Plasma Modification of Polyolefin Surfaces
"플라스마를 이용한 폴리올레핀 표면의 변용"

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Plasma Modification of Polyolefin Surfaces

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Polyolefins (Polyethylene and Polypropylene)

Advantage in use

General and cheap resin
Most widely used synthetic polymers for industrial and food packaging fields

Limitation for general use

Low surface energy ; poor printing, bonding and coating properties

Surface Treatment Techniques

To improve inferior functional characteristics
To increase their commodity value

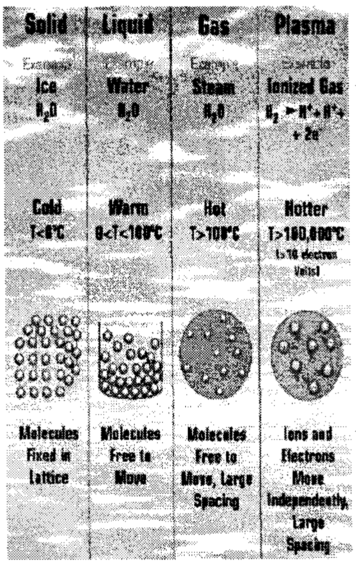
Dry physical treatments

Plasma, corona and flame discharge, photons, UV, ozone, laser, ion and electron beam irradiation, pressing between Al sheets etc.

Wet chemical treatments

Strong acids and bases like permanganic acid, chromic acid, Chlorosulfonic, sulfuric acid etc.

What is a plasma?



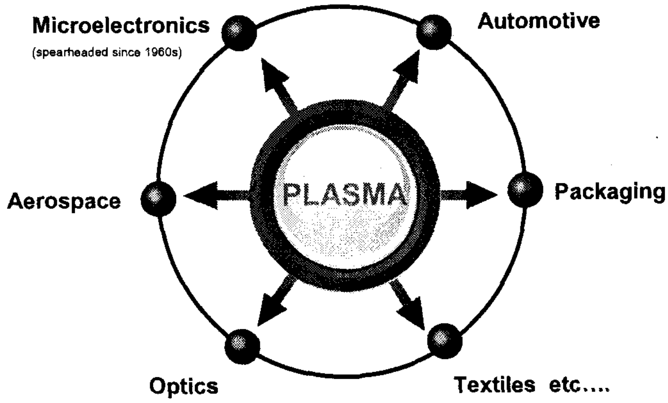
Plasma was identified as the fourth state of matter by Sir William Crookes in 1879.

Plasma consists of a collection of free-moving electrons and ions – atoms that have lost electrons. Energy is needed to strip electrons from atoms to make plasma. The energy can be of various origins: thermal, electrical, or light (ultraviolet light or intense visible light from a laser). With insufficient sustaining power, plasmas recombine into neutral gas.

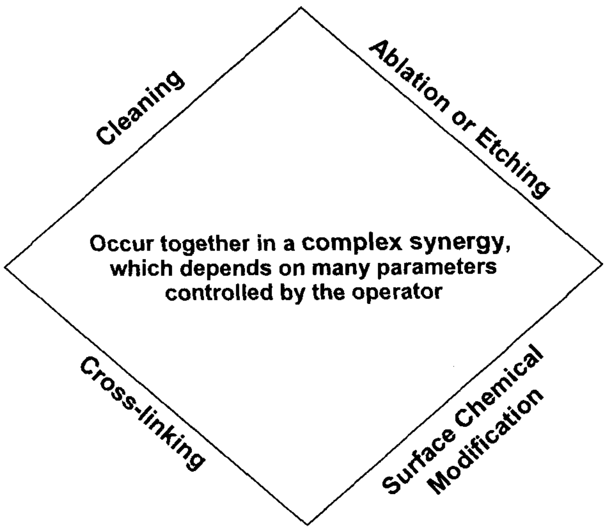
Plasma temperatures and densities range from relatively cool and tenuous (like aurora) to very hot and dense (like the central core of a star).

Plasma can be accelerated and steered by electric and magnetic fields.

Industrial Use of Plasma



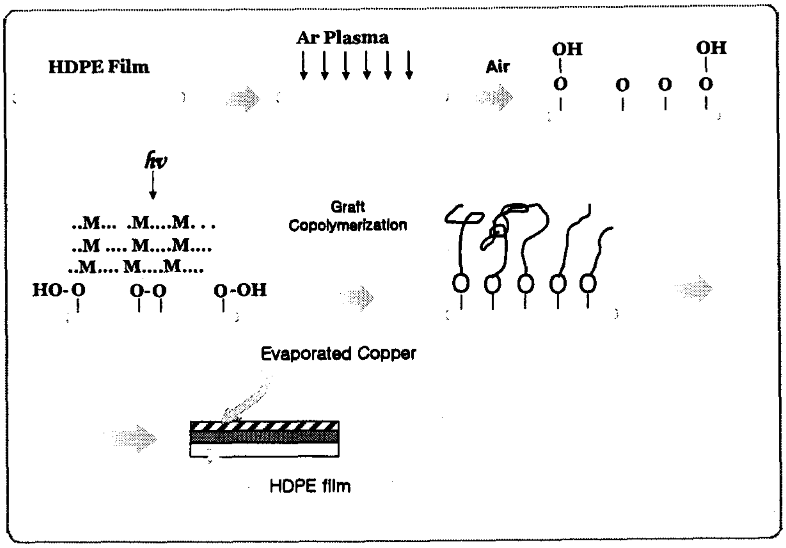
What effect has plasma?



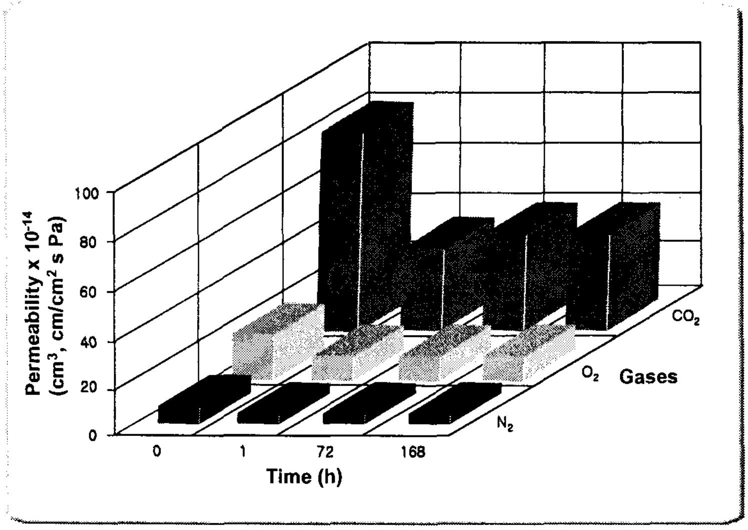
Effect of plasma treatments on polymers (Ozdemir et al., 1999)

Polymer type	Plasma type	Changes produced in material
Polyethylene	Air, O_2, N_2, CO_2, CF_4, NH_3, Ar	Increased polar groups and surface energy; improved wettability, adhesion, dyeability, and printability; enhanced peel strength; improved barrier properties
Polypropylene	O_2, N_2, H_2, NH_3, F_2+N_2, CF_6, SOF_2, SO_2	Enhanced wettability, adhesion, printability and dyeability; increased mechanical resistance and shear strength; improved barrier properties
Polyethylene terephthalate	Air, O_2, N_2, H_2, Ar, F_2+N_2, SF_6, SOF_2, SO_2, CF_4, C_2F_6, C_3F_6, C_4F_8	Increased surface energy; enhanced wettability, adhesion, dyeability, and peel strength; improved barrier properties
Polystyrene	O_2, N_2, CF_4, CO_2, Ar	Increased wettability, adhesion, and printability
Polycarbonate	O_2, CF_4, Ar, NH_3	Increased wettability, adhesion, and printability
Polyvinyl chloride	O_2, N_2, H_2, NH_3	Reduced migration of plasticizers; increased stability and peel strength
Ethylene vinyl alcohol	N_2	Improved surface properties; increased adhesion
Nylon	N_2	Increased surface energy; enhanced shear and peel strengths

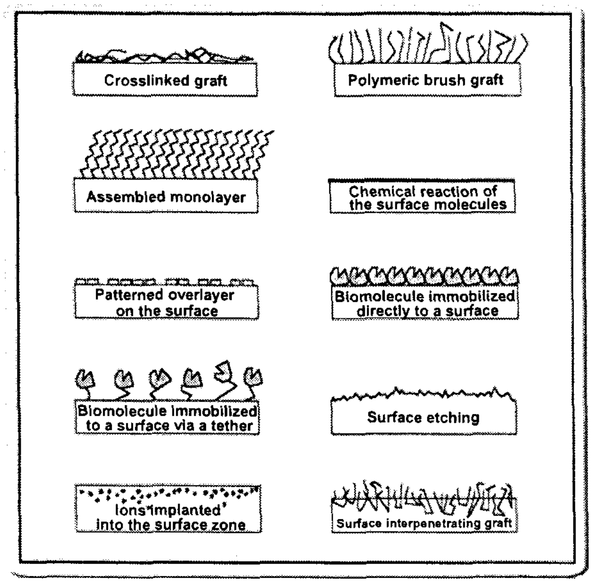
Schematic diagram of the UV-induced surface graft copolymerization and metallization processes (Ng et al., 2000)



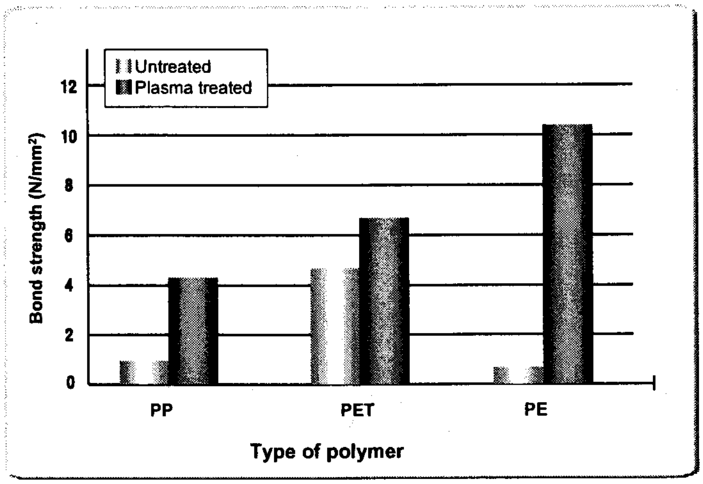
CO_2, O_2, and N_2 permeabilities of untreated and argon plasma-treated LDPE films at 30℃ (Rossi et al., 1995)



Possibilities for surface modification (Ratner, 1996)



Comparison of the bond strengths of untreated and O2 plasma-treated polymer films (Petasch et al., 1995)



Advantages of Plasma Treatment

- Versatile, uniform, reproducible, and environmentally benign method
- Improve surface energy, optical reflection, resistance to glazing, barrier properties, optical reflection, biocompatibility, adhesion to other materials
- Impart antimicrobial properties
- Maintaining bulk properties : modification depth very low

Flame	< Corona, Plasma	< UV/Ozone
2-4 nm	~ 10 nm	10 nm- 1 um

Current Drawbacks of Plasma Treatment

- Aging
- Requiring vacuum for operation and the high operation cost
- Difficulty in controlling the process parameters

Frequency of Plasma for Operation

- Low-frequency (LF, 50-450KH)
- Radio-frequency (RF, 13.56 or 27.12 MHz)
- Microwave frequency (MW, 915 MHz or 2.45 GHz)

Type and Purpose of Plasma

Oxygen and Nitrogen containing (NO_2, NO, NH_3..) plasma	Increase the surface energy
Fluorine containing (CFx) plasma	Decrease the surface energy and Improve the chemical inertness
Inert gas (Ar, He, Ne) plasma	Cross-linking

Oxygen Plasma

1) Etching :
the reactions of atomic oxygen with the surface carbon atoms, giving volatile reaction products

2) Formation of oxygen functional groups :
the reactions between the active species from the plasma and the surface atoms ;

C-O, C=O, O-C--O, C-O-O, and CO_3

Parameters Affecting the Surface Modification

Major

- Power
- Pressure
- Time
- Gas Type (Composition)

Minor

- Temperature
- Flow Rate
- Reactor Geometry
- Sample Location
- Plasma Type
- RF Vol. and Frequency

Optimum Process Condition

"Uncontrollable" plasma treatment : Many desirable changes and damage to the surface of polymers, such as degradation of polymer chains and etching of the surface materials.

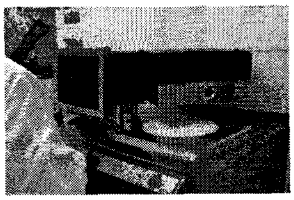
Plasma system with lower production costs and easily optimized and controlled treatment processes could lead to rapid growth in the utilization of plasma technologies on an industrial scale.

The development of the proper process : result of optimization tests

Film Material

Film	Blown low density polyethylene (LDPE) film	Casted polypropylene (CPP) film
Thickness	125 ㎛	125 ㎛,
Glass Transition Temperature	-110℃	-5~0℃
Melting Temperature	105℃	165℃
Crystallinity	45%	60%
Melt index	6.0 g/10min at 190℃	8.0 g/10min at 230℃
Density	0.916 g/㎤	0.9 g/㎤
Resin Type	Seetec XL 505 (Honam Petrochem. Co., Daejeon, Korea)	Hopelen FC-150B (Honam Petrochem. Co., Daejeon, Korea) Homo isotactic (>95wt%) PP

Plasma Treatment-1



1) Plasma Unit:

Capacitively-coupled, parallel-plate reactor with a radio-frequencyof 13.56 MHz

2) Plasma Type :

Oxygen plasma

3) Chamber and Reactor Configuration :

Chamber : aluminium alloy consisted of 490 mm inner dia. and 246 mm height, closed with two stainless-steel flanges.

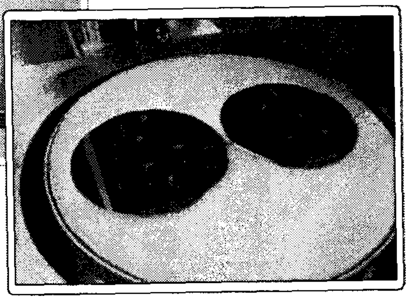
Upper electrode was located in the top cover- through which oxygen gas was flushed.

The size of bottom electrode : 20 mm thickness and 420 mm in dia. covered with ca. 5 mm quarz plate.

Evacuation and flush : 5 x 10-4 Torr with N_2

Oxygen etch procedure (150 W, 50 sccm O_2, 60 mTorr).

Plasma Treatment-2



5 pieces of film (2 x 2 cm each) were placed on the wafer and put onto the middle of plate of bottom electrode in chamber and oxygen gas was flushed from the top cover.

Operating Condition of Plasma Unit

Power : 50 to 300 W

Pressure : 50 to 500 mTorr

Treatment time : 10 sec to 12 min

Gas and flow rate : O_2 - 50 sccm

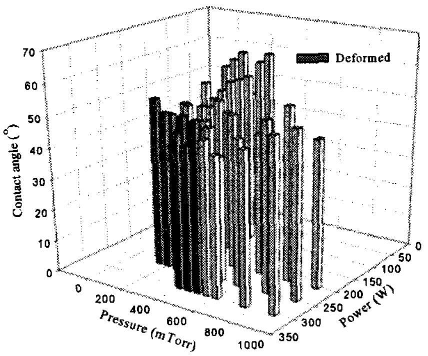
Cooling Temperature of Electrode : 10℃

Experimental Methods

Contact angle	Wetness
Toluidin-blue test	Carboxyl group
XPS and ATR-FTIR	XPS and ATR-FTIR

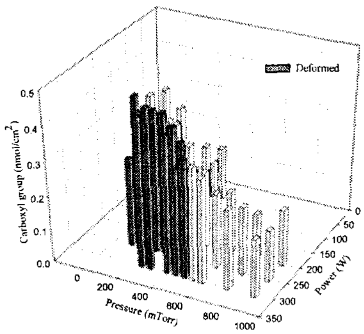
Contact angle as functions of pressure and power

LDPE



Carboxyl group as functions of pressure and power

LDPE



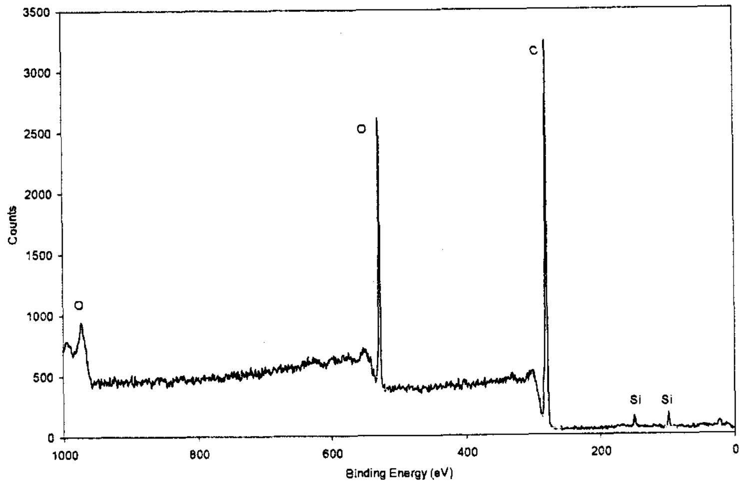
Contact angle and carboxyl group values of oxygen plasma-treated CPP film as a function of treatment time

(Treatment condition; 250 W, 50 mTorr, 50 sccm)

Time (min)	Contact Angle (°)	Carboxyl group ($nmol/cm^2$ COOH)
0.08	49.75	0.07
0.17	41.75	0.14
0.5	53.88	0.19
1	47.25	0.38
2	51.00	0.43
3	63.00	0.50
4*	58.76	0.51
5*	62.96	0.59

deformed

XPS survey scan for oxygen plasma-treated LDPE film

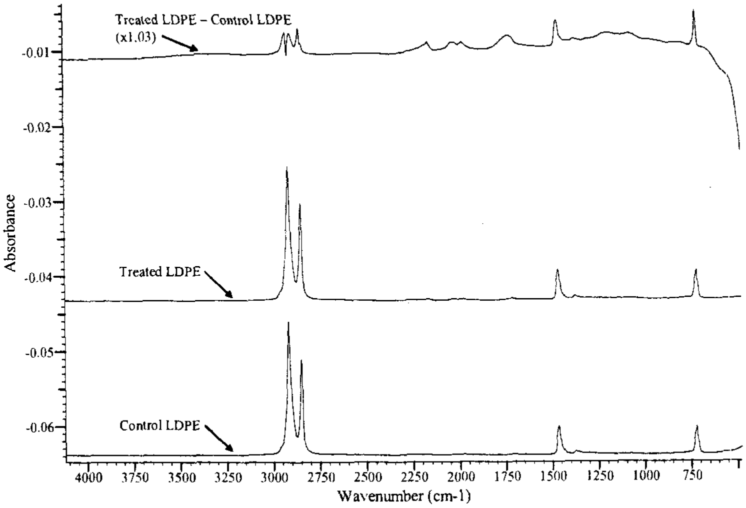


XPS-Approximate atom % surface compositions of oxygen plasma treated LDPE and CPP films

(%)

Atom	O	Si
LDPE Film		
- Control	< 0.5	---
- Treated	22.6	3.2
CPP Film		
- Control	< 0.5	---
- Treated	28.7	9.4

ATR-FTIR spectra of control and oxygen plasma-treated LDPE film



Critical zone for the oxygen plasma treatment of 125 um LDPE film specimens regarding deformation

(Treatment condition; 3min, 50sccm, 10C)

Power (W) \ Pressure (mTorr)	50	100	150	200	250	300	350	400	450	500	550	600
50												
100												
150												
200	xx	(x)	(x)									
250			xx	xx	x	x	x					
300						xx		x		x		

White zone : not deformed

Dark zone : deformed
((x): very slightly, almost not, x : slightly(5-10%), xx : moderately(10-40%), xxx : largely (more than 40%) and sticked to the wafer)

Critical zone for the oxygen plasma treatment of 125um CPP film specimens regarding deformation

(Treatment condition; 3min, 50sccm, 12C)

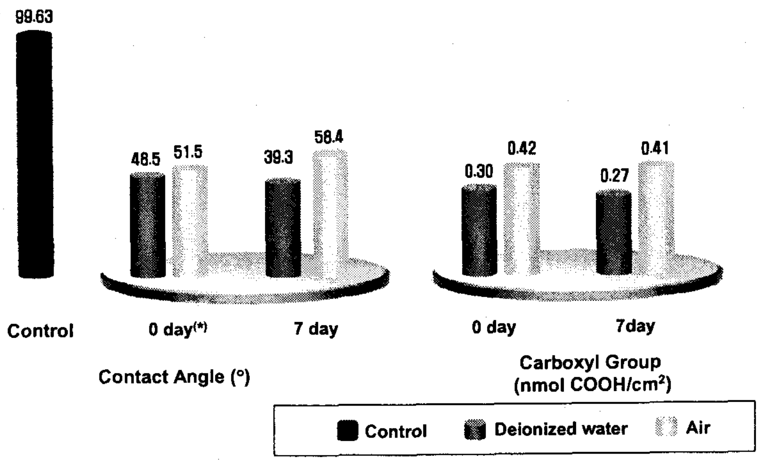
Power (W) \ Pressure (mTorr)	50	100	150	200	250	300	350	400	450	500	550	600
50												
100												
150												
200												
250												
300		*	*									

White zone : not deformed

Dark(red) zone : deformed
((x): very slightly, almost not, x : slightly(5-10%), xx : moderately(10-40%), xxx : largely (more than 40%) and sticked to the wafer

Slightly dark zone(*) : not defomed, but the treated side became opaque which turned again to be transparent after dipping in d.w.

Effect of contact milieu after plasma treatment of LDPE film on the contact angle and carboxyl group values



(*)Each measurement was done approximately 2hrs after plasma treatment.
The plasma-treated film samples were kept in a vial filled either with deionized water or air

Effect of repeated treatment on the contact angle and carboxyl group values of LDPE and CPP films

Film	Power (W)	Pressure (mTorr)	Treatment time (min)	Contact angle(°)	Carboxylic group (nmol COOH/㎠)
Low density polyethylene	200	200	3	53.0	0.37
			3+1	45.0	0.33
			3+1+1	44.4	0.33
	200	200	3	46.5	0.31
			3+2	48.9	0.36
			3+2+2	46.8	0.47
			3+2+2+2	44.6	0.45
Polypropylene	250	50	3	63.0	0.46
			3+3	48.0	0.63
			4+3	54.1	0.64
	250	50	3	59.8	0.51
			3+2.5	56.6	0.62
			3+2.5+2.5	43.6	0.59
			3+2.5+2.5+2.5	47.7	0.83
	250	50	2.5	55.9	0.48
			2.5+2.5	54.3	0.65
			2.5+2.5+2.5	45.3	0.60
			2.5+2.5+2.5+2.5	45.6	0.66
	250	50	3	61.6	0.47
			3+3	46.5	0.60
			3+3+3	48.1	0.64
			3+3+3+3	47.5	0.75
	250	50	3	54.6	0.48
			3+2	49.5	0.55
			3+2+2	43.4	0.72
			3+2+2+2	44.6	0.73

References

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