Polymer Bulletin 16, 499–505 (1986)

Polymer Bulletin

Grafting

Sorption and thermal polymerization of acrylic acid on polyethylene and on polyethylene-iron oxide composite
A comparison between grafting by radiation and thermal methods

Glaucione Gomes de Barros[1*] **and Fernando Galembeck**[2]

[1]Departamento de Química Orgânica e Inorgânica, Universidade Federal do Ceará, C.P. 3010, 60.000-Fortaleza, Brasil

[2]Instituto de Química, Universidade Estadual de Campinas, Campinas, Brasil

SUMMARY

Low density polyethylene can be modified by acrylic acid sorption and in situ thermal polymerization and grafting, at 60-90°C. Iron (III) oxide dispersed on low density polyethylene increases the extent of acrylic acid sorption and polymerization/grafting, both in (X-ray) preirradiated and non-preirradiated polyethylene. This effect is better observed at 60°C. The ratio between the weight gain on non irradiated and preirradiated matrix is higher at 60°C than at 90°C.

INTRODUCTION

Chemical, photochemical and radiochemical initiation are used in vinyl monomer grafting on solid polymers. Various modified polymers are thus obtained which have interesting properties. For instance,ion-exchange membranes are prepared by grafting acrylic acid,4-vinylpyridine and other monomers on polytetrafluoroethylene (PTFE) and polyethylene (PE) after exposure of the solid polymer to γ-irradiation (1-5).

Studies on solid polymer grafting have considered the following aspects: (i) grafting kinetics, in which both the chemical factors and the mass transfer rate (in monomer sorption) are relevant and (ii) chemical, thermal, mechanical, electrical, and other (ion-exchange,wettability) properties of the resulting grafted polymer (6-8).

Grafting kinetics is dependent of many factors. When using radiolytic initiation it is necessary to control irradiation (or preirradiation) dose, monomer concentration, temperature and film thickness. The effect of these variables on acrylic acid grafting in PE has been examined in detail to establish well-defined, reproducible grafting techniques (8). Optimal conditions to obtain acrylic acid-grafted PE films of both good strenght, elasticity and ion exchange capacity were also established (9,10).

Radiation-initiated grafting on PE is usually carried out in the 60-120°C temperature range (6,11,12). Grafting temperatures may be lowered to ca. 40°C by addition of redox reagents to the reaction system (13). Nevertheless little is known about the contribution of thermal polymerization per se in grafting processes. We have decided to verify the extent of PE modification by exposure to acrylic acid, at the temperatures used in radiation-initiated grafting but without use of initiator.

In addition the effect of Fe_2O_3, dispersed in solid PE, on the extent of acrylic acid incorporation to this polymer, both by thermal and radiation-initiated processes, was also examined. This was done for two reasons: first, the catalytic activity of Fe_2O_3 in methyl methacrylate polymerization is well documented (14,15); second, previous work demonstrated the feasibility of Fe_2O_3 incorporation to various solid,inert

---

[*] To whom offprint requests should be sent

polymers by Fe(CO)$_5$ sorption and in situ oxidation (16). This is a mild process which can be used with either formed or raw polymers.

EXPERIMENTAL

Acrylic acid (AA) (with 200ppm of hydroquinone monomethyl ether stabilizer) was obtained from Aldrich Co.. Other reagents were of analytical grade and used without further purification.

Low density polyethylene (LDPE) film (d = 0.918 g/cm^3, MI= 1.15 g/ 10 min) was from Poliolefinas (São Paulo). The identity and purity of the material was checked by IR spectroscopy and X-ray diffraction. The degree of crystallinity was 50% as measured by X-ray diffraction in a Philips instrument (Mod. 1130) using a Cuk$_\alpha$ tube operating at 40 KV and 20 mA.

The films were washed with ethanol and dried under reduced pressure before the sorption experiment. Fe$_2$O$_3$-doped LDPE films were prepared following the procedure described by Galembeck (16).

LDPE (either plain or Fe$_2$O$_3$-doped) films were immersed in 98% acrylic stock solution under nitrogen atmosphere at the specified temperature and times. After sorption, the samples were rinsed with water, ethanol and dried under reduced pressure 1 torr).

The film weight increase was calculated by:

$$\%\ \text{mass increase} = \frac{W-W_i}{W_i} \cdot 10^2 \,(\text{matrix}) \quad \text{or} \quad \frac{W-W_c}{W_c} \cdot 10^2 \,(\text{composite})$$

Where W_i is the initial weight of the LDPE film, W is the LDPE or LDPE-Fe$_2$O$_3$ film weight after monomer sorption and W_c is the composite film weight.

The homopolymer extraction was done with water, in a Soxhlet apparatus. X-ray film treatment was carried out under a tungsten source working at 30 KV and 12 mA. The field intensity, measured by LiF dosimeters, was 2.4 x 10^4 r/hr. The films were irradiated under reduced pressure (ca. 1 mmHg) at room temperature (25ºC). IR spectra were obtained on a Perkin-Elmer Model 283 spectrophotometer. All the spectra were compensated using in the reference beam a LDPE film.

RESULTS

The weight increase of LDPE film pieces after immersion in acrylic acid at 25ºC and 90ºC is shown in Fig. 1. A continuous weight increase is observed at 90ºC reaching 18.3% after six hours. Weight increase at 25ºC is much less, ca. 1.3%.

AA-treated (at 25ºC) PTFE films lose all sorbed monomer under reduced pressure (1 torr); films exposed to AA at 90ºC retain ca. 80% of the incorporated acid even under extended exposure to reduced pressure (20 hours and 1 torr) (Fig. 2).

Figure 3 shows the IR spectrum of an AA-treated (90°C, 4 hours immersion) LDPE film. The spectrum shows strong absorptions at 1770cm^{-1} (ν, C=O) and at 1230-1170cm^{-1} (ν, C=O and δ, OH). However, the absorption at 1630cm^{-1} (ν, C=C), characteristic of the monomer, is absent.Evidently the weight gain is due to either grafting or interpenetrating network formation. Part of this material (30-40%) may be extracted with water, as indicated in Table 1.

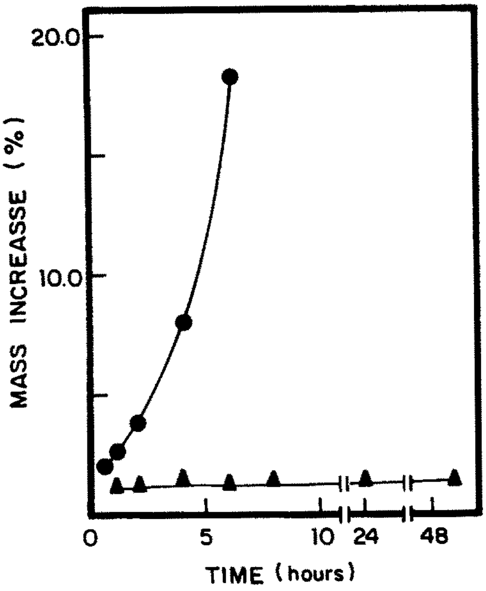

Figure 1 - Acrylic acid sorption on LDPE at 90°C (●) and 25°C (▲).

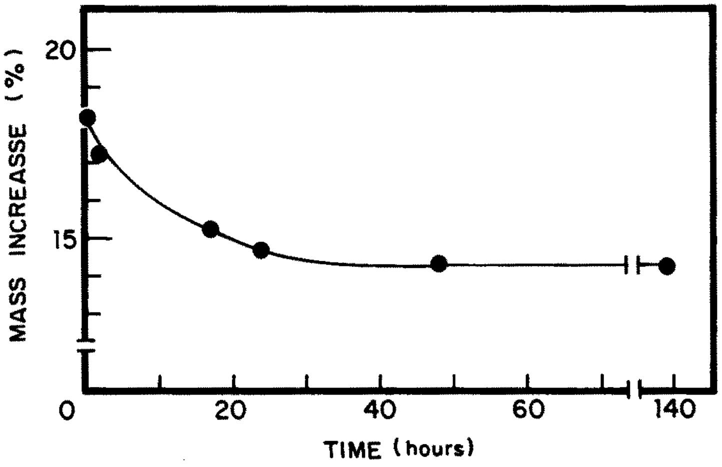

Figure 2 - Desorption of Acrylic acid from swollen LDPE, prepared by immersing LDPE films in AA for 6 h, at 90°C under N_2 atmosphere.

Acrylic acid-modified films were treated with 100 mM NaOH (29 hours immersion, 60°C). The IR spectrum of the dried film showed the appearance of a broad peak at 1530-1580 cm^{-1} indicating the conversion of -COOH to -COONa groups (Fig. 4). After the immersion of AA-modified films in 10 mM NaOH, under N_2 (120h, 60°C) the titration of excess NaOH with 10 mM

HCl allowed the determination of the carboxylic groups on the modified polymers films (Table 2). The titratable fraction of material incorporated to LDPE shows a considerable variation from sample to sample, perhaps due to intrinsic sample heterogeneity and wetting problems, as pointed out by Chapiro (17).

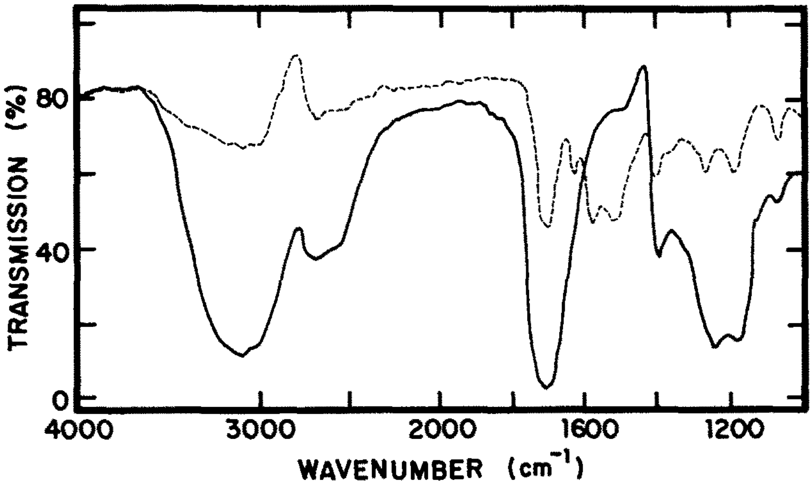

Figure 3 - Infrared spectra of LDPE and LDPE-iron oxide composite films after acrylic acid sorption at 90°C for 4 hours. (-) LDPE,7.5% weight increase; (---) LDPE-iron oxide,2.5% weight increase. Spectrum condition: LDPE film on the reference beam.

Table 1 - Water extraction of LDPE films after acrylic acid sorption and polymerization (6 hours/90°C).

Sample No.	$\frac{W-W_i}{W_i} \cdot 10^2$	$\frac{W_e - W_i}{W_i} \cdot 10^2$	$\frac{W_e - W_i}{W - W_i} \cdot 10^2$
1[a]	15	12	81
2[b]	13	9	69
3[b]	13	8	65
4[b]	10	7	67
5[b]	12	8	67

W_e, weight of the extracted film; extraction time: [a]26 hours, [b]39 hours.

Table 2 - NaOH titration of LDPE films after acrylic acid sorption and extraction in water.

Sample No.	initial matrix monomers moles	titrated matrix monomer moles	titrated moles (%)
6[a]	0.21	0.06	28
7[a]	0.25	0.19	56
8[a]	0.19	0.13	68
9[b]	0.22	0.09	41

extraction time: ^{a}53 hours; ^{b}64 hours.

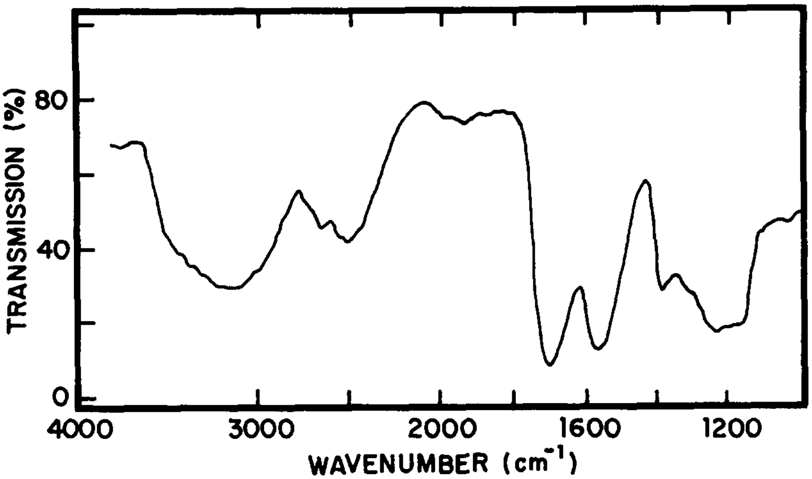

Figure 4 - Infrared spectrum of LDPE after acrylic acid sorption and immersion in 0.1 N NaOH at 60°C for 29 hours. Sorption conditions: 4 hours at 90°C under nitrogen atmosphere. Spectrum condition: LDPE film on the reference beam.

Grafting on preirradiated LDPE

The effect of preirradiation on LDPE film weight gain under exposure to acrylic acid over a 25-90°C range temperature was also examined (Table 3). No grafting or polymerization is detected at 25°C on both preirradiated and non-irradiated films whereas at 60°C and 90°C the preirradiated films exhibit large weight increases. The weight gain ratio between preirradiated and non-irradiated films is ca.10 fold at 60°C; at 90°C it is only 2-3 fold.

Table 3 - Effect of radiation and temperature on LDPE film mass increase after acrylic acid sorption.

Sample No.	$\frac{W-W_i}{W_i} .10^2$	$\frac{W_e-W_i}{W_i} . 10^2$	$\frac{W_e-W_i}{W_i} . 10^2$	Irradiation time (min)	Sorption temp. (°C)
10^{a}	1	-	-	-	25
11^{a}	1	-	-	20	25
12^{b}	3	2	66	-	60
13^{b}	20	18	91	20	60
14^{b}	22	20	89	20	60
15^{b}	77	60	79	-	90
16^{b}	107	89	83	-	90
17^{c}	144	102	71	-	90
18^{c}	309	191	62	20	90
19^{c}	340	171	50	20	90

extraction time: ^{2}0 hours; ^{b}48,5 hours; ^{c}38-41 hours.
sorption time: 6 hours.

From this, we conclude that AA undergoes thermal polymerization or grafting onto polyethylene, which can be well observed at 90°C. It may be responsible for 30-50% of the mass increases at 90°C and for ca. 10% at 60°C.

LDPE films immersed in AA become opaque when the film weight gain exceeds 10%; beyond 30% weight gain the dry films are brittle but become flexible and rubbery, when exposed to water.

Fe_2O_3-containing LDPE films were also preirradiated and immersed in AA, at various temperatures. The weight gains observed are presented in Table 4. The results show some major differences of the data in Table 3: (i) the maximum weight gain is obtained at 60°C for both preirradiated and non-irradiated LDPE-Fe_2O_3 films, (ii) rather effective thermally induced polymerization is found at 60°C, and (iii) iron oxide reduces the extent of acrylic acid sorption and polymerization at 90°C.

Table 4 - Effect of radiation and temperature on LDPE-Fe_2O_3 film mass increase after acrylic acid sorption.

Sample No.	$\frac{W-W_c}{W_i} \cdot 10^2$	$\frac{W_e-W_c}{W_i} \cdot 10^2$	$\frac{W_e-W_c}{W_i} \cdot 10^2$	Fe_2O_3 (%)	Irradiation time (min)	Sorption temp. (°C)
20^a	1	-	-	-	-	25
21^a	1	-	-	-	20	25
22^b	135	100	74	0.5	-	60
23^b	113	86	76	0.5	-	60
24^b	254	229	90	0.5	20	60
25^b	230	212	92	0.5	20	60
26^c	45	37	82	0.3	-	90
27^c	41	22	53	0.4	-	90
28^c	50	22	44	0.4	-	90
29^c	109	88	80	0.4	20	90
30^c	101	75	74	0.4	20	90

extraction time: [a]0 hours; [b]48.5 hours; [c]38-41 hours.
sorption time: 6 hours.

The IR spectrum of iron oxide-doped LDPE film after AA sorption at 90°C (Fig. 3) is similar to that of LDPE film subjected to the same treatment, with additional bands at 1520 and 1570 cm^{-1} (ν_a,COO^-), and at 1630 cm^{-1} (ν, C=C).

DISCUSSION

Exposure of LDPE films to AA at 60 and 90°C leads to appreciable film weight gain even on non-irradiated films. Our results do not allow the distinction between actual grafts and interspersed homopolymers. In any case, however, ion-exchange membrane-type materials are generated, independently upon addition of chemical initiators or the use of radiation.

The use of hydroquinone methyl ether prevents external bulk AA polymerization to occur but does not prevent polymerization within the LDPE matrix. Most likely, this is due to insolubility of the inhibitor in the LDPE films.

Rather striking results were obtained with Fe_2O_3-doped LDPE films. When compared to non-doped films they show higher weight gain at 60°C but lower gains at 90°C for both non-irradiated and preirradiated films. This behavior may be rationalized as follows: oxide particles can adsorb the monomer increasing its local concentration within the films and therefore the formation of polymer or graft at 60°C. However, at higher temperatures the oxide particles may yield iron acrylate and probably iron (III) hydroacrylate polymer which block further acrylic acid penetration. Also, 10-50% of the final weight gain in the grafts obtained by preirradiation should be due just to thermal polymerization.

We find thermal polymerization to be an effective and simple procedure to obtain ion-exchanging polyethylene-based films. This is much facilitated by adding Fe_2O_3 to the substrate polymer.

ACKNOWLEDGEMENTS

This work was supported by CNPq and FAPESP grants.

REFERENCES

1. A. Chapiro and P. Seidler, Eur. Polym. J. 1, 189 (1965).
2. G.Bex, A.Chapiro, M.B.Huglin, A.M. Jendrychowska-Bonamour and J.O'Neil J. Polymer Sci. C22, 493 (1968).
3. I. Ishigaki, N.Kamiya, T.Sugo and S.Machi, Polymer J. 10, 513 (1978).
4. A.M.Jendrychowska-Bonamour and J.Millequant, Eur. Polym. J. 16, 25 (1980).
5. A.M.Rabie, M.I.Aly, S.A.Hegazy and N.I. El-Awady, Polymer J. 11, 359 (1979).
6. G.H.Hisiue and W.K.Huang, J. Appl. Polym. Sci. 30, 1023 (1985).
7. Y.Nakano, H. Omichi and W.J. Mcknight, J. Appl. Polym. Sci. 29, 1041 (1984).
8. I. Ishigaki, T. Sugo, K. Senoo, T. Okada, J. Okamoto and S. Machi, J. Appl. Polym. Sci. 27, 1033 (1982).
9. I.F. Osipenko, A.P. Polikarpov, N.R. Prokopchuk and L.P. Krul, J. Polym. Sci. Polym. Lett. Ed. 21, 527 (1983).
10. A.P.Polikarpov, I.F. Osipenko and L.P. Krul, Vysokomol. Soyed A26, 1013 (1984).
11. J.K. Rieke, G.M. Hart and F.L. Saunders, J. Polym. Sci. Part. C4, 589 (1964).
12. L. Ivanova and H. Boudevska, Die Angew. Makrom. Chem. 103, 125 (1982).
13. V.A. Postnikov, N.Ju. Lukin, B.V. Maslov and N.A. Platé, Polym. Bull. 3, 75 (1980).
14. T. Yamaguchi, H. Tanaka, A.B., Moustafa, T. Ono, H. Ito, O. Itabashi,M. Endo, M. Ohuchi and L. Saito, Chem. & Ind. 619 (1974).
15. A.B. Moustafa and A.A. Adb-El-Hakin, J. Polym. Sci. Polym. Chem.Ed. 14, 433 (1976).
16. F. Galembeck, J. Polym. Sci. Chem. Ed. 16, 3015 (1978).
17. A.Chapiro, J. Polym. Sci. 29, 321 (1958).

Accepted October 7, 1986 K