METHOD OF CARBON NANOTUBES DISPERSION IN POLYMERIC MATRIX

Monica MURARESCU[1], Dumitru DIMA[1], Gabriel ANDREI[1], Adrian CIRCIUMARU[1]

[1]University "Dunarea de Jos" of Galati, Domneasca Street 47, Romania,
monica.murarescu@ugal.ro

Abstract: *In order to obtain better homogenous composite material, different carbon nanotubes (CNTs) dispersion techniques in the polymeric matrix are very well known. Due to the strong interactions between CNTs, the efficiency of these dispersion techniques is highly limited. The aim of this paper is to present improvement techniques considered as new step in the global dispersion process before the composite material final shape finalization. At this moment, it is very difficult to carry out a classical dispersion from technological point of view. In this paper, more than the acknowledged mechanical and ultrasonic dispersion method, the introduction of a genuine dispersion technique is proposed; it refers to an external vibrant magnetic field able to determine a vibration movement of CNTs covered by a molecular Fe (III) oxide. This external vibrant magnetic field is made by using a permanent magnet involved in a rotational movement around its own axis and also interacts with the individual CNTs own magnetic fields. The maintenance of a tensioned vibrating state at the individual CNT level contributes to a good dispersion state preservation and increases the connections and physical-chemical interactions hindering. The dispersion efficiency in a vibrant magnetic field was studied using the comparative methods, correlating the electronic microscopy analysis with the mechanical strength tests. With respect to the composite material obtained under these conditions, a significant quality improvement as well as a mechanical strength increase was observed.*

Keywords*:* *magnetic properties, composite material, polymer matrix composites.*

Introduction

Carbon nanotubes (CNTs) utilization in the polymeric matrix consists in the obtaining process of some unique properties as a main result of their nanometrical dimensions.

Their unusual structure along with a decreased density, a remarkable strength and stiffness, followed by electrical properties versatility contribute to a high interest on their use as ingenuous polymeric materials reinforcement. [1], [3]

The key element of this possibility consists in the mechanic, thermic and electric properties transmission from the CNTs to the polymeric composite material. Hereby, there are two problems that have to be solved in order to bring substantially improvement to the polymers material properties along with carbon nanotubes addition as fillers: the interfacial connection and moreover, the optimum CNTs individual dispersion in the polymeric matrix. [2]

The polymer interfacial adhesion can be substantially improved by the chemical functionalization of the nanotube surface. The influence of the chemical bond between nanotubes and the matrix on the interfacial adhesion was anticipated by the molecular dynamics simulations. [1], [5]

The particles having nanometrical dimensions present a large surface, with a higher size degree than conventional fillers surface. Their surface area actions as the transfer interface of the strains and it is responsible in the same time for the strong and natural CNTs tendency to make agglomerates. These properties efficient operation in polymers depends on their homogenous dispersion process in the matrix at the same time with the agglomerates destruction process and their wetting with polymeric substance.

Considering CNTs distribution process in a polymeric matrix, these elements would have to be evaluated: the nanotubes length, their disorder, the volume ratio, the matrix increased thickness, the attraction between CNTs themselves.[4]

The usual particles dispersion in the polymeric materials seems to be difficult and finally ends with both phases separation and agglomeration phenomenon. It was demonstrated that nanoparticles' thermodynamically stable dispersion in the polymeric liquid can be successfully obtained for the systems which lineal polymer radius of gyration is bigger than the nanoparticle radius.

The dispersed nanoparticles expand the lineal polymeric chains and the primarily result is a polymer which radius of gyration increases with nanoparticles volume ratio. It was suggested the fact that this process entropic disadvantageous is balanced by an enthalpy gain due to the increased number of molecular contacts between the dispersed nanoparticles surfaces in comparison with nanoparticles surfaces in the phase separation case. [2], [5] Even the dispersed state is thermodynamically stable; it is difficult to be obtained considering an inappropriate processing strategy, this one being one of the most important things referring to CNTs dispersion process into lineal polymers. [2], [6] Starting from a well-determined target like nanotubes dispersion, different work techniques are proposed: ultrasonication, mechanical stirring, etc.

Ultrasonication has a big energy local impact but introduces small quantities of shearing forces, so that this method is appropriate only for matrix with very low thickness and small volumes. The local energy input leads to CNTs breakage, decreasing their length. CNTs dispersion in an adequate solvent (like: dimethylketone, styrene) represents an appropriate way for ultrasonication technique application in order to obtain CNTs composite materials. In this way, it would be allowed an agglomerates separation due to the vibration energy. [3],[6] Decreased agglomerates dimensions can be easily obtained by using CNTs functionalization technique.

Mechanical stirring is a usual dispersion method of particles in the liquid systems and can be successfully used for nanoparticles dispersion. The dispersion result depends on the mixer shape and size as well as stirring speed. After an intensive CNTs stirring into the resin, they present the natural tendency of agglomerating and this flocculation phenomenon experimentally observed is primarily generated by the wearing contacts as well as elastic coalescence mechanisms. [7]

Calendaring becomes a working obtaining way of a good dispersion state. This method is a usual well-known method of microparticles dispersion in different matrix, like: colouring agent for cosmetics and paint. A major advantage of this method, apart from the improved dispersion results would be the efficient manufacture of a diversified nanocomposites range.

Other methods than the above supposed techniques of some energy type introduction in CNTs/polymeric matrix mixing process that would be able to realize an enthalpy/entropy optimum ratio. Furthermore, a good dispersion can be anticipated and realized in this way.

Materials and methods

In order to obtain nanocomposite materials with polymeric matrix we used an unsaturated polyesteric matrix AROPOL™ M105 TPB ASHLAND OLANDA – ROTTERDAM, a largely used resin at industrial level added with 1% catalyst 2-ethyl-cobalt hexanoat. We used methyl-ethyl ketone peroxide 2% as initial catalyst. Multi-wall carbon nanotubes (MWCNTs) were obtained from Cheaptubes Inc. USA, having the following characteristics: external diameter 8 – 15 nm, length 10 – 50 μm and purity over 95%. It was realized a covering process with a molecular layer of Fe_2O_3 in accordance with a technology that represent another scientific paper aim. In order to present carbon nanotubes optimum concentration value in the polyester matrix, we considered three types of concentration: 0.10; 0.15 and 0.20%.
We carried out 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 (fig.1).

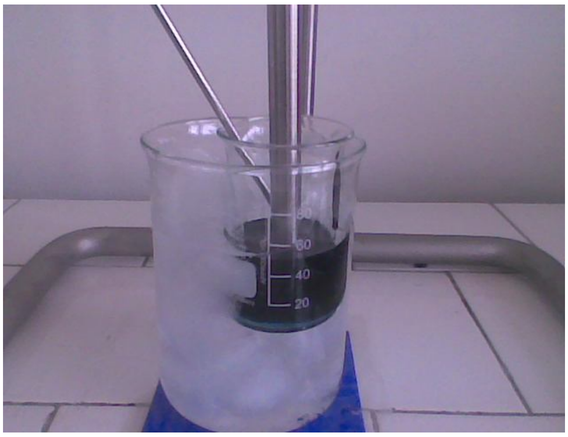


Fig.1 The dispersion by ultrasonication process in polyester matrix

At the end of these two different types of stirring, a dispersion process in a vibrant magnetic field (fig.2) took place. We made two experimental series coded with A and B using these three types of concentration for carbon nanotubes covered by a molecular layer of Fe_2O_3. The samples coded with B made by using three different types of concentration are different from the samples coded with A due to the fact that the dispersion technology contains an extra-phase represented by a supplementary dispersion in a vibrant magnetic field (fig.2).

Fig.2 The dispersion process of CNTs in polyester matrix in a vibrant magnetic field

The samples made in accordance with standards EN 63, ASTM D790-81, NFT 57-105 or NFT 51-001 from a dimensional and 3 point flexural test point of view were moulded in rubber matrices that were previously made-up by flush cutting procedure. After the samples were extracted from the matrices, they were dimensionally and chemically stabilized using a thermal treatment in the oven at 278K for 8 hours. For each experiment we used 10 samples for a statistically interpretation. The samples were fixed at 3 points flexural test on a testing machine "win Test™ Analysis – Testometric materials testing machines, England". The machine working parameters are: working speed – 2,500 mm/min, flexural load – 1,000N, span – 32,000mm.

Results and Discussion

The testing results were plotted and shown in the following shape (fig.3).
The experimental data at 3 points flexural test for the two series coded A and B are schematically presented in table 1.
It is easier to understand in this way the experimental data interpretation in order to justify the anticipated effect of an external vibrant magnetic field at carbon nanotubes dispersion technology.

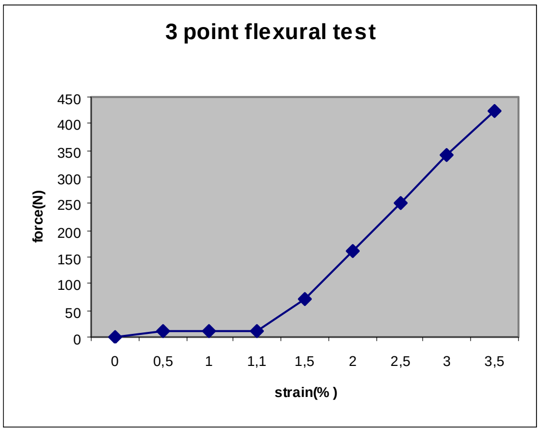


Fig.3 Three points flexural test. The variation of deformation plot (%) depending on the applied force (N)

Table 1

Bending modulus values

Sample	Bending Strength @ Break (N/mm²)	Bending Modulus (N/mm²)	Transv. Rupture Strength (N/mm²)
$A_{0,10\%}$	103.90	4168.64	103.90
$B_{0,10\%}$	105.04	4728.29	105.09
$A_{0,15\%}$	105.25	4305.62	105.45
$B_{0,15\%}$	109.24	4500.66	109.61
$A_{0,20\%}$	110.40	4605.21	110.44
$B_{0,20\%}$	111.50	4805.25	112.50

It was observed a bending modulus and other mechanical parameters increasing with carbon nanotubes concentration increasing. Moreover, at the same concentration values it was observed an increasing at B series in comparison with A series that demonstrates the vibrant magnetic field efficiency in the dispersion process of carbon nanotubes in polyester matrix. The increasing variation of mechanical parameters at 3 point flexural test is presented in table 2.
The highest value for bending modulus is observed at the concentration of 0.1%. This conclusion is explained by the fact that the vibrant magnetic field efficiency is quantified when the gaps between nanotubes clusters are large.

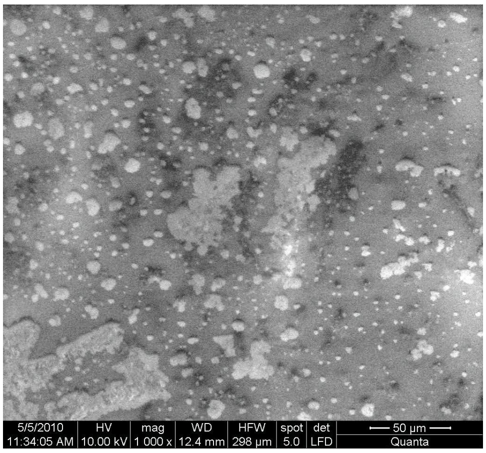
Table 2

Mechanical parameters variation at 3 points flexural test for the same version of B series in comparison with A series

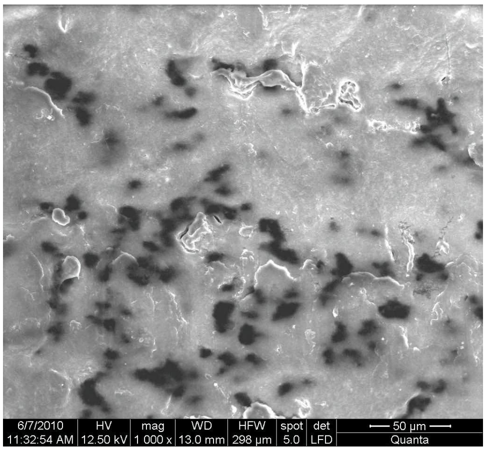
Conc.(%)	Bending strength variation (%)	Bending modulus variation (%)	Transv. rupture strength variation (%)
0.10	1.08	11.83	1.13
0.15	3.65	4.30	3.79
0.20	0.99	4.16	1.83

At the highest concentration values, that means 0.15% and 0.20%, the same parameter variation maintains quasi-constant; the explanation would be that gaps decreasing have important impacts on the vibrant magnetic field efficiency concerning the dispersion process of carbon nanotubes covered by a molecular layer of Fe_2O_3. SEM analysis (fig.4) confirms the experimental data obtained at 3 points flexural test; an improved carbon nanotubes distribution at B series in comparison with A series was observed.
In the samples of 0.10% and 0.15% from A series we observed a stronger agglomeration in comparison with the sample of 0.20% of the same set. This aspect is possible due to the equilibrium established by the attractive forces energy between the nanoparticles and the dispersion forces energy for 0.20% samples. In this case we made a comparison on the adverse energetic state for the dispersion forces considering the samples of 0.10% and 0.15% concentration. At B series, considering all

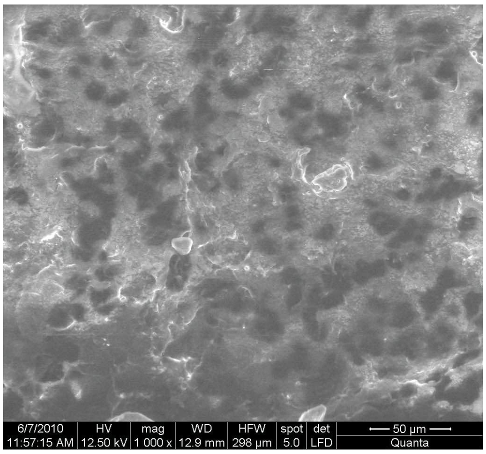
concentration values, a superior distribution at carbon nanotubes was observed.



$A_{0,1\%}$

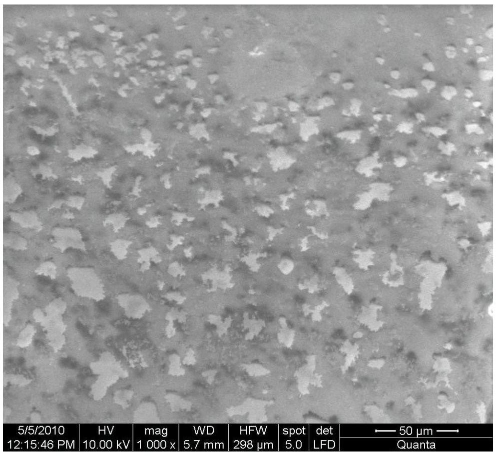


$A_{0,15\%}$

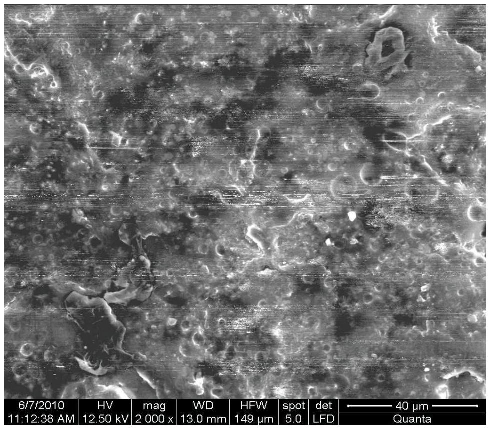


$A_{0,2\%}$

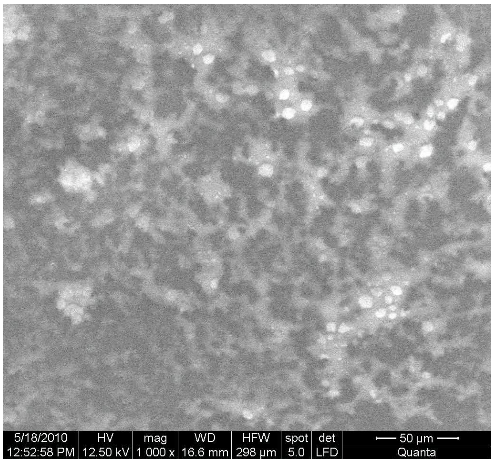
Fig.4 SEM analysis for A series samples of 0,10%, 0,15% and 0,20% concentration without the vibrant magnetic field presence



$B_{0,1\%}$



$B_{0,15\%}$



$B_{0,2\%}$

Fig. 5 SEM analysis for B series samples of 0,10%, 0,15% and 0,20% concentration in a vibrant magnetic field presence

From SEM analyses made by using Quanta™ 200 Scanning Electron Microscope (2006) we noticed that the non-agglomerated state of the particles from B series in comparison with A series demonstrates the fact that the enthalpic gain from the external vibrant magnetic field leads to the bond breakage between the nanoparticles participating in the clusters formation. This phenomenon is better observed at decreased concentration values of carbon nanotubes covered by a molecular layer of Fe (III) oxide. This is a consequence probably due to the vibrant magnetic field energy. It would be an interesting topic to be focused on, but considering the technological reasons we analyzed only a single type of magnetic stirrer.

Conclusions

The experimental data and the physical analysis confirm the theory of an optimum equilibrium existence between the dispersed system enthalpy and entropy. The mechanical, ultrasonic and external electro-magnetic field energy that is induced in the dispersed system due to carbon nanotubes covered with a molecular layer of Fe (III) oxide in the same time contribute at this target. This aspect is reflected by SEM analysis of the samples in / without a vibrant magnetic field and also by the flexural modulus and other mechanical parameters increasing resulted from three points flexural test.

In conclusion, we demonstrated that another technological step introduction in the dispersion process of carbon nanotubes covered with a molecular layer of Fe (III) oxide allows an improved distribution in the polyester matrix.

This supplementary stage in the technological dispersion process is responsible for the mechanical properties improvement and also the final product quality represented by nanocomposite material.

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