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Fabrication and characterization of metal-core carbon-shell nanoparticles reinforced epoxy nanocomposites

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Summary: Metal nanoparticles (NPs) were prepared starting from acrylamide complex of iron (FeAAm) nitrates. Precursors thermolysis at constant temperature in a self-generated atmosphere lead to formation of metal NPs, whose dimensions depend by the temperature and the time of synthesis. These NPs were used in different percentages to prepare epoxy resin based nanocomposites.

Transmission Electronic Microscopy (TEM) was employed to determine shape and dimensions of the synthetized NPs. Their internal structure was investigated using the X-Ray diffraction, and results have revealed a metal core/polymeric shell structure. These results were also confirmed by cross Thermogravimetric analysis (TGA) and vibrating sample magnetometer (VSM). Optical microscopy, performed on the NPs/epoxy resin system, was used to determine the obtained dispersion degree. Thermogravimetric analysis was employed to study the effect of NPs on the thermal stability of composites, showing that negligible variations are induced by their presence.

Thermomechanical characterization, performed using a Dynamic Mechanical Analyzer (DMA), have revealed a slight increase in the room temperature elastic modulus, while more remarkable variations are induced at high temperature. Glass transition temperature (Tg) does not result significantly affected by the presence of the nanoparticles. A complete fracture characterization was carried out to assess the effect of nanoparticles addition compared to the neat resin system, and the presence of NPs induces a global increase in the fracture energy: this effect is a consequence of the fracture path lengthening. However, higher filler contents are characterized by a lower increase in fracture energy, due to the coalescence of the voids around the debonded nanoparticles.

Magnetic tests, performed using a vibrating sample magnetometer, have revealed the ferromagnetic behavior of the iron particles based nanocomposites. In particular, saturation magnetization and coercivity were found dependent on the diameter of the iron core which depends, in turn, by the NPs pyrolysis temperature. Therefore nanocomposites filled with high temperature synthetized NPs show a stronger ferromagnetic behavior.

1 INTRODUCTION

Nanoparticles have obtained a great deal of attention during last years because their physical properties often differ from those of the corresponding bulk material [1, 2]. In particular metal and metal oxide nanoparticles exhibit unique properties in regard to sorption behaviors, magnetic activity, chemical reduction among others. Magnetic particles, consisting of magnetic elements such as iron, cobalt, nickel and their corresponding oxides [3, 4] have been the focus of research due to their attractive physicochemical properties.

Nanocomposites filled with inorganic nanoparticles have attracted much interest due to their high homogeneity, flexible processability and tunable physical properties such as mechanical, magnetic, optical, electric and electronic properties. However, metal and metal oxide nanoparticles lack chemical stability and mechanical strength. Moreover this kind of particles tend to aggregate, reducing the surface area to volume ratio and then the filler efficiency (in particular their magnetic properties). Appropriately dispersing nanoparticles in the hosting matrix allow overcoming many of these problems [5, 6, 7].

In this work, magnetic nanoparticles were prepared starting from acrylamide complex of iron nitrates. A controlled thermolysis at constant temperature was carried out in a self-generated atmosphere with the final size of the particles determined by the temperature and the time of thermolysis. A bisphenol A-based epoxy resin was considered as matrix to realize nanocomposite at different nanoparticles loading contents. The mechanical, magnetic and thermal properties of the neat system and filled nanocomposites were investigated to study the effect of thermalized nanoparticles. The mechanical performance of the filled system show an increase of the fracture toughness according to the level of loading and the typology of nanoparticles, whereas negligible changes in thermal stability where recorded by experimental tests.

Magnetic results reveal that, at room temperature, the saturation magnetization and coercivity vary according to the iron core diameter, which depends in turn by the preparation procedure of the nanoparticles.

2 MATERIALS AND METHODS

2.1 Sample preparation

Metal core/polymer shell nanoparticles were used as-received with no further treatments, and appears like finely dispersed black powders (Fig. 1). The epoxy resin employed during these tests was Cycom 977-20 by CYTEC, a monocomponent system designed for infusion process and with advanced aeronautical specifications.

Nanoparticles were prepared by controlled thermolysis of Acrylamide complexes Fe(III) nitrate (FeAAm), in the isothermal mode at 400 and 600°C in a self-generated atmosphere by a reported procedure [8]. The composition of synthesized nanoparticles was reported by the same authors in [3] and hereafter recalled: **iron(III) nitrate acrylamide complex (FeAAm)** Found (%): C, 27.4; H, 3.7; Fe, 10.6; N, 18.6. Fe(NO3)3(CH2=CHCONH2)4. Calculated (%): C, 27.0; H, 4.7; N, 16.5; Fe, 10.9. IR (KBr pellet), v/cm–1: 3190, 3320 (NH); 1660 (CO); 1385 (NO3); 280 (M—O).



Figure 1. Iron nanoparticles powders pyrolysed at a) 400°C and b) 600°C, respectively.

Nanocomposites were prepared by addition of 0.2wt% and 1wt% of nanoparticles in the epoxy resin, and then mixed for 30 mins by using a Misonix S3000 sonicator (Misonix Inc., New York, USA) equipped with a titanium tapped horn (instrument power: 15W). To obtain a better dispersion, sonication was performed at high temperature (90°C), in way to reduce the resin viscosity. The prepared system was poured in an aluminum mould, and then put in a vacuum oven at 90°C for 30 mins, in order to remove gases. Solution was then cured following the resin data sheet: 3 hours @180°C. A post cure of 3 hours @200°C was performed to remove the cure residual revealed by DSC.

2.2 Samples Characterization

Size and the shape of nanoparticles were investigated by TEM (TEM FEI Tecnai G12 Spirit Twin). Optical micrographs of nanoparticles and nanocomposites were taken by an optical Olimpus BX51 Inst. equipped with different magnitude oculars. A precise sawing was performed on the samples observed in transmission mode by optical microscopy. X-ray diffraction (XRD - DRON UM-2 and Philips PW 1050 diffractometers) was employed to analyze the crystal structure of the used nanoparticles.

Thermal stability of the nanoparticles and cured nanocomposites was studied by thermogravimetric analysis (TGA) using a TGA Q-500 by TA Instruments. DMA Q800 (TA Inst.) was employed to perform dynamic mechanical analysis in single cantilever mode. Mode-I fracture tests were conducted using single edge notched beam (SENB) specimen, according to the ASTM D5045-99 standard test method.

Vibrating sample magnetometer (VSM) M4500 EG&G PARC was used to perform magnetic tests on about 50 mg of nanocomposite samples. Tests were performed at room temperature.

3 RESULTS AND DISCUSSION

According to the TEM micrographs in Fig.2, the iron particles size depends by the preparation method: an increase of temperature determines an increase in iron particles dimensions.



Figure 2. TEM micrographs of nanoparticles.

The sizes and composition of nanoparticles, as well as the composition of the thermalized polymer matrix, depend on the specific type of metal-nanoparticles. Nanoparticles dimensions vary within a range of 5-20 nm depending on the nature of a metal and the thermolysis conditions [9]. Moreover, according to XRD results (see Fig.3), also the core/shell structure depends by the preparation method: in fact, the Fe_600_120 diffraction pattern highlights the presence of an iron carbide phase (Fe₃C) around the metal core. This inorganic shell is, in turn, wrapped by a polymeric shell.



Figure 3. X-Ray diffraction patterns for the products of thermolysis of the acrylamide complexes formed at different thermolysis temperatures: FeAAm at 500°C (*a*) and 600 °C (*b*). [10]

To investigate the thermal stability of the nanoparticles, thermogravimetric analysis were performed in oxidative atmosphere, and results are shown in Fig.4 and summarized in table 1. Due to the increase of weight residual, higher pyrolysis temperature induce formation of a larger metal core at expense of the polymeric shell thickness. Another feature that highlights the presence of a bigger metal core in NPs pyrolysed at 600°C is the strong oxidation undergone around 200°C: this reaction is also present in Fe_400_60 samples, but it is less relevant since there is less amount of iron in those nanoparticles.

	Residual in Air	T ^{end degradation}	
	[%]	[°C]	
Fe_400_60	32	416.9	
Fe_600_120	48.5	459.7	

Table 1. Residual obtained from TGA analysis on pristine nanoparticles.

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Figure 4. X-Ray diffraction patterns for the products of thermolysis

On the basis of these results, it is possible to schematize the configuration of the iron nanoparticles, pyrolysed at different temperatures, how reported in Fig.5.



Figure 5. Iron nanoparticles schematic illustration.

Fig. 6 shows optical micrographs of the resin/nanoparticles system: the amount of filler in each sample is 1wt%. It results that nanoparticles tend to form clusters with an average size of about 30 μ m. In all samples, the dispersion obtained with sonication results appreciable. However, is noteworthy that the samples filled with Fe_400_60 shows a better dispersion with largest aggregation not exceeding 35 μ m, in planar dimensions. In the case of samples filled with Fe_600_120, bigger agglomeration around also 60 – 70 μ m can be found. Formation of these larger clusters could be attributable to the magnetic interactions among the nanoparticles, which appear to have a stronger magnetic behavior compared to Fe_400_60 NPs.



Figure 6. Optical microscopy (5X and 20 X) of neat and filled epoxy resin.

Thermal stability of the nanocomposites was estimated using thermogravimetric analysis, performed both in nitrogen and air atmosphere. Tests results are summarized in table 2. All systems exhibit thermal degradation and significant weight loss with temperature with a single step (nitrogen atmosphere) and two steps (air atmosphere) degradation mechanism: T^{D}_{MAX} is the maximum degradation rate temperature obtained from tests performed in nitrogen atmosphere; instead, T^{I}_{MAX} and T^{II}_{MAX} are the maximum degradation rate temperatures for each degradation step in air atmosphere. The onset (T^{Onset}) and the end set ($T^{End Set}$) temperatures were determined from the intersection of the two tangents; peak degradation temperatures (T^{D}_{MAX} , T^{I}_{MAX} and T^{II}_{MAX}) were determined from the first derivative of the TGA curve. How is evident from table 2, the presence of nanoparticles does not affect significantly the thermal stability of the samples. Unique effect of the iron nanoparticles presence is a slight reduction of the maximum degradation rate temperatures, which result ~15° less (in nitrogen atmosphere) and ~30° less (in air atmosphere) than the neat epoxy resin. This effect could be attributable to the catalytic effect of the iron nanoparticles, which accelerates the degradation process.

	Nitrogen atmosphere			Air atmosphere		
	T ^{Onset} [°C]	T ^{End Set} [°C]	T ^D _{Max} [°C]	Char Yield [%]	$T^{I}_{Max}[^{\circ}C]$	$T^{II}_{Max}[^{\circ}C]$
Neat	356.9	401.4	383.4	22.07	359.6	524.8
977_20_ Fe_400_60	348.3	400.9	367.9	25.31	371.6	487.1
977_20_Fe_600_120	353.5	403.0	367.0	26.1	370.7	492.2

Table 2. TGA results of neat resin and nanocomposites (1%	(wt) both in nitrogen and a	ir atmosphere.
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Dynamic Mechanical Analysis, performed on neat and filled nanocomposites, has allowed to evaluate the mechanical modulus @40°C and @275°C and the glass transition temperature. Results are summarized in table 3. Presence of 1% of filler provides insignificant variations of the bending modulus @40°C, with a maximum increase of about 3.6%. Also modulus @275°C is not significantly affected by the presence of the iron nanoparticles, recording an increase of about 8% associated to the samples with Fe_600_120. Glass transition temperature (Tg) does not change significantly compared to the neat epoxy system.

	Tg [°C]	E' @40°C [MPa]	E' @275°C [MPa]	Δ E' @40°C [%]	Δ E' @275°C [%]
Neat	228.5	2880 ± 13	56.1 ± 3.5	-	-
Fe_400_60	231.8	2983 ± 24	55.94 ± 1.8	3.58	- 0.28
Fe_600_120	232.7	2836 ± 37	60.6 ± 0.8	- 1.53	8.02

Table 3. DMA results of neat resin and nanocomposites (1% wt).

As previously stated, Fracture tests were performed according the ASTM D5045-99 standard test method. Tests were performed using a three point bending test on neat epoxy and nanocomposite specimens and in both cases a brittle response was recorded. Since the fracture toughness behaviour as function of filler content can show unpredictable trends, as reported by Kim et al. [11], one another filler content (0.2wt%) was employed in these tests. Experimental values for the stress intensity factor are shown in Fig.7: it appears that K_{IC} value is slightly reduced increasing the amount of nanoparticles. This behaviour was predictable, as nanoparticles acting as stress concentrator, can behave as crack initiators.



Figure 7. K_{IC} behaviour obtained from fracture toughness test for neat resin and nanocomposites.

Fig.8 shows the critical strain energy release rate, G_{IC} , as function of nanoparticle contents. It is interesting to note that addition of NPs induces a global increase of G_{IC} : this effect is attributable to the tendency of the crack to propagate through these defects, increasing the crack propagation path and thus the extension of the fracture surfaces (lenghtning process). Anyway, if the particle concentration rises (1wt%), it occurs the coalescence of the voids around particles (due to the debonding of particle–polymer interface), and thus the reduction of the crack propagation path (bowing process). One another effect highlighted by Fig.8 is the higher G_{IC} values for samples filled with Fe_400_60 NPs, compared to those of Fe_600_120 based nanocomposites. To explain this phenomenon it is necessary to regard the nanoparticle structure of Fig.5: Fe_400_60 are characterized by a thicker and less degraded polymeric coating, able to absorb more energy, increasing the GIC value; moreover, iron NPs pyrolyzed at lower temperature are smaller, and therefore the lenghtning process is more efficient, with a further increasing of the G_{IC} values.



Figure 8. G_{IC} behaviour obtained from fracture toughness test for neat resin and nanocomposites

Vibrating sample magnetometer was employed to perform magnetic tests on nanocomposites. The thermo-magnetic curves in Fig.9 show the ferromagnetic behaviour of the sample under examination. Fe_600_120 based nanocomposites are characterized by higher maximal (or saturation, M_s) magnetization values, which are proportional to the mass of magnetic phase, according to published data by Pomogailo et al. [12]. A similar trend is

observable for the residual magnetization (M_r) and the coercivity H_c , how shown in table 4. It is interesting to note that increasing pyrolysis temperature results in a switch from superparamagnetic to ferromagnetic behavior, as revealed by analyzing the coercivity values that increase from 80 Oe to 623 Oe for the samples filled with 1wt% of iron nanoparticles. This behaviour is in agreement with the schematization of Fig.5, according to which higher temperature induce a larger metal core.



Figure 9. Magnetic flux density (B) vs. Magnetising force (H) curves measured at room temperature for the epoxy composites.

	Maximal magnetization	Residual magnetization	Coercivity
	[emu/g]	[emu/g]	[Oe]
977_20-Fe_400_60-0,2%	0.05±0.01	0.0066 ± 0.0008	67±5
977_20-Fe_400_60-1%	0.054 ± 0.005	0.006 ± 0.0006	80±4
977_20-Fe_600_120-0,2%	0.1 ± 0.01	0.038 ± 0.005	610±5
977_20-Fe_600_120-1%	0.255±0.001	0.086 ± 0.006	623±5

Table 4. Magnetic properties of the Fe-containing epoxy nanocomposites.

4 CONCLUSION

This work has shown interesting experimental results of a magnetic nanocomposite, obtained by dispersing iron containing nanoparticles in an epoxy matrix. Magnetic NPs has been synthetized performing a controlled thermolysis on acrylamide complex of iron (FeAAm) nitrates, in a self-controlled atmosphere at different temperatures. Trasmission electron microscopy has shown an increase of the particles size increasing the pyrolysis temperature. The growth of nanoparticles is attributable to the formation of a larger metal core, how demonstrated by thermogravimetric, XRD and mangetic analysis.

Optical microscopy was used to evaluate the dispersion of nanoparticles in the hosting matrix, obtained using sonication method, which was found uniform with an average cluster size within the range from $10\mu m$ to $30\mu m$. Thermal stability of the nanocomposites filled with nanoparticles was studied using thermogravimetric analysis, both in nitrogen and air atmosphere. Results have revealed a slight reduction of maximum degradation rate temperature, probably due to the iron catalytic effect. Not remarkable variation of elastic modules and glass transition temperature are revealed by dynamic mechanic analysis.

Fracture tests show a slight reduction of stress intensity factor (K_{IC}) whereas a more remarkable effect is revealed for the strain energy release rate (G_{IC}). An overall increase of the fracture energy is obtained with both filler content (0.2 and 1wt%), but this effect is more

evident for the samples filled with 0.2wt% of Fe_400_60 NPs.

Magnetic tests performed on iron filled nanocomposite have shown that the increase of pyrolysis temperature from 400°C to 600°C results in a switch from super-paramagnetic to ferromagnetic behavior as revealed by analyzing the coercivity values obtained at considered concentration for the different nanoparticles loaded composite samples. This phenomena is in agreement with the hypothesis that higher pyrolysis temperatures induce formation of a larger ferromagnetic metal core.

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