

Trifunctional Epoxy – SWNTs Composites. A New Non – Covalent SWNTs Integration Approach

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ABSTRACT

A novel non-covalent approach to integrate Single Walled Carbon nanotubes (SWNTs) into an epoxy system was addressed. It was based on the SWNT wrapping by a PEO-based Block copolymer (Pluronic F68) which provided highly debundled SWNTs. This procedure allowed performing the integration process without participation of organic solvents. The resulting nanocomposites were characterized by means of electrical and mechanical properties, and compared with different control samples. The reinforcement of the epoxy matrix with Pluronic-wrapped SWNTs provided higher electrical conductivity values and much lower percolation threshold than samples where SWNTs have been integrated without Pluronic. Storage moduli were decreased upon Pluronic incorporation in the control samples, but the presence of SWNTs compensated this plasticizing effect, maintaining the matrix stiffness. Tensile testing of the 0.5 wt% Pluronic-wrapped SWNTs sample revealed a toughness improvement of 276% with respect to the neat matrix.

Keywords: single-walled carbon nanotubes, block copolymer, wrapping, trifunctional epoxy, nanocomposites.

1 INTRODUCTION

Due to their unique physical properties, Carbon Nanotubes (CNTs) have great potential as property enhancers of polymers. However, properly dispersing CNTs within polymers, specifically epoxy matrices, is difficult. Surfactant dispersion of CNTs has been shown to be an effective non-covalent method to improve integration [1], using organic solvents. Block copolymers (BCs) have been treated as ordinary dispersants of CNTs in organic solvents and subsequently incorporated into epoxy resins in a few cases [2-4]. But it is well known that the use of solvents is harmful for the epoxy properties [5]. The solventfree non-covalent CNT-BC wrapping approach has not been used in epoxy resins reinforcement so far. Moreover, BCs exhibit a toughening effect by self-assembly nanostructure formation in epoxy resins [6] and

they can also be employed to obtain CNT powders with a high content on disentangled wrapped tubes [7,8]. Our aim is to take advantage of these features to manufacture high performance nano-filled thermoset materials. A novel non-covalent solventless integration technique, in which a block copolymer is used to wrap SWNTs, has been developed combining the SWNT debundling effect with the toughness enhancement of a BC. Characterization of nanocomposites physical properties has been also addressed.

2 EXPERIMENTAL SECTION

2.1 Materials

SWNTs were produced by the arc discharge technique at the Instituto de Carboquímica - CSIC (Zaragoza, Spain), using Ni/Y as catalysts in 2/0.5 atomic ratio. In order to increase purity and reduce metal content, these SWNTs were subjected to a refluxing HNO₃ treatment (1.5M, 2h) followed by centrifugation (10000 rpm, 4h). Acid-treated SWNTs were finally filtered through a polycarbonate membrane (Millipore, 3µm pore size) and thoroughly rinsed with deionised water. These acid-treated SWNTs will be called “SWNTs” hereafter.

The epoxy matrix consists of an aerospace-grade trifunctional epoxy monomer: triglycidyl-p-aminophenol (TGAP), and 4,4'-diaminodiphenyl sulfone was used as the curing agent. Both reagents were kindly provided by Hunstman Advanced Materials (Spain) and used as received.

2.2 Wrapping SWNTs in amphiphilic BC

The wrapping process was carried out by using an amphiphilic BC. A judicious selection of the respective blocks was made attending to their relative miscibility between the epoxy matrix and the SWNTs. Polyethylenoxide (PEO) was selected as the “epoxyphilic” block while Polypropilenoxide (PPO) was chosen as the block with more affinity to SWNTs. One BC which satisfies this composition, was the commercially available Pluronic F68 (Sigma-Aldrich, PEO-PPO-PEO, M_w = 8400

g/mol) used as purchased. SWNTs were dispersed in aqueous Pluronic F68 solution following an experimental procedure reported elsewhere [8], making use of tip sonication, centrifugation and filtering. The resulting wrapped SWNTs exhibited a high degree of debundling and contained 30 wt% of BC. The successful integration of Pluronic-wrapped SWNTs into the TGAP+DDS system was studied in terms of curing kinetics revealing an improvement in species mobility [8].

2.3 Nanocomposites preparation

The wrapping effect of Pluronic F68 over SWNTs greatly increased the miscibility of the filler with the epoxy medium, which allowed carrying out the integration process with no participation of organic solvents. The typical experimental protocol to manufacture TGAP-DDS-SWNT blends, which consisted of hot magnetic stirring (at 60°C) and mild tip sonication, can be found in reference [8]. Different filler ratios were incorporated into the epoxy system: 0.1, 0.25, 0.5, 1 and 2 wt% of bare SWNTs or Pluronic-wrapped SWNTs. Different control samples were also manufactured by adding to the TGAP-DDS epoxy system the same amounts of BC present in the different wrapped SWNTs ratios. Epoxy-CNT blends were cast on a homemade steel dish mould sealed by teflon plates. A curing process was carried out in a Perkin Elmer hydraulic press coupled to a Greaseby Specac controlled heater, under 3 Tm of pressure during 30 min. Then, sample specimens were transferred to a Carbolite LTH4/30 oven and postcured at 200°C for 4h.

2.4 Characterization techniques

Scanning electron microscopy (SEM) experiments were performed in a scanning electron microscope (Hitachi S3400N), working in the secondary electrons mode at a high voltage 15 kV and a distance of 5 mm. Cured samples were fractured and the edge was sputtered with a 10nm gold layer prior to their observation.

Dynamical Mechanical Analyses (DMA) were carried out using a Mettler DMA 861 dynamic mechanical analyzer, in the tensile mode at frequencies of 0.1, 1 and 10 Hz. The specimen dimension was $\sim 19.5 \times 5 \times 2 \text{ mm}^3$. The measurements were performed from -100 °C to the temperature at which the specimens degraded and broke, at a heating rate of 2 °C/min.

Tensile testing was made on an MTS 858 Table Top Servohydraulic test frame equipped with hydraulic grips. Samples were cured as a dog-bone coupon following the ASTM D638 standard [9]. Each dog-bone coupon was placed in the grips and tested in displacement control at a loading rate of 0.050 inches/min (1.27 mm/min) to failure. Up to 9 coupons were measured for each sample.

Electrical conductivity was registered with a Keithley 4200-SCS source measurement unit, working at 20V. The specimens were obtained from a dish mould with 8.8 x 8.8

x 2.9 mm³ holes. Nanocomposite samples were set in a sandwich-like arrangement using two copper sheets (0.2 mm thick). Measurements were carried out in a two point probe configuration, placing each probe in different 8.8 x 8.8 mm² square surfaces of the test sample.

3 RESULTS AND DISCUSSION

3.1 SEM observation

SEM images (Figure 1) clearly show how the integration of Pluronic-wrapped SWNTs leads to a much more homogeneous distribution of the filler. SWNTs bundles become thinner than unwrapped SWNTs, which tend to be present in the matrix as agglomerates of entangled bundles.

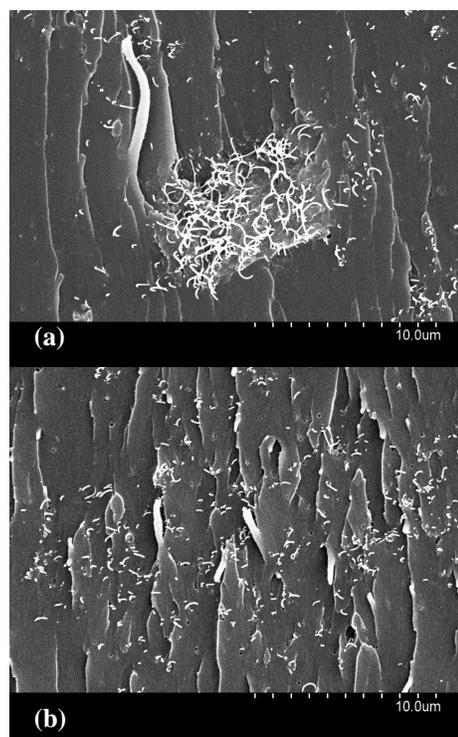


Figure 1: Typical SEM images of the nanocomposite sample containing: (a) 0.5 wt% SWNTs, and (b) 0.5 wt% Pluronic-wrapped SWNTs

3.2 Electrical conductivity

Table 1 shows electrical conductivity values for the different studied samples. The TGAP-DDS epoxy matrix exhibited a conductivity value of $9.7 \cdot 10^{-14} \text{ S/cm}$. Conductivity values for the nanocomposite samples showed higher improvements when using Pluronic-wrapped SWNTs as reinforcer. Samples without Pluronic have a less pronounced raise of conductivity values with increasing content of SWNTs, settling at 1 wt% ($\sim 10^{-7} \text{ S/cm}$). The

maximum conductivity values are achieved with Pluronic-wrapped SWNTs at lower filler content than SWNTs.

In all cases the BC-wrapping approach provides better overall conductivity values and a much lower percolation threshold. This threshold is reached below 0.1 wt% SWNTs in the case of Pluronic-wrapped SWNTs, since the effective SWNT content is lower considering the presence of BC (30 wt%). The conductivity raise of the sample containing 0.1 wt% wrapped SWNTs was about 4 orders of magnitude with respect to the neat matrix.

Filler content (wt%)	σ (S/cm)	
	SWNTs	Wrapped SWNTs
0.1	$6.70 \cdot 10^{-15}$	$1.38 \cdot 10^{-09}$
0.25	$5.73 \cdot 10^{-15}$	$6.85 \cdot 10^{-09}$
0.5	$1.04 \cdot 10^{-08}$	$2.91 \cdot 10^{-08}$
1	$1.78 \cdot 10^{-07}$	$2.62 \cdot 10^{-06}$
2	$1.11 \cdot 10^{-07}$	$1.60 \cdot 10^{-06}$

Table 1: Electrical conductivity values for the different epoxy nanocomposite samples. The filler content of SWNTs stands for the actual load. In wrapped SWNTs the filler content stands for 70 wt% SWNTs and 30 wt% BC.

3.3 Dynamical Mechanical Analysis

Figure 1 depicts the storage moduli data drawn from the DMA experiments in all samples. Three series of samples are represented: nanocomposite samples containing variable amounts of bare SWNTs, nanocomposites with variable amounts of Pluronic-wrapped SWNTs and blank samples made by incorporating the same amounts of Pluronic present in each of the wrapped SWNTs samples. Nanocomposite samples based on bare SWNTs showed a progressive and moderate modulus increase with increasing filler content. This series reaches a maximum modulus value at 1 wt% bare SWNTs (~4 GPa) which represents around a 30% improvement with respect to the neat TGAP+DDS matrix. On the other hand, the presence of Pluronic F68 within the epoxy matrix visibly decreased its storage modulus in ~ 30% due to a strong plasticizing effect

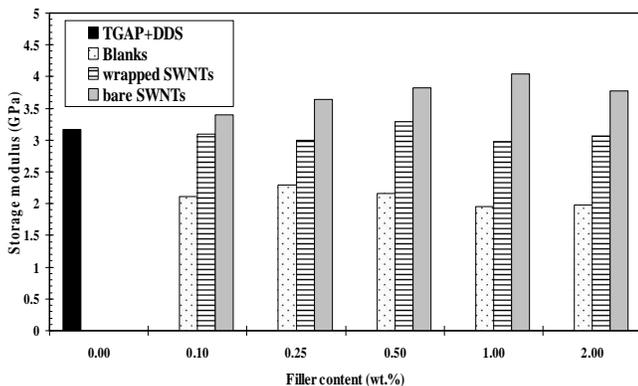


Figure 2: Storage moduli data drawn from DMA

caused by the BC. This effect has been previously observed by other authors working with other epoxy systems filled with PEO-based BCs [10]. This effect seems to be independent of the BC amount in the studied range. In Pluronic-wrapped SWNT samples, the storage moduli noticeably increase with respect to their respective blank samples. SWNTs compensate the effect of Pluronic BC, reaching the matrix stiffness (similar modulus value than TGAP+DDS), again with no clear dependence of the filler concentration. The DMA data are in good agreement with atomic force microscopy stiffness characterization of these nanocomposites (unpublished data).

3.4 Tensile tests

Tensile tests were carried out on the sample containing 0.5 wt% Pluronic-wrapped SWNTs (called Epoxy + wrapped SWNTs). Control samples consisted of several cases: the neat TGAP+DDS matrix (called Epoxy), the epoxy containing the same amount of BC present in the nanocomposite (called Epoxy + BC), and finally the epoxy nanocomposite containing 0.5 wt% SWNTs (called Epoxy + SWNTs). Stress (σ) – strain (ϵ) curves derived from the tensile analyses are represented in Figure 2.

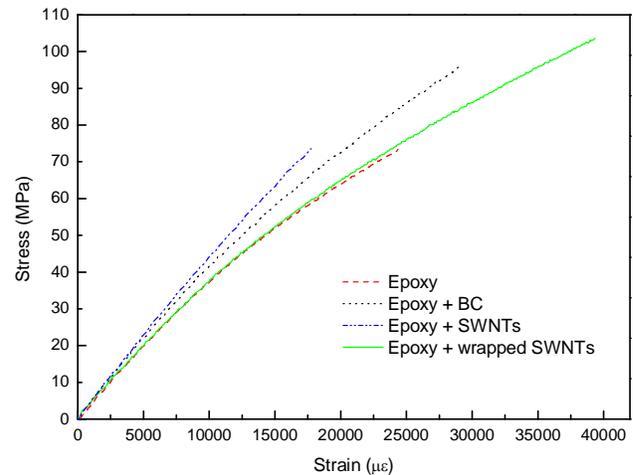


Figure 3: Representative $\sigma - \epsilon$ curves for the epoxy + 0.5 wt% Pluronic-wrapped SWNTs and its control samples

From the above curves, different mechanical parameters can be obtained. The Young's modulus (E) stands for the slope of the initial linear part of the curve (up to $5000 \mu\epsilon$), while toughness (G) is estimated by calculating the area under the curve. E and G data are collected in Table 2. It is clear how the incorporation of bare SWNTs slightly increases the TGAP+DDS Young's modulus and toughness by 4.7% and 35.3% respectively. The presence of the BC in the same amount as the Epoxy + wrapped SWNTs sample (0.15 wt% BC) has a more pronounced effect over toughness, causing an increase of 70.6% with respect to the neat matrix. This is consistent with the fact that BCs are

well known to toughen epoxy matrices at a nanoscale level by formation of self-assembled nanostructures [6]. In our case, Pluronic F68 itself is causing a noticeable toughness improvement despite the low amounts in which it is present. Young's modulus for Epoxy + BC sample, however, remains unchanged with respect to the neat matrix. Finally, for the Epoxy + wrapped SWNTs sample there is huge increase of toughness with respect to the neat matrix (276%), which evidences a synergic toughening effect between bare SWNTs and Pluronic F68. While bare SWNTs or BC are not separately causing much toughening, the combination of both (in the form of Pluronic-wrapped SWNTs) provides extremely high toughening effect. The elastic properties seem to be slightly worsened in this last case, since Young's modulus decreases a 7% with respect to the neat matrix.

Sample	Tensile Parameters	
	E (GPa)	G (MPa)
Epoxy	4.3 ± 0.4	0.34 ± 0.30
Epoxy + BC	4.3 ± 0.3	0.58 ± 0.52
Epoxy + bare SWNTs	4.5 ± 0.3	0.46 ± 0.15
Epoxy + wrapped SWNTs	4.0 ± 0.2	1.28 ± 0.74

Table 2: Tensile parameters extracted from $\sigma - \varepsilon$ curves for 0.5 wt% nanocomposite sample.

3.5 Thermo-oxidative stability

Thermogravimetric analysis (TGA) was applied in both inert and air atmospheres respectively to deepen into the degradation profile and its changes with the addition of SWNTs and/or Pluronic at a fixed loading. From the TGA profile (data not shown), isoconversional kinetics calculations [11] were applied and variations of the activation energy (AE) along the degradation process were obtained. Characterization data indicated that the thermo-oxidative profile of the nanocomposites degradation is composed by a very complex thermal stage (with, at least, two steps) followed by a neat single oxidative step (when registered in air) partially overlapped. The presence of SWNTs modifies the AE profile for both the degradation and oxidative steps, suggesting a mechanism alteration. The addition of Pluronic wrapped SWNTs increases the AE at lower conversions in each stage, whereas the control experiment with Pluronic evidenced an improvement in the stability as indicated by an AE increasing in the oxidative stage. It has also been drawn from the TGA data a significant improvement in the flame retardant ability of the composites when Pluronic-wrapped SWNTs are incorporated.

4 CONCLUSIONS

Successful preparation and characterization of novel nanocomposite materials based on a trifunctional epoxy resin and SWNTs was addressed through an integration

protocol which avoids the use of organic solvents. The approach consisted of the SWNTs wrapping by an amphiphilic BC (Pluronic F68). Samples containing BC-wrapped SWNTs possessed higher overall conductivity than samples without Pluronic, with a lower effective amount of SWNTs. Mechanical properties revealed that storage moduli remain unmodified for Pluronic-wrapped SWNT samples while toughness increased a 276% for the 0.5 wt% loading. This enhancement is a consequence of a synergic effect between bare SWNTs and the BC, since both components do not separately present such improvements. These features may be ascribed to the highly homogeneous distribution of SWNTs inside the epoxy matrix when incorporated as Pluronic-wrapped, far better than bare SWNTs (as determined by SEM). Storage and Young's moduli for samples without Pluronic are higher than the neat matrix. For a 0.5 wt% SWNTs epoxy nanocomposite, Storage and Young's moduli are increased by 30% and 35% respectively. The used approach allows enhancing the storage and Young's moduli, or toughness selectively depending on the incorporation of SWNTs with or without Pluronic F68. A thermal conductivity improvement is also expected. These measurements are currently under progress.

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