

Effect of synthesis conditions on the properties of magnetic crosslinked polystyrene microspheres

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Abstract

In this work, magnetic polymeric microspheres were prepared through the copolymerization of styrene and divinylbenzene in the presence of magnetite synthesized in our laboratory. The effects of magnetite modification with oleic acid, stirring speed, initiator concentration and stabilizer concentration on the particles' properties were studied. The magnetic microspheres were characterized according to morphology, thermal stability, particle size and distribution, and magnetic properties. The microspheres had spherical shape, micrometric size and superparamagnetic properties. Particle size was mainly affected by stirring speed, while particle size dispersion was strongly affected by initiator and stabilizer concentrations. The saturation magnetization of the microspheres was similar to the values reported in the literature for microspheres with the same content of magnetic material. The modification with oleic acid promoted the incorporation of magnetic material.

Keywords: *magnetic properties, magnetite, suspension polymerization, styrene-divinylbenzene copolymer.*

How to cite: Bouças, T. A. O., Costa, M. A. S., Cunha, H. A., Silva, M. R., Hui, W. S., & Castanharo, J. A. (2024). Effect of synthesis conditions on the properties of magnetic crosslinked polystyrene microspheres. *Polímeros: Ciência e Tecnologia*, 34(3), e20240033. <https://doi.org/10.1590/0104-1428.20230113>

1. Introduction

The production of non-magnetic polymeric microspheres has undergone major development during the last four decades, gaining a wide range of applications, from column packing to enzyme immobilization. These applications are based on the phenomenon of adsorption. Porous particles have been developed for this purpose, but they have drawbacks such as fouling, slow mass transfer and difficult pore cleaning. Microspheres with magnetic properties can overcome these problems, since they can be designed to be non-porous with high contact surface, and can be easily agglomerated or separated by the use of an electromagnetic field^[1,2].

There are three common ways of imparting magnetic properties to polymeric microspheres: the particles are designed to have polymeric shells and magnetic cores^[3,4]; the magnetic material is dispersed onto polymeric particles^[5-7]; or the magnetic material is formed *in situ* on the surface of the polymeric microspheres^[8]. The magnetic materials can be iron oxides^[9-12], ferrites^[13] and several other metal compounds and alloys. In some applications, the magnetic material is modified to be compatible with the polymeric matrix, which is produced by a large range of monomers and polymerization methods^[1]. Magnetic styrene-divinylbenzene

copolymers produced via suspension polymerization have been extensively studied regarding their ease of preparation, mechanical, thermal and chemical properties; porous structure and degree of particle size control^[4,6,14-16].

Classic suspension polymerization is generally free-radical initiated and involves two phases: an aqueous phase and an organic phase. The organic phase is a mixture of monomers, an initiator and sometimes diluents, while the aqueous phase contains a stabilizer and an inorganic salt to avoid coalescence and fragmentation of the monomer droplets. Mechanical stirring is used to create and maintain the suspension. Particle size and size distribution depend mainly on the stirring speed, and the nature and relative concentrations of the stabilizer and initiator. The proportion between the aqueous and organic phase and nature of the monomers and inorganic salt concentration also affect the particles' size^[15,17].

Magnetic polymer particles have wide applications in biomedical treatment and diagnosis and molecular and environmental separation. These applications require the magnetic polymer particles to have controlled size and size distribution for precise targeting and reproducibility^[18].

Conceição et al.^[15] prepared microspheres based on styrene and divinylbenzene (STY-DVB) containing carbonyl iron powder OX coated with 10% wt-Fe₂O₃ without diluents. They observed that the initiator concentration had an important influence on the microspheres' size distribution, in particular that increased initiator concentration assured narrower particle polydispersity. Ramos et al.^[16] also studied the variation of the initiator on magnetic poly(styrene-co-divinylbenzene) (P(STY-DVB)-M), but in this case diluents and maghemite were used. They concluded that the amount of initiator was the most important factor for the yield of resins, where higher concentrations of benzoyl peroxide (BPO) were associated with greater yield. In the present work, we used different percentages of BPO as initiator and magnetite as magnetic material. Magnetic microspheres based on the same monomers were also prepared by Santa Maria et al.^[14]. In their case, the initiator used was different than BPO, the magnetic material was carbonyl iron powder OX coated with 10% wt-Fe₂O₃, and different suspension agents were used. According to the authors, the composites showed good magnetic properties and the suspending agents and diluent system employed strongly influenced the microstructure and distribution of iron particles on the surface of the composite granules. Poly(vinyl alcohol) (PVA) was one of the suspending agents used in their study, but at a fixed concentration that was lower than in the present work. Formiga et al.^[4] also synthesized P(STY-DVB)-M with the main objective of producing core shells in two steps. In the first step, they employed a high stirring speed (800 rpm) to decrease the particle size of the cores and facilitate the increase in particle size of the subsequent shells.

Many other researchers have also investigated P(STY-DVB)-M. However, we did not find any study of P(STY-DVB)-M involving the behavior of microspheres in terms of particle size produced by variation of stirring speed and concentrations of suspending agent (PVA) and initiator (BPO) (4 and 6%), seeking to improve the size distribution in the suspension polymerization system.

2. Materials and Methods

2.1 Materials

Commercial styrene (STY) and divinylbenzene (DVB) were supplied by Sigma-Aldrich; commercial grade polyvinyl alcohol (PVA) was purchased from Air Products (São Paulo, Brazil), with hydrolysis degree = 85% and molecular weight = 80,000 to 125,000; and benzoyl peroxide (BPO) and other chemicals were purchased from Vetec Química Fina Ltda. (Rio de Janeiro, Brazil). All were used as received.

2.2 Magnetic material synthesis

Magnetite was produced according to the Massart method^[19], namely co-precipitation of iron (II) and iron (III) in a basic medium. FeSO₄ and FeCl₃ were the iron salts used, and NH₄OH assured the basic property of the solution. Magnetic precipitation was used to separate the magnetite produced. Magnetite modified with oleic acid was produced using the same method, but before magnetic precipitation oleic acid was mixed with magnetite by mechanical stirring and heating for 30 minutes^[20,21].

2.3 Magnetic microsphere synthesis

Microspheres were produced via suspension polymerization. The aqueous phase was a water solution of polyvinyl alcohol (PVA), 1, 2 or 3% w/v, and NaCl, 1% w/v. The organic phase was a mixture of styrene and divinylbenzene, in 9:1 molar proportion, containing 2, 4 or 6 mol% benzoyl peroxide (BPO) and 10% w/v magnetite modified with oleic acid. The aqueous to organic phase proportion was 4:1 by volume. The polymerization system was heated to 90 °C and mechanically stirred for 24 hours at 480, 600 or 720 rpm, respectively. The microspheres were washed and separated by filtration, and dried for 48 hours at 60 °C.

2.4 Particle size determination and scanning electronic microscopy (SEM)

Dried microspheres were segregated by size in an automatic sieve shaker (IPAS Retsch®) and size ranges from 500 to 75 micrometers were classified. The ranges with greatest percentage by mass were used in the characterizations. Microspheres selected from the most significant size ranges were analyzed using scanning electronic microscopy (Philips SEM, model XL-30). Samples were coated with a thin gold layer and submitted to acceleration voltage of 20 kV, high vacuum, and presence of secondary and backscattered electrons. Magnification of 60X, 200X, 800X or 5,000X was used.

2.5 Magnetic and thermal properties

Magnetic properties were analyzed with a Lake Shore model 7400 vibrating sample magnetometer (VSM) using cycle time of 1 second and hysteresis cycle time of 10 minutes. The magnetic field varied from 12,000 to -12,000 Oe. Thermogravimetric analysis was performed with a TA Instruments Q500 analyzer, where 20 to 30 grams of sample was heated in a nitrogen atmosphere to 600 °C at a rate of 10 °C/min (equipment error ± 4 °C).

3. Results and Discussion

This work presents the results of analyzing the influence of several parameters on the final properties of the microspheres. Thus, this section describes each parameter separately.

3.1 Stirring speed influence

It is known that stirring speed directly affects particle size (PS) and size distribution (PSD) in suspension polymerization systems^[17]. In this study, we evaluated stirring speeds of 480, 600 and 720 rpm while maintaining PVA and BPO concentrations at 1% and 2%, respectively. Figure 1 shows the influence of stirring speeds on particle size distribution of the polymer. The particle sizes of sample TR02 were mostly between 88 and 180 μm, while the other samples had predominant particle sizes smaller than 75 μm. As can be also observed in Figure 1, in sample TR02 most of the particles had two sizes (bimodal distribution). In suspension polymerization, the evolution of particle size comprises four stages. First there is the "transition stage", during which the average droplet size decreases according to the droplet breakup rate. The second is the "quasi-steady state", where

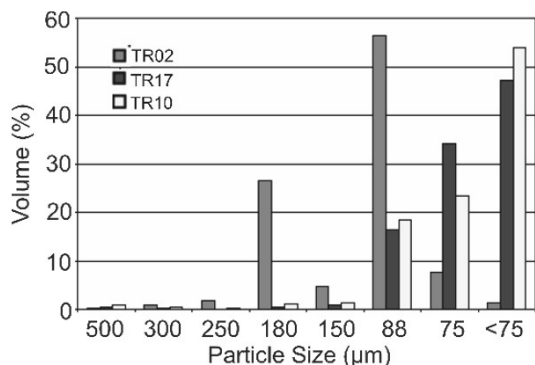


Figure 1. Polymer particle size distribution obtained by sieving with different stirring speeds: 480 rpm (TR02), 600 rpm (TR17) and 720 rpm (TR10).

the droplet rupture rate is equal to that of coalescence, resulting in a constant average droplet size. The fourth is the “growth or sticky stage”, in which the droplet breakup rate lags behind the coalescence rate due to increased droplet interference. This stage leads to larger droplets. Finally, there is the “point of identification”, where the viscous droplets resulting from the previous phase can no longer be broken or undergo coalescence. The sequence of these four stages is what often causes the size distribution of the droplets to become wider than that of the initial monomer droplets^[22]. Therefore, the size of the final droplets is determined by the contribution of rupture and coalescence. Both processes are related to the surface energy of the droplet, which is proportional to the interfacial tension. For low coalescence systems, bimodality is observed due to the droplet size distribution being attributed to the drop breakup process^[23]. Brown and Pitt^[24] also attributed bimodality in suspension systems to a breakup process that involves removal of small droplets whose sizes are approaching the maximum stable value. Thus, the production of a bimodal distribution from a rupture process must be assigned to erosive rupture involving the removal of a number of small drops to a larger one. This gives rise to two overlapping distributions with modes corresponding to daughter or satellite droplets, depending on the volume ratio^[23]. The TR17 and TR10 samples had significant yields and increased particle sizes smaller than 150 µm, with no significant variations. The concentration of particles gradually increased until it reached the smallest particle size range detectable by the analyzer.

In sample TR02, more than half of the concentrated mass of particles was between 88–180 µm, whereas sample TR17 had a significantly smaller amount in the range below 75 µm. Sample TR10 had a larger amount of particles concentrated in the smaller size range than sample TR02. These results indicate that increasing the stirring rate decreased the particle sizes. This can be attributed to the fact that stronger stirring produced smaller droplets in the suspension because the kinetic energy ruptured larger particles. They also were more uniform, since they were better distributed in the dispersed phase.

The particle size distribution and consequently the size of the polymer beads formed depend on the balance between the rates of breakage and coalescence of the

droplets. One of the factors that influences this mechanism is the stirring speed of the reaction mixture^[17]. Therefore, as can be seen in Figure 2, the SEM analyses showed that all particles had spherical morphology and no agglomerations. It can be concluded that the agitation mechanism remained balanced. In addition, these results corroborate the sieving result presented in Figure 1. It is evident that increasing the stirring speed during synthesis produced particle size distributions with narrower ranges. It can also be noted that sample TR02 (Figure 2a) had larger particle sizes than TR10 (Figure 2b) and TR17 (Figure 2c). It is also noteworthy that some material adhered to their surfaces (Figures 2a, 2b and 2c, highlighted), probably due to the presence of added magnetic material. Similar results were reported in the literature^[25].

Thermogravimetric analysis (Figure 3a) showed a single stage of thermal degradation of all the samples. There also was no significant variation in initial degradation temperatures (T_{ONSET}), which were approximately 310 °C; 300 °C and 317 °C for TR02, TR10 and TR17, respectively. In all cases, the residue content (magnetite) of the three samples was around 3%. The degradation temperatures varied by about 17 °C (5%) among the three samples values considered acceptable by the method. The T_{MAX} values also did not present significant variation (466 °C, 450 °C and 455 °C of TR02, TR10 and TR17, respectively). The residue was mainly due to the degradation of inorganic material present in the sample, in turn related to the content of Fe_3O_4 incorporated. The residue level was around 3%, showing that the incorporation of magnetite in these samples was much lower than expected (10% of the total mass of magnetic material added). These results are in agreement with previous reports in the literature^[15].

The analysis of the magnetic properties (Figure 3b) showed that samples TR10 and TR17 had slightly higher saturation magnetization than TR02, probably associated with the fact that smaller particle sizes mean a higher number of particles in the same mass of microspheres, and a greater amount of magnetite contained in that mass (considering constant content and size of magnetite particles). Therefore, a sample with smaller particle size has better magnetic properties, which are measured in relation to mass^[19]. The samples had low hysteresis (residual magnetization less than 0.1 emu/g) and saturation magnetization levels between 1.5 and 2.2 emu/g. Lee et al.^[26] obtained saturation magnetization values in the range of 1.2 to 4.0 emu/g. According to the authors, those results were adequate for the use of these materials as ion-exchange resins with magnetic properties.

3.2 Suspension agent content

In this study, the PVA was evaluated at 1, 2 and 3%w/v, maintaining stirring speed and BPO concentrations at 480 rpm and 2%, respectively.

Suspension agent concentration has been found to have a strong influence on suspension stability, thus being directly responsible for the average size and size distribution of monomer droplets (organic phase) inside the aqueous phase^[13]. When an inadequate amount of stabilizer is used, the suspension will be unstable and the monomer/polymer droplets will coalesce and become large^[27]. The suspension

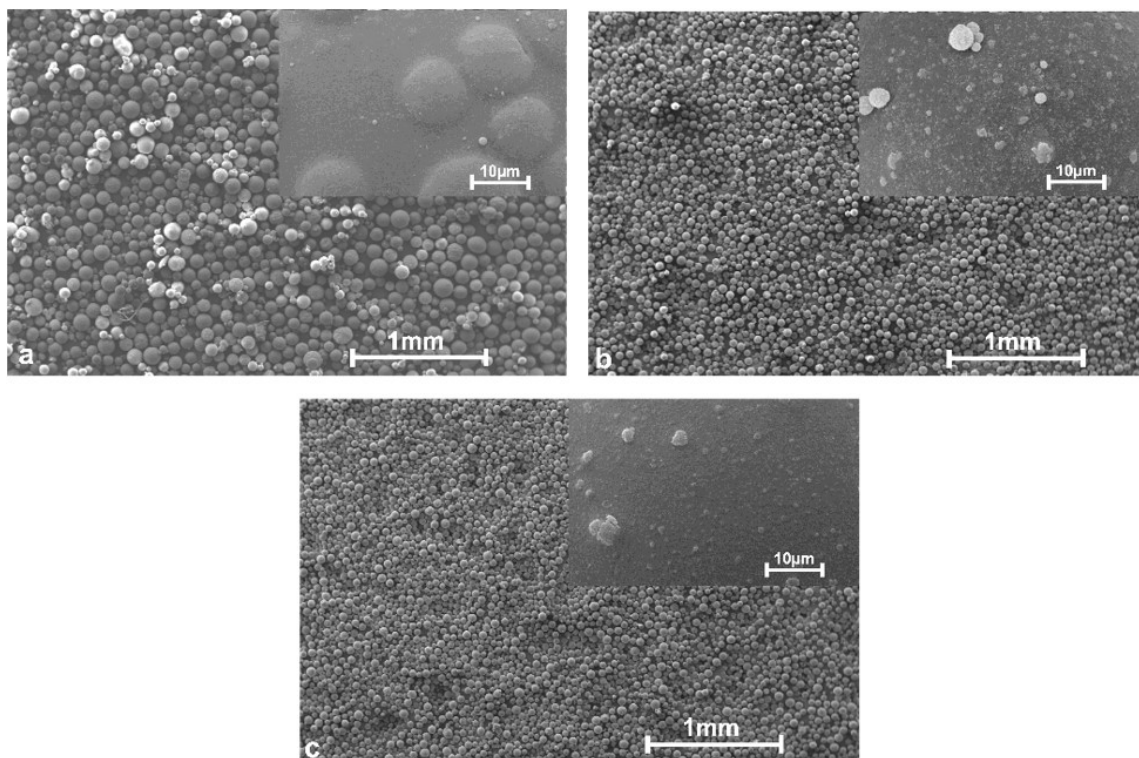


Figure 2. SEM micrographs of samples synthesized with different stirring speeds: (a) 480 rpm (TR02); (b) 720 rpm (TR10); (c) 600 rpm (TR17). General image at 60X magnification; Surface highlight at 5,000X magnification.

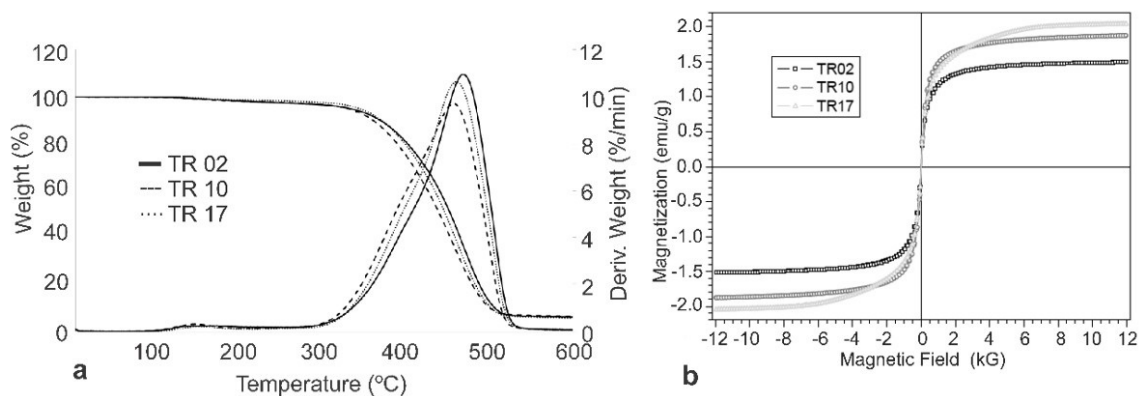


Figure 3. (a) TGA curves for polymeric particles obtained at different stirring speeds; (b) hysteresis curves obtained by VSM for samples produced with different stirring speeds (TR02=480 rpm, TR10=720 rpm and TR17=600 rpm).

agent used in this work was PVA, whose behavior depends on the extent to which the acetate groups are hydrolyzed^[28]. In this case, the hydrolysis degree was 85%, considered good for droplet stabilization in aqueous media, since the droplets can retain their integrity even when stirring speeds are increased^[29]. This could explain why none of the synthesized samples had collapsed spheres. As can be seen in Figure 4, SEM micrographs of the samples revealed particles with spherical shape as well as agglomeration, with

some microspheres having non-uniform surfaces (highlighted in Figures 4a and 4b) where 1 and 2% w/v PVA were used. Also, some of them were rough and some were smooth.

Figure 5 shows that the particle size distribution narrowed with increasing concentration of suspending agent to a certain point. In sample TR05, more than two-thirds of the particle size was in the 88 to 150 µm range, and had 2% PVA, while TR02, with 1% PVA, had two substantial peaks and less than 60% of the sizes in the same range. However, sample

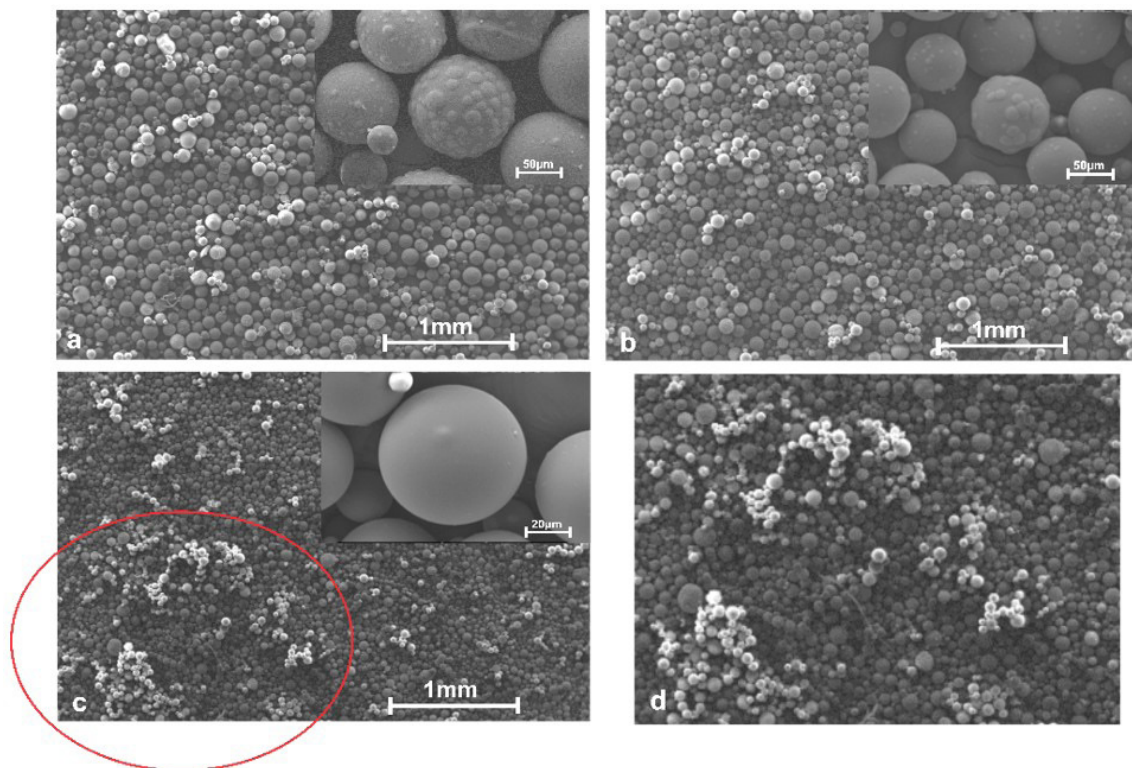


Figure 4. SEM micrographs of samples synthesized with different suspension agent concentrations: (a) 1% w/v PVA (TR02); (b) 2% w/v PVA (TR05); (c) 3% w/v PVA (TR18); (d) TR18 with sample area in red circle highlighted. General image at 60X magnification; Surface highlight at 800X magnification.

TR18, containing 3% PVA, had a wider distribution than the others, with two sample yield peaks and practically a third of the yield concentrated in the 180 to 250 μm range (the range with the best performance). The distribution followed the bimodal pattern of TR02, with particle size concentration in even larger ranges.

We observed an optimal PVA content, since overly high or low concentration of the suspension agent led to broader particle size distribution and larger particles^[30]. However, the presence of large amounts of polymeric material can have an opposite effect when the PVA solution is saturated. Excessive amounts of PVA can lead to aggregation of particles. This fact can explain why sample TR18, with higher PVA content, exhibited a more random particle size profile and higher yields of larger size fractions. This hypothesis is corroborated by Figure 4d, where agglomerated microspheres can be seen in sample TR18, but are not found in samples TR02 (Figure 4a) and TR05 (Figure 4b).

As can be seen in Figure 6a, thermogravimetric analysis showed a single stage of thermal degradation for all the samples. There was no significant variation between the degradation onset temperature of TR02 and TR05. Their T_{ONSET} values were approximately 280 $^{\circ}\text{C}$ and the residue content (magnetite) was around 5%. However, the T_{ONSET} of TR18 was around 325 $^{\circ}\text{C}$ (3% PVA). It is known that the nature of the sample (mass, volume or physical form) can affect TGA results. Therefore, it is possible that the significant polydispersion and also the greater volume of

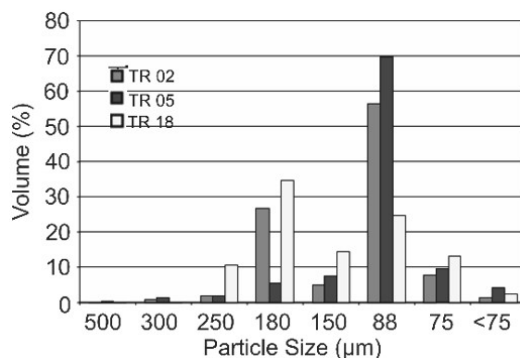


Figure 5. Polymer particle size distribution obtained by sieving with suspension agent content: 1% w/v PVA (TR02); 2% w/v PVA (TR05) and 3% w/v PVA (TR18).

agglomerations in TR18 may have influenced this result in relation to the other samples. The T_{MAX} value also did not vary significantly between samples TR02 and TR05 (both approximately 415 $^{\circ}\text{C}$). Sample TR18, on the other hand, presented a slightly different T_{MAX} of 420 $^{\circ}\text{C}$. The TGA graphs also showed that TR18, with the greatest suspension agent content, contained significantly lower solid residue (3%) than the other samples (5%), with lower PVA content. The residue was mainly attributed to degradation of the inorganic material present in the sample, and hence was

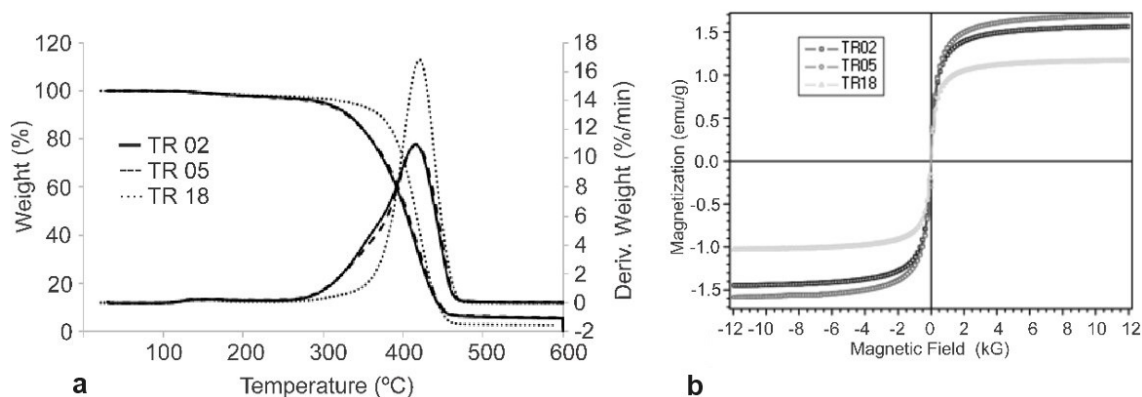


Figure 6. (a) TGA curves obtained for polymeric particles with different PVA concentrations; (b) Hysteresis curves obtained by VSM for samples obtained with PVA at different concentrations (1% w/v of TR02, 2% w/v of TR05 and 3% w/v of TR18).

related to the content of Fe_3O_4 incorporated. The residue values showed that the incorporation of magnetite in all the samples was much lower than we expected (10% of the total mass of magnetic material added). These results are in agreement with another study^[26]. There are two possible causes of this: either the agglomeration of particles reduced the amount of magnetite inside the spheres; or the sampling and selection of microspheres was poor and the relative number of non-magnetic particles was higher. Samples TR02 and TR05 had higher saturation magnetization (1.5 and 1.7 emu/g, respectively) than sample TR18 (1.1 emu/g) (Figure 6b). This can be an indication that TR18 had lower magnetic material content than the other two. Again, the samples showed typical superparamagnetic behavior at room temperature with any hysteresis loop.

3.3 Initiator content

In this study, the BPO was evaluated at 2, 4 and 6% mol, maintaining stirring speed and PVA concentrations at 480 rpm and 1% w/v, respectively. The content of initiator affects the number of threads started in the reaction medium, thus influencing the particles' sizes and their distribution^[15,31]. The higher the number of threads initiated, the smaller and more uniform the particles produced will be. We verified that similar to the suspension agent, the initiator content also had optimal values. High concentrations of BPO led to particle agglomeration and broader particle size distribution. Figure 7 shows that increasing the initiator concentration to a certain point narrowed the particle size distribution. Sample TR07, with 4% BPO, had a much narrower distribution than TR02, with 2%. More than three-quarters of the particle mass was concentrated in the 88-150 μm size range. Sample TR19, however, although having higher initiator content, had a much wider distribution, with less than half of the yield concentrated in the 88-150 μm range (the range containing the highest yield). Even so, the distribution gradually increased, both in larger and smaller ranges, unlike the bimodal pattern of sample TR02. According to the literature, increasing the initiator concentration causes an instantaneous increase in the concentration of oligomeric radicals, which consequently increases the rate of association of oligomers and the rate of coagulation of unstable particles, resulting

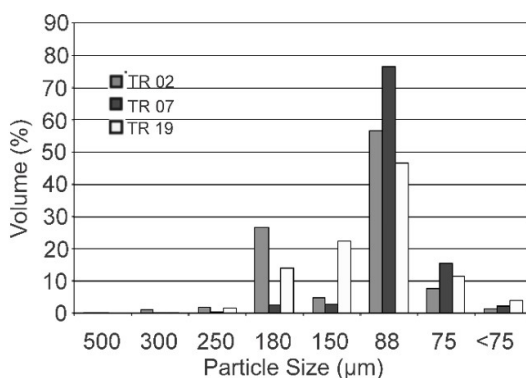


Figure 7. Polymer particle size distribution obtained by sieving with initiator content: 2% mol BPO (TR02); 4% mol BPO (TR07); and 6% mol BPO (TR19).

in larger particle sizes^[30]. The particle size distribution in this study, however, decreased when the initiator content increased from 2% to 4%, but the distribution increased with 6% initiator content. This is in line with the theory proposed by Liu et al.^[30]. The narrower distribution in TR07 can be attributed to the fact that 4% is the optimal initiator content for the system in question, below which there may be few radicals, so that chain junction termination is the most common termination mechanism, explaining the greater aggregation in sample TR02 (2% BPO) in relation to TR07 (4% BPO). Conceição et al.^[15], studying magnetic STY-DVB, reported a tendency for the polydispersion to decrease with increasing initiator concentration. We did not observe this behavior.

SEM micrographs of the samples (Figure 8) showed particles with spherical shape as well as agglomeration (surface highlight in Figures 8a, 8b and 8c). However, there was no uniformity of the microspheres' surface appearance. Some had rougher surfaces than others. The smallest and most uniform particles were produced with 4% BPO.

As shown in Figure 9a, all the samples had a single thermal degradation stage. The degradation onset values

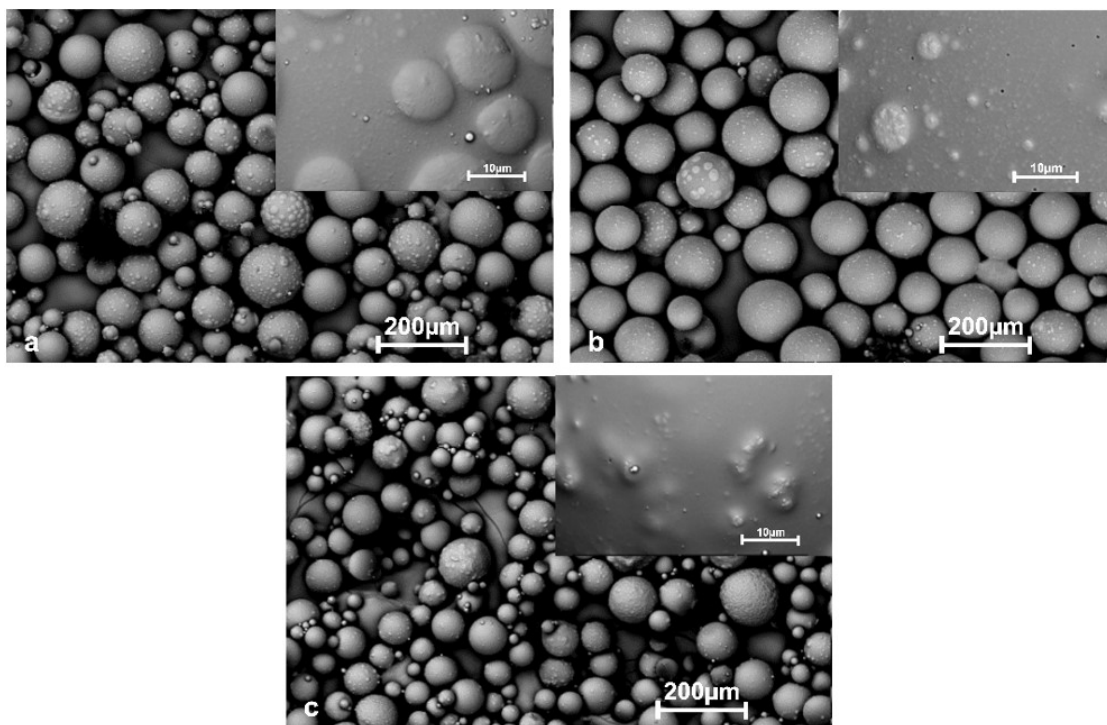


Figure 8. Micrographs of samples synthesized with different initiator concentrations: (a) 2% mol BPO (TR02); (b) 4% mol BPO (TR07); (c) 6% mol BPO (TR19). General image at 200X magnification; surface highlight at 5,000X magnification.

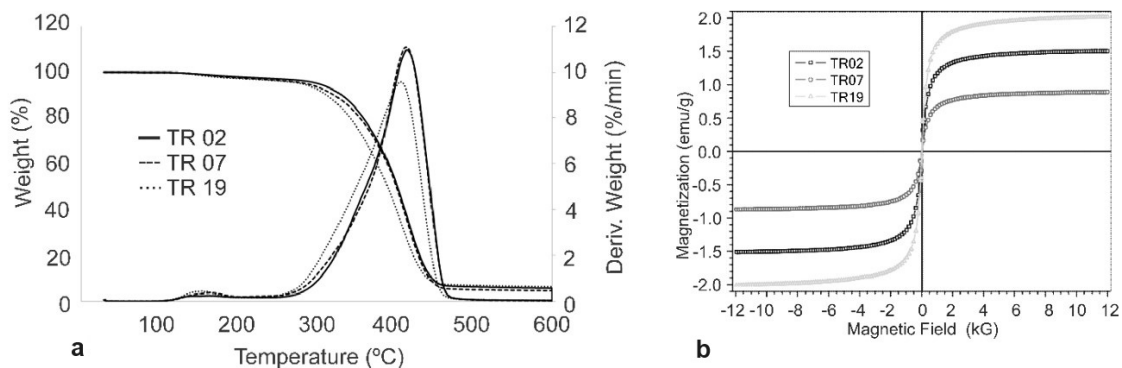


Figure 9. (a) TGA curves obtained for polymeric particles with different BPO concentrations; (b) hysteresis curves obtained by VSM for samples obtained with BPO concentrations (2% mol/mol BPO (TR02); 4% mol/mol BPO (TR07); and 6% mol/mol BPO (TR19)).

were around 280, 275 and 270 °C for TR02, TR07 and TR19, respectively, while their maximum degradation temperatures were 420 °C, 418 °C and 400 °C, respectively. Ramos et al.^[16] reported that a higher percentage of initiator caused a decrease in the degradation onset temperature. Only large differences in initiator concentration affected the thermal stability of the polymers formed in this study (TR02 compared to TR19). The VSM results (Figure 9b) showed no relationship between the increase in BPO concentration and saturation magnetization. This may be due to the selection of samples analyzed, reinforcing the previously described heterogeneous behavior of iron

incorporation in polymeric particles^[25]. The M_s values were 1.5, 0.7 and 2.0 emu/g for TR02, TR07 and TR19, respectively. Although the saturation magnetization results presented different values for all samples, the residues observed by TGA indicated no difference, reinforcing once again the heterogeneity of the incorporation of magnetic material in the microspheres.

4. Conclusions

The stirring speed was the main influence on the size of the obtained polymeric particles. At higher speeds,

smaller particles and narrower particle size distribution were obtained. The contents of initiator and suspending agent also influenced the particle size distribution of the synthesized copolymers. The initiator did not have a significant effect on the thermal stability of the polymers formed or on the amount of inorganic material incorporated. It was possible to obtain magnetic polymeric microspheres with behavior close to superparamagnetism for possible use in separation processes.

5. Author's Contribution

- **Conceptualization** – Thiago Alexandre de Oliveira Bouças; Marcos Antonio da Silva Costa.
- **Data curation** – NA.
- **Formal analysis** – Wang Shu Hui; Manoel Ribeiro da Silva; Thiago Alexandre de Oliveira Bouças.
- **Funding acquisition** - Marcos Antonio da Silva Costa.
- **Investigation** – Thiago Alexandre de Oliveira Bouças.
- **Methodology** – Thiago Alexandre de Oliveira Bouças; Marcos Antonio da Silva Costa.
- **Project administration** – Marcos Antonio da Silva Costa.
- **Resources** – Marcos Antonio da Silva Costa; Wang Shu Hui; Manoel Ribeiro da Silva.
- **Software** – NA.
- **Supervision** – Marcos Antonio da Silva Costa.
- **Validation** – NA.
- **Visualization** – Thiago Alexandre de Oliveira Bouças; Henrique Almeida Cunha; Jacira Aparecida Castanharo.
- **Writing – original draft** – Thiago Alexandre de Oliveira Bouças; Henrique Almeida Cunha.
- **Writing – review & editing** – Marcos Antonio da Silva Costa; Jacira Aparecida Castanharo; Wang Shu Hui; Manoel Ribeiro da Silva.

6. Acknowledgements

The authors thank the National Council for Scientific and Technological Development (CNPq), Office to Coordinate Improvement of Higher Education Personnel (CAPES), and Carlos Chagas Filho Research Foundation of the State of Rio de Janeiro (FAPERJ) (Proc. n° E-26-010.000982/2019, Cooperative Research Network on Nanostructured Materials and Device Engineering) for financial support.

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Received: Nov. 25, 2023

Revised: Mar. 28, 2024

Accepted: July 08, 2024