Thermal and Thermomechanical Properties of Epoxy Resin / Carbon Black Nanocomposites

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ABSTRACT

The thermomechanical properties and thermal stability of polymer nanocomposites, consisting of epoxy resin (ER) as matrix and carbon black (CB) nanoparticles as filler, were investigated by Thermogravimetric/ Differential Thermal Analysis (TGA/DTA) and Dynamic Mechanical Analysis (DMA). Our interest was focussed on the effect of different filler concentration on the thermomechanical properties, thermal stability and degradation processes of the nanocomposites. The addition of carbon nanofillers enhances, generally, the thermal behavior of the neat 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. Measurements were also performed at different heating rates. Kissinger decomposition model was used to determine the apparent activation energies.

Keywords: nanocomposites, carbon black nanoparticles, thermal stability, mechanical properties, activation energy

1 INTRODUCTION

Recently, polymer nanocomposites have attracted significant research interest, from both academic and industrial point of view. The reinforcement of polymer with nano-scaled fillers developed a new class of advanced multifunctional materials with improved properties [1, 2]. 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 [3, 4]. It is well known that the composite properties can change dramatically with the dispersion state, geometric shape, surface properties, particle size and distribution, etc.

Because of the commercial availability of nanoparticles, there is increasing interest in polymer nanocomposites. These composites have been shown to exhibit concurrent improvement on electrical, dielectric, mechanical, magnetic and optical properties, when compared with conventional polymer composites. At the same time, they perform enhanced thermal stability, flame retardancy, chemical resistance and permeability to gases, water and hydrocarbons [5-10].

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 nanoparticles have received much attention during the last decades. Extensive research and development efforts have been devoted to the use of CB as nanofillers to produce high-performance polymer nanocomposites for specific applications in numerous technological fields. Among the advantages of CB nanoparticles is their good adhesion with the polymer 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. Our interest was focussed on the effect of different carbon concentration on the thermomechanical properties, thermal stability and degradation behavior and 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 content. The activation energies during thermal decomposition process were calculated from measurements at different heating rates by using Kissinger method.

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

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 [11].

The DGEBA/TETA/CB nanocomposites were prepared by the dispersion of the determined amount of carbon nanoparticles in a glass vessel. Prior to that procedure, the pre-polymer was heated at 40 ^{o}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 CB agglomerates [11] and degassed again. The homogeneous liquid was poured in rectangular-shaped Teflon molds and the samples were cured at 60 ^{o}C for 20 h and at 150 ^{o}C for 2 h. Several specimens were prepared, with the filler content systematically varied between 0 % (pure resin) and 1 w/w % CB.

2.2   Experimental Techniques

The characterization of epoxy resin/carbon black nano-composites includes two different experimental techniques: 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 ^{o}C) up to 1400 ^{o}C under controlled dry nitrogen (N_2) flow and the weight loss was continuously monitored. For degradation kinetic analysis each sample was heated at five different heating rates, β, of 5, 10, 20, 30 and 40 ^{o}C/min.

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 ^{o}C/min was used. DMA measurements were performed from room temperature up to 200 ^{o}C and the resultant changes in the mechanical parameters (E′, E′′ and tanδ) were recorded.

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) technique. Heating rate dependence of relative TGA and derivative (DTGA) curves for epoxy nanocomposites filled with 0.2 w/w % CB nanoparticles are presented in Fig. 1. Similar curves have also been obtained for ER/CB nanocomposites with different CB contents. The results reveal that the samples show good thermal stability

for temperatures up to around 320 ^{o}C with a maximum decomposition temperature higher than 350 ^{o}C. A large weight loss occurs between 300-500 ^{o}C. Moreover, it was found that, independent from the heating rate, the intrinsic properties of the neat polymer matrix are improved after nanocomposite formation. Filled ER/CB nanocomposites show, generally, enhanced thermal stability (i.e. the degradation process starts at higher temperature), compared to the pure epoxy resin. The higher thermal stability of the nanocomposites can be attributed to the homogeneous dispersion of the carbon nanoparticles throughout the epoxy matrix. We also observe that the DTGA peak I quite asymmetric, i.e. there is a broadening at the right side, giving evidence for the existence of a double-mechanism behaviour.
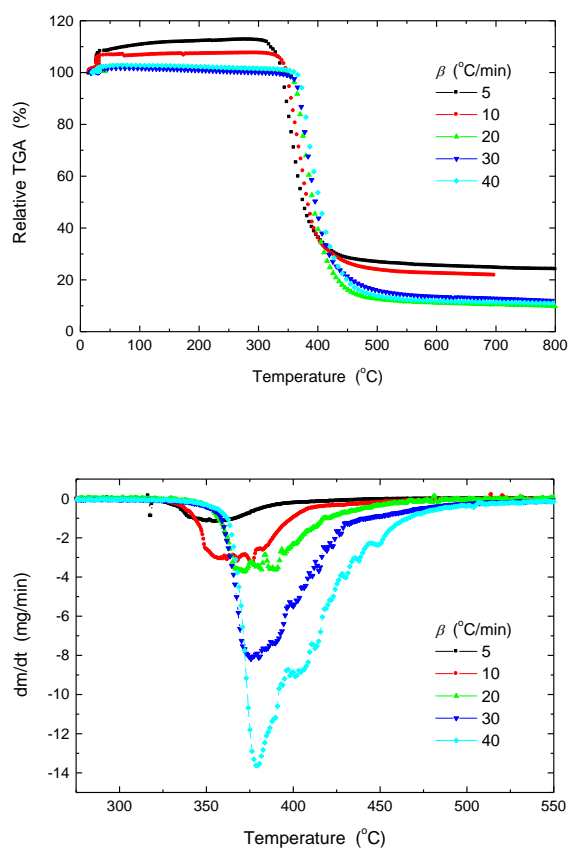

Figure 1: Comparative relative TGA (top) and DTGA (bottom) curves for ER/0.2CB nanocomposites at various heating rates, β, shown on the plots.

The decomposition (thermal degradation) temperature, T_P, corresponds to the peak temperature of the derivative mass loss (DTGA) curve, i.e. the temperature of the maximum weight loss rate. From DTGA curves (Fig. 1), the T_P can be determined. As it is clearly seen, the decomposition temperature increases with increasing heating rate. For all systems studied, when β= 5 ^{o}C/min, the

thermal degradation temperature is around 349 ℃, while for β= 40 ℃/min, T_P lies in the region 376-381 ℃.

In addition, the maximum mass loss rate (dm/dt) increases with increasing heating rate. In Fig. 2 the maximum weight loss rate (dm/dt) curve as a function of the filler concentration for ER/CB nanocomposites at heating rate equal to 20 ℃/min is presented. The small reduction observed for the samples with higher filler concentration is, probably, giving evidence for enhanced interactions between the pure polymer matrix and the carbon nanoparticles. It may be attributed to the fact that the degradation process of the nanocomposites is hampered by the increased carbon black content, because the filler nanoparticles form strong bonds with the epoxy matrix. This result is in good agreement with DMA measurements and glass transition temperature studies [11], to be discussed later.
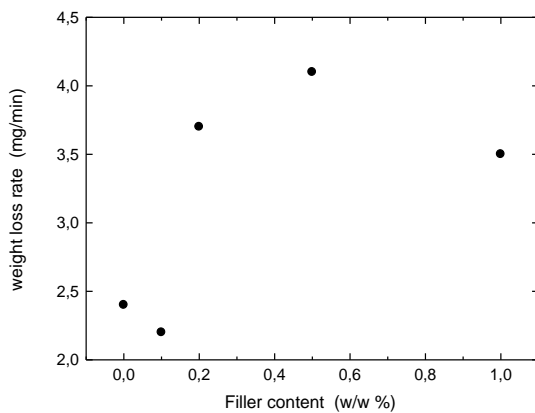

Figure 2: The maximum weight loss rate, dm/dt, as a function of the filler content for ER/CB nanocomposites at heating rate equal to 20 ℃/min.

For ER/CB nanocomposites, the yield of charred residue increases with increasing filler content (not shown here). This result coincides with DMA measurements and glass transition temperature studies [11]. It should also be mentioned that multi-walled carbon nanotubes were found [12] to have better dispersion within the epoxy matrix, compared to CB nanoparticles. It should also be mentioned that the modification of filler particles with specific chemical groups (such as amine groups) improves the compatibility with the polymer matrix and, thus, their dispersion within the polymer matrix.

One of the most common methods to calculate the apparent activation energy, E_{act}, during thermal degradation process is the Kissinger method [13]. This approach allows obtaining the dependence of the kinetic parameters from DTGA curves measured at different heating rates. This method does not require precise knowledge of the reaction mechanism. According to this method, E_{act} can be evaluated by the following equation:

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

where T_p is the temperature corresponding to the inflection point of the DTGA curves, i.e. maximum reaction rate, β is the heating rate and R is the gas constant (R= 8.314 J/K·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 the slope. In Fig. 3 such linear plots for neat epoxy resin and ER/CB nanocomposites are presented.

The apparent activation energy of the thermal degradation process for neat epoxy resin is: E_{act}= 201.15 kJ/mol. For ER/CB nanocomposites, activation energy values in the range of 216-237 kJ/mol were obtained. The higher values of E_{act} for the filled nanocomposites mean that the required energy to break the bonds in order for the resin to cure is higher for the filled samples. This result is consistent with the thermal analysis results described previously.

It is worth mentioning that Kissinger method is a special case for determining E_{act}, and it may not display the overall trend of E_{act}, due to the fact that data from a certain conversion rate are used. Therefore, results from Kissinger method are meaningful only in the case where E_{act} does not change within a wide range of conversion rate. However, the values of activation energy obtained in this work are useful, since they allow a better understanding of the thermal decomposition process of various ER/CB nano-composites used in technological applications. They also offer a tool in developing simplified models, in relation to composite processing. More results on the kinetic analysis of the degradation process are in progress and will be given in a future work.
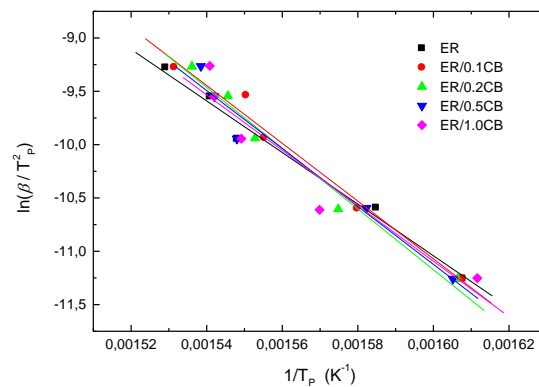

Figure 3: Linear Kissinger plots for determining activation energy during thermal decomposition process of neat ER and ER/CB nanocomposites.

The dynamic mechanical analysis generally reveals the amount of energy stored in the nanocomposises as elastic energy and the amount of energy dissipated during mechanical strain. In Fig. 4, characteristic plots of DMA measurements at constant frequency 10 Hz for ER/CB nanocomposites are presented. DMA measurements show that the storage modulus, E', is almost unaffected by the addition of carbon nanoparticles in the glassy state. On the other hand, it slightly increases in the rubbery one [11]. This again may support that there are favorable interactions between the carbon nanoparticles and the epoxy matrix. The peak temperature of $\tan\delta$ curves is considered as the glass transition temperature, T_g, of the samples. The glass transition temperature for the pristine epoxy matrix is: $T_g=$ 131.6 ^{o}C. After the formation of ER/CB nanocomposite, T_g increases ($T_g=$ 168.9 ^{o}C for CB concentration equal to 0.5 w/w %). This increase is more pronounced for low CB content. At the same time, $\tan\delta$ curve intensity (i.e. the maximum value of $\tan\delta$) becomes lower for the filled nanocomposites compared to the neat epoxy resin.
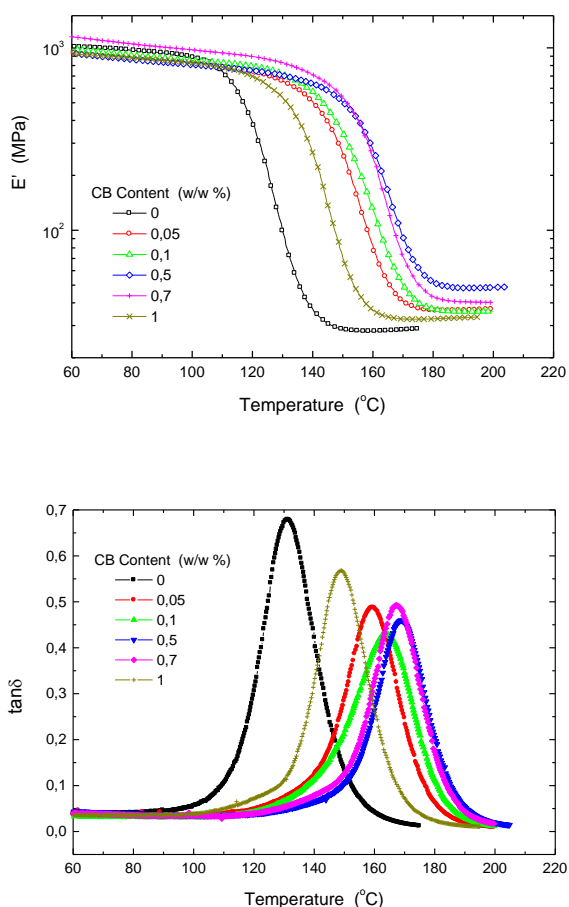

Figure 4: DMA spectra: E' (top) and $\tan\delta$ (bottom) as a function of temperature for ER/CB nanocomposites. Filler concentration is shown on the plots.

4 CONCLUSIONS

In this work, TGA and DMA techniques have been performed to investigate the thermal stability and dynamic mechanical behavior of ER/CB polymer nanocomposites. The addition of carbon nanoparticles enhances the thermal properties of the pure epoxy matrix. TGA results reveal that the system shows, for all heating rates, good thermal stability for temperatures up to 320 ^{o}C with a maximum decomposition temperature higher than 350 ^{o}C. The degradation process of ER/CB nanocomposites is probably hampered by the increased carbon content, because the interactions between the epoxy matrix and the filler nanoparticles are strong. The apparent activation energies of decomposition process were calculated by Kissinger method. The results demonstrate values of E_{act} in the range 216-237 kJ/mol for the filled nanocomposites, higher than that of the neat epoxy resin ($E_{act}=$ 201.15 kJ/mol). DMA measurements show that the storage modulus, E', is almost unaffected by the addition of carbon nanoparticles in the glassy state, but it slightly increases in the rubbery one. The glass transition temperature is higher for the ER/CB nanocomposites, compared to the neat epoxy resin.

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