

## Effect of iron(III) oxide on the thermal polymerization of methyl methacrylate in low density polyethylene matrix

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### ABSTRACT

The effects of the temperature and fine particles of  $\text{Fe}_2\text{O}_3$  upon methyl methacrylate(MMA) thermal polymerization in low density polyethylene(LDPE) matrix were investigated. The MMA mass increment in the composite matrix is a temperature dependent process. It reaches values 10 folds higher at  $90^\circ\text{C}$  compared to the mass increment at  $60^\circ\text{C}$ . The apparent polymerization rate is dependent of  $\text{Fe}_2\text{O}_3$  concentration reaching a maximum at 0.17-0.26 % of  $\text{Fe}_2\text{O}_3$  in the composite. The thermal process is catalysed by  $\text{Fe}_2\text{O}_3$ .

### INTRODUCTION

The effect of transition metals on the polymerization of vinyl monomers has been reported(1,2). Some of these studies showed catalytic activity of  $\text{Fe}_2\text{O}_3$  on the polymerization of methyl methacrylate(MMA) in aqueous media(3). Evidences for initiation of MMA polymerization by iron(III) salt have been discussed(4).

The modification of low density polyethylene(LDPE) by *in situ* sorption and thermal polymerization of acrylic acid(AA) has been studied(5). The kinetics of AA polymerization and the effect of  $\text{Fe}_2\text{O}_3$  particles doped matrix on the thermal polymerization were investigated(6,7). Interactions between  $\text{Fe}_2\text{O}_3$  particles and acrylic acid(AA) or poly(acrylic acid), (PAA), were evidenced.

In this paper we study the thermal modification of LDPE using MMA. The effect of iron(III) oxide particles on the thermal polymerization was investigated using the composite system LDPE- $\text{Fe}_2\text{O}_3$ .

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## EXPERIMENTAL

### Materials

MMA containing 10 ppm of hydroquinone monomethyl ether was purchased from Aldrich Chem. Co. LDPE sheets ( $d=0.918$  g/cm<sup>3</sup>, MI=1.15 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(8). The degree of crystallinity of LDPE was 50 %. Iron pentacarbonyl, Fe(CO)<sub>5</sub>, was supplied by BASF(Germany).

### Methods

The sorption and *in situ* oxidation of Fe(CO)<sub>5</sub> in LDPE films (3x4 cm) followed the procedure previously described(5). LDPE films(either plain or Fe<sub>2</sub>O<sub>3</sub> doped) were immersed in 99 % MMA under a nitrogen atmosphere at a specific temperature and time. The average film thickness was 200  $\mu$ m. After sorption, the samples were rinsed with acetone and dried under reduced pressure(1 torr). The mass increase of LDPE films was obtained gravimetrically as described(9). The surface homopolymer extraction was carried out in a Soxhlet apparatus using acetone as solvent.

### Physical Measurements

X-ray diffraction was done with a Philips instrument, Model 1130, using a CuK $\alpha$  tube operating at 40 KV and 20 mA. IR spectra were recorded on a Perkin Elmer Spectrophotometer, Model 283. A micrometer (J. T. Slocomb Co.) was used for thickness measurements.

## RESULTS

### a) Sorption and Thermal Polymerization of MMA in LDPE

LDPE films were immersed in MMA at 60 and 90°C for 1.0, 2.0, 4.0 and 6.0 hours and with an immersion frequency of 1 to 4 times. The mass increase as calculated by gravimetry is shown in Figures 1 and 2. Mass increment of 20.6 % and 18.3 % (wt % monomer by unit matrix weight) after monomer sorption (4x4 hours of reaction) at 60°C and 90°C were observed. A mass lost in the matrix during the first intervals of monomer sorption were noted (Figs. 1 and 2). The average of mass lost values were of 0.4 wt % and 3.0 wt % for the reaction temperatures of 60°C(Fig. 1) and 90°C(Fig. 2). Solubility tests at 30°C were carried out to check matrix(LDPE) and homopolymer(PMMA) solubilizations by the monomer.

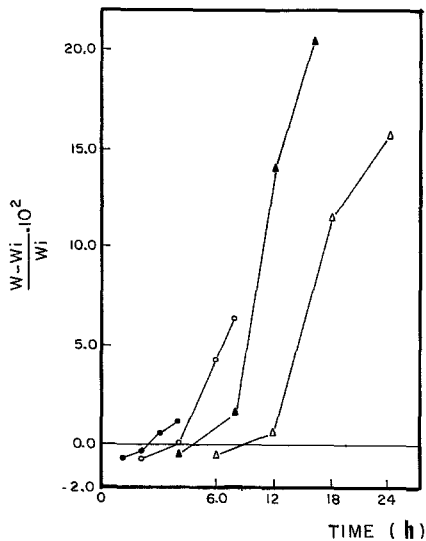


Fig.1 MMA Sorption in LDPE at 60°C. Sorption time: (●) 4 x 1.0 h; (○) 4 x 2.0 h; (▲) 4 x 4.0 h; (△) 4 x 6.0 h.

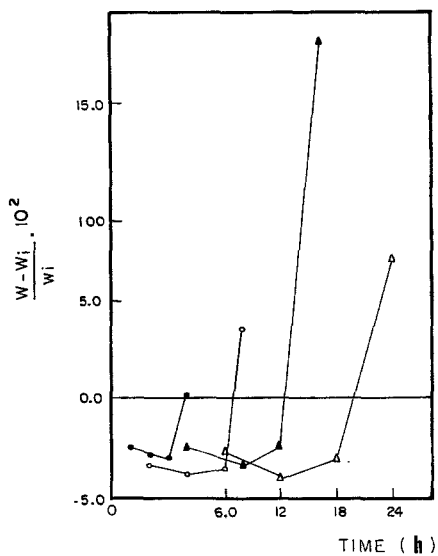


Fig.2 MMA Sorption in LDPE at 90°C. Sorption time: (●) 4 x 1.0 h; (○) 4 x 2.0 h; (▲) 4 x 4.0 h; (△) 4 x 6.0 h.

An average mass loss of 0.3 wt % was observed in the plain matrix and 1.7 wt % in the matrix previously submitted to the monomer thermal reaction. The evidence of some degree of solubilization of the matrix and homopolymer by MMA did not block the thermal polymerization in the LDPE matrix as shown by IR spectra (Fig. 3). The IR spectra of LDPE films after MMA sorption at 60°C (0.6 % of mass increase) presented a peak at  $1730\text{ cm}^{-1}$  ( $\nu$ , C=O), and showed absence of peaks at  $1630\text{ cm}^{-1}$  ( $\nu$ , C=C),  $960\text{ cm}^{-1}$  and  $825\text{ cm}^{-1}$  ( $\delta$ , C=C), Fig. 3a. The same profile was registered for samples after reaction at 90°C. Fig. 3b shows the spectrum of a sample with 4.0% mass loss (2 x 6.0 hours of reaction) and Fig. 3c shows the spectrum of a sample with a mass increment of 7.1 % (4 x 6.0 hours of reaction). The presence of carbonyl stretching ( $\nu_{\text{C=O}}$ ) and absence of unsaturation ( $\nu$  and  $\delta$  of C=C) can be seen in both samples.

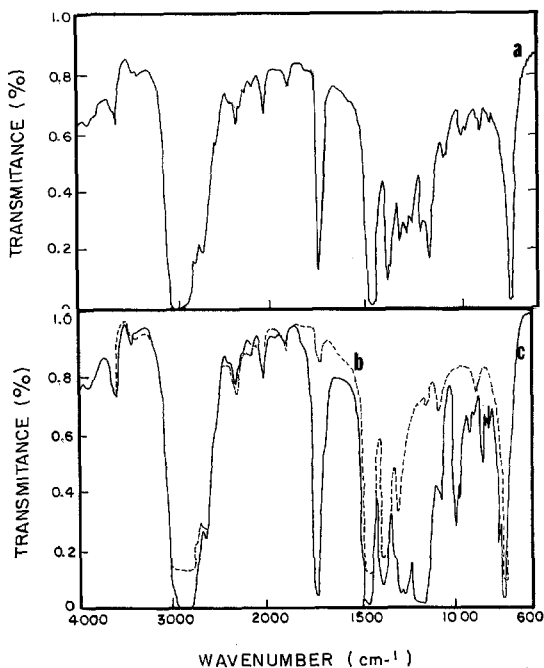


Fig.3 IR Spectra of LDPE after MMA Sorption.

(a) sorption temperature: 60°C; sorption time: 2 x 6.0 h; mass increment: 0.6 %. (b) sorption temperature 90°C; sorption time: 2 x 6.0 h; mass lost: 4.0 %. (c) sorption temperature: 90°C; sorption time: 4 x 6.0 h; mass increment: 7.1 %.

### b) Sorption and thermal polymerization of MMA in LDPE-Fe<sub>2</sub>O<sub>3</sub>

Films of LDPE containing 0.09-0.40 % finely dispersed Fe<sub>2</sub>O<sub>3</sub> particles(% of Fe<sub>2</sub>O<sub>3</sub> by weight of matrix) were immersed in a MMA solution for 0.5-6.0 hours at 60 and 90°C.

The mass increments versus reaction time at 60 and 90°C are shown in Figs. 4 and 5. A mass increment with time was observed in the composite matrix. It increases reaching 12.5 % in the composite matrix containing 0.26 % of Fe<sub>2</sub>O<sub>3</sub> (1 x 6.0 h of reaction at 60°C), Fig. 4, and 200.3 % of mass increase in the composite matrix containing 0.17 % of Fe<sub>2</sub>O<sub>3</sub> (1 x 6.0 h of reaction at 90°C), Fig. 5. These values are at least 1-2 order of magnitude higher than those observed in the pure matrix under the same conditions. The mass increment in the composite matrix was dependent of the temperature. A mass increment in the composite matrix of 10 times higher was observed at 90°C (Fig. 5) compared to that at 60°C (Fig. 4). As for the pure matrix, 0.4 % mass loss was observed in the composite matrix but only at short periods of time(0.5-1.0 h) and at 60°C (Fig. 4).

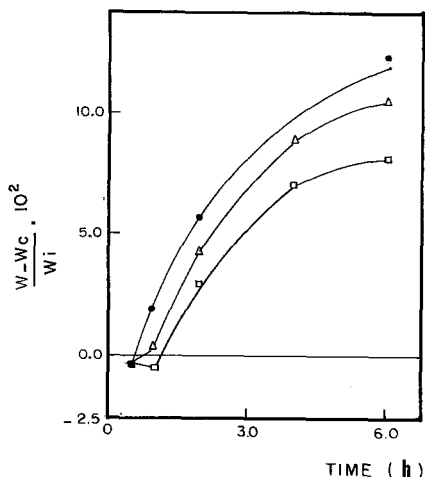


Fig.4 MMA Sorption in LDPE-Fe<sub>2</sub>O<sub>3</sub> at 60°C.

Fe<sub>2</sub>O<sub>3</sub> conc.: (□) 0.12 ± 0.01 %; (Δ) 0.26 ± 0.04 %; (●) 0.38 ± 0.03 %.

Evidence for homopolymer in the LDPE-Fe<sub>2</sub>O<sub>3</sub> modified matrix, either at 60 or 90°C, was shown by the IR spectrum which was similar to those in Fig.3.

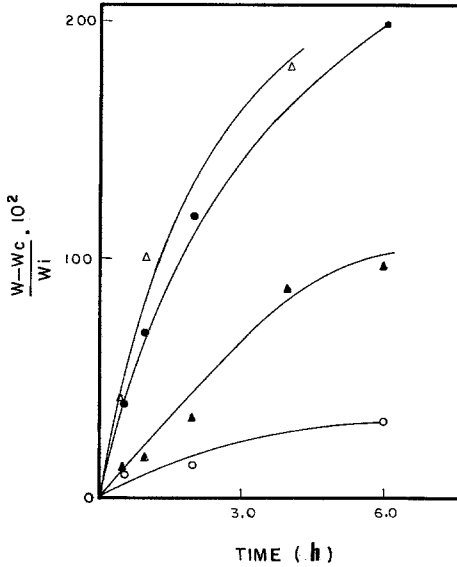


Fig. 5 MMA Sorption in LDPE-Fe<sub>2</sub>O<sub>3</sub> at 90°C.  
 Fe<sub>2</sub>O<sub>3</sub> conc.: (○) 0.09 ± 0.02 %; (●) 0.17 ± 0.02 %; (▲) 0.22 ± 0.01 %;  
 (△) 0.40 ± 0.04 %.

Figures 6 and 7 show the mass increment of the composite matrix versus Fe<sub>2</sub>O<sub>3</sub> concentration at 60 and 90°C. The mass increment of LDPE-Fe<sub>2</sub>O<sub>3</sub> increases with Fe<sub>2</sub>O<sub>3</sub> concentration until a maximum, then decreases at higher Fe<sub>2</sub>O<sub>3</sub> concentrations.

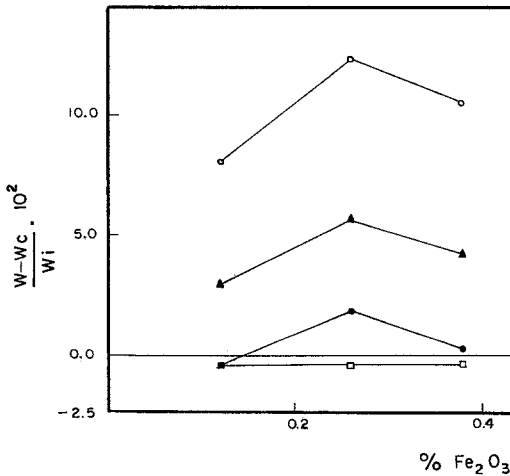


Fig. 6 MMA Mass Increment in LDPE-Fe<sub>2</sub>O<sub>3</sub> x % Fe<sub>2</sub>O<sub>3</sub> (60°C).  
 Sorption time: (□) 0.5 h; (●) 1.0 h; (▲) 2.0 h; (○) 6.0 h.

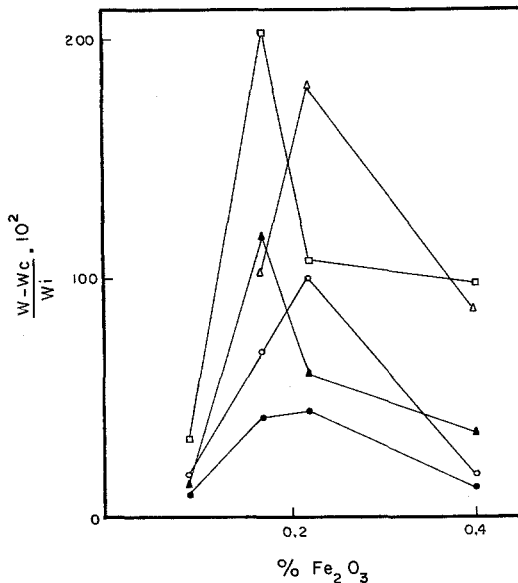


Fig. 7 MMA Mass Increment in LDPE-Fe<sub>2</sub>O<sub>3</sub> x % Fe<sub>2</sub>O<sub>3</sub> (90°C). Sorption time: (●) 0.5 h; (○) 1.0 h; (▲) 2.0 h; (△) 4.0 h; (◻) 6.0 h.

This behavior was observed at both temperatures (60 and 90°C). The maximum of mass increase was observed in the range of 0.12-0.26 Fe<sub>2</sub>O<sub>3</sub> at several times (Figs 6 and 7).

## DISCUSSION

The sorption and *in situ* thermal polymerization of MMA in pure LDPE and LDPE-doped Fe<sub>2</sub>O<sub>3</sub> was observed. The MMA polymerization in the pure and composite matrices, as proved by IR spectroscopy, indicates that the process occurs simultaneously with the solubilization of loosely linked polymer matrix chains on thermally produced homopolymer. The mass gain increases gradually with the time and frequency of the matrix immersion in the monomer solution.

The thermal polymerization in the composite matrix is directly dependent on temperature. The temperature effect upon the thermal polymerization of MMA in LDPE-Fe<sub>2</sub>O<sub>3</sub> is opposite to that observed using AA under the same conditions. In this case, a decrease of AA thermal polymerization with the temperature was observed.

This has been explained to be due to the formation of iron acrylate and probably iron(III) hydroacrylate polymers in LDPE-Fe<sub>2</sub>O<sub>3</sub> which blocks further AA diffusion and polymerization into the matrix(5). Based on the monomer structures, no reaction of MMA with Fe<sub>2</sub>O<sub>3</sub> particles are expected. In fact, previous studies by Mössbauer spectroscopy showed that iron(III) oxide remained unaltered after MMA sorption and thermal polymerization in LDPE-Fe<sub>2</sub>O<sub>3</sub> composite matrix(6). This confirms the absence of interaction between the MMA and Fe<sub>2</sub>O<sub>3</sub> particles leading to direct process control by temperature.

The data has also shown an increase of the apparent MMA polymerization rate in LDPE-Fe<sub>2</sub>O<sub>3</sub> with Fe<sub>2</sub>O<sub>3</sub> concentration reaching a maximum value at 0.17-0.26 % Fe<sub>2</sub>O<sub>3</sub> followed by a decrease at higher concentrations. It is confirmed that iron(III) oxide acts as a catalyst of the thermal radical polymerization lowering the activation energy as discussed previously(3, 6).

#### ACKNOWLEDGMENTS

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