

Effect of DC Glow Discharge Treatment on the Surface Energy and Surface Resistivity of Thin Film of Polypropylene

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ABSTRACT: A change in the surface energy and surface resistivity of a thin film of polypropylene (PP) of thickness 100 μm was investigated, using direct current (DC) glow discharge. The thin film of the PP was treated for various discharge powers and treatment time and the modification in the surface energy and the surface resistivity was observed. To investigate the modification in the surface energy after DC glow discharge treatment, contact angle of two test liquids formamide and de-ionized water over the surface of PP film was measured. By measuring the contact angle the change in surface energy and its two polar and dispersive components have been measured. It was observed that at a given power level of DC glow discharge

surface energy and its polar component increases with increase of the treatment time, attains a maximum value, and then becomes almost constant. Correspondingly, with increase in surface energy, a decrease in surface resistivity was observed. Also, a change in surface morphology was observed by atomic force microscopy and by FT-IR spectra generation of polar groups at the surface of PP film. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 767–772, 2007

Key words: polypropylene (PP); DC glow discharge treatment; surface modification; contact angle; surface resistivity

INTRODUCTION

It is well known that polymers are widely used both for high-technology and consumer product applications because of many desirable physical and chemical characteristics such as high strength-to-weight ratio, resistance to corrosion, and relatively low cost, etc., and they have replaced traditional engineering materials such as metals. Polymer surface is important in a number of applications such as adhesion promotion,¹ wetting,² colloidal stabilization,^{3–5} and biocompatibility.⁶ Polypropylene (PP) is one of the most widely used commodity thermoplastics, especially in automotive, electric, packaging, and consumer application. The reason for this can be found in its excellent properties, such as good processing, heat distortion temperature above 100°C, recycling ability and favorable price/performance ratio.⁷ Recently, studies on improving surface wettability on PP films using various surface modification techniques have been reported.^{8,9} In the present study DC glow discharge¹⁰ was employed to study the effect on the surface energy as well as resistivity of a thin 100 μm film of PP.

The surface energy of liquid adhesives and polymers is about 100 mJ/m^2 , while for ceramics and metals it is about 500 mJ/m^2 .¹¹ Therefore liquid adhesive spreads freely over the solid surfaces of the ceramic and metals, since there is a large decrease in the free energy of the system accompanying spreading, which shows high work of adhesion. But the surface energy of liquids is low and is comparable with that of polymers and the system shows nonspreading and low work of adhesion.

Adhesion is fundamentally a surface property that is governed by a layer of molecular dimensions.¹² Essentially adhesion of an adhesive to solid surface depends upon wetting.¹³ Wetting is qualitatively defined by reference to a sessile liquid drop resting on a solid surface at equilibrium. Information obtained from contact angle measurement for a wide range of solid substrates has proved vital to the formulation of biocompatible, adhesive and composite materials and in generating fundamental understanding of solid–solid and solid–liquid intermolecular interactions.^{14–20} For perfect wetting, contact angle θ should be zero. It also possible for liquid adhesives to spread and wet a solid surface when $\theta > 0^\circ$, but this requires the application of a force to the liquid adhesive to spread it forcibly over the solid surface.

Zisman²¹ gave a method for approximating the surface energy of solid substrate in the context of wetting,

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TABLE I
Surface Tension (γ_{LV}), Its Dispersive (γ_{LV}^D) and Polar (γ_{LV}^P) Components for Test Liquids

Liquid	Polar, γ_{LV}^P (mJ/m ²)	Dispersion, γ_{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

by introducing the concept of critical surface tension (γ_C), the minimum surface tension of a liquid by which the liquid spreads on solid spontaneously. The critical surface tension was taken as an approximate measure of the surface energy (γ_{SV}) of solid polymers having low surface energy. Thus these are difficult to wet and bond, as it requires adhesives 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 thereby exhibiting good bonding.

Introduction of various polar groups over the surface of polymers is necessary for better adhesion so as to increase the surface energy, since lower surface energy leads to poor adhesion.²² Numerous methods have been developed to modify polymer surfaces such as laser, corona, wet chemical, UV/ozone, and plasma treatments.^{22–28} Glow discharge method has become popular because of its better performance over the other methods as it results in better uniformity in the surface modification of polymers. Moreover, it is a dry treatment method, which is better suited for industrial applications. It is now well established that the discharge treatment creates physical and chemical changes such as crosslinking, degradation, and formation of new chemical functionalities.²⁹ The temperature of gases in the glow discharge generally remains low or ambient and plasma plays a predominant role in the surface modification of polymers. It is possible to create glow discharge with either DC or RF power sources. In industry, RF glow discharge is generally employed for surface modification of polymers. In the present study DC glow discharge was employed to see the effect on the surface energy as well as resistivity of a thin 100 μm film of polypropylene.

EXPERIMENTAL

In this investigation high density polypropylene thin film was used. The thickness of polypropylene film was about 100 μm . Drops of 5–7 μL volume of two test liquids, de-ionized water and formamide, of known polar and dispersion components of surface tension were used to evaluate the polar and dispersion components of surface energy of the PP film through measurement of their contact angle at a temperature of 27–30°C. The known components of surface tension of liquids are given in Table I.⁷

The DC glow discharge treatment of PP film was carried out in a vacuum chamber. The set-up contained a closed glass chamber of height 450 mm and diameter 300 mm. Through an inlet, air or other desired gases could be introduced into the glass chamber. A pair of 4-mm thick aluminum plates of diameter 80 mm was used as anode and cathode inside the glass chamber. The anode was fixed and an adjustable cathode was set to control the spacing between the two electrodes; in this study the spacing was kept at 100 mm. PP film cleaned by acetone was kept on the cathode. Inside the glass chamber, vacuum was created with the help of a rotary oil pump. A pressure of 0.3 Torr, measured by a Pirani gauge, was maintained inside the glass chamber. At this low pressure DC voltage exceeding 200 V was applied between the electrodes to ignite the glow discharge.

Surface modification of the polymer under DC glow discharge depends upon various process parameters, namely, duration of exposure, discharge power, spacing between the electrodes, and the type of the plasma gas. In this investigation the surface of PP film was modified using DC glow discharge treatment through air plasma, under different exposure times and powers, and the temperature through the whole process was 27–30°C. The schematic diagram for DC discharge chamber is shown in Figure 1. The different power levels and the exposure times used in the work are shown in the Table II.

Estimation of surface energy

Surface energy was estimated using the equation of state:

$$(1 + \cos \theta)\gamma_{LV} = 2(\gamma_S^D \gamma_{LV}^D)^{1/2} + 2(\gamma_S^P \gamma_{LV}^P)^{1/2} \quad (1)$$

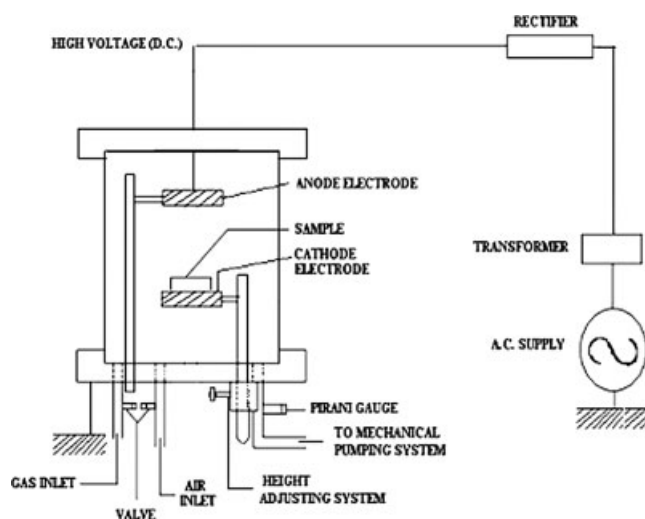


Figure 1 Schematic diagram for DC glow discharge treatment chamber.

TABLE II
Discharge Powers and Exposure Times

Discharge power (watt)	Duration of exposure (s)
1.0	5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 90, 110
3.0	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

At first, the contact angle (θ) of de-ionized water, was measured. Therefore, in this equation, θ is the measured contact angle of de-ionized water, where known surface tension of de-ionized water (γ_{LV}) and its two components namely polar (γ_{LV}^P) and dispersion (γ_{LV}^D) components were used from Table I. Therefore, the contact angle of de-ionized water results in a set of equations of two unknowns γ_S^P and γ_S^D of PP film surface. Again, the contact angle of formamide (θ) was measured on the PP film surface; θ was the measured contact angle of formamide and known surface tension of formamide (γ_{LV}) and its two components namely polar (γ_{LV}^P) and dispersion (γ_{LV}^D) were used from Table I. Therefore the contact angle of formamide results in another set of equation of two unknowns γ_S^P and γ_S^D of PP film surface. Solving these two equations, the unknown γ_S^P and γ_S^D of the PP film were calculated. Finally, total surface energy (γ_S) was estimated by adding γ_S^P and γ_S^D :

$$\gamma_S = \gamma_S^P + \gamma_S^D \quad (2)$$

The schematic diagram for contact angle measurement is shown in Figure 2. The contact angles for de-ionized water and formamide on untreated samples of the PP film are shown in the Figures 3 and 4. The surface energy and its components variation for different values of the power and exposure times are shown in Figures 5–7.

Measurement of resistivity

To study the effect of DC glow discharge treatment on the resistivity of the polypropylene thin film, the resistivity measurement was carried out. To study the effect of treatment on resistivity, the resistivity of both types of samples—treated as well as untreated—was measured. Before the measurement of resistivity, the

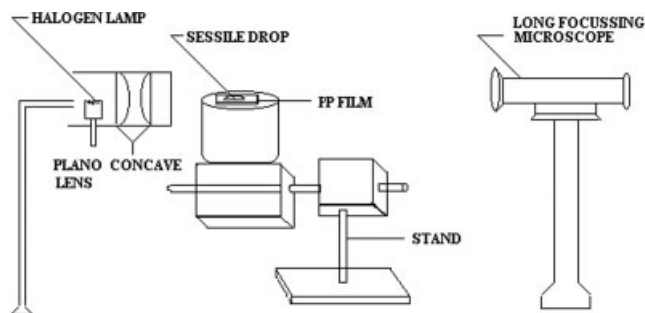


Figure 2 Schematic diagram for contact angle measurement.

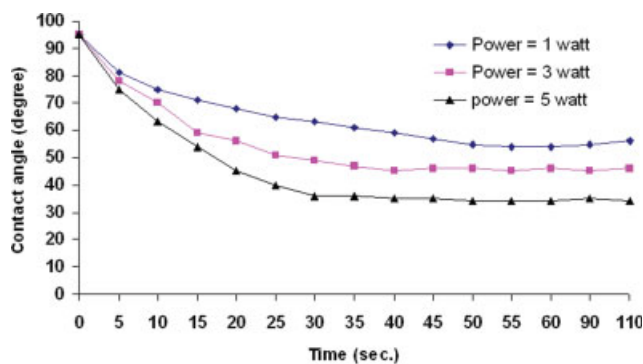


Figure 3 Contact angle versus treatment time for de-ionized water at different power levels. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

untreated and treated samples of polypropylene film were coated by aluminum from both sides in high vacuum, of the order of 10^{-6} mb, to make electrical contact. The coating was done using mask and the coating area was kept same. For measurement of resistivity, the resistance of samples was measured using high-resistance measuring electrometer capable of measuring resistance of order of 10^{16} Ω . The sample was mounted on a sample holder to make the electrical contacts and this sample holder was fixed on a self-made test fixture. The electrometer is capable of measuring the resistance of sample in two modes. In the first mode it can give the direct value of sample resistance; and in the second mode the source voltage of the electrometer is applied across the sample and current is measured through electrometer and then from I - V characteristics the value of resistance can be calculated. The resistance of the samples was measured using both measurement modes. The resistivity of treated samples of polypropylene for the different time exposures and power levels is shown in the Figure 8.

AFM and FT-IR analysis

The surface morphology of untreated and treated samples of PP films was characterized on a nanoscope III, a

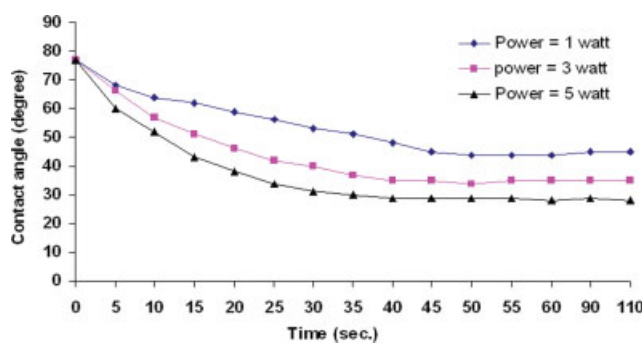


Figure 4 Contact angle versus treatment time for formamide at different power levels. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

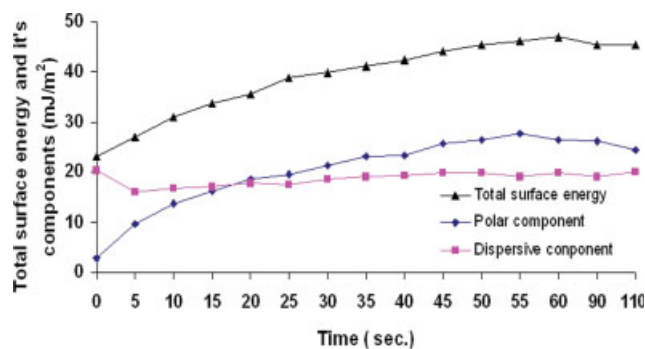


Figure 5 Surface energy and its components versus treatment time for power = 1 W. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

multimode atomic force microscope. In each case an area of $2 \times 2 \mu\text{m}^2$ was scanned using silicon tip in tapping mode. All measurements were conducted in normal air pressure and $27\text{--}28^\circ\text{C}$ temperature. The samples of the PP film were attached on a metal plate by an adhesive tape. Each sample treated at different power levels was measured with a new unused tip to avoid contamination. FT-IR was also used to observe the chemical changes by treatment on the samples.

RESULTS

Wetting characteristics of PP film are found to be significantly changed under exposure of DC glow discharge as evident from the lowering of contact angle of the test liquids, de-ionized water and formamide, indicating an increase in its surface energy. The extent of change in the surface energy and surface resistivity with the variation of conditions for glow discharge such as time of exposure and power was determined

The variation in contact angles of the two test liquids, de-ionized water and formamide, on treated PP film with respect to treatment time (exposure time) at different power level is shown in Figures 3 and 4, respectively. These plots show that at fixed power level, con-

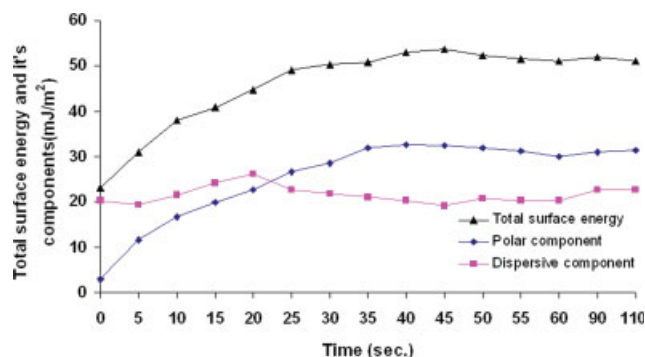


Figure 6 Surface energy and its components versus treatment time for power = 3 W. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

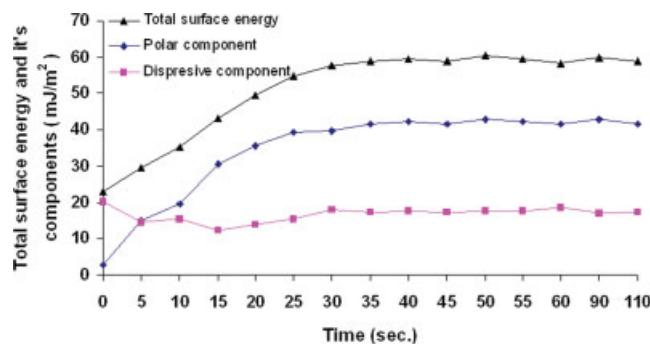


Figure 7 Surface energy and its components versus treatment time for power = 5 W. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tact angle decreases with treatment time for water as well as formamide. The contact angles for water and formamide on untreated samples of PP film were measured to be 95 and 77° respectively. When the power was 1 W the contact angle of water decreased to 53° for the treatment time of 60 s as shown in Figure 3, and it decreased to 43° in case of formamide for the same treatment time as in shown Figure 4. A further decrease in the contact angle with respect to treatment time was observed for the power values of 3 and 5 W. Also, it was observed that for high power levels the minimum value of the contact angle is found for low treatment times.

The variation in the total surface energy and its components (polar and dispersive) with respect to treatment time for different power levels was observed (Figs. 5–7). For power level of glow discharge of 1 W, the total surface energy was found to become 45 mJ/m^2 at 60 s of treatment time (Fig. 5). At 3 W of glow discharge the total surface energy was observed to be 52 mJ/m^2 for treatment time of 45 s (Fig. 6). The rise in the total surface energy for the glow discharge power 5 W was observed to be 60 mJ/m^2 for treatment time of 35 s (Fig. 7). It was observed that after certain time the total surface energy

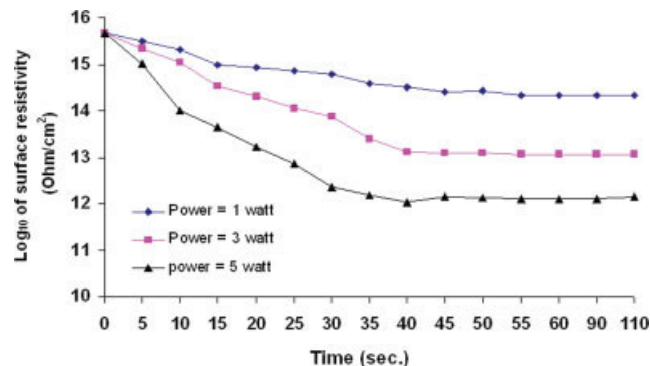


Figure 8 Variation in surface resistivity versus treatment time at different power levels. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

becomes almost constant. A similar variation in the polar component of the surface energy also was observed. In case of the dispersive component of the total surface energy the variation is found to be different. It was observed that its value first decreases and then becomes almost constant for all three power values.

The variation of surface resistivity with respect to treatment time is shown in Figure 8. It is clear from the plots that surface resistivity decreases with treatment time. For lower power of 1 W, surface resistivity decreases from 4.59×10^{15} ohm/cm² (on log₁₀ scale 15.6618) to 2.56×10^{14} ohm/cm² (on log₁₀ scale 14.4084) for the treatment time of nearly 60 s and for the further times it remains almost constant. For power of 3 W, it decreases up to 1.20×10^{13} ohm/cm² (on log₁₀ scale 13.0795) for treatment time of nearly 45 s. For the maximum power level that we have used in the experiment, that is, 5 W, the surface resistivity decreases to 1.24×10^{12} ohm/cm² (on log₁₀ scale 12.0941) for treatment time of nearly 35 s.

Figure 9(a) shows the AFM image of untreated PP film. Figure 9(b) shows the AFM image of sample treated for 60 s at power level 1 W, which depicts a change in surface morphology. Figures 9(c) and 9(d) show AFM images for treated samples for 45 and 35 s at

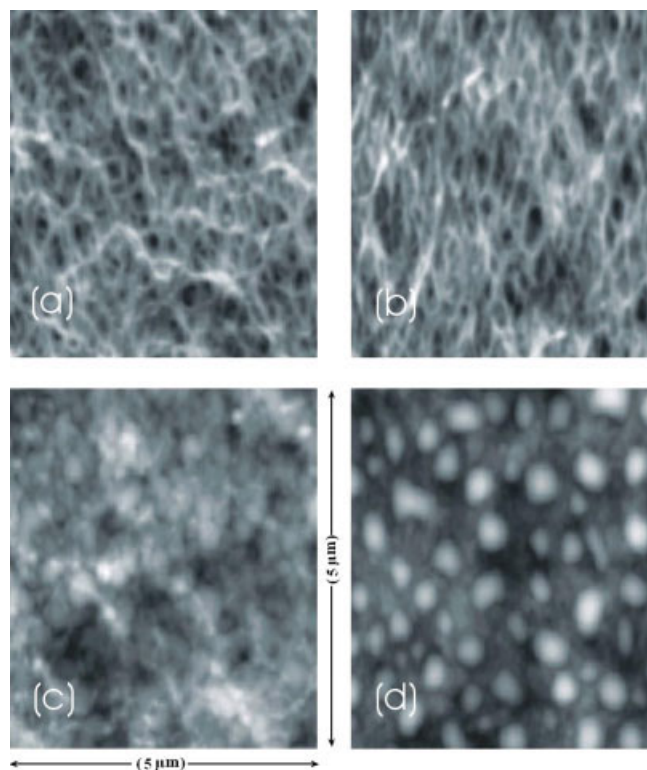


Figure 9 Topographic AFM images for (a) untreated, (b) treated for 60 s at 1 W, (c) treated for 45 s at 3 W, and (d) treated for 35 s at 5 W. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

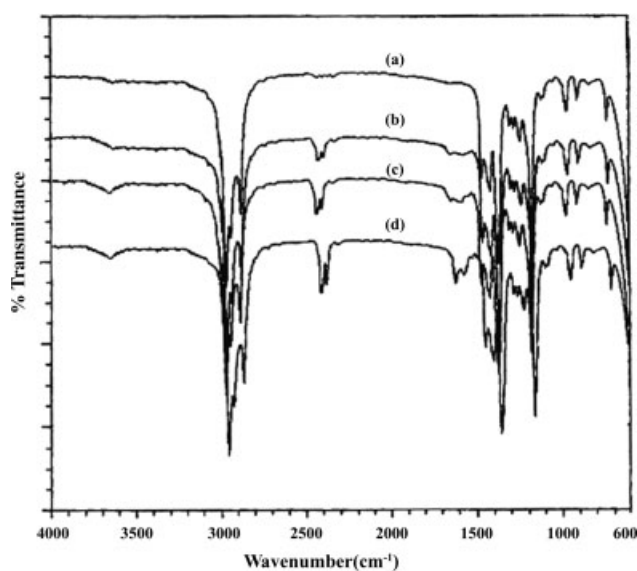


Figure 10 FTIR spectra for (a) untreated, (b) treated for 60 s at 1 W, (c) treated for 45 s at 3 W, and (d) treated for 35 s at 5 W.

power levels 3 W and 5 W respectively. Also, FT-IR spectra for the similar samples are shown in Figure 10. Figure 10(a) shows the FT-IR for untreated polypropylene sample. As the levels of treatment power were increased to 1, 3, and 5 W, some groups are generated at the surface of the treated samples as shown in Figures 10(b–d).

DISCUSSION

Polymers have very low surface energy and therefore show poor wetting characteristics. For many applications the surface energy of the polymers need to be increased so that the wetting characteristics of polymers could be increased. The surface modification of the PP film by exposure to DC glow discharge in air was carried out to alter the wetting characteristics and hence to increase the surface energy.

It was observed that the surface energy of untreated PP film is nearly 23 mJ/m², and after modification it increased up to 60 mJ/m² when exposed to DC glow discharge at power level of 5 W for 35 s.

The surface modification by exposure to DC glow discharge decreases the contact angle of de-ionized water and formamide on PP surface as shown in Figures 3 and 4. At a given power the contact angle of PP film surface with sessile drops of de-ionized water and formamide decreases.

The polar component of surface energy of PP film increases with increasing power as well as time of exposure of DC glow discharge, as shown in the Figures 5–7. It is clear from these figures that the polar component increases in the same fashion as the total surface energy

while the dispersion component remains constant except for small changes for the initial time values.

The total surface energy of the PP film and their polar component could be increased either by increasing the duration of exposure of DC glow discharge or by increasing its power. The cold plasma in glow discharge is a partially ionized fluid or, as a whole, is electrically neutral. The reactive species include electrons, ions, free radicals, and various neutral molecules characterized by low degree of ionization. The charged species under the electrical field gets accelerated and undergoes collisions among themselves and with the substrate polymer. If the colliding species has sufficiently high energy the collision may transfer sufficient energy to the atoms in the polymer chain to break the bonds. In oxygen abundant environments, the chain gets oxidized at the point of scission; when the duration of exposure increases, the number of collisions leading to breaking of bonds and oxidation increases. The power of glow discharge determines the energy of ions of the gaseous species and higher energy results in higher rate of collision capable of breaking bonds. Thus, from the Figures 5–7, it is clear that on increasing both the time of exposure as well as the power, leads to enhanced chain breaking and oxidation leading increased polar component of surface energy. It is clear from the results that the increase in surface energy and decrease in surface resistivity mainly depends on the polar component of the surface energy. AFM images for treated samples show the change of surface morphology. Figure 9(a) shows the AFM image for untreated sample. For the sample treated for 60 s at 1 W, nodule-like features emerge [Fig. 9(b)]. Increasing power level to 3 and 5 W, surface morphology is completely changed at 45 and 35 s of treatment time [Figs. 9(c) and 9(d)].

In FT-IR spectra (Fig. 10), the appearance of an absorption band in the 3600–3200 cm^{-1} regions is assigned to the hydrogen bonded O–H stretching vibration of generated alcoholic (–OH) and carboxylic (–COOH) group. The wide peak between 2400 and 2350 cm^{-1} represents the olefinic bonds and carbon–nitrogen groups or it may be the part of very broad and feeble intensity O–H of acidic group. A narrow band between 1720 and 1645 cm^{-1} confirms the presence of carbonyl (C=O) of the –COOH or ester (–COOR) group. Peak between 1200 and 1150 cm^{-1} represents the C–O stretching of carboxylic (–COOH) or ester (–COOR) group.

CONCLUSIONS

An increase in the surface energy and decrease in surface resistivity of a thin film of PP film was observed. The surface energy of PP film before the treatment was measured to be 23 mJ/m^2 and after the treatment under DC glow discharge it increased to 60 mJ/m^2 for treatment time of 35 s at power level

of 5 W. It was observed that the increase in surface energy is mainly dependent on its polar component. The surface resistivity before the treatment was measured to be 4.59×10^{15} ohm/cm^2 (on \log_{10} scale 15.6618), which after treatment was found to be 1.24×10^{12} ohm/cm^2 (on \log_{10} scale 12.0941) for the sample that was treated for 35 s at power level 5 W. So with the increase in surface energy, a corresponding decrease in surface resistivity was observed for the samples treated for maximum time of 35 s and power 5 W. Change in surface morphology and generation of polar groups was observed by AFM and FTIR analysis.

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