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# Modification of Surface Properties of Polymeric Materials

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## Abstract

Polymeric materials are successfully used in virtually all industries ranging from semiconductors, and coatings, to household appliances, automotive, and biomedical implants. Polymers generally have excellent bulk physical and chemical properties. However, certain properties of polymers such as low surface energy, low wettability, and high electrical resistivity sometimes limit their applications. Changing the bulk formulation of the polymers can alter some of these properties, but in general this is not acceptable as it can affect "desirable" bulk properties. Surface modification techniques have been used to alter polymer surfaces without affecting the bulk properties of the material. Most polymers have very high surface and bulk resistivity, which causes static charge problems in many applications. One such application is powder coating where the accumulation of excess charge causes an adverse impact on the appearance of the powder layer. Similarly the buildup of static charge during processing and application of polymer films in packaging industries is often harmful to sensitive electronic components such as those used in the computer industry. Charge buildup may be reduced by surface modification to control the surface resistivity. In this work, atmospheric plasma treatment was used to modify the surface resistivity of polymers. The surface resistivity of polyethylene film decreased from  $1.28 \times 10^{16} \Omega/\square$  to  $5.73 \times 10^{15} \Omega/\square$  at 18% RH.

## Introduction

In the last few decades synthetic polymers have replaced several materials, such as metals, and have extended their application to many innovative processes. This is due to their superior physical and chemical characteristics such as high strength to weight ratio, corrosion resistance and chemical inert nature. They are also relatively inexpensive and easy to process. At the same time some of these properties impose a limitation on applications in several new and high technology areas. Thus it is required that their surface properties be modified to suit a particular application without affecting their bulk properties. One such application is the use of conductive plastic packaging for protecting semiconductor chips against electrostatic discharge.

Surface modification is quite often used to create surfaces with properties considerably different from that of the bulk of the polymeric materials. Since the polymer surfaces are non-reactive, and surface modification involves chemical alteration of the surface layer, it requires the generation of high-energy species such as radicals, ions, and molecules in an excited electronic state to promote a surface reaction. This is achieved by techniques such as flame, plasma, UV, laser, X-ray and  $\gamma$ -ray, electron beam, ion beam, and corona treatment.

Plasma treatment is one of the most widely used surface treatment techniques. Plasma can be defined as a mixture of

charged and neutral species, such as electrons, positive ions, negative ions, radicals, neutral atoms and molecules. During plasma treatment, the composition and structure of a few molecular layers at or near the surface (approximately 10 nm) is modified due to the action of the energetic particles. This has been used to alter surface properties of polymers such as adhesion to metals and to other polymers, wettability, and printability, without changing their bulk properties (Briggs, 1982; Garbassi et al., 1996; Wu, 1982; Chan, 1994a, 1994b).

Typically most polymeric materials have extremely high electrical resistivity. Though high electrical resistivity of polymers is required in certain applications, such as insulative shielding on cables; it may be an undesirable property in other areas. The high surface resistivity can cause static charge problems in applications such as powder coating where typical powder paints (epoxy, acrylic, urethane or polyester) have high surface resistivities ( $\rho > 10^{14} \Omega/\square$ ). During the electrostatic powder deposition process, the highly resistive powder layer does not allow the electrostatic charge to decay at a rate fast enough to avoid the formation of back corona. The accumulation of excess charge has an adverse impact on the appearance of the powder layer (Cross, 1987; Bailey, 1998; Mazumder, 1998). Similarly, the buildup of static charge during processing and application of polymer films in the packaging industry is often harmful to sensitive electronic components such as those used in computers. Many times the buildup of static

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charge in the polyethylene packaging film damages the semiconductor chips (Fowler, 2001). This damage can be avoided by decreasing the surface resistivity of polymer films.

Various approaches have been utilized to decrease resistivity of polymers (Fowler, 2001; Ha, 2000). The electrical resistivity can be decreased by deposition of a thin layer of conductive polymer on the surface or by micro-encapsulation. Changing the chemical formulation could also decrease the resistivity of polymers. Long chain amines, such as POE, are used as anti-static agents. They are added to the bulk formulation during polymer synthesis. These additives have surfactant like structure with a polar head and a hydrocarbon chain. They migrate to the polymer surfaces where they form a micelle-like structure. The micelles act as moisture traps increasing the conductivity of the surface (Rosen, 1997). The above-mentioned approaches are not very well accepted due to cost and/or contamination considerations.

Previous studies on plasma treatment of polyethylene have shown the modification of chemical-surface structure to render the surface more hydrophilic (Liston et al., 1993; Foerch et al., 1993). A more hydrophilic surface will adsorb more moisture on the surface making it more conductive. Thus plasma treatment could decrease the electrical resistivity of polymer surfaces. The plasma treatment of polymers has been intensively studied using low-pressure plasmas, but very little work has been reported on plasma treatment under atmospheric conditions. In this work atmospheric plasma was used for surface modification of low-density polyethylene film.

### Materials and Methods

A plasma reactor was built for surface modification of polymer films with air as plasma gas. A low-density polyethylene (LDPE) film (100 mm thick), obtained from Fisher Scientific, was used for plasma treatment. The polymer film was exposed to plasma in the reactor, as shown in Fig. 1. The reactor is composed of a plasma generator and a grounded aluminum panel as an electrode. The plasma generator consists of a 200 mm long hemispherical Poly methyl methacrylate (PMMA) tube with 100 mm diameter stainless steel wire as the electrode. A high voltage (10 kV) AC power supply was used for generation of plasma. The surface resistivity of plasma-treated and untreated LDPE film was measured at various relative humidities to assess the effect of plasma treatment.

The polymer sample was plasma treated for 0.16, 0.5, 1, 2, 5, and 10 min, successively. After each treatment the film was exposed to an environment of known RH for 5 min in an environmental chamber before the surface resistivity was measured. RH values in the chamber were maintained

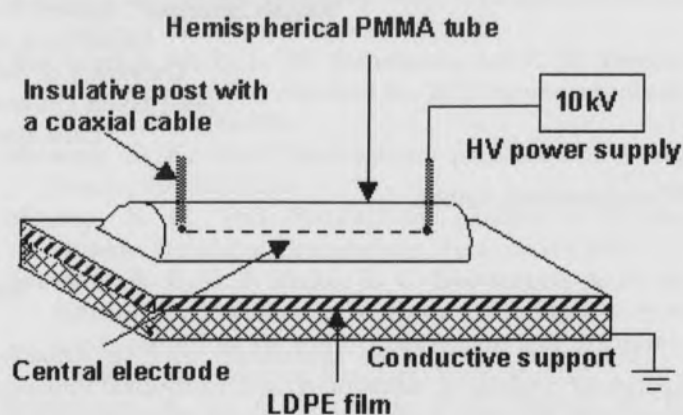


Fig. 1. Plasma treatment reactor for surface modification of Polymer films.

within  $\pm 1\%$  of the desired RH in the range of 50 – 90%.

The surface resistivity of a film was measured using the setup shown in Fig. 2. A surface resistivity instrument (Model 8009 by Keithley Instruments) was used along with an electrometer (Model 6517 of Keithley electrometer) in this setup. The measurements were also performed inside the environmental chamber.

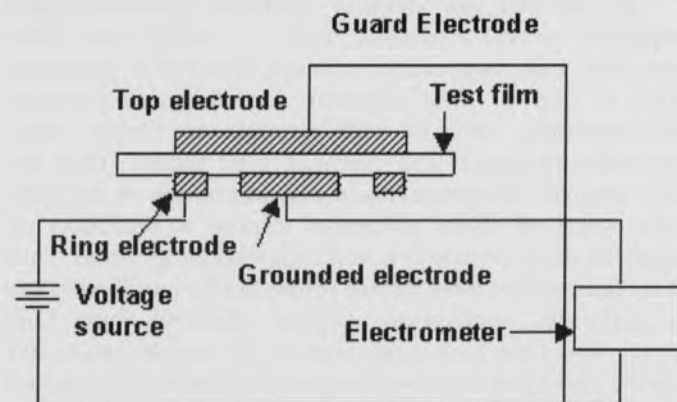


Fig. 2. Surface resistivity measurement setup.

To study the effect of plasma treatment on surface morphology, an untreated sample and a plasma treated sample of acrylic polymer were observed under an atomic force microscope.

### Results and Discussion

The surface resistivity of a polyethylene (LDPE) film was

measured at different relative humidity values varying between 18% and 90%. The surface resistivity was found to decrease with increasing humidity. The surface resistivity declined from  $1.28 \times 10^{16} \Omega/\square$  at 18% RH to  $2.73 \times 10^{12} \Omega/\square$  at 90% RH. The sample was plasma treated for 10 sec, and the surface resistivity was measured again. The surface

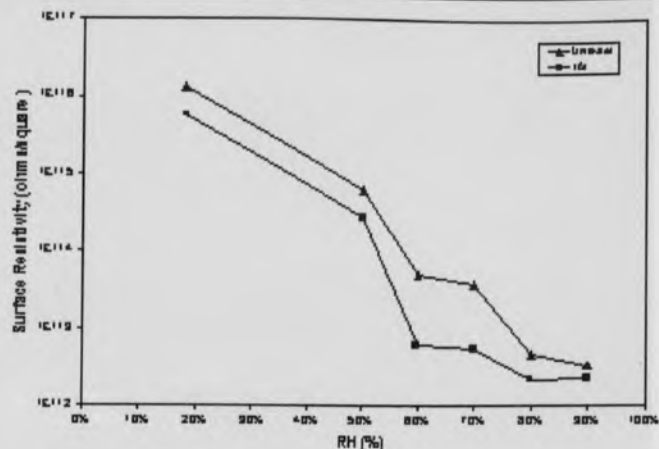


Fig. 3. Effect of plasma treatment on surface resistivity of LDPE film.

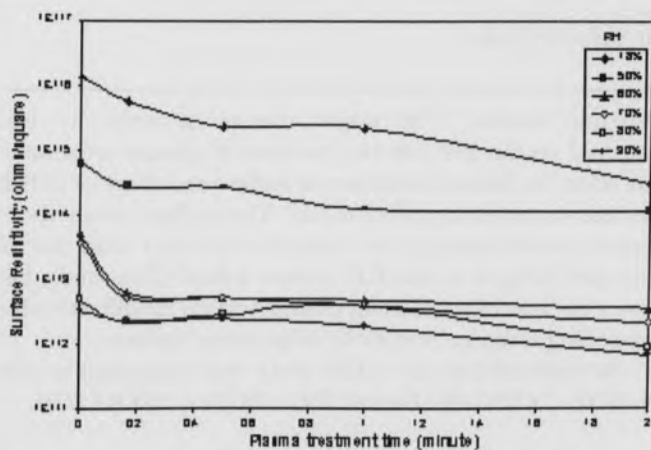


Fig. 4. Plasma treatment of LDPE films for different duration.

resistivity was found to decrease to  $5.73 \times 10^{15} \Omega/\square$  at 18% RH. The plasma treated sample was exposed to higher RH of 50, 60, 70, 80 and 90%. Similar to the untreated sample, a decrease in surface resistivity was observed with an increase in relative humidity. The surface resistivity of the plasma treated sample was lower than that of the untreated sample at all RH values tested (Fig. 3). Experiments with plasma treatment times of 30 sec, and 1, 2, 5, and 10 min showed insignificant changes after 2 min. A decrease in surface

resistivity was mainly observed for treatment times of less than 2 min (Fig. 4). An atomic force microscope (AFM) was used to characterize of surface roughness of treated and untreated sample. Plasma treated sample was found to be rougher than untreated sample (Fig. 5).

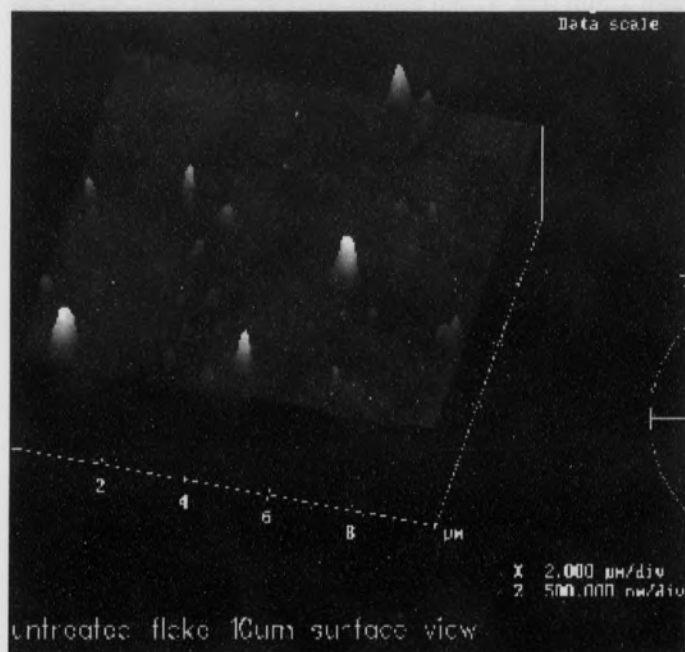
The decrease in surface resistivity with increasing relative humidity for the untreated sample could be due to formation of a conductive moisture layer over the sample surface. The change in surface resistivity with plasma treatment could be a result of processes at three different levels.

On the physical level, plasma treatment causes a change in the morphology of the surface. It distorts the surface leading to formation of micro-dents, which increases the surface roughness and the effective surface area. An increase in surface area results in more moisture adsorption, thereby increasing the surface conductivity. The AFM characterization of the plasma treated surface and the untreated surface substantiates the argument about the increase in surface roughness.

The change in surface chemistry of a polymer surface due to plasma treatment has been investigated in detail by several researchers (Wu 1982; Chan 1994a). Plasma treatment in air can generate several oxygen and nitrogen functionalities on the surface. It causes the uptake of oxygen by polymer surfaces leading to the formation of C-O-C (or C-OH), C=O and O-C=O groups. The plasma treatment is also known to increase the O/C ratio. More highly oxidized carbon increases with an increase in the O/C ratio. Initially the oxygen adds preferentially to specific carbon atoms unless no further C=O bonds can be formed. Further oxygen adds to the carbon that has already reacted leading to the formation of O-C=O species. Since the plasma treatment was carried out in air, the nitrogen also adds to the polymer as amine functional groups (C-NH<sub>2</sub>, C-NHR, C-NR<sub>2</sub>) and imines (C=N). These groups cause the increase in surface energy that makes the surface hydrophilic. The increase in surface energy results in the adsorption of more moisture on the surface making it more conductive. Besides the addition of polar functional groups, the plasma treatment also causes graphitization of the polymer surface, which strongly affects the electrical conductivity. There was a significant difference in surface resistivity of the plasma treated and the untreated sample at 18% RH. That could be due to the breaking of C-C bonds in polyethylene and the introduction of polar groups from the air making the surface hydrophilic. At higher RH there is not much difference in surface resistivity of plasma treated and untreated films. This could be due to attaining saturation in adsorption of the moisture layer. Longer treatment times, such as 5 or 10 minutes, could result in excessive chain scission leading to a layer of short chain oxidized material on the surface which has been referred as low-molecular-weight oxidized



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(A) Untreated Acrylic surface



(B) Plasma treated Acrylic surface

Fig. 5. AFM image of an (A) untreated and (B) plasma treated acrylic polymer flake.

material (LMWOM) by many researchers. The role of LMWOM on the polymer surface has not been very well understood (Chan, 1994a). There have been contradictory reports about their function of this material. But longer treatment time and higher RH are conducive to the formation of LMWOM.

On a molecular level the decrease in resistivity may also be explained on the basis of changes in electronic surface states. The addition of oxygen may create both occupied and unoccupied surface states that could change the Fermi level. A small concentration of nitrogen could create additional unoccupied surface states that again could change the Fermi level, bringing it closer to conduction band.

### Conclusions

Surface modification of the low-density polyethylene (LDPE) substrates was carried out using plasma treatment to lower the electrical resistivity. Plasma treatment decreased the surface resistivity of polyethylene film from  $1.28 \times 10^{16} \Omega/\square$  to  $5.73 \times 10^{15} \Omega/\square$  at 18% RH. The LDPE surface was plasma-treated for 0.16, 0.5, 1, 2, 5, and 10 minute successively. In all the cases it was found that the surface resistivity of plasma treated LDPE was lower than an

untreated surface. The major change in resistivity was observed within the first two minutes of plasma treatment. The effect of plasma treatment on surface resistivity of LDPE was also assessed at different RH. The surface resistivity of plasma treated sample was found to be lower than that of untreated sample at all RH values tested. This study has shown the feasibility of using plasma surface modification for controlling electrical resistivity of polymer surfaces.

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