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SURFACE MODIFICATION OF POLYCARBONATE USING MESH ELECTRODE AT ATMOSPHERIC PRESSURE DISCHARGE AT 50 HZ

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ABSTRACT

This paper reports the result of surface treatment of polycarbonate sample on atmospheric pressure dielectric barrier dischrge (APDBD) in argon environment. The discharge was generated in parallel plate DBD system with a fine metal mesh below a barrier using a high voltage power supply (0-20KV) operating at line frequency, 50Hz. The main objective of the study is to investigate improvement of the hydrophilic property of the polymer after the treatment in plasma. The plasma treated samples were characterized by gravimetric method and contact angle measurement with two test liquids and the contact angle data were used for the calculation of surface energy of the samples with its polar and dispersive components. Our result showed that the discharge produces significant improvement in hydrophilicity just after 2 minutes of treatment reducing the contact angle from 88.28^0 to less than 55^0. It was also found that the change in surface energy is mainly due to the increase in polar component of the surface energy.

Keywords: Contact angle, Surface energy, Dielectric barrier discharge, Surface polarity.

INTRODUCTION

Polymers are generally macromolecules formed by the repeated linking of large number of small molecules.[1] In recent years, polymers have become very attractive business article. The world production of polymers increases every year by 8-10% [2] because of their superior performance low cost, excellent breakage resistance, good transparency and low inflammability. However, the low hardness, low scratch resistance and easily degradation by ultraviolet radiation make a modification of polymer surface properties necessary.[3] The low surface energy of polymers results a low wettability, poor adhesion of additional coatings which have created numerous important technical challenges to be overcome by manufacturers. So it is necessary to change or improve the some of the surface properties without altering the bulk properties. Conventional methods of surface modification such as chemical treatment, mechanical roughening and treatment with the flame suffer from the problem of uniformity, reproducibility and cost effectiveness. But plasma surface modification of polymers offers a uniform, economic and environmentally friendly alternative.[4]

Kathmandu University
Journal of Science, Engineering and Technology
KUSET
Shrestha *et al.*, Vol.10, No.I, November, 2014, pp 15-19

Among various atmospheric pressure non-thermal plasma sources, atmospheric pressure plasma dielectric barrier discharge using line frequency (50Hz) is attractive for industrial applications as it avoids the high cost associated with vacuum-based plasmas and overcomes the power supply heating deficiency of the high frequency plasmas.[5] It offers an effective and versatile surface modification method by removing the volatile impurities, increasing surface roughness, breaking C-C and C-H bonds to form the stable cross linking surface structure and generating certain functional groups like the carbonyl (-C=O), carboxyl (-COOH), hydroxyl (-OH), and hydro-peroxide (-OOH) groups on the polymer surface which contributes to increase the wettability and adhesion. In this work APDBD with a metal mesh has been used to achieve homogenous discharge mode for the surface modification.

MATERIALS AND METHODS

The schemetic diagram of DBD reactor used in the present work is shown in Fig.1 and the nature of fine mesh electrode is shown in fig.2 in which gap of one space in fine mesh is 0.32mm. The discharge was produced in between two circular electrodes of stainless steel of diameter 10cm when the discharge gap is 2.5mm. A metallic fine mesh is kept in between dielectric (glass) of thickness 1.12 mm and metal electrode. Argon gas was introduced between the electrodes with a flow rate of 1litre/minute.

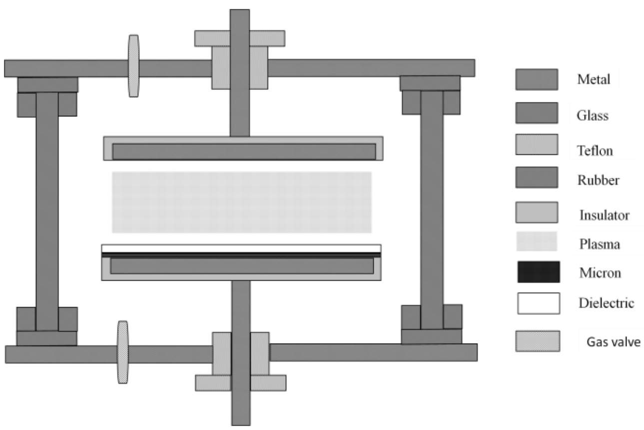

Fig. 1 Schematic diagram of DBD reactor

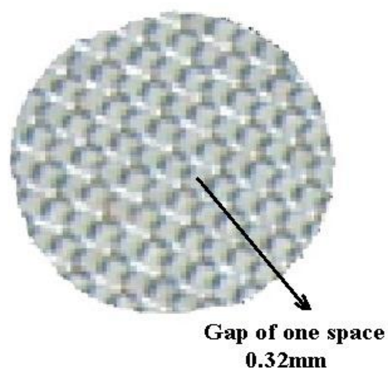

Fig. 2. Fine mesh electrode

The PC sample of thickness 2mm was cut into section of 3cm x 1.5cm for plasma treatment and ultrasonically washed in methanol and with doubly distilled water for 10 minutes and then dried in air before plasma treatment. The treatment of the PC sample was performed for various exposure times from 10 seconds to 10 minutes. The influence of the plasma treatment on the hydrophilicity at different voltage and treatment time was investigated by contact angle measurement using a rame-hart contact angle goniometer model: 200 taking two test liquids (distilled water and glycerol) on the surface of the PC. The total surface energy of the PC and its polar and dispersive components were determined using Owens-Wendt-Kaelble two liquids method by using Eq. 1.

Kathmandu University
Journal of Science, Engineering and Technology
KUSET
Shrestha *et al.*, Vol.10, No.I, November, 2014, pp 15-19

$$\gamma_l(1+\cos\theta) = 2\left(\gamma_l^d \gamma_s^d\right)^{1/2} + 2\left(\gamma_l^p \gamma_s^p\right)^{1/2} \ldots\ldots\ldots\ldots\ldots.(1)$$

where γ_l, γ_l^d and γ_l^p are the total, dispersive and polar components of surface energy of test liquids and its values are given in the table 1. γ_s, γ_s^d and γ_s^p are the same values for the PC under investigation and sum of γ_s^d and γ_s^p gives the total surface energy (γ_s).

Table 1.Surface tension and its polar and dispersive components for two test liquids. water and glycerol

Liquid	Total surface energy (mJ/m^2)	Polar component (mJ/m^2)	Dispersive component (mJ/m^2)
Water	72.8	51	21.8
Glycerol	63.4	29.7	33.6

RESULTS AND DISCUSSION

The loss in weight of the sample after the treatment is studied for different treatment time by gravimetric method and result is shown in Fig. 3. Figure clearly shows that there is increase in weight loss on increasing the treatment time. It might be due to etching effect, which is purely physical phenomenon created by inert gas plasma like argon by removing the volatile impurities from its surface or breaking up of bonds.

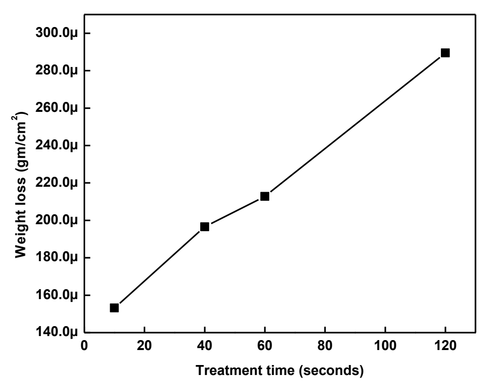

Fig. 1. Etching effect at applied voltage 14.09KV

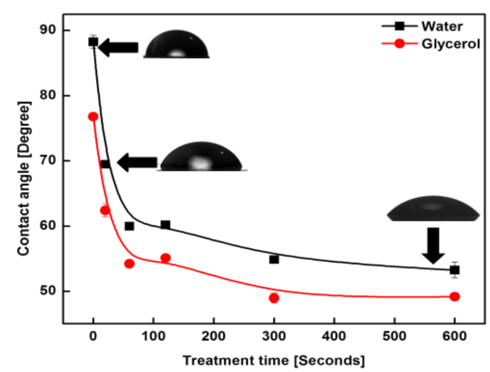

Fig. 4. Variation of contact angle with treatment time at 9.39KV

The atmospheric pressure dielectric barrier discharge can generate a wide range of active species including atomic oxygen, ozone, nitrogen oxides, neutral and metastable molecules, radicals and ultraviolet radiation in its discharge regimes. Therefore PC surface when exposed to a highly reactive regime, some chemical bonds on the surface are being cut off. The rearrangement of the cut-off bonds causes plasma etching on the surface resulting in the change of surface morphology, and in the meantime, some of them can be reacted with the active species like

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Shrestha *et al.*, Vol.10, No.I, November, 2014, pp 15-19

atomic O, OH, HO_2 etc resulting in the implantation of polar groups on the surface, which might be the main reason for the decrease of the static water contact angle. [6] Fig.4. shows the variation of the contact angle of the PC for water and glycerol at various treatment time at constant voltage 9.39KV. Initially contact angle of the untreated PC for water and glycerol was 88.28^0 and 76.8^0 but after plasma treatment it was significantly reduced to lower values, which suggests that a strong increase of wettability in the PC surface induced by the atmospheric pressure discharge treatment and after 2 minute treatment time contact angles reach a saturation state, suggesting that the physical and chemical changes induced by the plasma are also in saturation.[7] Fig. 4 also shows that glycerol has less contact angle than that of water. It is due to the fact that glycerol has less polar liquid as compared to the water so it has less surface energy as well as contact angle.

The variation of the surface energy with polar and dispersive component at 11.74KV is shown in the fig.5. There is inverse relation between contact angle and surface energy which can be obtained from eq.(1). Total surface energy increases from 28.1mJ/m^2 to 45.9mJ/m^2 during 10 minutes treatment time in plasma. Similar trend is also observed for the polar component and it is mainly due to the incorporation of the polar species like CO, COO and OH on the treated PC surface. Where as dispersive component initially decreases and becomes constant. It does not have any contribution to increase the wettability of the PC.

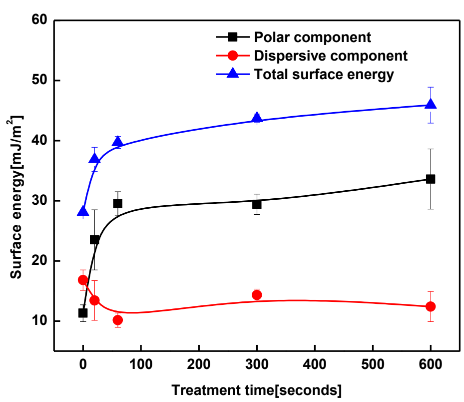

Fig. 2 Polar, dispersive and total surface energy of PC at 11.74KV

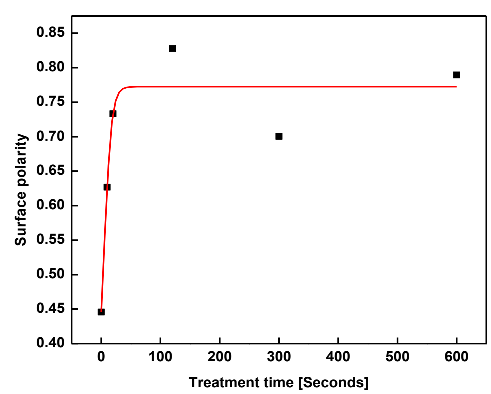

Fig. 6 Change of surface polarity with treatment time at 11.74KV

The change of surface polarity with treatment time is shown in Fig.6. The increase in surface polarity also gives the information of introduction of the new hydrophilic functional groups on the PC surface and gained the saturation after certain treatment time.It indicates that no mere hydrophilic functional groups are added in the PC surface.

CONCLUSION

Treatment of the PC in DBD using mesh electrode caused a significant improvement of the hydrophilic property and it strongly depends on the treatment time. The plasma treatment in the argon environment increased polar functional groups and the etching rate onto the surface causing the decrease in contact angle and increase in surface energy. All changes in surface improved the wettability of the PC.

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