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Spherical particles of phenolic resin treated with iron oxide

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Abstract This paper describes the preparation and characterization of phenolic resins' thermospheres covered by a magnetic phase of iron oxide. The thermospheres were prepared by allowing phenol and formaldehyde to react under dispersion polymerization conditions and the iron oxide phase was incorporated in situ onto the phenolic resin particles by adding concentrated NH_3 to $FeCl_2$ in DMSO. This reaction was conducted at 70 °C under nitrogen atmosphere in a controlled temperature vessel, and the modified resin was isolated and dried in vacuo. Both pure and modified resins were characterized by DRX, TG-DTA, and MEV/EDX. The modified particles were attracted by a magnetic field, indicating the fixation of magnetic iron oxide. No diffraction peaks were observed in DRX analysis; thermal analysis (DTA) of both pure and modified resins presented exothermic events between 300 and 680 °C, and 300 and 570 °C, respectively, indicating the microstructure of the resin was modified after the treatment. Thermogravimetric analysis (TGA) of the pure resin registered a 2.0% residue, compared to 8.0% for the modified resin. These residues correspond to about 7.0% of fixed iron oxide. MEV/EDX analyses confirm the modification of the resins by the process of fixing iron oxide.

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Introduction

Improvements on the characteristic of composites from a chemical composition stand point have contributed to the development of materials with specific properties to address a wide range of applications [1]. The development of methodologies for preparing and characterizing composites and specialty materials has made possible remarkable advances in the field of materials science.

The incorporation of fine particles has considerably improved the mechanical, electrical, optical, and magnetic properties of materials. However, the structuration and conformation of products are dependent on the type of interaction among the components by which they are formed, enhancing the general properties without losing their particular physico-chemical properties.

Magnetic iron oxides, such as magnetite and maghemite, find many applications as information storage medium [2], magnetic pigments [3], and contrasting agents in diagnosis for medical research [4, 5], to name just a few. Magnetic iron oxide sols of nanometric size stabilized in aqueous or non-aqueous media are called magnetic fluids or ferrocolloids [6], and have been used as magnetic seals, paints, and contrasting agents to detect flaws in metallic structures. The use of these sols as coating for several substrates through formation of thin films or by encapsulating the magnetic particles with polymers or another compound has enabled the preparation of hybrid material with magnetic properties [7, 8].

Magnetic iron oxide, in particular magnetite (Fe_3O_4), can be formed by the so-called "green rust" oxidative reaction [9, 10]. This involves treating a DMSO-water solution containing $FeCl_2 \cdot 6H_2O$ with ammonium hydroxide in the presence of air. Under such conditions a rapid oxidation takes place and is accompanied by hydrolyis which leads to base consumption. The partial dissolution of the $Fe(OH)_2$ coupled with the oxidation of the released Fe(II) to Fe(III), results in a magnetic phase in the form of magnetite nanometric particles.

In the present paper we investigate the formation of magnetic particles of iron oxide, using the "green rust" reaction on the surface of phenolic particles known as thermospheres.

Experimental

Phenolic thermospheres

The following procedure was adapted from Brode [11]. A 0.5-dm^3 three-necked round-bottomed flask equipped with a condenser, a thermocouple, and mechanical stirrer, was charged with phenol (40.0 g, 0.43 mol, Aldrich), paraformaldehyde (16.0 g, 0.53 mol, Riedel), NaOH 2.5 mol dm^{-3} (40×10^{-3} dm^3, 0.1 mol), gum arabic (0.5 g, 1.25 wt.% relative to phenol, Aldrich), and distilled water (20×10^{-3} dm^3). The mixture was kept under reflux with continuous stirring for 1 h, and then H_2SO_4 2.5 mol dm^{-3} (20×10^{-3} dm^3, 0.05 mol) was added. Following the phase inversion, the mixture was kept under reflux with continuous stirring for another hour to complete polymerization. The product was filtered off, washed exhaustively with water, and dried under vacuum in a desiccator.

Formation of the hybrid magnetite-phenolic resin

In a 0.15-dm^3 reaction flask kept at 70 °C, provided with a continuous flow of N_2 and a magnetic bar dimethylsulfoxide (DMSO, 0.1 dm^3, Merck) and 0.05 g of phenolic thermospheres were added, followed by an amount of ferrous chloride sufficient for a final concentration of about 0.05 mol dm^{-3}. After the salt, 20×10^{-3} dm^3 of concentrated ammonia was added to produce a magnetic phase of iron oxide. The suspension was stirred for 45 min and transferred to an erlenmeyer, which was sealed with a polyethylene film and left standing overnight. The resulting suspension was concentrated, the supernatant layer was discarded, and the resin particles were washed several times with distilled water before drying under vacuum in a desiccator.

Characterization

X-ray diffractograms of both unmodified (PR) and modified (MR) resins were obtained in the range 15–70 for 2Θ, with CuK monochromatic radiation from graphite crystal, using a diffractometer Siemens mod. d5000. Samples for scanning electron micrography (SEM) were prepared by depositing the resins on a sticky tape and attaching it to a glass slide which was fixed on metallic supports, before being metallized by deposition of a thin film of Au. Samples for X-ray dispersive energy analysis (EDX), were prepared in similar way, except for the metallization step. SE micrographs were taken from a JEOL microscope mod. JSM330 and for EDX analyses a NORAN probe was used. Specific surface areas of the samples were determined with a BET analyzer mod. CG2000. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) curves were obtained in synthetic air dynamic atmosphere (90×10^{-3} dm^3 min^{-1}) and heating speed of 20 °C min^{-1}, using an apparatus from TA Instruments, mod. TG/DTA 2960.

Results

The phenolic resins obtained consist of reddish brown microspheres of heterogeneous size. When dispersed in DMSO medium they formed a supernatant layer and upon addition of ferrous chloride the suspension turned slightly greenish. After concentrated ammonia was added, a dark green suspension was formed and 30 min later it became completely black. After this treatment the spherical resin particles were attracted by an external magnetic field.

As expected, no sharp peaks were observed in the X-ray diffraction pattern for the phenolic resins, since these are known to be completely amorphous. Even after the treatment, the same broad baseline pattern was observed.

In DTA and TGA curves of the unmodified resin (Fig. 1), four regions of weight loss can be identified, two appearing between 40 and 300 °C. The rate of maximum decomposition takes place between 300 and 600 °C, leaving about 2 wt.% as residue. The DTA and TGA curves for the modified resin (Fig. 2) bear some resemblance to those of the unmodified resin, but the rate of maximum decay is shifted to

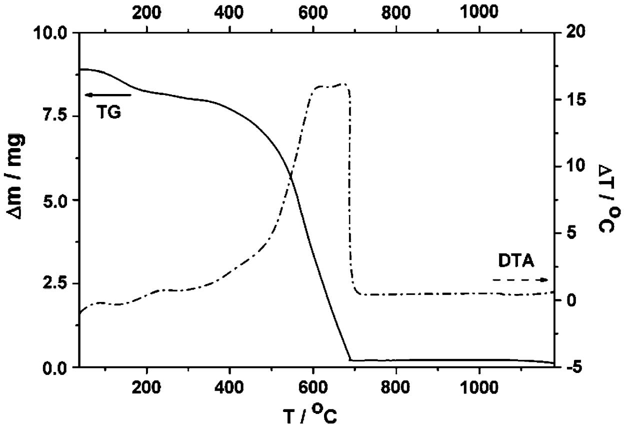


Fig. 1 Thermogravimetric and differential thermal analysis of the unmodified resin

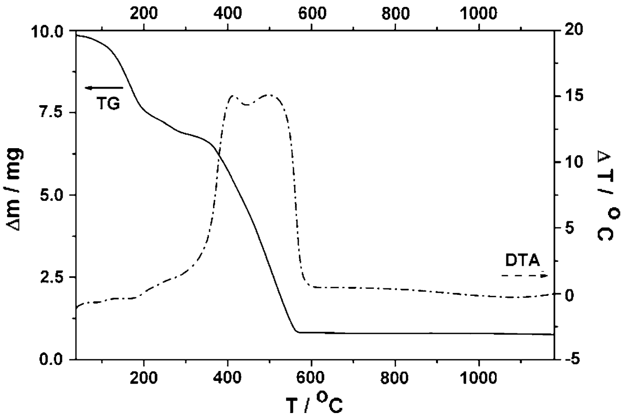


Fig. 2 Thermogravimetric and differential thermal analysis of the modified resin

a lower temperature and the residue, consisting of a reddish powder, increases to 8 wt.%.

Measurements of specific surface area for both unmodified and modified resins resulted in 1.0 and 2.0 $m^2 g^{-1}$, respectively. The size heterogeneity, surface state, and the internal structure of the spherical particles of both unmodified and modified resin, as well as EDX spectra are shown in Figs. 3 and 4.

Discussion

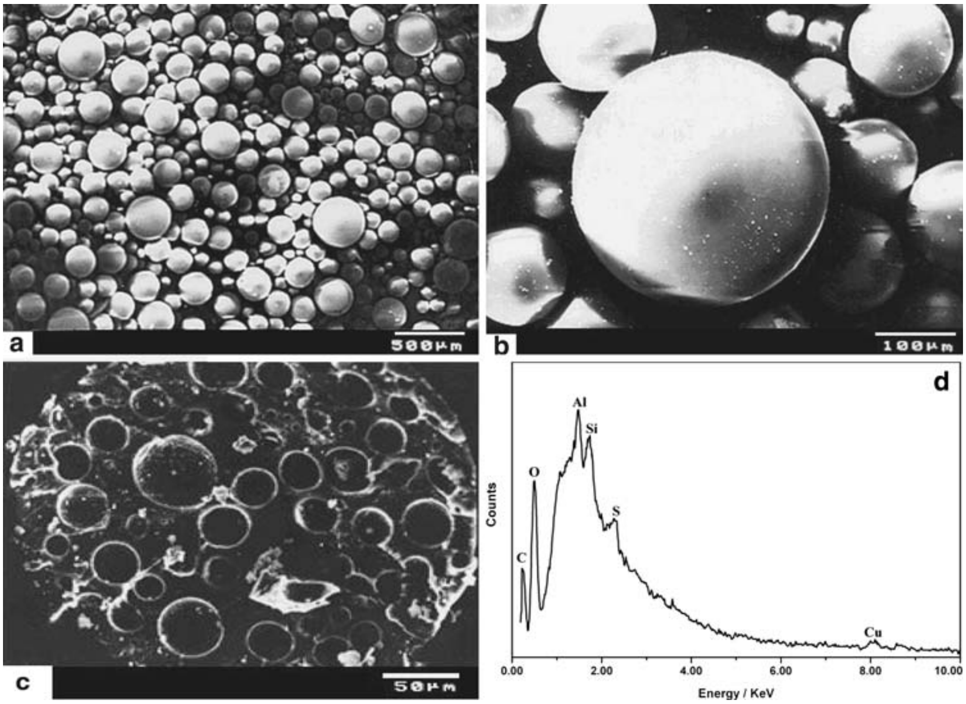
The attraction of the particles by an external magnetic field indicates that a magnetic layer was incorporated on their surfaces.

From the X-ray analysis it was not possible to identify crystalline phases in either of the samples and the widening of the baseline for the resins both before and after modification is typical of non-crystalline material. However the lack of diffraction peaks is not sufficient to conclude if the material is entirely amorphous, because this widening can occur in crystalline particles of nanometric size. It is possible that diffraction peaks of a nanometric crystalline phase may be masked and remain undetected due to the effect of an amorphous matrix or support that generates a highly noisy baseline.

In the DTA and TGA curves of the unmodified resin (Fig. 1), the degradation between 40 and 300 °C represents 11% of the total mass and corresponds to the loss of water and unchanged monomers (phenol and paraformaldehyde), that might have been occluded. Soon after the rate of maximum decomposition begins to increase, random chain scission takes place and the gaseous material given off consists mainly of water, carbon monoxide, carbon dioxide, methane, phenol, cresols, and xylenols [12]. These compounds are also released in the last stage of decomposition which starts above 600 °C. The DTA curve shows only exothermic events which can be correlated to the volatilization processes described above.

The DTA and TGA curves for the modified resin (Fig. 2) showed a first stage of decomposition corresponding to about 30% of the total mass. In this case DMSO is also released in the volatization processes and the reddish powder residue consists mainly of iron oxide. From a direct comparison between the residues of both resins we deduced

Fig. 3 Micrographs of the unmodified resin: (**a**) general view; (**b**) detail of one particle; (**c**) porous internal structure, and (**d**) EDX spectrum



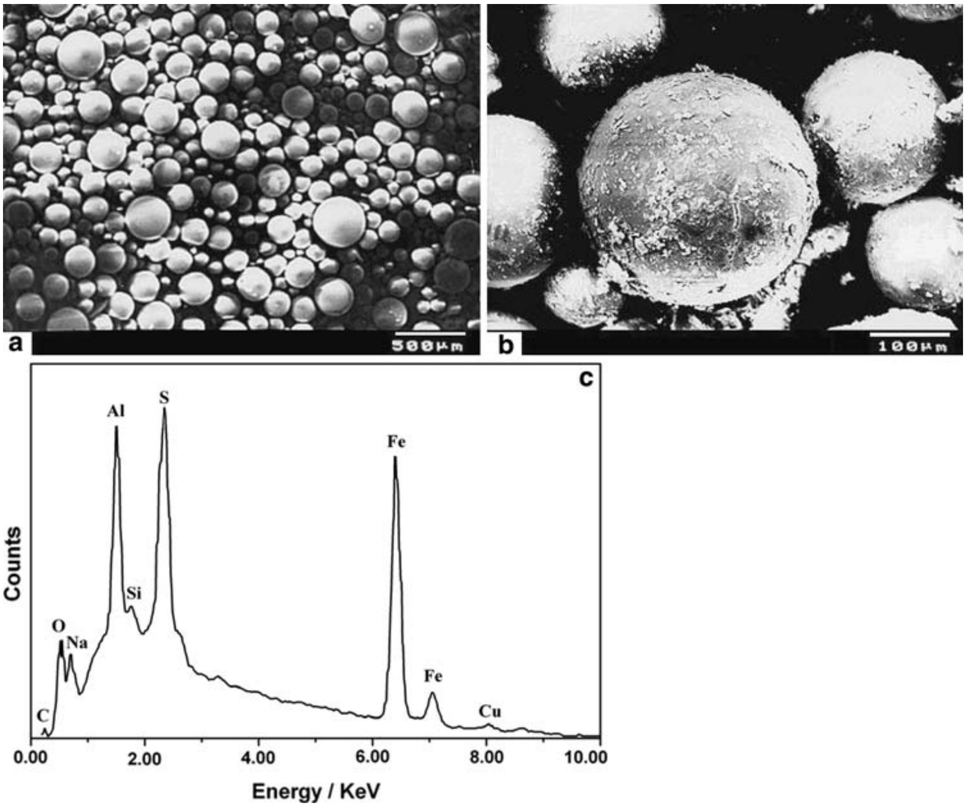


Fig. 4 Micrographs of the modified resin: (**a**) general view; (**b**) detail of one particle, and (**c**) EDX spectrum

that about 7% w/w of magnetic iron oxide (presumably magnetite) was incorporated by the phenolic resin.

The subtle difference in thermal behavior of the resins, as revealed by the TG curves, can be attributed to the incorporation of an oxide solid phase on a polymeric matrix, as well as the in situ process of oxide formation itself. The small reduction in the maximum decomposition temperature is associated to changes caused in the resin microstructure by the introduction of the oxide phase and by the DMSO solvent, due to its high penetrating power.

From the results of specific surface area it was not possible to evaluate any variation on the resins' macrostructure.

The spherical particles of unmodified phenolic resin showed a wide range of particle sizes, as revealed by Fig. 3a. Particle surfaces showed no imperfections (Fig. 3b), bearing out the low surface area obtained. Internally the particles are porous and show variable pore sizes (Fig. 3c). EDX spectrum (Fig. 3d) indicated the presence of C, O, S, and Na either from the resin structure or the residue from the synthetic process; the presence of Al, Si, and Cu is due to the mica sheet and the sample support.

The same heterogeneous size distribution was observed for the resin after modification, but the surface texture is drastically changed by the incorporation of the oxide phase (Fig. 4); in this case fractures and resin fragments deposited on the surfaces can be observed. Apart from the elements already noted in Fig. 3d, the EDX spectrum of the modified resin also showed a peak corresponding to the iron element, as a clear indication that the particle composition (surface and interior) was altered by an iron oxide phase.

Conclusions

The technique of dispersion polymerization was used to produce phenolic resin thermospheres. The material shows a wide particle size distribution and the average size is 50 (±5) µm. A hybrid material was produced by incorporating a magnetic layer of iron oxide on the phenolic particle surfaces, and the presence of iron was confirmed by thermal analysis and EDX analysis. The iron oxide phase was produced in situ and its magnetic properties were confirmed by applying a magnetic field on the sample. The presence of the oxide layer has a drastic influence on the microstructure of the resin and has a slight effect on its thermal behavior.

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