Investigation on gas plasma and liquid plasma treatment for polyether ether ketone (PEEK) surface for wettability enhancement

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Abstract. The results of liquid and gas plasma treatment on polyether ether ketone PEEK surfaces are reported. The experiments were conducted by using variation of treatment time (5 s to 60 s) using Helium as its working gas. The results were obtained by measuring the water contact angle (WCA) and the studying the surface morphology of the PEEK surface. Comparisons of WCA and Scanning Electron Microscopy (SEM) analysis were conducted for samples which undergone gas plasma treatment and liquid plasma treatment. After gas plasma treatment, WCA of the PEEK surface decreased from 65° to 21°. Results of WCA for liquid plasma treatment showed decrement from 65° to 45°. Images from SEM showed PEEK surface area after gas and liquid plasma showed surface area increment of 40% for gas plasma and 20% for liquid plasma. The decrement of WCA and increment of surface area showed that PEEK surface properties changed from hydrophobic to hydrophilic via wettability enhancement.

1. Introduction
PEEK has great physical and chemical properties, including outstanding mechanical properties, chemical resistance and thermal performance. It can withstand long term continuous temperatures of 248 °C as well as exposure to hot water or steam with low moisture absorption. PEEK also have good compatibility with all normal cleansing strategies, protection from erosion, and simplicity of framing by trim or machining and a thickness equivalent to human tissue.

In general, plasma is well known as the fourth state of matter. Plasma is also known as ionized gas. The plasma treatment conducted is atmospheric pressure low temperature process which could modify surface. To modify the surface properties of materials such as solid polymer, plasma treatment (low and atmospheric pressure) is extensively used [1]. Our previous work has shown that microorganism can be deactivated when plasma discharges is in water compared to discharge using gas. [2]. Thus, it is interesting to investigate its surface properties using WCA and SEM analysis. Another example of plasma treatment using air as its working gas also has shown promising results [3].

Plasma technique allows the surface to be more hydrophilic with the formation of new groups which can interact specifically with other groups when the reactive gases in the plasma such as Helium
or Argon are used. Plasma surface modification is getting more attention in biomedical engineering because it is an inexpensive and effective surface treatment technique for polymers. Plasma treatment is another simple technique used to modify polymers to the surface. Plasma treatment on PEEK has shown an increment of surface wettability at a fast rate and to create hydroxyl groups on the surface [4]. However, this depends on the type of material, the suitable choice of plasma, and time taken enable to increasing in hydrophobicity or hydrophilicity.

The surface property can be changed from hydrophobic to hydrophilic by using plasma treatment method [5]. In order to increase the wettability, while has little effect on its bulk properties, plasma is a relatively low cost tool, highly-efficient and easy to handle.

2. Plasma Technology and Surface Treatment

The transformations of non-thermal plasma at the atmospheric temperature plasma are significant. The economic and operational advantages compared to low pressure have led to the establishment of a variety of non-thermal atmospheric pressure plasma as a latest trend in research [6]. Atmospheric pressure plasma also produces reactive species to improve the material's surface characteristics and have an equivalent result in low pressure plasma treatment [7].

Atmospheric pressure plasma system was developed using a high voltage ignition coil power supply. This system can support plasma discharge by use of helium and argon as operating gas. The discharge temperature was found to be around 35 °C even in long term operation and the surface of thermal-sensitive materials such as polyethylene (PE) without altering its bulk properties can be modified using this type of non-thermal plasma. In an attempt to investigate the use of the plasma system to modify the PE surface, the results showed that the PE surface can be altered by 60 seconds of plasma treatment to a hydrophilic state. The reduction of water contact angle confirmed this [8].

Engineering of thermoplastic mostly show low energy surface and bad adhesion. Thus, it does not have the properties of surface that is needed in some application. In order to make the surface active, different methods are used. Non-thermal plasma is extensively used to modify the surface of various polymers to produce and improve the adhesion and wettabiliy properties without giving an effect to the bulk properties [9].

3. Methodology

To investigate the effect of treating PEEK surface by using atmospheric gas and liquid plasma, experiments on WCA and SEM were conducted as follows.

3.1. Preparation of PEEK before Plasma Treatment

A 1 cm thick PEEK was cut into 3 cm x 3 cm. The PEEK was placed on a glass plate before exposure to plasma. The center of each samples were exposed to atmospheric plasma. For liquid plasma, the PEEKs were submerged into the liquid. The samples were exposed to plasma for 5 to 60 seconds.

3.2. Plasma Surface Treatment

For gas plasma, the parameters of treatment such as helium gas flow rate, the working distance of the plasma discharge and treatment time were optimized. Helium gas flowed from a cylinder gas tank through the gas tube into the gas regulator at 1 L/min. Then, the gas travelled through the gas tube into the flow meter system then through quartz glass tube. Treatment time was varied, which are between 5 and 60 seconds. Plasma plumes on the surface of the PEEK sample is shown in Figure 1.

For liquid plasma, the quartz glass with the high voltage electrode and ground electrode was submerged into distilled water of 30 ml to activate the liquid. Then, the PEEK sample was inserted into the beaker as shown in Figure 2. Treatment time was varied, which are between 5 and 60 seconds.
Figure 1. PEEK sample exposed to gas plasma

Figure 2. PEEK sample submerged inside liquid plasma

3.3. Water Contact Angle (WCA) Measurements

The WCA measurements were conducted to determine the wettability of the surface. Untreated PEEK that acts as a control sample were placed on flat and a smooth surface, then 1 drop of distilled water were dropped by using a syringe on the surface of the sample. An example of image of the water droplet on the PEEK surface is shown in Figure 3. To determine the WCA the angle between the baseline of the droplet and the tangent of the drop boundary were determined using ImageJ1.52a software. Measurements were conducted 3 times and results are averaged values.

Figure 3. Water droplet on Untreated PEEK Surface

3.4. Scanning Electron Microscopy (SEM)

PEEK samples were coated with platinum before SEM analysis. This is because a direct exposure to electron will cause surface charge on PEEK surface. Images captured will be distorted due to this charging effect. By coating with platinum a conductive layer will be created on the PEEK enabling SEM image to be captured without distortion.

4. Results and Discussions

Each sample was treated by using Helium as working gas at flow rate of 1 L/min. The treatment time for each sample is 5, 15, 25, 35 and 60 seconds by using gas and liquid plasma. SEM images were taken only for treatment time 5s and 60s for gas and liquid experiments.

4.1. Comparison of Water Contact Angle (WCA) between Gas and Liquid Plasma of PEEK Surface

Figure 4 presents the results comparing WCA of PEEK after gas and liquid plasma treatment. It is shown that gas plasma treatment produces higher wettability compared to the liquid plasma treatment. Analyzing the treatment time, it is shown that gas plasma produces smaller WCA to the PEEK surface starting at 5 seconds compared to liquid plasma. Table 1 presents the results of WCA percentage decrement comparison between gas plasma and liquid plasma treatment. Surface processing using gas plasma produces smaller WCA faster.
Figure 4. Comparison of WCA and treatment time between gas plasma and liquid plasma treatment

Table 1. Percentage decrement of Water Contact Angle (WCA) of PEEK Surface after Gas and Liquid Plasma Treatment

| Treatment Time (s) | GAS PLASMA          | LIQUID PLASMA        |
|-------------------|---------------------|----------------------|
|                   | Water Contact Angle (°) | WCA decrement (°) | WCA decrement (%) | Water Contact Angle (°) | WCA decrement (°) | WCA decrement (%) |
| 0                 | 66.501              | -                   | -                  | 65.854              | -                   | -                  |
| 5                 | 61.049              | 5.45                | 8.02               | 63.435              | 2.42                | 3.67               |
| 15                | 44.307              | 22.19               | 33.37              | 60.255              | 5.60                | 8.61               |
| 25                | 42.879              | 23.62               | 35.52              | 57.804              | 8.05                | 12.22              |
| 35                | 33.690              | 32.81               | 49.34              | 53.130              | 12.72               | 19.32              |
| 60                | 21.434              | 45.07               | 67.77              | 45                  | 20.85               | 31.67              |

4.2. Comparison of Scanning Electron Microscopy (SEM)

Figure 5 and 6 shows the SEM images for PEEK samples after 5 s and 60 s of gas plasma treatment respectively. Figure 7 and 8 shows the SEM images for PEEK samples after 5 s and 60 s of liquid plasma treatment respectively. By referring to the SEM images in Figure 5 - Figure 8, the PEEK surface area after gas plasma and liquid plasma treatment were analyzed and the changes on the surface area were measured. The measurement results in Figure 9 showed that the PEEK surface area after gas plasma treatment is larger than liquid plasma treatment by approximately 40%. The results also showed the increasing value of surface area when the treatment time increased.
5. Conclusion

This paper presents a comparative study of surface treatment between gas plasma and liquid plasma. WCA and surface area measurements were conducted to evaluate the effect of both plasma treatments. When the water contact angle (WCA) decreases, the wettability of the surface increases. Subsequently, when the wettability of the surface increases, surface hydrophilic properties will also increases [9]. Our results showed that gas plasma treatment produces higher wettability compared to the liquid plasma treatment. It is because of the gas plasma can modify the surface of PEEK in short period of treatment time [3]. From SEM image analysis, the surface area of the treated PEEK showed the 40%
increment when treated with gas plasma. The longer treatment time, the larger the area of treated PEEK surface is produced. Gas plasma treatment is more effective plasma treatment because of the hydrophilic surface properties.

**Acknowledgement**

The author would like to acknowledge the support from the Fundamental Research Grant Scheme (FRGS) under grant number of FRGS/1/2015/SG02/UNIMAP/02/5 from the Ministry of Education Malaysia.

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