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DISPERSION OF CARBON NANOTUBES COATED WITH IRON (III) OXIDE INTO POLYMER COMPOSITE UNDER OSCILLATING MAGNETIC FIELD

DUMITRU DIMA[a], MONICA MURARESCU[a*], GABRIEL ANDREI[b]
[a]*Faculty of Sciences,* [b]*Faculty of Mechanical Engineering, University „Dunarea de Jos" of Galati, Domneasca 47, 800008, Galati, Romania*

A new strategy for nanoparticles dispersion into polymer matrix is described in this work. In order to improve the properties of the polyester composites, multiwall carbon nanotubes were chemically coated by a molecular layer of iron (III) oxide. Following a two phases method that includes energy supply into polymer, an optimum ratio between enthalpy and entropy was obtained. Considering physical-chemical interaction inside the dispersed system, during its evolution from raw material to nanocomposite, different types of energy, harmless for the system but acting in the proper direction for an effective dispersion, were applied. XRF, FTIR and SEM analysis were used to emphasis the effect of oscillating magnetic field on nanoparticles dispersion. Also, the influence of dispersion method on composite properties was discussed.

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1. Introduction

It is well known that carbon nanotubes are able to form agglomerates due to the big number of physical – chemical interactions, i.e. Van der Waals forces, as well as π-π and *p*-π chemical bonds [1]. A good dispersion of carbon nanotubes into various matrices (metallic, ceramic, polymeric) is a major concern of nanocomposites manufacturing technology [4]. In accordance with theory, the optimum value between dispersed system enthalpy and its entropy was obtained. This aspect is technological effective by choosing the most suitable steps regarding the compatibility process for the components of nanocomposite, i.e. carbon nanotubes and unsaturated polyester resin [2].

The first step of compatibility means the decrease of interactions and nanotube bonds [14-18]. Considering the mechanical energy input and chemical system that limit the interactions at reinforcement level, the second step of compatibility is the uniform distribution of particles. At this stage, reinforcement-unsaturated polyester interphase shows considerable modification. At the same time, reinforcement surface changes were observed [6].

According to current researches, a satisfactory carbon nanotubes dispersion, using different strategies that includes surface modification, functionalization and carbon nanotubes controlled cutting, was considered [10, 11, 5].

The main aim of this research was to obtain a good compatibility between multiwalled carbon nanotubes (MWCNTs) and unsaturated polyester matrix. After surface modification due to iron (III) oxide, chemically coated multiwalled carbon nanotubes (MWCNT-F_3) were obtained. An iron (III) thin oxid layer applied on carbon nanotubes surface, which could have a breaking effect on carbon nanotubes agglomerates was used. This is the main chemical process of the strategy that will be followed by physical and physical – chemical steps [3]. The technological steps have to consider both the efficiency and the real conditions allowed by the dispersed system whose properties are changing from a step to another. Considering this assumption, it was proposed a

* Corresponding author: monica.murarescu@ugal.ro

model of carbon nanotubes global dispersion into unsaturated polyester matrix schematically showed in Fig. 1.

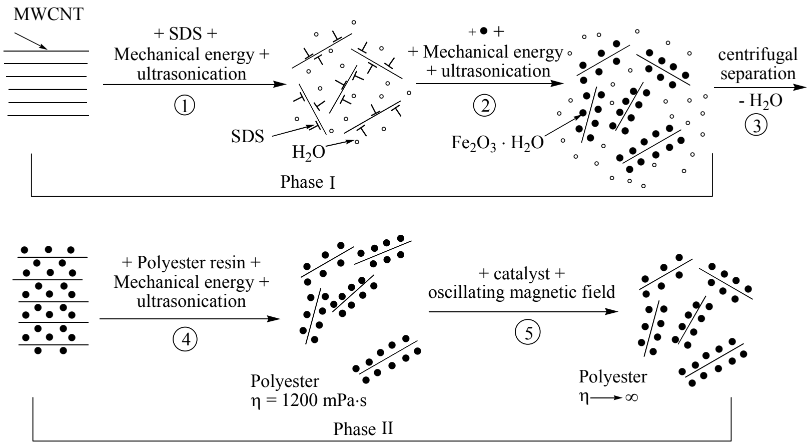


Fig.1 A schematically representation of the dispersion model for coated MWCNTs using iron (III) oxide in unsaturated polyester matrix

During the phase I, MWCNTs coated with Fe_2O_3 are obtained. Carbon nanotubes are dispersed in water by mechanical stirring and ultrasonication using an appropriate surfactant, sodium dodecyl sulfate (SDS) (1). Then, $Fe_2O_3 \cdot H_2O$ is chemical deposited in a molecular layer on MWCNT. The result is a dispersed MWCNT-F_3 in aqueous solution (2). By centrifugation method, water is removed (3) and the deposit is flushed by distilled water and ethylic alcohol followed by drying in oven, at 443 K for 8 hours. This is the end of the first stage of carbon nanotubes functionalization, that means MWCNTs transformation into MWCNT-F_3 [7, 8].

In the phase II, polyester - MWCNT-F_3 nanocomposite is obtained under the action of an oscillating magnetic field. Following steps are carried out: MWCNT-F_3 inclusion into polyester resin and mechanical grinding operation (4), then introducing the initiator catalyst into the system (5) so that a reticulation effect, due to styrene bridges by radical polymerization mechanism, is carried out. In case of usual techniques, the fast increase in system viscosity does not allow a good dispersion. A new dispersion method based on the action of an oscillating magnetic field in-line with the matrix was applied (Fig.4).

The magnetic field interacts with MWCNT-F_3 magnetic field due to iron (III) oxide and maintains the dispersed state in optimum conditions [3]. This fact is demonstrated by a comparative study of nanocomposite material obtained in the same conditions but without the action of oscillating magnetic field.

2. Experimental

2.1 Materials

In order to obtain satisfactory dispersion of carbon nanotubes into polyester matrix, the following materials were used:

– unsaturated polyester resin AROPOL™ M105 ASHLAND, currently used as a thermoplastic material with worldwide application; considering the polyester resin as a model, other different resins with similar physical, chemical and rheological properties provide the same results [13]; there are many preparation methods starting from the type of precursor catalyst; in this case, 2-ethyl cobalt hexanoat, methyl ethyl ketone peroxide (MEKP) catalyst and styrene, as reticulation agent, were used;

– MWCNTs were used due to the good properties assured by their nanometric dimensions and structural variety of C-C bonds [12];

– iron (III) oxide, included in ceramic materials category with good magnetic properties, was used in the dispersion process aiming to overcome the interference with supplementary energy without causing damages to nanocomposite material [9];

– sodium dodecyl sulphate (SDS) is well-known as one of the most used wet surface-active agent for carbon nanotubes dispersion in the aqueous solution, in order to be coated by iron (III) oxide.

2.2 Experimental steps

- **Carbon nanotube coating with iron (III) oxide**

The method intended to modify carbon nanotubes surface for an increased compatibility with polymeric matrix consists in covering technique with a molecular layer of Fe_2O_3. The first step of the method is the dispersion of carbon nanotubes using a solution of 1% sodium dodecyl sulphate, as surfactant agent, followed by ultrasonication, for 10 minutes, with BANDELIN HD3200 apparatus, as shown in Fig.2. Subsequently, a solution of $FeCl_3$ 1mol/L was added under a magnetic stirring, for 5 minutes. The obtained solution was submitted to ultrasonic treatment, for 10 minutes.

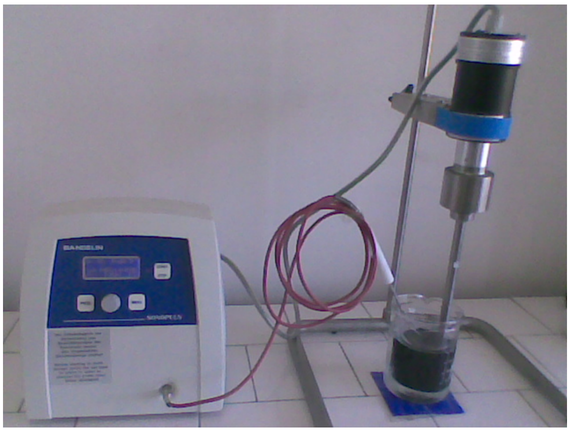


Fig.2 Ultrasonication of MWCNTs suspension using BANDELIN HD3200 generator

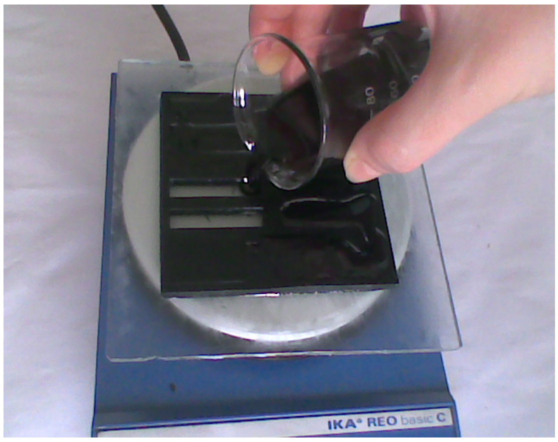


Fig.3 Dispersion of MWCNTs in polyester matrix under oscillating magnetic field

A solution of NH_3 was added followed by ultrasonication, until pH = 8.5 1mol/L. The final stage consists in a step by step flushing of nanotubes coated by molecular layer of Fe_2O_3 with bidistilled water, until pH = 5.5. Then, following operations were carried out: centrifugation at 6000 rpm, cleaning with anhydrous ethylic alcohol, drying in oven for 8 hours at 443 K and dry milling. The obtained nanotubes using the above method were noted with MWCNT-F_3.

- **MWCNT-F_3 dispersion into unsaturated polyester matrix**

Optimum concentration of MWCNTs in polyester matrix was selected after a careful analysis with following five values: 0.05; 0.10; 0.15; 0.20; 0.25%. The conclusion of the research is that the optimum concentration value is 0.20%. A new technique was used for dispersion method consisting of two different types of stirring: mechanical and ultrasonic.

At the end of two different types of stirring, the mixture was placed under the action of oscillating magnetic field (Fig.3). Two experimental series noted with A and B, considering the optimum concentration value for carbon nanotubes coated with a molecular layer of Fe_2O_3, were done. B samples are different compared to A samples due to the fact that the dispersion procedure implies supplementary dispersion under the action of oscillating magnetic field. The samples were dimensionally and chemically stabilized using a thermal treatment at 378 K in a drying oven, for 8 hours.

3. Results and discussion

X-ray fluorescence analysis (XRF) and IR transmission spectroscopy (FTIR) were used for a critical evaluation of MWCNTs surface modification due to coated iron (III). Similar results using iron (III) oxide as reinforcement were obtained by Guo et al. [3].

3.1 XRF analysis

Carbon nanotubes analysis by X-ray fluorescence was carried out using a NITON XLt 793 apparatus. Table 1 shows a brief representation of the average value of the data after 10 measurements. The analysis demonstrates elementary changes appeared as a result of chemical treatment applied for surface modification.

Table 1. Concentration (ppm) of metallic elements using XRF analysis

Material	Fe	Ni	Co	Mn	Cr	V	Ti	Ca	K
MWCNT	1120.15	7185.23	157.55	47.47	1302.86	424.23	1027.25	1901.15	225.16
MWCNT-F_3	55167.66	4109.67	27.85	244.58	610.21	437.52	3277.15	1255.14	2889.62

Fe concentration in MWCNT-F_3 is about 5.52%. The result is 50 times increased compared to MWCNT concentration that is 0.112%. Such increase of iron (III) oxide layer is enough to assure magnetic properties in the composite material structure, useful for manufacturing technology and for general properties of composite material.

The following elements show a decreased concentration due to Fe concentration increase: Ni and Cr 50% decrease, Co reduced 5.65 times and 34% decrease for Ca.

The increase in Mn concentration of about five times, Ti increase of about three times and K increase of twelve times is the result of contamination due to chemical reagents, as well as to distilled water, and finally to their low concentration in MWCNTs powder.

3.2 FTIR analysis

FTIR analysis was carried out on IR transmission spectrometer JASCO 660. The comparative study of the IR absorption spectrum for unmodified carbon nanotubes with the IR absorption spectrum for MWCNT-F_3 reveals the following modifications (Fig.4 and Fig.5):

– 1209 cm^{-1} band of MWCNT is more reduced in MWCNT-F_3; the appearance of two peaks, at 1159 cm^{-1} and 1119 cm^{-1} is explained by new bonds C-O formation at carbon nanotubes level with oxygen from iron (III) oxide chemically deposited on their surface;

– 598 cm^{-1}, 625 cm^{-1} and 685 cm^{-1} bands appear at MWCNT-F_3 and they could be resulted from 609cm^{-1} band that disappears or is removed;

– 500 cm^{-1} and 460 cm^{-1} bands are two very strong bands that could be explained by iron (III) oxide presence chemically bonded with carbon nanotubes;

– comparing MWCNT-F_3 to MWCNT, a band intensification at 1539 cm^{-1} and 1514 cm^{-1} was noticed;

– the characteristic band for H_2O, that is 3440 cm^{-1}, was seen at both carbon nanotube types;

– in case of MWCNT-F_3, a band around 1700 cm^{-1} that could be caused by C-O bond was observed.

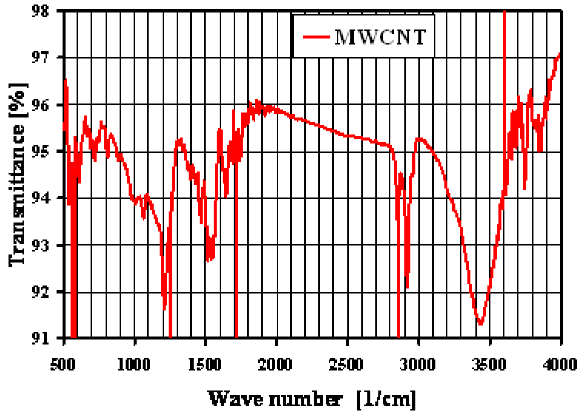


Fig.4 FTIR spectral analysis of MWCNT

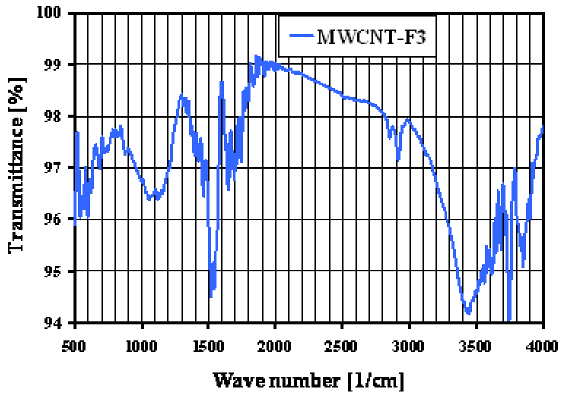
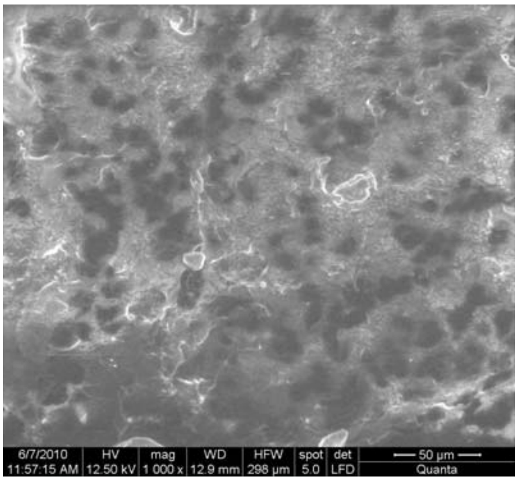


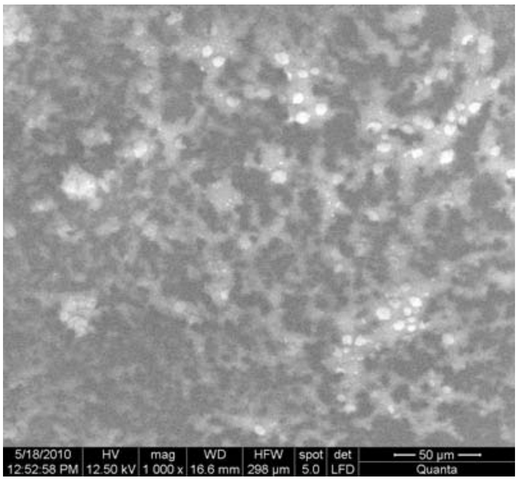
Fig.5 FTIR spectral analysis of MWCNT-F_3

3.3 SEM analysis

SEM analyses carried out on Quanta™ 200 Scanning Electron Microscope clearly reveal the uniform distribution of B series particles related to A series, that demonstrates the enthalpy gain due to the oscillating magnetic field action on the breaking of nanoparticles linkages (Fig.6). This phenomenon was better observed at lower concentration of carbon nanotubes coated with molecular layer of iron (III) oxide [1,2].



A



B

Fig.6 SEM analysis of nanocomposite samples: (A) MWCNT-F_3/polyester resin;(B) MWCNT-F_3/polyester resin under the action of oscillating magnetic field

4. Conclusions

The comparative study of XRF, FTIR and SEM analysis concludes on the optimum enthalpy -entropy equilibrium of the dispersed system carbon nanotubes - polymeric matrix due to the synergism obtained by modification of carbon nanotubes surface. Thus, the research was carried out in order to achieve a better compatibilization with polymeric matrix and to supply gradually dispersion energy into the system. The main result of the work was the dispersion improvement due to carbon nanotubes surface coating with an iron (III) oxide layer. The efficiency of coating method that assures the dispersion energy transfer to the system was confirmed by XRF and FTIR analysis. Quantitative and qualitative carbon nanotube surface transformation was obtained.

Acknowledgements

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