

# A COMPARATIVE STUDY OF WETTABILITY RESPONSES OF POLYETHYLENE AND POLYIMIDE SURFACES AFTER ION SHOWER TREATMENT

Alberto Amorsolo, Jr.<sup>1</sup>, Jose Cornelio Flores<sup>2</sup>, and Eric Miranda<sup>3</sup>

<sup>1,2,3</sup>Materials Science and Engineering Program, Department of Mining, Metallurgical and Materials Engineering, University of the Philippines, Diliman, Quezon City, Philippines  
Tel: 63-2-9818500 loc 3164,<sup>1</sup>e-mail: alberto.amorsolo@coe.upd.edu.ph

Received Date: October 9, 2014

## Abstract

Surface modification of polymers can be achieved by their exposure to different plasma systems in order to improve surface properties such as wettability and adhesion in a manner that can preserve desirable bulk properties. The paper presents the results concerning wettability responses after surface modification of low density polyethylene (LDPE) and Kapton polyimide (PI), using a DC ion shower system. Plasma source gases included argon and nitrogen, and wettability of the polymer surface after treatment was quantified in terms of the contact angle exhibited by water droplets on the polymer surface. Plasma treatment parameters investigated were accelerating voltage, exposure time and chamber pressure. The vicinity of the most promising setting from the initial variable screening experiments which used argon and nitrogen was further investigated using single-factor experiments (minimum of three levels per factor) to pinpoint more precisely a setting that would yield a minimum contact angle. Results showed that LDPE appears to be more resistant to surface modification than Kapton polyimide.

**Keywords:** Ion shower, Polyethylene, Polyimide, Surface modification, Wettability

## Introduction

### Significance of Study

The semiconductor and electronics industry in the Philippines is one of the key contributors to the country's economy, accounting for a big majority of the country's exports. The manufacturing activities undertaken by this sector mainly involve the assembly and packaging of semiconductor and electronic devices. As packaging materials, polymers are prominent candidates for they are relatively cheaper, lighter in weight and easy to form compared to other types of materials like metals or ceramics [1]. There are, however, issues concerning possible problems due to lower reliability and higher incidence of failure of polymer-packaged devices.

Polymers have relatively poor adhesion to metal surfaces leading to potential problems of delamination of interfaces involving them when adhesives are absent in the presence of thermal and mechanical stresses during service. There is also a difficulty in manufacturing composite systems involving polymers such as those found in printed circuit boards or printed wiring boards. For instance, adhesive layers are conventionally used to bind the polyimide substrate to metal layers such as copper. However, during other manufacturing steps that follow such as drilling operations, smearing of the adhesive layer may occur over via

structures [2] which could lead to high contact resistance if not removed completely. This would be eliminated if the adhesion property can be improved to a level in which no more adhesive layers are needed. Any research that can lead to better adhesion property of polymers through enhanced wettability or hydrophilicity is therefore going to be a welcome development in this industry where the technology is rapidly evolving with time. Thus, a research project was envisioned to look at the feasibility of using ion shower plasma technology to enhance surface properties of two important polymers, namely polyethylene and polyimide, considering that such facility was available in the Department of Mining, Metallurgical and Materials Engineering at the University of the Philippines Diliman campus. A previous exploratory study by Aceremo [3] showed initial promise of this technology for argon-polyethylene system. This study considered nitrogen as another plasma source gas and also looked at another type of polymer which is polyimide.

The significance of the study actually goes beyond applications in the semiconductor industry since surface modification can also improve other polymer properties such as dyeing ability and printability [4] and biocompatibility [5].

### **Theoretical Background**

The technology used in this study falls under plasma technology category. Plasma is a complex mix of ionized gas, neutral species and electrons, widely known as the fourth state of matter. Plasma technology is considered as environmentally friendly since it does not use harmful chemicals and solvents nor emits toxic wastes and effluents compared to other surface modification methods such as wet chemical treatment. Inert gases are used in this study such as argon and nitrogen. Plasma methods are considered to be controllable, relatively simple and economically competitive [3].

There are many ways of generating and sustaining plasma such as using radio frequency (RF), microwave and DC power sources [6-8]. In this study, the method uses a DC ion shower source and what further distinguishes it from the other plasma systems is the extraction of the positive ions from the plasma formed inside the vacuum chamber to form, using a system of Einzel lenses, a more focused ion shower directed towards the sample mounted on the stage. An ion beam is therefore essentially produced and directed downwards to the sample but the accelerating voltage is kept at sufficiently low level in order to modify the surface region only. This is in contrast to conventional ion implantation treatments for semiconductor materials for doping purposes where higher accelerating voltages are utilized and the plasma source gases contain toxic components such as arsine or diborane.

The principle of surface modification relies on the interaction of the species in the plasma with the atoms of the polymer molecules. The transfer of energy during collision can lead to several possible events such as breaking of bonds within the molecular chain creating radical species, sputtering of atoms from the polymer, removal of weakly bonded contaminants in the surface region and formation of functional groups on the polymer surface in the presence of reactive ions in the plasma [9,10]. Once bonds are broken, the surface free energy due to unsaturated bonds is expected to increase. This manifests as a drop in contact angle measured when a droplet of a liquid like water is placed on the treated polymer surface, indicating modification of the polymer to a more hydrophilic nature.

## **Polyethylene and Polyimide**

Polyethylene and polyimide are two polymers which have major importance in industry. The former is a typical thermoplastic while the latter is a typical thermoset. Polyethylene (PE), a linear polymer made only of carbon and hydrogen atoms, is a prototype wide-gap insulator with a number of important technological applications. It is used for containers, chemically resistant linings, films for packaging and electrical/electronic applications including cable insulation and cores in UHF cables [11,12]. The type of PE used in this study is low density polyethylene (LDPE) which exhibits both amorphous and crystalline regions in the solid. LDPE has the lowest degree of crystallinity among all types of polyethylenes. PE is a well-characterized material and frequently used as a standard test case for new technologies for polymers before considering polymers with more complicated structures [3].

Polyimide (PI) is valued for its extremely high thermal resistance and is utilized for packaging of devices where heat resistance is critical such as burn-in boards oil exploration electronics and military avionics [13,14]. The glass transition of PI is 260°C. In flexible-circuit carriers, it is the flexible dry film in which the printed circuit is deposited, which is found in popular customer products such as cameras, disk drives and older telephones. It is also used in printed wiring board in the same manner as other polymers like epoxy, aramid, cyanate, ester and BT (bismaleimide triazine) [15].

## **Objectives**

The study that will be discussed in this article is part of a bigger project that considered effects of ion shower treatment on the important surface properties of LDPE and Kapton PI which includes wettability, surface roughness, adhesion and hydrophobic recovery. However, the objective of this paper is only to make a comparison of the wettability responses of the two polymers after varying important treatment parameters, namely, accelerating voltage, exposure time and chamber pressure, using single-factor multi-level experiments. The wettability is quantified in terms of the contact angle exhibited by water droplets on the treated samples. It is also part of the objective to compare the optimum responses obtained after variable screening and optimization runs and rationalize the differences based on considerations of material structure and properties.

## **Scope of the Study**

The results to be presented cover only the contact angle response right after treatment. Other studies on surface modification using plasma in literature show that the treated surface is very dynamic in nature and will attempt to go back to its original surface energy configuration given sufficient time of aging. This phenomenon is known as hydrophobic recovery [16, 17] and by itself is a response worthy of another set of studies. This study will not also include other responses studied in the project such as the surface roughness from AFM analysis and ATR-FTIR spectra to limit the length of this article.

## **Methodology**

The methodology for this research consists of four different major steps. The first part involves the preparation of the ion shower system for surface modification runs following essentially the procedure of Aceremo [3]. The second part involves the set of single-factor experiments with at least three levels per factor that builds on the results of an earlier variable

screening experiment to determine in a more precise manner the location of the optimum setting of the single factor being investigated corresponding to the minimum contact angle. The third part includes the contact angle measurement right after treatment and the characterization of other properties of the untreated polymer samples by x-ray diffraction to ascertain the degree of crystallinity complemented by differential scanning calorimetry (DSC).

## Materials

Sample sheets of Kapton PI with thickness of about 0.05 mm or 50 microns as well as low density polyethylene (LDPE) were selected as substrates and were purchased from Goodfellow in the UK in the form of 12 inch x 12 inch sheets. Both polymers were certified to be additive free.

The study made use of argon and nitrogen as plasma gas sources in their high purity form only (no mixing was done). Ultra high purity nitrogen gas (UHP N<sub>2</sub>) and high purity argon gas (HP Ar) were used for generating the plasma in the first set of trials. Ultra high purity nitrogen gas was used as plasma source gas for the optimization runs which followed.

High purity nitrogen gas (HP N<sub>2</sub>) was used in leaking the chamber and purging the pumps. Methanol (CH<sub>3</sub>OH) solvent was used for leak testing and cleaning the external and internal parts of the ion shower system. Deionized water was used for determining the contact angle. Ethanol was a solvent used to detect leaks in the chamber.

## Sample Preparation and Storage

Two kinds of polymers were investigated in the study, low density polyethylene (LDPE) and Kapton polyimide (PI). The two are very different from each other, the former having linear polymeric chains and usually classified in the group called oligomers and the latter having more of a crosslinked network of benzene rings and amines. The chemical bonds of C–C/C–H, C–O, C=O and C–N are found specifically on the polyimide type of trademark called Kapton while only C–C and C–H bonds are found in LDPE.

The polymer sheets were cut into smaller samples of 1.5x1.5 cm<sup>2</sup> areas for plasma treatment. After the ion shower runs, the side that was not exposed to plasma was marked with a label.

In order to avoid contamination of the sample surface, anti-static, powder-free gloves were worn during handling and the stainless steel cutter was also ensured to be clean. After testing of the samples for contact angle, they were all kept inside Ziplock bags, of which one replicate was stored inside a dessicator while the other kept inside a drawer.

## The Ion Shower System

The major equipment used in the research was the ion shower system, designed and fabricated by Prof. Katsufusa Shono, a professor from Sophia University in Tokyo, Japan. Upon his retirement, he donated the system to the Department of Mining, Metallurgical and Materials Engineering under the College of Engineering of the University of the Philippines in Diliman campus. The system was originally designed for laboratory-scale doping of silicon semiconductor by an ion shower extracted from dopant gases like phosphine or diborane. Its original configuration for semiconductor doping is described in the dissertation of Madrid [18] and MS thesis of Diaz [19]. Later, Aceremo [3] looked at the feasibility of modifying the

system for surface modification of polymers upon the suggestion of Dr. Henry Ramos of the UP National Institute of Physics. The modified system, shown in Figure 1, is described in her MS thesis.

The ion shower has an 85mm diameter hot cathode ion source. The gas is introduced into the ion source by a leak valve and is ionized by electrons emitted from a tungsten filament. The ion source subsystem consists of the gas source, the gas injection system, and the components that will initiate the ionization process. Formation of ions is achieved when a potential difference across the anode and cathode terminals is applied in the discharge region of the ion source. When a suitable voltage is reached, neutral gas from the source breaks down from being an insulating dielectric to conducting plasma made up of ions, electrons, metastables, among others. Electrons from the tungsten filament are attracted to the anode biased at 150V. The magnetic field generated by the solenoid coil is then varied, the amount of current in the filament is also set, as well as the applied anode and solenoid voltage to control the rate of ionization of the input gas.



Figure 1. Ion shower system at UP DMMME

During plasma ionization, the filament assembly is cooled with chilled circulating water to prevent melting of the rubber O-ring. The series of electrostatic lenses focuses the generated ions to form a beam which is accelerated into the sample target placed on the stage.

The vacuum evacuation system is composed of a vane-type rotary pump (or roughing pump) and a turbo molecular pump. The vacuum system is necessary for ion bombardment processes as these require medium to high vacuum conditions. The vacuum allows for a contamination-free surface treatment of the substrate and for the ionization process to sustain the generated plasma.

The electrical power supply and control system is a DC system that converts AC current being supplied into direct current for the voltage sources for the filament, anode, solenoid, electrostatic lens and accelerator. A probe is attached to the shutter above the target material

to measure the current and current density inside the chamber. Ammeters are used to read current levels from the shutter, probe and stage.

A compact full range gauge is attached to one of the portholes at the side of the ion shower system with a connected measuring device and readout to measure the vacuum level, gas filling and discharge pressures. It is also used to monitor the performance of the rotary pump, check for leaks and in gas line purging.

The experimental procedure for plasma treatment using the ion shower system involves three sets: a) system start-up, b) plasma stability runs, and c) actual surface modification. The details of each can be found in the theses of Aceremo [3], Flores [2] and Bombita [20]. The system start-up consists of the necessary activities required to ensure efficient and stable plasma production. The plasma stability runs ensure a production of quiescent plasma and stable machine settings.

The schematic diagram of the ion shower system is given in Figure 2. Aside from the main chamber, it has a pumping station consisting of a roughing pump, turbomolecular pump, chiller and the gas tank. In Figure 2, the gas shown connected is argon but other gases may also be connected to the chamber depending on the intended treatment.

The system evacuation process involves two stages. In the first stage of evacuation, pressure is brought down from atmospheric pressure to a base pressure of  $10^{-3}$  Torr. High vacuum up to  $10^{-6}$  Torr is subsequently achieved by turning on the turbo-molecular pump (TMP). The TMP was used to achieve a clean chamber prior to the surface modification process, since the operating pressure while the plasma is generated and while the surface modification is taking place is only at  $10^{-2}$  Torr, and only the rotary vane pump is actually turned on during the exposure of the substrate.

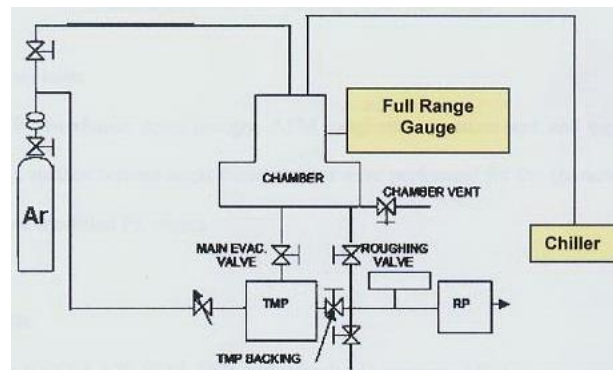


Figure 2. Schematic diagram of ion shower system [3]

Before doing actual surface modification, plasma stability runs were carried out in which the machine settings needed to produce quiescent plasma was determined by manipulating the combination of the filament current and voltage, anode current and voltage, upper and lower electrode currents and accelerator current and voltage at the set plasma source gas discharge pressure. Stable plasma with a pink to purple color in the electrostatic lens column and view porthole was observed in the case of nitrogen plasma. A typical image of the ion beam is shown in Figure 3 which shows the characteristic glow discharge of plasma.

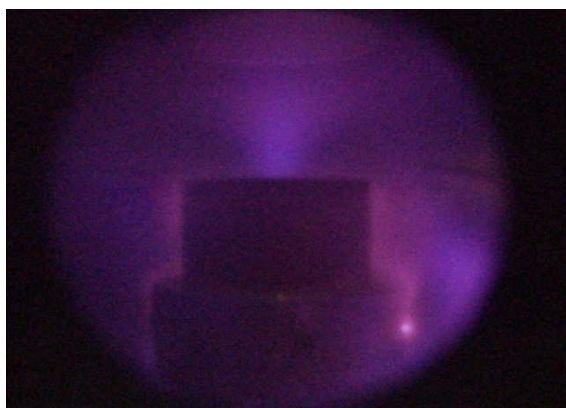


Figure 3. Typical nitrogen ion beam produced in the ion shower system [2]

### Surface Modification Procedure

The sample substrates of either LDPE or Kapton polyimide were loaded on the stage of the ion shower. The metal sleeve which was previously removed was then returned on the stage. Evacuation was performed down to a base pressure of  $10^{-3}$  Torr, and once this was achieved, the plasma source gas was injected at a flow rate corresponding to 5 psi until the desired discharge pressure/chamber pressure was achieved and made stable. High and low settings were set respectively. Chilled recirculating water was supplied. The filament voltage and current were also increased from the settings, with current in units of amperes increased from 0 to 31 with 1 min intervals between increments of 0-5, 5-12, 12-20 and lastly 20-31. The anode current and voltage, solenoid current and voltage, electrode currents for upper and lower lenses were also supplied. The ions generated were accelerated towards the stage by supplying the set accelerating voltage. When the quiescent plasma was generated and stable ammeter readings achieved, the shutter was opened to allow exposure of the samples to the ion shower for the designated exposure time setting.

### Experimental Design

A fractional factorial experiment (half of a  $2^4$  full factorial with two replications) [21] was initially used for the variable screening study to identify promising settings that yielded low contact angles. This initial set of experiments prior to the optimization runs investigated four factors, namely accelerating voltage, type of gas, exposure time and chamber pressure. The plasma source gases used were argon and nitrogen. The treatment settings are summarized in Table 1.

**Table 1. Low to High Settings of Treatment Parameters in the Fractional Factorial Experiment**

Plasma Source Gas	Accelerating Voltage (kV)	Exposure Time (min)	Chamber Pressure (mTorr)
Ar or N <sub>2</sub>	0.5-3.5	10-30	13-48

After the fractional factorial experiment was completed, single-factor multi-level experiments were carried out in the vicinity of the most promising combination that yielded the lowest contact angle. This was done for both LDPE and Kapton PI using only nitrogen plasma source gas since the results showed that this gas produced the lowest contact angle response. For this optimization phase, each set of runs involved varying the setting of one factor only while keeping the settings of the two other factors constant. There were a total of three sets of runs, each corresponding to either accelerating voltage, exposure time or chamber pressure as the single factor. A minimum of three levels were considered in each set of runs though for some sets up to five single-factor levels were used.

### Contact Angle Measurement and Other Characterization Methods

The samples for contact angle measurements were cut from starting sheets into 1.5 cm x 1.5 cm area. There was no wet cleaning done on the polymer samples since contact with a solvent like acetone could have an effect on the surface property. Any wiping of the water droplet after testing was done carefully using lint-free Kimwipes. After plasma treatment, the contact angles of the replicate samples were immediately measured and the time elapsed after bringing the samples out of the chamber and completing the measurement is estimated not to exceed 10 minutes. Each water droplet delivered by the syringe is about 7 microliters in terms of average volume.

The contact angle of a water droplet on a polymer film sample was measured by mounting the sample (treated or untreated) on a stage equipped with a microsyringe using a USB digital microscope attached to a laptop to magnify the droplet. The film was kept in a horizontal position and a small droplet of water was deposited on the surface. Two photos were taken of the water droplet for each replicate of a treatment combination after it spread on the surface based from an edge view of the polymer with droplet and the average droplet dimensions were reported (height and base diameter).

The droplet dimensions were measured from a magnified view of its digital microscope image in the computer screen to minimize the error. Based on the consideration that each droplet formed a spherical cap, the dimensions can yield the contact angle from geometry using a derived formula shown in Figure 4 which also shows the contact angle measurement set-up in the left side.

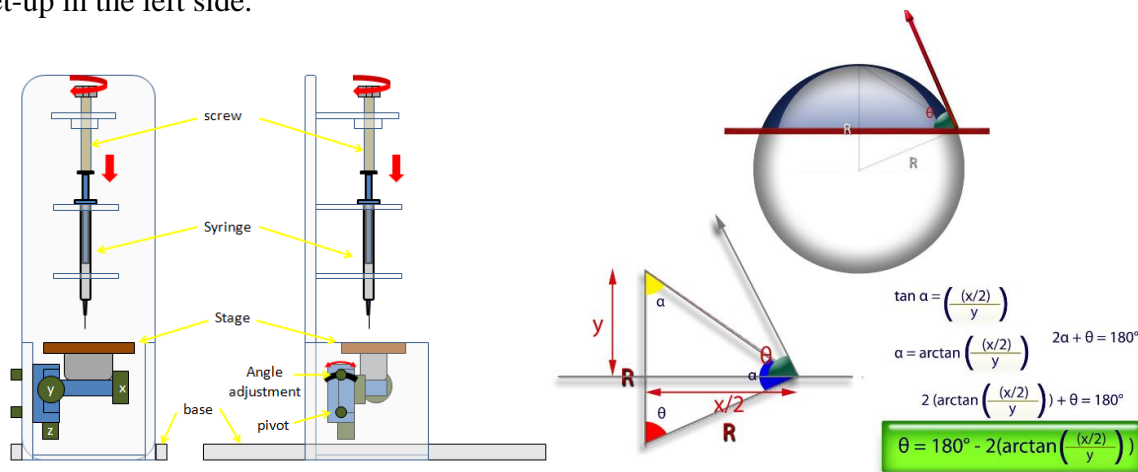


Figure 4. Set-up for measuring the contact angle (left) and formula for computing the contact angle from droplet dimensions (right) [22]



The untreated polymers were subjected to DSC analysis and also XRD analysis to gain better insight on the physical structure of the starting samples. DSC analysis was carried out at the UP Institute of Chemistry to ascertain the degree of crystallinity of the untreated samples.

Polymers are known to be semi-crystalline containing both amorphous and crystalline regions. Crystalline components will produce a well defined endothermic peak in the DSC spectrum corresponding to the melting of the crystal. A complementary analysis was also made by XRD method using the Shimadzu XRD 7000 diffractometer based on  $\text{CuK}\alpha$  radiation.

## Results and Discussion

### Promising Settings from Factorial Experiments using Argon and Nitrogen Gas

The factorial experiment using argon and nitrogen as plasma source gases showed that the treatment combination which yielded the lowest average contact angle for LDPE of about 17 degrees was the combination 3.5 kV, 30 minutes exposure and 48 mTorr chamber pressure using nitrogen as the plasma source gas. This is actually the setting where all factors have high levels in the factorial experiment. On the other hand, for Kapton PI, the experimental run which yielded the lowest contact angle of about 9-10 degrees corresponded to a setting of 0.5 kV, 10 minutes exposure and 48 mTorr setting, again using plasma source gas of nitrogen. It was seen from the results that nitrogen gas produced lower contact angle than argon and Kapton PI became more hydrophilic than LDPE after the same set of treatments. As a result of this initial set of experiments, the optimization runs were carried out only for nitrogen using the settings found for LDPE and Kapton PI as starting points for the single-factor experiments.

### Observed Trends from Fractional Factorial Experiment

A comparative summary of the preliminary settings mentioned in the previous sections is provided in Table 2. The average contact angle has been rounded off to the nearest digit. Looking at some trends from Table 2, the effect of the type of gas on the minimum contact angle is not as large for PI compared to LDPE.

**Table 2. Treatment Parameters which Yielded the Lowest Contact Angle Based on Data from the Fractional Factorial Experiment**

Polymer - Plasma Source Gas	Accelerating Voltage (kV)	Time (min)	Chamber Pressure (mTorr)	Ave. Contact Angle (deg)
LDPE - N <sub>2</sub>	3.5	30	48	17
LDPE - Ar	3.5	10	48	22
PI - N <sub>2</sub>	0.5	10	48	10
PI - Ar	0.5	30	48	14

Nitrogen as a plasma source gas is diatomic. One molecule of this gas has the potential of dissociating into two neutral atoms and eventually ionizing to form two positive ions per molecule. A greater number of bombarding species can of course lead to a higher degree of surface modification. In the case of argon, only one positive ion can be obtained per neutral atom of argon in the source gas. Though argon is a bigger atom than nitrogen, if the  $N_2$  is able to completely ionize, the effect of an increase in the number of nitrogen ions may lead to more surface modification than that of a beam with bigger ions but having lesser number.

### Results of Single-Factor Experiments Using Nitrogen

The results for both LDPE and Kapton PI are plotted in Figure 5. It is apparent from the plot for PI in the right that there is an optimum setting at around 0.5 kV. Below this voltage, the energy of the species is probably not sufficiently high to break enough bonds to create polar groups, thus contact angle is high. At higher accelerating voltages beyond the optimum, it is possible that more polar groups are able to recombine since they are effectively closer to each other on the average which results in a lower effective number of polar groups created that survived, making the surface not as hydrophilic as at the optimum setting.

In the case of the plot for LDPE on the left side of Figure 5, it appears that the contact angle can still go lower beyond 3.5 kV since a minimum has not been reached in the range. It was not possible to verify and increase the kV further due to limitations in the accelerating voltage power source that was just locally fabricated to replace the commercial high voltage source which reached the point of failure after the initial set of experiments was completed. On the other hand, if the accelerating voltage is further lowered below the range plotted, the contact angle is expected to increase already since at zero kV the contact angle should be closer to the untreated value of around 70 degrees. Runs outside the range are reserved for future studies but it is possible that for LDPE, two minima can be found beyond the region actually investigated.

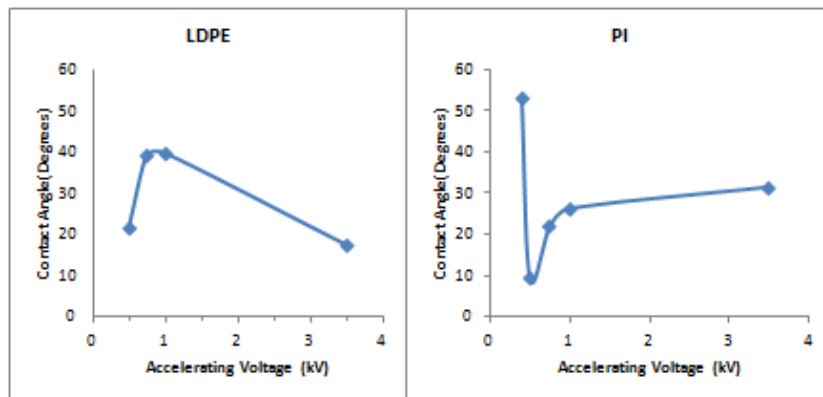


Figure 5. Contact angle versus accelerating voltage (30 min, 48 mTorr for LDPE and 10 min, 48 mTorr for PI)

The optimization results for exposure time shown in Figure 6 clearly show that this factor exhibits an optimum setting where the contact angle becomes a minimum. This is about 30 minutes for LDPE and only 10 minutes for Kapton PI. Longer time means more collisions have occurred that could lead to creation of polar groups. However, the longer the exposure

time, the greater also the opportunity for the polar groups to interact during this period that could lead to their annihilation such as by crosslinking with other adjacent polar groups. If the polar groups are not annihilated, they may also reorient themselves away from the surface through rotation of chain segments. This will therefore increase the contact angle beyond the optimum setting. The shorter optimum time and lower accelerating voltage requirement for Kapton PI also indicates this polymer is easier to modify than LDPE.

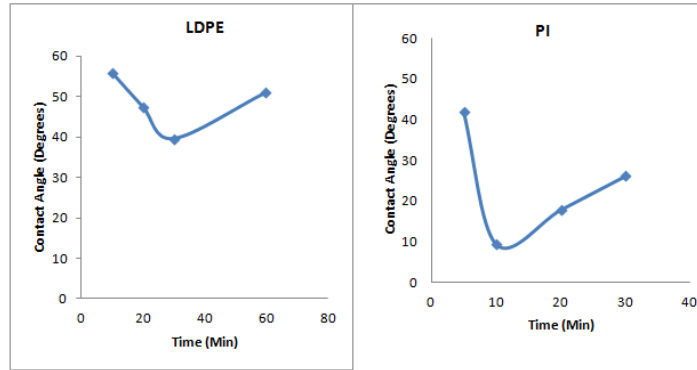


Figure 6. Effect of exposure time on contact angle using nitrogen (3.5 kV, 48 mTorr for LDPE and 0.5 kV, 48 mTorr for PI)

Finally, the results of the optimization runs using chamber pressure are shown in Figure 7. For LDPE, the plotted points define an essentially linear relationship with positive slope. The fact that the region is linear indicates that one is far from the optimum setting yet for this factor. An optimum setting is implied at lower chamber pressure settings than the range plotted. Theory tells us that going much lower than this optimum setting is also not going to work or will increase the contact angle towards the untreated value since there will be very few species produced to carry out surface modification. On the other hand, increasing the chamber pressure setting beyond this optimum will result in too many species in the plasma that leads to more collisions among the plasma species that could scatter the ions in the beam. A more scattered path downwards for the ions won't be as effective in terms of energy transfer as a more straightforward path without collisions. This could therefore explain the observed increase in contact angle as chamber pressure is increased for LDPE.

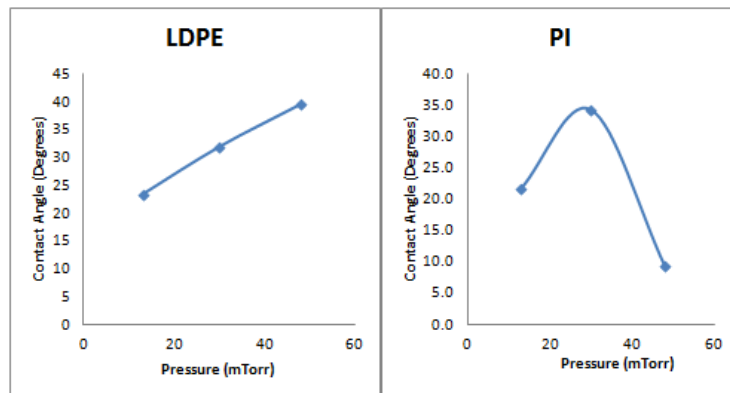


Figure 7. Effect of chamber pressure on contact angle using nitrogen (3.5 kV, 30 min for LDPE and 0.5 kV, 10 min for PI)

For PI, the range plotted exhibits a maximum. The profile actually appears to imply two minima, one at lower pressure settings and another at higher pressure setting above 48 mTorr. The second minima involving higher chamber pressure, if it indeed exists, can produce a more hydrophilic polymer than the implied first minima closer to 20 mTorr. Since the gas involved is nitrogen, the first minimum could correspond to plasma where not all of the dissociated nitrogen atoms are ionized and the other one to plasma where all of the dissociated ions are already ionized. LDPE does not exhibit this profile because it is harder to modify compared to PI.

### Rationalization of Observed Differences in Results for LDPE and Kapton PI

As presented in the earlier sections, LDPE appeared to be more resistant to surface modification than Kapton PI. One obvious difference between the two polymers is in their degree of crystallinity as discerned from Figure 8. The said figure is clear proof that Kapton PI is essentially amorphous while LDPE has higher crystallinity due to the very pronounced dip that corresponds to the melting point of the crystalline component of LDPE. In Kapton PI, the dip is only very shallow. The broad peaks in the XRD patterns are from the amorphous region while the sharper peaks are from the crystalline region. Though Kapton PI shows three secondary peaks riding on top of a broad peak, the intensities are much less than in LDPE indicating much lower degree of crystallinity than the latter.

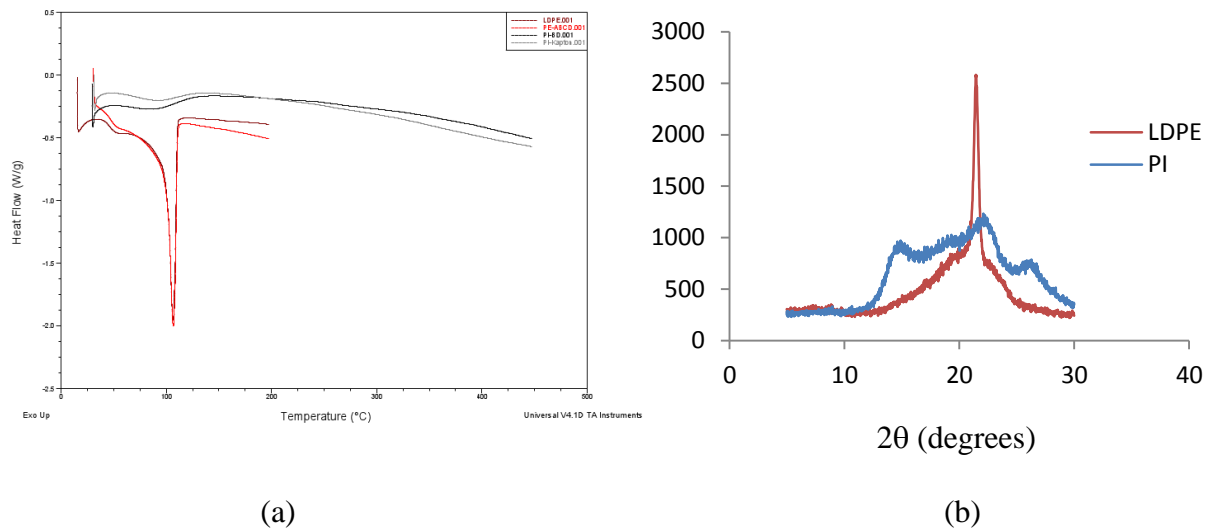


Figure 8. Comparison of untreated LDPE and Kapton PI: (a) Differential scanning calorimetry profiles from two trials per sample of LDPE (lower curves) and Kapton polyimide samples (upper curves), (b) X-ray diffraction patterns of LDPE (with sharp peak) and Kapton PI

It is easy to picture that denser crystalline regions will be relatively harder to disrupt by a beam of ions than an amorphous region which has less order and lower density because movement of atoms in the denser regions is more restricted. If molecular chains at the surface are fragmented by ion beam action, these fragments with radicals are less mobile in a crystalline region which has a denser packing. This can hamper movement needed for neighboring radicals to interact by mechanisms such as crosslinking which will result in their

annihilation. This should actually improve wettability since preservation of radicals is promoted. Also, a denser region will present more target atoms per unit area of the surface to the beam. Based on this analysis, LDPE should be easier to modify but the results show the opposite. This means another factor dominates with opposite effect.

A possible factor that could explain the difference is that LDPE is only made of C and H atoms while Kapton PI contains also some O and N elements in the molecule aside from C and H. Oxygen and nitrogen atoms are bigger in terms of atomic size than C and H. This will increase probability of collisions which promotes surface modification. In addition, the presence of oxygen itself already produces a polar group in the structure. In fact, the contact angle for polyimide in its untreated form is already lower than for low density polyethylene (68 degrees for Kapton PI versus 96 degrees for LDPE [22]). There are therefore more types of interactions that can occur in PI which has more types of bonds and this could also lead to more effective surface modification.

## Conclusions

The comparative study has clearly shown that the optimum settings to produce a more hydrophobic surface is different for LDPE and Kapton PI, with the latter appearing to be easier to modify and requiring relatively lower settings of exposure time based on optimization runs investigating this factor considering the results using nitrogen gas. For accelerating voltage, an optimum setting for this factor has been found for PI using nitrogen gas but for LDPE, it appears this optimum voltage setting could even exceed 3.5 kV. For chamber pressure factor using nitrogen gas, the range investigated is far from the optimum range for LDPE because of the absence of curvature in the response surface. For PI, however, a marked curvature was present in the response surface but a maximum contact angle was found rather than a minimum though the profile suggests two possible minimum settings, one at lower pressure and another one at even much higher chamber pressure than the one investigated. This could be due to more complicated interactions involving PI because of its oxygen and nitrogen content.

The differences observed between treated PI and LDPE are attributed mainly to the difference in composition of the two polymers in their untreated form, with PI containing oxygen and nitrogen atoms not found in LDPE. The observed difference in crystallinity does not explain why contact angles are lower and surface modification is easier to achieve for PI.

## Acknowledgement

The funding provided by DOST-PCIEERD of the Republic of the Philippines is gratefully acknowledged. The assistance of the research project staff: Krisette Anne de Chavez, Anna Monica Dipasupil, and Jeremiah Chan is likewise acknowledged. The assistance extended by Dr. Henry Ramos from UP NIP who served as consultant for the project is also acknowledged.

## References

- [1] G.Q. Blantocas, *Development of a Gas Discharge Compact Ion Shower Source for Low Energy Charged Particle Beam Studies and its Application as Modifier of Organic Materials*, Thesis (PhD), University of the Philippines, Diliman, Quezon City, Philippines, 2004.

- [2] J.C. Flores, *Surface Modification of Kapton Polyimide Using a DC-Powered Ion Shower System*, Thesis (Master's), University of the Philippines, Diliman, Quezon City, Philippines, 2011.
- [3] A.M. Aceremo, *Development of an Ion Shower System for Surface Modification of Polymer Materials*, Thesis (Master's), University of the Philippines, Diliman, Quezon City, Philippines, 2007.
- [4] L.-S. Shi, L.-Y. Wang, and Y.-N. Wang, "The investigation of argon plasma surface modification to polyethylene: Quantitative ATR-FTIR spectroscopic analysis," *European Polymer Journal*, Vol. 42, No. 7, pp. 1625-1633, 2006.
- [5] J.H. Loh, "Plasma surface modification in biomedical applications," *Medical Device Technology*, Vol. 10, No. 1, pp. 24-30, 1999.
- [6] F.S. Denes, and S. Manolache, "Macromolecular plasma-chemistry: An emerging field of polymer science," *Progress in Polymer Science*, Vol. 29, No. 8, pp. 815-885, 2004.
- [7] E. Nasser, *Fundamentals of Gaseous Ionization and Plasma Electronics*, Wiley-Interscience, New York, United States, 1971.
- [8] M. Venugopalan, *Reactions Under Plasma Conditions: Vol. 1*, Wiley-Interscience, New York, United States, 1971.
- [9] A. Kondyurin, V. Karmanov, and R. Guenzel, "Plasma immersion ion implantation of polyethylene," *Vacuum*, Vol. 64, No. 2, pp. 105-111, 2001.
- [10] E.M. Liston, L. Martinu, and M.R. Wertheimer, "Plasma surface modification of polymers for improved adhesion: A critical review," In *Plasma Surface Modification of Polymers: Relevance to Adhesion*, M. Strobel, C.S. Lyons, and K.L. Mittal, eds.: VSP, Utrecht, Netherlands, pp. 3-39, 1994.
- [11] M. Ataefard, S. Moradian, M. Mirabedini, M. Ebrahimi, and S. Asiaban, "Surface properties of low density polyethylene upon low-temperature plasma treatment with various gases," *Plasma Chemistry and Plasma Processing*, Vol. 28, No. 3, pp. 377-390, 2008.
- [12] K.S. Kim, and C.M. Ryu, "Investigation of crystallinity effects on the surface of oxygen plasma treated low density polyethylene using x-ray photoelectron spectroscopy," *Polymer*, Vol. 44, No. 20, pp. 6287-6295, 2003.
- [13] S.H. Kim, S.W. Na, N.-E. Lee, Y.W. Nam, and Y.-H. Kim, "Effect of surface roughness on the adhesion properties of Cu/Cr films on polyimide substrate treated by inductively coupled oxygen plasma," *Surface and Coatings Technology*, Vol. 200, No. 7, pp. 2072-2079, 2005.
- [14] Polyimide, *Data Sheet*, Goodfellow Co., Huntingdon, United Kingdom.
- [15] R.R. Tummala, *Fundamentals of Microsystems Packaging*, International Edition, McGraw-Hill Professional, New York, United States, 2001.
- [16] E. Occhiello, M. Morra, P. Cinquina, and F. Garbassi, "Hydrophobic recovery of oxygen-plasma-treated polystyrene," *Polymer*, Vol. 33, No. 14, pp. 3007-3015, 1992.
- [17] C. O'Connell, R. Sherlock, M.D. Ball, B. Aszalós-Kiss, U. Prendergast, and T.J. Glynn, "Investigation of the hydrophobic recovery of various polymeric biomaterials after 172 nm UV treatment using contact angle, surface free energy and XPS measurements," *Applied Surface Science*, Vol. 255, No. 8, pp. 4405-4413, 2009.
- [18] P.L. Madrid, *Mathematical Modeling of Implant Dose and Characterization of P-N Junctions Formed by Ion Shower Technology (IST)*, Thesis (PhD), University of the Philippines, Diliman, Quezon City, Philippines, 2000.

- [19] J.M.A. Diaz, *Characterization of Silicon P-N Junctions Fabricated by Ion Shower Doping*, Thesis (Master's), University of the Philippines, Diliman, Quezon City, 2003.
- [20] S.C. Bombita, *A Comparative Study on the Surface Modification of Polyethylene and Polyimide Using Helium Plasma in an Ion Shower System*, Thesis (Master's), University of the Philippines, Diliman, Quezon City, Philippines, 2011.
- [21] R.E. Walpole, R.H. Myers, S.L. Myers, and K. Ye, *Probability and Statistics for Engineers and Scientists*, 9<sup>th</sup> Edition, Prentice Hall, Boston, United States, 2011.
- [22] A.V. Amorsolo, Jr., *Modification of the Surface Properties of Polymer Materials by Plasma Treatment*, Year 1 Project Report, DOST-ERDT Program entitled High Value-Added Materials for the Semiconductor and Electronics Industry, 2010.