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# Monitoring the Mechanical Behaviour of Electrically Conductive Polymer Nanocomposites Under Ramp and Creep Conditions

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Various amounts of carbon black (CB) and carbon nanofibres (CNF) were dispersed in an epoxy resin to prepare nanocomposites whose mechanical behaviour, under ramp and creep conditions, was monitored by electrical measurements. The electrical resistivity of the epoxy resin was dramatically reduced by both nanofillers after the percolation threshold (1 wt% for CB and 0.5 wt% for CNF), reaching values in the range of  $10^3-10^4 \ \Omega \cdot cm$  for filler loadings higher than 2 wt%. Due to the synergistic effects between the nanofillers, an epoxy system containing a total nanofiller amount of 2 wt%, with a relative CB/CNF ratio of 90/10 was selected for the specific applications. A direct correlation between the tensile strain and the increase of the electrical resistance was observed over the whole experimental range, and also the final failure of the samples was clearly detected. Creep tests confirmed the possibility to monitor the various deformational stages under constant loads, with a strong dependency from the temperature and the applied stress. The obtained results are encouraging for a possible application of nanomodified epoxy resin as a matrix for the preparation of structural composites with sensing (i.e., damage-monitoring) capabilities.

**Keywords:** Epoxy, Nanocomposites, Electrical Properties, Mechanical Properties, Creep, Monitoring.

# 1. INTRODUCTION

In the last 20 years, there has been a strong emphasis on the development of polymeric nanocomposites (PNCs).<sup>1</sup> The rapid growth of experimental characterization techniques and theoretical prediction approaches promoted an extensive research in this field. Nanostructured materials are characterized by a very high surface-to-volume ratio. Therefore, strong molecular interactions and unconventional material properties may arise when nanofillers are dispersed in polymer matrices. It has been widely proven that the addition of a nanofiller to a polymeric matrix can increase its mechanical performances,<sup>2-4</sup> gas and solvents barrier properties,<sup>5,6</sup> degradation and chemical resistances.<sup>7</sup> Moreover, the above mentioned improvements can be obtained by adding relatively low amount of filler (generally less than 5 wt%), avoiding the typical drawbacks (embrittlement, loss of transparency, loss of lightness) associated to the usage of traditional organic microfillers.<sup>8</sup> In general, the resulting properties depend on the level of nanofiller dispersion within the matrix and on the degree of filler-matrix interfacial interaction.<sup>9</sup>

In the recent years, a considerable interest arose toward carbon based nanofillers due to their high thermal and electrical conductivities. In fact, various papers documented how the electrical conductivity of polymer matrices could be substantially improved through the introduction of conductive nanofillers, such as metal nanopowders, graphite nanoplatelets (GnP), carbon black (CB) and carbon nanofibres (CNF). The electrical behavior of these systems was successfully described referring to the percolation theory.<sup>10</sup> After a given filler content, the so-called percolation threshold, the conductive particles form a continuous network through the insulating matrix and the resistivity drastically decreases by several orders of magnitude. The simultaneous incorporation of two different nanofillers could lead to synergistic effects in the conductivity behavior of the resulting materials.<sup>11-16</sup> For instance, Li et al. investigated the effects of hybrid carbon nanotubes (CNTs) and graphite nanoplatelets (GnPs) on the mechanical and electrical properties of epoxy nanocomposites. When the total filler loading was fixed at 2 wt%, the nanocomposite containing 1% GnP and 1% CNT showed an electrical conductivity more than two orders of magnitude higher than that of nanocomposites with 2 wt% GnP alone.<sup>14</sup>

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In a recent work<sup>17</sup> we documented how the introduction of vapour grown carbon fibres (VGCF) and exfoliated graphite nanoplatelets (xGnP) in a poly(lactic acid) (PLA) matrix at a total filler content of 10 wt% could promote a further decrease of surface resistivity with respect to the effect played by the single nanofillers.

As polymer matrix composites are particularly sensitive to damages in the polymer matrix (such as matrix cracking), a reliable method for the detection and assessment of such failures is highly desirable.<sup>18</sup> Furthermore, an *in-situ* monitoring of the deformational behaviour and damage development could represent a useful tool to increase the reliability and lifetime as well as to ease the maintenance of structural components exposed to static and cyclic loading conditions. AC and DC electrical methods have been extensively used to study a variety of damage mechanisms under static and dynamic loading conditions.<sup>19-28</sup> If electrical conductivity methods have been widely investigated for the detection of failure in carbon fibre reinforced polymers (CFRPs), the application of an electrically conductive matrix allows one to extend the approach also to composites reinforced with non conductive fibres (i.e., glass or polymer fibres). Both nanoscaled<sup>23</sup> and microscaled<sup>29</sup> carbon black particles have been used to modify the matrix of glass-fibre reinforced thermosets. In these works, it was shown that external stress as well as apparent mechanical damage can be detected in these multiphase composites via electrical conductivity methods. Recently, Thostenson and Chou reported on the usage of carbon nanotube modified glass fibre reinforced epoxy composites and their potential for strain and damage sensing. It could be shown that with a weight fraction of 0.5% CNTs in the epoxy matrix, mechanical stresses/strains, as well as matrix failure can be detected via electrical conductivity measurements.<sup>30</sup>

Despite its practical importance, no papers can be found on the electrical monitoring of the mechanical behaviour of polymer composites under static (creep) loading conditions. Therefore, the analysis of the deformational behaviour of polymer matrices under constant loads could represent and important issue for the health monitoring of structural composites.

In the present paper, epoxy matrices modified with small amounts (up to 4 wt%) of conductive carbon nanofillers (CB and CNF) were prepared and thermo-mechanically characterized. After a preliminary optimization of the composition, combined mechanical/electrical tests were performed in order to evaluate the sensing potential of these multiphase composites both under quasi-static and creep conditions.

# 2. EXPERIMENTAL DETAILS

### 2.1. Materials and Sample Preparation

A bicomponent epoxy resin, supplied by Elantas Camattini SpA (Collecchio, Italy), was used as matrix. In particular,

**Table I.** Physical characteristics of epoxy resin cured at 24 h at room temperature followed by 15 h at 60 °C, according to the producer data sheet.

Property	Value
Density (g·cm <sup>-3</sup> )	1.08-1.12
Max $T_{\sigma}$ (°C)	92–98
Flexural modulus (GPa)	3.2–3.6
Tensile strength (MPa)	67–75
Ultimate elongation (%)	6.0-8.0

EC157 epoxy base (density =  $1.15 \text{ g} \cdot \text{cm}^{-3}$ , viscosity = 700 mPa  $\cdot$  s), constituted by a mixture of Bisphenol A/Bisphenol F/Hexanediol diglycidyl ether (equivalent epoxide weight (EEW) =  $165-180 \text{ g} \cdot \text{equiv}^{-1}$ ), was mixed with W152 LR amminic hardener (density =  $0.95 \text{ g} \cdot \text{cm}^{-3}$ , viscosity = 30 mPa  $\cdot$  s) at a weight ratio of 100:30. The main physical properties of the cured material according to the producer's datasheet are listed in Table I. Carbon black nanoparticles (Ketjenblack EC600JD) were provided by Akzo Nobel Chemicals Spa (Arese, Italy). This nanofiller is characterized by fine aggregates of spherical particles with typical dimension of around 30 nm and a density of 1.95 g  $\cdot$  cm<sup>-3</sup>. Vapor grown carbon nanofibres (1195JN) have been supplied by NanoAmor Inc. (Houston TX, USA). These fibres have a length of 5–40  $\mu$ m, a core diameter of 0.5-10 nm and an outside diameter of 240-500 nm. Table II summarizes the experimental data regarding density and specific surface area of the selected nanofillers. All materials were used as received.

The epoxy base, the hardener and the nanofiller were manually mixed for 5 minutes, then mechanically stirred for 5 min at 2000 rpm in a Dispermat<sup>®</sup> F1 mixer and finally degassed under vacuum for 10 min. The compound was then poured in the cavities of silicone molds and thermally cured in an oven for 2 h at 50 °C followed by 2 h at 100 °C. This accelerated thermal treatment was preferred over that suggested by the resin supplier (24 h at room temperature followed by 15 h at 60 °C) in order to speed up the preparation of the samples without affecting the final properties of the cured resin. Samples were designated with a code indicating the kind of matrix (Epoxy), the nanofiller type (CB or CNF), the weight ratio and total amount. For instance, Epoxy-CB-2 indicates a nanocomposite sample containing 2 wt% of CB, while Epoxy-CB/CNF-90/10-2 indicates the nanocomposite containing

 Table II. Density and specific surface area (SSA) of carbonaceous nanofillers used in this study.

Density <sup><i>a</i></sup> (g $\cdot$ cm <sup>-3</sup> )	$SSA^b (m^2 \cdot g^{-1})$
$1.95 \pm 0.06$	1353.1±4.3
$1.78\pm0.08$	$28.8\pm0.2$
	Density <sup>a</sup> $(g \cdot cm^{-3})$ 1.95 ± 0.06 1.78 ± 0.08

<sup>a</sup>Measured through a Micrometrics Accupyc<sup>®</sup> 1330 helium pycnometer. <sup>b</sup>Measured through an ASAP<sup>®</sup> 2010 Accelerated Surface Area and Porosimetry machine, following BET procedure.

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a CB/CNF mixture (at a ratio of 90/10) for a total nanofiller content of 2 wt%.

#### 2.2. Experimental Techniques

### 2.2.1. Thermo-Mechanical and Microstructural Characterization

Rheological measurements on uncured resin were conducted both on pure epoxy and on nanofilled mixtures in a Brookfield RVT coaxial viscosimeter (Middleboro, Massachussetts, USA), with an inner diameter of 17 mm and an outer diameter of 19 mm, in a shear rate interval between 0.1 and 100 rad  $\cdot$  s<sup>-1</sup>. For each composition, a sample volume of 8 ml was poured between the cylinders and tested at a temperature of 25 °C controlled by a thermostatic chamber.

Morphology of the cryofractured surfaces of fully cured materials were investigated by a Zeiss Supra 40 field emission scanning electronic microscope (FESEM), at an acceleration voltage of about 1 kV and a pressure of  $10^{-6}$  Torr. The lateral surfaces of the samples were metalized with a silver paste before the observations.

Thermal properties of the samples were evaluated through differential scanning calorimetry (DSC) tests, performed with a Mettler DSC30 apparatus (Schwerzenbach, Switzerland). A thermal cycle from 0 °C to 200 °C, at a heating rate of 10  $^{\circ}C \cdot min^{-1}$  under a nitrogen flow of 100 ml·min<sup>-1</sup>, was adopted. Quasi-static tensile tests were performed at 25 °C on ISO 527 1BA dogbone samples (5 mm wide and 2 mm thick, gage length of 30 mm) by using an Instron<sup>®</sup> 4502 tensile testing machine (Norwood, Massachusetts, USA), at a constant crosshead speed of 1 mm  $\cdot$  min<sup>-1</sup>. For the evaluation of the elastic modulus, the strain was recorded through an Instron 2620-601 extensometer (Norwood, Massachusetts, USA), with a gage length of 12.5 mm. According to ISO 527 standard, the elastic modulus was determined as a secant value between strain levels of 0.05% and 0.25%. When the deformation reached a value higher than 0.25%, the extensometer was removed and the deformation was monitored referring to the crosshead displacement. In this way, both the elastic modulus (E) and the quasi-static tensile properties at break  $(\sigma_h, \varepsilon_h)$  were determined.

### 2.2.2. Electrical Resistivity Measurements

Electrical bulk resistance measurements were performed at room temperature in direct-current mode. A 6 1/2-digit electrometer/high resistance system, supplied by Keithley Instruments Inc. (Cleveland, Ohio, USA) (model 6517A), was used. Because of the high electrical resistance of the samples and the relatively low contact resistance, a 2-point electrical measurement was chosen as test configuration. In order to decrease the contact resistance, the sample surfaces in contact with the electrodes were painted with a silver coating. Measurements were carried out on rectangular samples (cross section of 5 mm × 3 mm, length of 30 mm), and at least five specimens were tested for each sample. When the electrical resistance was lower than  $10^5 \Omega$ , measurements were carried out under an applied voltage of 10 V, and the resistance values were measured after a time lapse of 60 s, in order to minimize time-dependent effects. When the electrical resistance was between  $10^5$  and  $10^6 \Omega$ , measurements were carried out under an applied voltage of 100 V. When the electrical resistance was higher than  $10^6 \Omega$ , measurements with an applied voltage of 1000 V were taken on square film samples (length of 95 mm and thickness of 3 mm). In this latter case coaxial electrodes were used in order to minimize the amount of current flowing through the surface, using text fixtures according to ASTM 1D257 standard.

# 2.2.3. Ramp and Creep Mechanical Loading Ingentation

Quasi-static ramp and creep tensile tests were performed at 25 °C on ISO 527 1B dogbone specimens (10 mm wide and 4 mm thick) by using a MTS 858 Mini Bionix servohydraulic testing machine (Eden Prairie, Minnesota, USA), connected to a RT3 real-time digital control system by Trio Sistemi e Misure Srl (Bergamo, Italy). All test were performed inside an Instron model 3119 thermostatic chamber (Norwood, Massachusetts, USA) and strain was recorded through a MTS model n. 634.31F-24 extensometer (Eden Prairie, Minnesota, USA), with a gage length of 20 mm.

Ramp tests were performed at a crosshead speed of  $2 \text{ mm} \cdot \text{min}^{-1}$ . Monitoring of electrical resistance and temperature was performed through a Keithley 6517A multimeter. A representative image of the experimental setup is reported in Figure 1(a). As depicted in Figure 1(b), a voltage of 10 V was applied through two plastic clips covered by thin copper plates, within a distance of 30 mm. The electrical contact zones were painted with a silver conductive coating. The thermocouple of the multimeter was placed into the thermostatic chamber in proximity of the specimen (Fig. 1(b)). Both electrical resistance and temperature signals were acquired with a frequency of 10 Hz.

Creep tests were performed at various stress levels (from 30 MPa to 50 MPa), in a temperature range between 20 and 50 °C, for a loading time of 3600 s. Both electrical resistance and temperature signals were acquired with a frequency of 1 Hz. Tensile creep compliance D(t) was computed by dividing the time dependent strain  $\varepsilon(t)$  by the constant applied stress  $\sigma_0$ . Due to the large deformation of the samples during the creep tests at high stresses or at elevated temperatures, the deformation was monitored normalizing the crosshead displacement for the gage length of the samples (80 mm). The electrical resistance of undeformed specimens at various temperatures was monitored by using the same equipment. In this way it was



nanocomposites.

**Fig. 1.** (a) Setup for the monitoring of the electrical conductivity during tensile mechanical tests under ramp and creep conditions. (b) Particular of a clamped specimen.

possible to correct electrical resistance data acquired during tensile and creep tests, taking into account only the effects associated to the mechanical deformation.

Moreover, in order to evaluate the capability of the tested samples to recover creep deformation, strain recovery tests were also performed for a time of 9 h after unloading.

# 3. RESULTS AND DISCUSSION

# 3.1. Thermo-Mechanical Behavior and Microstructural Features of Nanocomposites

Shear viscosity values of neat epoxy and nanocomposites filled with CB and CNF are plotted in Figures 2(a) and (b),

respectively. Some points are missing on the plots because the instrument was not able to measure the viscosity of highly viscous systems at elevated shear rates. The static viscosity of the neat resin is about 1700 mPa · s, which is a value quite higher than that declared by the producer (150-250 mPa · s at 25 °C). We suppose that the adopted high-rate mixing producer may have produced a heating of the compound, with some crosslinking. As it commonly happens in nanofilled systems,<sup>31</sup> the viscosity of both CB and CNF composites increases with the filler content over the whole range of shear rates. It is interesting to note that, at a given nanofiller content, CNF samples show higher viscosity values than the corresponding CB compounds. This effect could be attributed to the different aspect ratio of the selected nanofillers: in general a continuous network can be created by CNF at lower filler contents with respect to those required for particular fillers such as CB.<sup>32</sup>

cosity values of (•) Epoxy, (▲) Epoxy-CNF-0.5 and (♦) Epoxy-CNF-1



**Fig. 3.** ESEM images of the fracture surfaces of (a) Epoxy, (b) Epoxy-CB-0.5, (c) Epoxy-CB-3, (d) Epoxy-CNF-2 and (e) Epoxy-CB/CNF-90/10-2 nanocomposites.

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Information on the dependency of the morphology from the filler content and type, have been collected by electron microscopy. FESEM micrographs of neat resin, Epoxy-CB-0.5, Epoxy-CB-3, Epoxy-CNF-2 and Epoxy-CB/CNF-90/10-2 samples are shown in Figures 3(a)-(e). As often reported in the scientific literature, the fracture surface of neat epoxy appears quite smooth (Fig. 3(a)), while the microstructure of CB nanomodified systems is characterized by the presence of primary particles arranged in aggregates and agglomerates, homogeneously distributed within the polymer matrix. Epoxy-CB-0.5 system is characterized by the presence of tiny and pale primary particles with average diameter of about 30 nm, organized in agglomerates of about 150 nm. Epoxy-CB-3 system manifests a higher particle density and a higher tendency of the particles to form agglomerates. In fact, the agglomerates are larger in size with respect to the systems at lower nanofiller content (about 250 nm). Epoxy-CNF-2 system exhibits a rather complex microstructure. Even if some cavities due to fiber-matrix debonding phenomena are detectable on the fracture surface (Fig. 3(d)), it is very difficult to assess the presence of the nanofibres and to have information about their dispersion state. Also in the Epoxy-CB/CNF-90/10-2 ternary composite it is rather difficult to detect the presence of nanofibres (Fig. 3(e)). Table III summarizes the average dimension of the agglomerates of CB nanofilled systems. As mentioned before, the size of the agglomerates tends to increase with the nanofiller content, and Epoxy-CB/CNF-90/10-2 presents an agglomerate size very similar to that of Epoxy-CB-2 composite. As often reported for particulate filled nanocomposites,<sup>33</sup> as the filler amount increases the mean interparticle distance diminishes and the probability of aggregation is therefore enhanced.

Table IV summarize glass transition temperatures of neat epoxy and relative nanocomposites, collected during the first  $(T_{g1})$  and second  $(T_{g2})$  heating scans of DSC tests. In agreement with the producer's data sheet, neat resin shows  $T_{g1}$  and  $T_{g2}$  values of 82 °C and 89 °C, respectively. If CB and CNF based nanocomposites are compared at the same filler content, no substantial differences can be found. In fact,  $T_{g1}$  and  $T_{g2}$  values increase for both materials until a nanofiller concentration of 1 wt% and then it starts to decrease, reaching a minimum for a nanofiller amount of 3 wt%. A similar trend has been previously observed and reported by our group for various nanofilled

 Table III.
 Average dimension of the agglomerates detected on the tested samples.

Sample	Avg. agglomerates size (nm)
Epoxy-CB-0.5	$148 \pm 12$
Epoxy-CB-1	$144 \pm 50$
Epoxy-CB-2	$171 \pm 28$
Epoxy-CB-3	$252 \pm 82$
Epoxy-CB/CNF-90/10-2	$157 \pm 29$

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**Table IV.** Glass transition values of neat Epoxy and relative nanocomposites from DSC tests.  $T_{g1}$  and  $T_{g2}$  refer to the first and the second heating cycle, respectively.

Table V.	Quasi-static tensile properties of neat Epoxy, Epoxy-CB- <i>x</i> and
Epoxy-CN	NF- $x$ ( $x = 0.5, 1, 2, 3 \text{ wt\%}$ ) nanocomposites.

Sample	$T_{g1}$ (°C)	$T_{\rm g2}~(^{\circ}{\rm C})$
Ероху	82.0	88.7
Epoxy-CB-0.5	82.5	89.4
Epoxy-CB-1	84.2	90.5
Epoxy-CB-2	81.3	88.3
Epoxy-CB-3	80.2	88.2
Epoxy-CNF-0.5	82.5	89.2
Epoxy-CNF-1	85.5	92.5
Epoxy-CNF-2	82.2	89.0
Epoxy-CNF-3	78.9	87.8

E (GPa)	$\sigma_b$ (MPa)	$\varepsilon_{b}$ (%)
$3.03 \pm 0.17$	$59.6 \pm 0.8$	$5.3 \pm 0.1$
$2.96 \pm 0.04$	$67.4 \pm 1.7$	$5.7 \pm 0.2$
$3.23 \pm 0.11$	$69.7 \pm 0.4$	$5.7 \pm 0.1$
$3.61 \pm 0.10$	$58.7\pm0.5$	$4.2 \pm 0.1$
$3.80\pm0.15$	$55.0\pm0.5$	$4.0\pm0.1$
$2.85\pm0.05$	$62.4 \pm 0.4$	$4.9 \pm 0.1$
$3.10 \pm 0.08$	$62.0 \pm 2.3$	$5.6 \pm 0.2$
$3.31 \pm 0.05$	$50.2 \pm 2.4$	$3.5 \pm 0.1$
$3.42\pm0.10$	$44.7\pm1.5$	$2.8\pm0.1$
	E (GPa) 3.03 ± 0.17 2.96 ± 0.04 3.23 ± 0.11 3.61 ± 0.10 3.80 ± 0.15 2.85 ± 0.05 3.10 ± 0.08 3.31 ± 0.05 3.42 ± 0.10	E (GPa) $\sigma_b$ (MPa) $3.03 \pm 0.17$ $59.6 \pm 0.8$ $2.96 \pm 0.04$ $67.4 \pm 1.7$ $3.23 \pm 0.11$ $69.7 \pm 0.4$ $3.61 \pm 0.10$ $58.7 \pm 0.5$ $3.80 \pm 0.15$ $55.0 \pm 0.5$ $2.85 \pm 0.05$ $62.4 \pm 0.4$ $3.10 \pm 0.08$ $62.0 \pm 2.3$ $3.31 \pm 0.05$ $50.2 \pm 2.4$ $3.42 \pm 0.10$ $44.7 \pm 1.5$

thermosets.<sup>9, 34–37</sup> It could be hypothesized that for elevated filler amounts the crosslinking process is partially hindered by the nanofiller. In other words, the observed  $T_g$  trends could be explained considering the occurrence of two concurrent phenomena: as the filler content increases the chainby blocking effect is likely to increase thus inducing a slight<sub>T</sub>  $T_g$  increase, while, at the same time, polymer-filler chemi-2.6 cal interactions and the viscosity increase may reduce the 20 crosslinking degree of the matrix, with a consequent reduction of its  $T_g$ .

Representative stress–strain curves of quasi-static ramp tensile tests on neat epoxy and of CB filled nanocomposites are reported in Figure 4, while the most important mechanical parameters are collected in Table V. As often observed with nanofilled systems,<sup>38, 39</sup> the elastic modulus of both CB and CNF nanocomposites progressively increases with the filler content, reaching a maximum for a nanofiller content of 3 wt%. In particular, an increase of 13% and 25% can be observed with respect to the neat epoxy resin for CNF and CB systems, respectively. For as concern ultimate mechanical properties such as stress and strain at break values, for both nanofillers a similar



**Fig. 4.** Representative stress–strain curves of quasi-static tensile ramp tests of neat epoxy and Epoxy-CB-*x* nanocomposites (x = 1-3 wt%).

trend can be observed, with a maximum for a concentration of 1 wt%. The reduction of the tensile properties at break at elevated filler contents is more pronounced when CNFs are utilized. As previously reported by our group,<sup>2, 33–35, 40</sup> the progressive embrittlement of nanocomposite systems at elevated filler amounts could be induced by nanofiller aggregation. If ternary systems with a total nanofiller amount of 2 wt% are considered (Table VI), it can be concluded that both elastic modulus and ultimate tensile properties follow a rule of mixture.

## 3.2. Electrical Resistivity of Nanocomposites

In Figure 5(a) the electrical resistivity of the neat epoxy and of nanocomposites is plotted as a function of the content of CB or CNF nanofillers. The electrical resistivity of the neat matrix is about  $10^{16} \Omega \cdot cm$ , in the typical range generally reported for epoxy resins.<sup>41</sup> CB filled nanocomposites show a percolation threshold at a filler concentration between 1 and 2 wt%, with a resistivity drop of more than eight orders of magnitude from 1 to 2 wt%, reaching a plateau value at around  $10^3 \Omega \cdot cm$  for nanofiller contents higher than 2 wt%. On the other hand, CNF based nanocomposites show a percolation threshold lower than 0.5 wt%. For both fillers, the electrical resistivity diminishes down to about  $10^4 \ \Omega \cdot cm$  for a filler content of 4 wt%. As reported in literature,<sup>11, 14</sup> it is probable that the higher aspect ratio of CNF with respect to CB nanoparticles leads the formation of a conductive path

**Table VI.** Quasi-static tensile properties of the nanocomposites containing both CB and CNF, with a total nanofiller content of 2 wt%.

Sample	E (GPa)	$\sigma_b~({ m MPa})$	$arepsilon_b\ (\%)$
Epoxy-CNF-2	$3.31 \pm 0.05$	$50.2 \pm 2.4$	$3.5 \pm 0.1$
Epoxy-CB/CNF-20/80-2	$3.30 \pm 0.10$	$51.6 \pm 1.2$	$3.6\pm0.1$
Epoxy-CB/CNF-50/50-2	$3.38\pm0.05$	$52.8 \pm 1.3$	$3.7 \pm 0.1$
Epoxy-CB/CNF-60/40-2	$3.37 \pm 0.08$	$54.6 \pm 1.5$	$3.8 \pm 0.1$
Epoxy-CB/CNF-70/30-2	$3.40 \pm 0.12$	$55.1 \pm 1.1$	$3.9\pm0.1$
Epoxy-CB/CNF-80/20-2	$3.54 \pm 0.10$	$57.8 \pm 1.3$	$4.0 \pm 0.1$
Epoxy-CB/CNF-90/10-2	$3.58 \pm 0.10$	$58.6 \pm 1.5$	$4.1\pm0.1$
Epoxy-CB-2	$3.61\pm0.10$	$58.7\pm0.5$	$4.2\pm0.1$



Fig. 5. (a) Electrical resistivity as a function of the nanofiller content for ( $\blacktriangle$ ) Epoxy-CB-x nanocomposites (x = 1-5 wt%), (•) Epoxy-CNF-x nanocomposites (x = 1-4 wt%). (b) Electrical resistivity as a function of the CB/CNF ratio for nanocomposites with  $(\blacklozenge) 0.5 \text{ wt\%}, (\blacktriangle) 1 \text{ wt\%},$ (•) 2 wt%, (■) 3 wt% total amounts of nanofillers.

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AME at lower filler loadings, but after the percolation threshold the contribution of the two nanofillers on the electrical conductivity of the composites is practically the same. According to the literature data, matrices with an electrical resistivity as low as  $10^4 \ \Omega \cdot cm$  seem suitable for electrical monitoring,18,42-44 therefore both CB and CNF nanocomposites at filler concentrations higher than 2 wt% could be considered as good candidates for self-monitoring applications.

In Figure 5(b) the electrical resistivity of the nanocomposite systems containing both CB and CNF are plotted as a function of CB relative amount. In most cases, it can be seen how electrical resistivity roughly follows the rule of mixtures. Interestingly, a negative deviation from linearity can be detected for the systems with a total filler content of 2 wt%. Resistivity data follow a linear trend until a CB relative amount of 60-70% is reached, and then a minimum is detected for a CB/CNF ratio of 90/10. As reported by Sumfleth et al.,<sup>16</sup> it can be hypothesized that the fine dispersion of CB and CNF leads to the formation of co-supporting networks, in which CB agglomerates are interconnected by CNF dispersed in the interparticle region. Under these conditions the formation of a conductive path within the matrix is favoured.

On the basis of thermo-mechanical and electrical characterization, it emerges that 2 wt% nanofilled systems display good conductivity values with acceptable values of tensile strength and glass transition temperature. Therefore, Epoxy-CB/CNF-90/10-2 sample was chosen for the subsequent characterization of the electrical monitoring of tensile mechanical behavior under ramp and creep loading conditions.

# 3.3. Monitoring the Mechanical Response **Under Ramp and Creep Conditions Through Electrical Resistivity**

Ramp (i.e., constant strain rate) tensile tests were performed on Epoxy-CB/CNF-90/10-2 samples. Stress-strain curve and the relative electrical resistance variation  $(\Delta R/R_0)$  during tensile test on the nanocomposite samples are compared in Figure 6. It can be noticed that  $\Delta R/R_0$ follows a linear trend for small deformations (i.e., lower than 0.5%), and that for higher strain levels the slope of the curves slightly decreases. When the final failure is approached, a sudden increase of  $\Delta R/R_0$  values, probably due to a rapid damage evolution within the matrix, can be detected. As reported by Nanni et al.,<sup>44</sup> the separation between conductive particles at an increasing strain results in a higher electrical resistance. Sensitivity is enhanced since the conductive particles gradually separate under strain, with a consequent enhancement of the electrical resistivity. Moreover, as the stress at break is approached, a permanent separation between particles occurs due to cracks nucleation, with a sudden increase of the resistance values. It can be therefore concluded that the selected nanocomposite system can be electrically monitored when a ramp load is applied.



Fig. 6. Stress-strain curve and relative resistance variation during ramp tensile test on Epoxy-CB/CNF-90/10-2 sample.

Room temperature creep compliance of neat matrix and Epoxy-CB/CNF-90/10-2 nanocomposite are compared at various stress levels in Figure 7(a), while creep compliance data at 50 °C are reported in Figure 7(b) for two different stress levels. Both at room temperature and at 50 °C, nanofilled sample manifests an interesting improvement of the creep stability with respect to the neat matrix. In fact, both elastic and viscoelastic components of the creep compliance are remarkably reduced by nanofiller introduction. As previously reported,<sup>38,45</sup> the stabilizing effect provided by a nanofiller in a polymer matrix is more evident at elevated stress levels or at elevated test temperatures. Therefore, an appropriate combination of carbon nanofillers can be exploited for preparing moderately conductive materials, concurrently enhancing their creep stability.

In Figure 8, creep compliance and electrical resistance variation of Epoxy-CB/CNF-90/10-2 sample are reported on the same plot for creep tests at various stresses performed at room temperature (Fig. 8(a)) and at 50 °C (Fig. 8(b)). At room temperature, a sudden increase of the



**Fig. 7.** Comparison of the creep compliance of the neat matrix (--) and of the Epoxy-CB/CNF-90/10-2 nanocomposite (—) at (a) room temperature and (b) at 50 °C, for different applied stresses.



**Fig. 8.** Creep compliance and resistance variation during creep loading of Epoxy-CB/CNF-90/10-2 sample at various applied stresses at (a) room temperature and (b) at 50 °C.

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electrical resistance upon load application can be observed, proportionally to the stress level. It is interesting to note how  $\Delta R/R_0$  tends to decrease with creep time for applied stresses of 30 and 40 MPa, while at 50 MPa an almost flat plot can be detected. At 50 °C creep compliance values are noticeably higher than those registered at room temperature, and a progressive increase of  $\Delta R/R_0$  with time can be observed, regardless the stress level. It can be therefore concluded that the creep monitoring capability of the selected nanocomposites is strongly affected by the applied stress and the temperature. Different deformation and conduction mechanisms could be tentatively invoked to explain the trend of the electrical resistivity under creep conditions. It is well known that both microstructure and electrical conduction behaviour of polymeric materials is strongly influenced by time dependent mechanisms.<sup>46</sup> It can be hypothesized that, as a consequence of the instantaneous application of the creep load, the conductive network within the polymer matrix is destroyed and a resistivity increase is observed. When the kinetics of deformational processes is low (i.e., at low temperatures

and/or at low stresses), nanoparticles are able to re-form a conductive network, thus inducing a progressive decrease of the electrical resistance. On the other hand, at elevated creep stresses and/or temperatures, the higher kinetics of the deformational processes may hinder interparticle interactions and the subsequent re-formation of the conductive path, with a progressive increase of  $\Delta R/R_0$  values with time. In any case, further investigations are needed to gain a better comprehension of the observed phenomenon.

In order to investigate the potential of the selected nanocomposite system for monitoring the strain recovery processes after creep loading, some tests were performed. In Figure 9(a) the plots of the deformation of the Epoxy-CB/CNF-90/10-2 sample during creep and recovery tests performed both at room temperature and at 50 °C are reported, while in Figure 9(b) the correspondent relative resistance values are represented. When the



**Fig. 9.** (a) Relative deformation and (b) relative values of the electrical resistance of the Epoxy-CB/CNF-90/10-2 sample for a creep test and following recovery performed at room temperature and at 50 °C (applied stress of 20 MPa).

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creep test is performed at room temperature, the sample is able to recover practically all the applied deformation after unloading, while a remarkable residual deformation remains at the end of the recovery stage if the test is carried out at 50 °C. It is interesting to note how the electrical resistance measured at the end of the recovery at 20 °C is similar to the  $\Delta R/R_0$  value registered before the application of the load. On the other hand, at 50 °C the final resistance is considerably higher than that determined at the beginning of the creep stage. This permanent increase of the electrical resistance registered at elevated temperature is clearly related to the permanent deformation and/or damage evolution within the epoxy matrix accumulated during the loading stage.

# 4. CONCLUSIONS

Electrically conductive nanocomposites were prepared by by adding various amounts of carbon black and carbon nanofiersit bres in an epoxy matrix. The mechanical characterization 2.6 of the resulting composites highlighted how both CB and 2 2 CNF were able to improve the elastic modulus of the neat matrix, with a positive effect on its ultimate properties up to a filler content of 1 wt%. The introduction of both the nanofillers lead to a dramatic decrease of the electrical resistivity down to values of  $10^3-10^4 \ \Omega \cdot cm$  for filler loadings higher than 2 wt%. Moreover, a positive synergistic effect was detected for epoxy systems containing a total nanofiller amount of 2 wt% with a relative CB/CNF ratio of 90/10.

The monitoring of tensile tests under ramp conditions highlighted a direct correlation between the tensile strain and the increase of the electrical resistance over the whole duration of the tests. Monitoring of tensile creep tests evidenced a complex electrical response depending on the temperature and applied stress levels. Moreover, the epoxy nanocomposite under investigation allowed also an electrical monitoring of the strain recovery process after unloading. These results are encouraging for a possible application of the nanomodified epoxy for the preparation of fibre reinforced structural composites with damagesensing capabilities.

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