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MWCNT DISPERSION METHOD WITH IRON(III) OXIDE IN UNSATURATED POLYESTER MATRIX

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Abstract: *The aim of this work is to obtain a better compatibility between MWCNTs and the unsaturated polyester matrix by their surface modification using the coating technology with iron (III) oxide, followed by clearing and separation process from the aqueous dispersion. The coating efficiency by chemical deposition of carbon nano-tubes was analyzed by XRF and FTIR analyses. The iron (III) oxide coated carbon nano-tubes dispersion was realized by a mechanical blending followed by ultrasonic treatment and finally a tension state maintenance by a vibrant magnetic field introducing in the unsaturated polyester matrix reticulation process. It was realized different technological versions, in order to relieve the vibrant magnetic field influence.*
Key words: *dispersion, MWCNT, polyester, magnetic field*

1. INTRODUCTION

It was demonstrated by recent scientific papers that improved carbon nano-tubes dispersion is obtained using different strategies including physical and chemical methods (Mackay et al., 2006). Physical methods consider nano-tubes direct mixing using a mechanical force (Andrady, 2008). Chemical methods are carried out by surfactants action, functionalization and carbon nano-tubes surface modification, and polymer wrapping technology (Guo et al., 2008). The aim of this paper is to realize a good compatibility between MWCNTs and the unsaturated polyester matrix by their surface modification due to iron (III) oxide coating process chemically deposited (Goddard et al., 2007). Moreover, it was proved a suitable physical and chemical processes succession in the dispersed system iron (III) oxide/MWCNT, that means MWCNT-F_3 (Gogotsi, 2006). In this way, the target was an iron (III) oxide thin layer obtaining on carbon nano-tubes surface, a monomolecular layer ideally, which could act like a failure on carbon nano-tubes agglomerates (Advani, 2007). In fact, this is the main chemical process used in this dispersion strategy (Kelsall, 2005).

2. EXPERIMENTAL

2.1 Materials

In order to obtain improved carbon nano-tubes dispersion in a polyester matrix, it was used the following materials (Mai & Yu, 2006):

- unsaturated polyester resin AROPOL^{TM} M105;
- MWCNTs from Cheaptubes Inc. USA;
- sodium dodecyl sulphate (SDS) from Sigma Aldrich.

2.2 Methods

- ***Carbon nano-tube coating process using iron (III) oxide***

A method of modifying carbon nano-tubes surface for an increased compatibility with the polymeric matrix consists in covering technique with a molecular layer of Fe_2O_3.

The first step of this method is represented by carbon nano-tubes dispersion using a solution of 1% sodium dodecyl sulphate (SDS) as surfactant followed by ultrasonic treatment process for 10 minutes with BANDELIN HD 3200, with 40% amplitude. Subsequently, a solution of $FeCl_3$ 1mol/L was quantitative added under a magnetic stirring for 5 minutes and the resulted solution is ultrasonic treated for 10 minutes. The final stage consists in a step to step washing process of the nano-tubes coated by a molecular layer of iron (III) oxide particles using bi-distilled water till pH = 5,5. It follows a centrifugation process of the nano-tubes from the solution at 6000 rpm, the final washing with anhydrous ethylic alcohol, the oven drying for 8 hours at 443K and finally the dry milling process. The final product is MWCNT-F_3.

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

In order to present carbon nano-tubes optimum concentration in the polyester matrix, it was tested the following values: 0,05; 0,10; 0,15; 0,20; 0,25% . MWCNTs optimum concentration in polymeric matrix can be determined using a viscosity variation ($\Delta\eta$) study in relation to nano-tubes concentration from the polymeric resin. The optimum concentration value (0,2 %) is obtained at a maximum viscosity increasing, after that a constant value is registered or even a decreasing value is possible. The experimental data are synthetically presented in fig.1. In MWCNT-F_3 case, iron (III) oxide presence can generate contradictory effects, which mean: Van der Waals and π-π interactions decreasing between carbon nano-tubes due to oxide layers separating effect and the magnetic interactions that are responsible of clusters generation in the matrix added with covered nano-tubes. That is the reason because new dispersion energy must be introduced in order to block clusters formation; this target is technological realizable due to the introduction of an external vibrant magnetic field. It was accomplished the dispersion process considering a self-technology represented by two different types of stirring, starting with a mechanical one and followed by a ultrasonic type of stirring. At the end of these two different types of stirring, it was realized a dispersion process in a vibrant magnetic field.

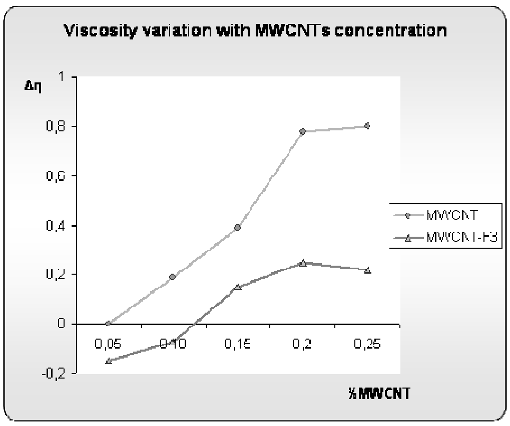

Fig.1. Viscosity variation depending on MWCNT-F_3 concentration

Two experimental series, A and B, were realized considering the optimum concentration of carbon nanotubes covered with a molecular layer of iron (III) oxide. B samples are different from A samples due to the fact that the dispersion technology contains an extra-phase represented by a supplementary dispersion in a vibrant magnetic field. The samples were molded in silicone rubber mould. After this process, the samples were dimensional and chemical stabilized using a thermal treatment at 278K in a drying chamber for 8 hours.

3. RESULTS AND DISCUSSIONS

The critical evaluation of MWCNTs surface modifications due to iron (III) oxid plating having the final result MWCNT-F_3 coded samples was realized by X ray fluorescence analyses (XRF) and IR transmission spectrum (FTIR). These analyses confirmed the quantitative and qualitative carbon nanotube surface transformations.

3.1 XRF analysis

Carbon nanotubes analysis by X-ray fluorescence was carried out by NITON XLt 793 apparatus. This analysis demonstrates the elementary changes appeared as a result of the chemical treatments applied for MWCNTs surface modifications.

Fe concentration in MWCNT-F_3 is about 5,52%. The result is 50 times increased compared to MWCNT concentration that is 0,112%. This increase represents the iron (III) oxide layer enough for generating magnetic properties in the composite material structure, useful for the manufacturing technology and for the general properties of the composite material. The following elements present a decreased concentration (Ni, Cr a 50% decrease, Co ~ 5-6 times) due to Fe concentration increase. The increased Mn concentration of about 5 times, Ti of about 3 times is the result of contamination due to the chemical reagents used, also to the distilled water and finally to their low concentrations in MWCNT.

3.2 FTIR analysis

FTIR spectrum was realized using an IR transmission spectrometer JASCO 660 Plus. A comparative study of IR absorption spectrum for carbon nano-tubes unmodified with the same IR absorption spectrum for carbon nano-tubes plated with iron (III) oxide (fig.2) relieves the following modifications:

- 1209 cm^{-1} band of MWCNT is more reduced in MWCNT-F_3 and moreover, it was observed the appearance of a two new peaks, at 1159 cm^{-1} and 1119 cm^{-1} explained by new bonds C-O formation at carbon nano-tubes level with oxygen from iron (III) oxide chemically deposited on their surfaces;
- 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 moved;
- 500 cm^{-1} and 460 cm^{-1} bands are two very strong bands that could be attributed to iron (III) oxide presence chemically bonded by carbon nano-tubes;

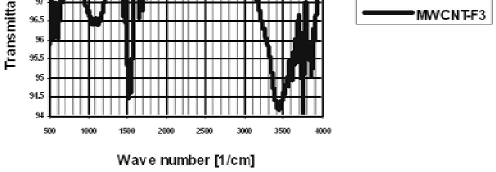

Fig.2. FTIR spectrum of MWCNT-F_3

- comparing MWCNT-F_3 with MWCNT it was observed a band intensification at 1539 cm^{-1} and 1514 cm^{-1};
- at the both carbon nano-tube types it was seen the characteristic band for water, that is 3440 cm^{-1};
- at MWCNT-F_3 it was observed a band around 1700 cm^{-1} that could be attributed to C-O bond.

4. CONCLUSIONS

The comparative study of these three types of analyses concludes on the optimum enthalpy/entropy equilibrium maintenance of the dispersed system carbon nano-tubes / polymeric matrix. This balance is technological realizable due to the synergism obtained using carbon nano-tubes surface modification in order to increase the compatibility process with polymeric matrix and the gradually introduction of dispersion energy into the system. In this way, it was carried on the coating process with a molecular layer of iron (III) oxide on carbon nano-tubes surface that was confirmed by XRF and FTIR analysis. MWCNTs optimum concentration in the unsaturated polyester matrix was determined at 0,2%. This optimum value was demonstrated by viscosity maximum variation ($\Delta\eta$). XRF analysis confirms the quantitative and qualitative substance modifications at MWCNTs. FTIR analysis confirms that iron (III) oxide chemically deposited do not realize a mechanical mixture with MWCNTs. Iron (III) oxide is bonded by physical-chemical forces by MWCNTs surface, that is very important in the dispersion process. MWCNTs surface modifications required a new technological chain that offers the possibility of an efficiently transfer of the dispersion energy to the reactive system. The improved dispersion is obtained by a new energy introducing at the final technological stage of the nano-composite material by an external vibrant magnetic field.

5. ACKNOWLEDGEMENTS

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