

# Thermomechanical Properties of Epoxy Resin / Carbon Nanotubes / Clay Nanocomposites

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## ABSTRACT

Polymer nanocomposite systems based on epoxy resin (ER), reinforced with amine-modified multi-walled carbon nanotubes (MWCNT) and/or nanoclays were studied by Dynamic Mechanical Analysis (DMA) and Thermogravimetric/Differential Thermal Analysis (TGA/DTA). For comparison, three different nanocomposite systems (ER/MWCNT ER/clay and ER/MWCNT+clay) were examined. 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. The addition of a small amount of nanoclays to ER/MWCNT composites enhances nanotubes dispersion without harming electrical conductivity or mechanical performance of the composites. Kissinger method was used to analyze the kinetics of decomposition mechanism. Apparent activation energies during the thermal degradation process were calculated.

**Keywords:** epoxy nanocomposites, carbon nanotubes, clay, thermal stability, degradation behaviour

## 1 INTRODUCTION

Epoxy resin (ER) is one of the most commonly used matrices for the preparation of polymer composites, because of its easy processability excellent mechanical properties, high thermal stability and their good balance between properties and cost [1, 2]. Thermosetting epoxy resins are widely used for many applications, including high strength adhesives, lightweight foams, surface coatings and durable laminates [3]. In recent years, polymer nanocomposites reinforced with surface-treated nanofillers have received significant attention because of the substantial improvements they can achieve in mechanical, thermal and barrier properties when compared with the unmodified polymer [4].

Multi-walled carbon nanotubes (MWCNT) are typical representatives of widely-used fillers for significant improvement of mechanical, thermal and electrical properties of the nanocomposites. Extensive research and development efforts have been devoted to the use of MWCNT as nanofillers to produce a variety of high-

performance polymer nanocomposites for specific technological applications. Among the advantages of MWCNT is their high aspect ratio which can induce better adhesion with the polymeric matrix. This is an important factor for effective enhancement of the nanocomposites properties.

There are some indications [3, 5] that the incorporation of small amount of nanoclays to polymer-MWCNT nanocomposites can enhance the nanotubes dispersion. The selection of layered silicate nanoclays as reinforcements is highly attractive because of their relatively low-cost, high thermal inertness, ready availability and environment-friendly characteristics [2, 6]. Dispersed nanoclay platelets into the matrix prevent the nanotubes aggregation, after breaking the bundles by steering and sonication, through attractive forces. In the present study, organo-modified montmorillonite clays: Cloisite 30B was introduced into ER/MWCNT composites to improve nanotube dispersion without harming electrical conductivity or mechanical performance.

Cloisite 30B is methyl-hydrogenated tallow bishydroxyethylammonium chlorine 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 most effective in achieving exfoliation. This clay morphology seems to enhance the nanotubes dispersion as pointed out for epoxy-CNT composites [2].

MWCNT appear to have an affinity for clay that causes them to become more exfoliated and better networked in these composites. This clay-nanotube synergy may make these composites better suited for a variety of industrial applications.

This study investigates the effect that the addition of commercially available nanoclays has on the mechanical and thermal properties of an epoxy polymer-MWCNT composite. For comparison, three different nanocomposite systems (ER/MWCNT, ER/Cloisite 30B and ER/MWCNT+ Cloisite 30B) were studied by means of Thermogravimetric Thermal Analysis (TGA) and Dynamic Mechanical Analysis (DMA) techniques. Our interest was focused on the effect of nanoclays incorporation on thermal stability, dynamics of the degradation behaviour and mechanical properties of the composites.

## 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  $\mu\text{m}$ ) 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 ( $-\text{NH}_2$ ) groups. The modified nanoclays Cloisite 30B were supplied by Southern Clay Products, USA. All the components of the systems studied are commercial products and were used without any purification. Three different nanocomposite systems were prepared (ER/MWCNT, ER/ Cloisite 30B and ER/MWCNT+ clay, respectively) [7, 8].

In order to prepare the DGEBA/TETA/MWCNT nanocomposites the pre-polymer was heated at 40  $^{\circ}\text{C}$  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 [8], 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  $^{\circ}\text{C}$  for 20 hours, whereas some of the samples were subjected to an additional post-curing heat treatment at 150  $^{\circ}\text{C}$  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, ER/ Cloisite 30B and ER/MWCNT+Cloisite 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 ( $\sim 20^{\circ}\text{C}$ ) up to 1400  $^{\circ}\text{C}$  under controlled dry nitrogen ( $\text{N}_2$ ) flow and the weight loss was continuously monitored. TGA experiments were performed at different values of the heating rate,  $\beta$  (from 5 up to 40 K/min).

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 ( $\tan\delta$ ) were performed from room temperature up to 200  $^{\circ}\text{C}$ . Standard operating conditions were: scanning rate 2  $^{\circ}\text{C}/\text{min}$ , frequency 10 Hz and strain  $4\times$ . 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. Heating rate is equal to 40 K/min.

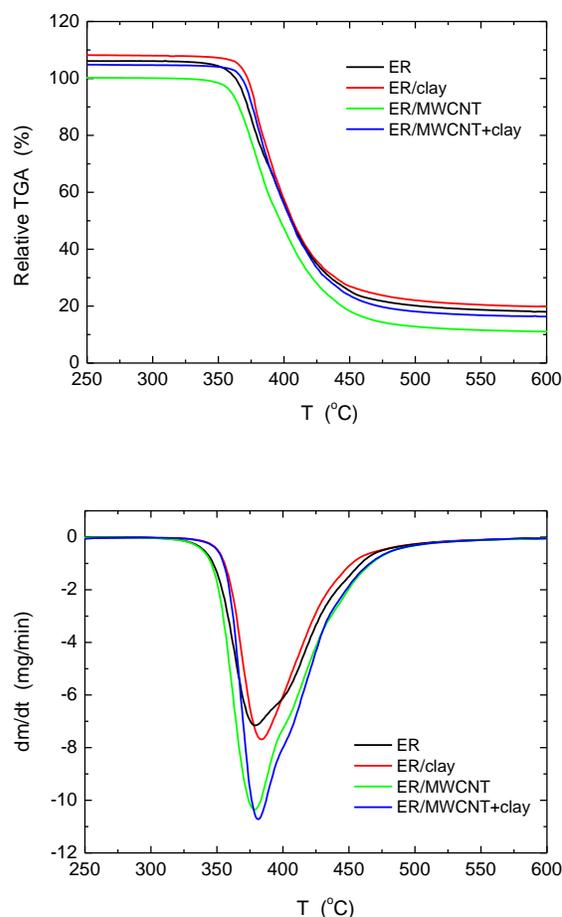


Figure 1: Comparative relative (top) and differential (bottom) TGA curves as a function of temperature for all the nanocomposites studied. Heating rate is 40 K/min.

Relative TGA results reveal that the samples show good thermal stability for temperatures up to around 335 °C, followed by a sudden weight loss between 360-480 °C.

As it is clearly shown, the addition of nanofillers enhances, generally, the thermal properties of the neat epoxy matrix. It is also interesting to note that the incorporation of clay nanoplatelets improves filler dispersion within the epoxy matrix. This is attributed to the enhanced synergy between carbon nanotubes and the clay.

The decomposition temperature,  $T_p$ , is the temperature corresponding to the inflection point of the thermal degradation curves. It is considered as the temperature of the peak of the derivative mass loss (DTGA) curve, i.e. the temperature of the maximum reaction (weight loss) rate. In all case maximum decomposition temperature is found to be higher than 370 °C.

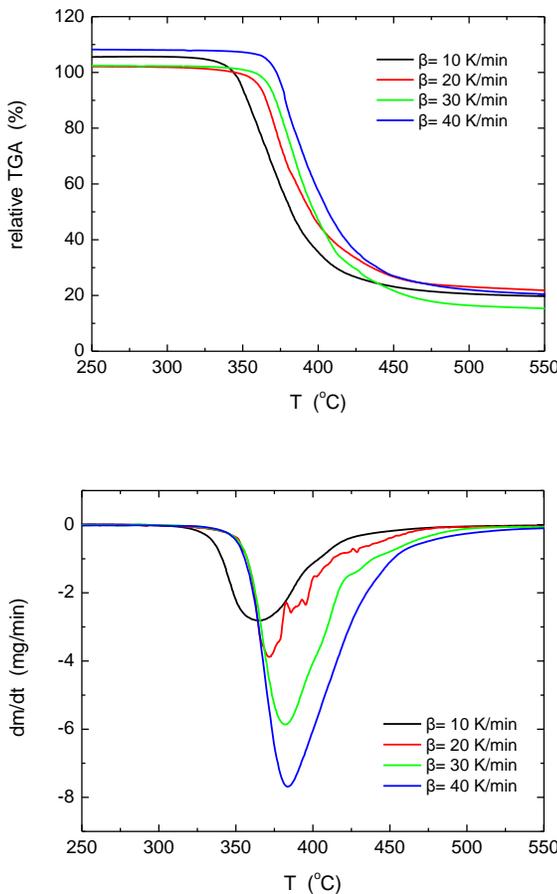


Figure 2: Relative (top) and differential (bottom) TGA curves as a function of temperature for ER/Closite 30B nanocomposites for various values of the heating rate shown on the plot.

It can also be concluded from Fig. 1 that the composites containing Closite 30B nanoclay seems to have, generally, superior thermal properties, compared to the other systems.

The higher thermal stability of the nanocomposites may be attributed to the homogeneous dispersion of intercalated silicate layers, which by nature have much higher thermal stability [9]. The nano-dispersed lamellae of clay within the epoxy matrix may change the decomposition process of the polymer, since the silicate layers act as thermal hindlers.

The curves in Fig. 1 have similar shape for all the heating rates examined. The influence of the heating rate,  $\beta$ , on the thermal process parameters is depicted in Fig. 2. It is obvious that the characteristic decomposition temperature shifts to higher values with increasing heating rate. At the same time, maximum weight loss rate ( $dm/dt$ ) increases, too.

It should be mentioned that, independent from the heating rate, the addition of nanoparticles enhances the thermal properties of the epoxy matrix. We also observe that the DTGA peak is quite asymmetric, giving, thus, evidence for existence of a double mechanism behavior.

In our case, only a small amount (2 w/w %) of Closite 30B clay is sufficient to improve nanotube dispersion into ER/MWCNT composites [3, 5]. This is due to the chemical nature of the clay, which leads to easy exfoliation of carbon nanotubes. Probably, clay nanoplatelets prevent carbon nanotubes to reform aggregates. Consequently, carbon nanotubes are better networked within the epoxy matrix. Thus the presence of nanoclay changes the physical nature of the formed crosslinked network and could lead to enhanced chain mobility [3, 5].

TGA measurements at nanocomposites with different filler concentration show that the degradation mechanism is hampered by the increased filler content, because filler nanoparticles form strong bonds with the epoxy matrix. As a result, a more complex network structure is created. This result is in agreement with dynamic mechanical analysis (DMA) measurements and glass transition temperature studies [8].

One of the most common methods to calculate the apparent activation energy,  $E_{act}$ , during thermal degradation process is the Kissinger method [10]. This approach allows obtaining the dependence of the kinetic parameters from DTGA curves measured at different heating rates. The main advantage of this method is that it does not require precise knowledge of the reaction function and order. According to this method,  $E_{act}$  can be obtained by the following equation:

$$\frac{d\left(\ln \frac{\beta}{T_p^2}\right)}{d\left(\frac{1}{T_p}\right)} = -\frac{E_{act}}{R} \quad (1)$$

where  $T_p$  is the decomposition temperature corresponding to the inflection point (maximum weight loss rate) of the TGA curves,  $\beta$  is the heating rate and  $R$  is the gas constant ( $R= 8.314 \text{ J/K}\cdot\text{mol}$ ).

From a plot of  $\ln(\beta/T_p^2)$  versus  $1/T_p$  and fitting to a straight line,  $E_{act}$  can be easily calculated from its slope. In Fig. 3 such linear plots for the neat epoxy resin and the

prepared nanocomposites are presented. The apparent activation energy of the thermal degradation process for the neat epoxy matrix is:  $E_{act} \approx 354$  kJ/mol. For all the filled nanocomposites, activation energy values in the range 190-222 kJ/mol were obtained. The lower activation energy values for the filled nanocomposite may be related to strong interactions between nanoparticles and the free radicals formed during degradation, giving rise to the nanoparticles having a catalytic effect on the sample degradation [11]. To fully understand the reaction mechanism, calculations at different conversions values should be done.

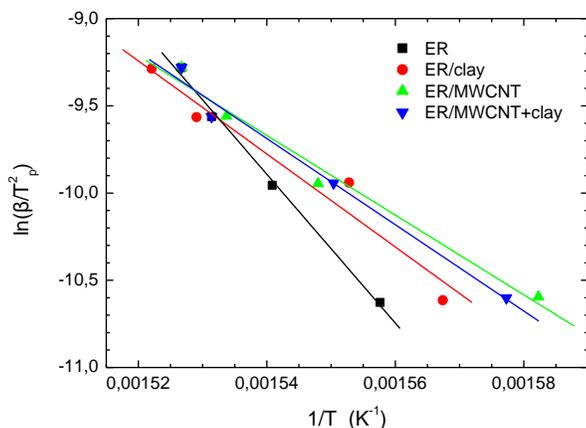


Figure 3: Linear Kissinger plots for determining activation energy during thermal decomposition process for all the nanocomposites studied.

DMA measurements were performed to estimate the glass transition temperature,  $T_g$ , of the composite systems studied. The glass transition temperature was calculated from the peak temperature of  $\tan\delta$  curves (not shown here). For the filled samples it was found to be about 2-3 °C lower than that of the neat epoxy matrix ( $\approx 163$  °C). This is in accordance with observations in similar epoxy/nanoclay systems [2, 12]. As soon as clay platelets are embedded into the epoxy matrix, they act as restrictions to polymer chain mobility. The more intercalated or exfoliated the clays are, the more the restrictions they generate [13]. The decrease in  $T_g$  values observed may be an indication that there are rather poor interactions between the polymer and the filler nanoparticles.

Sarathi et al. [6] have reported an increase in  $T_g$  with the addition of clays, which is attributed to the good adhesion of the polymer matrix and the particles acting as restrictions for chain mobility. An increase in  $T_g$ , tensile strength and elastic moduli, with the addition of clay in epoxy nanocomposites, has been recently reported in the literature [13].

The variation of  $T_g$  values depends, generally, on two contradictious factors: (i) free volume increase and (ii) interactions between the components. In our case, the decrease in  $T_g$  values observed for the filled composite systems may 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 chain motions.

## 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 means of Thermogravimetric/Differential Thermal Analysis (TGA/DTA) and Dynamic Mechanical Analysis (DMA). Cloisite 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 335 °C. ER/MWCNT+clay composite seems to have superior thermal properties, compared to the other systems. In the presence of clay nanoplatelets, carbon nanotubes seem to be more easily exfoliated and better networked within the epoxy matrix. Kissinger method was used to analyze the kinetics of the degradation process and apparent activation energies were calculated. Glass transition temperature for the filled composite systems are 2-3 °C lower than that of the pure epoxy matrix. This can be explained in terms of free volume increase.

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