

Influence of Carbon Nanoparticles on Thermogravimetric Properties of Epoxy Nanocomposites

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ABSTRACT

The thermomechanical properties and thermal stability of polymer nanocomposites, based on epoxy resin (ER) as matrix, were investigated by Thermogravimetric/Differential Thermal Analysis (TGA/DTA) and Dynamic Mechanical Analysis (DMA). For comparison, carbon nanotubes (MWCNTs) or carbon black (CB) nanoparticles were used as filler. Our interest was focussed on the effect of different filler on the thermomechanical properties, degradation behavior and thermal stability of the nanocomposites. 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 nanofillers enhances, generally, the thermal behavior of the epoxy matrix. The dispersion of nanoparticles and the interactions between them and the epoxy matrix seem to play an important role on the thermal properties and molecular dynamics mechanisms, especially for higher filler concentrations.

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

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 electrical, dielectric, mechanical, magnetic and optical properties and enhanced thermal stability, flame retardancy, chemical resistance and permeability to gases, water and hydrocarbons [3-8].

Epoxy resin (ER) is one of the most commonly used matrices for the preparation of polymer nanocomposites, because of its easy processability and excellent mechanical properties. Carbon black (CB) nanoparticles are typical representatives of widely-used fillers for significant

improvement of mechanical, thermal and electrical properties of the nanocomposites. Carbon nanotubes (MWCNTs) have received much attention during the last decades. Extensive research and development efforts have been devoted to the use of MWCNTs as nanofillers to produce high-performance polymer nanocomposites for specific applications in numerous technological fields. 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 carbon black nanoparticles or amine-modified multi-walled carbon nanotubes. Our interest was focussed on the effect of different filler particles on the thermomechanical properties, degradation behavior and thermal stability of the nanocomposites. The filler content, the dispersion of nanoparticles and the interactions between them and the epoxy matrix seem to play an important role on the thermal properties and molecular dynamics mechanisms, especially for higher filler concentrations.

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 μ m) was supplied by Nanocyl SA. The extra conductive carbon black (particle size 25–75 nm) was obtained from Degussa, Germany. All the components of the system are commercial products and were used without any purification [9].

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 prepolymer 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 [6] 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. Similar preparation procedure was followed for the ER/CB nanocomposites. Several specimens were prepared, with the filler content systematically varied between 0 % (pure resin) and 1 w/w %.

2.2 Experimental Techniques

The characterization of epoxy nanocomposites includes two different experimental techniques: Thermogravimetric/Differential Thermal Analysis (TGA/DTA) 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 20 to 1400 °C under dry nitrogen (N₂) atmosphere at a heating rate of 20 °C/min and the weight loss was monitored.

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. DMA measurements were performed from room temperature up to 200°C and the resultant changes in the mechanical parameters (E', E'' and tanδ) were plotted.

3 RESULTS AND DISCUSSION

The thermal and mechanical properties of epoxy nanocomposites are changed, due to the filler particles contribution to crosslinking procedure and the existence of an interfacial layer between the nanoparticles and the polymer matrix.

The effect of carbon nanoparticles on thermal stability of the nanocomposites was studied using thermogravimetric analysis (TGA). Relative TGA and derivative (DTGA) curves for neat epoxy and the prepared ER/CB nanocomposites are presented in Fig. 1. Similar curves have also been obtained for epoxy resin nanocomposites filled with carbon nanotubes (ER/MWCNTs) [10]. The results reveal that the samples show good thermal stability for temperatures up to around 350 °C with a maximum decomposition temperature higher than 375 °C. A large weight loss occurs between 350-550 °C.

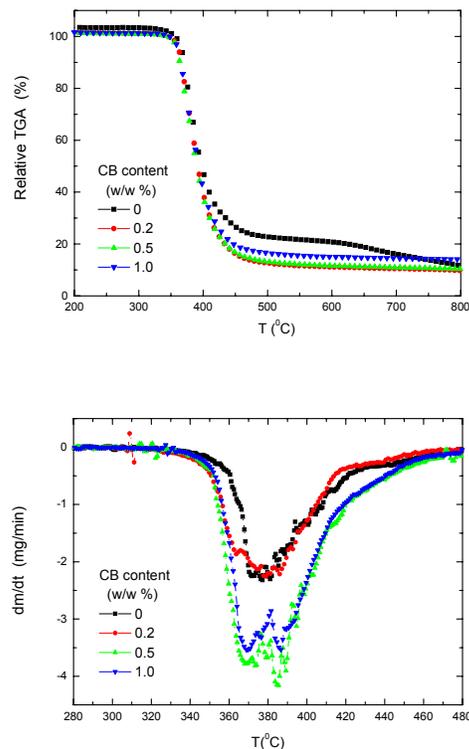


Figure 1: Comparative relative TGA (top) and DTGA (bottom) curves for ER/CB nanocomposites with various filler concentrations shown on the plots.

The decomposition (thermal degradation) temperature corresponds to the peak temperature of the derivative mass loss (DTGA) curve, i.e. the temperature of the maximum weight loss rate. Fig. 2 shows a comparative DTGA thermogram for nanocomposites with 0.5 w/w % filler concentration. Similar curves have also been obtained for other compositions. The thermal degradation temperatures of the pure epoxy and the prepared nanocomposites are similar, within experimental errors (± 1.5 °C).

In Fig. 3 the mass loss rate (dm/dt) curve as a function of the filler content for both systems is presented. It is, generally, significantly higher for ER/MWCNTs samples, compared to ER/CB nanocomposites. The reduction observed for the samples with higher filler concentration is probably attributed to the fact that the degradation process of the nanocomposites is hampered by the increased filler content, because the interactions between the epoxy matrix and the filler particles are stronger. The 1.0 w/w % nanocomposites show the reverse behavior, giving evidence for enhanced interactions between the pure polymer matrix and carbon nanoparticles. This result is in agreement with

DMA measurements and glass transition temperature studies [9].

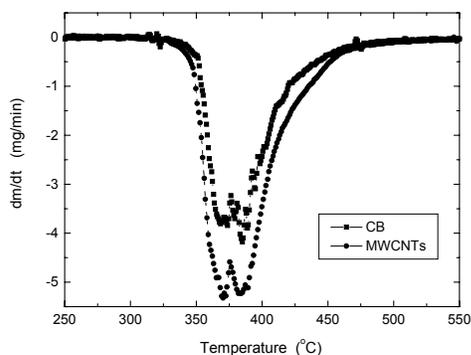


Figure 2: Comparative differential TGA curves for ER/CB and ER/MWCNTs nanocomposites reinforced with 0.5 w/w % of filler.

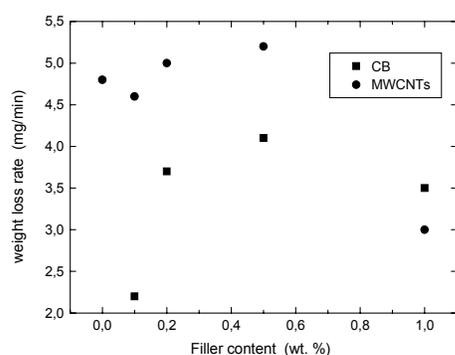


Figure 3: The maximum weight loss rate as a function of the filler content for the nanocomposite systems studied.

Fig. 4 presents the temperature corresponding to 5 % initial mass loss (onset of TGA curves) as a function of filler content for both nanocomposite systems. It indicates the thermal stability of the samples. The degradation process starts at higher temperatures for ER/CB nanocomposites, compared to ER/MWCNTs. Data reveal that filled ER/CB nanocomposites show, generally, enhanced thermal stability (i.e. the degradation starts at higher temperatures), compared to the pure epoxy matrix. The opposite occurs for ER/MWCNTs nanocomposites. Moreover, the $T_{5\%}$ temperature slightly decreases by the addition of MWCNTs nanoparticles [10].

The variation of residual mass (char content) with filler content is presented in Fig. 5. The residual weight is indicative for the degradation level and the flammability

resistance of the samples. The char formation mechanism is enhanced for filler content higher than 0.2 w/w %. The residual mass for ER/MWCNTs nanocomposites is significant higher compared to that of ER/CB samples and decrease with increasing filler content. This reduction is probably attributed to the fact that the degradation process of the nanocomposites is hampered by the increased filler concentration [10]. On the contrary, for ER/CB nanocomposites, the char content increases with increasing filler content. This result is in agreement with DMA measurements and glass transition temperature studies [9].

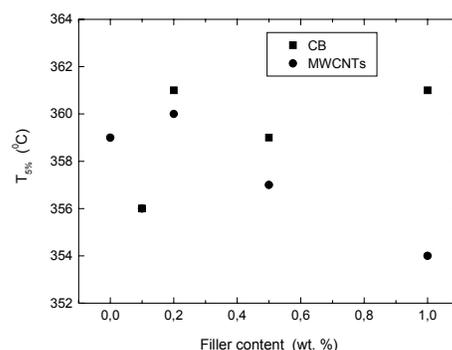


Figure 4: The temperature corresponding to 5 % initial mass loss as a function of the filler concentration for ER/CB and ER/MWCNTs nanocomposites.

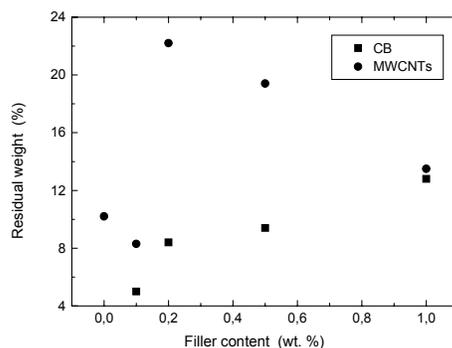


Figure 5: The residual weight at temperature 1000 °C as a function of the filler content for ER/CB and ER/MWCNTs nanocomposites.

It should also be mentioned that MWCNTs were found to have better dispersion within the epoxy matrix, compared to CB nanoparticles. The variation of residual mass for the two systems tend to be similar at higher filler content (1.0 w/w %). This observation maybe attributed to the different

filler arrangement (from dispersed to agglomerated state), which occurs for higher CB contents (greater than 0.7 w/w %). This result is in agreement with glass transition temperature studies [9].

DMA measurements for ER/CB system show that the storage modulus, E' , is unaffected by the addition of filler nanoparticles in the glassy state, but it increases in the rubbery one [9]. The opposite occurs for ER/MWCNTs nanocomposites [10]. In Fig. 6, characteristic plots of DMA measurements at constant frequency 10 Hz for ER/CB and ER/MWCNTs nanocomposites are presented. The glass transition temperature, T_g , is determined by the peak temperature of $\tan\delta$ curves. We observe that, for ER/CB nanocomposites, the glass transition temperature is higher, compared to the pure polymer matrix and the intensity becomes lower.

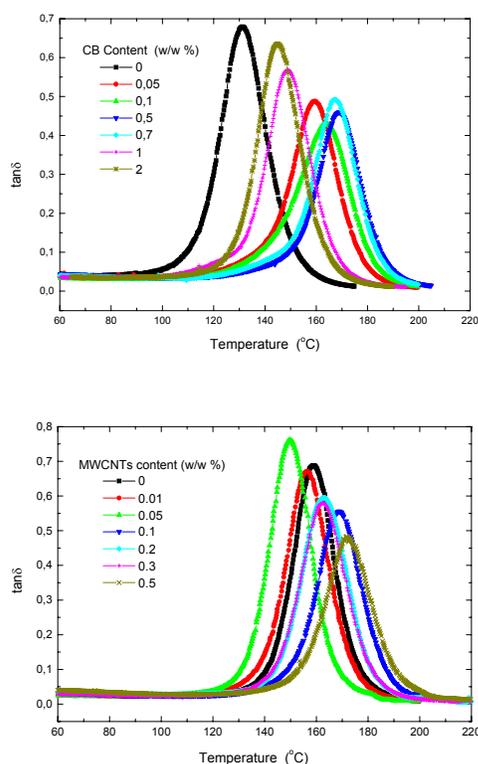


Figure 6: DMA spectra: $\tan\delta$ as a function of temperature for ER/CB (top) and ER/MWCNTs (bottom) nanocomposites. Filler content is shown on the plots.

For ER/MWCNTs nanocomposites and for 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. It is also clear that the minimum value of $\tan\delta$ 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 nanofillers on the glass transition and the relaxation behavior of the polymer matrix will be given in a future work.

4 CONCLUSIONS

In this work, the thermal stability and dynamic mechanical behavior of ER/MWCNTs and ER/CB polymer nanocomposites were investigated by means of TGA and DMA techniques. The addition of nanoparticles enhances the thermal properties of the pure epoxy matrix. TGA results reveal that both systems show good thermal stability for temperatures up to 350 °C with a maximum decomposition temperature higher than 370 °C. Weight loss rate is higher for ER/MWCNTs, compared to ER/CB nanocomposites, but it decreases with increasing filler content. This probably means that the degradation process of the nanocomposites is hampered by the increased filler concentration. The char formation mechanism is enhanced with the addition of nanoparticles higher than 0.2 w/w %. For higher filler concentrations, the interactions between the neat polymer matrix and the carbon nanoparticles play an important role. DMA measurements show that, for ER/CB system, the storage modulus, E' , is unaffected by the addition of filler particles in the glassy state, but it increases in the rubbery one. The opposite behavior was observed for ER/MWCNTs nanocomposites. Finally, the glass transition temperatures of the nanocomposites are, generally, higher than that of the pure epoxy matrix.

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