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A Study of the Initiator Concentration's Effect on Styrene-Divinylbenzene Polymerization with Iron Particles

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Abstract: This paper describes the preparation of magnetic copolymer obtained from suspension polymerization of styrene (Sty) and divinylbenzene (DVB) in the presence of iron particles treated and not treated with oleic acid. The magnetic copolymers were characterized according to their morphology, particle size distribution and magnetic properties. The results show that incorporation of iron particles significantly changed the particles' morphology. All samples presented higher saturation magnetization than the values reported in the literature and the particle size distribution was more monodisperse when the polymerization was conducted with 5%wt of benzoyl peroxide (BPO).

Keywords: Magnetic copolymers, suspension polymerization, iron, composite.

Introduction

Magnetic copolymers are composites based on polymers as the matrix and inorganic magnet materials, such as Fe_2O_4 , Fe_2O_3 , nickel and cobalt, which exhibit the characteristics of both polymers and the magnets^[1-4]. These materials have many potential technological applications, such as water treatment, cell labeling, cell separation, enzyme immunoassaying and drug targeting^[5-14]. Many different polymerization methods can be used to prepare magnetic copolymers, such as emulsion polymerization, dispersion polymerization and suspension polymerization, among others. Of these methods, suspension polymerization is simplest and allows easiest preparation and control of the surface areas and pore structure than the others^[15-22].

The most important parameters for application of magnetic copolymers are size, size distribution, morphological aspects, hydrophobicity/hydrophilicity, density of reactive surface groups and magnetic properties^[4,15]. Some authors have shown that the reaction kinetics has a greater influence on particle size distribution when the initiator's concentration is increased, because the viscosity increase rate is higher than the coalescence rate, causing a decrease in particle size^[23-24].

In this work, we investigate the effect of initiator concentration on the synthesis of magnetic copolymers.

Experimental

Materials

Styrene, divinylbenzene and carbonyl iron powder OX were kindly provided by Petroflex, Nitriflex and Basf, respectively, and used as received. The carbonyl iron powder OX consists of iron particles coated by 10% wt- Fe_2O_3 with 4 μm average particle size. Benzoyl peroxide (BPO), poly (vinyl alcohol) (PVA), oleic acid and ethanol were purchased commercially and also used as received.

Preparation of iron composite

Reaction of iron and oleic acid

Iron (20 g) was soaked with oleic acid (260 mL) in distilled water (500 mL) and the solution was stirred for 24 hours. Then the material was repeatedly washed with ethanol to remove the nonreacted oleic acid and dried at 60 °C.

Preparation of iron composite materials

The styrene and divinylbenzene copolymerizations were performed in a 500 mL, three-necked, round-bottomed flask reactor fitted with a mechanical stirrer and reflux condenser, placed in a silicon oil bath. The organic phase (OP) consisted of 90% mol of styrene, 10% mol of divinylbenzene, benzoyl peroxide as initiator and iron particles treated or not with oleic acid (20% in relation to monomers). The aqueous phase (AP) was prepared by addition of PVA (0.2% wt/v in relation to water). The organic phase and iron were added to the reactor under stirring (360 rpm) at room temperature during 30 minutes. Then the aqueous phase was added and the suspension system was kept under stirring at the same rate at 80 °C during 24 hours. The resin beads were washed with hot water (8 portions of 500 mL) and ethanol and then were dried at 50 °C.

The amounts of benzoyl peroxide employed were 1% (BA-13 and BA-16), 3% (BA-14 and BA-17) and 5% (BA-15 and BA-18) in relation to the monomers. The copolymers BA-13, BA-14 and BA-15 were synthesized with iron not treated with oleic acid.

Characterization

The apparent density was determined according to the ASTM D1895 method. The magnetic properties were determined by a vibrating sample magnetometer (Lake Shore VSM, model 7400) at room temperature (frequency = 1 segundo and hysteresis cycle

time = 10 minutes). The morphology and iron particle distribution on the surface were observed by scanning electron microscopy (Philips SEM, model XL-30). The samples were dispersed on conductive tape and submitted to gold sputtering to make them conductive prior to the analyses. The average particle size was determined by scattering (Malvern Instruments, model 2000) and the reaction of oleic acid and iron was confirmed through diffuse-reflectance FTIR spectroscopy (Perkin Elmer model Spectrum One). The degradation temperature was determined by thermogravimetric analysis (TA Instruments, model Q50). The samples were heated in a nitrogen atmosphere from 10 to 950 °C at a rate of 10 °C/min.

Results and Discussion

The spectrum of carboxylic acids displays a strong and large band for the -OH stretch in the region 3300-2500 cm^{-1} . This band is usually centered at about 3000 cm^{-1} . The C=O axial stretching appears at 1760 cm^{-1} , while the C-O-H stretching is observed at 1315-1280 cm^{-1} . In the case of long chains, this band appears as a double peak. Another characteristic of carboxylic acid spectra is the appearance of large or medium intensity bands near 920 cm^{-1} , which correspond to angular deformation out of the plane of the -OH group^[25] (Figure 1a). The diffuse-reflectance FTIR spectrum of iron modified by oleic acid is shown in Figure 1b. The spectrum shows a peak at 1630 cm^{-1} , which corresponds to the symmetric and asymmetric stretching of carboxylate groups. The strong C = O stretching vibration ($\approx 1750 \text{ cm}^{-1}$) is absent and the broad stretching near 3500-3300 cm^{-1} can be a sign of absorption of water and hydroxyl groups on the iron. Therefore, it is possible to confirm the incorporation of oleic acid on the surface of the iron particles due to the formation carboxylate.

According to literature, treatment with oleic acid or other organic compounds makes the iron surface hydrophobic and increases its affinity for the organic phase. This surfactant can also prevent agglomeration of iron particles, which are attracted by Van der Waals bonding^[4,15,16,26-28].

The particle size distribution depends on the polymerization conditions. Differences in morphology depend on the combination of suspension agents, types and concentration as well as the stirring speed. Normally, the polymerization conditions are suitable to produce copolymer beads but the introduction of a new component (e.g. iron particles) can disturb the polymerization process, producing particles without defined shape.

Figure 2 shows SEM micrographs of copolymer BA-13 synthesized with 20% iron without oleic acid treatment. It can be seen that some particles are agglomerated and do not present a defined shape (Figure 2a). This trouble occurred because of the addition of iron, which does not have any affinity for the organic phase and thus alters the particles' morphology. It was possible to see iron particles dispersed on the bead surfaces (Figure 2b). Figure 3 shows SEM micrographs corresponding to copolymer BA-16 synthesized with 20% iron treated with oleic acid. It is possible observe that the particles are not agglomerated and have a more homogeneous bead size distribution. However, this last copolymer has some particles without defined shape. This behavior is not so marked, indicating that the iron treated with acid oleic allowed better morphological control due to its repellent action. It was possible to see iron particles dispersed on the bead surfaces (external part) and in the interior of copolymers synthesized with iron treated or not with oleic acid (Figure 4).

The TGA's curves showed that the percentage of residual mass was lower for BA-16 (0.87 mg – 11.25%) than (1.24 mg – 13.31%),

meaning that the BA-16 copolymer contains less iron because this metal holds some oleic acid on its surface (Figures 5 and 6).

Even with a smaller amount of iron, the BA-16 copolymer presented a saturation magnetization result ($M_s = 18.87 \text{ emu.g}^{-1}$) closer to that of BA-13 copolymer ($M_s = 17.38 \text{ emu.g}^{-1}$), which means that the iron treated with oleic acid allowed the particles to become spherical without agglomeration, as well as permitting saturation magnetization closer to that of the copolymer containing iron particles not treated with oleic acid. The employment of acid improves the copolymer's final magnetic properties (Figure 7).

Alvarez and co-workers^[23] noticed that the reaction kinetics' influence on particle size distribution is higher when the initiator's concentration is multiplied by four, while keeping the other conditions constant. This result could be attributed to an increased polymerization rate, which accelerates the monomer-polymer mixture's viscosity gain, making the gel effect more noticeable in the beginning of the reaction. Because of this, the viscosity increase rate is higher than the coalescence rate, decreasing the particles' size. Ober and Hair^[24] also observed this behavior when the initiator amount was doubled.

The Figure 8a shows the particle size distribution curves of copolymers BA-13, BA-14 and BA-15 synthesized with iron without oleic acid treatment. It is possible to observe that copolymer BA-15 had a narrower particle size distribution compared to copolymers BA-13 and BA-14. As mentioned in the literature, iron can act as a strong reaction inhibitor due to adsorption of free radicals during the polymerization, reducing the polymerization rate considerably. As a consequence, a broadening enlargement of the pearls size distribution is observed^[18]. As the polymer was obtained with higher initiator concentration, reaction rate was probably higher, producing a narrow particle size distribution. Figure 8b shows the particle size distribution curves of copolymers BA-16, BA-17 and BA-18 synthesized with iron treated with oleic acid. The distribution curves are very similar. However, the particle size distribution range of these copolymers (BA-16, BA-17 and BA-18) shifted to smaller values when the initiator concentration was increased. The particle size distribution curves of copolymers BA-16, BA-17 and BA-18 showed that these copolymers present more homogeneous particles when compared with the copolymers synthesized with iron without oleic acid treatment (BA-13, BA-14 and BA-15).

The apparent density results and particle size distribution are shown in Table 1. Copolymer BA-18 presented the smallest particle size of all the copolymers as well as the largest apparent density. Based on these results, it can be concluded that the increase of the initiator concentration assured narrower polydispersity of particles for copolymer BA-15 and smaller particle size for BA-18.

As shown previously, the addition of iron particles caused a disturbance in the shape of the beads formed. Because of that, we measured the degradation temperature of all copolymers. The results are presented in Table 1. Styrene-divinylbenzene copolymers presented a degradation temperature around 413 °C. The degradation temperature was increased by the addition of iron, meaning the iron kept the copolymers thermally stable.

The magnetization curves of all samples are shown in Figures 9 and 10. The saturation magnetization was approximately 23.0 emu.g^{-1} . None of these evaluated samples showed hysteresis and the remanence magnetization values were close to zero, suggesting that they have superparamagnetic properties (Table 1). The saturation magnetization (23.0 emu.g^{-1}) is higher than the values reported in other similar studies (15.0 – 17.0 emu.g^{-1})^[17-18]. All magnetic composites responded very rapidly to a magnetic field.

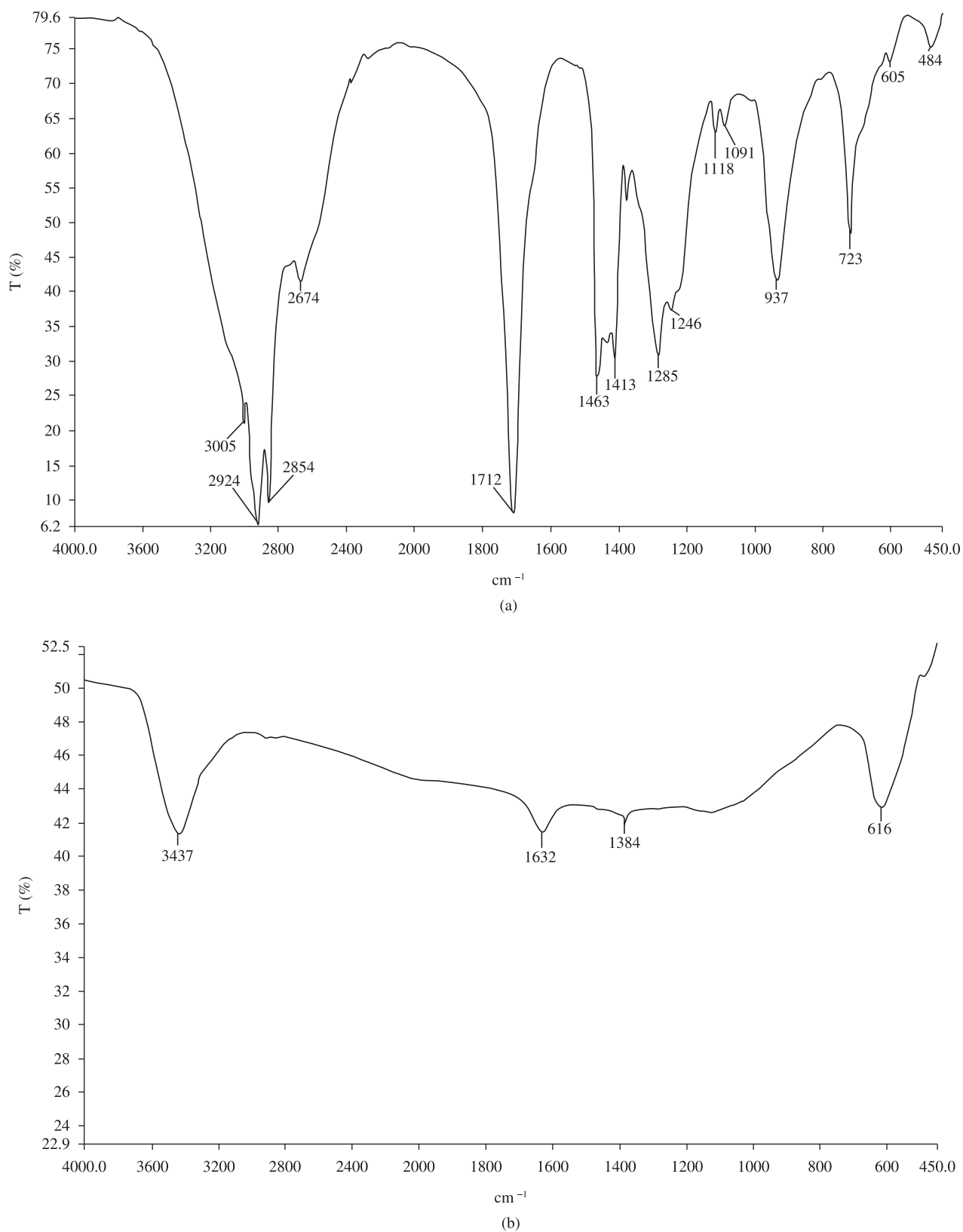


Figure 1. Diffuse IR spectrum. a) Oleic acid; and b) modified iron with oleic acid.

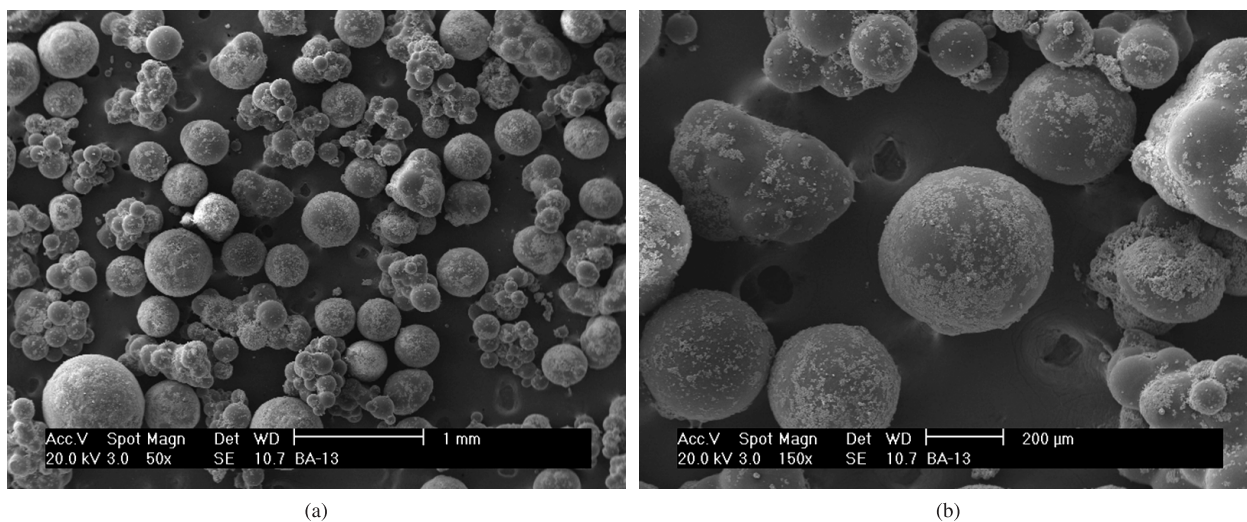


Figure 2. Scanning electronic micrograph of composite synthesized with 20% iron without oleic acid treatment (BA-13). a) Overview of polymeric particles; and b) surface details.

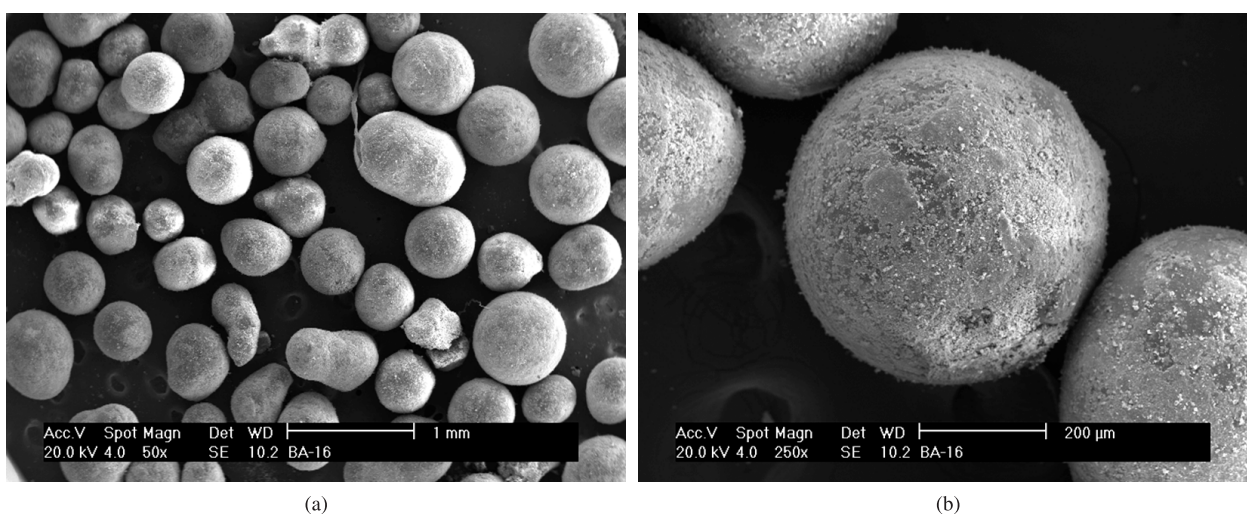


Figure 3. Scanning electronic micrograph of composite synthesized with 20% iron oleic acid treatment and benzoyl peroxide 1% (BA-16). a) Overview; and b) surface details.

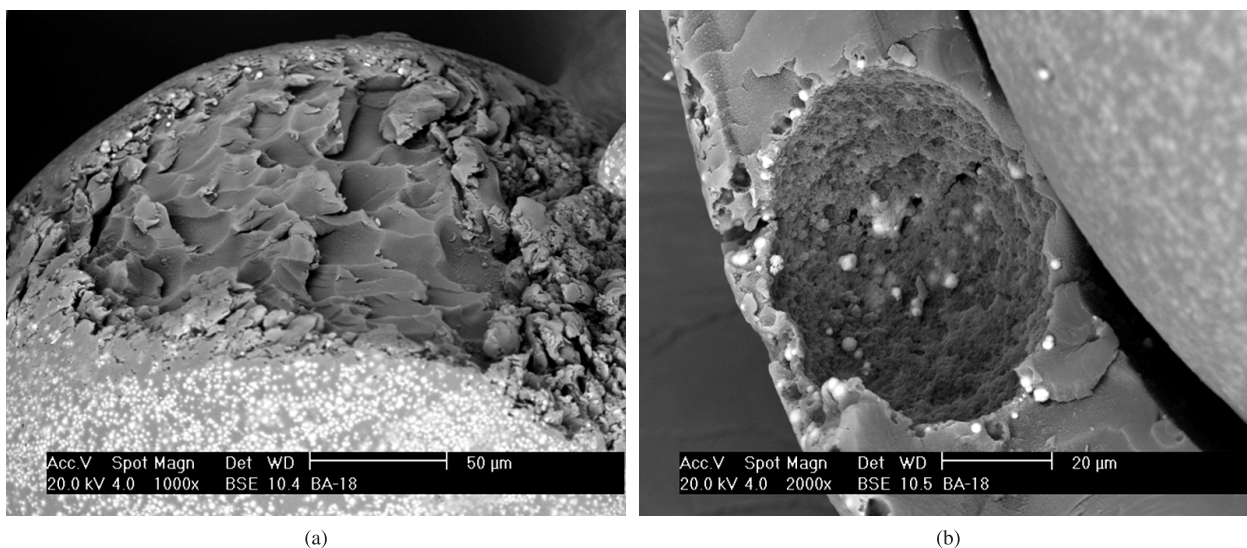


Figure 4. Scanning electronic micrograph of external part of composite synthesized with 20% iron oleic acid treatment and benzoyl peroxide 5% (BA-18). a) Surface details; and b) interior details.

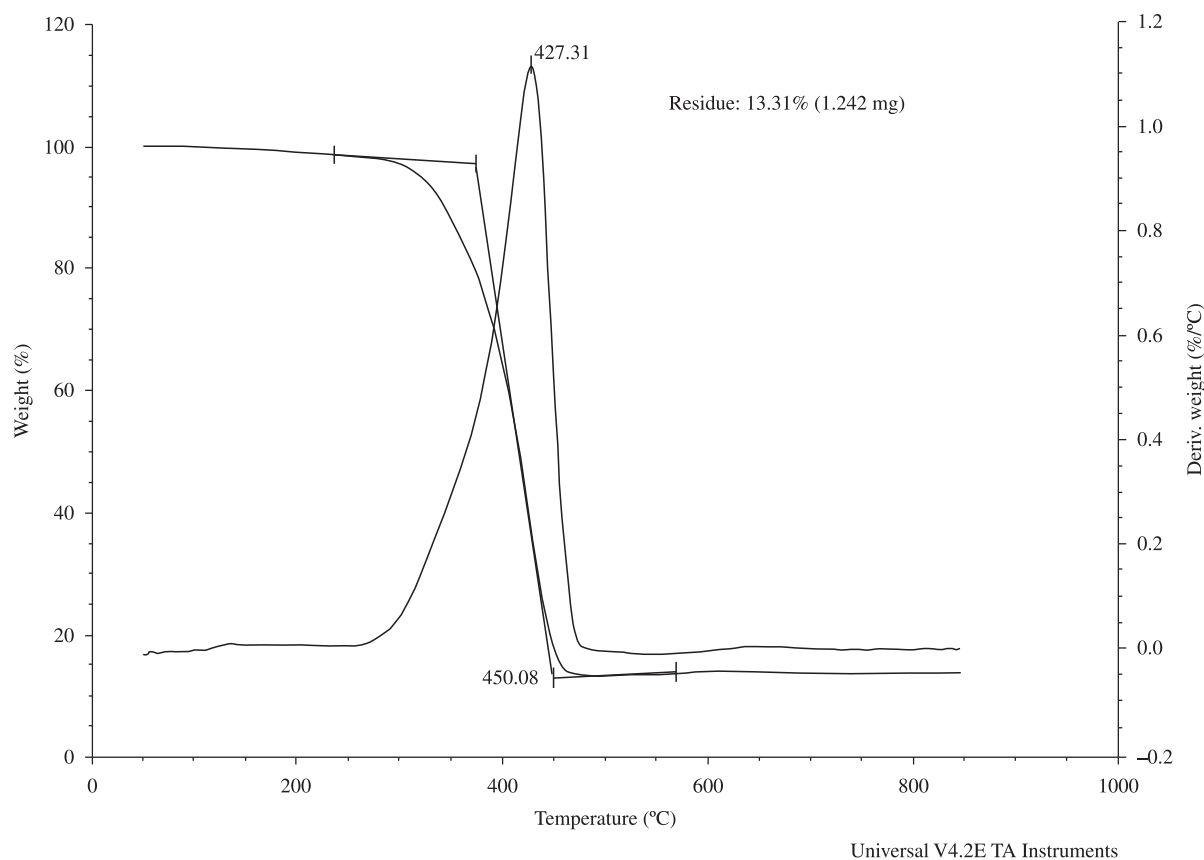


Figure 5. TG curve of composite with 20% iron without oleic acid treatment (BA-13).

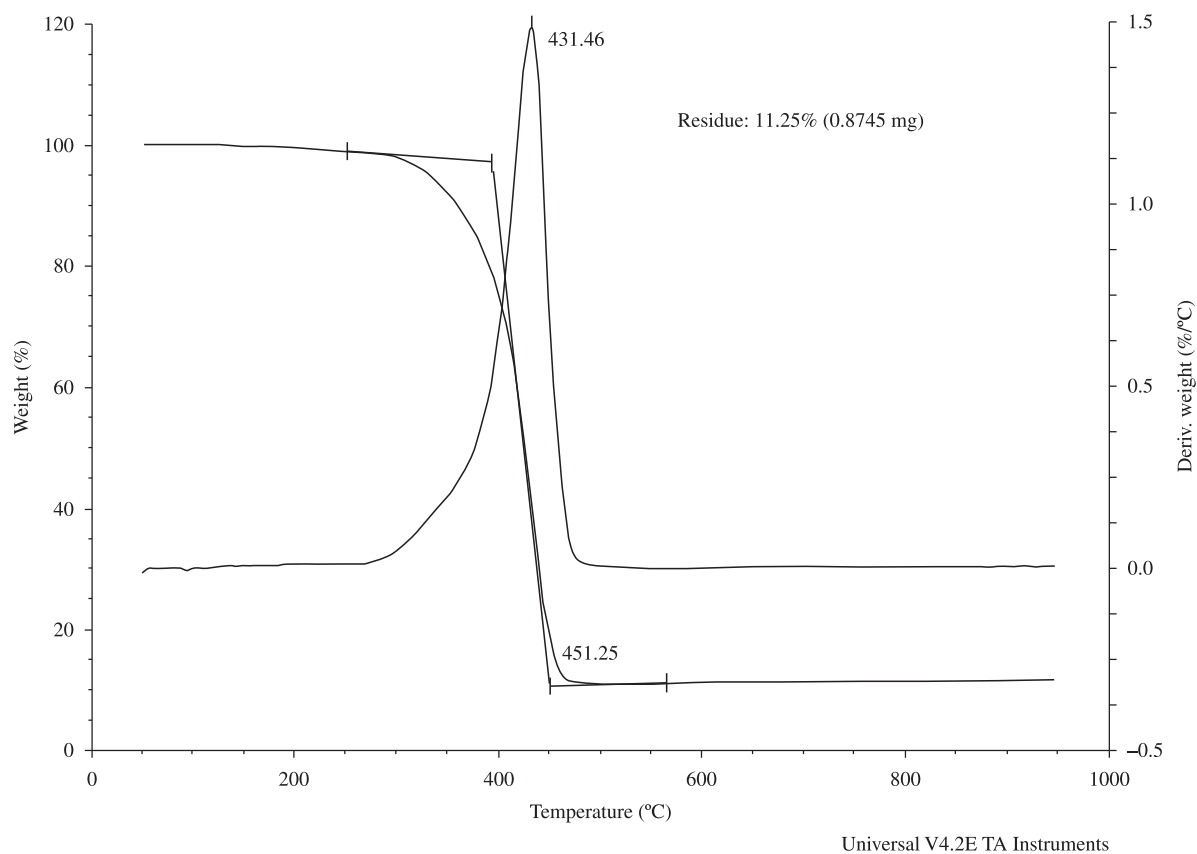


Figure 6. TG curve of composite with 20% iron treated with oleic acid (BA-16).

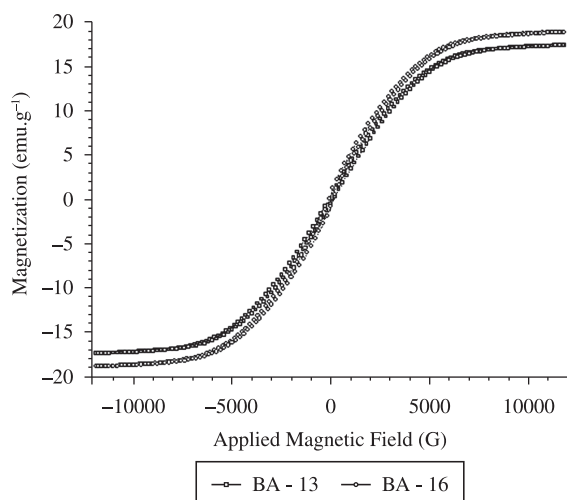
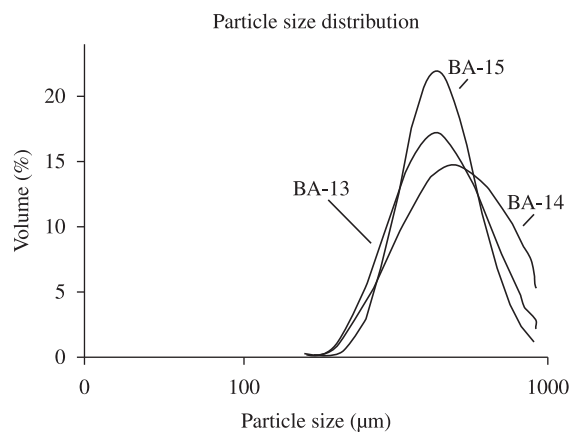
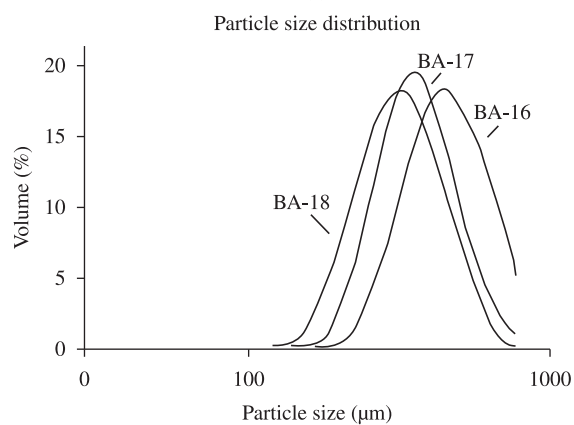


Figure 7. Magnetization curves of composites synthesized with 20% iron without (BA-13) and with oleic acid treatment (BA-16).



(a)



(b)

Figure 8. Particle size distribution curves. a) Copolymers BA-13, BA-14 and BA-15 synthesized with iron without oleic acid treatment; and b) Copolymers BA-16, BA-17 and BA-18 copolymers synthesized with iron treated with oleic acid.

Conclusion

This study showed that the initiator's concentration affects the particle size distribution. The particle sizes of the copolymers synthesized with iron treated with oleic acid (BA-16, BA-17 and

Table 1. Synthesis parameters and physics characteristics.

Composite	BPO* (%)	D-50 (mm)	M _s (emu.g ⁻¹)	M _r (emu.g ⁻¹)	Density (g.cm ⁻³)	Degradation temperature (°C)
BA-13	1	0.44	17.38	0.45	0.62	427
BA-14	2	0.49	22.05	0.76	0.66	425
BA-15	3	0.44	21.47	0.61	0.70	422
BA-16	1	0.52	18.87	0.71	0.72	431
BA-17	3	0.49	23.02	0.86	0.60	425
BA-18	5	0.37	23.07	0.59	0.80	423

Polymerization condition: STY – 90% mol; DVB – 10% mol; initiator = BPO* (% in relation to monomers); Organic Phase/Aqueous Phase = ¼; temperature = 80 °C; time = 24 hours; D-50 – medium particle size; M_s – saturation magnetization; M_r – remanence magnetization. The composites BA-16, BA-17 and BA-18 were treated with oleic acid.

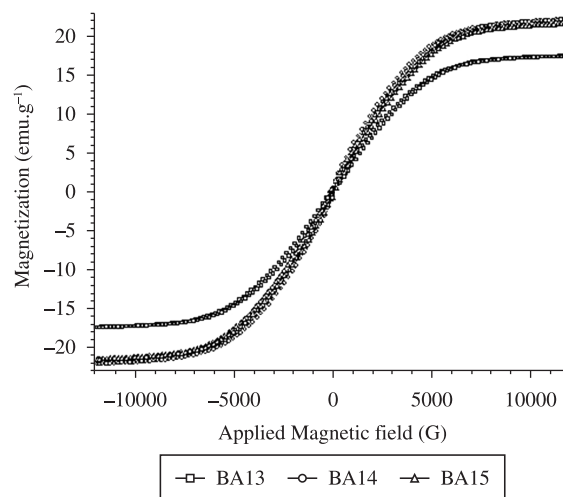


Figure 9. Magnetization curves of composites synthesized with iron not treated with oleic acid.

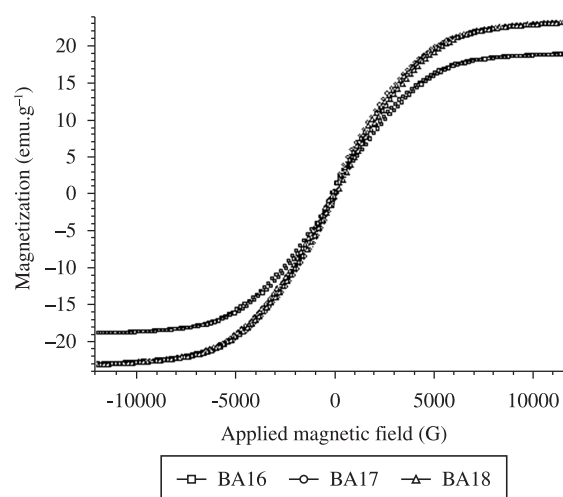


Figure 10. Magnetization curves of composites synthesized with iron treated with oleic acid.

BA-18) were smaller but the copolymers synthesized with iron without treatment with oleic acid (BA-13, BA-14 and BA-15) had a narrower size distribution. In the both cases, the best results were obtained when the initiator concentration was increased to 5% wt.

The use of oleic acid allowed the formation of non-agglomerated particles and produced more homogeneous sizes. The magnetic polymeric particles also exhibit superparamagnetic properties.

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