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SURFACE MODIFICATION OF POLYETHER ETHER KETONE (PEEK) FILAMENT YARN

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ABSTRACT

Foisal ABM (2014) Surface modification of polyether ether ketone (peek) filament yarn. *Ins. Engg. Tech.* 4(2), 1-7.

The aim of this work is to develop wettability and adhesion between the surface of inert Polyether ether ketone (PEEK) filaments and elementary silver (Ag) particles by applying the atmospheric pressure corona plasma. It has been tried also to modify surface of PEEK by Formic acid but the result is insignificant which has been stated on this work. The wettability of plasma treated PEEK is investigated by means of contact angle and surface free energy measurement. The tensile test of the plasma modified PEEK filament is carried out to determine the influence of the modification on its mechanical properties. Surface roughness of PEEK is observed using scanning electron microscopy (SEM).

Key words: *PEEK, plasma, surface topography*

INTRODUCTION

Aryl Polyether ether ketone (PEEK) is an organic semi crystalline (~35%) thermoplastic polymer (Patel *et al*. 2011). Aromatic poly ethers are relatively new groups of polymers in the field of engineering plastics. The initial chemistry for PEEK synthesis was developed by ICI in the late 1970s. PEEK is a tough high molecular weight polymer with excellent mechanical, thermal and chemical properties. PEEK polymer has a glass transition temperature (Tg) at around 143°C, a continuous p temperature of 260°C, melts at around (Tm) 343°C and onset of decomposition temperature between 575 and 580°C and thus, is one of the most thermally stable thermoplastic polymers. PEEK's excellent thermal properties are attributed to the stability of the aromatic backbone consists of ether and carbonyl groups in the monomer unit, shown in Fig. 1 (Patel *et al*. 2011, Pawson *et al*. 1992).

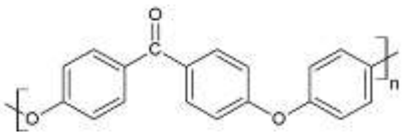

Fig. 1. The structure of PEEK

High performance polymers like PEEK have a low surface free energy and very often do not possess the desired surface properties in terms of strong adhesive bonding. They are hydrophobic in nature. PEEK possesses two units, a phenyl ether group and a benzophenone group, with an oxygen atom and a carbonyl group (C=O) existing between the two phenyl groups (Fig. 1). The C-O bond in the phenyl ether group and the C-C bond in the benzophenone group are relatively weak because the electronegativity of oxygen elements is strong and the phenyl and carbonyl groups (C=O) have resonant structure. The bonding energy of the C-C bond in the phenyl groups is 120 kcal/mol. The bonding energies of C-O bond in the PEEK main chain (the phenyl ether group) and the C-C bond in the benzophenone group are 84 kcal/mol and 102 kcal/mol respectively. These bonding energies indicate that the C-O bond in the phenyl ether group and the C-C bond in the benzophenone group are weak (Narushima *et al*. 2002).

However, it is not easy to modify the surface of aromatic polymers containing phenyl groups. This is because the radicals in the plasma are poor at removing hydrogen atoms from phenyl groups due to the chemically stable structure of the phenyl group. One of the methods that may be used to form hydrophilic functional groups on the aromatic polymers is to increase the power applied via the plasma process (Narushima *et al*. 2002). The surface energy of untreated PEEK lies between 34-38 mN/m, with surface treatments (plasma, corona etc.) this can be increased to ~60 mN/m. A surface energy of 55 mN/m should be high enough for all finishing processes encountered. The critical effect of most surface treatments is to increase the polar portion of the surface free energy, to provide active species that can act as sites for the bonding to take place between the PEEK filaments and liquids. There are various methods that may be employed for the modification of PEEK polymeric materials such as atmospheric pressure plasmatreatment, corona discharge, flame, mechanical surface roughening/etching, chemical etching, primers, etc. (Golzer 2004, Narushima *et al*. 2002) and (Jha *et al.* 2010) have modified PEEK polymer films with the help of plasma method. In this work PEEK filaments are treated by formic acid and atmospheric pressure corona plasma to modify their surface properties, in order to increase adhesion between the surface of filaments and elementary silver (Ag).

Plasma containing electrons, ions, radicals, and neutral molecules strongly interacts with polymer surfaces, and as a result, physical and chemical modifications occur in the surfaces. Like gas, plasma does not have a definite shape or a definite volume unless enclosed in a container; unlike gas, under the influence of a magnetic field, it may form structures such as filaments, beams, and double layer. The main purpose of plasma treatment is to modify the surfaces of materials. Properties enhanced like wettability, adhesion, bio-compatibility, protection, and anti wear, sterilization, and chemical affinity or inertness. Most of the industrially used plasma technologies for surface processing are non thermal reactive plasmas. Plasma processing is a technology used in a large number of industries, such as semiconductor device fabrication for computers, automotive, paper, plastics, ceramics, textiles, food packaging, biomedical, polymers, and solar energy (Biswas *et al.* 2011; Rausher *et al*. 2010).

A corona is a process by which a current flows from an electrode with a high potential into a neutral fluid, usually air, by ionizing that fluid so as to create a region of plasma around the electrode. Corona plasma treatment is the longest established and most widely used plasma treatment (Labay *et al.* 2010). Fig. 2 shows the schematic diagram of corona plasma process.

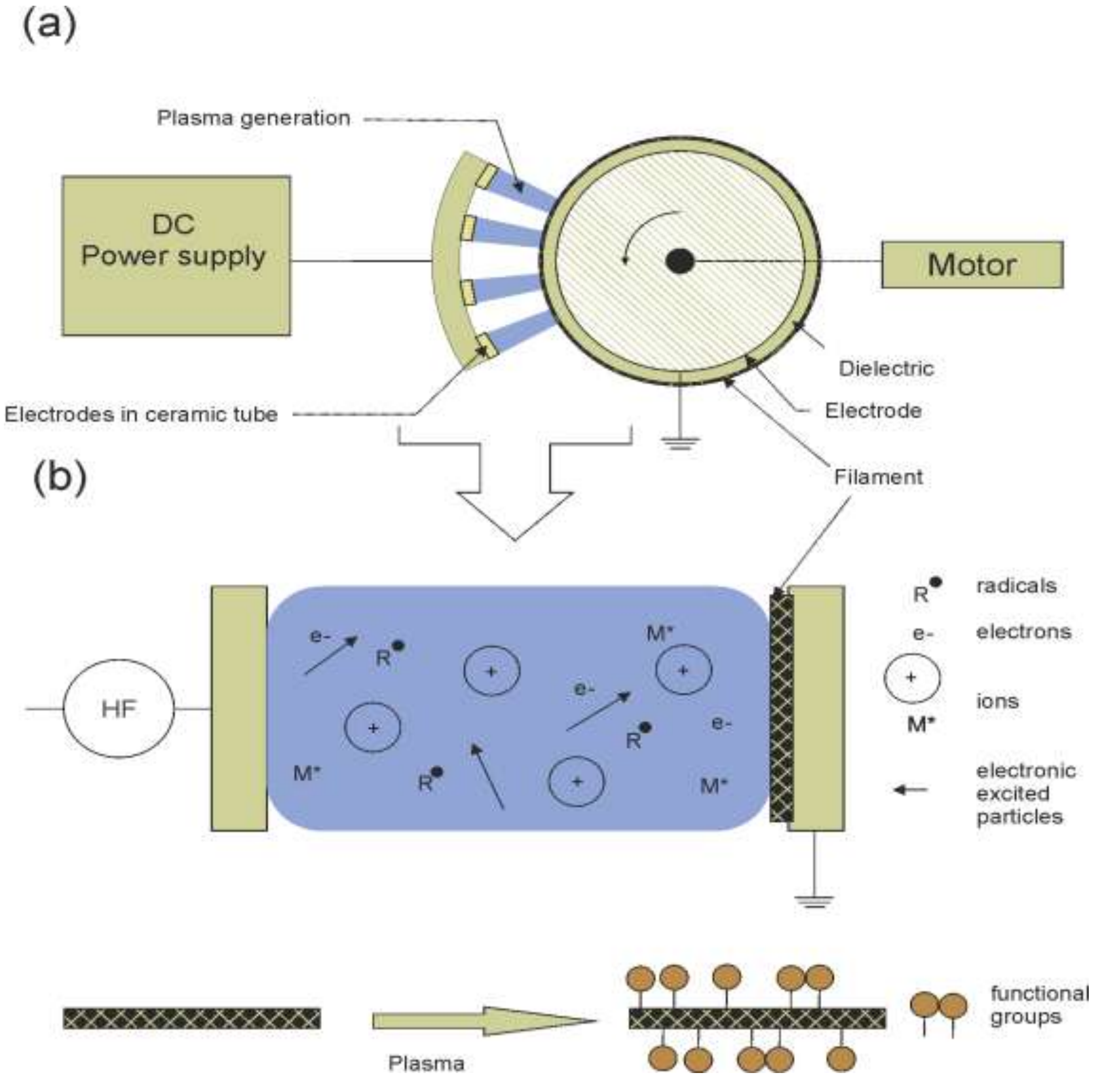

Fig. 2. a) Schematic diagram of corona plasma treatment on PEEK filaments and b) Different reactive species present in the plasma generation zone

Plasma contains activated species such as electrons, ions and radicals. Ions, which have high kinetic energies given by the electrical field in the plasma, degrade the polymer chains of the PEEK surface by ionic bombardment. Very reactive radicals are formed on the polymer surface to modify the surface with functional groups. At the same time as the formation of the functional groups and degradation reactions of polymer chains occur on the surface when irradiated with plasma, because there are always ions present with the radicals in plasma (Narushima *et al*. 2002).

The surface treatment on PEEK improves the surface energy and 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 (Labay *et al.* 2010). The optimum adhesion is obtained when the surface energy of the PEEK is greater than the surface tension of the liquid (water) to enable good wetting onto the PEEK filaments (Golzer 2004) shows the schematic diagram of possible degradation reaction of PEEK filaments on the surface during plasma irradiation.

However, PEEK filaments also undergo the scission of ether groups to form two radicals in intermediate products (Fig. 4). Each of these radicals will subsequently convert into oxygen functional groups due to the oxidation and will remain in PEEK filaments surface because of their high stability due to delocalization. Aromatic groups in the polymer chains play an important role in the modification by plasma. The delocalization and stabilization of radicals by aromatic groups may contribute to the formation of oxygen contained functional groups in PEEK polymer chain (Inagaki *et al.* 2003). The PEEK filaments surface is expected to become more hydrophilic (low water contact angle) after modification.

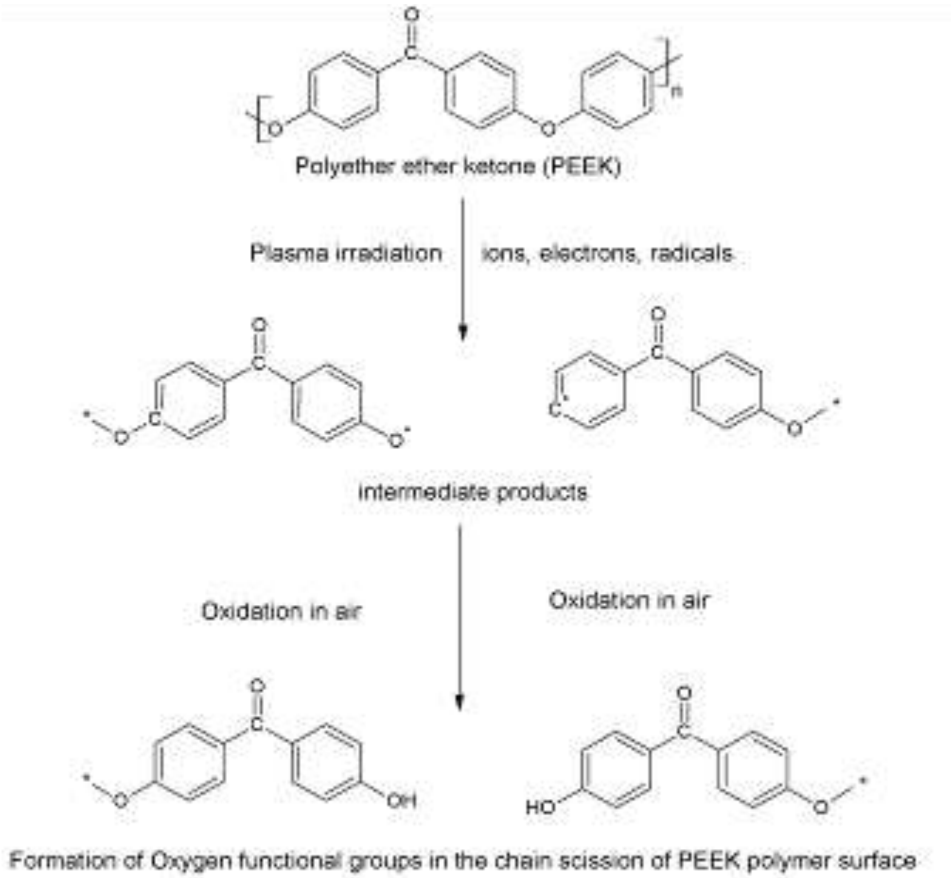

Fig. 3. Possible degradation reactions occurring on PEEK filaments surfaces during plasma irradiation

MATERIALS AND METHODS

Two types of PEEK filament yarns have been used in this work, Multifilaments (30 Filaments, 46 Tex) and monofilament (diameter 0.50 mm, 265 Tex) yarn collected from Zyex Ltd. (A part of the multinational ICI),

Stone house, United Kingdom.

Formic Acid treatment

The original PEEK filament surface is modified with formic acid (5%) solution at room temperature about 20 minutes and then washed and dried at room temperature.

Plasma treatment of PEEK filaments

The plasma treatments are carried out using atmospheric pressure plasma (APP) system “Corona pretreatment system-AS Coating star (ASCS)”, Ahlbrandt, Germany. The working principle of this plasma system is based on the dielectric barrier discharge (DBD) system.

Contact angle and surface energy measurement

The contact angle and surface energy of single PEEK filament is measured by the instrument Tensiometer (K100), Kruess, Germany. Ten individual measurements are taken at randomly chosen filaments to calculate the mean value.

Investigation of stress-strain behavior of PEEK

'TextechnoFafegrph ME' material testing machine is used to determine the stress-strain behavior of original PEEK and plasma treated PEEK. The breaking force (forces to break the filaments) versus elongation is recorded during testing.

Scanning Electron Microscopy (SEM)

To assess the changes in surface topography of surface modified PEEK filaments, the scanning electron microscopy (SEM) is done.

RESULTS AND DISCUSSION

Results of contact angle

The Fig. 4 represents the graphical comparison among different types of modification of PEEK filaments. It reveals that the contact angle is highest on untreated PEEK filaments and with water and diiodo methane, which is 83.4° and 41.1° respectively. Due to acetone treatment the contact angle of water and diiodo methane decreases to 64.2° and 21.0° respectively. The change in contact angle by formic acid treatment is insignificant on the original multifilament PEEK. Due to the surface modification of PEEK filaments by atmospheric pressure plasma the contact angle in both water and diiodo methane solution decreases significantly. The contact angle of untreated PEEK filaments with water has decreased due to the plasma modification from 83.4° to 49.9°, 47.9°, 51.7° at 2kW, 3kW and 4kW plasma treatment for 2 minutes respectively. However, the difference in wetting properties for different discharge power is relatively insignificant. Though the contact angle after acetone wash reduces by about 20°, however, due to plasma modification on the desized sample, the change in contact angle is less compared to that of plasma modified sample on original multifilament PEEK. In case of plasma treated monofilament the contact angle with water and diiodo methane is 60.5° and 50.2° respectively. As plasma treated surface becomes more oxidized, or has more ionizable groups introduced to it, hydrogen bonding with water becomes easier and the droplet spreads along the hydrophilic surface, resulting in a lower contact angle (Wang *et al.* 2010). Lower contact angle of polar liquids means a higher amount of hydrophilic groups formed on the surface of PEEK and increased wetting properties.

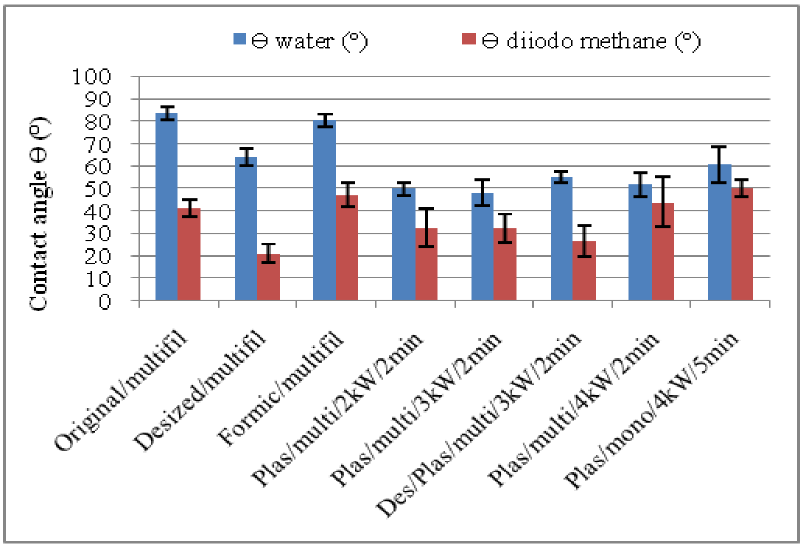

Fig. 4. Graphical representation of contact angle measurement

Results of surface energy

Fig. 5 shows the total surface free energy including polar and dispersive parts of differently surface modified filaments. Formic acid treatment does not increase polar parts significantly. It can be seen that the polar parts and surface energies increase simultaneously by plasma treatment on undesized PEEK multifilaments at 2kW, 3kW and 4kW for 2 minutes. The polar parts increased to 16.8, 17.7, and 18.2 mN/m respectively. 3kW plasma for 2 minutes has also been applied on desized PEEK multifilaments but the polar parts are less increased than that in undesized filaments and the value is 13.1 mN/m. In terms of plasma treated monofilament the polar part is 14.2 mN/m. The higher surface energy results in stronger adhesion between two surfaces. Generally, plasma treatments introduce unpaired electrons and create new polar groups (especially when using oxygen containing atmospheres) on the surface, which leads to an increase in the surface energy and a decrease in water contact angle. From this experiment it can be concluded that the PEEK filaments with plasma treatment at different power can increase the polar and dispersive parts as well as the free surface energy on the surface of PEEK filaments.

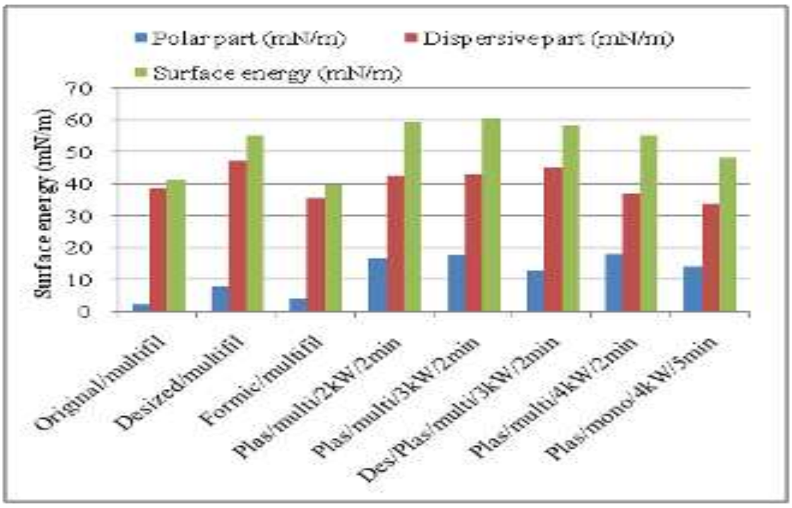

Fig. 5. Graphical representation of surface energy measurement

Influence of surface modification on tensile properties of multifilament

Fig. 6 shows the comparison of breaking force and elongation of original PEEK with formic acid and different kW plasma treatment on the multifilament. It shows that the changes of breaking force and elongation due to different modifications are not significantly different. Plasma treatment at different kW for 2 minutes on both undesized and desized PEEK filaments has almost no effect on the breaking force and elongation.

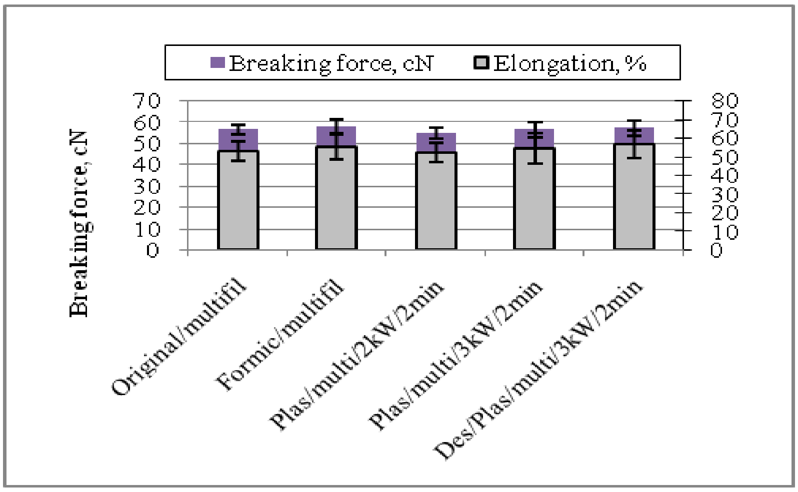

Fig. 6. Graphical representation of breaking force and elongation of modified multifilament PEEK

Surface topography

The change of surface topography due to the plasma treatment on multifilament and monofilament PEEK investigated by SEM images is discussed as follows:

Images of PEEK multifilaments

The surface topography of original multifilament PEEK (as received), 1.2 kW, and 3 kW plasma treated for 2 minutes on desized PEEK multifilaments which are studied under SEM at different magnifications are shown in Fig. 7 with different magnifications. From Figure 7a, it can be seen that the original PEEK filament (as received) has a homogenous surface with some particles like substances adhering over the filament surface (indicated by A), which are intrinsically produced at the time of melt spinning. However, no obvious grooves and ruts can be observed on the unmodified PEEK.

Fig. 7 (b, c) show the desized PEEK filament surface modified by plasma treatment with 1.2 kW and 3 kW for 2 minutes respectively. From Fig. 7 (b, c) it can be seen that, most of the adhering particles are removed after plasma modification. They present uneven and rough surfaces (indicated by B), that are clearly different from unmodified one. Surface roughness is significantly enhanced at the plasma modification (Fig. 7 b, c).

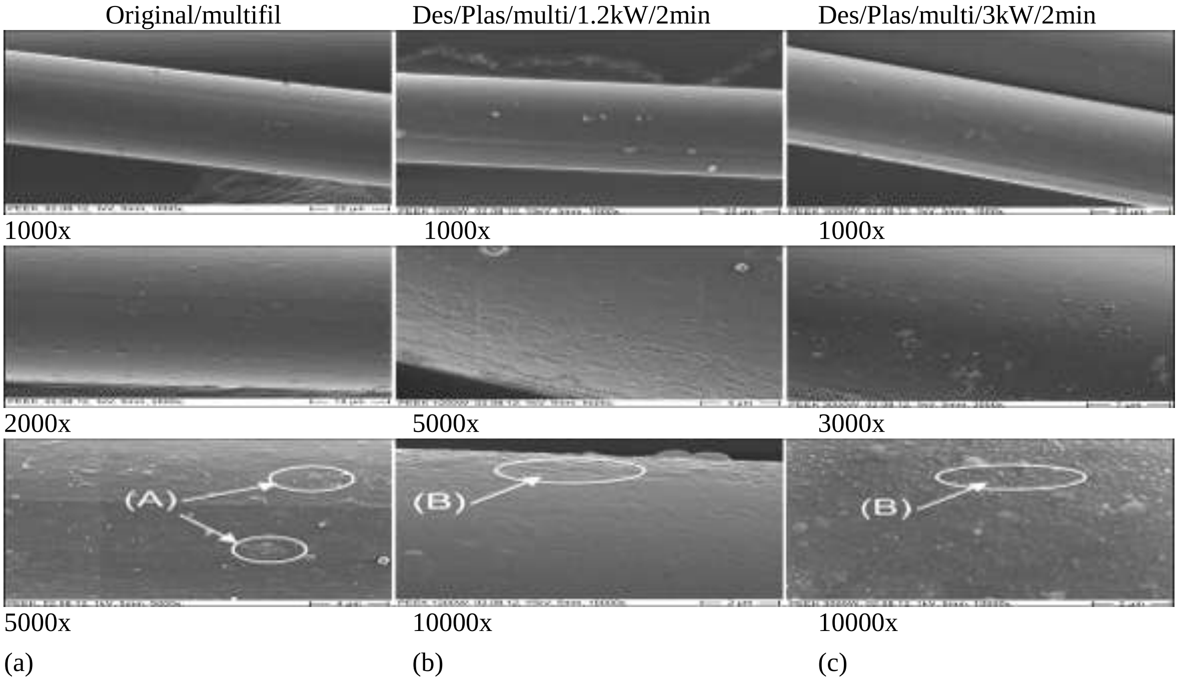

Fig. 7. SEM images of original and plasma treated on desized PEEK multifilaments

Images of PEEK monofilaments

Fig. 8 shows the SEM images of original and plasma treated monofilament PEEK at different kW for 5 minutes.

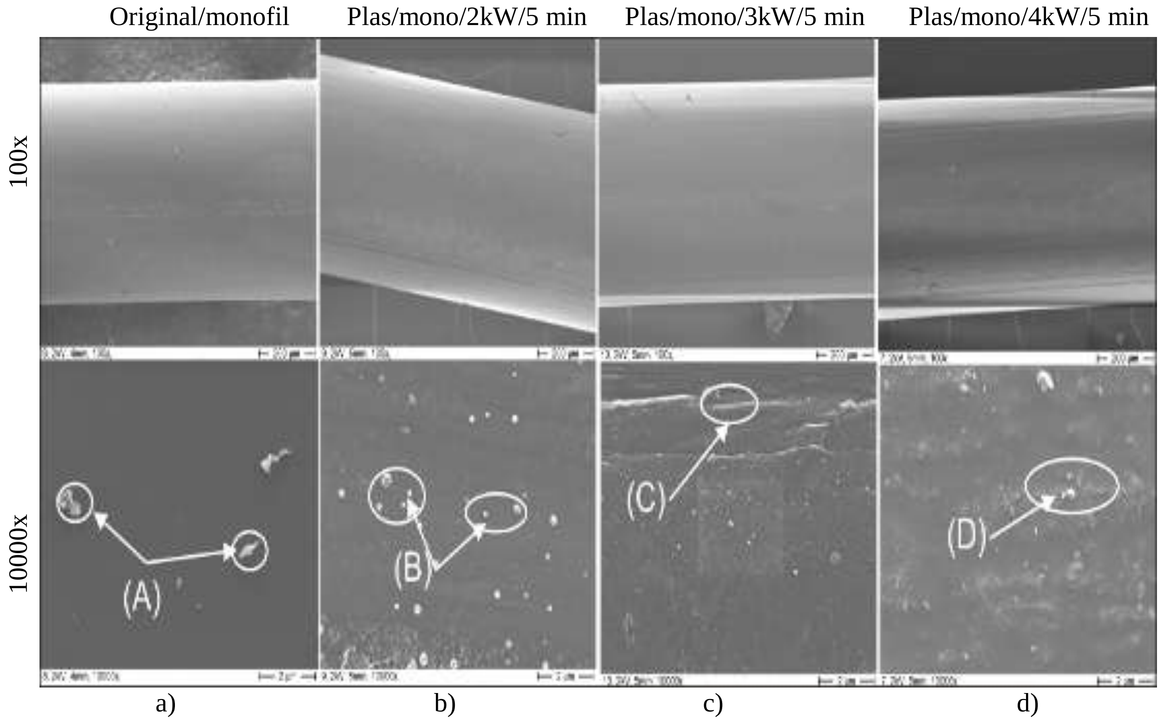

Fig. 8. SEM images of original and 5 minute plasma treated PEEK monofilament at different powers at 100 and 10000 fold magnifications

From Fig. 8 a) it can be seen that the surface of the original monofilament PEEK is smooth with some particles adhering to it (indicated by A). The size of the adhering particles seems to be small with 2 kW plasma treatments. Fig. 8 b) which is indicated by B. Fig. 8 c) and d) show that there is presence of some grooves and bulges indicated by C and D respectively which are the results of higher level of electrical power used during plasma modifications.

CONCLUSION

The test results of contact angle measurement and surface free energy of surface modified PEEK show that due to plasma treatment, polar parts can be increased significantly which is most important for the wettability of PEEK. The tensile test results of breaking force and elongation due to plasma treatment on multifilament PEEK show very less difference in compare to those of the original PEEK. However, tenacity of PEEK increased remarkably with the power increased of plasma due to decrease of filament fineness. From the SEM images, the difference between original PEEK and plasma treated PEEK can be clearly observed. The roughness and functional groups induced due to plasma treatment on the surface of PEEK filament Atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) are necessary to examine on the surface.

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