed in a tabular form in **Table 1**, the data for which has been compiled from the suppliers Parker-TexLoc and Victrex data sheet.

In spite of the excellent properties, PEEK, like any other polymer, in general exhibit insufficient adhesive bond strength due to its reasonably low surface energy. Recent advances in the use of polymers and the resulting requirement for hydrophilic surfaces for adequate adhesion has fuelled the development of the plasma surface modification to different industries [2]. Plasma contains active species, such as electrons, ions, radicals, photons, etc., which are able to initiate chemical and physical modification at the polymer surface [3-5]. It is observed that polar component of surface energy leading to total surface energy of the polymer increases significantly due to generation of new functional groups under the carbon cleaning effect and surface oxidation effect by reactive species in the plasma. In this regard, the surface of PEEK

sheet is modified by low pressure plasma for 30 and 120 sec at 100 W of power. After the surface modification, it is necessary to determine the chemical changes introduced on the polymer surface by Plasma. For this, the polymeric specimen is characterised by Contact angle measurement and Surface energy estimation. The polymeric specimen with the highest surface energy is then subjected to Energy Dispersive Spectroscopy (EDS) study using Scanning Electron microscope to determine the chemical changes introduced by the plasma treatment.

Experimental

Low pressure plasma treatment under RF (radio frequency) glow discharge

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 as shown in **Fig. 1**. 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}

Table 1. Table showing different properties of PEEK.

General properties									
Density	Water Absorption	Refractive Index	Limiting Oxygen Index %	Cost Per Unit Mass	Cost Per Unit Volume	Chemical/Solvent Resistance			
1320 kg/m ³ (82.5 lb/ft ³)	24h, %: 0.5	2.15	24	60 US\$/kg (27.2 US\$/lb)	79200 US\$/m ³ (2800000 US\$/ft ³)	Excellent			
Mechanical properties									
Young's Modulus	Tensile Yield Strength	Ultimate Tensile Strength	Compressive Strength	Shear Modulus	Ductility	Flexural Strength	Poisson's Ratio	Hardness	Specific Gravity
3.6 GPa (0.522 × 10 ⁶ psi)	89.6 MPa (13 × 10 ³ psi)	100 MPa (14.5 × 10 ³ psi)	118 MPa (17.1 × 10 ³ psi)	1.4 GPa (0.203 × 10 ⁶ psi)	50% elongation at break	98 MPa (14.2 × 10 ³ psi)	0.39	99 Rockwell M	1.30~1.32
Thermal properties									
Maximum Working Temperature	Thermal Conductivity	Thermal Expansion	Specific Heat Capacity	Melting Point					
260 °C (500 °F)	0.245 W/m-K (BTU-in/hr-ft ² -°F)	1.7 × 10 ⁻⁶ /°C (2.6E-11-10 ⁻⁶ /°F)	1470 J/kg-K (0.351 BTU/lb-°F)	340 °C (644 °F)					
Electrical properties									
Electrical Conductivity	Electrical Resistivity	Dielectric Strength	Dielectric Constant	Volume Resistivity	Surface Resistivity				
3.45 E-21% IACS	5.0E+23 nΩ-m	19.7 MV/m (0.0005 MV/mil)	3.20~3.30	4.9 × 10 ¹⁶ ohm-cm	2.0 × 10 ¹⁶ ohm/sq				
Calculated values									
Strength-to-Weight Ratio	Stiffness-to-Weight Ratio	Resilience		Rupture Work					
67.9 kN-m/kg	2.73 MN-m/kg	12.4 kJ/m ³		48.3 MJ/m ³					

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 and 120 sec of exposure with 100 W of power. 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 four hours to dry. The specimens were then placed under the low pressure plasma chambers and treated with plasma using air.

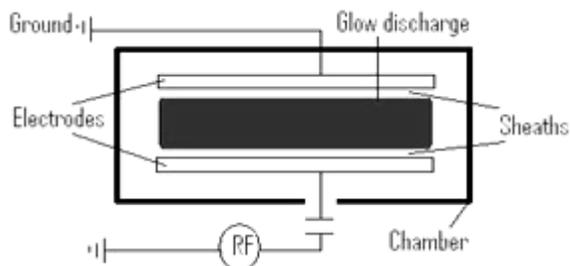


Fig. 1. Schematic diagram of RF glow discharge.

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 and low pressure plasma treated polymers using deionized water and formamide as test liquids. The polar and dispersion components of surface tensions of de-ionised water and formamide are listed in **Table 2**.

Table 2. Polar γ_{LV}^P , dispersion γ_{LV}^D and total surface tension γ_{LV} 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

The surface energy and the polar and dispersion components of the polymer were calculated using the following Equation.

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

Firstly, the contact angle of de-ionised water θ was measured on the polymer surface. Therefore in this equation θ is the measured contact angle of de-ionised 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 surface. Secondly, the contact angle of formamide θ was

measured on the polymer 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 surface. Thereby solving these two equations, the unknowns γ_S^P and γ_S^D of the polymer were calculated. Finally, the total surface energy γ_S was estimated by the following equation (2):

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

Energy dispersive spectroscopy (EDS) study using scanning electron microscope

The combination of the SEM and X-ray analysis using either energy-dispersive X-ray spectroscopy (EDS) provides a powerful tool for local microchemical analysis [6]. The energy dispersive X-ray spectroscopy (EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. In EDS analysis, the first step involved the coating of the base material i.e. untreated PEEK and low pressure plasma treated PEEK with platinum by applying a current of 40 mamp for 60 sec. This gives the sheets with platinum coating of 30 nm thickness. The samples were then introduced separately in to the SEM (Scanning Electron Microscope) chamber. EDS analysis was carried out at an accelerating voltage of 5 keV kept at a working distance of 20 mm and a high vacuum mode was used.

Results

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

Surface energy and its polar and dispersion components of untreated PEEK and low pressure plasma treated PEEK for 30, 60, 120, 240 and 480 sec of exposure were calculated using contact angle measurements. **Fig. 2(a)** and **(b)** show that the contact angle on the surface of Untreated PEEK is 70.6° with water and 51.3° with Formamide. **Fig. 3(a)** and **(b)** show that the contact angle on the surface of Low pressure plasma treated PEEK for 120 sec, decreases to 40° with water and 34.2° with formamide. In the case of low pressure plasma treated PEEK, it is observed from **Table 3** that polar component of surface energy leading to total surface energy of PEEK increases up to 120 seconds of exposure, thereafter it decreases with increasing exposure time due to the sputtering of Cu on the surface of PEEK [7].

EDS analysis

Table 4 and **5** show that the atomic % as well as weight % of the element ‘‘C’’ decreases with plasma treatment where as the atomic % as well as weight % of the element ‘‘O’’ increases with the plasma treatment. This may be due to the increase in the oxygen containing functional groups due to the interaction of the plasma with the surface. **Fig. 4** and **Fig. 5** are the SEM images of untreated and low pressure

plasma treated PEEK along with their corresponding graphs. While, there is not much change noticed in the surface morphology of the PEEK surfaces as can be seen in **Fig. 4** and **Fig. 5**, there is certainly a change in the peaks of carbon and oxygen in the corresponding graphs of the two figures.

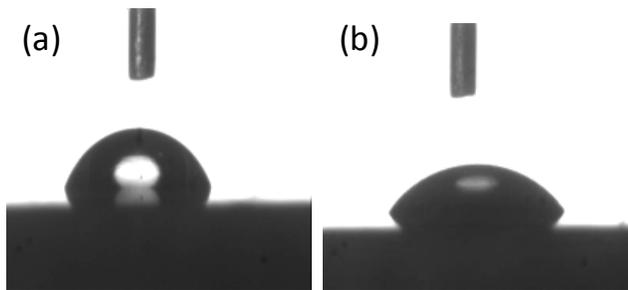


Fig. 2. Contact angle on untreated PEEK (a) using water: 70.6° and (b) using Formamide: 51.3°.

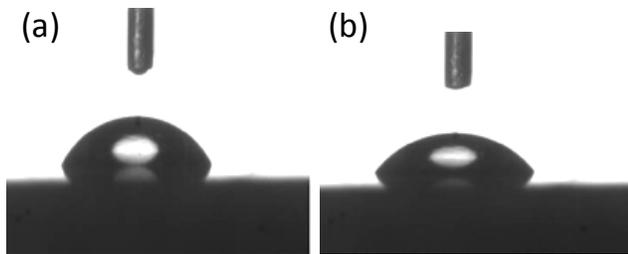


Fig. 3. Contact angle on low pressure plasma treated PEEK (a) using water: 40° and (b) formamide: 34.2°.

Table 3. Surface energy measurements on PEEK sheet.

Item	Treatment time (Sec)	γ_S^P mJ/m ²	γ_S^D mJ/m ²	γ_S mJ/m ²
Basic PEEK	0	4.3	46.83	51.14
Low pressure plasma treated PEEK	30 Sec	24	29	53
	60 Sec	30	26.2	56.2
	120 Sec	40	25.5	66.5
	240 Sec	35	24	59
	480 Sec	32	23	55

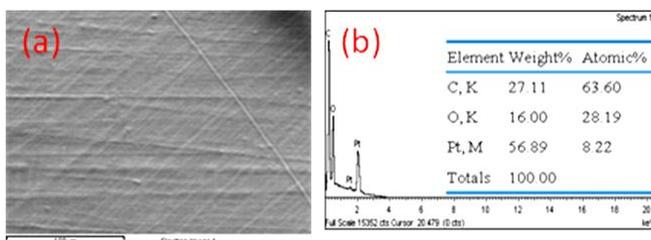


Fig. 4. (a) SEM image and (b) weight% and atomic% of elements of untreated PEEK.

Discussion

Polymer composites are being widely used in automotive and aerospace sectors. They appear to be materials of choice 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 [10]. 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]. 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].

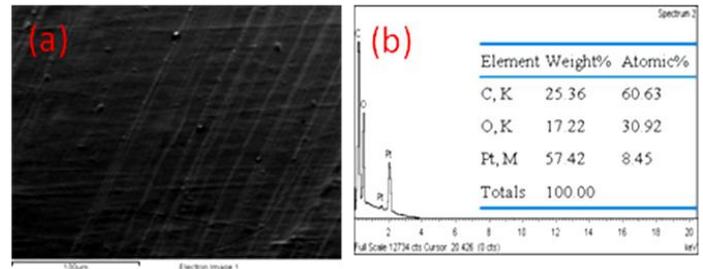


Fig. 5. (a) SEM image and (b) weight% and atomic% of elements of Low pressure plasma treated PEEK for 120 sec.

Therefore, in order to improve the surface energy of polymers, surface of PEEK has to be modified. There are different surface treatment methods which had been used to modify the surface of PEEK. Literature shows that chemical treatment [15], mechanical surface roughening [16, 17], corona treatment [18], cold gas plasma treatment [17], laser treatment [19] and UV treatment [20] methods had been used to modify the surface of PEEK. Although these methods had resulted in the improvement of adhesive bonding of PEEK, but it's not clear which modification technique would be superior to others. But, dry plasma treatment methods using plasma appears to be promising field. Glow discharge under low pressure plasma is a popular technique, which results in better uniformity in surface modification of the polymers [21-24]. Moreover, it is a dry treatment method, which is better suited for industrial applications. It is now well established that the glow discharge treatment creates physical and chemical changes such as crosslinking, degradation, formation of free radicals and oxygen functionalisation [25-29]. The temperature of gases in a glow discharge generally remains low and the plasma plays a predominant role in the surface modification of polymers. The advantage of this technique is that plasma treatment is confined to top several hundred angstrom and bulk properties of the material remain the same [9]. Therefore, the modification depth of the plasma treatment is only a few nanometers [11, 12]. The improvement in adhesion properties is attributed to the formation of polar groups on the polymer surfaces [8]. Low pressure air discharge methods have been used [30, 31] to modify the surface of polycarbonate and PET respectively. Therefore, the above study has been carried out keeping all these factors in to consideration.

After the modification, the surface characterisation is done as it helps to know the changes (active species) that have been brought about on the surface by the Plasma. EDS analysis of the modified surface can be a suitable method of identifying the functional groups that have been introduced on the surface. The present study gives an insight in to the

elements present in the sample along with their atomic and weight % in the sample. The change in surface chemistry of a polymer surface due to plasma treatment has been investigated in detail by several researchers [13, 14]. Plasma treatment in air can generate several oxygen and nitrogen functionalities on the surface. It causes the uptake of oxygen by polymer surfaces leading to the formation of C-O-C (or C-OH), C=O and O-C=O groups. This must be reason for the increase in atomic% of oxygen after treatment of the polymer surface with plasma.

Conclusion

The above study shows that with the plasma treatment there is definitely an increase in the percentage of oxygen which could have been due to increase in oxygen functional groups. EDS study, as a surface characterisation technique does give an idea about the chemical composition of the sample but doesn't give any information on how the elements are connected. Another option for functional group identification on the modified surface is XPS (X-ray Photoelectron Spectroscopy) owing to its low analysing depth with a sampling volume that extends from the surface to a depth of approx. 50-70 Å and thus carrying out XPS analysis of the samples is next step of our study.

Acknowledgement

The corresponding author acknowledges the research grant awarded to her by Department of Science and Technology (DST), Government of India under the WOS-A scheme (CS-43/2009). The author is also thankful to BIT Mesra, Ranchi and SMIT, Sikkim for providing lab facilities for carrying out the experiments.

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