THERMAL BEHAVIOR OF THERMOSETTING RESIN REINFORCED WITH CARBON NANOTUBES AND GRAPHENE NANOPLATELETS

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For two decades, numerous researches are being carried out about the addition of carbon nanotubes (CNT) into epoxy matrix in order to enhance the electrical, mechanical and thermal properties [1]. Recently, graphene nanoplatelets (GNP) become in interesting candidates to nanofiller of these polymer matrix. Actually, it is known that the CNT/epoxy composites can present enhanced mechanical properties and good electrical conductivity. However, their effect of the thermal properties is not clear. On the other hand, controversial results are actually being published about the effect of the GNP addition on the thermal behavior. In principle, it is expected that the thermal conductivity should increase due to the very high thermal conductivity of both nanofillers (GNP: 2000 $W \cdot m^{-1} \cdot K^{-1}$ and CNT: 385 $W \cdot m^{-1} \cdot K^{-1}$ at room temperature). However, these nanofillers present a high aspect ratio and therefore this property depends on the spatial direction. Also, it is well known that the properties of composites reinforced with nanofillers are strongly dependent on the experimental conditions, such as dispersion degree, nanofiller content, etc.

In this work, we study the effect of the addition of GNP and CNT in an epoxy matrix. The influence of the content added of these nanofillers on the glass transition temperature and degradation temperature is analysed. Moreover, the thermal conductivity of these nanocomposites is determined.

Experimental

Epoxy resin was obtained from a basic DGBEA monomer (Araldite LY556) cured with an aromatic amine (Araldite XB3473), both purchased from Huntsman. GNPs powder grade M25, with an average thickness in the range of 6-8 nm and an average lateral size of 25 µm, were provided by XGScience.

The dispersion procedure used was based in a method previously published [2,3]. The method is based on several cycles of calandering with different rollers gaps of from 15 to 5 µm and an increasing velocity per cycle: 250, 300 and 350 rpm. The dispersion procedure was carried out on the monomer of the resin. Once the dispersion was completed, the mixture was degassed under vacuum at 80 °C for 15 minutes. After the elimination of the occluded gases, hardener was added in a 100:23 (LY556:XB3473) in weight to achieve the stoichiometric ratio and the cured at 140 °C for 8 h in a plate.

Thermomechanical behavior was studied by Dynamic Mechanical Thermal Analysis (DMTA, Q800 V7.1 from TA Instruments) in a single cantilever bending mode. The experiments were carried at 1 Hz frequency, scanning from 20 to 250 ºC using a heating rate of 2 ºC/min. The dimensions of samples were 35 x 12 x 1.5 mm^3. The maximum of tandδ vs. temperature plots was used to identify the α-relaxation associated to the glass transition.

The degradation temperature was determined by Thermogravimetry (TGA, TA) while the thermal conductivity was measured through thermal diffusivity, using Laserflash LFA 457 MicroFlash equipment (Netzsch, Selb, Bavaria, Germany) applying a temperature scanning from 20 ºC to 200 ºC.

A TA Instruments Thermal Mechanical Analyser (TMA Q400) was applied for measuring the coefficient of thermal expansion (CTE). The measurement was carried out for a temperature range from 25 ºC to 200 ºC and a heating rate of 10 $ºC \cdot min^{-1}$.

Results and Discussion

The thermal expansion coefficient (CTE) of neat epoxy resin is $110 \cdot 10^{-6}$ K^{-1} while the CNT addition induces a light increase to $140 \cdot 10^{-6}$ K^{-1}. Not great differences are observed as a function of CNT content added. GNP addition modifies lightly the expansion coefficient, whose value reaches $120 \cdot 10^{-6}$ K^{-1} but in this system a high anisotropy is observed. CTE measured in the x, y axis is different than the measured one in z-direction. This is due to the self-orientation of graphene nanoparticles. This effect is not observed with CNT, when they are homogenously dispersed.

The degradation temperature increases by the addition of GNP and CNT. This effect is marker with GNP. The incorporation of a low concentration of graphene induces an important thermal stabilization, increasing the degradation temperature. This enhancement can be attributed to the so-called ‘‘tortuous’’ path effect, which limits the entry of oxygen and delays the escape of volatile degradation products and also char formation. The graphene nanoplatelets are more effective fillers as barriers than the graphene nanotubes, due to their planar geometry.

The glass transition temperature is also modified by the addition of graphitic nanofillers. In this case, the increase is important with the CNT incorporation. The explanation is the introduction of nanotubes into the free volume of thermosetting resin, hindering the mobility of polymer chain segments and therefore increasing the glass transition temperature.

Finally, the thermal conductivity is also increased on the composites reinforced with CNT and GNP regard to neat epoxy resin. The neat epoxy resin presents conductivity close to 0.13 $W \cdot m^{-1} \cdot K^{-1}$ while the composite reinforced with 10% GNP reaches 0.668 $W \cdot m^{-1} \cdot K^{-1}$.

Conclusions

Composites reinforced with CNT or GNP present thermal properties enhanced regard to neat epoxy resin. Both graphitic nanofillers induce an increase of thermal conductivity and degradation temperature.

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