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Polypropylene-based ferromagnetic composites

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Abstract Microcomposites of polypropylene (PP) and magnetite (Fe_3O_4) in different concentration were prepared by one-step melt blending of magnetite powders and polypropylene. Morphology of the composites was studied by means of scanning electron microscope (SEM) to investigate magnetite dispersion within the polypropylene matrix. Thermoxidative stability and mechanical properties were investigated, showing improved thermal stability and enhanced stiffness. Magnetic properties characterization showed a ferromagnetic behavior with coercive field of 116 Oe and saturation magnetizations linearly dependent on the content of magnetic phase.

Keywords Polymer composites · Melt blending · Magnetite ·
Magnetic properties · Ferromagnetism

Introduction

Polymer composites are a well-known reality in which the typical characteristics of a polymer (such as low density, good specific mechanical properties, and processability) are combined with the high stiffness and thermal stability of inorganic fibers or particles. In the last few years, the need to obtain new lightweight, easily-processable, and inexpensive magnetic materials promoted the development of magnetic polymer-based composites. Indeed, traditional permanent magnets present major drawbacks in their high density, brittleness, and processing costs. In this frame, polymeric materials may bring some significant benefits, extending the application of magnetic devices to

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applications where low cost and lightweight is a must. Unfortunately, an intrinsically magnetic polymer appears not to be easily feasible, as discussed by Mataga et al. [1], due to the fact that most organic polymers present a closed-shell electronic structure with a singlet ground state with all electron spins paired and therefore have diamagnetic properties. Discoveries of purely organic ferromagnetic materials have been reported; in 1968 Mataga proposed theoretically several magnetic polymer structure containing high spin blocks as shown in Fig. 1.

In 1987, Ovchinnikov et al. announced the discovery of the first ferromagnetic organic polymer based on polydiacetylene chain with dangling nitroxyl radicals [2, 3]. Also Torrance et al. reported the synthesis of an organic ferromagnet by iodine oxidation of 1,3,5-triaminobenzene [4]. Iwamura obtained fully characterized ferromagnetically coupled oligomers of polycarbenes [5, 6].

However, all those results were unconvincing because of the poor characterization and problems with reproducibility of results. In most cases, well-characterized polymers showed weak antiferromagnetic behavior [7]. Recently, an example of a magnetic polymer, which contained a large number of cross-links and alternating connectivity of radical molecules, was reported [8]. However, at present the simplest and best promising way to obtain a magnetic polymer with tailored magnetic properties is to fill it with magnetic particles to obtain a composite.

In the recent years, magnetic-particle-filled polymers, mostly thermosets, were studied and developed to obtain a class of materials called soft magnetic composite

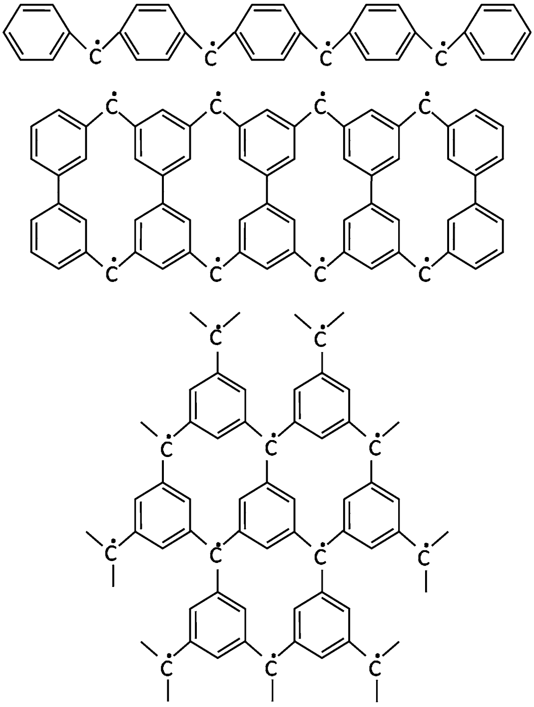

Fig. 1 Theoretical magnetic polymeric structures

material (SMCm). This field has been recently reviewed [9]. Among all the particles used for the production of SMCm, magnetite is certainly the most important and widely used, owing to its well-known synthesis [10, 11] and magnetic properties [12]. The survey of polymer-based magnetic composites also covers hard magnetic behaviors with the use of Nd–Fe–B nanostructured powders [13, 14]. However, most of the work has been focused only on magnetic properties, whereas only few papers [15, 16] reported a complete composite characterization, including other physical properties such as mechanical and thermal behaviors, which are of interest for practical applications.

This article addresses the preparation and characterization of polypropylene (PP)/magnetite (Fe_3O_4) composites (referred as to PP/Fe_3O_4 in the following) in terms of magnetic properties as well as morphology, mechanical properties, and thermoxidative stability.

Experimental

Magnetite (Fe_3O_4) powder with particle size ≤ 1 μm was purchased from Sigma-Aldrich and used as received. Polypropylene was a Moplen HP456H by LyondellBasell, Italy (MFI 2.4 g/10 min @ 230 °C/2.16 kg).

The composites were prepared by mixing polypropylene and different concentrations of magnetite (5, 10, and 25 wt%) in a DSM 15cc twin-screw microextruder (process conditions: 190 °C, 5 min, 100 rpm); neat PP was processed in the same condition and used as a reference material.

The morphology of the microcomposites was characterized using a scanning electron microscope (SEM) model 1450VP by Leo, equipped with a back scattered electron detector. Specimens were prepared using cryogenic fragile fracture to avoid plastic deformation.

Thermogravimetric analyses were performed on a TGA Q500 by TA instrument operating from 50 to 800 °C at 10 °C/min, in platinum crucibles containing ca. 10 mg of sample with gas fluxes of 60 mL/min for sample gas (nitrogen or air) and 40 mL/min for balance protection gas (nitrogen).

In the following, T_{onset} is defined as the temperature corresponding to 5% weight loss and $T_{\max}$ as the temperature at maximum weight loss rate.

Specimen for tensile test (ISO527-2, type 5A) were prepared by injection molding on a Cronoplast Babyplast 6/10 injection molding machine; tensile tests were performed on a Zwick Roell model Z/0101 dynamometer, with a 10 kN load cell, at a deformation speed of 1 mm/min in the elastic region ($\varepsilon < 0.0025$) and 50 mm/min in the plastic region, in agreement with ISO527-2 standard [17].

The magnetic characterization was performed on a vibrating sample magnetometer model 7410 produced by LakeShore. All measurements were done at room temperature under a maximum applied field of 18 kOe. Samples had an irregular shape (each dimension <3 mm), but given their composite structure the exact shape of the plastic matrix does not affect magnetization results. Magnetic properties turned out to be independent on the direction of the applied magnetic field.

Results and discussion

Morphology

The microcomposites were morphologically characterized by means of scanning electron microscopy to evaluate magnetite particle distribution and the presence of aggregated particles. SEM micrographs for PP/Fe_3O_4 composites, taken at 5000× magnification, are reported in Fig. 2. PP/Fe_3O_4 prepared with 5 wt% of magnetite shows a homogeneous distribution of submicronic primary particles of magnetite (Fig. 2a).

Increasing magnetite loading to 10 wt% (Fig. 2b) and to 25 wt% (Fig. 2c) a similar distribution of primary particles is achieved, increasing the total loading an increased density of dispersed primary particles is observed. However, the presence of few micronic aggregates of primary particles is also observable as pointed out by arrows in Fig. 2b and c; these residual aggregates may be due to unoptimised melt blending conditions.

The dispersion of the magnetic phase could be further optimised using organic coated magnetite [18–20], thus increasing the affinity between the inorganic phase and the polymeric matrix. However, the use of such organic-functionalized particles is beyond the objective of this article and will be the matter of a future work.

Thermal stability

The thermal stability of the composites has been studied by means of thermogravimetric analysis in oxidative conditions. The weight loss curves and the derivative

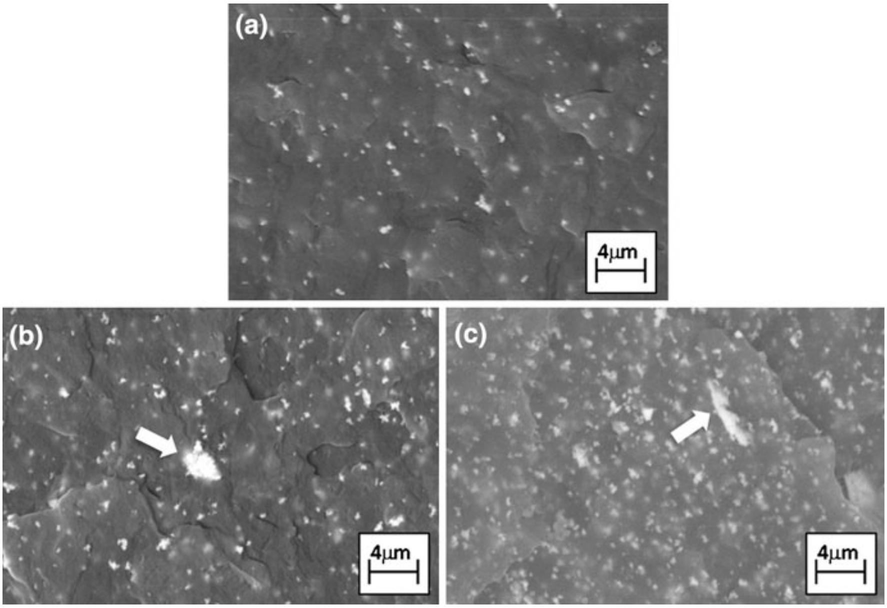

Fig. 2 SEM micrograph of PP/Fe_3O_4 at different weigh loadings: **a** 5%, **b** 10%, **c** 25%

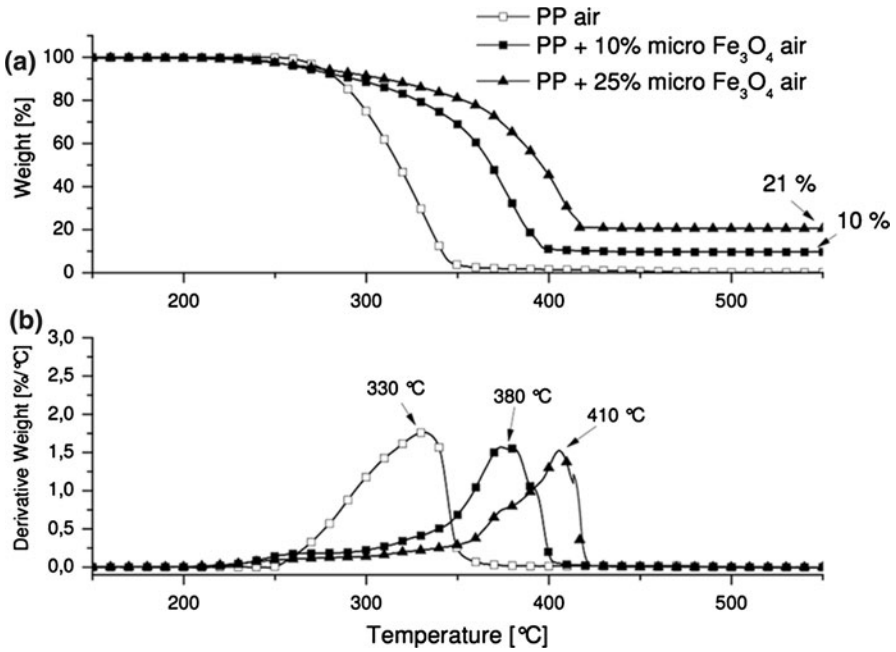

Fig. 3 TGA analysis of PP/Fe_3O_4 composites: **a** mass loss curve and **b** derivative weight curve

weight curves for microcomposites with 10 and 25 wt% of magnetite, compared to neat polypropylene, are reported in Fig. 3. Despite a slight reduction of the T_{onset}, the presence of magnetite clearly induces delay in mass loss for both PP/Fe_3O_4 composites compared with pure PP. The maximum weight loss rate (Fig. 3b), T_{max}, is shifted from 330 °C for polypropylene to 380 and 410 °C for the samples with 10 and 25 wt% filler loadings, respectively. This behavior is attributed to the formation of a protective layer by the accumulation of magnetite particles on the surface of the samples during polymer thermoxidative degradation [21–24]. The inorganic layer acts as a barrier protecting the underlying polymer from oxygen diffusion: since oxygen highly accelerates radical scission of PP [25] a reduction in oxygen concentration directly results in a lower degradation rate, thus delaying the mass loss.

The final residue for pure polypropylene is negligible, whereas significant residues are obtained for the microcomposites, approximately reflecting the initial content of magnetite.

Tensile test

Tensile tests were performed on the micrcomposite filled with 10 wt% of magnetite to estimate the effect of particles on the mechanical properties of polypropylene; Table 1 reports the elastic modulus, maximum load, deformation at max load, fracture load, and deformation at break for the composite and for the neat polymer.

Table 1 Tensile test result for PP and PP + 10% micro Fe_3O_4

Sample	Elastic modulus (N/mm^2)	Maximum load (N/mm^2)	Fracture load (N/mm^2)	Elongation at break (%)
PP	950 ± 20	38 ± 1	24 ± 2	457 ± 21
PP 10% micro Fe_3O_4	1095 ± 20	40 ± 1	31 ± 4	19 ± 3

It is clearly observable that the elastic modulus of PP/Fe_3O_4 is about 15% higher than reference PP, evidencing an increased stiffness, whereas elongation at break is significantly decreased.

The change in the observed mechanical properties matches the typical reinforcement effect of polymer microcomposites, due to the formation of a stiff interphase between the particles and the matrix. Adhesion and hindered mobility of interphase absorbed polymer chains decreases deformability and increases the strength of the interphase resulting in a stiffer and more brittle composite [26].

Magnetic properties

The magnetic properties of the PP/Fe_3O_4 composites were characterized by means of vibrating sample magnetometry. Figure 4 reports the magnetization curves of PP/Fe_3O_4 at different loadings: the composites present an hysteresis loop typical of ferromagnetic materials with coercive fields of about 116 Oe. The values of magnetization, which are 4.1 for PP + 5 wt% Fe_3O_4, 7.7 for PP + 10 wt% Fe_3O_4, and 16.4 emu/g_{tot} for PP + 25 wt% Fe_3O_4, show a linear dependency from the concentration of magnetic phase, showing that the amount of magnetic material filling the PP matrix properly scales with the magnetite used during the mixing process. The hysteresis loops are typical for particulate systems, characterized by a slow approach to saturation and a small hysteresis. Given the size of the magnetite particles, a superparamagnetic behavior is not to be expected. On the contrary, the employed magnetite particles should all be in their single-domain magnetic state [27–29], thus a Stoner–Wohlfarth like behavior is expected. For a random distribution of easy axis orientation in the solid angle, the remanence to saturation ratio should be close to 0.6 in the case of non-interacting, single domain particles. As it can be seen in Fig. 4, a much lower M_r/M_s ratio is observed (of the order of $\cong$0.12–0.14), indicating the presence of either much larger magnetite particles, in the multidomain state, or aggregates of single-domain particles which, because of their interactions, display a collective behavior, where magnetization reversal is driven by domain nucleation-like processes involving the switching of a subset of the particles of an agglomerate, thus reducing the magnetic remanence. This observation is in agreement with the SEM micrographs shown in Fig. 2. It is worth noting that a magnetic remanence exactly equal to zero is to be expected only in the case of superparamagnetic, non-interacting magnetite particles. This is not our case, mainly because the size of the particles is too large. Any residual magnetization has to be attributed to the multi-domain nature of either the particles or their aggregates, which are too small (and possibly too disordered) to effectively average out

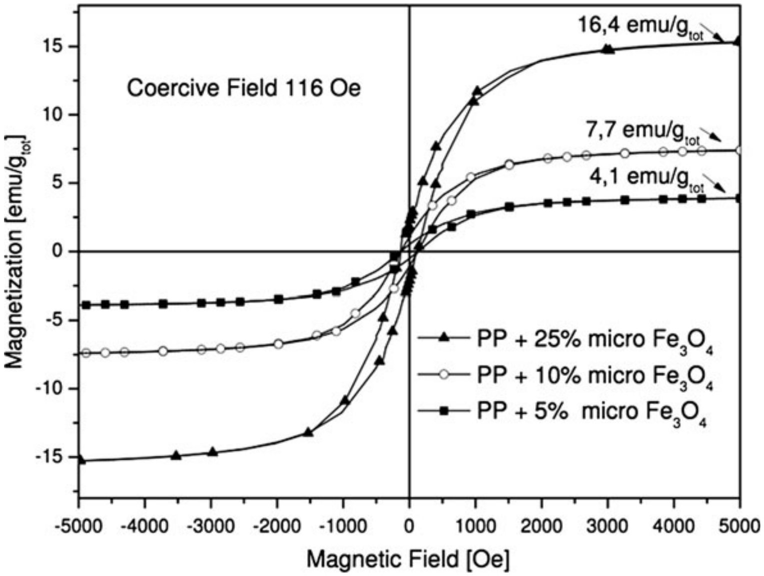

Fig. 4 Hysteresis loops of PP + 5, 10 and 25% micro Fe_3O_4

rigorously at zero their remanence. The independence of the M_r/M_s ratio on magnetite concentration in the composite material is an indication that the most important role in the magnetization process is played by the primary particles (see Fig. 2), which are approximately the same in shape and size in all studied samples. The increased density of primary particles on increasing magnetite content does not lead to a qualitative change of the magnetization process, indicating that even in the sample with a 25 wt% loading the average distance among the primary particles is too large to induce significant interaction effects. Similarly, the micronic aggregates that have been observed in the 10 and 25 wt% loaded samples, although quite large, do not significantly affect the hysteresis loops shapes, indicating that the fraction of magnetite particles that constitute these micronic aggregates is negligible.

Conclusions

In this article, the preparation and characterization of polypropylene/magnetite microcomposites by one-step melt-blending were explored. Despite no organic functionalization on magnetite, an homogeneous distribution of magnetite particles within the polymer matrix was obtained, even increasing the amount of magnetite in the composite to 25 wt%, as evidenced by morphological analysis showing good dispersion of magnetite primary particles. Limited particle aggregation in few-micron-size aggregates is possible, particularly in samples with a higher concentration of particles.

Thermogravimetric analysis showed an improvement in thermoxidative stability, due to the formation of an oxygen-protective barrier during heating, made of oxide particles. The use of micrometric magnetite enhances material stiffness, thus producing a reinforcement of polymer composites. Magnetic properties showed a ferromagnetic behavior with a saturation magnetization which is linearly dependent on the content of magnetic phase. Although the micronic aggregates do not significantly affect the magnetic properties of the studied composites, they are an indication that further homogenization of the distribution of the particles in the polymeric matrix would be recommended, so that higher loads could be achieved. This goal would certainly benefit potential applications, such as lightweight weak permanent magnets or radiofrequency absorbers. Moreover, a better control of the aggregation process of the particles would lead to the possibility of either further reducing the M_r/M_s ratio or increasing it, depending on the requirements of the application.

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