Epoxy composites with covalently anchored amino-functionalized SWNTs: towards the tailoring of physical properties through targeted functionalization

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Functionalization of single-walled carbon nanotubes (SWNTs) with covalently grafted amine moieties provides reactive fillers with potential covalent anchoring to an epoxy matrix. Manufacturing and characterization of a high performance epoxy system reinforced with as-grown and aminated SWNTs are presented through four different approaches. Epoxy composite materials incorporating SWNTs aminated through sidewall addition reactions present enhanced mechanical, thermal and electrical properties, beyond the effect of unfunctionalized SWNTs. The functionalization pathways studied here lead to a composite with specific improvements in some of the physical properties of the epoxy matrix, which enables the tailored design of the composites properties through functionalization. The amination via diazonium reaction with 4-aminobenzyl amine is especially effective in enhancing the tensile and impact properties of the epoxy composites (44% improvement in impact strength at 0.1 wt % loading) and leads to the highest increase in elastic modulus reported so far for the integration of aminated nanotubes into epoxy resin. Composites incorporating aminated SWNTs throughout the 1,3-dipolar cycloaddition reaction stand out for their thermo-oxidative stability and thermomechanical properties The incorporation of as-produced arc-discharge SWNTs into the TGAP/DDS epoxy matrix leads to composite materials with the highest electrical conductivity among all the studied samples.

Introduction

Epoxy resins are a classic example of thermosetting polymers for light-weight applications in aerospace and automotive industries. Epoxy monomers with high number of oxirane rings per molecule (multifunctional monomers) are currently being utilized in this field of applications. Their use includes structural applications, coatings, adhesives, insulation, etc. However, fundamental flaws in epoxy performance (such as high brittleness, moduli and stiffness below the required level, excessively high electrical resistance, among others) often restrict their range of use. The addition of a filler to enhance physical properties has been carried out extensively in recent decades. Within this context, single-walled carbon nanotubes (SWNTs) will become ideal candidates because of their extraordinary properties [1,2] and their potential reinforcing role if a suitable transfer of properties is achieved from the nano to the macroscale.

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This is indeed a major challenge when dealing with polymer/SWNT composites, where the bundling tendency, insolubility in most of liquid media and lack of adhesion to the matrix reported for SWNTs represent the main obstacles for the full exploitation of these materials. Thus, the reported results are still inferior to those predicted from theoretical studies.[3]

Numerous pre-processing procedures have been applied in order to address this problem and ameliorate the features of the composite, among which SWNT covalent modifications are increasingly being employed.[4] The covalent grafting of amine groups on SWNT surfaces has a special advantage since these functional groups are able to actively participate in the curing process, reacting with the oxirane rings and becoming an integrated element in the matrix owing to covalent bonds between the filler and the crosslinked epoxy structure. The functionalization of carbon nanotubes (CNTs), either SWNTs or multi-walled carbon nanotubes (MWNTs), with amines has been observed to lower the degree of agglomeration and to enhance the filler-matrix adhesion,[5] leading to remarkable improvements in the mechanical properties of epoxy matrices at low loadings.[6] Other studies also state significant improvements of epoxy/amine-CNT as compared to the parent matrix,[7] i.e. from ~25-70% improvement in storage modulus to ~10-45% improvement in tensile strength. However, to date, only very few studies have been reported on the integration of covalently aminated SWNTs into epoxy matrices [6,8] Works related to epoxy/amine-SWNT composites involving multifunctional epoxy networks, which have scarcely been reported in the literature, are of particular interest for high-performance applications.

Table 1: Data extracted from TGA plots in air and N_2 atmosphere of the neat matrix and composites with 0.5 wt % SWNTs. T_{10} = temperature corresponding to 10% weight loss; T_{max} = temperature of maximum rate of weight loss; the subscripts 1 and 2 refer to the first and second degradation stages, respectively. ΔT is the difference between T_{max1} and T_{max2}. R_{700} = residue at 700ºC

The general aim of covalently grafting amine groups onto CNTs is to seek an enhancement of SWNT miscibility and dispersability in organic media, together with providing a matrix-

4) 1,3-dipolar cycloaddition of azomethyne ylides with a specifically chosen α-aminoacid (SWNT-dca).

	Air atmosphere					N₂ atmosphere			
	T_{10} (ºC)	$T_{max}1$ (ºC)	$T_{max}2$ (ºC)	ΔT (ºC)	R_{700} (wt%)	T_{10} (ºC)	T_{max} (ºC)	R_{700} (wt%)	OI (%)
Neat TGAP/DDS	348±2	364±2	534±4	170	0.10±0.06	350±2	386±2	23.7±0.1	26.7
TGAP/DDS/SWNT-asg	353±2	375±2	544±4	170	0.92±0.06	352±2	392±2	27.5±0.1	28.5
TGAP/DDS/SWNT-oxa	352±2	364±2	541±4	177	0.65±0.06	353±2	394±2	25.8±0.1	27.8
TGAP/DDS/SWNT-dca	351±2	386±2	545±4	158	0.73±0.06	355±2	395±2	26.5±0.1	28.1
TGAP/DDS/SWNT-dba	352±2	371±2	547±4	176	0.85±0.06	353±2	394±2	27.2±0.1	28.4
TGAP/DDS/SWNT-nfp	351±2	381±2	537±4	156	1.28±0.06	351±2	393±2	26.4±0.1	28.1

reactive filler. This feature is exploited towards the integration of functionalized SWNTs in the epoxy, usually by the use of solvents. However, the presence of organic solvents in the epoxy matrix usually presents some disadvantages (inhomogeneous filler distribution upon evaporating[9] or decreases in parameters such as Vickers hardness,[10] flexural modulus[10] and glass transition temperature T_g[11]); for this reason, the resulting performance of the composite may be aggravated as compared to what is expected. This paper aims to provide a comprehensive characterization of a series of amine-SWNT/epoxy composites with covalent anchoring to the matrix for the design of composite materials suitable for aerospace applications. The integration of functionalized SWNTs was carried out without organic solvents in order to ascertain the property improvements as a direct consequence of the SWNT functionalization. Discussion is given in relation to the filler-matrix dispersion behaviour and chemical affinity, which is a direct consequence of the functionalization route, as previously shown by differential scanning calorimetry (DSC).[12]

Experimental section

Materials and reagents

SWNTs were produced at the Instituto de Carboquímica (Zaragoza, Spain) by the arc-discharge technique, using graphite as the carbon source, and Ni /Y as metal catalysts in 4/1 atomic ratio. Additional characterization information on these SWNTs is given in Supplementary Information (Table S1). The epoxy system was an aerospace-grade resin based on a trifunctional precursor, triglycidyl-p-aminophenol (TGAP), with 4,4'-diaminodiphenyl sulfone (DDS) as the curing agent. Both were supplied by Huntsman and used as received.

Functionalization of SWNTs

Functionalization of as-grown arc-discharge SWNTs (SWNT-asg) was conducted through several procedures, consisting of the covalent grafting of primary amine-ended moieties: 1) Nitric acid oxidation, carboxylic activation with $SOCl_2$ and amide formation using N-boc-1,6-diaminohexane (SWNT-oxa). 2) Alkaline reduction with sodium-naphthalide ions and sidewall radical addition of aminohexanoic acid-derived acyl peroxide (SWNT-nfp). 3) Sidewall addition of benzylamine through *in situ* generated diazonium salt of 4-aminobenzylamine (SWNT-dba).

A detailed description of the functionalization procedures and SWNT characterization can be found elsewhere.[12] All the aforementioned covalent modifications are shown in Chart 1. A diagram of functionalization protocols are given in Table S2 (Supplementary Information).

Composites preparation

Neat baseline epoxy (TGAP + DDS) was prepared by directly blending TGAP and DDS in a stoichiometric functionality ratio (100/67) at 60ºC for 15 minutes. Different nanocomposites containing 0.1, 0.5 and 1 wt % of as-grown or functionalized SWNTs were prepared by a solvent-free method including stirring at 60ºC and tip sonication.[13] In a typical experiment, 1g of TGAP was mixed with the required filler amount and magnetically stirred at 60ºC for 45min. Then, the mixture was subjected to tip sonication (Hielscher DRH-UP400S ultrasounds tip, with 3mm tip diameter, 400W maximum power and 24kHz maximum frequency) at 50% amplitude, in continuous regime, for 15min, having external refrigeration with a water bath at room temperature. After a couple of minutes of stirring at 60ºC, the DDS (0.67g) is slowly incorporated stepwise, within a time period no longer than 30min. The initial amount of SWCNTs is taken so that the final wt% in the TGAP/DDS mixture is the desired. The epoxy blank sample was prepared using the same procedure but without adding SWNTs, in order to verify the effect of the preparation protocol on the properties of the matrix. The curing was performed by casting the epoxy or composite blends into a steel dish mould (2 mm thick) sealed by 3-mm thick teflon plates, followed by curing at 160ºC for 45 minutes and 200ºC for 30 minutes in a Perkin Elmer hydraulic press coupled to a Greaseby Specac controlled heater, under 3 tonnes of pressure. The samples were removed from the mould, transferred to a Carbolite LHT4/30 oven and postcured at 200ºC for 4 hours.

Characterization techniques

SEM experiments were made 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.

TGA experiments were performed in both nitrogen and air atmospheres (at 50 ml/min flow rate) using a Setaram Setsys Evolution 16/18 device at a heating rate of 10ºC/min, in the range from 25 to 900ºC.

The dynamic mechanical performance of the samples was analysed using a Mettler DMA 861 dynamo-mechanical analyser. Experiments were performed in the tensile mode at a frequency of 1 Hz. A dynamic force of 6 N oscillating at fixed frequency and amplitude of 30 μm was used. The relaxation spectra were recorded in the temperature range between -100ºC and 325ºC, at a heating rate of 2 ºC/min. The specimen dimensions were ~19.5 × 5 × 2 mm^3.

Tensile mechanical properties of the composites were measured with an INSTRON 4204 tester at room temperature (23 ± 2ºC), using a crosshead speed of 1 mm/min and a load cell of 1 kN. Dogbone specimens (Type 1BB) were employed, as specified in the UNE-EN ISO 527-2 standard. Both sample surfaces were surface-polished prior to the measurements. At least five specimens for each type of composite were tested to ensure repeatability.

Charpy impact strength measurements were carried out using a CEAST Fractovis dart impact tester. A hammer mass of 1.096 kg impacted at a constant velocity of 3.60 ms^{-1} (giving a total kinetic energy at impact of 7.10 J) on notched specimen bars with dimensions 33 × 10 × 3 mm^3, as described in the UNE-EN ISO 179 standard. Measurements were performed at 23 ± 2ºC and 50 ± 5% relative humidity. The presented data correspond to the average value of at least 5 specimens.

Electrical conductivity was measured with a Keithley 4200-SCS source measurement unit, working at 20V. The specimens were ~19.5 × 5 × 2 mm^3. Measurements were carried out in a two-probe configuration Nanocomposite test samples were placed in a sandwich-like arrangement using two copper sheets (0.2 mm thick).

AFM measurements were performed with a Multimode SPM from Veeco Instruments (Santa Barbara, US), equipped with Nanoscope V controller and JV-scanner (130μm scan size in XY, and 6μm Z-range), The system included the HarmoniX option which allows force-distance curves to be acquired in real time during tapping mode operation and map mechanical properties to be extracted as additional data channels.[14] Soft silicon tapping mode cantilevers with off-axis tip design and reflective backside Al-coating (tip radius 10 nm, spring constant 4 N/m, fundamental vertical resonance 70kHz, torsional resonance 1200 kHz) were used, optimized for large bandwidth acquisition of the force distance data (type HMX, Veeco Probes, Camarillo, US). Probes were mounted in a cantilever holder with large dither piezo (model MFMA, Veeco Instruments, Santa Barbara, US). Electrical mapping was carried out using tips Using cantilever SCM-PIC made of Sb-doped W with 0.01-0.025 Ω·cm resistivity coated with 20 nm of Pt/Ir and 3nm Cr. Cured composites were cut with an ultramicrotome, thoroughly polished and attached to a steel sample holder with silver painting prior to the AFM measurements. Calibration of the modulus was performed by comparing the HarmoniX-data with a polymer sample of known modulus in the expected range.

Results and discussion

Microscopic observations

Scanning electron microscopy (SEM) images were taken of fractured edge surfaces of the composites and representative examples are shown in Figure 1. The epoxy composite-containing SWNT-asg (Fig. 1a) exhibits a very irregular distribution of the filler, with frequent entanglements (highlighted with circles in Fig. 1a). The filler consists of long SWNT bundles that appear to have been pulled out from the bulk matrix. The incorporation of SWNT-oxa gives a similar fracture edge overview (not shown), much like that of solvent-free integrated nitric acid-treated SWNTs in the same epoxy resin.[15] Epoxy composites with the other functionalized SWNTs exhibit substantially different features. The fracture edge contains randomly dispersed SWNTs without visible agglomerates. The length of bundles is noticeably shorter, which could be indicative of breakage, instead of a pulling-out. Thus, the epoxy composites containing sidewall-functionalized SWNTs would present better filler-matrix adhesion and enhanced dispersion within the matrix, as a direct consequence of functionalization. It is worthy of note that the SWNT-dba composite (Fig. 1d) shows a larger dispersion enhancement, as most of its fracture surface contains lower distribution density. Furthermore, the protruded bundles across the fracture edge appear extremely short (mostly as dots), indicative of a higher breakage of the SWNTs spawned by a more efficient covalent anchoring.

Thermal and thermo-oxidative performance

Information about thermal and thermo-oxidative features can be inferred from thermogravimetric analysis (TGA) in nitrogen and air atmospheres. In general, thermograms obtained in inert environment exhibit a single weight loss centred at about 390ºC, while those registered in oxidative atmosphere show two consecutive weight losses, centred around 370ºC and 440ºC respectively.[16] Table 1 indicates the different parameters obtained from the TGA plots, including the temperatures of maximum rate of weight loss (T_{max}) and the temperatures corresponding to 10% weight loss (T_{10}), for composites with 0.5 wt % SWNTs. The solvent-free incorporation of SWNT-asg leads to an enhancement in thermal and thermo-oxidative stability since T_{max} increases ~6ºC and T_{max1} and T_{max2} rise ~10ºC each. The incorporation of functionalized SWNTs leads to higher degradation temperatures in most cases as compared to the neat epoxy matrix or the epoxy composites containing SWNT-asg. The most remarkable features are those coming from SWNT-dca composites in nitrogen atmosphere, where T_{10} increases by about 5ºC and T_{max} rises by 9ºC as compared to the TGAP/DDS sample. This is approximately 3ºC higher than the SWNT-asg composite in both parameters at 0.5 wt % loading. The rest of composites containing functionalized SWNTs do not exhibit significant improvements in comparison to the TGAP/DDS/SWNT-asg sample, but all of them possess higher thermal stability than the parent matrix. Moreover, composites incorporating SWNT-oxa and SWNT-dba exhibit the largest differences between T_{max1} and T_{max2} (ΔT), suggesting a slowing down of the degradation process. Interestingly, in air environment, the SWNT-dca composite shows the highest T_{max1} value, which is 22ºC higher than the neat matrix and 12ºC higher than the composite with the same amount of unfunctionalized SWNTs. This indicates that the SWNT-dca composites are more suitable for high-temperature applications in oxidative environments than pristine epoxy.
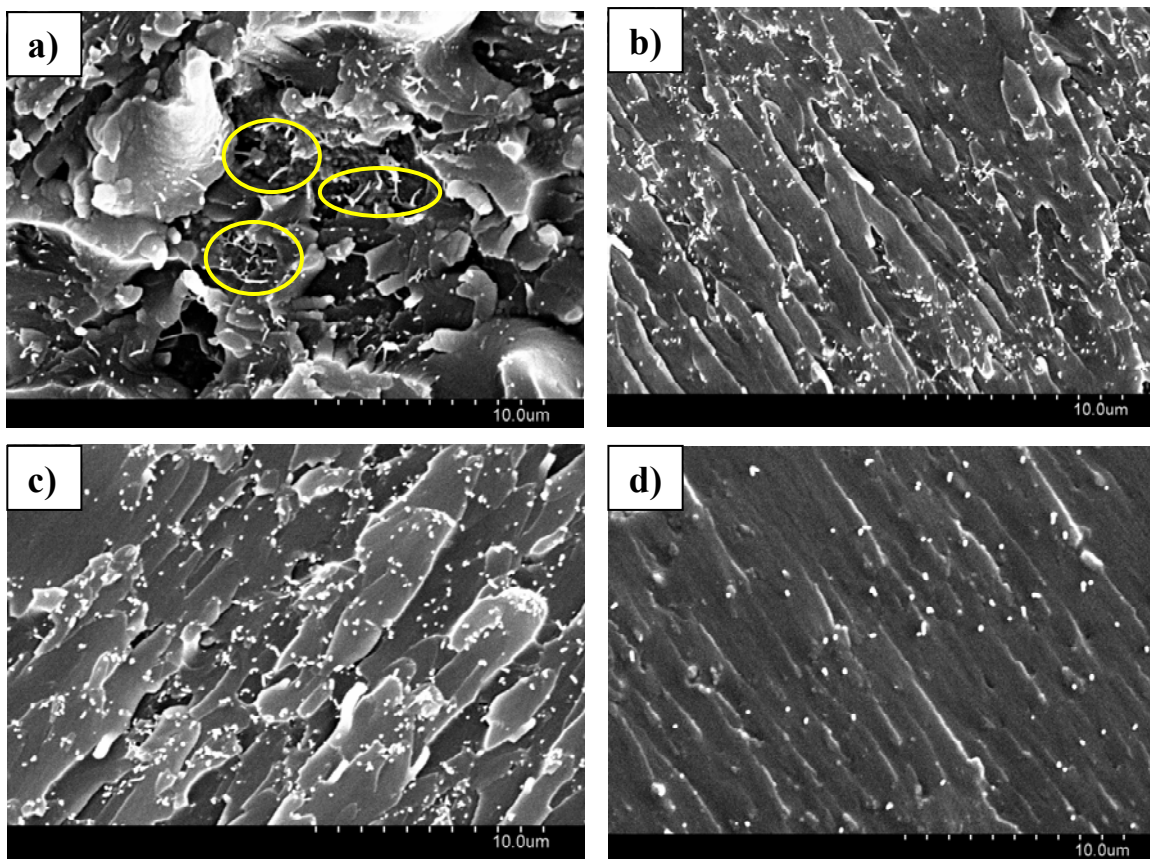
Figure 1: Fracture surface SEM images of epoxy composites containing (a) 1 wt % SWNT-asg; (b) 0.5 wt % SWNT-dca; (c) 1 wt % SWNT-nfp; (d) 0.5 wt % SWNT-dba

In contrast, the thermo-oxidative stability of SWNT-oxa composite only improves marginally, and the SWNT-nfp composite exhibits a sensibly higher oxidative sensitivity (T_{max2} is only 3ºC higher than the TGAP/DDS sample). However, in the latter sample, the R_{700} value is the highest (12-fold that of the neat matrix), suggesting that this functionalized filler is more efficient in preventing the total oxidation of the sample despite having a lower oxidative stability. The thermo-oxidative stability (regarding T_{max2}) of the epoxy composites may be related to the chemical nature of the amine grafted moiety on SWNT surfaces. SWNT-nfp provides the lowest enhancement, since this purely aliphatic moiety would be the most sensitive to oxidative environments. SWNT-oxa, SWNT-asg and SWNT-dca exhibit higher T_{max2} increase, possibly owing to the prevalence of oxygen and heterocyclic groups on their surface, which are more resistant to thermal oxidation. Finally, the highest T_{max2} is found for SWNT-dba, most likely owing to the aromatic character of the grafted moiety, which provides additional resistance to oxidative environments at elevated temperatures.

From the char residue wt % at 700ºC in inert atmosphere, the flame retardant ability of a material can be estimated through the oxygen index (OI). This parameter can be easily calculated through the Van Krevelen empirical equation.[17] The limiting OI (in %), at which a material can be considered flammable, is ≤26%. The TGAP/DDS sample exhibits an OI value close to the flammable behaviour, and all the composite samples show visible non-flammable behaviour. This enhancement has no dependence on the functionalization route except for the SWNT-oxa composite, which exhibits lower enhancement. This OI improvement is similar to that achieved by incorporating block copolymer-wrapped SWNTs into the same epoxy resin,[16] although in this case with even lower amounts (less than half) of SWNTs.

Dynamic mechanical analysis

The dynamic mechanical properties of the different epoxy/SWNT composites were studied in order to ascertain changes in their stiffness as a function of temperature. Dynamic mechanical Analysis (DMA) tests over a wide temperature range are sensitive to the transitions and relaxation processes of the resin in the composite, and provide information about the CNT-matrix interfacial bonding. The summary of the room temperature storage moduli (E´) and glass transition temperatures (T_g) of the different composites is shown in Figure 2. E´ of the neat epoxy matrix (Fig. 2a) is 3.42 GPa, and it decreases by ~18% upon subjecting the matrix to the same preparation procedure as the composite samples. This indicates that the hot stirring and sonication steps cause damage to the parent matrix with the present curing cycle. This damage could arise from the polymer chains scission upon heating and/or sonication, which would lower the cross-linking degree at a given TGAP/DDS ratio, hence diminishing the matrix stiffness. A focus on the composites incorporating a 0.1 wt % SWNT loading clearly shows that all

functionalized SWNTs are able to compensate this effect, and to raise E´ close to the value of the neat matrix, with the exception of SWNT-oxa, whose composite shows similar E´ to that of the blank sample. At higher loadings, the differences between the various samples are more pronounced. At 0.5 wt % loading, the SWNT-oxa composite still remains below the neat matrix, despite having storage modulus above the blank sample. All the other composite samples exhibit similar E´ values, which are on average 58% higher than that of the blank sample. With respect to the 1 wt % loading, the largest E´ enhancement is found for the SWNT-dca composite (77% improvement in comparison to the blank sample). The SWNT-oxa composite slightly surpasses the matrix modulus, while the other composites exhibit a very high E´, with those of samples containing functionalized SWNTs clearly above that of the composite with non-functionalized SWNTs. This significant increase in the storage modulus, hence in the composite stiffness, results from improved interfacial bonding CNT-epoxy, since the amino groups grafted on the CNT surface reacted with the epoxy group during the solvent-free mixing and subsequent curing processes. It is worthy of note that E´ improvements achieved in some of our composites with functionalized SWNTs are the highest reported for analogous epoxy composites containing other amino-functionalized CNTs with similar loading.[6,8,18,19] For composites with 0.5 wt % of aminated SWNTs loading, the highest E´ increment is achieved for the SWNT-dba composites, exhibiting higher E´ improvement than that obtained by Wang et al [8] at the same loading. For composites with a 1 wt % CNT loading, the SWNT-dca composite showed higher enhancement than those composites reported by Zhu et al,[6] Liu et al [19] and Spitalsky et al [18]. Working with aminated MWNTs, those authors [18] reported much higher improvement using functionalization with aryl diazonium than with carboxylation + amidation, which is in agreement with our results. A brief comparison of mechanical and thermomechanical results between our samples and relevant literature data is provided in Table S3 (Supplementary Information).

The evolution of the damping factor (tan δ, ratio of loss to storage modulus) as a function of temperature (Fig. 3) displays three relaxations peaks. The transition at the lowest temperatures (β relaxation) is related to the crankshaft rotation of the hydroxyl ether segments of the crosslinked network in the glassy state.[20] The relaxation that appears at the highest temperatures (α_1 relaxation) corresponds to the glass transition, while the other relaxation is the α_2 transition of the cured network.[21] The addition of SWNTs leads to an increase in both β and α_1 transition temperatures of the neat epoxy (initially at about -50ºC and 251ºC, respectively), whilst the α_2 transition temperature remains generally almost unchanged. Figure 2b compares the T_g values for the different samples prepared. It can be observed that the blank sample shows a T_g that is about 4 ºC lower than the neat epoxy, owing to the processing steps. T_g data for the composites with the lowest loadings (0.1 wt %) are in the range between the values of the neat epoxy and the blank sample, except for the composite with non-functionalized SWNTs, which exhibits a noticeable decrease. At higher loadings, composite materials exhibit significant increases in the T_g as compared to the reference sample, with the increments being more pronounced for samples with 1 wt % loading. The functionalized nanotubes are incorporated into the matrix through the formation of strong covalent bonds, becoming part of the crosslinked network and hence leading to an increase in the T_g. The largest increment is obtained for the composite incorporating 1 wt % of SWNT-dba (about 16.5ºC higher than the blank sample), with the other samples with functionalized SWNTs possessing similar T_g values, which are higher than the T_g value of the composite with non-functionalized SWNTs. The increments observed in the T_g are higher than those reported for analogous epoxy/amino-
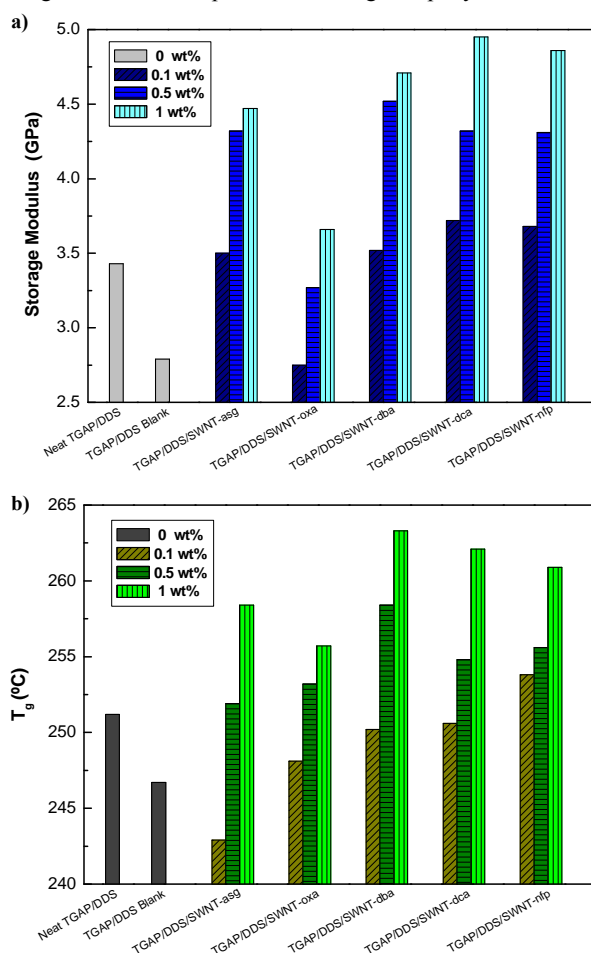
Figure 2: Data extracted from the DMA tests: (a) Storage moduli E´; and (b) Glass transition temperatures, T_g

functionalized CNT composites,[8,22-24] (see Table S3, Supplementary Information), which showed lower increases and, in some cases, a reduction in T_g values.[8,19] Data from Table S3 show that amine functionalization by the 1,3-dipolar cycloaddition reaction of an azomethine ylide has shown to be the best route for improving T_g, not only among the routes reported in this paper, but also using others reported in the literature involving plasma processing[24] or carboxylation-amidation with several aliphatic and aromatic diamines.[22,23] This reasserts the reinforcing potential of our fillers, which behave as powerful enhancers for crosslinking and adhesion to the matrix.

A comparison of tan δ curve for neat epoxy and the two composite systems that possess the highest and lowest T_g is shown in Figure 3. The height of the α_1 peak decreases with the addition of the SWNTs, owing to an increase in the rigidity of the systems. In the case of SWNT-oxa reinforced composites, the height of this peak remains almost unaffected by increasing SWNT content, whereas there is a noticeable decrease in height for those incorporating SWNT-dba as the concentration rises. This reflects the more effective chain restriction ability caused by SWNT-dba functionalization, ascribed to the CNT-epoxy interfacial covalent bonding that strongly hinders molecular movements. Moreover, this fact is consistent with the higher T_g values of composites with SWNT-dba in comparison to those
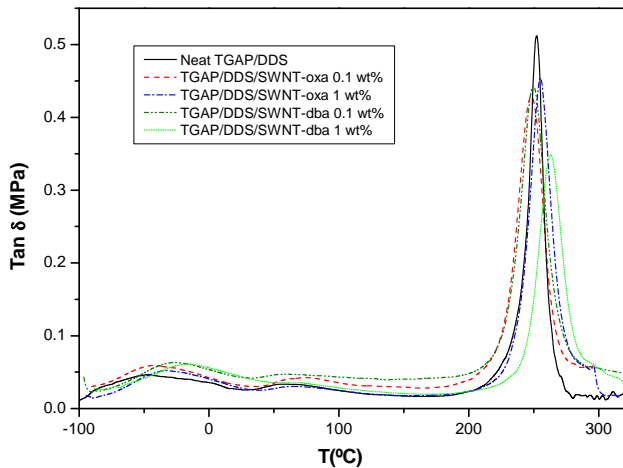
Figure 3: Damping factor (tan δ) curves vs temperature for the neat epoxy matrix and some composite samples containing SWNT-oxa and SWNT-dba

including SWNT-oxa. On the other hand, the broadening of the α_1 peak with the addition of CNTs is also related to restrained chain mobility that occurs in the composites, hence covering a wider temperature range.[25] The SWNTs disturb the relaxation of adjacent polymer chains, which would behave differently from those farther away from the nanofiller, leading to a broadening in the relaxation peaks. Similar phenomena have been reported for other composites incorporating covalently grafted SWNTs to the polymer matrix.[26]

Tensile properties

The static mechanical properties of the composites were also studied, with representative stress-strain curves of samples incorporating 0.5 wt % loading given in Figure 4. The Young's modulus (YM), elongation at break (ε_b) and strain to failure (σ_y) obtained from all performed tensile tests are listed in Table 2. YM of the neat epoxy matrix is about 3.1 GPa, decreasing by ~14% with the sonication and stirring processes. The incorporation of 0.5 wt % unfunctionalized SWNTs causes a ~30% increase in YM, as compared to the neat matrix (48% in comparison to the blank sample). This improvement is comparable to those attained by the addition of the same amount of SWNT-nfp or SWNT-dca. However, the incorporation of SWNT-oxa leads to a marginal YM enhancement (barely a 4% increase) probably owing to inhomogeneous dispersion of the filler and undeveloped SWNT-matrix interfacial bonding, hence poor load transfer ability. The largest increase in YM for a 0.5 wt % loading is found for the SWNT-dba composite, which exhibits nearly 38% improvement as compared to the neat TGAP/DDS sample (about 60% improvement in comparison to the blank). This is an increase of 8% compared to the composite containing unfunctionalized SWNTs, suggesting that the diazonium route is the functionalization that leads to the highest degree of anchoring (at 0.5 wt % loading). Similar behaviour was found for the other concentrations tested. At 1 wt % loading, the SWNT-dba composite exhibits about 75% higher modulus than the blank sample, while the increment for the SWNT-asg composite is around 64%. The exceptional modulus enhancements attained in these composites indicate the existence of strong epoxy-CNT interfacial bonding, capable of transferring the stress load and preventing the sliding of nanotube bundles during tension. With regard to the tensile strength, the trends observed are similar to

those described for the modulus. The σ_y value of the blank sample is slightly lower than that of neat TGAP/DDS, and it experiences an increase of around 35% upon addition of 0.5 wt % SWNT-asg (21% increase in comparison to the TGAP/DDS matrix). Comparable results in σ_y are found again for composites with the same amount of SWNT-nfp and SWNT-dca, while the largest increase is observed for the SWNT-dba composite (29% and 9% improvement as compared to the neat matrix and the SWNT-asg composite, respectively, and 44% enhancement with regard to the blank sample). At 1 wt % loading, this type of composite shows 43% strength enhancement in comparison with the neat epoxy (10% higher modulus than the composite incorporating unfunctionalized SWNTs and almost 60% higher than the blank sample). The aforementioned improvements for YM values are the highest reported in the literature for other amino-functionalized CNTs/epoxy composites [6,27,28,30-32] at the same filler loading (see Table S3, Supplementary Information). The data regarding σ_y improvement are generally higher than those reported using other aminated CNTs, except for reference [18] where MWNTs have been aminated by both carboxylation + amidation and diazonium route + amidation, and reference [24] aminated by plasma + diamine treatment (see Table S3, Supplementary Information). This suggests that most of the functionalization routes employed in this work are especially effective in improving the SWNT dispersability and the SWNT-epoxy interfacial adhesion, resulting in greater improvement to the tensile strength. The SWNT-dba composite is capable of absorbing larger amounts of energy before breaking, beyond the effect of unfunctionalized SWNTs, which is also reflected in the ε_b values. This latter parameter is about 4% and 3.6% for the neat matrix and the blank sample, respectively. For composites with 0.5 wt % loading, the use of SWNT-dba as the filler provides the closest value to the neat matrix (only ~8% decrease in ε_b), whereas the unfunctionalized nanotubes lead to a 22% decrease; this means that the former filler induces the most ductile fracture among all the studied samples. This is a very significant result as the general trend in epoxy/SWNT composites is the drastic reduction of ε_b upon filler incorporation,[6,33,34] providing a more fragile fracture behaviour and being detrimental to materials toughness in most cases. Similar trends were found for the other concentrations tested. Moreover, at 0.1 wt % loading, the SWNT-dba composite shows an increase in elongation at break up to
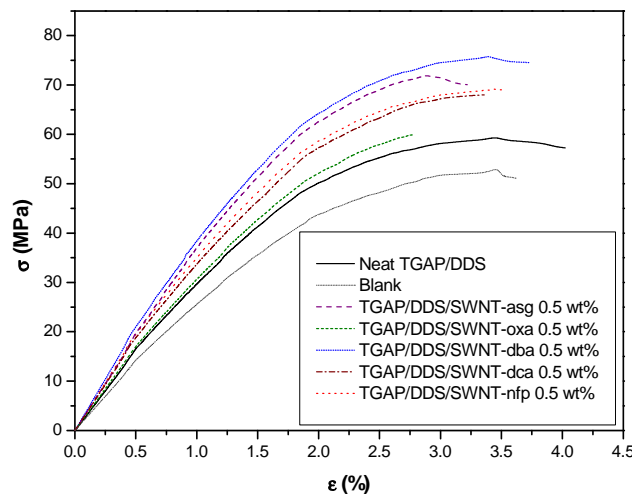

Figure 4: Representative stress-strain curves for the neat epoxy matrix and the different studied composites at 0.5 wt % loading.

Table 2: Tensile parameters for the neat epoxy matrix and nanocomposite samples at different SWNT loadings

	Filler loading (wt%)	YM (GPa)	σ_y (MPa)	ε_b (%)
Neat TGAP/DDS	0	3.1 ± 0.1	58 ± 1	4.0 ± 0.2
Blank	0	2.7 ± 0.3	52 ± 4	3.6 ± 0.4
TGAP/DDS/SWNT-asg	0.1	3.2 ± 0.2	60 ± 3	4.5 ± 0.2
	0.5	4.1 ± 0.4	70 ± 5	3.1 ± 0.4
	1	4.5 ± 0.2	76 ± 3	2.5 ± 0.5
TGAP/DDS/SWNT-oxa	0.5	3.3 ± 0.3	62 ± 4	2.8 ± 0.2
TGAP/DDS/SWNT-nfp	0.5	4.0 ± 0.2	69 ± 3	3.6 ± 0.3
TGAP/DDS/SWNT-dba	0.1	3.4 ± 0.1	61 ± 5	4.9 ± 0.4
	0.5	4.3 ± 0.1	75 ± 2	3.7 ± 0.2
	1	4.8 ± 0.3	83 ± 4	3.1 ± 0.3
TGAP/DDS/SWNT-dca	0.5	4.0 ± 0.3	66 ± 3	3.4 ± 0.4

~5%, which is a 22% increment as compared to the relatively brittle neat epoxy matrix. This fact would point to an effective breakage of SWNTs during the material failure, instead of a simple pull-out (in consonance with microscopic observations), which again shows the strong reinforcement effect by these amino-functionalized SWNTs and the potential of these TGAP/DDS composites in high-stress structural applications at room temperature. From the area under the stress-strain curve, first evidence is given for improved toughness of the SWNT-dba composites in comparison to the neat matrix. With strong covalent bonding, the functionalized nanotubes can maintain or even increase the strain to failure, thus leading to an increase in impact resistance. A detailed discussion is given in the following section. In short, DMA and tensile measurements demonstrate that the solvent-free dispersion of as-grown arc-discharge SWNTs leads to visible enhancements in the mechanical and thermomechanical properties of the TGAP/DDS matrix. Covalent amination of SWNTs can improve these parameters beyond the effect of unfunctionalized SWNTs. In contrast, SWNTs aminated on tips and defect sites show poor improvement in mechanical performance, ascribed to poor dispersability. These results are consistent with the literature, which reports better results for sidewall covalent amination rather than tip-defect amination.[18]

Impact strenght

Epoxy resins possess high strength and stiffness, although a relatively low toughness, which is a crucial and limiting factor for the design of structural components. Therefore, an improvement in the impact strength of epoxies is a desired goal. CNTs have certain potential to improve the toughness of epoxy systems owing to their excellent mechanical properties, high aspect ratio and the large interface provided.To evaluate the toughness of the different composites, room temperature Charpy impact tests were performed and quantitative results were obtained for the SWNT-dba and SWNT-asg composites, shown in Figure 5. The impact strength of the pure resin is approximately 2 kJ/m², and decreases by almost 25% for the blank sample, since the integration process leads to some damage on the epoxy network, hence premature failure. Non-functionalized nanotubes lead to an increase in the epoxy toughness at low nanofiller loadings (about 21% at 0.1 wt % SWNT content), while it decreases at higher filler contents. The composites with 1 wt % SWNT-asg exhibit similar toughness to the blank sample.
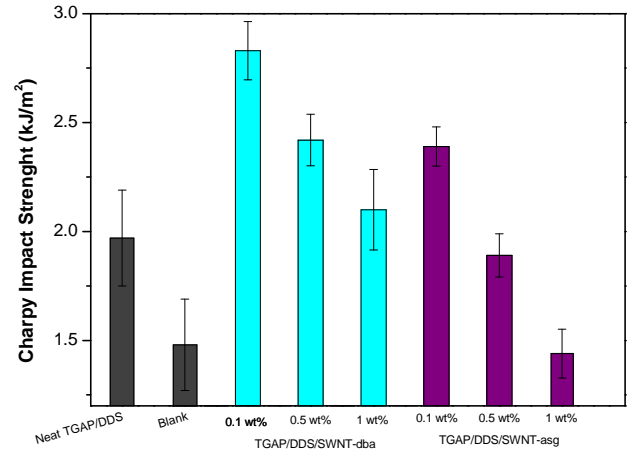
Figure 5: Charpy impact strength for the neat epoxy, the SWNT-dba and SWNT-asg composites at different nanotube loadings. Error bars represent confidence intervals calculated using Student's "t-test" (statistical significance = 0.1).

Toughness is very sensitive to the state of dispersion of the nanofillers and their interfacial adhesion with the matrix. At very low loadings, the non-functionalized nanotubes should be well-dispersed through the matrix, leading to a large epoxy-CNT surface area, thus minimizing the stress concentration nuclei. However, when the filler concentration increases, aggregate formation is favoured. These aggregates serve as stress concentration sites that promote the formation of dimples and nucleate cracks. This aggravates the brittleness under high strain rates, resulting in a small decrease in the impact strength and premature system failure. In contrast, composites incorporating SWNT-dba show improved toughness compared to the matrix for all the concentrations studied. Thus, at 0.1 wt % loading, a 44% improvement in impact strength is observed in comparison to the neat matrix (about a 90% increase as compared to the blank sample). This is consistent with the increase in elongation at break at 0.1 wt % loading. The enhancement is less significant at higher loadings, only about 7% at 1 wt % SWNT content. The improved behaviour found for composites reinforced with these

amino-functionalized SWNTs is probably related to their improved dispersability within the matrix as well as the CNT-
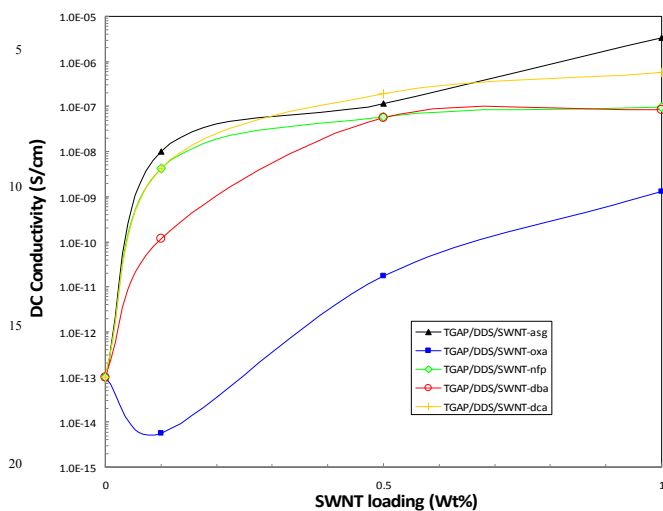

Figure 6: DC conductivity values as a function of SWNT loading

matrix covalent bonding, hence a higher effective interfacial area, which provides a strong barrier for pinning and bifurcation of the advancing cracks. Moreover, these composites absorb more energy during fracturing, owing to the additional rupture of the strong covalent bonds between the amino groups of the SWNTs and the epoxide moieties. These results demonstrate that it is possible to enhance the impact resistance of epoxy composites by means of strong interfacial bonding at the molecular level with crosslinked polymer chains. The simultaneous increase in stiffness, strength and toughness observed for composites obtained through the diazonium route makes them particularly attractive for structural applications, such as aeronautical and aerospace industries.

Other approaches can be used in the pursuit of improving epoxy mechanical properties in addition to covalent functionalization. Recently,[15] we have reported that the incorporation of an acid-treated SWNT filler wrapped with Pluronic F68 block copolymer drastically enhances epoxy toughness with no detrimental effect on the elastic properties. A wider tailoring of the physical properties can be further achieved also taking non-covalent approaches into account toward the design of an epoxy/SWNT nanocomposite with specifically enhanced features.

Electrical conductivity

Direct current (DC) conductivity measurements were conducted on the different composite samples and the obtained results are given in Figure 6. As a general observation, all composite samples show higher electrical conductivity than the bare matrix, and those containing functionalized SWNTs exhibit equal or lower conductivity than samples containing unfunctionalized SWNTs. This is explained on the basis that covalent modifications to the structure of SWNTs lead to an impurity state near the Fermi level that can lead to dramatic changes in conductive properties.[35,36] The functionalization procedure can play an active role in conductivity values of the composites. In the entire range of studied compositions, it is clear how epoxy composites containing SWNT-oxa as filler present the lowest conductivities observed, with a detrimental effect at the lowest loading. This confirms the poor dispersability of this filler, which

hinders its potential to create conductive pathways within the bulk matrix, and also the fact that this functionalization route induces a high level of damage to SWNTs. Indeed, the nitric acid treatment is known to be particularly harmful to the conductive properties of epoxy/CNT composites.[15,37] The sidewall functionalization of SWNTs does not cause particular damage to conductive properties, except for the diazonium route (at the lowest loading). The diazonium reaction on SWNT sidewalls has been reported to occur preferentially over SWNTs with metallic behaviour,[38] which are mainly responsible for the macroscopic conductive properties in bulk SWNT samples, so this fact would explain the lowered conductivity of epoxy composite with 0.1 wt % of SWNT-dba. At higher loadings, the effect of enhanced filler-matrix interactions (owing to functionalization) would compensate for the chemical inhibition of metallic tubes, leading to conductivity values within the same order of magnitude as that belonging to SWNT-asg composites. At the highest loading (1 wt %), the epoxy composite containing SWNT-dca as filler exhibits the closest conductivity value to that of the SWNT-asg composite. The former exhibits only one order of magnitude difference compared to the latter, which points to the 1,3-dipolar cycloaddition as a suitable functionalization means for preserving the conductive properties of epoxy/SWNT composites at high loadings while enhancing other physical properties.

Atomic force microscopy (AFM) characterization

Figure 7 presents comparative AFM images of the epoxy nanocomposite with 1 wt% SWNTs-nfp. Figures 7a and 7b show the topography image and its associated stiffness map, respectively. The stiffness map for the neat epoxy (image not shown) reveals a very homogeneous profile with a stiffness average value close to 3 GPa. The nanocomposite sample stiffness mapping shows different features; there is a green area (showing comparatively higher stiffness than the neat matrix) and small areas in pink with higher stiffness (about 5 GPa) that seem to correspond to small (around 200 nm) aggregates of SWNTs. The comparison with the composites bulk stiffness (obtained from DMA) reveals that these nanostructures are the main responsible of the macroscopic behaviour, as their stiffness correlates with the composites storage modulus at 1 wt% loading (Fig. 2a). Therefore, a proper transfer of properties is suggested owing to the covalent bonding between matrix and the filler, despite a higher level of dispersion could still be achieved. Figures 7c and 7d show electrical current mapping and the corresponding profile of another area in the same composite, respectively. In the current map, it is possible to see areas of higher conductivity corresponding to the presence of SWNTs surrounding by areas of lower conductivity but higher than the rest of the composite, which confirms the observations in Figure 7b concerning the formation of aggregates or non-disaggregated SWNTs bundles. AFM observations correlate with those made by scanning electron microscopy (SEM) in terms of the different state of dispersion between SWNT-nfp and SWNT-dba.

Conclusions

The solvent-free incorporation of as-produced arc-discharge SWNTs into the TGAP/DDS epoxy matrix leads to composite materials with fairly enhanced mechanical and thermal properties together with the highest electrical conductivity from among all the studied samples. The previous functionalization of these SWNTs by sidewall covalently grafting amine moieties provides

epoxy composites with improved performance as compared to those containing as-grown SWNTs. With the exception of the
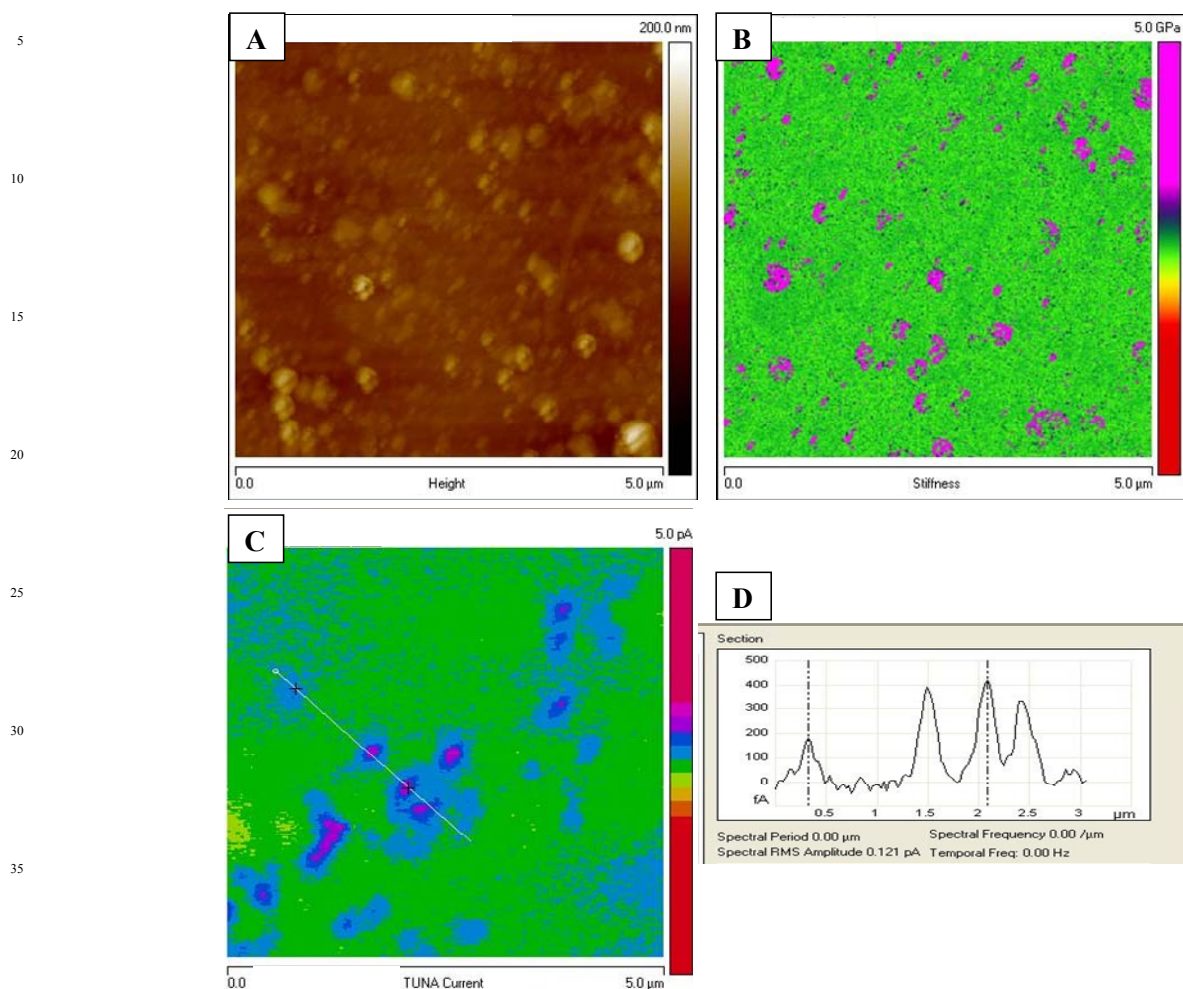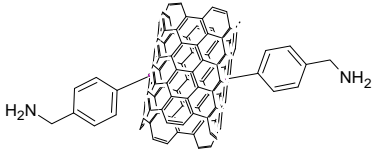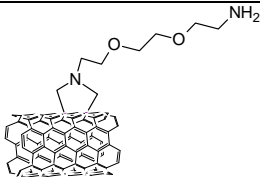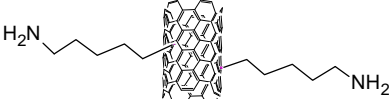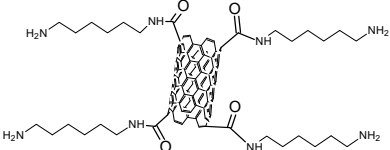

Figure 7: AFM images corresponding to SWNTs- nfp composite at 1 wt % loading A) topography image; B) stiffness map of the same area as Fig. 7A; C) current map; D) current profile as indicated in Fig. 7C.

SWNT-oxa sample, covalently aminated SWNTs present better direct dispersability in the epoxy medium. The chemical nature of the grafted moieties promotes the SWNT reaction with the matrix epoxide groups, leading to covalent anchoring to the matrix, during the crosslinking reactions.[12] This study shows that specific amino-functionalization can be applied to preferentially enhance specific features of the epoxy matrix. Amination via diazonium reaction with 4-aminobenzyl amine is especially effective in enhancing the mechanical performance of the epoxy composites with enhanced stiffness (especially at medium-high SWNT loadings) and the highest YM ever reported for aminated CNTs integrated in epoxy resin at 1 wt%. The highest T_g and tensile parameters measured in this study correspond to composites prepared with SWNT-dba as filler and the increments observed in T_g are the highest reported for similar epoxy/amino-functionalized CNT composites. The excellent mechanical features of this series of composites are supported by impact resistance tests and also by SEM, where the lowest bundle pull-out and degree of agglomeration were observed. As a matter of fact, a noticeable increase in the impact strength is observed with only 0.1 wt % of SWNT-dba, coupled with a more ductile fracture behaviour as inferred from ε_b values. These composites would be particularly useful for structural applications in the aerospace or automotive industries. On the other hand, composites incorporating aminated SWNTs throughout the 1,3-dipolar cycloaddition reaction stand out for their thermal, thermo-oxidative (between 6 and 12 ºC higher $T_{max}1$ than the rest of samples) and electrical properties only one order of magnitude lower conductivity than the SWNT-asg composite at 1 wt %, and about six orders of magnitude higher than the neat matrix at this SWNT loading), while possessing excellent mechanical performance (the highest storage modulus at 1 wt %). In this regard, composites with SWNT-dca as fillers are particularly attractive as coatings or adhesives with mechanical resistance and conductive properties. The amination of SWNTs via alkaline reduction + diacyl peroxides provides a filler whose epoxy composites display a well-balanced whole of physical properties, with some emphasis in the stiffness at the lowest loadings (highest T_g and nearly the highest storage modulus at 0.1 wt %). AFM and SEM observations indicate that the improvement of mechanical performance is determined by the degree of dispersion of the SWNTs in the matrix and, thus, by the chemical nature of the amine.

Chart 1. Amino-functionalized types of SWNTs used and their specific improvements in the epoxy matrix

Sample Nomenclature	Functionalization route and outcome		Specific improvements
SWNT-dba	In situ formation and reaction with an aryl diazonium salt		**Best tensile and impact properties** - 45% increase of Young's Modulus (1 wt %) - 44% increase in impact strenght (0.1 wt %) **And, highly enhanced dynamic mechanical properties** - 10ºC increase in Tg (1 wt %) - 40% increase in Storage Modulus (1 wt %)
SWNT-dca	1,3-dipolar cycloaddition reaction of an azomethine ylide		**Best thermo-oxidative and thermomechanical performance** - 45% increase of Storage Modulus (1 wt %) - 22ºC increase in $T_{max}1$ (air) at 1 wt %
SWNT-nfp	Alkaline reduction and subsequent reaction with a diacyl peroxide		**Good balance of physical properties**, with enhanced stiffness at the lowest loading
SWNT-oxa	Chemical oxidation followed by carboxylic activation and amidation		None

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