Thermomechanical Properties of Epoxy Resin/MWCNTs Nanocomposites

H. Zois[*], A. Kanapitsas[*] and C.G. Delides[**]

[*]Technological Educational Institute (T.E.I.) of Lamia, 3rd km Old National Road Lamia-Athens, 35 100 Lamia, Greece, kanapitsas@teilam.gr
[**]Technological Educational Institute (T.E.I.) of West Macedonia, Laboratories of Physics and Materials Technology, 50100 Kila, Kozani, Greece, kdelidis@yahoo.com

ABSTRACT

The thermomechanical properties and thermal stability of a nanocomposite system, which consist of epoxy resin (ER) as matrix and carbon nanotubes (MWCNTs) as filler, were investigated by Thermogravimetric/Differential Thermal Analysis (TGA/DTA) and Dynamic Mechanical Analysis (DMA). The dependence of the thermal properties (i.e. weight loss rate, decomposition temperature, residual mass) of the nanocomposites is associated with the filler content. The addition of carbon nanotubes improves generally, the thermal behavior of the epoxy matrix. The results were discussed in terms of the epoxy resin-MWCNTs interactions. The interactions between the polymer matrix and the filler nanoparticles seem to play an important role, especially for the higher MWCNTs concentration,

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

1 INTRODUCTION

Polymer nanocomposites show different properties than the bulk polymer matrix, due to the small size of the filler and the corresponding increase of their surface area [1, 2]. It is well known that the composite properties can change dramatically with the dispersion state, geometric shape, surface properties, particle size, and particle size distribution. Because of the recent commercial availability of nanoparticles, there is increasing interest in polymer nanocomposites. These composites have been shown to undergo substantial improvements in mechanical properties such as the strength, modulus and dimensional stability, permeability to gases, water and hydrocarbons, thermal stability, flame retardancy, chemical resistance and electrical, dielectric, magnetic and optical properties [3-8].

Epoxy resin (ER) is one of the most commonly used matrices for the preparation of polymer composites, because of its easy processability and excellent mechanical properties. Carbon nanotubes (MWCNTs) have received much attention since their discovery by Ijiima in 1992 [9]. Extensive research and development efforts have been devoted to the use of MWCNTs as nanofillers to produce a variety of high-performance polymer nanocomposites for specific technological applications. Among the advantages of MWCNTs is their high aspect ratio (as high as 1000), which can induce better adhesion with the polymeric matrix. This is an important factor for effective enhancement of the nanocomposites properties. The modification of filler particles with specific chemical groups (such as amine groups) improves the compatibility with the epoxy resin and, thus, their dispersion within the polymer matrix.

The main aim of the present work is to investigate the thermomechanical properties and thermal stability of nanocomposite materials based on epoxy resin matrix filled with amine-modified multi-walled carbon nanotubes. We also focus on the influence of filler content on the thermal and mechanical behavior of the systems studied.

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. The hardener used was triethylenetetramine (TETA) supplied by Sigma Aldrich. The amine-modified multi-walled carbon nanotubes (average diameter 9.5 nm and average length < 1 μm) was supplied by Nanocyl SA. All the components of the system are commercial products and were used without any purification.

The DGEBA/TETA/MWCNTs nanocomposites were prepared by the dispersion of the determined amount of carbon in a glass vessel. Prior to that procedure, the pre-polymer was heated at 40 °C in order to decrease its viscosity. The stoichiometric amount of TETA (14 phr) was added to the DGEBA matrix, and then the mixture was mechanically stirred for 1 h at 2000 rpm and degassed under vacuum for 15 min. Finally, the mixture was sonicated for 30 min in order to break up the MWCNTs agglomerates [10] and degassed again. The homogeneous liquid was poured in rectangular-shaped Teflon molds and the samples were cured at 60 °C for 20 h and at 150 °C for 2 h. Several specimens were prepared, with the filler content systematically varied between 0 % (pure resin) and 1 % w/w MWCNTs.

2.2   Experimental Techniques

The characterization of the ER/MWCNTs nanocomposites includes two different experimental techniques: Thermogravimetric/Differential Thermal Analysis (TGA/DTA) and Dynamic Mechanical Analysis (DMA).

A Polymer Laboratories dynamic mechanical thermal analyzer MK III operating at a frequency of 10 Hz, a strain of 4× and a scanning rate of 2°C/min was used. Measurements were performed from room temperature up to 200°C and the resultant changes in the mechanical parameters (E′, E′′ and tanδ) were plotted.

Thermogravimetric and Differential Thermal Analysis measurements were performed on a simultaneous thermal analyzer (TGA/DTA) STA 503 device (BAEHR ThermoAnalyse GmbH, Germany). TGA tests were conducted in temperature range from 20 to 1400 ^{o}C under dry nitrogen (N_2) atmosphere at a heating rate of 20 ^{o}C/min and the weight loss was monitored.

3   RESULTS AND DISCUSSION

The thermomechanical properties of the ER/MWCNTs nanocomposites are changed, due to the MWCNTs' contribution to crosslinking procedure and the existence of an interfacial layer between the nanoparticles and the polymer matrix.

The effect of MWCNTs on the thermal stability of the nanocomposites was studied using thermogravimetric analysis (TGA). Relative TGA and derivative (DTGA) curves for neat epoxy and the prepared ER/MWCNTs nanocomposites are presented in Fig. 1a and 1b, respectively. Similar curves have also been obtained for epoxy resin nanocomposites filled with carbon black (ER/CB) [11]. The results reveal that the samples show good thermal stability for temperatures up to around 340 ^{o}C with a maximum decomposition temperature higher than 375 ^{o}C. A large weight loss occurs between 350-550 ^{o}C. 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. The thermal degradation temperatures of the pure epoxy and the ER/MWCNTs nanocomposites are similar, within experimental errors (± 1.5 ^{o}C). The higher the filler content is, the lower the weight loss rate is (dm/dt peak magnitude decreases).

The temperature corresponding to 5 % initial mass loss, $T_{5\%}$, (onset of the TGA curve) indicates the thermal stability of the samples. The variation of $T_{5\%}$ with MWCNTs content are shown in Fig. 2. The data reveals that the pure epoxy matrix shows, generally, higher weight loss onset (i.e. the degradation starts at higher temperatures), compared to the ER/MWCNTs nano-composites. The $T_{5\%}$ temperature is slightly decreases by the addition of MWCNTs.
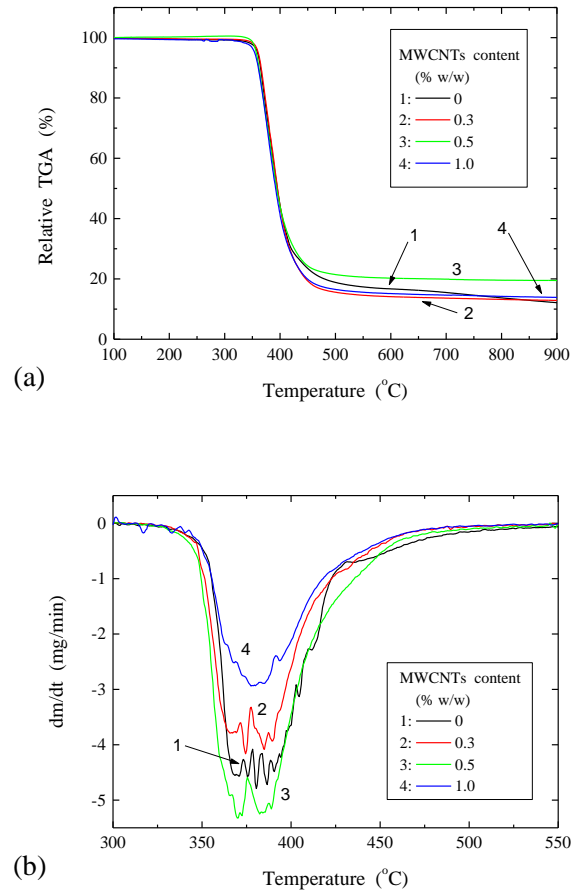

Figure 1: Comparative relative TGA (a) and DTGA (b) curves for ER/MWCNTs nanocomposites with various filler contents shown on the plots.
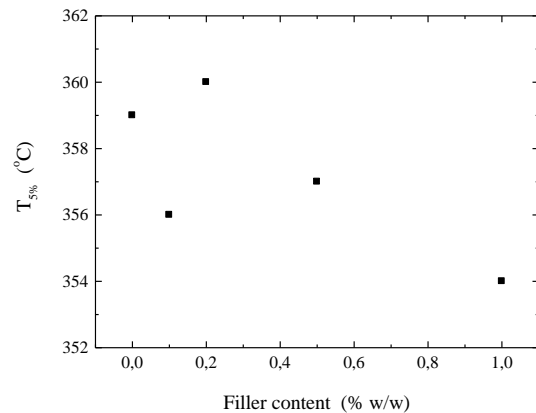

Figure 2: The temperature corresponding to 5 % initial mass loss as a function of the filler content for ER/MWCNTs nanocomposites.

Fig. 3 shows the variation of residual mass (char content) of the nanocomposites at 1000 $^\circ$C as a function of the filler composition. The char content are indicative of the degradation level and the flammability resistance of the samples. The char formation mechanism is, generally, enhanced when adding filler particles, however the values of the residual mass for the ER/MWCNTs nanocomposites decrease with increasing filler content.

The reduction observed for the samples with higher MWCNTs content is probably attributed to the fact that the degradation process of the nanocomposites is hampered by the increased filler concentration, because the interactions between the ER matrix and the MWCNTs filler particles are stronger. This result is in agreement with DMA measurements and glass transition temperature studies [10]. It should also be mentioned that MWCNTs were found to have better dispersion within the polymer matrix, compared to ER/CB nanocomposites [11]. A complete comparison of the thermomechanical properties and thermal stability of ER/MWCNTs and ER/CB nanocomposites can be found in [11].

In Fig. 4, characteristic plots of DMTA measurements for ER/MWCNTs nanocomposites are presented. It was found that the storage modulus, E′, decreases significantly in the glassy state. On the contrary, it is slightly affected by the filler content in the rubbery state.

The glass transition temperature, T_g, is determined by the peak of the tanδ curves. It varies in a strange way. The glass transition temperature as a function of the filler content is presented in Fig. 5. For the samples with filler content up to 0,05 % w/w, the glass transition temperature decreases, compared to the pure polymer matrix. For the samples with higher MWCNTs content, T_g is higher compared to the pure epoxy matrix and varies slightly with increasing filler content.
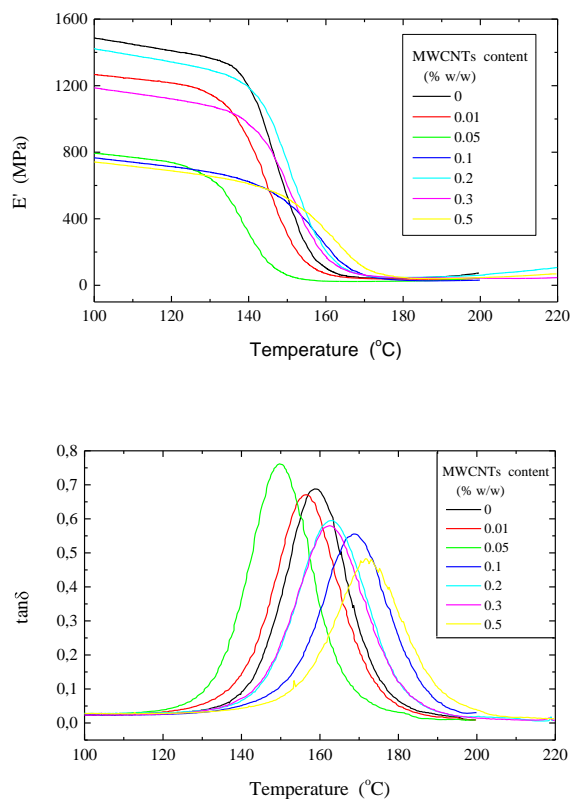

Figure 4: DMA spectra: E′ (top) and tanδ (bottom) as a function of temperature at constant frequency of 10 Hz for ER/MWCNTs nanocomposites and various filler contents shown on the plots.
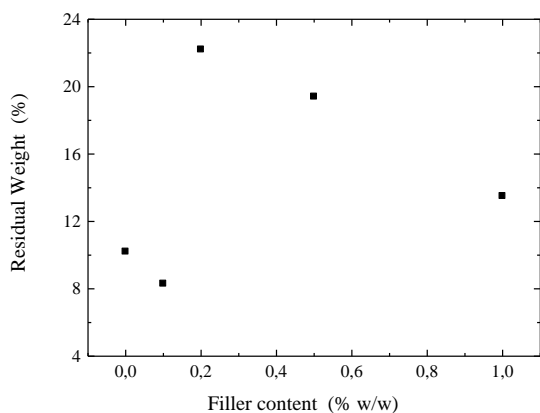

Figure 3: The residual weight at temperature 1000 $^\circ$C as a function of the filler content for ER/MWCNTs nanocomposites.
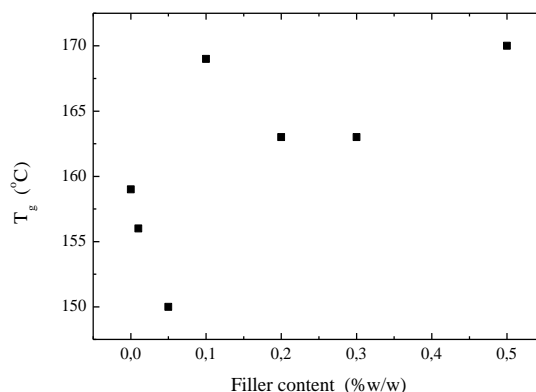

Figure 5: The glass transition temperature as a function of the filler content for ER/MWCNTs nanocomposites.

Filler Content (% w/w)	0	0.1	0.2	0.5	1.0
Maximum weight loss rate (mg/min)	4.8	4.6	5.0	5.2	3.0
Decomposition temperature (^{o}C)	380	379	382	378	379
$T_{5\%}$ (^{o}C)	359	356	360	357	354
Residual mass (%)	10.2	8.3	22.2	19.4	13.5
T_{g} (^{o}C)	159	169	163	170	-

Table 1: The characteristic values of TGA parameters for ER/CNTs nanocomposites

It is also clear that the minimum value of tanδ is observed for the sample with higher glass transition temperature. These results are, probably, attributed to the formation of MWCNTs aggregates within the epoxy matrix. More results on the effect of the nanofillers on the glass transition and the relaxation behavior of the polymer matrix will be given in a future work.

In the Table 1 above the values of the characteristic parameters of TGA measurements for ER/MWCNTs nanocomposites are summarized. It is also included the glass transition temperatures obtained from DMA measurements.

4 CONCLUSIONS

In this work, the thermal stability and dynamic mechanical behaviour of epoxy resin/multi-walled carbon nanotubes (ER/MWCNTs) composites was systematically investigated. The dependence of thermal properties on the filler content was also studied. It was found that the addition of carbon nanotubes enhances the thermal properties of the epoxy matrix. The degradation starts at higher temperatures and the char formation mechanism is enhanced when adding filler particles. For higher MWCNTs content, the interactions between the polymer matrix and the filler particles play an important role and the degradation process becomes slower. From DMA measurements it was found that the addition of MWCNTs increases the glass transition temperature of the pure polymer matrix and decreases the storage modulus in the glassy state. The interactions between the filler particles and the epoxy matrix seem to play an important role on the thermal properties and molecular dynamics mechanisms.

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