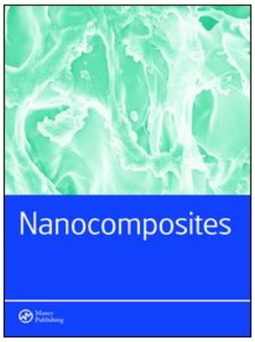

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Nanocomposites

ISSN: 2055-0324 (Print) 2055-0332 (Online) Journal homepage: http://www.tandfonline.com/loi/ynan20

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To cite this article: L. Dumas, L. Bonnaud & P. Dubois (2016): Novel porous nanohybrid materials with unexpected mechanical and electrical performance by pyrolysis of carbon nanotube-filled benzoxazine thermosets, Nanocomposites, DOI: 10.1080/20550324.2016.1254927

To link to this article: http://dx.doi.org/10.1080/20550324.2016.1254927

Novel porous nanohybrid materials with unexpected mechanical and electrical performance by pyrolysis of carbon nanotube-filled benzoxazine thermosets

L. Dumas*, L. Bonnaud and P. Dubois

Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers (CIRMAP), Materia Nova Research Center & University of Mons, 23 Place du Parc, B-7000 Mons, Belgium

Abstract In this communication, we highlight the remarkable and unexpected mechanical and electrical properties of new porous nanohybrid materials as readily obtained by a two-step preparation procedure. Neat multi-wall carbon nanotube (CNT)-reinforced benzoxazine nanocomposites were first produced. At a CNT content of 5 wt%, pyrolysis of the nanocomposites allowed for recovering porous monolithic nanohybrid materials exhibiting outstanding mechanical resistance (elastic modulus of ca. 50 MPa) for an electrical conductivity as high as 30 S cm^{-1}. Interestingly, long CNTs were found to build up an internal scaffold limiting the deformation of the foamed structure and preserving the geometric shape and dimensional integrity of the sample along the pyrolysis process. The concept of this novel approach paves the way for the production of a very promising choice of viable (nano)materials for use as domains as versatile as in energy storage, catalysis, or shielding applications.

Keywords Nanohybrid foam, Benzoxazine, Carbon nanotubes, Electrical conductivity, Porous materials, Pyrolysis

Cite this article L. Dumas, L. Bonnaud and P. Dubois: *Nanocomposites*, doi: 10.1080/20550324.2016.1254927

Introduction

Due to their exceptional mechanical, thermal, and electrical properties, carbon nanotubes (CNTs) have received a major attention in the field of materials science. Indeed, the resulting structures fabricated from these nanofillers hold technological promise for a variety of applications from structural composites to energy storage, through nanoelectronic.[1–3] However, to fully exploit the potential of such a kind of nanofillers, the control of their interactions with the matrix has to be achieved without altering the intrinsic properties of the individual tubes.[4,5] In polymer science, two main approaches have been developed to enhance the CNT/matrix interactions: namely the covalent and non-covalent chemical functionalization.[6–8] While the first method allows the establishment of strong linkages to the matrix, the number of covalent bonds generated is relatively low and the modification of the CNT surface is also known to disrupt its electrical properties. Conversely, the non-covalent approach maintains the CNT intrinsic properties with numerous supramolecular interactions but also introduces an additional interface between the filler and the matrix. The most promising and effective method is therefore to obtain naturally strong interactions between the CNTs and the matrix. Interestingly, a few polymers and precursors of polymerization are able to intrinsically establish these kinds of interactions with CNTs such as for instance benzoxazine resins with a high aromatic content.[9]

Benzoxazine resins are a new class of thermosetting resins that have recently gained a renewed interest due to their capacity to combine the excellent properties of traditional epoxy and phenolic resins. They exhibit near-zero volumic shrinkage during curing, low water absorption, high char yield, low coefficient of thermal expansion, easy curing without the need of hardeners or catalysts, and for some benzoxazines the T_g is even higher than the curing temperature.[10–12] Other interesting features are the great versatility of monomer molecular design afforded by the rather easy Mannich condensation of a phenol and an amine in presence of formaldehyde, with the possibility to incorporate additional functionalities or to use bio-based resources.[13,14] By selecting appropriate reagents bearing specific functional groups, it becomes relatively simple

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*Corresponding author, email ludovic.dumas@outlook.fr

Received 17 September 2016; accepted 24 October 2016
DOI: 10.1080/20550324.2016.1254927

to adjust the monomer architecture and its subsequent interactions with nanofillers. In a previous study,[15] we found that a diamino-based benzoxazine synthesized from phenol and p-phenylene diamine (coined as P-pPDA) was able to establish strong supramolecular interactions with CNTs leading to a significant enhancement of the properties of the resulting nanocomposite network. More specifically, a increase of more than 50 °C of the glass transition temperature was observed in the presence of very low content in CNTs, i.e. 0.5 wt%. In addition, upon thermal exposure to high temperature (i.e. 300–1000 °C), the shape of the nanocomposite is maintained although it degrades and turns into an abundant and highly cohesive char. Nevertheless, the electrical properties of the nanocomposite proved relatively restricted with a conductivity of 10^{-4} S cm^{-1} limiting possible advanced applications.

In this contribution, the remarkable CNT/P-pPDA interactions were leveraged to prepare a nanocomposite with a much higher (and unusual) CNT content, actually as high as 5 wt%, and to submit it to pyrolysis. This unique two-step preparation generates a porous nanohybrid foam with a controlled shape combining easy process preparation with excellent electrical conductivity and remarkable mechanical resistance and stiffness.

Experimental section

Materials

The following chemicals were purchased from Aldrich and used without further purification: 1,4-phenylenediamine (99%), phenol (99%) and paraformaldéhyde (95%). Technical chloroform was purchased from VWR and used as received. Multi-walled CNTs (MWCNTs) were provided by Nanocyl (NC7000) and were used without any further purification. According to the supplier, the CNTs have an average diameter of 9.5 nm, mean length of 1.5 μm, surface area ranging from 250 to 300 m^2/g and purity of min. 90%. The P-pPDA synthesis procedure can be found elsewhere.[15]

The pyrolysis of the nanocomposite samples was performed using a thermogravimetric analyzer (TGA) Q50 device from TA Instruments. Samples of 10 * 10 * 3 mm^3 were submitted to a temperature ramp from 25 to 1000 °C at a heating rate of 10°C/min under a nitrogen flow of 60 mL/min.

Characterizations

Thermomechanical properties were investigated using a dynamic mechanical thermal analysis (DMTA) apparatus (DMA 2980 Dynamical Mechanical Analyzer from TA Instruments). Specimens (70 × 12 × 3 mm^3) were tested in a dual cantilever configuration with a dual cantilever length of 35 mm. The thermal transitions were studied in the temperature range of 25–350 °C at a heating rate of 3 °C/min and at a fixed frequency of 1 Hz. An amplitude of 18 μm was used corresponding to a strain of 0.043%.

The three-point bending stress–strain curves of nanocomposites were recorded at 20 °C at a constant deformation rate of 1 mm/min with a Lloyd LR 10 K tensile tester using rectangular-shaped specimens according to the NF EN ISO 14125:198 standard: 60 * 11.25 * 3 mm^3 with a useful length of 48 mm. The compression tests were carried out on squared samples of 10 * 10 * 3 mm^3 with a deformation rate of 1 mm/min. All mechanical data were determined based on the average of five independent measurements allowing calculation of error bars.

SEM–FEG images were obtained with a Hitachi SU8020 instrument using an accelerating voltage of 20 kV.

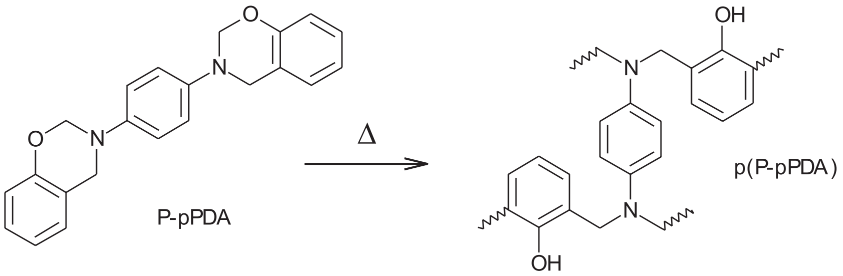
Four-probe dc measurements were performed using a Keithley BAG1 source Meter-2400 as the constant current source with a tension voltage of 40 V, and a Keithley 2010 multimeter to measure the voltage drop across the inner probes separated by 1.59 mm. At least five measures were made for each sample, recording *V*–*I* curve for each injected intensity.

Results and discussion

Nanocomposites preparation and characterization

The preparation process of the nanocomposite containing 5 wt% of CNTs involves the incorporation and dispersion of the CNTs into the P-pPDA resin following an ultrasonication step in chloroform using a finger-tip sonifier (Synaptec Nextgen Inside 500 equipment, 500 W, 20 kHz, 13 mm diameter ultrasonic-probe), for 2 min. The presence of solvent helps to dissipate the increase in temperature due to the powerful sonication and limits the subsequent auto-curing of the resin. The residual solvent is evaporated under vacuum at 140 °C and the nanofilled resin, in the form of a viscous paste, is then transferred into a stainless steel mold. If a higher CNT content is used, the viscosity of the uncured resin become too elevated and the material cannot be easily processed and degassed. A further degassing is carried out under vacuum in temperature before closing the mold and finally the nanocomposite is step cured in an air-circulating oven until the maximum cross-linking degree is reached (1 h at 140 °C, 2 h at 180 °C, 2 h at 220 °C, and 30 min at 230 °C) (Scheme 1).

To characterize the dispersion quality of CNTs, high resolution scanning electronic microscopy (SEM–FEG) was performed. As shown in Fig. 1, CNTs appear to be well dispersed



Scheme 1 Representation of the thermal ring opening polymerization of the P-pPDA resin

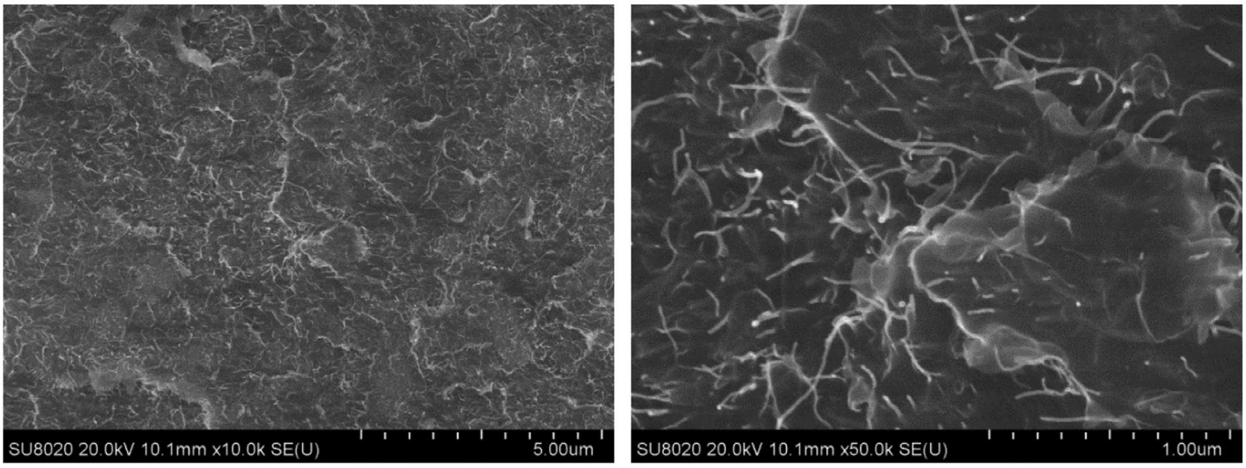


Figure 1 Representative SEM–FEG images of a breaking profile of p(P-pPDA) containing 5 wt% of CNTs at two different magnifications

and distributed within the whole cross-linked polybenzoxazine network: the long nanotubes are relatively well individualized while the dispersion state appears to be uniform. This homogeneous dispersion and high aspect ratio of CNTs in the nanocomposite enable a dense percolation network favorable for the preparation of an electrically conductive nanocomposite. It is noteworthy that without the help of any kind of external chemical functionalization, a relatively high content of CNTs, i.e. as high as 5 wt%, can be dispersed within P-pPDA precursors and similarly to previous works (with much lower CNT content) presented elsewhere,[9,15,16,21] the dispersion is found to be preserved during the curing process.

Additionally, mechanical and thermomechanical properties were characterized to investigate and evaluate both the performance of the nanofilled resin and the effect of high CNT content. The results were compared to those of p(P-pPDA) systems without CNT and with 0.5 wt% of CNTs. As can be seen in Fig. 2(a), the thermomechanical stability of the 5 wt% CNT-based nanocomposite is further enhanced compared to both the pristine matrix and the 0.5 wt% CNT-based nanocomposite. More specifically, the thermal stability is in this case higher than 275 °C while the thermomechanical transition temperature T_α reaches 340 °C representing a shift of more than 80 °C when compared to the pristine matrix and nearly 30 °C higher than the nanocomposite containing 0.5 wt% CNTs. This result appears of high interest since an optimal CNT content of 0.5 wt% was previously observed for CNT contents lower than 1 wt%.[16] In this low-CNT content range, the observed optimum was correlated to the coexistence of two mechanisms, namely interfacial constrains and free volume increase[17] but it seems that for a much higher CNT content, actually 5 wt% CNTs, the polymer chains must be still constrained and the network properties can be further reinforced.

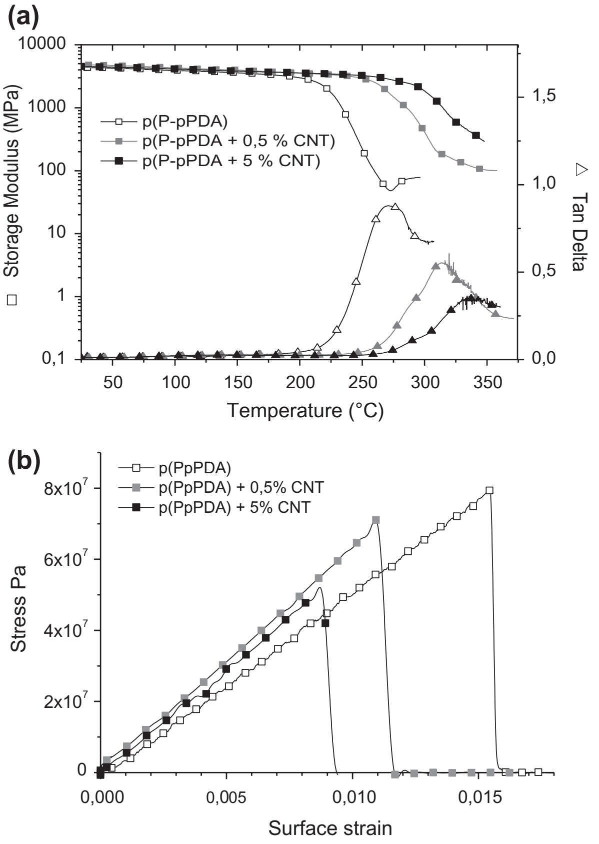


Figure 2 (a) Thermomechanical behavior of the p(P-pPDA) based nanocomposites obtained in dual cantilever mode (1 Hz, 3 °C min^{-1}, strain of 4.3 10^{-2}%). (b) Representative three-point bending stress–strain curves of p(P-pPDA) with different CNT contents

The steady mechanical tests in three-point bending mode attests for the mechanical resistance of the prepared nanocomposites with a maximal flexural strength of (60 ± 20) MPa for the 5 wt% CNT nanocomposite. This value appears slightly lower than the (85 ± 20) MPa and the (75 ± 30) MPa of the pristine matrix and the nanocomposite with 0.5 wt% of CNT, respectively, but as it can be seen on the maximal strain, the more the CNT content is increased, the more the material becomes brittle, i.e. it breaks at lower deformation rates. The value achieved (ca. 60 MPa) is higher than the typical targeted flexural strength of 25 MPa for electrochemical devices such as bipolar plates as defined by the US Department of Energy.[18] A slight variation in the elastic modulus is also noticeable with the incorporation of CNTs which increases from (5.5 ± 0.3) GPa for the pristine resin, to (6.3 ± 0.3) GPa for the two investigated nanocomposites. Although this 15% increase seems relatively moderate and lower than the expected value of 12 GPa according to the Halpin–Tsai model[19] for a randomly oriented nanocomposite prepared with such multi-wall CNT with an intrinsic modulus of 450 GPa, this value is found to be in good agreement with what is reported in the literature. Indeed, the modulus increase recorded for other polybenzoxazine resins (*prepared with bisphenol A and 3-aminophenoxyphthalonitrile*) filled with CNTs was also reported to be quite limited.[20] For other resins such as epoxy, the literature is more abundant but the increase in the mechanical properties appears also to be limited. As examples, Allaoui *et al*.[21] measured an increase in modulus from 0.12 GPa to 0.47 GPa on addition of 4 wt.% nanotubes; Breton *et al*.[21] observed an increase in modulus from 2.75 to 4.13 GPa with addition of 6 wt% of CNT and Xu *et al*.[22] observed in their side a significant increase in modulus from 4.2 to 5 GPa at only 0.1 wt.%. Nevertheless, the main aim on this study was not to reinforce the mechanical properties of the P-pPDA resin with 5 wt% of CNT, which constitute an important amount for a nanocomposite point of view, but to show that the material filled with this high CNT content still presents sufficient mechanical properties, i.e. which are not degraded.

The electrical conductivity of the nanocomposite based on P-pPDA was evaluated and the results are gathered in Table 1. More specifically, the four-probe measurements with a direct current indicate a large increase in the electrical conductivity in the case of the 5 wt% CNT nanocomposite which reaches 0.2 S cm^{-1}. To the best of our knowledge, such a conductivity has never been reported for polybenzoxazine nanocomposites containing a carbon content maintained below 10 wt%, where the maximal conductivity mentioned is 10^{-3} S cm^{-1}.[9,16,23] It is only in the case of nanocomposites prepared with other types of polymer matrices that similar conductivities are achieved. For instance, a polydimethylsiloxane matrix is found to reach a conductivity of around 10^{-1} S cm^{-1} in the presence of 5 wt% CNTs.[24] Higher electrical conductivity may be obtained by increasing dramatically the CNT content, up to 50 wt%, entering in this case the area of the so-called buckypapers. For example, Chapertegui *et al*.[25,26] were able to prepare a CNT-Benzoxazine buckypaper showing a very interesting electrical conductivity, close to 30 S cm^{-1}. Interestingly, the maximal current allowed before breakdown is severely increased for the 5 wt% CNT-based polybenzoxazine nanocomposite stressing the possible transfer of higher energy through the material without altering its integrity.

Table 1 **Electrical properties of nanocomposites and nanohybrid samples with different CNT contents**

Samples	Conductivity, S cm^{-1}	Maximal current, mA (V = 40 V)
Bulk materials		
p(P-pPDA)	Not conductive	–
p(P-pPDA) + 0.5 wt% CNT	(5 ± 1) 10^{-4}	0.5
p(P-pPDA) + 5 wt% CNT	(2.0 ± 0.5) 10^{-1}	100
Pyrolyzed samples		
p(P-pPDA)	Not measurable	–
p(P-pPDA) + 0.5 wt% CNT	8.0 ± 0.4	>1000
p(P-pPDA) + 5 wt% CNT	30 ± 5	>1000

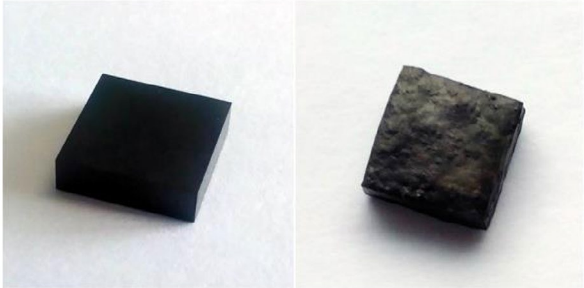


Figure 3 **Illustration of the sample shape preservation on a sample of 1 cm². Left: before pyrolysis, right after a pyrolysis at 1000 °C under N$_2$**

From nanocomposite to nanohybrid

Table 1 highlights also the remarkable increase in the electrical conductivity of the different materials after the one-step pyrolysis treatment until 1000 °C. This type of behavior is only achieved with P-pPDA resin containing CNTs, which allows a shape preservation during pyrolysis on a useful macroscopic scale as pointed out by Fig. 3. For other benzoxazine resins or for the CNT-deprived p(P-pPDA), the thermal treatment degrades severely the sample while the shape loses its integrity and is easily collapsible.[15] As a result, the pyrolyzed p(P-pPDA) cannot be subjected to the electrical conductivity measurement due to insufficient mechanical resistance. The conservation of the shape integrity is also correlated to experimental issues, and mainly related to the homogeneity of the heating on the sample. As a TGA furnace is used to perform the pyrolysis, the material dimensions must be sufficiently restricted to be located in the homogeneously heated area.

In addition to the preservation of the shape after pyrolysis, the main relevant result lies in the sharp increase in several decades of the electrical conductivity which reaches (30 ± 5) S cm^{-1} for the 5 wt% CNT nanohybrid. Such a value constitutes a real progress in the field of polybenzoxazines and carbon nanofillers as it is similar to the conductivity of CNT buckypapers.[26] For other comparison, the electrical conductivity of a pellet of CNTs obtained by compression was only of 10 S cm^{-1} which is close to the reported value of the macroscopic electrical conductivity of MWCNTs.[24] The relatively low conductivity of the pellet of CNTs compared to the conductivity of one single tube may be imparted to a poor contact between each tube. The pyrolysis appears thus to generate a carbonaceous cement binding the CNTs all together, forming a dense network and therefore promoting good electrical contact. Moreover, an increase in the CNT concentration led to a higher electrical conductivity of the pyrolyzed sample while the maximal current before breakdown was relatively similar and reached in fact the maximal available value from the system apparatus of 1 A keeping the linear relation between tension and current.

Carbonization of nanocomposites made of CNTs is currently a hot topic as these materials can lead to highly conductive porous nanohybrids with a main interest in energy field due to the combination of high electrical conductivity with large surface areas. Cao *et al*.[27] have prepared a nanohybrid film by an *in situ* carbonization of a cellulose nanofiber/CNT

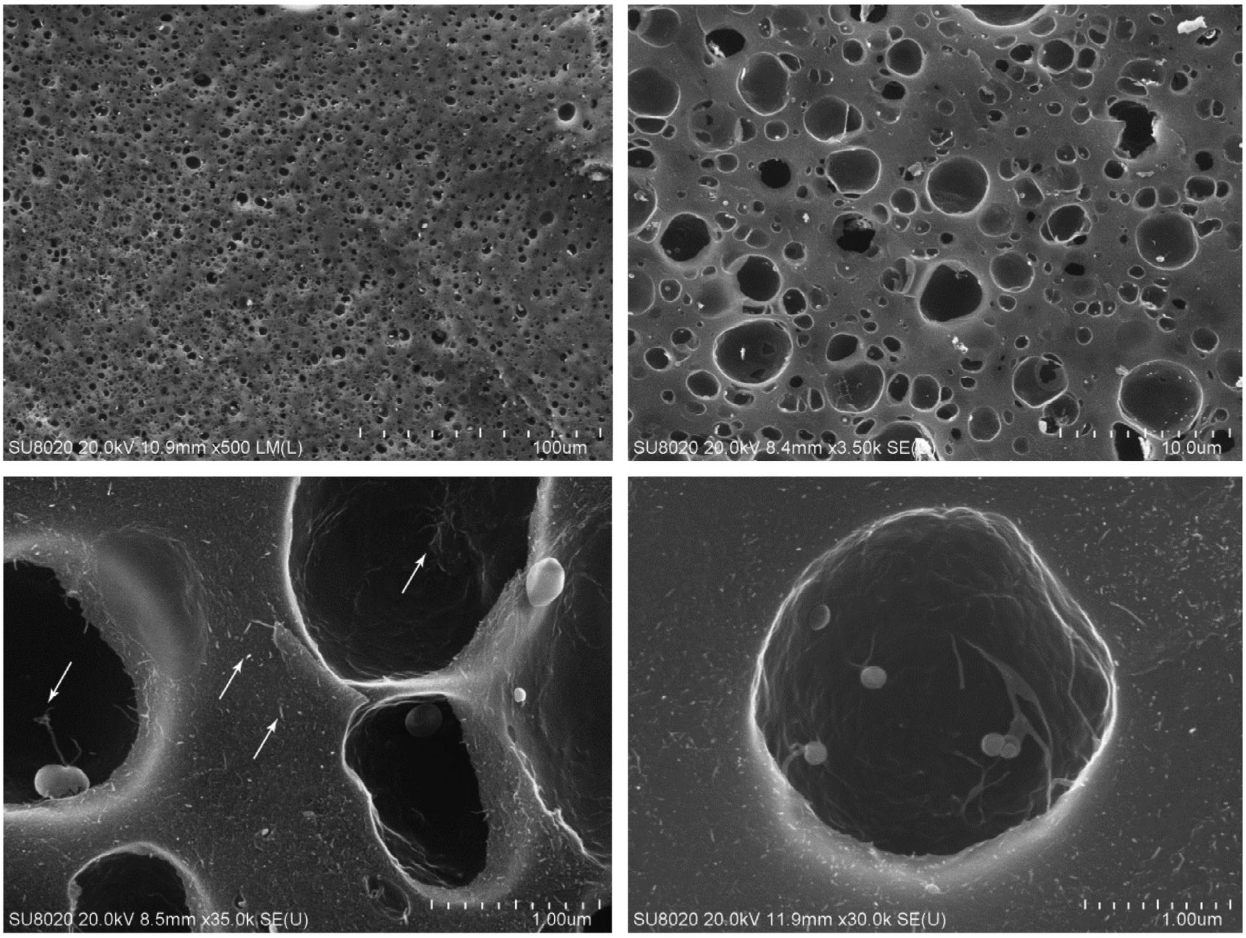


Figure 4 SEM–FEG images of the pyrolyzed nanohybrid containing an initial content of 5 wt% of CNT at different magnification. Arrows highlight the presence of CNTs both in cell wall and on the surface inside pores

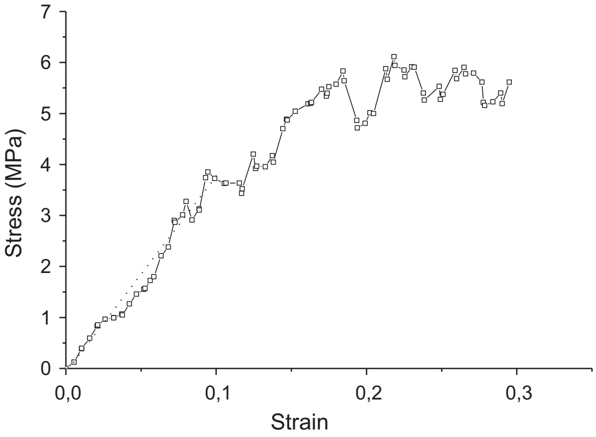


Figure 5 Representative compression curve of the nanohybrid prepared with 5 wt% of CNT

blend with a 1:2 ratio (corresponding to a 66 wt% CNT content). They obtained a flexible film with a conductivity of about 32 S cm^{-1} after the carbonization procedure. Another interesting strategy was developed by Worsley *et al*.[28,29] It consists in the preparation of a super-elastic foam, thanks to the carbonization of an assembly of CNTs, or graphene, maintained by a phenol/formaldehyde resin which was obtained through a dispersion in water. The pyrolyzed materials exhibited electrical conductivities from 0.8 to 3 S cm^{-1} for a 30 wt% CNT content depending on the foam density. These different strategies allow the preparation of CNT-based nanohybrids combining three main properties at different levels: high electrical conductivity, porosity, and sufficient mechanical properties allowing their auto support. The benzoxazine nanohybrid prepared with 5 wt% of CNT combines also these special features.

Indeed, as illustrated in Fig. 4, the diameter of the pores varies from *ca.* 5 μm to 10 nm while the interior of the pores is covered with bristling nanotubes offering an increased surface area. The macroscopic porosity rate is about 50% (a weight loss of 50% is recorded during the pyrolysis at 1000 °C) for a bulk density of about 0.6 as determined from the physical dimensions and mass of each sample. The cell walls are constituted of the char residues of the pyrolyzed p(P-pPDA) armored with an internal scaffold of CNTs. This internal scaffold presents two advantages. First, as discussed in the introduction, it limits the volumic change in the sample during the pyrolysis (the measured macroscopic volumic shrinkage is lower than 6%) and secondly, it brings a mechanical reinforcement to the foam.

A mechanical characterization in compression was carried out in order to evaluate the mechanical resistance of the pyrolyzed nanohybrid prepared with 5 wt% CNTs. As shown in Fig. 5, the foam presents a remarkable mechanical strength although it is issued from a thermally degraded material. The average mechanical strength is about (6.0 ± 0.5) MPa. In other words, it means that a sample of 1 cm^2 of area (typically the sample presented in Fig. 3) can support a weight of 60 kg without collapsing. This result is very promising and it can be related to the mechanical resistance of 15.6 MPa reported in the literature for an optimized and well-defined porous carbon monolith also obtained through the pyrolysis of a poly(benzoxazine-co-resol) made material obtained through an emulsion–gelification process.[30] The potential of these new nanohybrids lies in the combination of interesting thermal stability and the convenience of the preparation following a simple and direct method contrary to the mult-istep and long sol–gel preparation method required for carbon areogels.[29,31,32] Furthermore, and despite some irregularities of the curve due to un-optimized surface state, an elastic modulus of about (50 ± 10) MPa was calculated with a strain at the limit of elasticity comprised between 0.1 and 0.2. The sample stiffness appears firstly to be quite limited, but the mechanical properties are known to be closely related to the porous structure which is itself dependent on the heating rate of the pyrolysis process due to a competition between gas evolution and gas diffusion.[33] In our case, the pyrolysis was by no means optimized and the unexpected mechanical resistance offered by the as formed porous structure lets expect a very promising way of improvement and further control of both the porosity and the resulting mechanical properties.

Conclusions

In this communication, we demonstrated a convenient and scalable two-step method to prepare a moldable nanocomposite based on the P-pPDA polybenzoxazine resin and CNTs which can be turned into a nanohybrid foam using a simple pyrolysis process. This approach takes advantage of the special interactions between CNTs and the selected P-pPDA resin conferring on a macroscopic scale, an excellent structural cohesion of the material during the pyrolysis despite a rapid heating rate. The resulting nanohybrid foam combines a multi-scale porosity, high electrical conductivity, and a remarkable mechanical resistance. This new concept, the viability of the process and the robustness of the foam can open new strategies for applications in various fields such as electromagnetic interference shielding,[34,35] electrochemistry,[36,37] catalysis,[38,39] or CO_2 capture.[40,41]

Acknowledgments

The authors wish to thank Wallonie and European Community for general support in the frame of the "Fonds de maturation: NANOBENZO project", the FEDER 2014–2020 program: HYBRITIMESURF, MACOBIO, BIOMAT and BIORG-EL projects, the INTERREG V program (BIOCOMPAL project) and the "Programme d'Excellence FLYCOAT" and the Interuniversity Attraction Pole Program initiated by the Belgian Science Policy Office.

Disclosure statement

No potential conflict of interest was reported by the authors.

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