

**STUDY ON THE SYNERGISTIC EFFECT OF BORON NITRIDE
AND CARBON NANOTUBES IN THE IMPROVEMENT OF THE
THERMAL CONDUCTIVITY OF EPOXY COMPOSITES**

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3 **Referee: 1**
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7 **COMMENTS FOR AUTHORS**

8 **This manuscript presents a study on the synergistic effect of mixed nanofillers between**
9 **boron nitride and carbon nanotubes for their improvement on thermal conductivity of epoxy**
10 **nanocomposites. It is an interesting topic to be studied, while gaining thermal conductivity**
11 **with electrical insulating nature is also of interest for some applications.**

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13
14 **Although some important results (i.e. evidence of sufficient dispersion after only 20s**
15 **sonication of nanoparticles in epoxy) are missing, while the language and writing style**
16 **should to be improved as well, it is suggested to have a major revision before this**
17 **manuscript to be considered for publication.**

18
19
20 First, we would like to thank the reviewers for their great job and the help given us to improve
21 the quality of the manuscript. As mentioned in the paper (Page 8, 4th line from the bottom),
22 preliminary studies of the sonication dispersion were performed. As it is said, too long
23 sonication times can lead to a premature homopolymerization. Despite the viscosity varies at
24 each filler concentration, micrographs of the composites demonstrated a good dispersion of
25 the nanofillers in the matrix.

26
27 The text has been revised completely.

28
29 **Please find list of suggestions as follow:**

30
31 **Title, please use the term “synergistic” rather than “cooperative” for clear message to**
32 **audience.**

33
34 Substituted.

35
36 **P1, line 41, abstract, if the main purpose is to achieve thermal conductivity without**
37 **introducing electrical conductivity, why pristine CNT (with excellent electrical properties and**
38 **difficulties in dispersion) was employed?**

39
40 Pristine CNTs were used because of the high thermal conductivity they present. The use of
41 chemically modified CNTs, although better for dispersion, increases the price and it is
42 undesirable at industrial scale. As we proved in an earlier article with expanded graphite, the
43 combination with BN can limit the electrical conductivity, acting as a barrier. Moreover, the
44 thermal conductivity of CNTs is much higher than that of graphite.

45
46
47 **P1, line 49, abstract, the statement of “Nevertheless, in the presence of BN, it was possible**
48 **to increase the proportion of CNTs in the formulation without deterioration of the electrical**
49 **resistivity” needs more justification to avoid misleading. Which CNTs are referred here?**
50 **What proportion of CNTs without increasing the electrical conductivity?**

51
52 Text revised for a clear understanding.

53
54 **P2, introduction, overall writing needs to be improved. i.e. first paragraph of intro, bit**
55 **random with non-scientific writing. What is reinforced epoxy polymers? Thermoset micro or**
56 **nanocomposites? Would be better to highlight the needs first (high thermal conductivity),**
57 **then lack of performance from ceramic fillers, with some literature of using carbon based**
58 **fillers as later section (probably even after second paragraph introducing why CNTs).**
59
60

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3 Introduction revised following the feedbacks. Some references have been added.
4

5 **P2, line 47, "grow nanotubes directly on a surface..." these are irrelevant to current work..**
6 **Why synthesis been discussed here? Also how could CNTs have improved interaction with**
7 **matrix if they have less "defects", if functional groups remained at the surface of pristine**
8 **CNTs as defects? Please remove these sentences to make a clear storyline for audience.**
9

10 Sentence removed. The following sentence is maintained since CVD manufacturing is the one
11 that produces more imperfections in the atomic structure, improving the interface capabilities.
12 Not necessarily meaning that the defects are functional groups anchored in the surface.
13 Vacancies, interstitial atoms, impurities ... modify the structure introducing point or linear
14 defects as dislocations or interfacial defects.
15
16

17 **P4, line 3, what were the reasons of these "contradictory results"? Even by the end of this**
18 **study, no clear answer was provided to address this. Authors need to clarify the aim bit**
19 **better in the introduction section.**
20

21 Thank you, we agree with the reviewer that no contradictory results were found. Only
22 different results were obtained by Su et al, when modifying BN particles. We have eliminated
23 the sentence about the contradictory results.
24
25

26 **P5, line 29, 35% amplitude for 20s was enough to disperse nanoparticles in epoxy system?**
27 **According to what research? Where is the evidence to support?**
28

29 As mentioned before, preliminary studies were performed although not presented. Each epoxy
30 system would present different behavior. The amplitude of the sonifier was high enough,
31 taking into account the amount of sample, approximately 10 grams of mixture. The amplitude
32 was selected according to the experience of the group of MATERIA NOVA in Mons, where this
33 part of the work has been performed. Micrographs of the final material were the evidence of a
34 good dispersion.
35
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37 **P17, line 32 and figure 6, related to previous comment, cannot see any evidence of CNT was**
38 **well dispersed when BN was introduced. Need to include these results.**
39

40 As the CNTs were dispersed previously in the epoxy matrix, the addition of BN did not produce
41 a deterioration in the dispersion. In figure 6 it can be observed how the o-CNTs are well
42 dispersed within the matrix (see Figure 6A). See Figure 6C where nanotubes can be clearly
43 observed and well distributed in the epoxy matrix on a BN particle surface.
44
45

46 **P17, line 42, what is the percolation threshold of CNT for these two systems?**
47

48 We have not determined the percolation threshold of CNTs by rheology in DGEBA mixtures.
49 Only the rheological threshold in the ECC system was studied, thanks to the different
50 concentrations added, and was found to be between 0.1 and 0.25 wt. % of CNTs. However, the
51 rheological percolation is not always equivalent to electrical percolation, since tunneling effect
52 can occur, when electrical conductive particles are close enough to each other. In this case, the
53 addition of 0.05 wt. % in ECC matrices overpassed the electrical percolation, diminishing
54 several orders of magnitude the electrical resistivity in these composites. In the case of the
55 DGEBA system, the addition of 1 wt. % of CNTs has already overpassed that point.
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3 **P18, figure 7B, where are CNTs in this image? Please highlight or use arrows to guide.**
4

5 The magnifications of this micrograph did not allow to clearly observe CNTs. What is clearly
6 observed is the complex morphology of the sample breakage, meaning the rupture is not as
7 fragile as the neat epoxy in figure 7A. We have experienced problems in the acquisition of the
8 micrographs by ESEM at higher magnifications due to the electron back-scattering in
9 DGEBA/CNTs composites, as commented in the text.
10

11 **P19, line 35, cannot see the reasons for the statement “we could prove that the addition of**
12 **BN allowed us to ...” was that due to the network formation? Also please revise the writing**
13 **style of this statement. Same issue in page 22 line 55, please do not use the term “anyway”.**
14
15

16 P19-Thanks for your observation, it has been clarified.
17

18 P22. Revised.
19

20 **Referee: 2**
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22
23 **COMMENTS FOR AUTHORS**
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25 **This paper reports a deep investigation of the synergistic effect of CNTs and BN particles**
26 **dispersed in crosslinked epoxy matrices with the aim to improve thermal conductivity**
27 **without compromising electrical insulating properties. The paper is very interesting and very**
28 **well written. it takes into account the very limited documents about this topic in literature**
29 **and for this reason it is an important paper which should be published in this journal in the**
30 **present form without any modifications.**
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33 Thank you very much for your positive opinion of the work done.
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STUDY ON THE **SYNERGISTIC** EFFECT OF BORON NITRIDE AND CARBON NANOTUBES IN THE IMPROVEMENT OF THE THERMAL CONDUCTIVITY OF EPOXY COMPOSITES

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Abstract

The enhancement of the thermal conductivity, keeping electrical insulation, of epoxy thermosets through the addition of pristine and oxidized carbon nanotubes (CNTs) and micro-platelets of boron nitride (BN) was studied. Two different epoxy resins were selected: a cycloaliphatic (ECC) and a glycidic (DGEBA) epoxy resins. The characteristics of the composites prepared were evaluated and compared in terms of thermal, thermo-mechanical, rheological and electrical properties. Two different dispersion methods were used in the addition of pristine and oxidized CNTs depending on the type of epoxy resin used. Slight changes in the kinetics of the curing reaction were observed in the presence of fillers. The addition of pristine CNTs led to a greater enhancement of the mechanical properties of ECC composites whereas the oxidized CNTs presented a higher effect in the DGEBA matrix. The addition of CNTs alone drastically led to a drop of the electrical resistivity of the composites. Nevertheless, in the presence of BN, **which is an electrical insulating material**, it was possible to increase the proportion of **pristine** CNTs **till 0.25 wt. %** in the formulation without deterioration of the electrical resistivity. A low but significant synergic effect was determined when both fillers were added together. Improvements of about 750% and 400% in thermal conductivity were obtained in reference to the neat epoxy matrix for the ECC and DGEBA composites, respectively.

Keywords: Thermal conductivity; carbon nanotubes; boron nitride; epoxy resins; composites.

1. Introduction

One of the most challenging issues in **thermosets** consists in the enhancement of **their** thermal conductivity (TC), because **these materials have** intrinsically insulating characteristics. It should be mentioned that to improve the thermal management is crucial in the rapid evolution of modern electronics and other applications that involve the **reduction** of working temperature ranges.¹ **The reduction or maintenance of this temperature improves directly efficiency, reliability and useful operation time of electronic devices.** In the last two decades great efforts have been devoted to enhance the **TC capability** in reinforced epoxy polymers, **mostly by adding micro- and nanofillers, which is the best economical way applicable at industrial scale.**^{2,3} Since the thermal conductivity of traditional ceramic fillers (Al_2O_3 , SiO_2 , AlN , BN , SiC ...) is becoming insufficient for this purpose, even at high loadings, other alternatives are sought. That is why many studies have been performed using carbon materials including carbon nanotubes (CNTs),⁴ carbon nano-fibers,⁵ graphene,⁶ graphite,⁷ expanded graphite (EG),⁸ carbon black,⁹ etc., as they exhibit an exceptional thermal transport ability.¹⁰

CNTs are characterized by a high aspect ratio, excellent mechanical properties, remarkable thermal and electric conductivities, low density and good corrosion resistance against oxidative environments.^{3,11} Although these properties depend on the synthetic method used (chemical vapor deposition, laser ablation, arch discharge, etc.) and manufacturing quality, CNTs can improve the properties of epoxy composites such as: Young's modulus, tensile and yield strengths, fracture toughness, hardness, flexibility, adhesion, vibrational damping, hydrophobicity, piezoelectricity for sensors, etc.¹¹⁻¹⁶ These characteristics make them very interesting materials in the development of nanotechnology, nanoscience and microelectronics. According to their exceptional properties, they can be used in a wide range of different applications in the fields of aerospace, automotive and naval engineering, light emitting diodes (LEDs) and bio-medicine, among others.^{17,18} Besides the different synthetic methodologies, chemical vapor deposition appears as the most convenient, since it is the most economical ~~it is able to grow nanotubes directly on a surface~~ and the obtained nanotubes have more defects, which improves the interaction capability with the matrix, increasing the interface properties.^{19,20} One of the main problems to be solved in the preparation of composites is the dispersion of CNTs in the matrix due to their high surface area and their strong tendency to agglomerate via Van der Waals forces.^{11,13} The other important issue is the high interfacial thermal resistance between the nanofiller and the polymeric matrix.^{1,4}

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3 Previous published studies^{21,22} showed that pristine CNTs at low concentration can enhance TC when
4 good dispersion is reached. Nonetheless, a beneficial method to improve the epoxy-CNT interactions and
5 thus the dispersion of CNTs is their functionalization (usually by oxidizing the surface), which can
6 preserve CNT pristine structure, through the delocalized π -bonds interactions.^{11,23} It is important to stress
7 that not all functionalization types contribute in a positive way to the enhancement of TC.^{24,25}
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13 Heat transport in carbon materials is dominated by electron transport due to the sp^2 hybridization of
14 carbon atoms, while in polymer composites this phenomenon is governed through phonons.^{1,26} Despite
15 the high thermal conductivity of CNTs, composite conductivities presented much lower values than those
16 estimated by theoretical calculations.^{1,27} This fact is caused by the phonon scattering produced in the
17 CNT-matrix and CNT-CNT interfaces and their high interface thermal resistances. The origin of these
18 resistances is the high difference of the frequency modes that obstruct the phonon-phonon coupling
19 before exchanging heat in each interface.^{27,28} Lattice defects and impurities should not be underestimated,
20 since they are points at which phonons can be scattered.¹
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30 Up to now, there are only few publications combining boron nitride (BN) and CNTs in epoxy matrices.
31 However, a synergistic improvement in the thermal conductivity using these two fillers has been
32 demonstrated in polyphenylene sulfide matrices.²⁹ This improvement seems to strongly depend on the
33 surface treatment of the MWCNTs. Teng et al.³⁰ used BN and functionalized MWCNTs to prepare epoxy
34 composites and a synergistic effect in the thermal conductivity was observed in the composite containing
35 30 vol. % of BN and 1 vol.% of MWCNTs, reaching a value of TC of 1.91 W/m·K, but electrical
36 conductivity was not determined. Li et al.³¹ studied how the addition of fillers (BN/CNT), fabricated by
37 in-situ growing of CNTs onto BN surfaces, to epoxy resins affected the mechanical characteristics and
38 TC. The materials with BN/CNT particles showed better thermal performance than pure BN composites
39 even with CNTs loading as low as 2 wt. %. The prepared composites had a large electrical resistivity
40 because BN particles blocked the current paths of CNTs bonded to the inorganic particles. Mechanical
41 properties of the samples were also improved. The Su's group reported different results when adding BN
42 particles and CNTs to epoxy matrices.^{32,33} In both papers, CNTs were modified with amino groups at the
43 surface, whereas BN was modified with iron oxide in one of the works and unmodified in the other. By
44 using a 30 wt. % of modified BN, the addition of CNTs led to a reduction in TC, whereas when 35 wt. %
45 of pristine BN was used, a synergistic effect of about 40% of increase was observed. They described that
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3 the increase in the proportion of BN in the matrix reduced the electrical conductivity in the composites
4
5 with CNTs.
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8 According to the scarce number of studies on the synergism between BN and CNTs, and the effect on
9
10 electrical characteristics, we have considered interesting to go deeper into this topic. Thus, the aim of the
11
12 present work is the preparation of epoxy composites with a high thermal conductivity keeping electrical
13
14 insulation using different proportions of these particles. The study also aims to investigate which changes
15
16 in the matrix and in the fillers affect these characteristics and if there are some kind of synergistic effects
17
18 among them. As the matrix, two different epoxy systems based on diglycidylether of bisphenol A
19
20 (DGEBA) and a cycloaliphatic resin (ECC) cationically homopolymerized have been tested, which were
21
22 previously optimized using a cationic initiator, CXC1612, and adding BN microplatelets as the filler.³⁴⁻³⁶
23
24 In the present work, BN particles, with a larger size, and pristine and oxidized MWCNT's are selected.
25
26 The kinetics of the curing of the different formulations have been determined by calorimetry. Rheological
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28 studies have allowed us to determine the effect of the addition of fillers to the formulations on their
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30 viscoelastic characteristics and to determine the rheological percolation threshold in ECC formulations.
31
32 The materials obtained have been characterized from the thermal and thermomechanical point of view
33
34 and thermal conductivity and electrical resistivity were also determined.

35 2. Materials and methods

36 2.1. Materials

37
38 Cycloaliphatic epoxy resin (3,4-epoxy cyclohexylmethyl 3,4-epoxycyclohexane carboxylate, ECC)
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40 (EEW=126.15 g/epoxy equivalent) was supplied from Sigma Aldrich Inc. (Darmstadt, Germany).
41
42 Diglycidyl ether of bisphenol A (DGEBA) EPIKOTE Resin 828 (EEW=187g/epoxy equivalent) was
43
44 purchased from Hexion Specialty Chemicals (Stuttgart, Germany). The initiator N-(4-methoxybenzyl)-
45
46 N,N-dimethylanilinium hexafluoroantimonate (CXC1612), from King Industries Inc. (Norwalk, CT,
47
48 USA), was dissolved in propylene carbonate at 50 wt. %. Propylene carbonate and triethanolamine (TEA)
49
50 were provided by Sigma Aldrich Inc. and both purified by distillation before use. Glycerol (Gly) and
51
52 hydrogen peroxide solution of 30 wt. % were supplied by Sigma Aldrich Inc. and used as received.
53
54 Multiwalled carbon nanotubes (MWCNT, see **Figure 1A**) were provided by Nanocyl SA (Sambreville,
55
56 Belgium), with 9.5 nm and 1.5 μm of diameter and length averages, respectively, and specific surface
57
58 area (SSA) in the range of 250-300 m^2/g . Platelets of hexagonal boron nitride (BN, **Figure 1B**) with an
59
60 average size of 30 μm (PCTP30) were purchased from Saint-Gobain (Valley Forge, PA, USA).

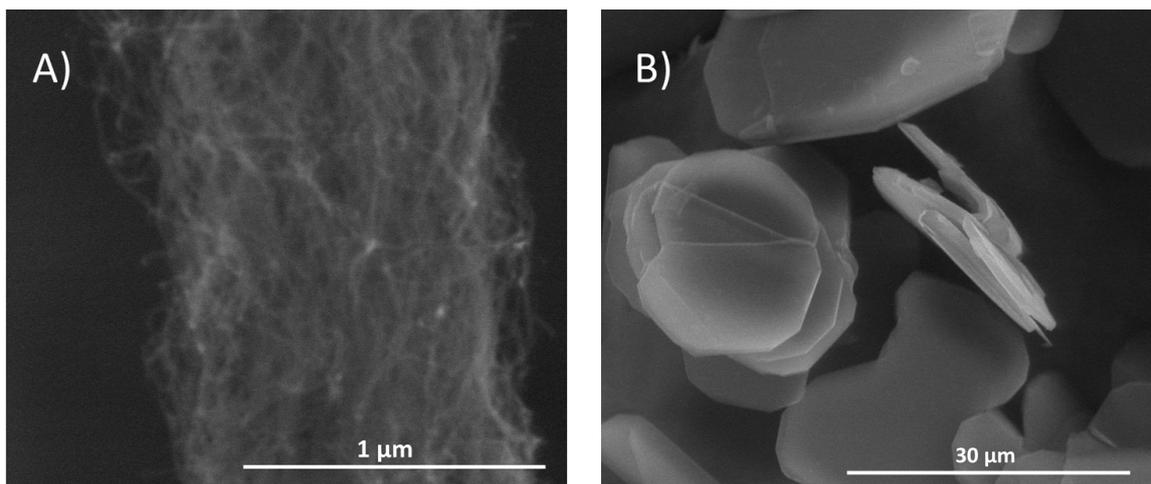


Figure 1. A) Pristine CNT agglomerate in powder form. B) Micro-sized platelets of h-BN.

2.2. Sample preparation

The cycloaliphatic epoxy system was prepared by mixing 1 phr of CXC1612 (parts of initiator per hundred parts of resin) and 0.1 phr of TEA. Proportions between 0.05-1 wt. % of CNT were added to the epoxy system as is schematized in **Figure 2A**. CNTs were dispersed in the resin by direct sonication (Digital Sonifier 250/450 from Branson Ultrasonic Corporation, Danbury, CT, USA), using 35% of amplitude during 20 s, divided in four equal batches of 5 s. Vacuum at room temperature was applied during 1 h to remove bubbles formed by the dispersion procedure. The mixtures of ECC-CNT were used to form new mixtures by using 60 wt. % of them with the 40 wt. % of BN particles. In this case, mechanical stirring until homogeneity was performed. The curing of the samples was carried out in metallic molds and following an optimized multi-step temperature schedule at 80, 100, 120, 150, 180 and 200 °C, with a dwelling time of 1 h at each temperature.

DGEBA resin formulation was prepared following a previous procedure by mixing 3 phr of CXC1612 and 2 phr of Gly. A maximum proportion of 1 wt. % of CNTs, and 40 wt. % of BN were added. The curing was performed at 120 °C for 1 h, followed by a post curing at 150 °C for 1 h. The preparation procedure is schematized in **Figure 2B**.

CNTs were oxidized following the procedure described by Pak *et. al.*²⁹ using a mild treatment of the CNTs with hydrogen peroxide at 30% in a sonicator bath. 1 wt. % of oxidized carbon nanotubes (o-CNTs) was added to neat ECC and DGEBA epoxy formulations, and to these formulations containing a 40 wt. % of BN.

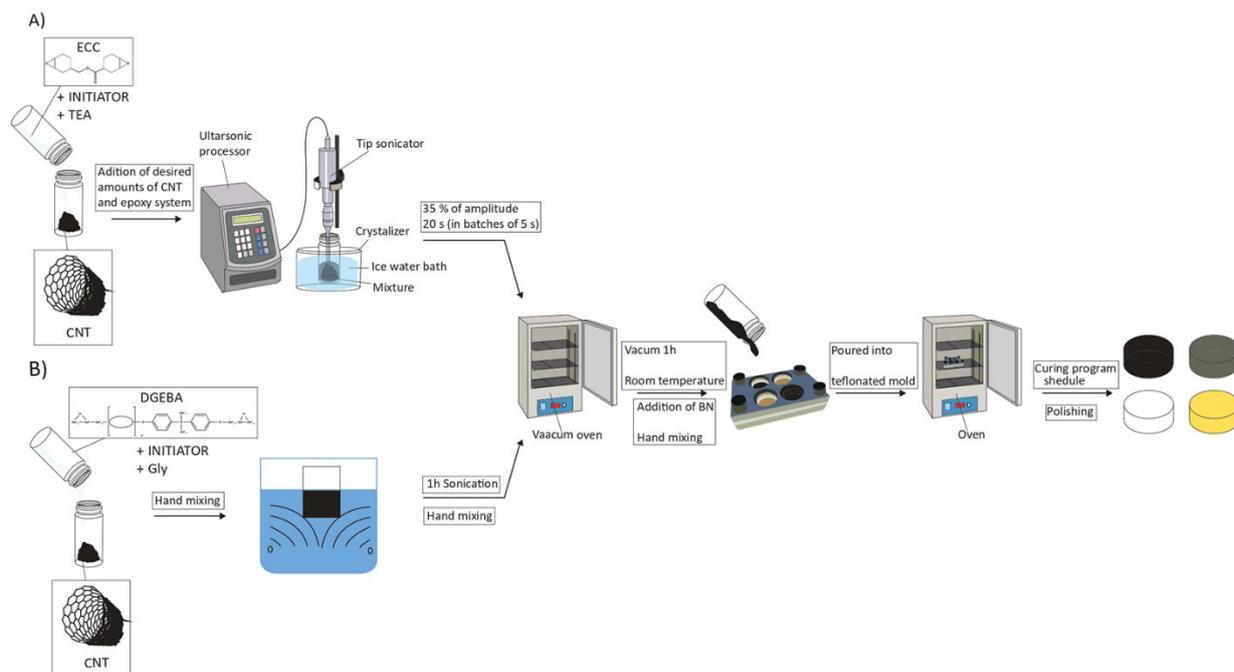


Figure 2. Scheme of sample preparation of ECC (A) and DGEBA mixtures (B).

2.3. Characterization techniques

A modulated differential scanning calorimeter (DSC, Mettler Toledo, Columbus, OH, USA) Mettler DSC-3+ was used to analyze the epoxy reaction evolution. Samples of ca. 3-5 mg were tested in aluminum pans with a pierced lid in a nitrogen atmosphere with a gas flow of 50 mL/min. The dynamic studies were performed in the range of 30-250 °C with a heating rate of 10 K/min. Enthalpy released on curing the samples (Δh) was calculated integrating the calorimetric signal (dh/dt) using a straight baseline in the range of the exotherm, with the help of the STARE software.

Rheologic experiments were carried out for ECC-CNT formulations in parallel aluminium plates (20 mm diameter) in oscillatory mode with an AR G2 rheometer equipped with a peltier temperature controller accessory from TA Instruments (New Castle, DE, USA). The linear viscoelastic range (LVR) was determined at 1 Hz and 30 °C varying the strain applied. Viscoelastic properties, shear elastic modulus (G') and viscous modulus (G'') were determined in the LVR in frequency sweep experiments at 30 °C.

Dynamic mechanical thermal analyses (DMTA) were performed with a TA Instruments DMA Q800 analyzer. The prismatic rectangular samples (20 x 4.5 x 2.5 mm³) were analyzed by 3-point bending clamp at a heating rate of 3 K/min from 30 to 300 °C, using a frequency of 1 Hz and an oscillation of 0.1% of sample deformation. The Young's modulus (E) was determined at 30 °C by means of a force ramp at constant rate, 1 N/min, until reaching a deformation that never exceeds 0.25% of strain, to

guarantee that only the elastic part of the material is evaluated. E was calculated taken the slope between 0.1 and 0.2 % of the deformation curve in accordance with the equation:

$$E = \frac{L^3 m}{4bt^3} \text{ (Eq. 1)}$$

where E is the elastic modulus of epoxy sample (MPa), L is the support span (mm), b and t are the width and the thickness of test sample (mm) and m is the gradient of the slope (N/mm).

Surface hardness was evaluated through Knoop microindentation analysis being consistent with ASTM D1474-13. A minimum of 12 determinations were considered with a confidence level of 95% for each material. Knoop microindentation hardness (KHN) was calculated as follows:

$$KHN = \frac{L}{A_p} = \frac{L}{l^2 C_p} \text{ (Eq. 2)}$$

where L is the load applied by the indenter (0.025 Kg), A_p is the area of indentation in mm² and C_p the indenter constant relating l^2 with A_p .

Thermomechanical analyses (TMA) were carried out on a Mettler TMA40 thermomechanical analyzer. Square cured samples (9 x 9 x 2.3 mm³) were supported by the clamp and a silica disc to distribute uniformly the force and heated at 5 K/min from 35 to 100 °C. A minimum force of 0.01 N was applied to avoid results distortion. The thermal expansion coefficients (CTEs) in the glassy state of the material were calculated as follows:

$$CTE = \frac{1}{L_0} \cdot \frac{dL}{dT} = \frac{1}{L_0} \cdot \frac{dL/dt}{dT/dt} \text{ (Eq. 3)}$$

where L is the thickness of sample, L_0 the initial length, t the time, T the temperature and dT/dt the heating rate.

Thermal stability of cured samples was evaluated in a Mettler TGA2 thermobalance. All the experiments were carried out under N₂ atmosphere (50 mL/min). Pieces of cured samples of 3-6 mg were heated between 30 and 600 °C at a heating rate of 10 °C/min.

Environmental scanning electron microscopy (ESEM) was used to examine the fillers and breaking surfaces of the materials prepared. A Quanta 600 environmental scanning electron microscopy (FEI Company, Hillsboro, OR, USA) allows collect micrographs at 10-20 kV and low vacuum mode without the need to coat the samples with poor electrical conductivity.

Electrical resistance of materials was tested using a multimeter 34410A 6½ Digit from Agilent Technologies (Santa Clara, CA, USA) at room temperature and based on ASTM D257-14. The samples with higher electrical resistance ($>10^8 \Omega \cdot \text{m}$) were evaluated with a Megohmmeter Resistomat 24508 (Gernsbach, Germany) at room temperature and the same standard. Samples of approximately 14 mm of diameter were tested between two stainless steel electrodes with a surface area of 19.635 mm². A voltage of 500 V during 5 min was applied to thermoset composites. Electrical resistivity (ρ) was determined as follows:

$$\rho = R \frac{A}{l} \quad (\text{Eq. 4})$$

where R is the electrical resistance measured by the device, A the electrode area and l the sample thickness.

Thermal conductivity was measured using the Transient Hot Bridge method by a THB 100 device from Linseis Messgeräte GmbH (Selb, Germany). A HTP G 9161 sensor was used with a 3 x 3 mm² of area calibrated with poly(methyl methacrylate) (PMMA), borosilicate crown glass, marble, Ti-Al alloy and titanium. Two equal polished rectangular samples (9 x 9 x 2.3 mm³) were placed in each face of the sensor. Due to the small size of sensor, side effect can be neglected. A measuring time of 100 s with a current of 10 mA was applied to the five measures done for the different formulations.

3. Results and discussion

3.1. Calorimetric analysis by DSC

The initiator selected, CXC1612, has proved to present a markedly thermal latent character in an ECC formulation in the presence of TEA until reaching temperatures over 100 °C (determined by DSC).³⁴ According to that, the formulation presents a long storage stability at room temperature. For this reason, this system was selected for direct sonication to disperse carbon nanotubes, taking advantage of the low viscosity of ECC resin. Ultrasonication is considered an efficient dispersion method, less time consuming compared to other techniques, although it is known to damage CNTs introducing defects and reducing lengths.^{25,37} The formation of defects represents an advantage providing bonding sites between the filler and the matrix, to the already imperfect CNT made by CVD. After preliminary investigations it was decided to apply 20 s of ultrasonication, divided in batches of 5 s, at the high amplitude of 35% to all the ECC-CNT mixtures (see compositions in **Table 1**). Lengthen sonication time increased the temperature by the mechanical action and the homopolymerization reaction was initiated despite having the curing

system the latent character. CNT suspensions, which were degassed under vacuum, could be stored at room temperature for three months without observing any sign of filler precipitation, which confirmed the good dispersion reached. To ECC-CNT mixtures a 40 wt. % of BN was added and the compositions of the different formulations are detailed in Table 1.

The curing of the formulations prepared was studied by DSC in dynamic mode. **Table 1** contains the most important data extracted from these experiments. It should be mentioned, that the curing exotherms are narrow and high, due to the latent character and quick reaction.³⁴

Table 1. Composition of the ECC formulations and DSC data for all the mixtures.

Sample	T _{peak} ^a (°C)	Δh ^b (J/g)	Δh ^b (kJ/ee)
Neat epoxy	122.4	603	76.1
0.05% CNT	121.6	599	75.6
0.10% CNT	120.5	594	75.1
0.25% CNT	121.0	592	74.9
0.50% CNT	120.5	594	75.3
0.75% CNT	120.1	593	75.4
1.00% CNT	120.5	593	75.5
1.00% o-CNT	120.4	601	76.5
40% BN	120.2	364	76.5
0.05% CNT / 40% BN	120.9	363	76.4
0.10% CNT / 40% BN	120.6	363	76.4
0.25% CNT / 40% BN	120.8	363	76.7
0.50% CNT / 40% BN	120.2	354	75.0
0.75% CNT / 40% BN	120.8	353	75.3
1.00% CNT / 40% BN	120.9	350	74.8
1.00% o-CNT / 40% BN	118.9	353	75.5

^a Temperature of the maximum of the curing exotherm.

^b Enthalpy evolved on curing per gram of mixture or epoxy equivalent (ee).

Some authors studied the curing behavior of epoxy systems filled with CNTs.³⁸ When the filler was well dispersed no variation in the curing process was observed. However, when CNTs agglomerate conflicting results were reported, diminishing or increasing the enthalpy evolved during curing. In Table 1 it can be observed how the addition of CNTs barely change the temperature of the maximum of the curing exotherm and the heat evolved during the cure, which support the good CNT dispersion. The addition of o-CNTs does not lead to great differences when added to the curing formulation. In all the CNTs filled formulations the temperature of the maximum of the peak is reduced only in 2 °C, which indicates a slight activation of the curing process as reported previously.³⁹ The addition of a 40% of BN to the neat epoxy leads to a similar decrease in the temperature of the peak, but there is any influence on the CNTs filled formulations. The sample of 1 wt. % o-CNT/40 wt. % BN seems to be the most reactive, since a reduction of 3 °C in the temperature of the exotherm can be observed in reference to the neat epoxy. It

seems to indicate a slight cooperative effect between both fillers. It is known, that the presence of protons, formed in the CNT oxidation, can help to catalyze the ring-opening polymerization.^{40,41} It must be mentioned that DSC did not allow to determine the T_g of the cured material, due to the constrained network formed.³⁴

DGEBA formulations were also tested to know the effect of the fillers on the curing behavior. The high viscosity of DGEBA makes more difficult the CNT dispersion. Since the use of solvents must be avoided, it was decided to combine mechanical mixing and the action of bath sonication to reach a good dispersion (see Figure 2B). In this case, only the formulations with a 1 wt. % of CNT or o-CNTs were studied (see **Table 2**). The addition of fillers to the DGEBA-CNT curing system produces higher differences in the DSC characteristics than in the previous formulations, probably as a consequence of a worst dispersion and the influence of the structure of this resin (**Figure 3** and Table 2). In contrast to ECC mixtures, the storage stability of these formulations is limited to some days. Unlike ECC-CNT samples, in DGEBA formulations the fillers shift the reaction to higher temperatures, delaying the curing. The delay is more noticeable in BN formulations, which could be explained by the dilution effect of the high quantity of filler. The differences in ECC and DGEBA mixtures could be related to the highest reactivity of ECC resins in cationic homopolymerizations. The curing achieved in all the formulations seems to be quite similar, because there is no difference in the enthalpies evolved per epoxy equivalent in the different formulations. In these materials, T_g could be appreciated and the presence of filler seems not to influence much the values, although the highest T_g was reached in samples containing both BN and CNTs.

Table 2. Composition of the DGEBA formulations and DSC data for all the mixtures.

Sample	T_{peak}^a (°C)	Δh^b (J/g)	Δh^b (kJ/ee)	T_g^c (°C)
Neat epoxy	121	542	101.3	132
1% CNT	126	530	100.1	132
40% BN	133	318	99.0	130
1% CNT / 40% BN	134	314	99.5	134
1% o-CNT	126	540	102.0	132
1% o-CNT / 40% BN	134	317	100.4	134

^a Temperature of the maximum of the curing exotherm.

^b Enthalpy evolved on curing per gram of mixture or epoxy equivalent (ee).

^c Glass transition temperature determined by DSC of samples cured isothermally in the oven.

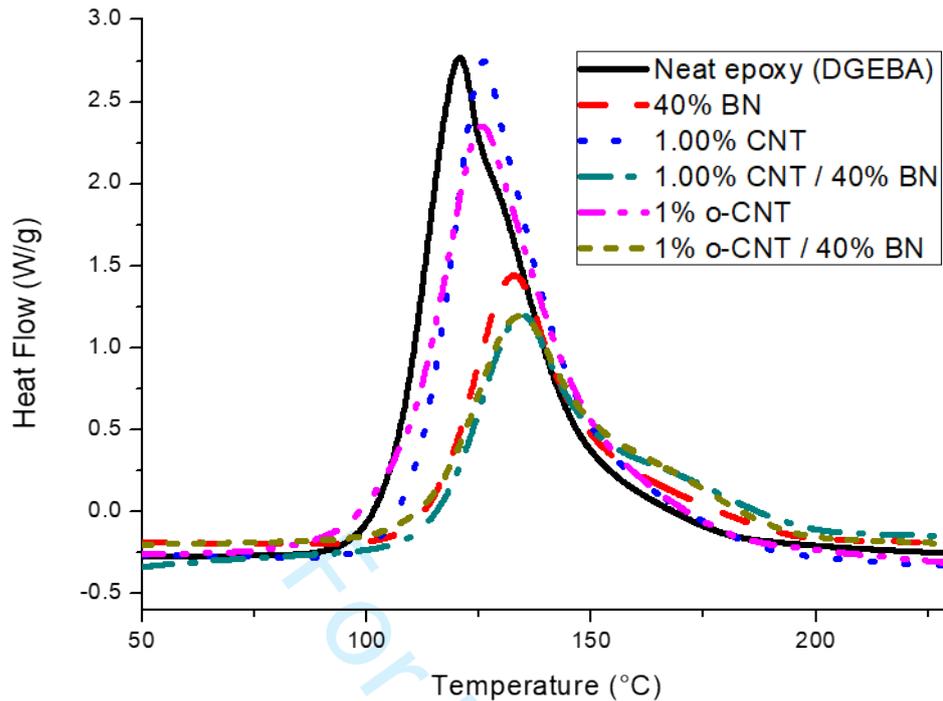


Figure 3. DSC curing exotherms of DGEBA formulations.

3.2. Rheologic study

The rheological behavior of polymers loaded with nanoparticles is one of the most important factors when these mixtures have to be processed. From the viscoelastic properties in oscillatory experiments it can be determined at what concentration for each type of particles the percolation is reached. It is known that not only the shape, particle and matrix interactions, microstructure formed, and dispersion can determine the viscoelastic behavior of resin-particles mixtures, but temperature is a very important influence factor, and as a consequence, the concentration at the percolation can vary.^{42,43}

In the present case, tube-like particles (CNTs) are used as fillers and they can be dispersed randomly or aligned thanks to the high aspect ratio and therefore, percolation threshold is expected to be reached at low concentration. The determination of this point is of the main importance since a sudden change in different properties could occur. In this study, the percolation threshold of the CNTs in the ECC solution has been determined, since it is important to be under this threshold to keep the electrical insulation character of the composites prepared. A temperature closely to room temperature (30 °C) was used considering industrial processing. Only the mixtures of ECC-CNT were evaluated since, the amount of BN added (40 wt. %) as filler exceeded the percolation threshold as was determined in a previous study.³⁴

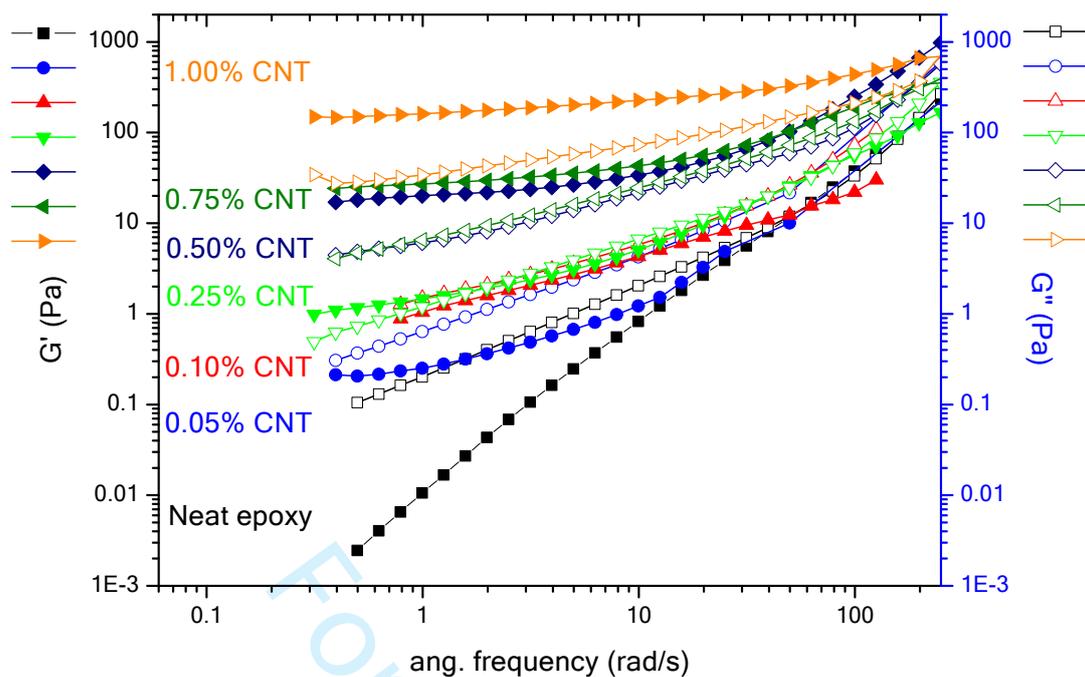


Figure 4. Storage modulus (G') and loss modulus (G'') against frequency (ω) of the ECC-CNT mixtures at 30°C.

All the mixtures were tested varying the amplitude at a fixed frequency (1 Hz) to determine the linear viscoelastic range (LVR), mandatory to determine the viscoelastic properties such as storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) in experiments changing the frequency (ω) applied.

Figure 4 represents G' and G'' towards the ω for all the mixtures. It can be observed at which concentration G' is over G'' at low frequencies (<1 rad/s), sign that percolation threshold is surpassed.^{36,44} This transition, from liquid like behavior ($G'' > G'$) to solid like ($G' > G''$), is located between the wt. % of 0.10 to 0.25 of CNT. It must be considered that this behavior is characteristic for this epoxy system with this type of particles, the dispersion method applied (sonication) and the temperature at which the mixtures were examined.

As expected, the concentration of CNTs necessary to reach the percolation is quite low, common of nanoparticles with high surface area. In contrast, micro-sized particles, like 6 μm hexagonal BN platelets, in the same type of resin and at the same temperature, the percolation was reached at a proportion of 14.4 wt. %.³⁴

The plot of η^* against ω for 1 wt. % of CNT and o-CNT are represented in **Figure 5**. The plot shows a lower viscosity for the non-oxidized nanotubes. This means that the percolation with this filler would result in higher concentrations than the untreated filler, as it is common with functionalized CNT.⁴⁵ The

increase of the concentration to achieve the rheological percolation threshold in modified particles is explained as the changes in particles during the processing, the enlargement of particle-matrix interactions and, as consequence, as an improvement of filler dispersion.^{43,46}

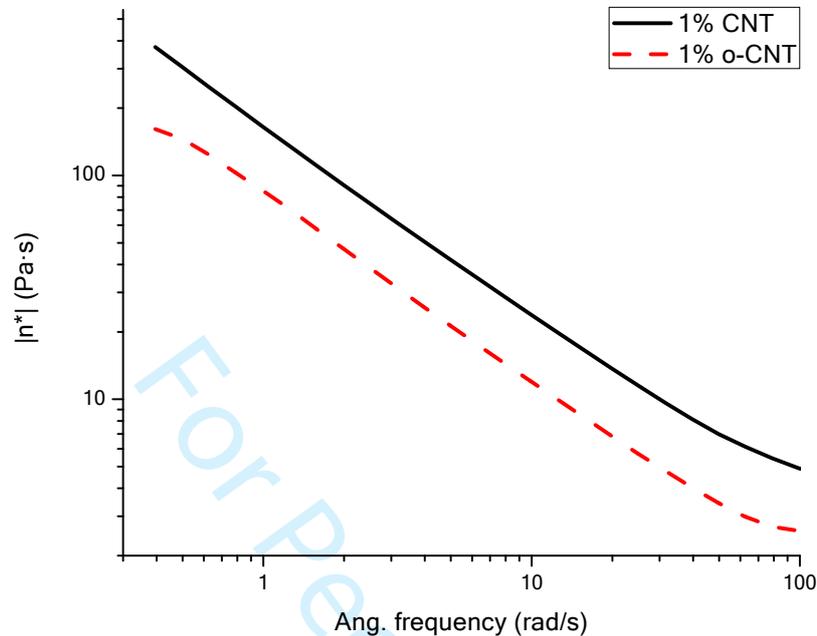


Figure 5. Complex viscosity against frequency of treated and untreated CNT in ECC matrix.

3.3. Thermal and thermomechanical analysis

Thermal and thermomechanical properties of all the cured composites were determined. The most important information of the experiments performed by DMTA, TGA and TMA in the ECC-CNT samples are collected in **Table 3**. Nanoparticles added in polymer matrices, and specifically CNTs in this study, are known to greatly increase a wide range of properties which include mechanical and thermal characteristics using lower concentrations than the conventional micro-sized fillers.¹²

The values of Young's modulus show an enhancement with the increasing addition of CNTs, up to a maximum at the proportion of 0.75 wt. % of CNT with an improvement of a 37.5 % in reference to the neat epoxy sample. Similar results were described by Ulus et al. were small proportions of CNT results in better mechanical behavior than increasing the concentration of nanofillers.^{47,48} On increasing the CNT content, the viscosity of the formulation becomes higher and the possibility of the formation of agglomerates increases, which influence the processing and the final properties.⁴⁹ The use of o-CNT leads to a diminution of the rigidity, probably due to the deterioration of the structure of the particles. This seems to indicate that the hydroxyl and acid groups on the surface do not produce any improvement in the

interaction. With the addition of 40 wt. % of BN the rigidity is highly improved, more than twice of neat material as observed in previous studies,^{34,44} as the result of the reinforcing role of the filler. The use of both CNTs and BN particles has a complementary effect in the rigidity of the samples, slightly increasing their value with the same trend as the composites with only CNTs as filler, which reach the maximum rigidity at 0.75 wt. % proportion.

Table 3. Mechanical and thermomechanical characterization of ECC-CNT composites.

Sample	E ^a (GPa)	tan δ _{peak} ^b (°C)	T _{5%} ^c (°C)	Char yield ^c (%)	KHN ^d	CTE _{glass} ^e (10 ⁻⁶ ·K ⁻¹)
Neat epoxy (ECC)	2.42 ± 0.02	210	352	1.8	12.9 ± 0.8	108
0.05% CNT	2.73 ± 0.08	209	346	2.0	18.0 ± 0.9	101
0.10% CNT	2.95 ± 0.04	214	342	1.8	21.4 ± 0.8	100
0.25% CNT	3.04 ± 0.02	212	336	2.8	21.8 ± 0.9	100
0.50% CNT	3.06 ± 0.04	214	330	3.1	22.9 ± 0.7	87
0.75% CNT	3.33 ± 0.05	214	332	3.5	26.0 ± 0.9	85
1.00% CNT	3.17 ± 0.03	215	329	3.6	25.2 ± 1.2	83
1.00% o-CNT	2.92 ± 0.01	214	318	3.1	25.0 ± 1.3	82
40% BN	6.50 ± 0.11	215	361	41.9	22.7 ± 0.7	78
0.05% CNT / 40% BN	6.58 ± 0.12	212	359	44.1	24.3 ± 1.4	77
0.10% CNT / 40% BN	6.61 ± 0.16	211	357	43.8	25.1 ± 1.8	72
0.25% CNT / 40% BN	6.98 ± 0.39	210	351	44.4	25.0 ± 1.2	69
0.50% CNT / 40% BN	7.01 ± 0.47	211	346	43.4	25.8 ± 1.6	69
0.75% CNT / 40% BN	7.16 ± 0.14	212	342	45.0	25.9 ± 1.4	67
1.00% CNT / 40% BN	6.68 ± 0.11	215	343	44.3	24.9 ± 1.1	64
1.00% o-CNT / 40% BN	6.61 ± 0.41	212	340	44.1	24.0 ± 1.0	65

^a Young's modulus determined at 30°C in DMTA with a controlled force experiment in the elastic material range.

^b Temperature of the maximum of the tan δ peak determined at 1 Hz in an oscillatory experiment by DMTA.

^c Temperature of 5 wt.% loss and final residue in TGA test at 10 K/min in nitrogen atmosphere.

^d Microindentation Knoop hardness.

^e Coefficient of thermal expansion (CTE) in the glassy state (50-75°C) determined by TMA.

The rigidity of the composites with DGEBA as the matrix was also determined and the values obtained are collected in **Table 4**.

Table 4. DMTA, TGA and TMA results from DGEBA-CNT composites.

Sample	E ^a (GPa)	tan δ _{peak} ^b (°C)	T _{5%} ^c (°C)	Char yield ^c (%)	KHN ^d	CTE _{glass} ^e (10 ⁻⁶ ·K ⁻¹)
Neat DGEBA	2.17 ± 0.05	131	376	13.1	21.9 ± 0.9	80
1% CNT	2.26 ± 0.04	145	372	18.9	21.9 ± 0.7	78
1% o-CNT	2.37 ± 0.03	144	381	17.5	25.7 ± 1.0	72
40% BN	5.49 ± 0.12	148	399	48.8	24.5 ± 1.3	72
1% CNT / 40% BN	5.63 ± 0.09	146	386	48.2	24.6 ± 1.1	56
1% o-CNT / 40% BN	6.26 ± 0.21	145	395	51.0	25.7 ± 0.9	57

^a Young's modulus determined at 30°C in DTMA with a controlled force experiment in the elastic materials range.

^b Temperature of the maximum of the tan δ peak determined at 1 Hz in an oscillatory experiment by DMTA.

^c Temperature of 5 wt.% loss and final residue in TGA test at 10 K/min in nitrogen atmosphere.

^d Microindentation Knoop hardness.

^e Coefficient of thermal expansion (CTE) in the glassy state (50-75°C) determined by TMA.

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3 Young modulus barely increases with the addition of 1 wt. % of CNT. However, the oxidation of CNTs
4 leads to a slightly higher rigidity. The results obtained seem to indicate that there is no interaction
5 between the electronic density of phenylene rings in the resin and the electronic density of CNTs, which
6 does not meet our expectations, but the presence of reactive groups in o-CNTs can lead to covalent
7 bonding with the resin to some extent.
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13 The T_g s of the composites derived from ECC (Table 3), which could not be determined by DSC due to
14 the tight network formed, could be visualized by DMTA. The values remained within a narrow range of
15 temperatures (209-215 °C) according to the rigidity and high crosslinking density of the epoxy matrix.
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17 The small variation by the addition of filler confirms the low interaction between fillers and matrix. On
18 the other hand, the temperature of $\tan \delta$ peaks of DGEBA materials (Table 4) shows an increase of about
19 15 °C when the fillers were added, but in this case the temperatures were lower (131-148 °C). Both the
20 addition of 1 wt. % of pristine and oxidized CNTs affects the $\tan \delta$ values in a similar way than 40 wt. %
21 of BN and any synergetic effect between the fillers could be appreciated. In DGEBA composites, the
22 addition of fillers increases more the $\tan \delta$ temperature than the T_g determined by DSC (Table 2). This
23 can be related to the fact that these fillers somehow interact with the resin producing a more pronounced
24 effect on thermomechanical tests than in techniques based on the change of the heat capacity, indicating
25 their higher mechanical effect close to the relaxation temperature range.
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37 The thermal stability of the composites was studied by TGA under inert atmosphere (see Tables 3 and 4).
38 This is an important characteristic which determines the service life of a material when it is exposed to
39 high temperature. It is known that the addition of CNTs to polymer matrices increases the thermal
40 resistance of the composites mainly attributable to the good dispersion and interactions between the filler
41 and the polymer matrix.^{50,51} Nevertheless, the impurities that remain in the nanofiller, due to the
42 manufacturing technique, can accelerate the degradation process.⁵² The two types of composite matrices
43 present a monomodal decomposition derivative plot, with an only pronounced step of weight loss. In
44 Table 3, the TGA data for ECC samples are collected. As we can see, the initial decomposition
45 temperature ($T_{5\%}$) decreases proportionally to the amount of CNTs added, but the addition of BN particles
46 delays the decomposition process. The addition of the partially oxidized CNTs accelerates even more the
47 degradation. The char yield exhibits its dependence with the amount of filler. It should be noted the
48 carbonaceous residue that promotes the addition of pristine CNTs. In contrast, although the addition of
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3 CNTs accelerates the degradation process and BN particles stabilize thermally the composites, the
4 addition of o-CNTs increases moderately their thermal stability, which is a sign that functionalization of
5 nanotubes is more valuable with aromatic epoxy matrices. The notable difference in the residues formed
6 with ECC and the DGEBA composites leads to a predictable higher flame retardancy for the latter.
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11 For coating applications, the surface hardness is one of the main characteristics to ensure durability. The
12 values determined for both types of composites are collected in the previous tables. In the case of ECC
13 composites, the minimum addition of CNTs greatly increases the hardness, from 12.9 to 18.0 KHN and
14 there is progressive increase, reaching a maximum at the 0.75 wt. % CNT proportion (26.0 KHN). When
15 BN was added, the enhancement in hardness on adding increasingly proportions of CNTs gets lost, and
16 the maximum value is limited to 25.9 KHN with a 0.75 wt. % of CNT. The results with DGEBA resin
17 make a difference. The addition of CNTs did not produce any change in hardness in reference to the neat
18 epoxy (21.9 KHN). However, when o-CNTs were added, there is a notable enhancement (25.7 KHN),
19 showing again that the modification has a greater effect when DGEBA is the matrix.
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30 The thermal expansion coefficient of the composites was analyzed by TMA experiments. The reduction
31 of this coefficient is desirable since polymers expand more than metals or ceramics on increasing
32 temperature. Thus, when they are used to join or coat surfaces of metallic or ceramic materials,
33 temperature fluctuations can cause deadhesion, warping, cracking or the creation of internal stresses that
34 over time can result in critical failures. In Table 3 a reducing trend in the CTE with the addition of both
35 type of fillers can be observed. The most important change in CTE was found between the proportions of
36 0.25 and 0.50 wt. % of CNT. A 40 wt. % of BN leads to a high reduction of the CTE value but
37 proportionally, CNTs play a more important role in this improvement. In fact, the size and shape of the
38 particles greatly affect this property, since in previous studies with the same epoxy system, using a 6 μm
39 sized BN, the reduction was greater.³⁴ DGEBA materials have a lower CTE value and is slightly reduced
40 by the presence of one of the fillers. The combination of CNT and BN has a synergistic effect on the CTE
41 reduction. The CTE of neat DGEBA drops in a 30 % when both fillers were added.
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53 3.4. Microscopic inspection of composites

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56 It has been previously explained, that the dispersion of fillers in the matrix is one of the most important
57 requirements to improve the final composite characteristics. To prove that a good dispersion has been
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reached, electronic microscopy inspection (ESEM) is highly recommended. **Figure 6** shows some of the most representative micrographs of the fracture surface of the materials prepared with ECC as the matrix.

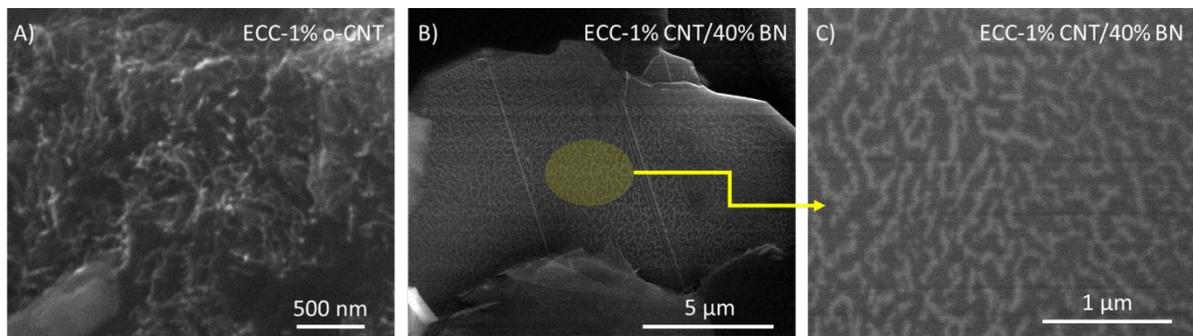


Figure 6. A) ECC with 1 wt. % of o-CNTs at 50k magnifications. B) ECC with 1 wt. % of pristine CNTs and 40 wt. % of BN at 10k magnifications, and the amplification of the same sample at 50k magnifications.

As we can see, there is a good dispersion of oxidized nanotubes in the matrix (Figure 6A). When both pristine CNTs and BN were added to composites, both fillers are well dispersed in the matrix (micrograph not shown), but which is intriguing is the distribution of nanotubes on the BN surface. Figure 6B shows the surface of a BN platelet (in the inner of the composite) with a thin layer of resin containing nanotubes, and Fig 6C shows an amplification of the BN particle surface. It can be observed how nanotubes are well distributed forming a co-continuous morphology of CNT-ECC matrix. It is also clear that CNTs have surpassed the percolation threshold.

Figure 7 shows some selected micrographs of broken surfaces of DGEBA composites.

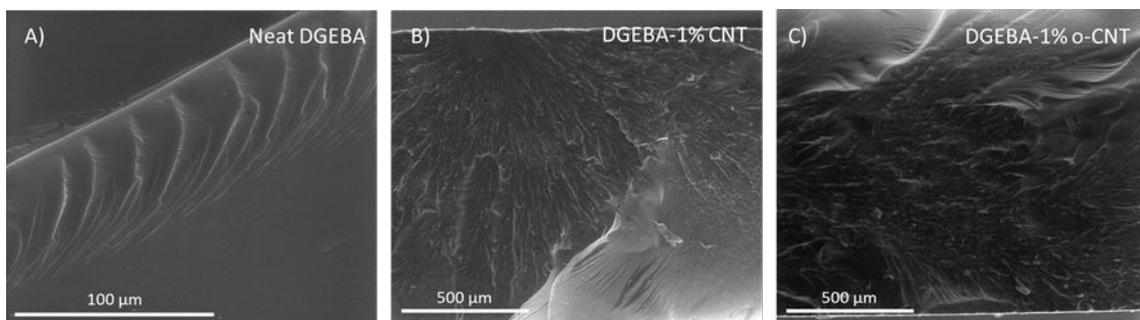


Figure 7. A) Neat DGEBA resin at 800 magnifications. B) DGEBA composite with pristine CNTs at 100 magnifications. C) DGEBA composite with o-CNTs at 100 magnifications.

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3 In this case, the figures show that the addition of pristine and oxidized CNTs leads to an improvement of
4 toughness, since the crack propagation in Figures 7B and 7C is more complex with more tortuous ways.

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7 In case of DGEBA, although a good dispersion of the nanotubes in the matrix could be observed, it was
8 not possible to get clear images of them by this technique.
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10 11 **3.5. Electrical resistivity**

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13 The technological application of the materials developed in the present work **requires to achieve the**
14 **maximum thermal conductivity without affecting their electrical insulating character.** For this reason, it is
15 imperative to know the maximum amount of CNTs able to keep electrical insulation. By rheology we
16 could determine that the percolation threshold in ECC/CNT mixtures was between 0.10 and 0.25 wt. %.
17 However, this value can slightly differ from the proportion of CNTs to reach the electrical percolation,
18 **because of the possibility of tunneling effect.** Thus, we selected different formulations with proportions of
19 CNTs varying from 0.05 to 1 wt. % **to determine their electrical characteristics.** **Figure 8** represents the
20 values of electrical resistivity for ECC mixtures (red bars). It can be seen, that even the minimum
21 concentration of nanotubes added to the formulation (0.05 wt. %) sharply decreases the electrical
22 resistance by 7 orders of magnitude, which is no longer suitable for high insulation applications. This
23 means that the electrical percolation threshold of the system is lower than 0.05 wt. % of CNT, under the
24 rheological percolation. A good dispersion plays against the electrical insulation, since if the distance
25 between the CNTs is close, the electrons can circulate by tunneling effect at a lower energy level,
26 producing short-circuits in electronic devices. Between 0.10 and 0.25 wt. %, range of the rheological
27 percolation, another fall of one order of magnitude is observed, and finally in the concentration range
28 between 0.5 and 1 wt. % of CNTs the resistivity values are in the range 10^2 - $10^1 \Omega \cdot m$. The use of partially
29 oxidized nanotubes improves to $10^2 \Omega \cdot m$ the resistivity, due to the fact that the oxidation of the nanotube
30 surfaces disturbs the electronic transmission.
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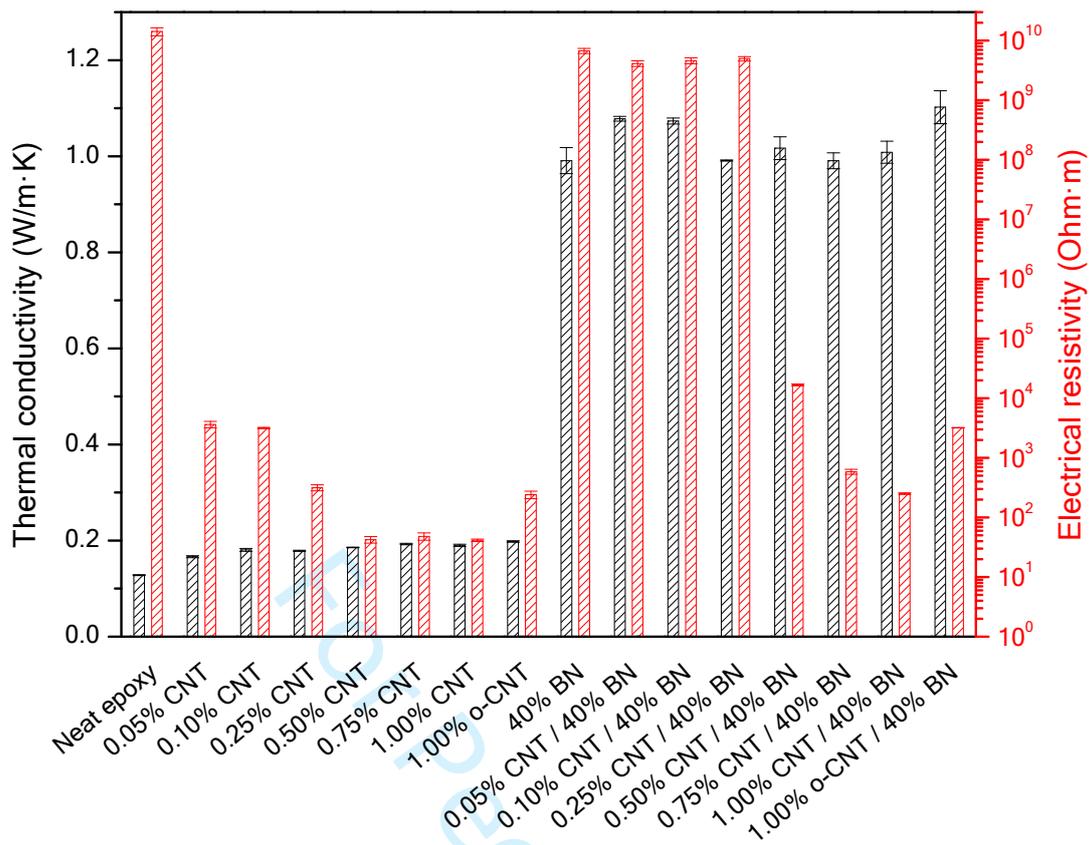


Figure 8. Thermal conductivities and electrical resistivities of ECC-CNT/BN composites measured at room temperature.

In a previous work,⁸ in which expanded graphite and BN were combined as fillers in epoxy composites, we proved that the addition of 70% of BN to the mixture allowed to maintain a sufficient electrical resistivity even when a 5 wt. % of expanded graphite was added. Other authors also reported that the addition of electrically insulating BN considerably increases the insulation character for graphene composites.⁵³ Figure 8 shows that in BN containing samples, as far as the concentration of CNTs is under 0.50 wt. % the electrical resistivity is kept just one order of magnitude lower than the neat epoxy, 10⁹ Ω·m, high enough to maintain good insulating characteristics. BN particles act as a barrier that prevents the circulation and tunneling effect of electrons between the conductive particles. At 0.50 wt. % of CNT in the sample with 40 wt. % of BN the resistivity falls down 5 orders of magnitude, going down further with the increasing content of nanotubes, but with higher values than CNT/epoxy composites. The addition of 1 wt. % of oxidized CNTs to the BN formulation leads to resistivity values one order of magnitude higher than a similar formulation with non-treated CNTs. From these results it can be summarized that formulations containing 0.25 wt. % CNTs or below and 40% BN could be the most adequate in terms of electrical insulation from all the ECC composites prepared.

Similar trends can be observed in **Figure 9** for DGEBA composites, although in this case less compositions were tested. While neat DGEBA epoxy resistivity is similar to neat ECC epoxy ($10^{10} \Omega \cdot m$) the addition of 1 wt. % CNT reduces drastically the resistivity 9 orders of magnitude. As in the ECC mixtures the resistivity is slightly higher when the CNTs were previously oxidized. The addition of BN, as in the previous ECC composites, acts as a barrier to the transmission of the electrical current, but its effect is less pronounced.

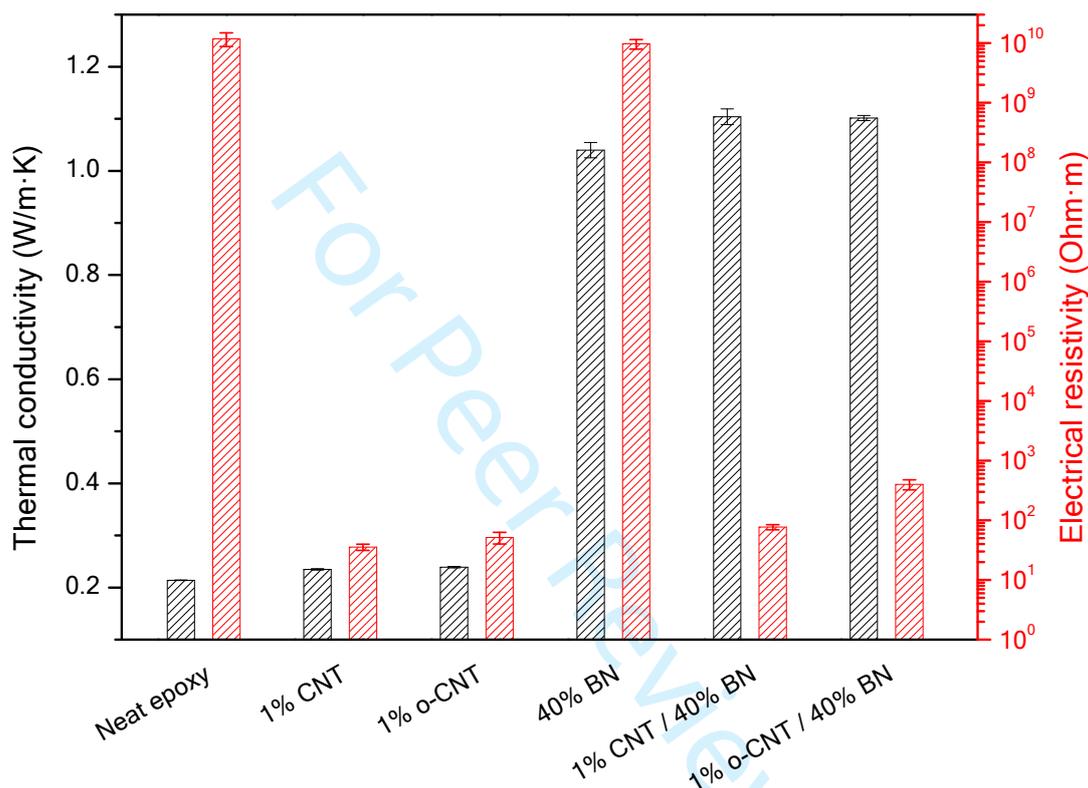


Figure 9. Thermal conductivities and electrical resistivities of DGEBA samples at room temperature.

3.6. Thermal conductivity

The large aspect ratio of one-dimensional filler such as CNTs is expected to enhance the TC of polymers at relatively low filler fractions for the high thermal conductivity they possess, which is reported to be around $6000 \text{ W/m}\cdot\text{K}$.⁵⁴ Figure 8 collects the results of TC of composites with different proportions of CNTs dispersed in the ECC matrix. The presence of CNTs in the composite enhances the thermal conductivity from $0.13 \text{ W/m}\cdot\text{K}$ for the neat epoxy to a maximum of $0.20 \text{ W/m}\cdot\text{K}$, when 1 wt. % of o-CNT was added to the formulation, which is more than a 50% of improvement in TC. The composites with non-modified CNTs showed a maximum in TC of 0.19 , when 0.75 or 1 wt. % of CNT were added. The addition of 40 wt. % of BN enhanced the conductivity up to values around of $1 \text{ W/m}\cdot\text{K}$, with a

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3 maximum with a 1 wt. % of o-CNT of 1.102 W/m·K. No appreciable differences were observed on
4 increasing the amount of CNT in BN filled composites. Although a slight synergistic effect of BN and
5 CNT of 8-11% is observed in the present study, the synergistic effect is much lower than that reported by
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7 Teng et al.³⁰ with values of TC about 1.91 W/m·K, using a 30 wt. % of BN and 1 vol. % of CNTs.
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9 However, they do not measure electrical resistivity characteristics of the composites and they added
10 epoxy functionalized CNTs and amino functionalized BN particles to the epoxy resin, which enhance the
11 interactions between the matrix and fillers, necessary to get good thermal conductivity. However, the
12 chemical modification of fillers could not be desirable for technological applications due to the high cost
13 and the low availability of industrial modified fillers.
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21 If we consider both thermal and electrical conductivities, the samples containing between 0.05 and 0.1 wt.
22 % of CNTs and 40 wt. % of BN are the best ones that fulfill the performance requirements for the
23 applications desired. It should be noted that CNTs increase much the viscosity, which is a drawback for
24 their application. Thus, taking all of this into account, the best formulation is the one with 0.05 wt. % of
25 CNTs and 40 % of BN. The composites obtained shows an improvement in thermal conductivity of
26 around 750 %, keeping good electrical insulating characteristics.
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33 In case of using DGEBA as the epoxy matrix, we can see in Figure 9 that the addition of CNT scarcely
34 affects the TC value, just about 10% of improvement. No significant differences were observed with the
35 oxidation of the nanotubes. The addition of BN alone leads to a TC of 1.04 W/m·K and the further
36 addition of CNTs improves this property to approximately up to 1.10 W/m·K, which means an
37 improvement higher than 400% in reference to the neat formulation. However, the synergistic effect of
38 BN and CNTs is of only 6 %, which is even less than in case of ECC formulations. Although we
39 hypothesized the existence of π - π interaction between phenylene units in DGEBA and CNTs to improve
40 filler-matrix interactions, finally these effects have not been noticed in the results obtained with this type
41 of resin.
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51 52 53 **4. Conclusions**

54 In the present study, the combined addition of CNTs and BN particles to ECC and DGEBA epoxy
55 matrices have been studied with the aim to improve their thermal conductivity without deteriorating other
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3 properties of the thermoset systems such as their electrical insulating character or their mechanical and
4 thermal properties.

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6 A low amount of 0.05 wt. % of CNTs well dispersed within epoxy matrix makes **these materials**
7 electrically conductive. However, on adding a 40 % of BN to the system, it is possible to increase up to a
8 0.25 wt. % the amount of CNTs to the system to improve significantly its thermal conductivity while
9 keeping its electrical insulating character. More precisely, the most promising combinations of CNTs and
10 BN achieved in this work lead to a synergistic effect of 11% in ECC matrix and of 6% in DGEBA. They
11 are composed of 0.05 or 0.10 wt. % of CNTs and 40 wt.% of BN in ECC matrix, with a value of 1.07
12 W/m·K, which means an improvement of 750 % in reference to the unfilled material. The replacement of
13 pristine CNTs by oxidized nanotubes further improves the thermal conductivity of the formulation to 1.10
14 W/m·K. In the case of DGEBA matrix, the best thermal conductivity achieved is 1.10 W/m·K, which
15 represents an improvement higher than 400% in reference to the corresponding unfilled system.

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17 Regarding the mechanical properties of the composites, the stiffness of cured ECC-CNT composites is
18 found to be enhanced with both individual or joint addition of fillers but the highest improvement of
19 Young's modulus is achieved for the systems containing a combination of CNTs and BN particles.

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21 In addition, pristine CNTs seem to have a slightly higher influence on the improvement of mechanical
22 characteristics in ECC composites whereas o-CNTs are found to have a higher influence in the
23 mechanical properties of DGEBA systems. This result suggests that reactive groups generated on the
24 surface of o-CNTs could be involved in covalent bonding in the case of DGEBA matrix.

25
26 Interestingly, the thermal expansion coefficient of the composites is found to be positively reduced with
27 the addition of BN and CNTs. DGEBA materials show a synergic effect of both fillers in the
28 improvement of this parameter.

29
30 Finally, regarding the thermal stability of the composites, the presence of CNTs leads to a dual and
31 antagonist contribution. More precisely, the CNTs are found to promote the formation of carbonaceous
32 residues (the char yield under pyrolysis conditions is significantly increased) but at the same time, they
33 are found to deteriorate the initial temperature of decomposition of the composites proportionally to their
34 amount in the composites. In addition, o-CNTs are found to accelerate even more the degradation of the
35 composites. **However**, the presence of BN particles allows to delay and attenuate this last effect in the
36 composites containing both CNT and BN particles.

All these results clearly highlight that CNT and BN make a valuable combination of particles to enhance the thermal conductivity of thermoset materials without sacrificing other properties of such systems.

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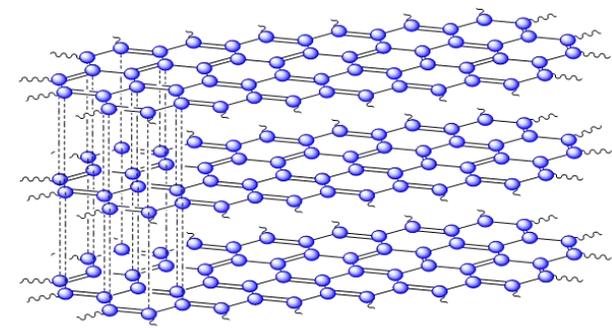
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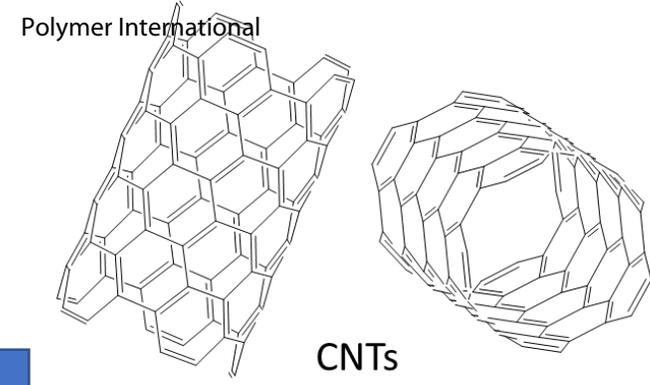
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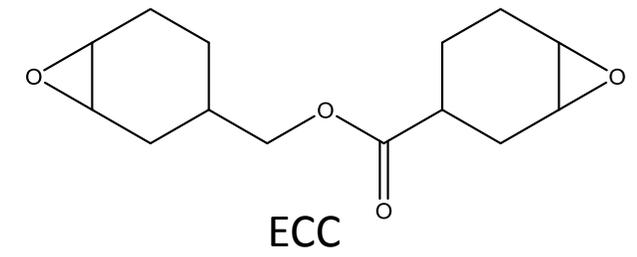
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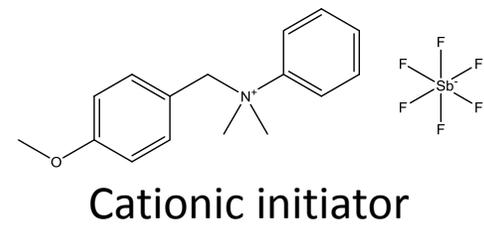
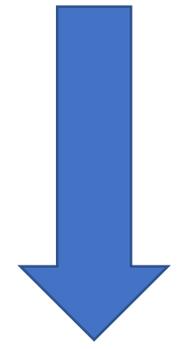
h-BN



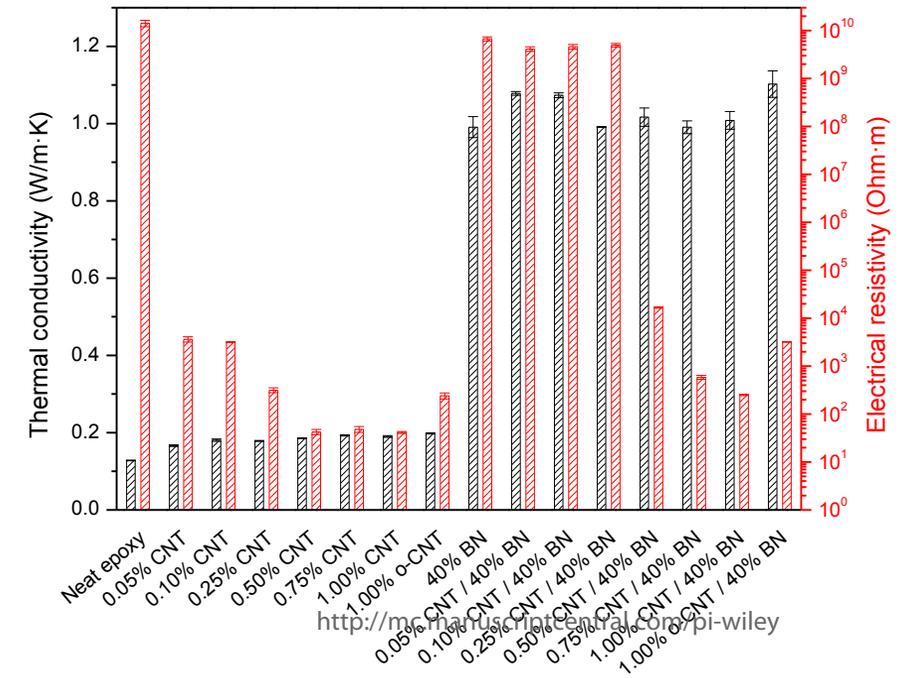
CNTs



ECC



Cationic initiator



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3 **Study on the cooperative effect of boron nitride and carbon nanotubes in the improvement of the**
4 **thermal conductivity of epoxy composites**
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6 Isaac Isarn, Leïla Bonnaud, Lluís Massagués, Àngels Serra* and Francesc Ferrando
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8 The enhancement of the thermal conductivity of epoxy resins, keeping electrical insulation, has been
9 studied by adding pristine and oxidized carbon nanotubes (CNTs) and micro-platelets of boron nitride
10 (BN).
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