

Mössbauer spectral changes in X-ray preirradiated polytetrafluoroethylene iron (III) oxide composite-interactions with acrylic acid

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ABSTRACT

The Mössbauer spectrum of Fe₂O₃ dispersed in PTFE is a doublet (IS = 0.33 – 0.35 mm/s; QS = 0.89 – 0.90 mm/s) and is unaltered by prolonged exposure to acrylic acid. Under exposure to X-rays, a new Fe (III) site is found, which differs from the preextant site in having a different microenvironment asymmetry. Acrylic acid treatment of preirradiated PTFE-iron (III) oxide composite generates an environment of a great distortion around iron nuclei as shown by the quadrupole splitting (QS = 1.11 mm/s). These results show that X-rays sensitize Fe(III) towards asymmetric sites in finely dispersed iron (III) oxide particles in the amorphous region of the matrix.

Introduction

The observation that the Mössbauer effect can be detected on iron nuclei inserted into light atom matrices has marked the evolution of Mössbauer investigation on polymeric matrices (1). Mössbauer spectroscopy was employed to study the amount of poly(iron methacrylate) prepared by the irradiation of the precursor monomer (2), as well as the extent of polymerization (3). It was also observed by this technique that the interactions involving poly(vinylpyridine) and iron centers are weak (4) and that Fe(III) complexes inserted into polyacetylene matrix undergo partial conversion to a high spin Fe(II) form (5). The nature of the anion introduced by doping into polyacetylene with iron complexes was also clearly revealed by Mössbauer spectroscopy (6,7).

Iron (III) oxide doped polytetrafluoroethylene (PTFE) by sorption and *in situ* oxidation of iron pentacarbonyl (8) appeared as a doublet in the Mössbauer spectrum (9), typical of superparamagnetic particles (IS = 0.36 mm/s; QS = 0.68 mm/s). More recently, by the same technique, the interaction of acrylic acid with iron oxide into a PTFE matrix was shown to be a surface process not involving extensive oxide reaction(10). The Mössbauer spectra of the composite containing or not containing acrylic acid (AA) had the same profile and similar Mössbauer parameters, IS = 0.33–0.35 mm/s; QS = 0.88–0.90 mm/s (10). Nevertheless, the iron (III) oxide affects the rate of acrylic acid polymerization in PTFE preirradiated with X-rays or irradiated by UV.

The purpose of this paper is to employ Mössbauer spectroscopy to study the effect of X-ray preirradiation on PTFE-Fe₂O₃ composites with and without acrylic acid (AA) introduced by sorption of aqueous acrylic acid into the composite.

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Experimental

Acrylic acid (AA) (stabilized by 200ppm of hydroquinone monomethyl ether) was purchased from Aldrich Chem. Co.. The monomer was used without dilution.

Polytetrafluoroethylene (PTFE) sheets (2x3x0.14 cm) made of Dupont Teflon by Incoflon (São Paulo), were used after the treatment described in reference (10). The impregnation of PTFE sheets (of 50% and 70% crystallinity) with Fe_2O_3 and the sorption of AA in virgin or composite polymer followed the procedure previously described (10,11).

PTFE- Fe_2O_3 films were preirradiated with X-rays using a tungsten source (Philips) working at 30kV and 12mA. The radiation intensity measured by LiF dosimeters was 2.4×10^5 R/hr. The films were irradiated under reduced pressure (0.1 mmHg) at room temperature.

Infrared spectra were recorded on a Perkin-Elmer Mod. 283 spectrophotometer; differential spectra were measured using a bare PTFE film in the reference beam.

Mössbauer spectra of preirradiated PTFE- Fe_2O_3 were run before and after AA sorption, at room temperature. The required iron content in the sample was 5 mg/cm², which was reached by piling up a number of films. A calibration spectrum utilizing an iron sheet absorber gave the iron line width of $\Gamma = 0.26$ mm/s. The isomer shifts given are referred to the iron absorber.

Results and Discussion

Fig. 1 shows Mössbauer spectra of preirradiated PTFE- Fe_2O_3 for 400 sec., before acrylic acid sorption of 70% and 50% PTFE crystallinity (samples S_1 and S_3). The spectra of both samples are very similar irrespective of PTFE crystallinity. Both consist of similar quadrupole doublets with a splitting, $QS = 0.85 \pm 0.01$ mm/s and isomer shift, $IS = 0.33 \pm 0.02$ mm/s (Table 1). The doublet remained unaltered after AA sorption on the polymer-metal oxide composite of 70% of PTFE crystallinity (S_2 in Fig. 1). As expected, iron ions maintain their ferric state as indicated by the IS value. The high value of QS is consistent with an environment of high electronic asymmetry for the iron nuclei similar to those observed in references (9) and (10).

However, the main feature of the spectrum of 400 sec preirradiated PTFE- Fe_2O_3 (50% PTFE crystallinity) followed by AA sorption, resulted in a slightly distorted doublet which can be resolved into two distinct doublets (Fig. 2). Albeit, not yet satisfactorily adjusted as two doublets one might infer this to be an indication of a distinct, new site for the iron nuclei. The resolved doublets had similar IS values (0.36 ± 0.07 mm/s) typical of Fe^{3+} nuclei but distinct QS values of (0.58 ± 0.05 and 0.96 ± 0.05 mm/s) suggesting a quite different asymmetric charge environment (Table 1; S_4). A more detailed examination of this fact was carried out using longer irradiation periods of the composite matrices with 50% PTFE crystallinity.

Upon 1200s preirradiation, the PTFE- Fe_2O_3 spectrum was adjusted as two doublets: doublet a ($IS = 0.38 \pm 0.01$ mm/s and $QS = 0.66 \pm 0.00$ mm/s) and doublet b ($IS = 0.31 \pm 0.01$ mm/s and $QS = 0.86 \pm 0.00$ mm/s), Fig. 3 and Table 2. Doublet (b) had Mössbauer parameters in the same range as those found for non-irradiated PTFE- Fe_2O_3 samples whether treated or not with AA (10), Table 2. However, the first doublet (a) showed quite different QS (0.66 mm/s) and IS (0.38 mm/s) values. These data indicate

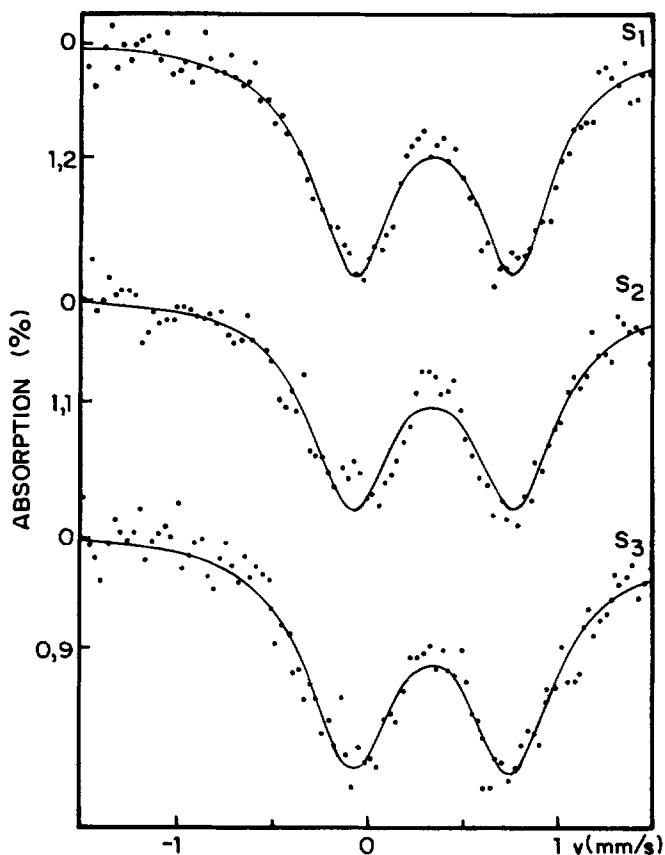


Fig. 1 - Mössbauer spectra
 PTFE- Fe_2O_3 (S_1), PTFE- Fe_2O_3 after AA sorption (S_2), 70% PTFE
 crystallinity; PTFE- Fe_2O_3 , 50% PTFE crystallinity (S_3) ;
 preirradiation time: 400 sec.; AA sorption time: 6h/90°C.

possible structural changes in the microenvironment of the iron oxide particles dispersed in PTFE, induced by X-ray irradiation. This may be explained by distinct iron oxide particles sites dispersed in crystalline or amorphous regions of PTFE matrix which may differ with respect to electron density and symmetry environment of iron(III) nuclei.

The Mössbauer spectrum of preirradiated PTFE- Fe_2O_3 followed by exposure to AA showed significant change. The asymmetric doublet (Fig.4) can be resolved to two doublets: (a) IS = 0.38 mm/s, QS = 0.66 mm/s; (b) IS = 0.34 mm/s, QS = 1.11 mm/s (Table 2). These data show that these samples also contain two iron sites (termed a and b) as in the case of preirradiated PTFE- Fe_2O_3 . Nevertheless, site b, exhibits a higher QS value (1.11 mm/s) indicating a great distortion around Fe (III) ion possibly related to amorphous iron (III) oxide, $\text{Fe}(\text{OH})_3$ (12). It could also be interpreted with restrictions as low spin Fe(II) ion. The later possibility seems to be highly unlikely since no low spin Fe(II) oxides

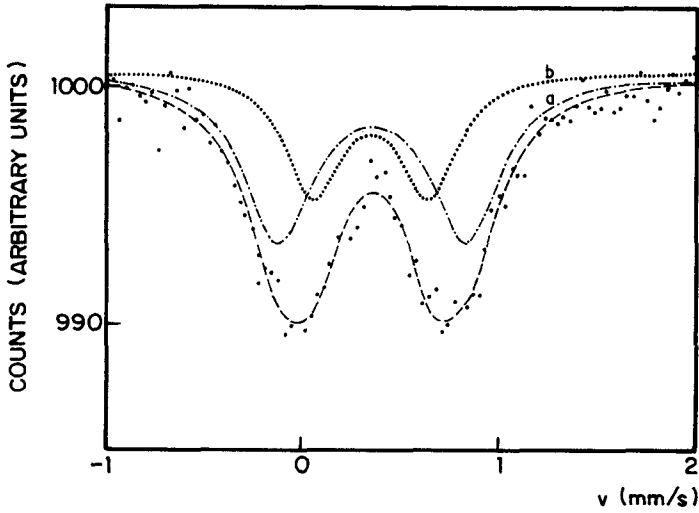


Fig. 2 - Mössbauer spectrum of preirradiated PTFE-Fe₂O₃, after AA sorption (S₄); preirradiation time 400 sec.; AA sorption for 6h at 90°C.

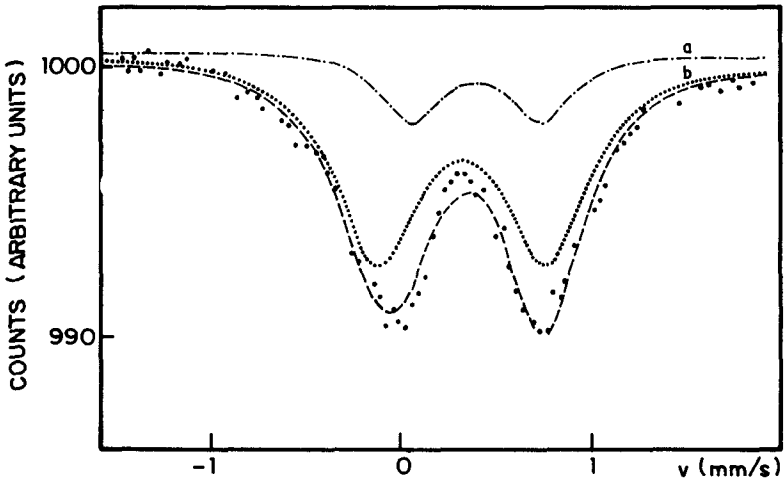


Fig. 3 - Mössbauer spectrum of preirradiated PTFE-Fe₂O₃ (S₅), preirradiation time 1200 sec; 50% PTFE crystallinity.

TABLE 1 - Mössbauer parameters

Nº	Sample	%Fe ₂ O ₃	$\frac{W - W_c}{W_i} \cdot 10^2$	IS (mm/s)	QS (mm/s)	Γ (mm/s)
S ₁	PTFE-Fe ₂ O ₃	1.1	-	0.33±0.01	0.85±0.00	0.52±0.02
S ₂	PTFE-Fe ₂ O ₃ After PA sorption	1.2	1.7	0.34±0.02	0.86±0.01	0.55±0.02
S ₃	PTFE-Fe ₂ O ₃	1.6	-	0.33±0.02	0.85±0.01	0.55±0.02
S ₄	PTFE-Fe ₂ O ₃ After AA sorption	1.5	2.0	0.36 ^a ±0.06 0.36 ^b ±0.07	0.58 ^a ±0.05 0.96 ^b ±0.05	0.35 ^a ±0.09 0.45 ^b ±0.05

Sorption time: 6h/90° under nitrogen atmosphere; preirradiation time: 400 sec.; PTFE crystallinity: (S₁), (S₂), 70%; (S₃), (S₄), 50%.

TABLE 2 - Mössbauer parameters

nº	Sample	%Fe ₂ O ₃	$\frac{W - W_c}{W_i} \cdot 10^2$	IS (mm/s)	QS (mm/s)	Γ (mm/s)
S ₅	PTFE-Fe ₂ O ₃	1.6	-	0.38 ^a ±0.01 0.31 ^b ±0.01	0.66 ^a ±0.00 0.86 ^b ±0.00	0.36 ^a ±0.02 0.54 ^b ±0.01
S ₆	PTFE-Fe ₂ O ₃ After AA sorption	1.6	10.4	0.38 ^a ±0.02 0.34 ^b ±0.02	0.66 ^a ±0.00 1.11 ^b ±0.01	0.36 ^a ±0.02 0.49 ^b ±0.02

Sorption time, 8h/90°C in a nitrogen atmosphere; preirradiation time 1200 sec..

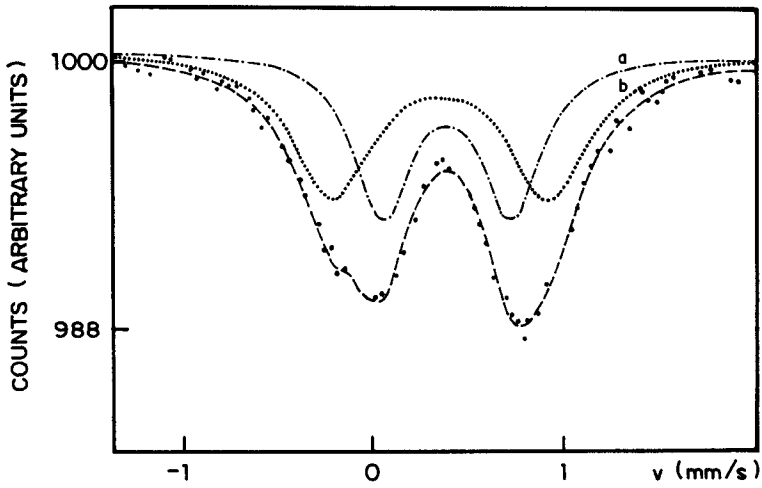


Fig. 4 - Mössbauer spectrum of preirradiated PTFE-Fe₂O₃ after AA sorption (S₆), preirradiation time 1200 sec.; 50% PTFE crystallinity; AA sorption 8h at 90°C.

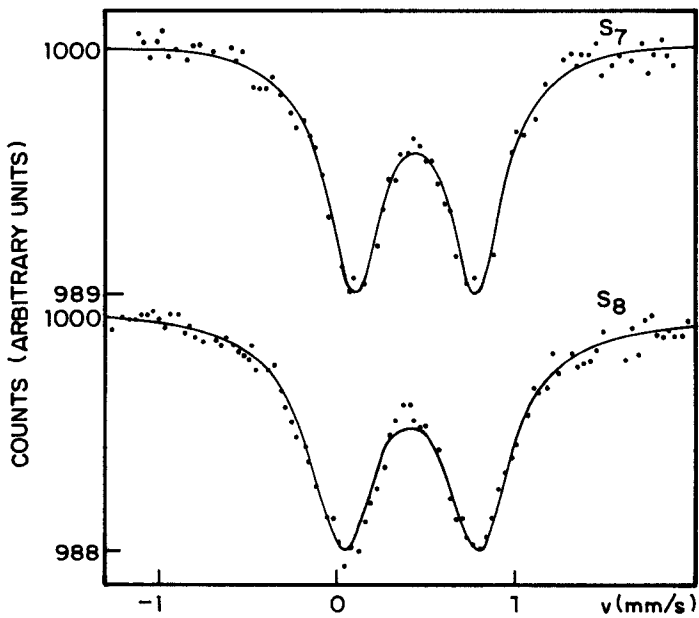
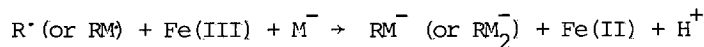


Fig. 5 - Mössbauer spectra of preirradiated PTFE-Fe₂O₃ after acetic acid sorption, 8h/90°C (S₇) and 32h/90°C (S₈); preirradiation time 1200 sec. .

have been reported as far as we know. The AA could then act as just a PTFE plasticizing agent rather than an electron source for iron (III) producing iron (II) ions as proposed on our previous work (10):



where: M = acrylic acid.

It is possible that the iron oxide particles which have been exposed to AA are dispersed into the amorphous region of PTFE (site b) while those iron (III) oxide particles, with corresponding Mössbauer parameters values referred as site a, and which remained unaltered after AA sorption, are dispersed into the crystalline region.

Mössbauer spectra were also obtained for preirradiated (1200 sec.) PTFE-Fe₂O₃ treated with acetic acid, 8h and 32h at 90°C (Fig. 5). The spectra showed just a symmetric doublet with IS = 0.40-0.42 mm/s and QS = 0.66-0.73mm/s (Table 3). These values are within the range found for non-irradiated PTFE-Fe₂O₃ after acetic acid sorption reported previously as due to iron (III) acetate formation (10) and also in agreement with the values found for iron (III) acrylate IS = 0.40 mm/s and QS = 0.65 mm/s (13). We conclude that preexposure to X-rays does not affect the effect of acetic acid on the composite polymer-iron oxide. That means iron (III) oxide species react with acetic acid irrespective of the micro-environment in which it is contained. This is different from the case of preirradiated PTFE-Fe₂O₃ after AA sorption.

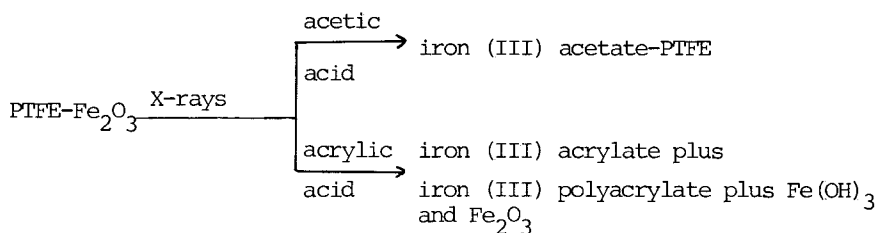
TABLE 3 - Mössbauer parameters

n°	Sample	%Fe ₂ O ₃	%Acetic acid mass increment	IS (mm/s)	QS (mm/s)	Γ (mm/s)
S ₇	After acetic acid sorption	1.6	1.8	0.42±0.00	0.66±0.00	0.38±0.00
S ₈	After acetic acid sorption	1.7	3.1	0.40±0.00	0.73±0.00	0.44±0.00

Sorption temperature, 90°C; sorption time, (S₇) 8h and (S₈) 32h; x-ray preirradiation 1200 sec..

In contrast, the IR spectrum of preirradiated PTFE-Fe₂O₃ after AA sorption showed the same features as the non-irradiated samples, such as the peaks assigned to carboxylate groups (1580 and 1510cm⁻¹), carbonyl group (1710cm⁻¹) and unsaturation at 1635cm⁻¹ (10).

This can be summarized as follows:



It is thus clear that X-rays affect Fe₂O₃ particles dispersed in PTFE leading to structural modifications in the iron nuclei microenvironment. This result may be relevant in regard to *in situ* polymerization and protection of partly oxidized iron plates of interest to coatings technology.

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