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Surface Modification of Polycarbonate by Treatment with 50Hz Dielectric Barrier Discharge at Near Atmospheric Pressure

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Abstract: ***The samples of Poly-Carbonate (PC) were treated with Dielectric Barrier Discharge produced at 1000V at a near atmospheric pressure. The discharge thus produced was of glow type. Nature of the discharge was studied by using electrical characterization techniques and the electron density of discharge was calculated. Surface characterization of the sample was done using contact angle measurement and Raman spectroscopic analysis. The hydrophilicity of the sample increased rapidly for a certain treatment time and reached to its saturation point. The surface of the treated and untreated samples was found to be Raman active for the shorter treatment time and the activity vanished after further treatment.***

Keywords: PC, DBD, Contact Angle, Surface Free Energy, Hydrophilicity, Wettability, Raman Spectroscopy, Electrical Characterization

1. Introduction

Discharge characterization of Dielectric Barrier discharge (DBD) can be done using both numerical [1] and experimental methods [2]. The experimental method includes techniques like electrical [3] and optical characterization. The high electron temperature in non-thermal plasma [4] causes changes on the surface properties [5] of treated sample while its bulk properties remaining unaffected due to the low ion temperature. Most of the polymers treated industrially are heat sensitive [6], so treating them with hot plasma does not yield good results. The pressure inside a custom designed plasma reactor was reduced to few orders of magnitude (around 40 torr) using a vacuum pump. Reduction of pressure helps in the reduction of breakdown voltage [7]. Thus produced plasma is more uniform in comparison to the plasma produced at atmospheric pressure. Uniform glow discharge plasma is ideal for material processing [8].

The surface modification of polymer includes change in wettability and adhesion [9] as well as the enhancement or reduction of friction on the polymer surface. The surface energy of the polymer can be either increased or decreased [10] according to the need of the experiment and the functional groups can be either added or wiped out from the surfaces [11].

2. Experimental

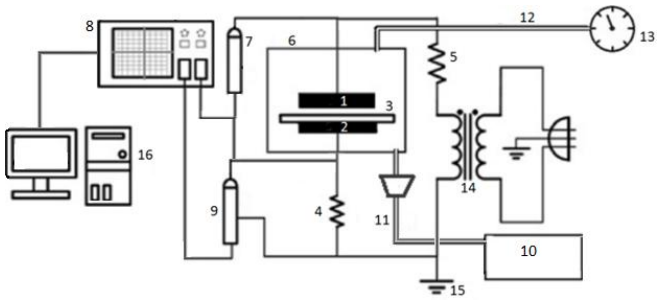

Figure 1: Experimental Setup

1. Circular upper electrode 2. Ground electrode 3. Dielectric sheet 4. Ballast Resistor 5. Resistor 6. Reaction Chamber 7. 10-times voltage Probe 8. Oscilloscope 9. Current Probe 10. Vacuum Pump 11&12. Pipe 13. Pressure Gauge 14. High Voltage Transformer 15. Ground 16. Computer Interfacing .

The experimental setup of the research is as shown as in figure 1. A cylindrical polycarbonate tube is used as the plasma chamber. The PC chamber is preferred due to its transparent nature allowing the experimentalist to see what is happening inside the chamber. Two circular copper electrodes, each of diameter 5cm and thickness 1cm are 4.5mm apart and a glass sheet of thickness 1mm is used as dielectric. The reactor is vacuum shielded and is connected to a vacuum pump and an analogue pressure gauge. The working voltage for the entire experiment is set to be 1000V. Reduction of pressure inside the chamber makes the generation of plasma at such a comparatively low voltage possible. Current and voltage waveforms are obtained using the digital oscilloscope (Tektronix TDS2000). A high voltage probe (PINTEK HVP-28HF) is used for the reduction of the voltage by 1000 times in order to prevent the oscilloscope from getting damaged due to the high voltage.

The samples of polycarbonate are cut into (3cm$\times$ 1.5cm) rectangular pieces. They are then washed by methanol and put into an ultrasonicator for further cleaning. samples are placed on the glass sheet between the electrodes. Thus treated sample are taken for surface characterization. Contact angle is measured using a contact angle goniometer (Rame-hart Model 200) [12] and Raman spectra of the surface is generated using Raman Spectrometer (RIRM Spectrometer, RI Instruments, India)

3. Results and Discussion

a) Electrical Characterization

The value of electron density (n_e) has been calculated by using Power Balance Method. The balance between the

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input power from high voltage power supply (P) and power lost in the plasma leads to

$$n_e = \frac{P}{2Aev_bE_{lost}} \text{.....(1)}$$

Using this equation electron density is calculated. The calculation was made by using the values give below:
The discharge gap = 3.5 mm, Applied frequency = 50 Hz
Area of each electrode =20.43cm^2
Bohm velocity = 2×10^5 cms^{-1}.
E_{lost} = 50eV (in our condition).
The calculated value of electron density (n_e) was found to be 3.21×10^{12}cm^{-3}.

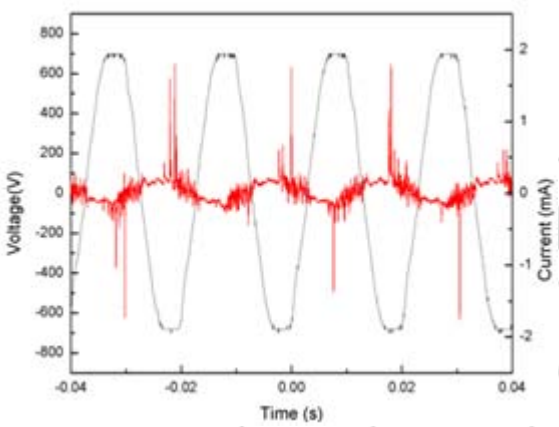

Figure 2: Current and voltage waveforms as the function of time

b) Contact Angle Measurements

Static contact angle of the water and glycerol on the surface of the polymer samples are measured using contact angle goniometer immediately after treating the surface with plasma. The surface free energy (γ) of the surface is measured in terms of polar (γ^p) and dispersive (γ^d) components using Fowkes equation [13]. The sum of these two components gives the value of total surface free energy of the sample. The surface free energy is calculated from the Harmonic mean method using the contact angle [14]. Figure 3 and 4 shows the variation of water contact angle and surface free energy of PC surface as the function of treatment time. The contact angle decreases on increasing the treatment time. The rate of decrease in contact angle becomes lower on increasing the treatment time and it finally reaches to its saturation point. The surface free energy increases on increasing the treatment which is due to the functionalization of the polymer surface with hydrophilic groups. It is found that the further treatment of PC also does not lead to any significant changes in the surface free energy. Figure 5 shows the variation of ratio of the polar and dispersive components of surface free energy as a function of treatment time. The increment in the value of the ratio signifies that there is a dominance of chemical change with respect to physical change on the surface of polymer sample. So, more treatment of sample is needed to get more chemical change on the surface of the PC polymer.

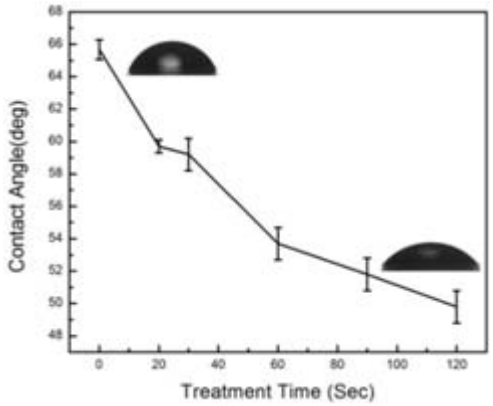

Figure 3: Contact angle of PC surface as a function of treatment time for 50 Hz DBD at near-atmospheric pressure.

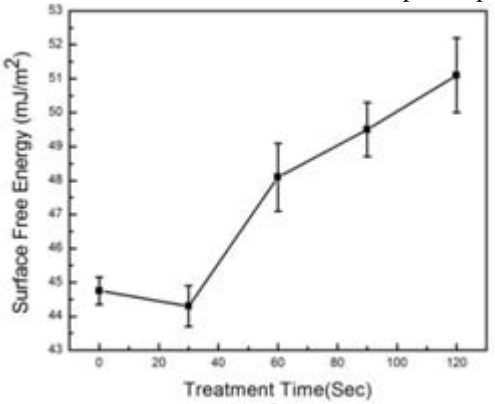

Figure 4: Surface free energy (γ) of PC surface as a function of treatment time for 50 Hz DBD at near-atmospheric pressure.

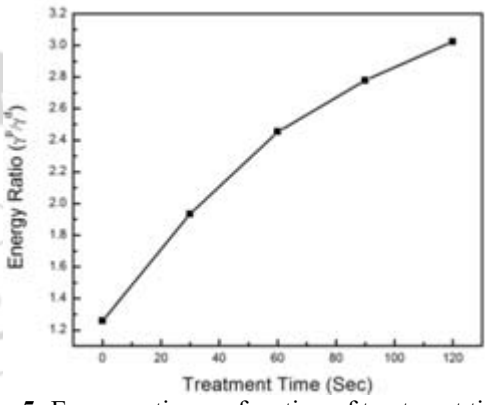

Figure 5: Energy ratio as a function of treatment time for 50Hz DBD at near-atmospheric pressure.

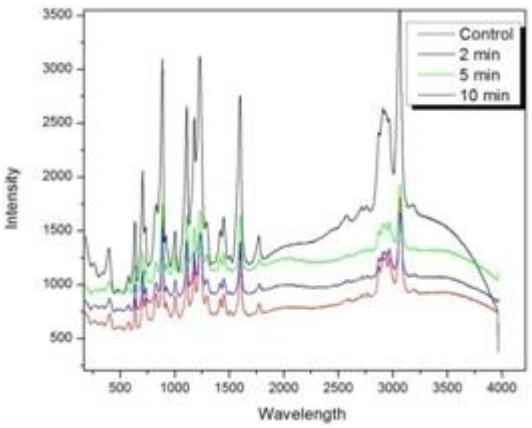

Figure 6: Raman spectra of the PC sample for various treatment time.

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c) Raman Spectroscopy

Both the untreated and treated samples of PC were probed by a Raman Spectrometer. The graphs obtained are shown in the figure 6. It can be seen that the intensity increases for certain treatment time. Increase in intensity implies that the surface of PC becomes Raman active after plasma treatment. The Raman activity is maximum for the 2 minute treatment time. It then decreases for 5 minutes treatment and finally loses its activity after 10 minutes of treatment.

4. Conclusions

Contact angle of the surface changes drastically for the initial treatment time and reaches to its saturation time on further treatment. The polymer industries can therefore save the energy by calculating the optimal treatment time for the sample over which there is noticeable change on the surface properties. From Raman spectroscopic analysis it was noticed that the surface becomes Raman active for certain treatment time and finally loses the activity on further treatment.

5. Acknowledgement

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