

Effects of Film Thickness and Inhibitor Concentration on the Sorption and Thermal Polymerization of Acrylic Acid in Low-Density Polyethylene

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SYNOPSIS

We investigated the effects of hydroquinone monomethyl ether concentration and film thickness upon the thermal polymerization of acrylic acid on low-density polyethylene. The thermal polymerization of acrylic acid on low-density polyethylene depended on the concentration of hydroquinone monomethyl ether inhibitor. It was a free-radical reaction with initiation on the film surface and then proceeding to the bulk matrix. The process was not controlled by monomer diffusion for the range of film thickness of 90–200 μm . It became a diffusion-controlled process at higher film thicknesses ($> 200 \mu\text{m}$). A film layer of up to 100 μm was proposed as the limiting thickness for a diffusion-free process. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Several studies were carried out on polyethylene (PE) in order to produce materials exhibiting new properties.^{1,2} However, information concerning the factors that could affect the kinetics of the polyethylene modification by the grafting reaction is not well understood.^{3–5} It was recently proposed to modify low-density polyethylene by thermal polymerization of acrylic acid in the matrix.⁶ It was observed that iron (III) oxide has a strong effect on the radical reaction, increasing the extent of thermal polymerization of acrylic acid on low-density polyethylene, which is better observed at 60°C. This new method to obtain modified PE lacks information about the effect of factors that could interfere with the thermal polymerization reaction. In this paper, we investigate the effect of factors such as inhibition of the radical polymerization reaction and thickness of the matrix film, which could affect the kinetics of the thermal polymerization, in order to obtain better control of the properties and the amounts produced of this new material.

EXPERIMENTAL

Materials

Acrylic acid (AA) was supplied by Cia. Química Rhodia Brasileira and was distilled under vacuum before use. Hydroquinone monomethyl ether (HMME) was supplied by Cia. Rhodia Brasileira and was purified by recrystallization in acetone. Low-density polyethylene (LDPE) sheets ($d = 0.918 \text{ g/cm}^3$, $\text{MI} = 1.15 \text{ g/10 min}$) were supplied by Poliolefinas (São Paulo). The films were immersed in toluene for 24 h and dried before use. The characteristics of the polymer were checked by IR spectroscopy and X-ray diffraction.^{6,7} The degree of crystallinity was 50% as measured by X-ray diffraction.

Methods

The sorption and thermal polymerization of AA (80% by unit volume of aqueous solution containing 350 or 500 ppm of HMME) in LDPE films followed the method described in our previous work.⁶ The average thicknesses of the films used were 90, 200, 250, and 310 μm . The mass increase on LDPE films was obtained gravimetrically as described in the literature.⁸

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The surface homopolymer extraction was carried out in a Soxhlet apparatus using water as solvent. The swelling measurements of the samples after the reaction and extraction procedures were done by weighing the films and placing them in water at room temperature for 48 h. The films were quickly blotted dry with absorbent tissue and then weighed again. The percent swelling of the polymer was calculated according to Odian et al.⁹ The swelling ratio (q) is defined as the ratio of the volume of swollen film to the volume of unswollen film.

Physical Measurements

X-ray diffraction was done with a Philips instrument Model 1130 using $\text{CuK}\alpha$ tube operating at 40 KV and 20 mA. IR spectra were recorded in a Perkin-Elmer spectrophotometer Model 283B. A micrometer (J. T. Slocumb Co.) was used for the thickness measurements.

RESULTS

A. Effect of Hydroquinone Monomethyl Ether (HMME) on the Thermal Polymerization of AA in LDPE

LDPE films (3×4 cm) with thicknesses of 90, 200, 250, and 310 μm were immersed in an 80% by volume

Table I AA Sorption and Thermal Polymerization in LDPE at 90°C (Inhibitor Concentration 350 ppm of HMME)

Film Thickness (μm)	Mass Increase (%)	Reaction Time (h)	Mass Increase after Extraction (%)
90	0.1	1	0.1
	0.2	2	0.2
	0.9	4	0.9
	1.8	6	1.7
200	0.0	1	0.0
	4.4	2	4.3
	4.1	4	4.0
	12.9	6	12.9
250	0.1	1	0.1
	0.4	2	0.4
	2.5	4	2.4
	10.9	6	10.7
310	0.1	1	0.1
	0.4	2	0.4
	2.9	4	2.7
	7.3	6	7.3

Table II AA Sorption and Thermal Polymerization in LDPE at 90°C (Inhibitor Concentration 500 ppm of HMME)

Film Thickness (μm)	Mass Increase (%)	Reaction Time (h)	Mass Increase after Extraction (%)
90	0.5	1	0.2
	0.6	2	0.4
	0.9	4	0.8
	1.1	6	1.0
200	0.5	1	0.5
	2.0	2	2.0
	4.5	4	4.4
	1.3	6	1.2
250	0.3	1	0.3
	0.3	2	0.3
	3.1	4	3.1
	2.9	6	2.9
310	0.0	1	0.0
	0.6	2	0.6
	1.0	4	1.0
	1.5	6	1.5

of AA aqueous solution, containing 350 and 500 ppm of HMME, at 90°C. After reaction, the films were washed and the homopolymer from the surface was extracted for 24 h using water as the solvent. The average mass increase remaining in the sample was 93 wt % (cf. Table I). The thermal polymerization of AA on LDPE films was confirmed by the IR spectra of the samples, which showed the absence of the peak at 1630 cm^{-1} (stretching of vinyl $\text{C}=\text{C}$) and the presence of the carbonyl group at 1770 cm^{-1} . The mass increases of LDPE after AA sorption and thermal polymerization using several LDPE film thicknesses and HMME concentration of 350 and 500 ppm on the solution are shown in Tables I and II.

Figure 1 shows the mass increases of LDPE films after sorption and thermal polymerization of AA at 90°C containing 350 ppm of HMME vs. time. A continuous weight increase was observed on the films with different thicknesses (90, 200, 250, and 310 μm). A mass increase of 12.9 wt % was reached after 6 h of reaction (thickness of 200 μm). The same behavior was observed using an HMME concentration of 500 ppm in the AA solution (80%) (Fig. 2). However, a much lower extent of polymerization was observed (no more than 5 wt % of a mass increase was reached at the same reaction conditions). A linear behavior mass increase with

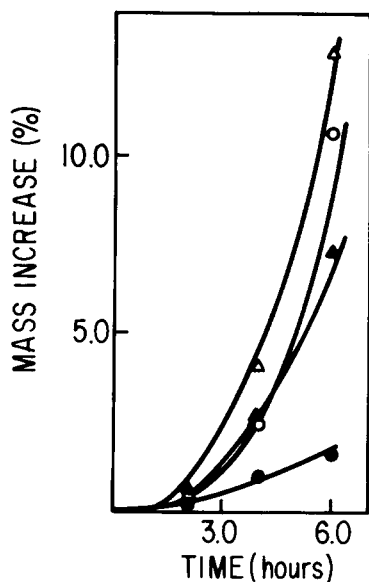


Figure 1 AA sorption and thermal polymerization in LDPE at 90°C. Inhibitor concentration: 350 ppm HMME. Film thicknesses: (●) 90 μm ; (Δ) 200 μm ; (○) 250 μm ; (\blacktriangle) 310 μm .

time was observed on the LDPE film that was 90 μm thick, independent of the inhibitor concentration (350 or 500 ppm of HMME) (Fig. 3). The apparent polymerization rate is higher at lower HMME concentration in the AA solution. The decrease of the apparent polymerization rate observed as the inhibitor concentration increases in the reaction media indicates that the thermal polymerization in LDPE is a free-radical process. In other words, the poly-

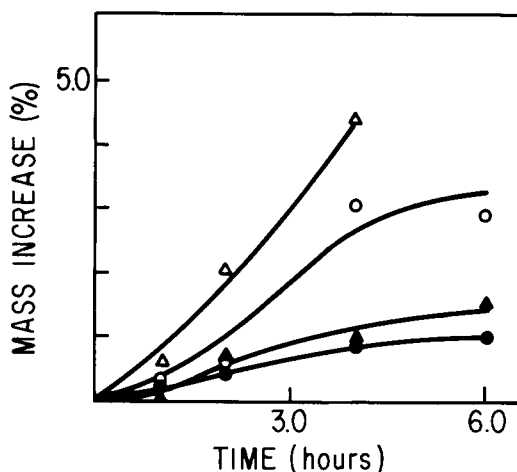


Figure 2 AA sorption and thermal polymerization in LDPE at 90°C. Inhibitor concentration: 500 ppm HMME. Film thicknesses: (●) 90 μm ; (Δ) 200 μm ; (○) 250 μm ; (\blacktriangle) 310 μm .

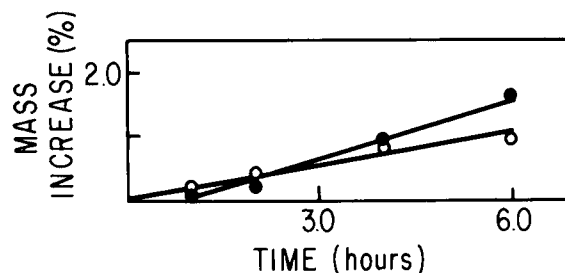


Figure 3 AA sorption and thermal polymerization in LDPE film (90 μm) at 90°C. Inhibitor concentration: (●) 350 ppm HMME; (○) 500 ppm HMME.

merization in the matrix is initiated by radical species, produced by heating the monomer solution.

B. Effect of Film Thickness on the Thermal Polymerization of AA on LDPE Films

Figures 1 and 2 also show the effect of film thickness on the sorption and thermal polymerization of AA on LDPE. A larger polymerization rate was observed on films 90–200 μm thick as compared with a smaller polymerization rate on films 250 and 310 μm thick. The decrease of the polymerization rate suggests that the thermal polymerization of AA on the LDPE matrix is controlled by the monomer diffusion into the matrix.

The thermal polymerization reaction in films 90 μm thick appears to be a diffusion-independent process in which the reaction rate is also independent of the monomer concentration in the matrix. In this case, the polymerization occurs mainly on the surface or on film layers near the surface. An increase of the polymerization rate was observed in films 90–200 μm thick.

C. Swelling Measurements of LDPE Films after Sorption and Thermal Polymerization of AA on LDPE

Figure 4 shows the percent swelling of modified LDPE film as a function of mass increase in LDPE after AA sorption and thermal polymerization (350 ppm of HMME in AA aqueous solution). A proportional increase of percent swelling of polymer with the mass increase of matrix was observed. However, the swelling ratio exhibited higher values on the samples of lower thickness. The same behavior was observed on the modified LDPE by using 500 ppm HMME in the AA aqueous solution (Fig. 5). The swelling ratio was found to be independent of film thickness up to a 1.5% of mass increase. A

decrease of swelling ratio with an increase of film thickness was observed for higher mass increase values ($> 1.5\%$).

DISCUSSION

The extent of AA thermal polymerization on LDPE film depends on the inhibitor concentration; it appears to be higher at lower concentrations of HMME. This suggests that a radical initiation reaction occurs mainly on the LDPE film surface or near to it with a propagation reaction proceeding subsequently in the bulk matrix. The literature shows HMME as possessing inhibitory activity only in the presence of oxygen.^{10,11} In this way, radicals such as RO_2^{\cdot} , and RO^{\cdot} are proposed to initiate the AA thermal polymerization on the matrix.

The effect of film thickness on the polymerization rate is identical for both inhibitor concentration (350 and 500 ppm of HMME) used. However, an unusual increase of the polymerization rate is observed on films 90–200 μm thick. According to Odian et al.,¹² a diffusion process is described by the following grafting rate:

$$R_p = [(k_p/k_t^{1/2})R_i^{1/2}M][\tanh(A)]/(A)$$

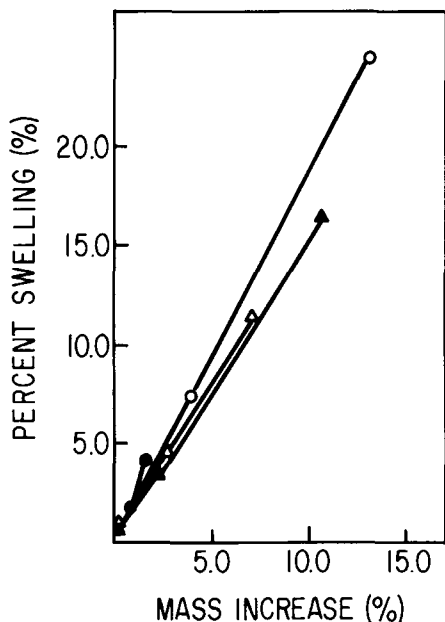


Figure 4 Percent swelling in water of LDPE films modified by sorption and thermal polymerization of acrylic acid at 90°C . Inhibitor concentration: 350 ppm. Film thicknesses: (●) 90 μm ; (○) 200 μm ; (▲) 250 μm ; (△) 310 μm .

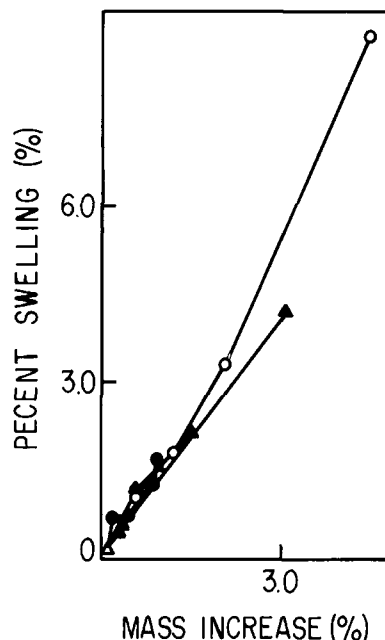


Figure 5 Percent swelling in water of LDPE films modified by sorption and thermal polymerization of acrylic acid at 90°C . Inhibitor concentration: 550 ppm. Film thickness: (●) 90 μm ; (○) 200 μm ; (▲) 250 μm ; (△) 310 μm .

where $A = [(k_p/k_t^{1/2})(R_i/D)]^{1/2}L/2$; k_p and k_t are the constants of propagation and termination rates, respectively; R_i , the initiation rate; D , the monomer diffusion coefficient; and L , the film thickness. For a diffusion-free process ($A < 0.1$), this equation reduces to

$$R_p = (k_p/k_t^{1/2})R_i^{1/2}M$$

and the following conditions are expected: (i) small film thickness, and (ii) slow polymerization rate relative to the monomer diffusion rate, i.e., R_p and $k_i/k_t^{1/2}$ have small values and D is high.

For a diffusion-controlled process ($A > 3.0$), the equation reduces to

$$R_p = (k_p/k_t^{1/2})R_i^{1/2}M/A$$

or

$$R_p = 2(k_p/k_t^{1/2})^{1/2}R_i^{1/4}MD^{1/2}/L$$

The following conditions are expected: (i) high film thickness, and (ii) the polymerization rate is faster than the diffusion rate, i.e., R_i and $k_p/k_t^{1/2}$ have high values and D is small.

On this basis, we suggest a diffusion-free process for the AA thermal polymerization on LDPE films using film thicknesses in the range 90–200 μm , even if the polymerization rate is not kept constant during the process. As the thermal polymerization is observed mainly in the surface or near to that, we propose a limiting value of the thickness, $\Delta(L)$, in which the process is independent of monomer diffusion of $\Delta(L/2) = 100 \mu\text{m}$. It is possible in this region that a variation of the radical concentration, which could be trapped within the film layer, and, consequently, an increase of the initiation and polymerization rates, R_i and R_p , could occur.

Also, the swelling measurements confirm a graft or interspersed poly(AA)–LDPE material with polymerization observed mainly on the surface of LDPE films or near to that for lower film thickness ($\leq 200 \mu\text{m}$).

We thank CNPq (Brazilian Research Council) for the financial support.

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Received May 22, 1991

Accepted April 10, 1992