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Immobilization and Grafting of Acrylic Acid on Polyethylene Surface by Ar-plasma Treatment

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polyethylene(PE)
ATR
가 .
가 PE
PE 47 53° PE 23 26°
가
가
PE peel test
ablation 가

ABSTRACT : For surface modification of polymers with hydrophilic functional groups, acrylic acid was grafted and immobilized on the surface of polyethylene(PE) by cold-plasma treatment using Ar gas. The modifications were identified by analysis of ATR - IR spectrum and by the measurement of contact angles. Compared to virgin PE, significant decreases in contact angle were observed for both the grafted PE and the immobilized PE. The decreases of contact angle were in the range of 47-53° for grafted PE and 23-26° for immobilized PE. The degree of hydrophilicity depended strongly on the plasma-treating time and discharge power. For the case of grafting it has shown that the longer plasma-treating time, the higher hydrophilic character. For the case of immobilization, whereas, higher discharge power and longer exposure to plasma have shown the detrimental effect for the preparation of hydrophilic PE surface due to the decrease of carboxyl group by ablation effect. The decrease in adhesion strength of immobilized PE, compared to grafted PE, was also attributed to the ablation of carboxyl group.

Keywords : acrylic acid, surface modification, immobilization, grafting, adhesion.

bulk property
bulk property
가
가
가¹⁻⁴₅₋₇
가 (glow discharge)
가
가⁸⁻¹⁶
poisoning⁸
-COOH, -CO-, -OCO-, -OH -O-
Seo^{17,18} C₁ C₄
OH
10 15%
Cho¹⁰
-COOH, -CO-,
-OCO-, -OH -O-
가

ma immobilization)
가
가
PE
75
cm, 3.8 cm Pyrex
13.56 MHz
(Auto Electric, ST - 350) (LC - 500),
(MKS MFC1159), (Welch Model No.1400) (MKS Baratron)
^{13,14}
5 mTorr
(PE) hot
press 3 mm KRS -
5 crystal 4.7×2.0 cm
5.5×2.0 cm
- 10
40 W, 240 mTorr
1, 2
3 20 mTorr
PE
PE 40 W, 240 mTorr
25 W, 240 mTorr 40
W, 240 mTorr 30, 60, 90 120
PE

PE

PE

PE

PE

PE Soxhlet

PE

PE

1 μm 20

ATR (Jasco A - 202, ATR - 6, 24
) KRS - 5(48 wt%
thallium bromide + 52 wt% thallium iodide)

가

23 \pm 1 8 mL

$\pm 2^\circ$ (Erma
180 $^\circ$
peel test KS
A1107 2 cm
(OPP , 0.2 kgf/cm SUS
#302) PE UTM(H5K -S,
Hounsfield test equipment) 300 mm/min

PE 가

PM3 (fragment)

multiplicity triplet state, UHF
(unrestricted Hartree - Fock), siglet
state, RHF(restricted Hartree - Fock)
convergence limit=0.01,
Polak - Ribiere

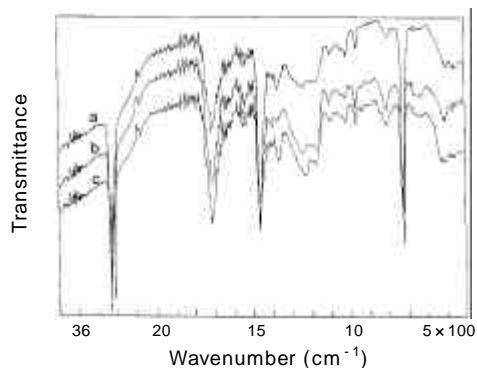


Figure 1. ATR - IR spectra of grafted acrylic acid on PE surface by Ar plasma treatment. (a) exposed for 1 min, (b) exposed for 2 min, and (c) exposed for 3 min.

Table 1. Relative Absorbances for Characteristic Absorption Bands(unit: $\text{cm}^{-1}/\text{cm}^{-1}$)

sample	band		
	2850/2920	735/721	1710/2920
virgin PE	0.92	0.71	-
grafting (1 min)	0.88	0.72	0.21
grafting (2 min)	0.83	0.71	0.32
grafting (3 min)	0.79	0.65	0.39

PE

a, b c PE

1 , 2 , 3

가 1710 cm^{-1}
가 가

21

가 , Table 1
(1710/2920 cm^{-1})

2850/2920 cm^{-1} -CH₂-

735/
721 cm^{-1} PE -CH₂-

rocking Table 1
ATR
KRS - 5 crystal

Figure 1 ATR
40 W, 240 mTorr

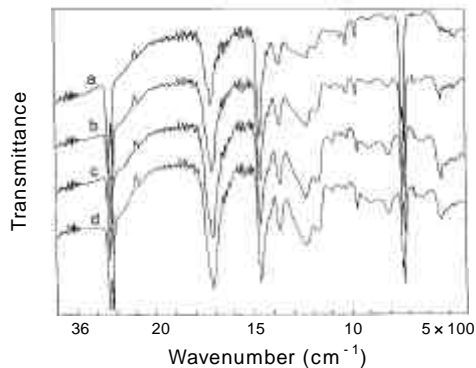


Figure 2. ATR-IR spectra of immobilized PE surface. (a) 30sec, (b) 60 sec, (c) 90 sec, and (d) 120 sec at 240 mTorr, 25 W.

Table 2. Relative Absorbances for Characteristic Absorption Bands, Ar Plasma Treated at 25 W, 240 mTorr

sample	band		
	2850/2920	735/721	1710/2920
virgin PE	0.92	0.71	-
immobilization(30 sec)	0.87	0.71	0.33
immobilization(60 sec)	0.86	0.71	0.46
immobilization(90 sec)	0.84	0.68	0.70
immobilization(120 sec)	0.91	0.69	0.63

Table 3. Relative Absorbances for Characteristic Absorption Bands, Ar Plasma Treated at 40 W, 240 mTorr

sample	band		
	2850/2920	735/721	1710/2920
virgin PE	0.92	0.71	-
immobilization(30 sec)	0.83	0.70	0.24
immobilization(60 sec)	0.83	0.70	0.27
immobilization(90 sec)	0.83	0.78	0.22
immobilization(120 sec)	0.87	0.74	0.11

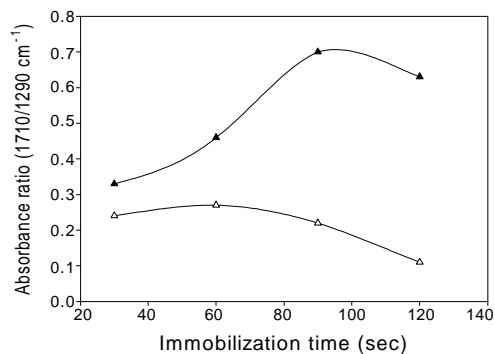


Figure 3. Variation of absorbance ratio(1710/2920 cm^{-1}) with immobilization time and discharge power(: 25 W, 240 mTorr, : 40 W, 240 mTorr).

PE crystal 가 가
 PE -CH₂- 가 (reference)
 Figure 2 25 W, 240 mTorr 3
 PE 240 mTorr
 25 W
 (30, 60, 90 120)
 Table 2 Figure 2
 , Table 3 40 W
 . 40 W, 240
 mTorr

Figure 2 Table 2 3
 . 25 W (Figure 2)
 가 1700, 1100 - 1300
 800 cm^{-1} - C -
 O- -COOH 22 가
 가 가 120
 Table 2 1710/2920 cm^{-1} 0.33,
 0.46, 0.70 가 가 0.63
 . 40 W (Table 3)
 가 1710/2920 cm^{-1}
 0.24 0.11
 25 W 40 W 가
 120 1710/2920 cm^{-1}
 1/6

Figure 2

Figure 3
 25 W 40 W
 가

ablation

가 ablation^{8,12,23}

PE

가 가

1 Table 2 1710/2920 cm⁻¹

가

40 W

ablation

가 ablation

가 가 PE

가 CAP mechanism⁸

가 ablation 가

(Semi - Empirical Quantum Mechanical Calculation) PM3

(102.00 kcal/mol) abla-

tion 가

Figure 4 가

1 7 π triplet

1 가 66.08 kcal/mol 가

가

2, 3, . . .

2 가

가

1

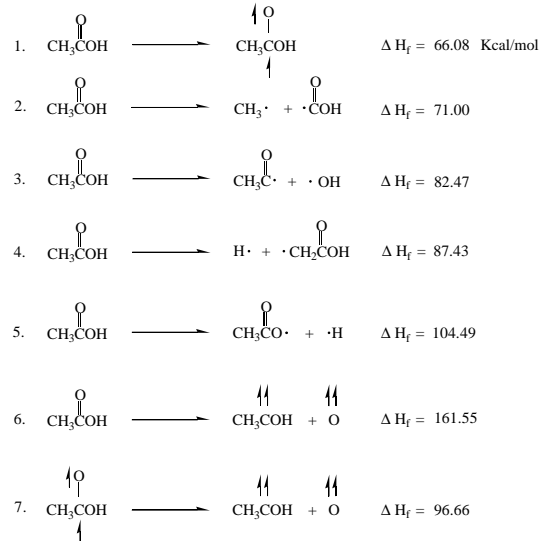


Figure 4. Heats of formation calculated semi-empirically by PM3 method.

7 25.66 kcal/mol 7 2 Boltzmann

7

1 71.00 kcal/mol 가

2가

가

가

가

가

fragmentation

ATR ESCA

ATR

,²⁰ d, d ≈ 1/10

가

가 400 4000 cm⁻¹

0.25 2.5 μm

가

ESCA

가

ESCA X 가 50

Table 4. Contact Angle of Water Droplet Wetted on Grafted PE Surface (Plasma Discharge Condition: 240 mTorr; 40 W)

treating time	virgin	1 min	2 min	3 min
contact - angle (°)	95	48	45	42

Table 5. Contact Angle of Water Droplet on Immobilized PE Surface (Plasma Discharge Condition: *, 240 mTorr; 25 W, ** 240 mTorr; 40 W)

treating time	30 sec	60 sec	90 sec	120 sec
contact - angle (°)*	72	71	71	69
contact - angle (°)**	71	73	73	71

Table 6. Data for Adhesion Strength of PE Samples by 180° Peel Test

sample	adhesion strength(kg/cm)
virgin PE	0.156
grafted PE(1 min)	0.219
grafted PE(2 min)	0.232
grafted PE(3 min)	0.221
immobilized PE(25W/240mTorr/30 sec)	0.211
immobilized PE(25W/240mTorr/60 sec)	0.213
immobilized PE(25W/240mTorr/90 sec)	0.216
immobilized PE(25W/240mTorr/120 sec)	0.210
immobilized PE(40W/240mTorr/30 sec)	0.193
immobilized PE(40W/240mTorr/60 sec)	0.205
immobilized PE(40W/240mTorr/90 sec)	0.209
immobilized PE(40W/240mTorr/120 sec)	0.200

60 가 ATR
가
24,25

5 10
Table 4
PE, Table 5
PE 가

가
PE

, Table 1 Figure 1
1710/2920 cm⁻¹ 가

20°
가, 가

20°
PE 가
가

PE
가
PE
가

ablation PE
가 가

Table 6 peel test
180°
PE PE
가 가

PE가 가
25 W PE 40 W

PE
PE> PE(25W)> PE(40W)>

가 가 PE
가 가

Table 1, 2 3
(1710/2920 cm⁻¹), 25

W PE가 가
가

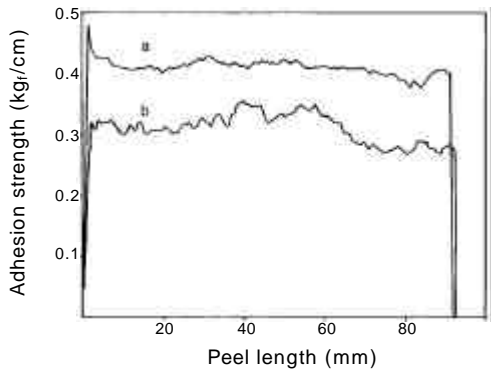


Figure 5. Spectra of peel strength. (a) immobilized PE at 240 mTorr, 40 W for 60 sec and (b) virgin PE.

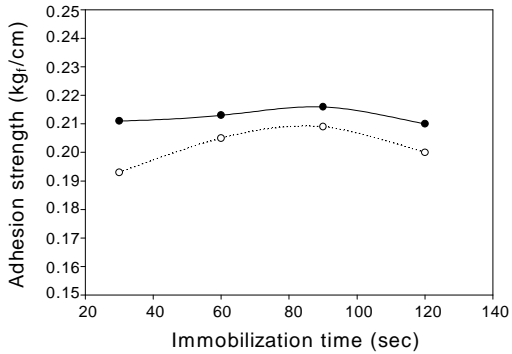


Figure 6. Adhesion strength of immobilized PE sample with treating time. 240 mTorr, 25 W (—), 240 mTorr, 40 W (1/4).

(1710/2920 cm^{-1})
 25 W PE가 40 W
 W PE
 Figure 5 40 W, 60 (a)
 (b)

PE
 Figure 6

가
 PE
 Park 24
 LDPE
 가
 PE
 ATR , PM3
 peel test
 1.
 PE 가 가
 가 가
 2.
 가 가 40 W,
 240 mTorr 가 25 W,
 240 mTorr 가
 가 가 가
 ablation 가 가 가
 가
 3. peel test
 PE가 가
 PE > PE(25W) > PE(40W) >

a b

: 1999

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