Influence of Nanoclay’s Incorporation on Mechanical and Thermogravimetric Properties of ER/MWCNT Composites


*Merchant Marine Academy of Epirus, Vathi, GR-481 00 Preveza, Greece, hariszois@gmail.com
**Technological Educational Institute (T.E.I.) of West Macedonia, Laboratories of Physics and Materials Technology, GR-501 00 Kila, Kozani, Greece, kdelidis@yahoo.com & adamstimoniaris@gmail.com
***Technological Educational Institute (T.E.I.) of Lamia, Department of Electronics, 3rd km Old National Road Lamia-Athens, GR-351 00 Lamia, Greece, kanapitsas@teilam.gr

ABSTRACT

Polymer nanocomposite systems based on epoxy resin (ER), reinforced with amine-modified multi-walled carbon nanotubes (MWCNT) and/or nanoclays were studied by Thermogravimetric/Differential Thermal Analysis (TGA/DTA) and Dynamic Mechanical Analysis (DMA). For comparison, two different nanocomposite systems were examined (ER/MWCNT and ER/MWCNT+clay). The main aim of the present work is to investigate the effect of nanoclays’ incorporation on the degradation behaviour, thermal stability and thermomechanical properties of the nanocomposites. It was found that the addition of a small amount of nanoclays to ER/MWCNT composites enhances nanotubes dispersion without harming electrical conductivity or mechanical performance of the nanocomposites.

Keywords: nanocomposites, carbon nanotubes, mechanical properties, thermal stability

1 INTRODUCTION

The reinforcement of a polymer with nano-scaled fillers developed a new class of advanced multifunctional materials with improved properties [1-3]. These materials are subject of extensive research, because they can be used in many fields of technological applications. It is well known that the properties of a nanocomposite system may vary significantly from those of the bulk matrix, because of the small size of the filler and the increase of the interfacial area [4-6]. However, their unique properties depend strongly on the dispersion of nanoparticles and the interactions between them and the epoxy matrix.

Among the most versatile thermosetting matrices are epoxy resins, because of their good balance between properties and cost, high thermal stability, excellent mechanical strength low density and ease in processability [6, 7]. On the other hand, among nanofillers, carbon nanotubes (MWCNT) are an especially attractive class of inclusions, because of their excellent mechanical, thermal and electrical properties. The addition of carbon nanotubes is widely investigated in the literature [8]. Extensive research and development efforts have been devoted to the use of MWCNT as nanofillers to produce a variety of high-performance polymer nanocomposites with novel properties for specific industrial applications. Among the advantages of MWCNT is their high aspect ratio (as high as 1000), which can induce better adhesion with the polymeric matrix [3, 4]. This is an important factor for effective enhancement of the nanocomposite properties.

Functionalization of carbon nanotubes seems to be the most effective way to overcome some problems related to the difficulty in manufacturing these composites and the architecture of the formed network [3, 6]. Fillers’ modification allows a uniform dispersion of the carbon nanoparticles into the matrix, but it also plays an important role to the formation of an interface and a secondary crosslinking network. These two factors seem to strongly affect also the properties of the final product [2, 8].

In previous works [9, 10] the thermomechanical properties of epoxy nanocomposites reinforced with amino-modified MWCNT were studied. It was found that the addition of carbon nanotubes improves the mechanical behaviour and simultaneously decreases the electrical percolation threshold of these composites. This effect was attributed to better nanotubes’ dispersion and stronger epoxy-MWCNT interaction after functionalization, because the amine groups on the fillers surface act as an additional curing agent. In some cases a mixture of nanofillers leads to superior results. There are some indications [11] that the incorporation of small amount of nanoclay to ER/MWCNT composites can enhance even more the nanotubes’ dispersion. Carbon nanotubes appear to have an affinity for clay that causes them to become more exfoliated and better networked in these composites. Possibly, the platelets of nanoclays, as soon as they are embedded into the epoxy matrix, prevent the nanotubes to reform aggregates. This clay-nanotube synergy may make these composites better suited for a variety of technological applications.

In the present study, clay nanoparticles (Closite 30B) were introduced into ER/MWCNT composites in order to improve nanotubes’ dispersion without harming electrical conductivity or mechanical performance. For comparison, two different nanocomposite systems were studied (ER/MWCNT and ER/MWCNT+clay) by means of TGA and DMA techniques. Our interest was focused on the effect of nanoclays’ incorporation on thermal stability.
degradation behaviour and mechanical properties of the nanocomposites.

2 EXPERIMENTAL

2.1 Sample Preparation

The pre-polymer D.E.R. 332 used in this work is diglycidyl ether of bisphenol A (DGEBA) supplied by Fluka SA, USA. The hardener used was triethylene-tetramine (TETA) supplied by Sigma Aldrich, USA. The multi-walled carbon nanotubes (average diameter 9.5 nm and average length less than 1 μm) were supplied by Nanocyl SA, Belgium. The nanotubes, as mentioned by the manufacturer, were prepared via a CCVD technique and, then, they were functionalized with amine (–NH₂) groups. The modified nanoclays Closite 30B were supplied by Southern Clay Products, USA. All the components of the systems studied are commercial products and were used without any purification. Two different nanocomposite systems were prepared (ER/MWCNT and ER/MWCNT+clay, respectively) [9, 12].

In order to prepare the DGEBA/TETA/MWCNT nanocomposites the pre-polymer was heated at 40 °C in order to decrease its viscosity. The stoichiometric amount of TETA (14 phr) and MWCNT was added to the DGEBA matrix, and then the mixture was mechanically stirred for 1 hour at 2000 rpm and degassed under vacuum for 15 minutes. Finally, the mixture was sonicated for 30 minutes, in order to suppress the possible formation of MWCNT agglomerates and bundles [12], and degassed again. This process accomplishes the best possible dispersion of the carbon nanotubes within the epoxy resin matrix. The produced homogeneous liquid was poured in rectangular-shaped Teflon molds and the samples were cured at 60 °C for 20 hours, whereas some of the samples were subjected to an additional post-curing heat treatment at 150 °C for 2 hours.

In all the systems prepared, the nanotubes content was 0.1 w/w %, while the clay’s concentration was 2 w/w %.

2.2 Experimental Techniques

For the characterization of the fabricated ER/MWCNT and ER/MWCNT+Closite 30B composites two different, complementary experimental techniques were used: Thermogravimetric/Differential Thermal Analysis (TGA) and Dynamic Mechanical Analysis (DMA).

Thermogravimetric and Differential Thermal Analysis measurements were performed on a simultaneous thermal analyzer (TGA/DTA) STA 503 device (BAEHR Thermo-Analyse GmbH, Germany). TGA tests were conducted in temperature range from ambient temperature (~20 °C) up to 1400 °C under controlled dry nitrogen (N₂) flow at a constant heating rate of 20 °C/min and the weight loss was continuously monitored.

For DMA experiments a Polymer Laboratories dynamic mechanical thermal analyzer MK III was used. Measurements of the tensile storage and loss modulus (E’ and E”) as well as loss tangent (tanδ) were performed from room temperature up to 200 °C. Standard operating conditions were: scanning rate 2 °C/min, frequency 10 Hz and strain 4×. In each of the tests, at least three different samples were tested, and the average results were recorded.

3 RESULTS AND DISCUSSION

Thermal stability and degradation behaviour of the nanocomposites were examined by thermogravimetric analysis (TGA). The behaviour of the composites includes contributions from both the epoxy matrix and the presence of the reinforcing phases. Filler nanoparticles affect the crosslinking procedure and, as a result, an interfacial layer between the nanoparticles and the matrix is formed.

Typical traces of the TGA measurements for the pristine epoxy resin and the ER/MWCNT, ER/clay and ER/MWCNT+clay composite systems are shown in Fig. 1. It was found that the addition of nanofillers enhances, generally, the thermal properties of the neat epoxy matrix.

![Figure 1: Comparative relative (top) and differential (bottom) TGA curves as a function of temperature for all the nanocomposites studied.](image-url)
Relative TGA results reveal that the samples show good thermal stability for temperatures up to around 340 °C, followed by a great weight loss between 350-550 °C. It is interesting to note that for ER+clay system, a new “step” appears at about 600 °C. This is clearly due to the contribution of the nanoclay.

The decomposition (thermal degradation) temperature corresponds to the temperature of the peak of the derivative mass loss (DTGA) curve, i.e. the temperature of the maximum weight loss rate. Maximum decomposition temperature is found to be higher than 375 °C.

It can also be concluded from Fig. 1 that ER/MWCNT+ clay composite seems to have superior thermal properties, compared to the other systems, i.e. degradation temperature becomes higher and residual mass (char content) increases, too.

When only a small amount (2 w/w %) of Cloisite 30B clay is embedded into ER/MWCNT composites, nanotube dispersion is improved. Cloisite 30B is methyl hydrogenated tallow bishydroxyethyl ammonium chloride clay. The single long chain has a potential of stabilization of the dispersion of the clay platelets and the two hydroxyethyl groups anchor the chain firmly to the clay surface. This organic modification appears to be the most effective way in achieving exfoliation. This clay morphology seems to enhance the nanotubes dispersion as pointed out by Liu and Grunlan [11] for epoxy/single-walled carbon nanotubes composites.

Furthermore, in the presence of nanoclay, carbon nanotubes seem to be more easily exfoliated and better networked within the epoxy matrix. Possibly, the platelets of nanoclays, as soon as they are embedded into the epoxy matrix, prevent the nanotubes, after breaking the bundles by mechanical steering and sonication, to reform aggregates through attractive forces. Thus, the incorporation of a small amount of nanoclay into ER/MWCNT composite significantly enhances the nanotubes’ dispersion. It is worth mentioning that the presence of nanoclay changes the physical nature of the formed crosslinked network and could lead to enhanced chain mobility.

Results of DMA measurements are presented in Fig. 2 and summarized in Table 1. The storage (E’) and loss (E’’) modulus in both the glassy and the rubbery state are significantly lower for ER/MWCNT and ER/MWCNT+ clay samples, compared to the unfilled epoxy matrix. This behaviour may be attributed to a large increase of the free volume and/or may be indicative of poor interactions between the polymer and the filler nanoparticles in this particular complex system.

At the same time, the glass transition temperature (T_g) values of the nanocomposites studied (calculated from the peak temperature of tanδ curves, see Fig. 2c) were found to be about 2-3 °C lower than that of the pure epoxy matrix (163 °C). This is in complete accordance with observations in similar epoxy/nanoclay systems [4, 11]. For the filled systems studied, the peak height values increase, too.
<table>
<thead>
<tr>
<th>Composite System</th>
<th>$\tan \delta$</th>
<th>$E'$ (10$^9$ Pa)</th>
<th>$E''$ (10$^8$ Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ER</td>
<td>0.66</td>
<td>162.8</td>
<td>1.40</td>
</tr>
<tr>
<td>ER+clay</td>
<td>0.68</td>
<td>159.7</td>
<td>1.25</td>
</tr>
<tr>
<td>ER/MWCNT</td>
<td>0.69</td>
<td>160.3</td>
<td>1.04</td>
</tr>
<tr>
<td>ER/MWCNT+clay</td>
<td>0.71</td>
<td>160.2</td>
<td>1.08</td>
</tr>
</tbody>
</table>

Table 1: Characteristic values from DMA spectra.

The variation of $T_g$ values depends on two contradictious factors: free volume increase and interactions between the components. The decrease in $T_g$ values observed for the filled composite systems can be explained in terms of free volume. It seems that the effect of free volume increase due to incorporation of the filler particles dominates compared to the effect of interactions within the interlayers formed around the filler nanoparticles, which restrict segmental motions.

DMA measurements on epoxy composites filled with multi-walled carbon nanotubes and clay nanoparticles show that different fillers could lead to different plasticization / antiplasticization results that also depend on their concentration [9].

### 4 CONCLUSIONS

In this work polymer nanocomposite systems based on epoxy resin (ER), reinforced with amine-modified multi-walled carbon nanotubes (MWCNT) were studied by Thermogravimetric/Differential Thermal Analysis (TGA/DTA) and Dynamic Mechanical Analysis (DMA). Clay Closite 30B was introduced into ER/MWCNT composites in order to achieve uniform nanotubes’ dispersion. The addition of nanofillers enhances, generally, the thermal properties of the pristine epoxy matrix. Samples show good thermal stability for temperatures up to around 340 °C.

ER/MWCNT+clay composite seems to have superior thermal properties, compared to the other systems. In the presence of nanoclay, carbon nanotubes seem to be more easily exfoliated and better networked within the epoxy matrix. Glass transition temperature for the filled composite systems are 2-3 °C lower than that of the pure epoxy matrix. Improved mechanical properties for the clay-filled systems are attributed to uniform nanotubes’ dispersion and stronger epoxy-MWCNT interactions after incorporation of the nanoclay.

### REFERENCES