ASSESSMENT OF CARBON NANOTUBES FUNCTIONALIZATION THROUGH BENDING AND WEAR TESTS ON POLYESTER NANOCOMPOSITES

Monica MURARESCU1, Dumitru DIMA1, Gabriel ANDREI2, Luminita CIUPAGEA2

1) „Dunărea de Jos” University of Galati, Romania, Faculty of Sciences and Environment, ROMANIA
2) „Dunărea de Jos” University of Galati, Romania, Faculty of Mechanical Engineering, ROMANIA

gabriel.andrei@ugal.ro

ABSTRACT

The aim of this paper is to investigate the influence of MWCNTs functionalization in order to improve their dispersion in a polyester matrix. Improved dispersion determines physical-chemical properties increase of the obtained nanocomposite. A method of MWCNTs functionalization by coating with a layer of iron (III) oxide is presented and the influence of an oscillating magnetic field applying in nanocomposite technology is investigated. Mechanical and tribological properties of nanocomposites with functionalized MWCNTs were analyzed by comparative testing and oscillating magnetic field influence as technological stage of dispersion was investigated.

Keywords: Polyester, Nanocomposite, Wear, Carbon Nanotubes

1. INTRODUCTION

The literature presents two major problems in terms of polymer/MWCNT nanocomposite materials, whose resolution leads to an increase of their properties: the interfacial connection and moreover, the optimum MWCNTs individual dispersion in the polymeric matrix [3].

The influence of the chemical bond between nanotubes and the matrix on the interfacial adhesion was anticipated by the molecular dynamics simulations [9]-[15], [1].

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 by the strong and natural MWCNTs tendency to realize agglomerates. These properties efficient operation in the polymers depends on their homogenous dispersion process in the matrix in the same time with the agglomerates destruction process and their wetting with polymeric substance. Considering MWCNTs 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 MWCNTs themselves [16].

The usual particles dispersion in the polymeric materials seems to be difficult and finally ends with both phases separation and agglomeration phenomenon.

Starting from a well-determined target like nanotubes dispersion, it will be proposed different work techniques: ultrasonication, mechanical stirring, calendaring etc. [7], [8].

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 lead to MWCNTs breakage, decreasing their length. MWCNTs dispersion in an adequate solvent (like: dimethylketone, styrene) represents an appropriate way for ultrasonication technique application in order to obtain MWCNTs composite materials. In this way, it would be allowed an
agglomerates separation due to the vibration energy [6], [2]. Decreased agglomerates dimensions can be easily obtained using MWCNTs functionalization technique [17], [18].

Mechanical stirring is an usual dispersion method of the particles in the liquid systems and can be successfully used for nanoparticles dispersion. The dispersion result depends by the mixer shape and size as well as stirring speed. After an intensive MWCNTs 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 [5]. The main idea of this paper is that another energy type introduced into the disperse system in the composite material obtaining process is used from the outside part of nanocomposite material. External electromagnetic field energy that is induced in the dispersed system due to carbon nanotubes covered with a molecular layer of iron (III) oxide contributes at an improved carbon nanotubes dispersion into the matrix system [19], [20].

2. SAMPLES AND TECHNIQUES

Method of modifying carbon nanotubes surface for an increased compatibility with the polymeric matrix consists in covering technique with a molecular layer of iron(III) oxide. The first step of this method is represented by carbon nanotubes dispersion using a solution of 1% sodium dodecyl sulphate (SDS) as surfactant agent followed by ultrasonication process for 10 minutes with BANDELIN HD3200, having 40% amplitude. Subsequently, a solution of FeCl3 1mol/L was quantitative added under a magnetic stirring for 5 minutes and the resulted solution is ultrasonicated for 10 minutes using the same ultrasounds generator, at the same parameters. After that, it was quantitative added a solution of NH3 1mol/L till pH = 8.5, followed by the same ultrasonication process. The final stage consists in a step to step washing process of the nanotubes covered by a molecular layer of iron(III) oxide particles using bidistilled water till pH = 5.5, followed by a centrifugation process. In order to obtain nanocomposite materials with polymeric matrix it was used an unsaturated polyesteric matrix AROPOLTM M105, a largely used resin at industrial level added with 1.5% catalyst 2-ethyl-cobalt hexanoat. It was used methyl-ethyl ketone peroxide 1.5% as the initial catalyst. Multiwall 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 iron(III) oxide in accordance with a technology that represent another scientific paper aim. In order to present carbon nanotubes optimum concentration value in the polyester matrix, it was considered three types of concentration: 0.10; 0.15 and 0.20%.

It was realized the dispersion process considering a self-technology represented by two different types of stirring, starting with a mechanical one and followed by an 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. It was realized two experimental series A and B using these three types of concentration for carbon nanotubes covered with a molecular layer of iron(III) oxide. B samples realized using three different types of concentration are different from A samples due to the fact that the dispersion technology contains an extra-phase represented by a supplementary dispersion in an oscillating magnetic field.

The samples realized 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 dimensional and chemical stabilized using a thermal treatment in the oven at 323K for 24 hours. For each experiment it was worked using 10 samples for a statistically interpretation. The samples were stand at 3 points flexural test on a testing machine Win TestTM Analysis.

3. RESULTS AND DISCUSSION

The obtained materials in accord with these methods presented above were analyzed in order to show the modifications appeared in comparison with the initial MWCNTs. For this reason, it was used analysis techniques of the functional groups from MWCNTs surface level as the oxidative decoupling result of C-C bonds localized at MWCNTs external tube level. The unoxidized inner side tubes maintain the MWCNTs initial properties and the functionalized or covered with a molecular layer of iron(III) oxide external tube realizes a better compatibility between matrix and nanotubes. In order to present the modifications suffered by MWCNTs
surfaces after these three different treatments applied, it was realized an XRF analysis with NITON XLt.

The samples covered with a molecular layer of iron(III) oxide (MWCNT-F3), Fe concentration is about 5%. This covering layer represents a consistent deposit of iron(III) oxide. This layer has magnetic properties, it is interacting with oscillating magnetic field and realizes a vibration movement of MWCNTs. In this way, an improved dispersion is assessed.

The optimum value of carbon nanotubes concentration in the polyester resin in order to correspond to the technological requests for a nanocomposite material obtaining process. MWCNTs optimum concentration value in polymeric matrix can be determined using a viscosity variation study in relation to nanotubes concentration from the polymeric resin. This variation viscosity value is evaluated in percentage in comparison with the pure resin.

The experimental values are synthetically presented in Fig.1.

The experimental data at 3 points flexural test for the two series A and B are schematically presented in Table 1.

Table 1. Bending modulus values

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bending Strength at Break (N/mm²)</th>
<th>Bending Modulus (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0.10%</td>
<td>103.9</td>
<td>4168.64</td>
</tr>
<tr>
<td>B0.10%</td>
<td>105.0</td>
<td>4728.29</td>
</tr>
<tr>
<td>A0.15%</td>
<td>105.2</td>
<td>4305.62</td>
</tr>
<tr>
<td>B0.15%</td>
<td>109.2</td>
<td>4500.66</td>
</tr>
<tr>
<td>A0.20%</td>
<td>110.4</td>
<td>4605.21</td>
</tr>
<tr>
<td>B0.20%</td>
<td>111.5</td>
<td>4805.25</td>
</tr>
</tbody>
</table>

Table 2. Results of mechanical tests

<table>
<thead>
<tr>
<th>Conc. MWCNT (%)</th>
<th>Bending strength (%)</th>
<th>Bending modulus (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>1.08</td>
<td>11.83</td>
</tr>
<tr>
<td>0.15</td>
<td>3.65</td>
<td>4.30</td>
</tr>
<tr>
<td>0.20</td>
<td>0.99</td>
<td>4.16</td>
</tr>
</tbody>
</table>

The highest value for bending modulus is observed at a concentration of 0.1%.

This conclusion is explained by the fact that the oscillating magnetic field efficiency is quantified when the gaps between nanotubes clusters are large.

At highest concentration values, that means 0.15% and 0.20%, the same parameter variation maintains quasi-constant; the explanation would be that gaps decreasing presents important impacts on the oscillating magnetic field efficiency concerning the dispersion process of carbon nanotubes covered by a molecular layer of iron (III) oxide.

In order to determine the friction coefficient, MWCNT-F3 nanocomposite samples were tested using pin-on-disk tribometer as a module of the equipment UMT - Multi-Specimen Test System (CETR, 2007, USA).
As a general behaviour, the friction coefficient decrease at all the concentration types was observed, starting with the samples without any external oscillating magnetic field till the samples under this magnetic field presence.

A similar behaviour with/without the oscillating magnetic field presence till a moment was observed at the samples whose MWCNT-F3 concentration is higher than 0.1%. This critical point is obtained for the samples with 0.15% MWCNT-F3 at 700 meters and for the samples with 0.20% MWCNT-F3 at 200 meters. After this moment, a dramatic friction coefficient increase is obtained and this value of 0.7 maintains almost constant till the experiment end.

This high increase is obtained due to MWCNT-F3 nanocomposite material flaw.

The different concentration of MWCNT-F3 nanocomposite materials were comparatively studied in Fig.3 and a decrease friction coefficient was obtained from 0.10% to 0.15% till 0.20%.

Figure 4 presents a good behaviour of MWCNT-F3 nanocomposite in the oscillating
magnetic field presence, especially at 0.10% MWCNT-F3, in comparison with 0.15% and 0.20%.

4. CONCLUSION

The viscosity variation study concluded on the optimum concentration. Considering the experimental data analysis and processing, an optimum concentration value about 0.15% MWCNT in MWCNT-F3 systems respectively was obtained, excepting MWCNT-pure system whose optimum value was registered at 0.20% MWCNT.

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 iron(III) oxide in the same time contribute at a new improved dispersion method. Tribological analysis presents MWCNT-F3 nanocomposite materials as having the best behaviour in the oscillating magnetic field presence in comparison with the same samples without this magnetic field influence.

All these analyses confirm that the oscillating magnetic field introduction at magnetic nanoparticles composites contributes at an improved dispersion obtaining.

In conclusion, it was demonstrated that another technological step introduction in the dispersion process of carbon nanotubes coated with a molecular layer of iron (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.

REFERENCES

2. ASGARI S., 2005, Composite materials containing carbon nanoparticles, Provisional applications No.60/643,842.