

Effect of various gas plasma treatment on the surface property and process parameter for Polyethylene- A Review

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Abstract— In present paper we have tried to review plasma surface modification of Polyethylene with plasma of different gases. The five gases have been observed: oxygen, Nitrogen, Argon, Freon and atmospheric air. The selection of five gases is done on the basis of their characteristics. The combination of process parameters like exposer time, wave power and frequency have been made in order to improve the surface properties like wettability, strength, roughness and hardness. Wettability is measured in terms of contact angle with the liquid while other properties are the observed by functional group preset at the surface of the polyethylene and the contents of these groups are influenced by the gas used for the plasma treatment. The ATR FTir is used for measuring the functional group present at the layer of polyethylene. Effect of various gases have been also observed like vise Argon plasma surface treatment is known as CASING process and Oxygen plasma treatment promotes roughness while ammonia plasma reduces the surface roughness.

Keywords- Plasma gas, Polyethylene, contact angle, functional group, Exposer time, treatment power, wettability

I. INTRODUCTION

Surface modification is the act of modifying the surface of a material by bringing physical, chemical or biological characteristics different from the original surface of a material. The surface modification of the plastic materials is promising approach for improving surface property such as wettability, adhesion and other surface characteristics likewise resistivity and anti-bacterial property. In the surface modification method the surface characteristics can be improved while the property of the bulk material remains unchanged so it is not susceptible to cracking.

There are various methods are available for the surface deposition of the polymers. It can be classified in to 1) Physic chemical method. 2) Mechanical method. 3) Biological method. Plasma deposition method is one of the Physic chemical methods. And it is extensively used because of its following advantages

- Easy preparation
- Unique film chemistry
- Coated on unique substrates with good adhesion
- Conformal and pin-hole free films
- Excellent permeation barriers with low level of leachable⁷

And it's accurate result and improved surface characteristics along with the good surface finish and wide range of property variations allows this method to use for the surface modification of the Polymers. As far as concerned to the Polyethylene the mechanical method for the surface modification is not advisable in this case the Gas Plasma discharge is most efficient and accurate method for the surface modification for obtaining desired surface properties.

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, resistivity, without changing their bulk properties.⁶

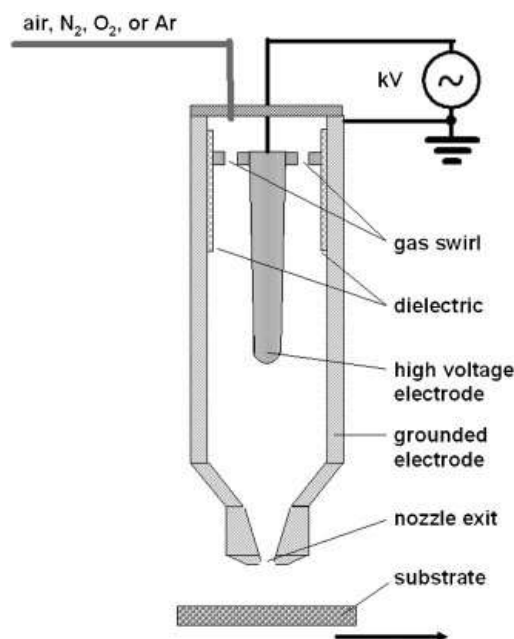


Fig 1 Schematic drawing of plasma jet³

II. LITERATURE REVIEW

During the plasma treatment there are three distinct processes have been takes place, depending upon the treating time and composition of the gas discharge plasma. At a short time of period one process of the Surface modification takes place. While other two are depending upon the gas being used for the plasma whether it is etching process or polymerization process because these two

processes is also contributing for the surface modification so it is necessary to consider them.⁵

For above reason in this paper we have chosen the five different gases for the evaluation these are:

Table 1 gases and its charectoristics⁵

1	Argon	Representative of Inert gases.
2	Oxygen	Representative of Chemical Active gases.
3	Nitrogen	
4	Freon	Representative of chemical active and Organic polymer creating gases
5	Air	Representative of the Mixed compounds.

A. Material and Measurement

Polyethylene has been selected for the plasma treatment because it's wide application and has certain good property such as high chemical resistance, high impact strength and flexibility with the low cost.

Wettability refers to as a surface adhesion and it can be easily characterized by measuring the contact angle of surface with the liquid. Different device have been used for Dynamic contact angle measurements.

During the plasma treatment the wide range of the reactive spices have been generated at the interface depending upon the active gas compounds used in the treatment. These spices plays important role so known as a Functional group and it is necessary to measure all these functional groups is detected by the ATR FTIR (Attenuated total reflection Fourier transform infrared spectroscopy) and this device is used to measure the concentration of the Functional group.

B. Flowing gas Discharge regime

Different gas have been used for the changing the number of process parameter like viz. increasing the depth of penetration, reducing the treatment time, reducing the power, increasing the hardness and strength etc. Surface finish and surface roughness varies with the gas used in the plasma treatment.

1) Argon

It is an inert gas so no qualitative change has been observed in the surface of the chemical composition of PE. During the experiment the Argon is flowing along with the 2.45GHz wave and microwave power used for the surface modification exposer time is sufficient to abstract hydrogen and to form free radicals at near the surface which interact to form cross links and unsaturated groups. Plasma also removes the low molecular weight material and converts it in to the high molecular weight. This treatment has been known as CASING (cross linkage by activated spices of inert gases) The contact angle value decreases with the increase in microwave power and also observed that the for a longer periods or at higher microwave power, deteriorates the surface of the polymers so microwave power should be confined with certain range of power and treatment time. The functional groups that take places are similar to oxygen that are Hydroxyl, carboxyl and carbonyl and it is due to the presence of residual gases in the reactor.⁴

2) Oxygen

Oxygen is the Chemical active gas used extensively for the plasma treatment. With the Oxygen plasma treatment there are addition to the surface activation of polymer surface, fictionalization of polymer occurs due to the active nature of

plasma gas used. Oxygen plasma is produced with the 2.45 GHz wave and 60A current. There are mainly carboxyl, hydroxyl and carbonyl formed as a functional group at the surface of the polymer and these groups have higher energy as compared to the functional group formed with the Argon. Oxygen plasma can reacts with the polymer surface to produce number of atomic oxygen functional group. Two processes occur simultaneously etching of polymer surfaces one and another is formation of oxygen functional groups. Oxygen is become more etched and rough surfaced with increase in the treatment time so that exposer time is limited to about 1 min for the 50W power and 0.3-0.9 torr pressure otherwise it will causes rough surface and mechanical interlocking. For the same contact angle oxygen plasma needs less power and treatment time as compare to the argon plasma so that improved wettability is obtained. In addition to wettability the hardness of the surface is also increased and it is depends upon the flow rate for the 20 min exposer time with 5 to 10W.^{1,4}

Treatment time (seconds)	Argon plasma treated			Oxygen plasma treated		
	Microwave power (watt)			Microwave power (watt)		
	100	150	200	100	150	200
0	66	66	66	66	66	66
60	64	63	57	52	49	46
120	62	54	51	44	40	36
180	58	51	47	41	36	35

Table 2 water contact angle for polyethylene for O2 and Ar4

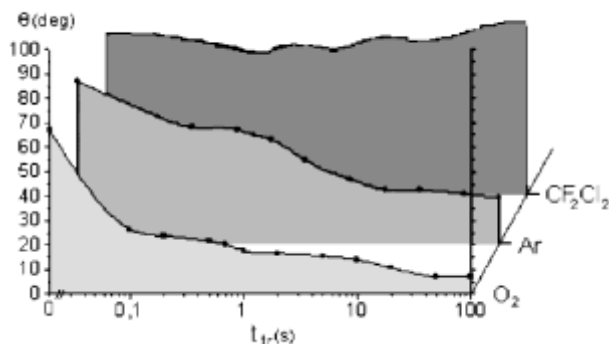
3) Nitrogen

Nitrogen plasma treatment is done at the 17 and 22 kHz excitation frequency and input pressure of 5.9 bars as a result of this treatment the formation of functional group nitrile and at the surface of the polymer. With addition to these functional groups the large amount of oxygen concentration are also observed in nitrogen plasma treated sample. This is due to diffusion of oxygen in plasma and/or reaction of substrate surface with the ambient atmosphere. For the same amount of the contact angle nitrogen plasma requires more treatment time/power as compare to the oxygen plasma. Strength of oxygen treated sample is higher than nitrogen treated sample.^{1,3}

4) Freon

Freon is taken in to observation as a representative of organic polymer creating gas. During the Freon gas treatment the power is 100W and 0.5 torr is kept and surface modification is done by polymerization which changes the surface qualitatively. It have large rate of polymerization and despite the fact that they are chemically active, they take smaller part in other possible chemical reactions and with other compound at the time of polymerization.

Plasma Treatment of Polymer Surfaces in Different Gases



are formed at the surface of Polyethylene. The decreasing of Surface tension can be obtained by displacing of already created oxygen group with carbon-fluorine, carbon-chlorine or mixed carbon-chlorine-fluorine these will lead to change kinetic physical-chemical mechanism. But whole time interval is greater than oxygen and argon plasma treatment time.¹

5) Atmospheric Air

Atmospheric air is taken in to consideration as compound gases. During the process reaction takes place in two ways. Those are

- Reaction when substrate is hit by plasma jet
- Reaction outside the plasma jet after the treatment

The atmospheric air is taken under the pressure of 0.5 torr and 17 to 22 KHz and microwave power of 5kV range. Number of gas compounds are available in the atmospheric air results in higher total concentration of hetero atoms especially oxygen, incorporated in to substrate surface of the air. Total numbers of heterogeneous functional groups are higher. so that the surface tension is higher in the Atmospheric air plasma treatment. In the air plasma, simultaneous existence of reactive oxygen and nitrogen species in the air plasma result is the formation of Oxim, imine and amide in addition to carboxyl, nitrile, hydroxyl and carbonyl. Since the strength of the surface is of very low range due to presence of large number of functional groups.³

6) Miscellaneous gases

Since there are number of other gases which have been observed likewise oxides(oxygen and air), carbon dioxides, ammonia etc. for the oxides plasma treatment there is increment in micro hardness and micro roughness.² while carbon dioxide plasma introduce several oxygen containing functional group including carboxylic acid, ketone /aldehyde, and hydroxyl/epoxide groups. The wettability of the plasma-treated surfaces decreases upon storage in air.⁹ Ammonia plasma treatment; carboxyl or amino functional groups were incorporated on the PE surface. Amino groups (NH) formed at first were followed by formation of imino groups (N=) in a secondary reaction. The surface roughness of PE samples decreased through ammonia plasma treatment.⁸

III. CONCLUSION

From the above reviews we are come on the conclusion as follows.

1. It is found that oxygen is more reactive in etching the polyethylene surface. With the plasma time and power the wettability is increased and micro hardness is also increased which depends upon the flow.

Fig.2– comparison of different gases for the contact angle and treatment time. ⁵

Due to polymerization effect there is increase in the layer of homogenous structure. Since gas mixture is created from the different organic compound including non-saturated compounds also there are large number of functional groups

2. For the same contact angle and strength nitrogen plasma needs more treatment time/power as compare to oxygen plasma.
3. With the argon plasma the surface wettability is increased due to process of CASING and it is less as compare to oxygen plasma for same treatment time and power.
4. For the nitrogen plasma have a lower surface energy but yields a better bond strength as compare to air plasma
5. Freon plasma leads to change of the kinetic physical chemical mechanism which turns increase the modification time.
6. Air plasma have good surface energy is due to hetero atomic functional group present in atmospheric air.
7. Oxide plasma treatment should perform under optimum range of power and time otherwise etching is produced which increases roughness of the polyethylene surface.
8. Wettability of the carbon dioxide plasma treated sample decreases when storage in air
9. Roughness of the polyethylene surface decreases when it is treated with ammonia plasma.

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