Change in surface free energy and surface resistivity of polycarbonate and polypropylene sheets after plasma exposure

R. S. BISHT, R. KUMAR[a*], N. THAKUR[b]

T.B.R.L Chandigarh 160030, India
[a]Jaypee University of Information Technology, Waknaghat, Solan (H.P.) 173215, India
[b]Himachal Pradesh University, Shimla (H.P.) 171005, India

Sheets of polypropylene (PP) and polycarbonate (PC) of thickness 2 mm have been exposed to direct current (DC) plasma. Glow discharge plasma was generated at a pressure 200 Pa to modify the surface of polymer sheets at room temperature. Low pressure allows a relatively long free path for accelerated electrons and ions inside the chamber. The measurements of surface energy and surface resistivity were carried out for the thin sheets which were exposed at different discharge powers and exposure time in oxygen plasma. It has been observed that for lowest discharge power (1 watt), the variations in surface energy (along with its components) for PC are small then that for PP sheet, while at 5 watt of discharge power no significant difference has been observed. The resistivity has been found to decrease with the exposure time as well as with the discharge power for both the samples. The surface free energy of PP has been found to increase to 50 mJ/m^2 and in case of PC 52 mJ/m^2 For maximum power (i.e. 5 watt used in this study) the surface resistivity of PP has been found to decrease to 1.26×10^9 Ω/cm^2 and for PC it decreased to 1.83×10^{11} Ω/cm^2. Before the treatment the resistivity of PP and PC were measured 1.24×10^{12} Ω/cm^2 and 1.32×10^{15} Ω/cm^2 respectively.

1. Introduction

It is well known that the polymers show many desirable physical and chemical characteristics such as high strength to weight ratio, resistance to corrosion, and relatively low cost etc. Polymers are widely used both for high-tech and consumer product applications and they have been able to replace more traditional engineering materials (1). There is still fundamental difference between polymers and engineering materials which is still challenging. The characteristics low surface free energy and the high surface resistivity are still the point of research. Because of low surface free energy the polymers show poor adhesion. Adhesion can be estimated by contact angle between the surface tangent of sessile drop and the solid substrate hosting the drop. Conducting polymers can be used as driving electrodes for polymer dispersed liquid crystal display devices.

Contact angle measurement has been observed to be one of the best methods for estimating the chemical changes which occurs at the modified surface of polymers by plasma (2). Using contact angle Zisman (3) gave a method for approximating the surface energy of solid substrate in context of wetting, by introducing the concept of critical surface tension (γ_C), the minimum surface tension of a liquid blow which the liquid spreads on solid spontaneously. Different intermolecular interactions such as Van-der Walls interactions, electrostatic interactions etc (4-10) can be obtained by this method. The critical surface tension has been taken as approximate measure of the surface energy (γ_{SV}) of solid. Polymers having low surface energy are difficult to wet and bond as it requires adhesive of surface tension $\gamma \leq \gamma_C = \gamma_{SV}$. Metals and ceramics have high value of γ_{SV} and may be readily wetted by many organic adhesives exhibiting good bonding.

In the literature the modification of polymer surfaces have been done using different methods such as atmosphere pressure plasma treatment, wet chemical etching, laser treatment, dry discharge treatment etc (11-21). The most effective method among these methods is glow direct current (DC) glow discharge plasma treatment due to the uniformity of treatment on the polymer surface. As we know that inside glow discharge plasma there exist ions, electrons and neutral species. The ions (in some cases) introduce functional group at the surface as well as they do cross linking of the polymer molecules. In some cases they degrade the polymer surface by chain scission and change its crystallinity (22,23). Addition of functional groups and breaking of chain at surface increases the surface energy of the polymers. In this study we have used (DC) glow discharge (24) to modify the surface free energy and surface resistivity of thin sheets of PP and PC. The experiment was performed at two discharge powers levels. The contact angle measurement of de-ionized water and formamide has been used to monitor the effect of (DC) glow discharge on the surface thin sheets.

2. Experimental

We used thin sheets of PP and PC with an area of approximately 1.5×1.5 mm^2 and thickness about 2 mm. Ethanol (C_2H_5OH) was used to remove the surface contaminations. Two test liquids de-ionized water and formamide with known polar and dispersion components of their surface tensions were used to evaluate the polar and dispersion components of surface free energy of PP and PC through the measurement of their contact angles. After cleaning with C_2H_5OH, the samples were transferred to a glass chamber (vacuum chamber) to expose them in DC glow discharge plasma. The closed glass chamber contained a height of 450 mm and diameter of 300 mm. Through an inlet oxygen gas was introduced into the glass chamber. The cathode was kept fixed and the spacing between the two electrodes could be controlled by adjustable anode vertically upward to the cathode. In this experiment the spacing between the electrodes was kept 20 mm. Cleaned PP and PC samples were kept on the cathode. A pressure of 200 Pa was produced inside the glass chamber at room temperature. Then a DC voltage 250 V was applied to generate glow discharges between the electrodes. The treatment of polymer sheets was carried out at two power levels (1 and 5 watts) for different exposure times. The power levels with exposure time are shown in Table 1.

Table 1. Discharge powers and exposure times.

Discharge power (Watt)	Duration of exposure (seconds)
1.0	5,10,15,20,25,30,35,40,45,50,55,60,,90,110
5.0	5,10,15,20,25,30,35,40,45,50,55,60,,90,110

Firstly, the measurement of surface energy and its components was carried out. Initially, without exposing samples to the glow discharge the contact angles of the test liquids droplets of size 5-8 μl on the surface of PC and PP were measures with the help of a stereo zoom microscopy. Then after treating the samples for different power levels and exposure times the same experiment of contact angle measurement was performed. The liquid drops on the surface of the samples were placed with the help of a syringe, and the estimation of the surface energy and its polar and dispersive components for both samples was done using the following equations.

$$(1+ \mathbf{Cos}\,\theta)\ \gamma_{LV} = 2(\gamma_S^{\ D}\,\gamma_{LV}^{\ D})^{1/2} + 2(\gamma_S^{\ P}\,\gamma_{LV}^{\ P})^{1/2} \tag{1}$$

and

$$\gamma_S = \gamma_S^{\ P} + \gamma_S^{\ D}. \tag{2}$$

The method for estimating the surface energy and its components is described elsewhere [21]. In the above equations θ is the contact angle and $\gamma_{LV}^{\ P}$ and $\gamma_{LV}^{\ D}$ are known for the test liquids. Which are given in Table 2.

Table 2. Surface tension (γ_{LV}), it's dispersive ($\gamma_{LV}^{\ D}$) and polar ($\gamma_{LV}^{\ P}$) component for test liquids.

Liquid	polar $\gamma_{LV}^{\ P}$ (mJ/m^2)	dispersion $\gamma_{LV}^{\ D}$ (mJ/m^2)	total surface tension γ_{LV} (mJ/m^2)
Water	51.0	21.80	72.8
Formamide	19.0	39.0	58.0

Secondly, electrical surface resistivity of the samples was measured. To make electrical contacts both the untreated and treated samples of PP and PC sheets were coated with silver film at one side. After coating the sheets were placed on a plane surface of glass sheet. The whole set-up was kept in a self made test fixture. Pressure contacts were used to make electrical contacts with the sample surface which were connected to a high resistance measuring electrometer. The electrometer could measure the resistance up to $10^{-16}\ \Omega$.

3. Results and discussion

A significant variation has been observed in the surface free energy (along with its components) and the surface resistivity of both the samples PP and PC. At the minimum treatment power of 1 watt the surface free energy of PP sample for 55 seconds of exposure time increases with the time as shown in Fig. 1. Also for PC sample at the same treatment power and time the surface free energy increases as shown in Fig. 2.
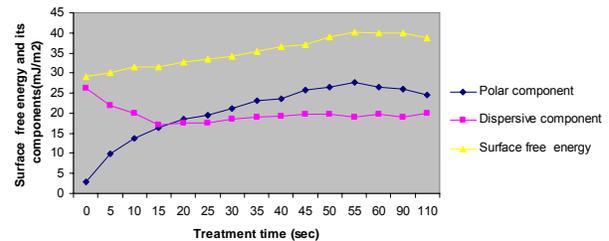
Fig. 1. Variation in surface free energy and its components for Polypropylene at power = 1 Watt.
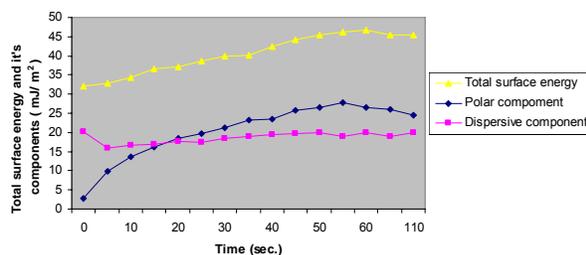
Fig. 2. Variation in surface free energy and its components for Polycarbonate power = 1 Watt.

In case of power level 5 watt the surface free energy of PP sheet has been observed to reaches to 50 mJ/m^2 for exposure time of 55 seconds as shown in Fig. 3. Similarly for PC it has been observed to reaches to 52 mJ/m^2 for 55 seconds of treatment time as shown in Fig. 4. The polar component for both the samples changes almost in the same fashion as the surface free energy changes. While the dispersion component changes in a random way.
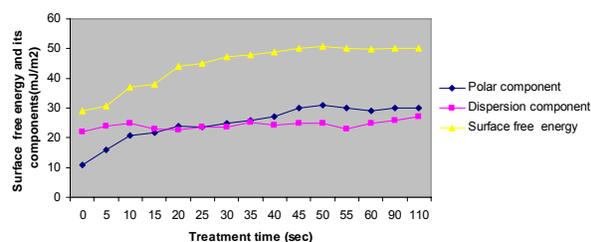
Fig. 3. Variation in surface free energy and its components for Polypropylene at power = 5Watt.
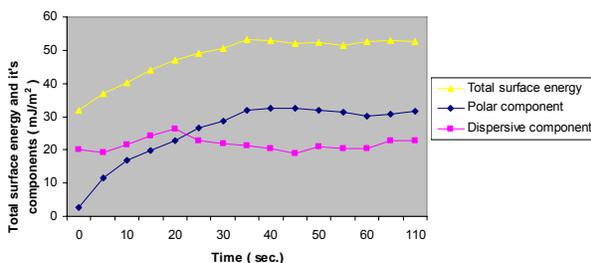
Fig. 4. Variation in surface energy and its components for Polycarbonate power = 5 Watt.

Figs. 5 and 6 shows the change in the surface resistivity of the thin sheets of PP and PC. It has been observed that surface resistivity for both the samples decrease with the increase in exposure time. Also with the increase of treatment power the surface resistivity decreases to large value as compared to small treatment power, which has been observed for small treatment times. For PP sheet at power level of 1 watt the surface resistivity decreases from 1.24×10^{12} Ω/cm^2 to $2.38 \times 10^{11}\Omega$/cm^2 at the exposure time of 55 seconds and at large values of time it remains almost constant. In case of PC the surface resistivity decreases from 1.32×10^{15} Ω/cm^2 to 1.30×10^{13} Ω/cm^2 for the same treatment power and exposure time. At higher power level of 5 watt the surface resistivity of PP is

observed to decrease to a value of 1.26×10^{9} Ω/cm^2 and for PC to a value of 1.83×10^{11} Ω/cm^2 for of 55 seconds of exposure time for both the samples.
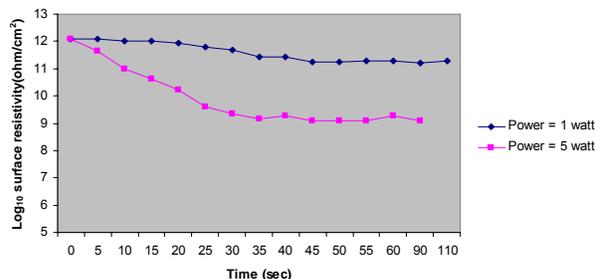
Fig. 5. Variation in the surface resistivity of polypropylene at different power levels.
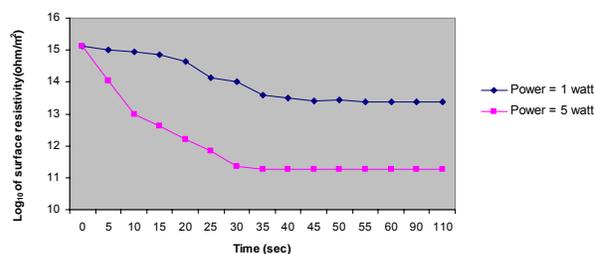
Fig. 6. Variation in the surface resistivity of polycarbonate at different power levels.

For 55 seconds of exposure time at 5 watt power the surface free energy of PP has been found to increase to 50 mJ/m^2 while for untreated PP sample it was measured to be 29.90 mJ/m^2. Similarly the surface energy of PC thin sheet for the same exposure time and power level has been observed to be increased to 52 mJ/m^2 while for untreated sample it was only 34 mJ/m^2.

The surface free energy of thin sheets of PP and PC and their polar components have been found to be increased with increase of both exposure time and treatment power. The reason behind this is believed the presence of the charged species in plasma of oxygen abundance. Charged species gets accelerated between electrodes when a DC voltage is applied between them and transfers their energies to the atoms of the polymer chain which results in chain breaking. The chain gets oxidizes at the points of chain scission in the oxygen abundance environment. So the increase in the treatment time and treatment power leads to enhancement of polar group at the polymers surfaces, which results in the increase of the surface free energy and a decrease in the surface resistivity.

4. Conclusions

A significant change in the surface resistivity of thin sheets of PP and PC has been observed. The surface resistivity of untreated sheet of PP was measured to be 1.24×10^{12} Ω/cm^2 which has been found to decrease to

1.26×10^9 Ω/cm^2 when it was treated for 55 second at power level of 5 watt. Similarly for untreated PC thin sheet the surface resistivity was measured to be 1.32×10^{15} Ω/cm^2 but after treatment at power level 5 watt for 55 seconds it decreased to 1.83×10^{11} Ω/cm^2. So the surface resistivity of thin sheets of both PP and PC has been found to decrease and the surface free energy has been observed to increase at the same power level and the treatment time. The decrease of the surface resistivity is assumed to be caused by polar component of the surface free energy as it changes in the same fashion as the surface resistivity.

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[*]Corresponding author: rajeshkumarf11@gmail.com