Influence of carbon nanotubes on the properties of epoxy based composites reinforced with a semicrystalline thermoplastic

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Abstract. Novel ternary nanocomposites based on a thermoset (TS) system composed of triglycidyl p-aminophenol (TGAP) epoxy resin and 4,4’-diaminodiphenylsulfone (DDS) curing agent incorporating 5 wt% of a semicrystalline thermoplastic (TP), an ethylene/1-octene copolymer, and 0.5 or 1.0 wt% multi-walled carbon nanotubes (MWCNTs) have been prepared via physical blending and curing. The influence of the TP and the MWCNTs on the curing process, morphology, thermal and mechanical properties of the hybrid nanocomposites has been analyzed. Different morphologies evolved depending on the CNT content: the material with 0.5 wt% MWCNTs showed a matrix-dispersed droplet-like morphology with well-dispersed nanofiller that selectively located at the TS/TP interphase, while that with 1.0 wt% MWCNTs exhibited coarse dendritic TP areas containing agglomerated MWCNTs. Although the cure reaction was accelerated in its early stage by the nanofillers, curing occurred at a lower rate since these obstructed chain crosslinking. The nanocomposite with lower nanotube content displayed two crystallization peaks at lower temperature than that of pure TP, while a single peak appearing at similar temperature to that of TP was observed for the blend with higher nanotube loading. The highest thermal stability was found for TS/TP (5.0 wt%)/MWCNTs (0.5 wt%), due to a synergistic barrier effect of both TP and the nanofiller. Moreover, this nanocomposite displayed the best mechanical properties, with an optimal combination of stiffness, strength and toughness. However, poorer performance was found for TS/TP (5.0 wt%)/MWCNTs (1.0 wt%) due to the less effective reinforcement of the agglomerated nanotubes and the coalescence of the TP particles into large areas. Therefore, finely tuned morphologies and properties can be obtained by adjusting the nanotube content in the TS/TP blends, leading to high-performance hybrid nanocomposites suitable for structural and high-temperature applications.

1. Introduction
Epoxy resins are versatile thermosetting polymers widely used in structural applications because of their high stiffness, chemical and heat resistance derived from the cross-linked structure, and easy processability. However, they are inherently brittle and have low wear resistance, which hinder their use for certain structural, adhesive, or coating applications. To address this problem, thermoplastic modifiers [1], rubber particles [2] or hyperbranched polymers [3] have been blended with epoxy resins. On the other hand, multi-walled carbon nanotubes (MWNTs) have outstanding mechanical, thermal and electrical properties and low density, thus are ideal candidates for reinforcing polymer matrices. Poor nanofiller-matrix interfacial adhesion and MWCNT agglomeration are generally the main challenges when dealing with nanotube-reinforced polymer composites. However, it has been recently demonstrated [4,5] that the uneven or asymmetric distribution of nanofillers within the matrix can lead to significant improvements in key properties. In the present work, we have followed this approach in order to achieve property improvements in an aerospace-grade high performance epoxy system. To attain this goal, the resin has been modified with a semicrystalline thermoplastic, an ethylene/1-octene copolymer and MWCNTs. An extensive characterization has been carried out in order to analyze the effect of MWCNT content, location and level of dispersion on the morphology, thermal and mechanical properties of the resulting hybrid composites.
2. Experimental
The epoxy (TS) system consisted of a high-performance trifunctional epoxy, triglycidyl p-aminophenol (TGAP) with a 4,4’-diaminodiphenyl sulfone (DDS) curing agent, supplied by Huntsman Advanced Materials, LLC. CVD MWCNTs were obtained from Cheap Tubes Inc (VT, USA). The thermoplastic (TP), an ethylene/1-octene copolymer with commercial name DOWLEX SC2107, was provided by Dow Chemical. The TP particle size was reduced using a cryogenic impact mill.

The neat TS was prepared by blending TGAP and DDS (100/49 resin/hardener wt% ratio) in a planetary centrifugal mixer for 5 min at 300 rpm and room temperature. The mixture was then poured into silicone moulds and cured in an oven at 130 °C for 1.5 h, followed by postcuring at 177 °C for 2 h. Blends of TS/TP (5 wt%) were prepared in a two-stage process: The TP powder was initially mixed with the TGAP in the planetary centrifuge for 10 min at 500 rpm. After a few minutes of stirring at 130 °C, DDS was added stepwise under continuous stirring until a homogeneous mixture was obtained, and the blend was then subjected to the above indicated curing cycle. Regarding TS/TP/MWCNT composites, the TP powder was initially blended with TGAP in the planetary mixer for 10 min at 500 rpm; afterward, the MWCNTs were added and the mixing continued for another 10 min. Subsequently, the mixture was stirred at 130 °C and the curing agent was added, and finally it was cured under the same conditions.

3. Results and discussion
The effect of the TP and MWCNTs on the curing behaviour of TS was investigated by differential scanning calorimetry (DSC), and the calorimetric parameters derived from the non-isothermal thermograms are collected in Table 1: curing enthalpy (ΔH), curing onset (T_o) and the slope of the curve in the region of the curing peak (m). The neat resin begins the curing at 130 °C, and shows a single step process with a slope of -0.55 W/g °C. Similar behaviour is observed for the TS/TP binary mixture, with the curing occurring at a slightly lower rate. However, composites incorporating MWCNTs start the curing at a lower temperature, and exhibit a two-stage process, the first step taking place at a significantly lower rate and the second at similar rate to that of the neat TS. These results hint that the MWCNTs have a dual effect: firstly, due to their higher thermal conductivity, they accelerate the onset of the curing process, which is initiated in those regions where CNTs are preferentially located. Secondly, they appear to impose a certain hindrance in the epoxy crosslinking that takes place at a lower rate. Afterwards, since curing is a dynamic process, it is extended to the entire composite, occurring at similar rate and the same temperature for all the samples compared to the neat matrix. Interestingly, as the CNT content increases, the aforementioned effects are stronger: T_o shifts to lower temperature and the slope of the first stage decreases. This is related to the morphology of the composites, as discussed later. Further, ΔH decreases in the presence of the MWCNTs, also pointing towards a hampering of the epoxy crosslinking. In fact, it has been reported [6] that well-dispersed CNTs can act as a physical hindrance to the monomer mobility and thus lower the heat of reaction.

Table 1. Thermal data derived from DSC experiments

| SAMPLE | ΔH (J/g) | T_o (°C) | m (W/g °C) | T_m (°C) | T_c (°C) | X_c (%) |
|--------|----------|----------|------------|----------|----------|---------|
| TS     | 203      | 130      | -0.55      | 121      | 99       | 39      |
| TP     | 121      | 99       | 39         | 121      | 99       | 39      |
| TS/TP (5 wt%) | 177 | 130 | -0.46 | 115 | 72/16 | 41 |
| TS/TP (5 wt%)/MWCNT (0.5 wt%) | 175 | 128 | -0.023/-0.45 | 123 | 82/23 | 48 |
| TS/TP (5 wt%)/MWCNT (1.0 wt%) | 189 | 124 | -0.015/-0.48 | 112 | 93 | 36 |

* Determined from non-isothermal curing thermograms. ΔH: curing enthalpy; T_o: curing onset; m: slope of the non-isothermal curve in the region of the curing peak. T_c and T_m: crystallization and melting temperatures, respectively. X_c: degree of crystallinity.
The morphology of the samples was analyzed by scanning electron microscope (SEM), and typical images of ternary composites with 0.5 and 1.0 wt% are shown in Fig. 1. In TS/TP (5.0 wt%)/MWCNT (0.5 wt%) nanocomposite (Fig. 1a and 1b), the TP particles are randomly and homogenously dispersed within the TS, showing matrix-dispersed droplet type morphology. The MWCNTs appear to be preferentially located at the TS/TP interphase (see Fig. 1b), probably due to their higher affinity with the TP owing to their hydrophobic nature. This phenomenon has been regarded as a mechanism to reduce the size of the minor polymer phase. Further, no MWCNT aggregates were observed in the whole examined regions. The well-dispersed nanofillers act as a solid barrier around the TP particles, thereby preventing the coalescence. However, SEM micrographs of TS/TP (5.0 wt%)/MWCNTs (1.0 wt%) show a very different morphology (Fig. 1c and 1d). The size of the TP domains is considerably larger, and they appear interconnected due to the coalescence of several particles, leading to a gross dendritic morphology. The MWCNTs are located within the TP phase (Fig. 1d), and appear quite aggregated. A plausible explanation could be that the higher CNT concentration resulted in higher viscosity of the phases, hindering their diffusion and migration over the composite.

Fig. 1 SEM micrographs at different magnifications of: (a) and (b) TS/TP (5 wt%)/MWCNT (0.5 wt%); (c) and (d) TS/TP (5 wt%)/MWCNT (1.0 wt%).

The crystallization behaviour of the composites was investigated by DSC (Fig. 2). Neat TP shows a sharp crystallization peak $T_c$ at about 100 °C, with a slight tail corresponding to smaller crystal sizes at the lower temperature side. On the contrary, TS/TP (5.0 wt%) displays two small, broad exothermic peaks at much lower temperatures than that of the neat TP, around 72 and 16 °C (Table 1). These are probably related to two populations of crystals with different average crystal sizes. According to the SEM images, the TP phase forms isolated and well-dispersed micro domains confined within the epoxy phase. Each domain can have a different nucleating activity depending on the size, degree of dispersion, presence of impurities, etc. An analogous behaviour has been reported for immiscible polymer blends where the crystalline polymer is finely dispersed in small domains (at the micro- or nanoscale), and is
denominated “confined or fractionated crystallization” [7]. TS/TP (5 wt%)/MWCNT (0.5 wt%) also shows two broad crystallization peaks related with TP particles with different crystal sizes, hence different degrees of confinement. Besides, the \( T_c \) is shifted to higher values, probably due to the nucleating effect of the nanofillers. However, TS/TP (5 wt%)/MWCNT (1.0 wt%) only exhibits a single crystallization. The disappearance of the lower temperature exotherms on increasing the MWCNT content is indicative of the elimination of the confinement effect in this sample. From the SEM images, both TP and the MWCNTs are agglomerated, with considerably large TP domains, hence the polymer crystallizes in a similar manner to neat TP. Further, the \( T_c \) is slightly higher than that of TS/TP(5.0 wt%)/MWCNTs(0.5 wt%), which could be related to the dispersion of the nanofillers inside the TP domains.

![Fig. 2 Dynamic DSC cooling (bottom) scans for the different samples](image)

The thermal stability of the samples was investigated under nitrogen atmosphere and the results are presented in Fig. 3. The initial degradation temperature of TS increases upon addition of both TP and MWCNTs, due to the higher thermal stability of these materials compared to the neat resin. The hybrid containing 0.5 wt% MWCNTs shows around 25 °C increment compared to that of neat TS. This outstanding increase is attributed to a synergetic stabilizing effect of the isolated TP domains and the well-dispersed MWCNTs that can act as a barrier and effectively hinder the diffusion of the degradation products from the bulk of the matrix to the gas phase. Further, the increase in thermal conductivity due to the presence of the MWCNTs facilitates heat dissipation within the nanocomposite. However, for the hybrid with 1.0 wt% MWCNTs the improvement is smaller (~15 °C), since both the TP and the MWCNTs are quite agglomerated, hence exert a less efficient barrier effect. Qualitatively similar trends are found for the temperatures corresponding to 10% weight loss and the maximum rate of weight loss.
The mechanical properties of the hybrids were characterized by tensile tests (Fig. 4). The Young’s modulus (E) of TS is ~2.8 GPa. The TP acts as a plasticizer and causes a 16% decrease in the matrix modulus. In contrast, the incorporation of MWCNTs imparts the high stiffness of the fillers to the matrix, and the TS/TP (5 wt%)/MWCNT (0.5 wt%) has ~12% higher E than TS. In this case, the nanotubes are predominantly located at the TS/TP interphase and might improve the matrix-TP interfacial adhesion. However, for the nanocomposite with 1.0 wt% MWCNTs, E is slightly lower than that of the matrix due to the less effective reinforcement of the agglomerated nanotubes that are mainly located inside the TP domains. Regarding the tensile strength (σ_y), the trends observed are similar to those found for the modulus, albeit the percentage increments attained are higher, i.e. ~24% for TS/TP (0.5 wt%)/MWCNT (0.5 wt%) compared to neat TS, suggesting that the nanotubes are more efficient in enhancing the matrix strength.

Focusing on the elongation at break (ε_b), a noticeable improvement is attained upon addition of the TP to TS due to its higher ductility. Nevertheless, TS/TP/MWCNT samples display lower ε_b than TS/TP (0.5 wt%), the reduction being more pronounced for that with higher nanotube loading since agglomerates strongly obstruct the plastic deformation of the matrix. The area under the tensile curve is a measure of the toughness of the material. As expected, TS/TP (0.5 wt%) shows higher toughness than the neat matrix (about 45%); the incorporation of 1.0 wt% MWCNTs to TS or TS/TP results in moderate toughness reductions, since the presence of agglomerates nucleates cracks, resulting in premature failure hence lower impact resistance. However, TS/TP (5.0 wt%)/MWCNT (0.5 wt%) shows ~52% higher value than that of TS. It seems that the toughening effect is boosted in this sample due to a synergistic action between the TP and the MWCNTs. Moreover, this superior performance could be related to the matrix-dispersed droplet type morphology observed for this composite, where small TP domains were found to be homogeneously dispersed within the matrix.
4. Conclusions
Novel ternary nanocomposites based on a thermoset epoxy matrix toughened with a semicrystalline thermoplastic copolymer and reinforced with MWCNTs have been developed. A significant change in the phase morphology of TS/TP blends from droplet-dispersed type to agglomerated TP domains with dendritic structure was found when the CNT concentration was increased from 0.5 to 1.0 wt%. The MWCNTs have a dual effect on the epoxy curing process: they accelerated the cure onset albeit hindered its progress since they impeded chain crosslinking. The nanocomposite with the lowest nanotube content showed two crystallization peaks at lower temperature than that of neat TP, related to confined crystallization of isolated domains with different average crystal sizes. However, a single peak appearing at similar temperature to that of TP was observed for that with 1.0 wt% MWCNTs, since the coalescence of the TP domains eliminated the confinement effect. The highest thermal stability and best mechanical properties were found for TS/TP (5.0 wt%)/MWCNTs (0.5 wt%) nanocomposite, due to synergistic effects of both TP and the nanofiller.

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