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STUDIES ON DISPERSION AND IMPROVED MECHANICAL AND THERMAL PROPERTIES OF POLYMER / CNT NANOCOMPOSITE

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Abstract

It is known that an important factor in nanocomposites obtaining technology is the dispersion of nanoparticles in the matrix. The paper proposes a new technology in the dispersion of carbon nanotubes in a polymer matrix. It was used multiwall carbon nanotubes (MWCNT) that based on a particular technology, have been coated with iron oxide (III) resulting so-called plated or coated nanotubes (MWCNT-F3). MWCNT-F3 carbon nanotubes were used to obtain a polymer/MWCNT-F3 nanocomposite material by dispersion in a polymer matrix represented by polyester resin. Oscillating magnetic field interacting with carbon nanotubes coated with iron oxide (III) own fields performs a vibrating movement thereof. Dispersion was carried out in steps by mechanical and ultrasonic mixing, with and without applying an oscillating magnetic field in polyester resin curing phase. The dispersion degree was qualitatively analyzed by SEM analysis. Influence of dispersion on the mechanical and thermal properties was performed by three points bending test and by measuring the thermal conductivity. Polymer/MWCNT-F3 nanocomposite systems were studied at different concentrations of carbon nanotubes, namely: 0,10%; 0,15; 0,20%. These nanocomposite systems were obtained in two technological variants: in the absence and in presence of oscillating magnetic field. The influence of oscillating magnetic field was qualitative emphasized by comparative analysis of SEM results of the two variants. In quantitative terms, the dispersion degree was analyzed by the results obtained from three points bending test and calorimetric measurements.

Keywords: dispersion, MWCNT-F3, oscillating magnetic field, thermal properties

1. 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 ingenious 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 resolved in order to realize a substantially improvement of 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 a 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 by the strong and natural CNTs 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 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] Starting from a well-determined target like nanotubes dispersion, it will be proposed different work techniques: mechanical stirring, ultrasonication, oscillating magnetic field etc. 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 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] 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 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 using CNTs functionalization technique. Oscillating magnetic field is the third dispersion energy form which can be introduced into the system only when an interaction between nanoparticles exists, that means magnetic properties existence. In order to accomplish these conditions, it were used coated CNTs with iron (III) oxide in this paper. Oscillating magnetic field efficiency concerning dispersion improvement was comparatively studied by SEM analysis, 3 points flexural test and calorimetric analysis.

2. MATERIALS AND METHODS

In order to obtain nanocomposite materials with polymeric matrix it was used an unsaturated polyesteric matrix AROPOLTM M105 TPB ASHLAND OLANDA – ROTTERDAM, a largely used resin at industrial level added with 1% catalyst 2-ethyl-cobalt hexanoat. It was used methyl-ethyl ketone peroxide 2% 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 Fe₂O₃ 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 a ultrasonic type of stirring (Fig 1.).

At the end of these two different types of stirring, it was realized a dispersion process in a vibrant magnetic field (Fig 2.). It was realized two experimental series coded with A and A* using these three types of concentration for carbon nanotubes covered with a molecular layer of Fe₂O₃. The samples coded with A* realized 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.). The samples were stand at 3 points flexural test on a testing machine “win TestTM Analysis – Testometric materials testing machines, England”. results and discussions

The experimental data at 3 points flexural test for the two series coded A and A* 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. 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 A* 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.

Table 1 Bending modulus values

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_{0.10%}$</th>
<th>$A^{*}_{0.10%}$</th>
<th>$A_{0.15%}$</th>
<th>$A^{*}_{0.15%}$</th>
<th>$A_{0.20%}$</th>
<th>$A^{*}_{0.20%}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bending Strength @ Break (MPa)</td>
<td>103.90</td>
<td>105.04</td>
<td>105.25</td>
<td>109.24</td>
<td>110.40</td>
<td>111.50</td>
</tr>
<tr>
<td>Bending Modulus (MPa)</td>
<td>4168.64</td>
<td>4728.29</td>
<td>4305.62</td>
<td>4500.66</td>
<td>4605.21</td>
<td>4805.25</td>
</tr>
<tr>
<td>Transv. Rupture Strength (MPa)</td>
<td>103.90</td>
<td>105.09</td>
<td>105.45</td>
<td>109.61</td>
<td>110.44</td>
<td>112.50</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 vibrant 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 vibrant magnetic field efficiency concerning the dispersion process of carbon nanotubes covered by a molecular layer of $\text{Fe}_3\text{O}_4$. SEM analysis (Fig 3. and Fig 4.) confirms the experimental data obtained at 3 points flexural test; an improved carbon nanotubes distribution at A* series in comparison with A series was observed.

Table 2 Mechanical parameters variation at 3 points flexural test for the same version of A* series in comparison with A series

<table>
<thead>
<tr>
<th>Conc.(%)</th>
<th>Bending strength variation (%)</th>
<th>Bending modulus variation (%)</th>
<th>Transv.rupture strength variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>1.08</td>
<td>11.83</td>
<td>1.13</td>
</tr>
<tr>
<td>0.15</td>
<td>3.65</td>
<td>4.30</td>
<td>3.79</td>
</tr>
<tr>
<td>0.20</td>
<td>0.99</td>
<td>4.16</td>
<td>1.83</td>
</tr>
</tbody>
</table>

At the samples of 0.10% and 0.15% from A series it was observed a stronger agglomeration in comparison with the sample of 0.20% of the same set. This aspect is possible due to the realized equilibrium among the attractive forces energy between the nanoparticles and the dispersion forces energy for 0.20% samples. This case was presented in comparison with adverse energetic state for the dispersion forces considering the samples of 0.10% and 0.15% concentration. At A* series, considering all concentration values, a superior distribution at carbon nanotubes was observed.

Fig. 3 SEM analysis for A series samples of 0.10%, 0.15% and 0.20% concentration without the vibrant magnetic field presence
From SEM analyses realized using Quanta™ 200 Scanning Electron Microscope (2006) was observed the non-agglomerated state of the particles from A* series in comparison with A series that demonstrates the fact that the enthalpic gain from the external vibrant magnetic field conduces to the bond breaking between the nanoparticles participating at the clusters formation. This phenomenon is better observed at decreased concentration values of carbon nanotubes covered with 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 it was analyzed only a single type of magnetic stirrer.

Polymer/MWCNT-F3 nanocomposite materials calorimetric analysis at different concentrations and different technological conditions were done using DSC 823 Mettler Toledo USA calorimetric analyzer.

Considering thermal conductivity tests, resulted an increasing variation for all three polymer/MWCNT-F3 nanocomposite systems with concentrations increasing of MWCNT-F3 carbon nanotubes (0,10; 0,15; 0,20%), both under the oscillating magnetic field and in his absence. Increasing variation of thermal conductivity for all three polymer/MWCNT-F3 nanocomposite systems, with MWCNT-F3 concentration increasing is plotted in Fig 5. Note that the thermal conductivity increasing in oscillating magnetic field presence is higher than in its absence at the same concentrations of MWCNT-F3 carbon nanotubes.

The percentage increase of thermal conductivity ($\Delta \lambda$) at polymer / MWCNT-F3 nanocomposite systems for three MWCNT-F3 concentrations (0,10; 0,15 and 0,20%) in the presence / absence of the oscillating magnetic field was determined using the following relation:

$$\Delta \lambda_i = \frac{\lambda_i - \lambda_0}{\lambda_0} \cdot 100 \%, \text{ in growth percent (\%)}$$

where:

$\lambda_i$ = thermal conductivity of polymer / MWCNT-F3 nanocomposite system at the three MWCNT-F3 concentrations ($i = 0,10; 0,15 \text{ and } 0,20\%$);

$\lambda_0$ = thermal conductivity of pure resin (0,00% MWCNT-F3) in terms of specified technological conditions in presence / absence of oscillating magnetic field during the resin curing process.

It was observed a continuous thermal conductivity increase both in the presence / absence of the oscillating magnetic field. This is an expected consequence of the fact that thermal conductivity increase is related to
MWCNT-F3 concentration variation. Moreover, a systematically higher thermal conductivity increase was observed at all nanocomposite systems to which an oscillating magnetic field influence was additional introduced.

Graphic representation of thermal conductivity increase of the polymer/MWCNT-F3 nanocomposite systems with different concentrations of MWCNT-F3 carbon nanotubes (0,10; 0,15; 0,20%) with carbon nanotubes concentration increasing is summarized in Fig 6.

To highlight the influence of the oscillating magnetic field on thermal conductivity increase of a polymer / MWCNT-F3 nanocomposite system at three MWCNT-F3 concentrations (i = 0,10; 0,15 and 0,20%), its growth rate was calculated using the following relation:

\[
\% \lambda_i = \frac{\lambda_{CMOi} - \lambda}{\lambda_{CMOi}} \cdot 100, \text{ in growth percent (\%)},
\]

where:

\(\lambda_{CMOi}\) = thermal conductivity of the polymer / MWCNT-F3 nanocomposite system, in the oscillating magnetic field presence, at three MWCNT-F3 concentrations (i = 0,10; 0,15 and 0,20%);

\(\lambda\) = thermal conductivity of the polymer / MWCNT-F3 nanocomposite system, in the oscillating magnetic field absence, at three MWCNT-F3 concentrations (i = 0,10; 0,15 and 0,20%);

In summary the influence of oscillating magnetic field is represented by thermal conductivity variation (\(\% \lambda_i\)) of polymer/MWCNT-F3 nanocomposite systems with different concentrations of MWCNT-F3 carbon nanotubes in Fig 7.

From Fig 7., unequivocally emerges the oscillating magnetic field influence through the linear increase of thermal conductivity increase percentage for polymer/MWCNT-F3 nanocomposite systems in this oscillating magnetic field presence to those in its absence, at the same MWCNT-F3 concentration.

This analysis was performed for all three polymer / MWCNT-F3 nanocomposite systems at three MWCNT-F3 concentrations (0,10; 0,15 and 0,20%).

It shows a linear increase in the percentage variation of thermal conductivity (\(\% \lambda_i\)) in the presence of oscillating magnetic field with increasing concentration of MWCNT-F3.

3. CONCLUSIONS

This paper has analyzed thermal conductivity variation for polymer/MWCNT-F3 nanocomposite system at three concentrations of carbon nanotubes coated with iron (III) oxide (0,10%, 0,15%, 0,20%) in two technological variants, respectively in the presence and absence of oscillating magnetic field. In both technological cases conductivity increased with carbon nanotubes concentration increasing, which is expected from the theoretical point of view.
The aim of this paper is to emphasize the oscillating magnetic field influence on carbon nanotubes dispersion process, their surface being modified by coating with iron (III) oxide. A comparative study and some growth indices choice of thermal conductivity demonstrated the unassailable effect of oscillating magnetic field on modified carbon nanotube dispersion in polymer matrix.

It was determined a linear increase of thermal conductivity by oscillating magnetic field applying which shows that its introduction in the process is an independent factor in achieving good dispersion of carbon nanotubes.

SEM analysis qualitatively confirmed the thermal conductivity linear increase by an improved dispersion highlighting due to oscillating magnetic field applying during polymer/MWCNT-F3 nanocomposites obtaining process.

ACKNOWLEDGEMENTS

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LITERATURE


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