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Surface Modification of PET and PP by Atmospheric Pressure Cold Plasma in Argon Environment

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Abstract **-This paper presents a DBD system used to generate plasma at atmospheric pressure in argon environment. The discharge was produced by applying high voltage power supply (7kV) to the electrodes separated by distance of 3 mm. The lower electrode was covered by a glass plate of thickness 1.5mm which served as the dielectric barrier. Argon was supplied at a flow rate of 2liter per minute. Two types of polymer samples, PET and PP were treated for different time ranging from 5sec-1minute.Contact angle of both the samples before and after treatment were measured. In our experimental results, it has been shown that plasma treatment produces remarkable improvement in wettability. The change in surface morphology of the sample was investigated by SEM analysis. SEM images showed that roughness of the sample increases appreciably after the treatment in plasma for both the polymers. The stability of plasma modified sample was also studied by measuring the hydrophobic recovery of the sample up to several days after the treatment.**

Keywords **- Surface modification, Plasma treatment, Hydrophilic material, polymers property, Dielectric barrier discharge, Surface Energy.**

I. INTRODUCTION

Polymeric materials are used as plastic and fibers in intensively increasing amounts. They have been used to replace traditional engineering materials like metals and glass because of high strength to weight ratio, resistance to corrosion, possibility of recycling, excellent breakage resistance, good transparency, low inflammability and their relatively low cost. They have been used successfully in fields such as adhesion, biomaterials, protective coatings, friction and wear-resistant composites, microelectronic devices and thin film technology. Especially, packaging industry is experiencing a technological revolution aimed at increasing consumer convenience and protection, and delivering new solutions for manufacturing and the distribution chain. Even in newly manufactured stuff made of polymers the recycled polymers are added to a certain amount, which may degrade their properties [1]. Many wetting and adhesion issues are therefore emerging, which require an additional surface processing to promote wetting of inks and coating and enhance adhesion with these and other substances. In order to improve adhesion strength, before applying any coatings the polymer surface need an adequate modification through treatments. This paper is about modification of polymer surface in order to increase its adhesion and wettability by plasma treatment technique [2-3].

Many of the common methods such as mechanical abrasion, solvent wiping, solvent swell that was followed by acid or caustic etching, flame treatment, or corona surface treatment are accompanied by safety and environmental risks, increased risk of part damage, and expensive pollution and disposal problems. For many industrial purposes where surface adhesion bonding is a prime concern, cold plasma treatment is the best process. Since plasma treatment is a process of surface

modification, the bulk properties of the material are retained. The nature of the process also allows precise control of the process parameters and ensures repeatability of the process in industrial applications [4].

Typically, a plasma referred to as the fourth state of matter is composed of a large concentration of highly excited atomic, molecular, ionic, and radical species, which upon collision with the surfaces of polymers placed in the plasma environment break covalent chemical bonds, thus creating free radicals on the polymer surface [5]. The free radicals will then undergo additional reactions, de- pending on the gases present in the plasma or subsequent exposure to gases in the atmosphere. The result is that these gas radical reactions form a surface that is potentially very different from that of the starting bulk polymer [4]. The surface modification of solid substrates by plasma exposure is mostly used for etching, cross linking, surface activation (radical formation) and as pre-deposition process. The modification processes is not restricted to plasma irradiation, since the performed air exposure also leads to significant surface changes [6-8]. To study such chemical changes, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy are used to study the surface chemical composition [9]. The depth of modification arises from plasma power and exposure time. Typically it is few hundred of Angstroms (determined by RBS, Rutherford backscattering). Scanning Electron microscopy (SEM) and atomic force microscopy (AFM) are used to investigate the surface morphology of the material at the atomic scale. All these methods require relatively expensive equipment, skilled technicians and quite sophisticated techniques to interpret the data. Now days, most popular plasma for this process are obtained from Argon, helium, Nitrogen, Oxygen, Carbon dioxide and air [1].

A good understanding of the surface properties of a solid can be obtained relatively inexpensively from the measurement of the surface free energy. Therefore contact angle measurement has been used in the study of surface free energy, wettability and adhesion of low surface energy materials.[10]. The contact angle is an angle that a liquid creates with a solid surface or capillary walls of a porous material when both materials come in contact together. Here two liquids model, also known as Owens-Wendt-Kaelble model was used to find the work of adhesion W_A expressed in terms of polar and dispersive components of surface energy [11]. i.e.

$$\mathrm{Y}_l(1 + \cos\theta) = 2\left[(\mathrm{Y}_l^d)(\mathrm{Y}_s^d)\right]^{\frac{1}{2}} + 2\left[(\mathrm{Y}_l^p)(\mathrm{Y}_s^p)\right]^{\frac{1}{2}}$$

Where, Y_l^p and Y_l^d are the polar and dispersion components of the surface tension of the test liquid. Similarly Y_s^p and Y_s^d are the polar and dispersion components of the surface energy of the solid.

Atmospheric Pressure Dielectric barrier discharge (APDBD) was used in our research as it has been emphasized in practical applications because it minimizes the need for vacuum systems and enables the treatment of materials continuously. In general, a stable glow discharge is easily achieved in low pressure of less than few mbar [12].

We have used two polymers Polypropylene (PP) and Polyethylene Terephthalate (PET) for our experimental purposes. PP is well applicable as plastic and as a fiber and PET is used for fibers or fabrics, and as ”PET Resin” in making bottles, jars, containers and packaging. Beside their many useful properties they have poor impact resistance at low temperature, are difficult paint or bond with adhesives and their molded surface is not smooth with glass reinforcement [13-14]

II. EXPERIMENTAL

A. Preparation and Treatment of Sample

Polypropylene (PP) and polyethylene Terephthalate (PET) were cut into the sample size of 60 mm by 15 mm and 140 mm by 15 mm. The samples were washed firstly in methanol for 5 minutes, secondly in acetone for 5 minutes finally in distilled water at ultrasonic bath for 10 minutes at an ambient temperature. They were then dried for few minutes and made ready for the plasma treatment by DBD. The discharge is made of brass with smooth surface. The lower electrode is fixed and upper electrode is movable. The lower electrode was covered by a glass plate of thickness 1.5 mm which

served as the dielectric barrier. The discharge was produced by applying high voltage power supply (≈7kV) to the electrodes separated by distance of 3 mm. Argon was supplied at a flow rate of 2 liter per minute. Two types of polymer samples, PET and PP were treated for different time ranging from 5sec, 10sec, 20sec, 40 sec and 1minute.

B. Measurement and Characterization

The effect of plasma treatment was investigated by comparing the contact angles of the treated and untreated samples with distilled water and glycerol. Sessile drop of 4 micro liters was made by using standard micro-syringe to place the water droplet in the samples. Contact angles of drops with reference to flat polymer surface were measured by the help of rame-hart contact angle Goniometer model 200. This unit is equipped with standard software to analyze the drop image for the calculation of surface energy. The system offers a high level of computer aided precision in measuring contact angle while facilitating the calculation of surface energy using different model equation by solving Owenes-Wendt-Kaelble model. In our work, contact angle was measured by two test liquid models, using distilled water and glycerol. Two samples of same polymer were kept in DBD and treated under similar conditions. One sample was used for SEM image and another was used for the measurement of contact angle.

C. Effect of Treatment time

Plot of treatment time and contact angle of PET with water and glycerol is illustrated in the fig.1 and 2 respectively. For a fixed power supply of ≈7kV, sample-electrode distance of 3mm and rate of Argon gas flow as 2 liter per minute, the contact angles were found to decrease exponentially. The result showed that contact angle of water with PET decreased from 76^{o}to 27^{o} and 65^{o} to 38^{o} to glycerol after 1 minute of treatment. Comparison of exponential decay of contact angles for both water and glycerol with treatment time can be made from fig.3. A more illustrative graph for the contact angles and the treatment time of water is shown in fig. 4. Besides, in our data there is anomaly at the treatment time of 40 seconds on both the graphs.

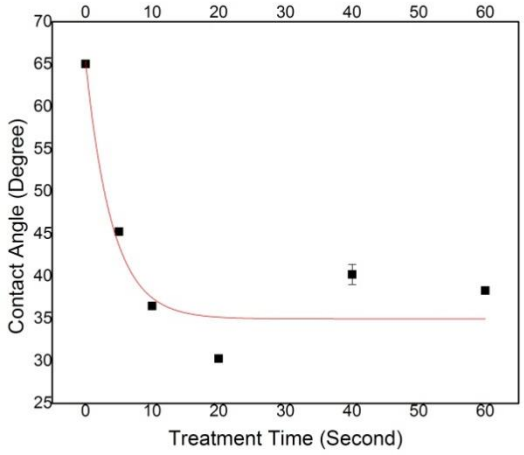


Fig.1. Contact angle of water drop on PET substrate as a function of treatment time. The applied voltage was ≈7kV, the inter-electrode spacing was 3mm and the gas flow rate was 2 liter per minute.

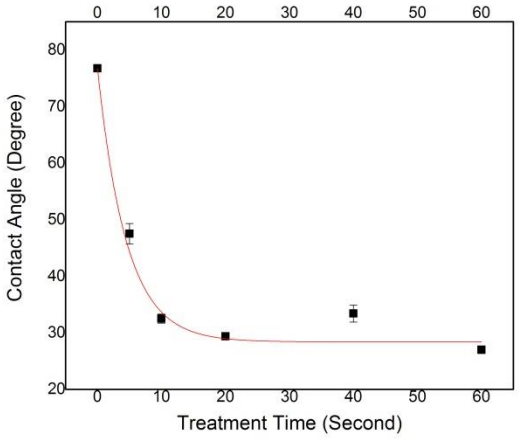


Fig.2. Contact angle of glycerol drop on PET substrate as a function of treatment time. The applied voltage was ≈7kV, the inter-electrode spacing was 3mm and the gas flow rate was 2 liter per minute.

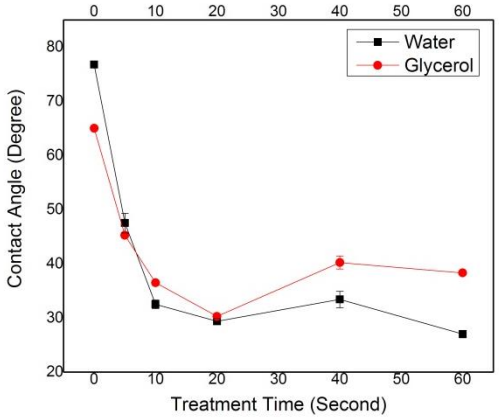


Fig .3. Variation of contact angle as the function of Treatment time

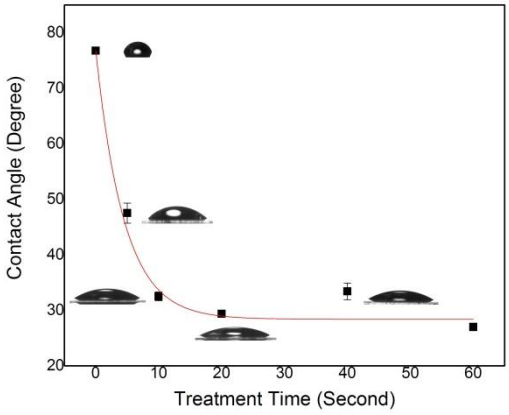


Fig. 4. Plot of contact angle as a function of treatment time of water along with the snapshot from Goniometer software in PET

D. Treatment time and Surface energy

Plot of contact angle and surface energy as a function of treatment time is given in fig.5. Applied voltage, inter electrode distance and rate of flow of argon were kept constant while the treatment time was varied form 5 sec to 1 minute. We can see an exponential decrease in contact angle and an increase in surface energy. Surface energy of PET increased from 37 mJ/m^2 to 76 mJ/m^2. The decrease in contact angle can be attributed to increase in surface roughness and incorporation of hydrophilic functional groups. This interaction of polymer surface with plasma might have caused hydrogen separation from polymeric chains and free radical creation. Radicals are created due to Ar+ or electron impacts, the CC and CH bonds being disrupted. With the CASING phenomenon (Cross-linking by activated species of inert gases) radicals interact with each other [15]. Exposure to plasma discharge can lead to the introduction of chemical functionalities, the nature of the functionalities highly depending on the chemical composition of the biomaterial and the process gas. This effect is time dependent as indicated in the graph. However a saturation value is obtained beyond 10 seconds of treatment which may be due to the equilibrium between the formation of hydrophilic functional groups on the surface and their removal by etching. Fig.5 demonstrates varying polar and dispersive components as functions of treatment time. Both polar and dispersive components sum up to give the total surface energy of the sample. For treatment time up to 10 seconds the surface energy increases rapidly and there is no appreciable amount of increase after that. This increase in surface energy results in increase in wettability of the sample.

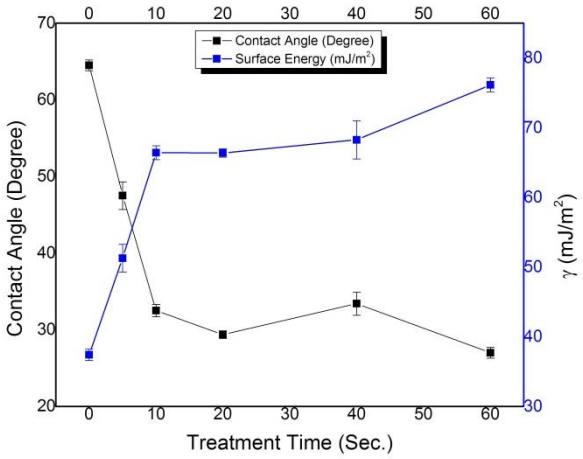


Fig.5. Plot of contact angle and surface energy as the function of treatment time at fixed applied voltage of ≈7kV, sample-electrode distance of 3mm and rate of Argon gas flow 2 liter per minute.

E. Study of surface morphology changes

To know more about the surface morphological changes due to plasma treatment, Scanning Electron Microscope (SEM) images were analyzed. While observing SEM images of PET and PP, surface

roughness was found to change with an increase in treatment time. From fig. 7 of PET sample, smooth surface can be observed on the untreated sample. While increasing the treatment time, the roughness has increased. There seems to be formation of small granules like structure after plasma treatment which might be there as on behind the increment in the surface roughness ultimately resulting in the increase in surface energy. SEM image so fun treated and plasma treated PP is shown in fig. 8 respectively. The roughness of the samples is found to be much higher that of PET samples.

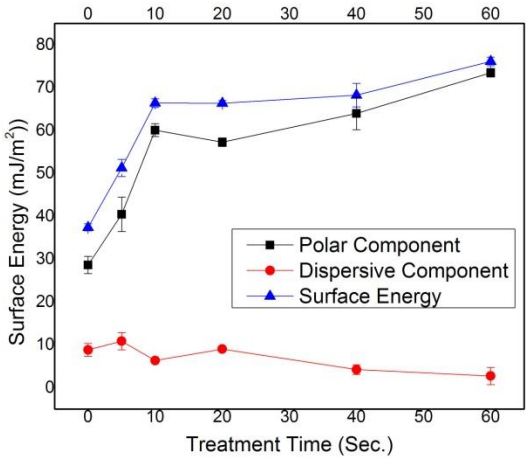
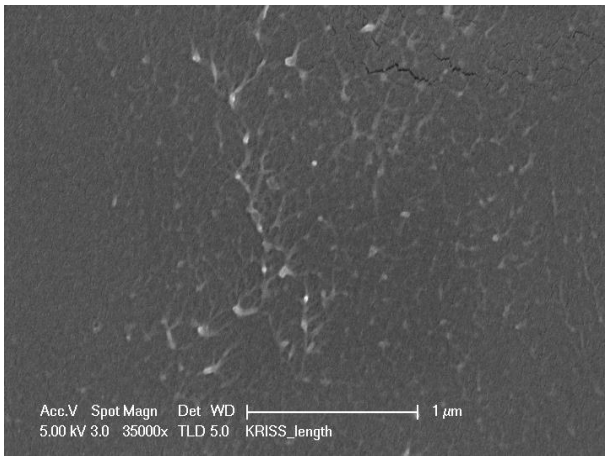


Fig.6. Plot of surface energy displaying both the polar and dispersive component as the function of treatment time



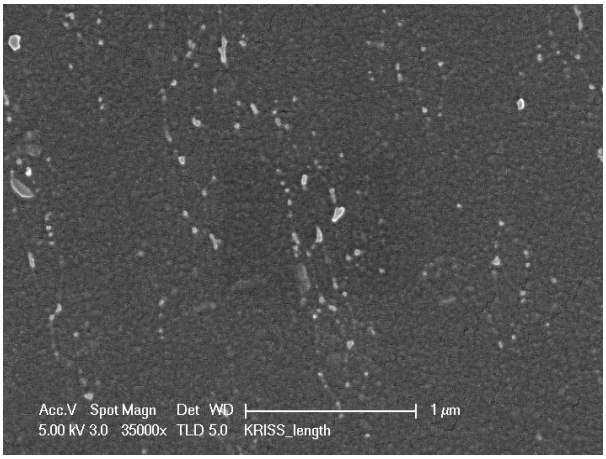


Fig.7. SEM images of PET sample untreated (top) and after 1 minute treatment (bottom) in plasma

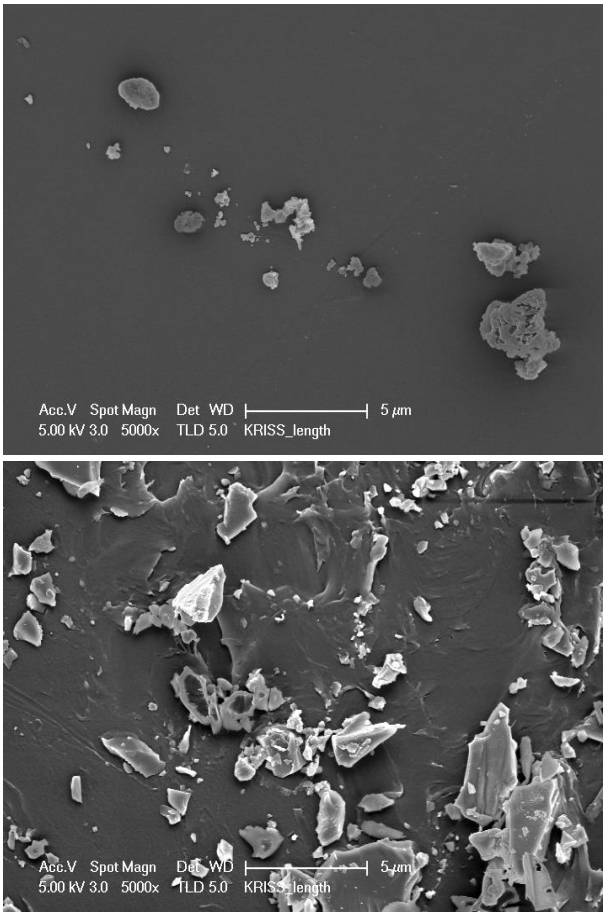


Fig.8. SEM images of PP sample untreated (top) and after 1 minute treatment (bottom) in plasma

F. Aging effect

As shown in fig. 9 contact angle is increasing with time. We can closely observe firstly, contact angle increase abruptly from 32.2° to 54.4° within 1 day after the treatment. There was no discernible change in the contact angle as its maximum change was 10° in the next 23 days. It has been reported that ageing is due to (i) thermodynamically driven reorientation of polar species away from the surface to the subsurface, (ii) diffusion of mobile additives from the polymer bulk to the surface, and (iii) the reaction of residual free radicals with the ambient (Spell and Christension 1979).

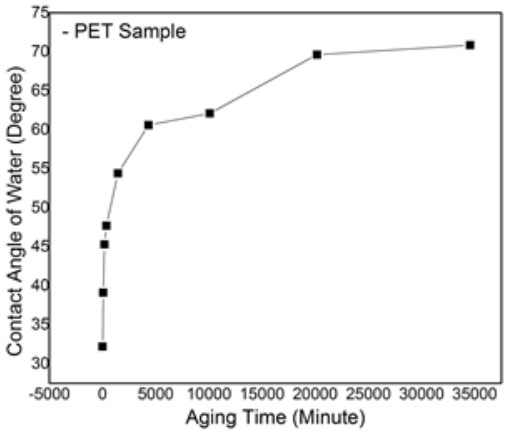


Fig.9. Ageing of contact angle of water on PET after treatment by plasma in Argon environment

III. CONCLUSION

The treatment of PET and PP by atmospheric pressure cold plasma in Argon environment caused decrease in contact angle and increase in surface energy. We were able to decrease contact angle of water from 76° to 27° and of glycerol from 65° to 38° in PET and increase surface energy from 37 mJ/m^2to76 mJ/m^2. It was seen that decrease of contact angle was exponential. This also shows that improvement of wettability of PET and PP strongly depends on the treatment time/etching effect. We concluded that plasma treatment causes temporary effect in decreasing the contact angle of liquid on polymer observing the ageing effect.

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