

Multiscale benzoxazine composites: the role of pristine CNTs as efficient reinforcing agents for high-performance applications.

Ludovic Dumas,^{*a,b} Leïla Bonnaud,^a Marjorie Olivier,^b Marc Poorteman,^b and Philippe Dubois^{a,c}

^a *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.*

Fax: +32 (0)65 37 3484; Tel: +32 (0)65 374984; E-mail: ludovic.dumas@outlook.fr.

^b *Department of Materials Science, Materials Engineering Research Center (CRIM), University of Mons, 23 Place du Parc, B-7000, Mons, Belgium.*

^c *Department Materials Research & Technology, Luxembourg Institute of Science and Technology LIST, 41 Rue du Brill, L-4220 Belvaux, Luxembourg*

Abstract. A convenient and efficient approach is presented in this study for developing advanced thermosetting composite laminates reinforced or not with 0.5 wt% of pristine CNTs. A highly aromatic benzoxazine monomer was selected as the matrix for the preparation of carbon fiber composites due to its strong intrinsic affinities with CNTs. Fine CNT dispersion was achieved within the whole composite after fabric impregnation leading to a considerable increase of the glass transition temperature of about 50°C. The resulting multiscale composite exhibits an improved thermomechanical stability, up to 300°C and its room temperature flexural strength is enhanced from 520 to 700 MPa. Moreover, the confinement of neat CNTs within the whole composite is also found to have a beneficial effect on the fire properties and the water sensitivity of the composite. These promising results highlight that when neat CNTs are able to develop strong interactions with the aromatic resin, the resulting system can provide a new and efficient way to design and improve the properties of composite laminates.

Keywords: Benzoxazine, carbon fiber composite, nanoreinforced, carbon nanotube, prepreg.

Introduction

Carbon fiber-reinforced polymer composites have been extensively used in many high performance applications that require a combination of light weight, high thermal properties and excellent mechanical performances. They emerge as candidates of choice in structural applications, especially in aerospace and aeronautic, because of their excellent specific modulus and specific strength, but they are also widely used in automotive, extreme sports, and many other fields.¹⁻⁵ Usually, thermosetting matrix resins used for the manufacture of fiber-reinforced composites include unsaturated polyester, epoxy resin, phenolic resin, bismaleimide, etc. Nevertheless, the continuous increase in the performance requirements of advanced materials is a main driving force for the design of new matrix resins allowing to combine superior targeted properties such as high strength, high modulus, high-temperature performances as well as a ease of processability.

In this frame, benzoxazine resins, a relatively new class of thermosets, benefit from a growing interest as they allow for combining the main advantages of both traditional epoxy and phenolic resins. The characteristic functional group of these resins consists in a heterocyclic six-membered oxazine ring fused to a benzene ring, which homopolymerizes by a ring-opening reaction without the need of hardeners or catalysts. First prepared by Holly and Cope in 1944 for chemical purposes⁶, they were mainly popularized as thermosetting resins by Ning and Ishida in the 90's who introduced a solventless synthesis process and highlighted their excellent balance of material properties.^{7, 8}

Their henceforth well-known main features are: i) easy thermal curing, ii) limited shrinkage during curing, iii) high glass transition temperature, iv) low water absorption, v) high charring yield, vi) low thermal expansion coefficient and vii) low dielectric constant.⁹⁻¹² Nevertheless, the main interesting characteristic of benzoxazines is their easy and versatile synthesis by a Mannich-like condensation of three elementary compounds: a phenol, an amine and formaldehyde offering thereby an extraordinary monomer design flexibility that allows for tailoring a large range of properties.¹³ Benzoxazine resins present thus several advantages for the preparation of high performance composites. Compared to unmodified epoxies, they can have a 2.5 fold higher toughness, higher modulus and lower moisture absorption, and can outperform other comparable resin systems as a composite matrix.¹⁴

Following the success of the benzoxazine development in the scientific community, different studies on composites were readily driven in parallel. From the pioneer work of Shen and Ishida in 1996, where laminates were prepared from prepregs of unidirectional carbon fibers, the newly developed polybenzoxazine composites appeared to be able to exceed the performances of bismaleimide composites and compete with polyimide ones while retaining a good processability.¹⁵ Thenceforth, diverse benzoxazine-based composites were prepared, mostly with a prepreg route, starting from different fibers: carbon fibers (CF)¹⁴⁻²² and glass fibers (GF)²³⁻²⁷ but also natural fibers²⁸⁻³² as well as wood particles^{33, 34}. Some authors were also interested in the possibility to reinforce the composite properties by adding carbon nanotubes (CNTs) into the matrix

due to their exceptional mechanical properties combined with additional excellent thermal and electrical conductivities.^{35, 36} Xu et al. improved the interfacial properties of a carbon fiber composite by introducing partially reduced graphene oxide into a benzoxazine matrix prepared with phenol and methylene diamine. An increase of the mechanical strength and toughness was found for low nanoparticle contents (<0.5wt%).³⁷ Li et al. introduced CNT-doped polyethersulfone films in a CF-based benzoxazine/epoxy composite.³⁸ The CNTs improved greatly the fire properties of the composite material by stabilizing the formation of an insulating and cohesive char. The use of CNTs was also reported in case of GF composites. Xu et al. covalently grafted a benzoxazine molecule to the surface of CNTs and used it as a polymer matrix for glass fiber-reinforced laminates. A significant increase of 44% of the flexural strength was recorded with a rate of CNTs around 6 wt% while the thermo-oxidative stability was also enhanced.

Due to their high aromatic content, benzoxazine resins are likely to present excellent affinities with CNTs leading in certain cases to an outstanding nanoreinforcement.³⁹ In previous studies, a new benzoxazine monomer prepared with phenol and paraphenylene diamine (P-pPDA) was found to establish so strong interactions with unmodified CNTs that the network properties, and particularly the glass transition temperature, displayed an outstanding improvement with a positive shift of more than 50 °C ($T_g > 300^\circ\text{C}$) with the addition of only 0.5wt% of CNTs leading to an increased thermomechanical stability up to 250°C.^{40, 41} This exceptional behaviour seemed to be an interesting stepping stone for a further exploration of the development of advanced structural composites with the P-pPDA resin nanoreinforced with a small amount of CNTs.

Herewith we propose the complete preparation of a benzoxazine-based structural composite nanoreinforced by carbon nanotubes, from the synthesis of the resin, dispersion of CNTs, prepregs elaboration, to the final characterization of selected macroscopic material properties.

Experimental

Materials

The following chemicals were purchased from Aldrich and used without any further purification: 1,4-phenylenediamine (99%), paraformaldehyde (95%) and phenol (99%). Technical chloroform was purchased from VWR and used as received. Multiwalled carbon nanotubes (CNTs) 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%. Carbon fiber plain woven fabrics Twill Balanced IM7 12k from Bally Ribbon Mills was kindly provided by Techspace Aero, Safran.

Characterization

Thermo-mechanical properties were investigated using a dynamic mechanical thermal analysis (DMTA) apparatus (DMA 2980 Dynamical Mechanical Analyzer from TA Instruments). Specimens ($70 \times 12 \times 3 \text{ mm}^3$) were tested in a dual cantilever configuration with a dual cantilever length of 35 mm. The

thermal transitions were measured 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 %. One representative sample was used for the measurements.

The 3-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 14125:1998 standard: $60 \times 11.25 \times 3 \text{ mm}^3$ with a useful length of 48mm. A displacement sensor was used to determine the real sample strain.

The apparent interlaminar shear strength was evaluated in 3-point bending mode using small span-to-depth ratios according to the standard EN ISO 14130:1997 on specimens of $30 \times 20 \times 3 \text{ mm}^3$ with a useful length of 15 mm and a deformation rate of 1 mm/min. The compliance of the flexural machine was subtracted. 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.

The preliminary fire testing was conducted on a mass loss calorimeter (Fire Testing Technology Ltd.) following the ISO 13927:2015 procedure. Specimens with dimensions of $100 \times 100 \times 3 \text{ mm}^3$ were irradiated with a heat flow of 50 kW/m^2 . From this test, the time to ignition (TTI), heat release rate peak (PHRR), time to heat release rate peak (T-PHRR), and total heat release (THR) could be acquired.

The water sensitivity was evaluated on rectangular specimen immersed in refluxing water (100 °C) during different periods of time: 24h. After that, the samples were surface dried with paper, weighed and analysed by DMA.

Prepreg and composite manufacture - CF/p(P-pPDA).

The benzoxazine resin P-pPDA was synthesized following a procedure described in a previous study.⁴¹ The resin was then dissolved in chloroform with a 30 wt% concentration until a clear homogenous mixture was obtained. The carbon fabric patterns ($10 \times 15 \text{ cm}^2$) were impregnated by the resin by immersion into the P-pPDA solution. The solvent was then partially evaporated at ambient temperature followed by a conditioning under vacuum at 140 °C during 5 min leading to convenient handling prepregs.

Composite laminates composed of nine prepregs (fibre content: 65 wt%, 55 vol%, determined by the weight measurement of all the carbon fabrics and the final composite), were preheated at 140 °C, manually compressed before degassing in a vacuum oven at 140 °C for 5 min and finally compressed using an hydraulic press under 150 bars. The mold was then maintained with clamps and cured using the following cycle in a ventilated oven: 1h at 140 °C, 2h at 180, 2h at 200°C 30 min at 220°C and 30 min at 230 °C to ensure complete polymerization of the P-pPDA resin. Thereafter, the samples were slowly cooled down to room temperature before their unloading.

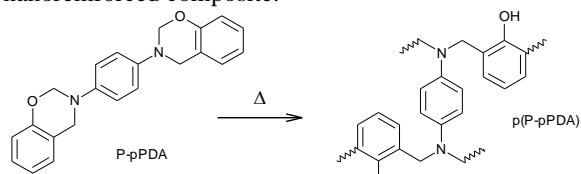
Nanoreinforced prepreg and composite preparation - CF/p(P-pPDA)/CNT.

The dispersion of 0.5wt% CNTs into P-pPDA was carried out by an ultrasonication step (Synaptec Nextgen Inside 500 equipment, 500 W, 20 kHz, 13 mm diameter ultrasonic-probe), in chloroform for 2 min.^{40, 41} An adequate amount of the obtained viscous solution was deposited and spread onto a carbon fabric. As the viscosity of the solution did not allow depositing a sufficiently thin layer of nanoreinforced resin, an additional fabric was deposited on the top surface, covering the resin. A small pressure was applied with a hand roll, helping the impregnation of the second carbon fabric and equalizing the resin quantity between the two fabrics. Depending on the initial resin quantity, additional carbon fabrics were added to prepreg leading to a semi product constituted of 3 to 4 carbon fabrics imbibed with the nanoreinforced resins. The so obtained “thick” prepreg was then degassed in a vacuum oven at 140 °C for 5 to 10 min. The preparation and curing procedure of the nanoreinforced composite laminate are performed following the conditions described in the previous paragraph and it contains as many layers as the unfilled composite laminate. A composite reinforced with 0.5wt% of CNT (with respect to P-pPDA) is obtained. The carbon fiber content is about 65 wt%.

Results and Discussion

Morphology of the composites

The P-pPDA resin used in this study is presented in scheme 1. The structure of the network after polymerization p(P-pPDA) is also shown. For the prepreg elaboration, the resin is dissolved in chloroform and the whole process is illustrated in Fig. 1, from the fabric impregnation to the final cured composite or nanoreinforced composite.



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

Fig. 1 b and e illustrate also the convenient and efficient handling of the prepregs which are rigid and unstacky due to the vitrification of the resin at ambient temperature ($T_g \sim 45^\circ\text{C}$). The resin content deposited onto the carbon fabric is for both the unfilled and CNT nanoreinforced composites around 35 wt% as determined by a simple macroscopic weighing. The final composite plates obtained after curing presented a regular surface covering with a global satisfying aspect and no macroscopic voids or defects were found when the plate was cut into several specimens.

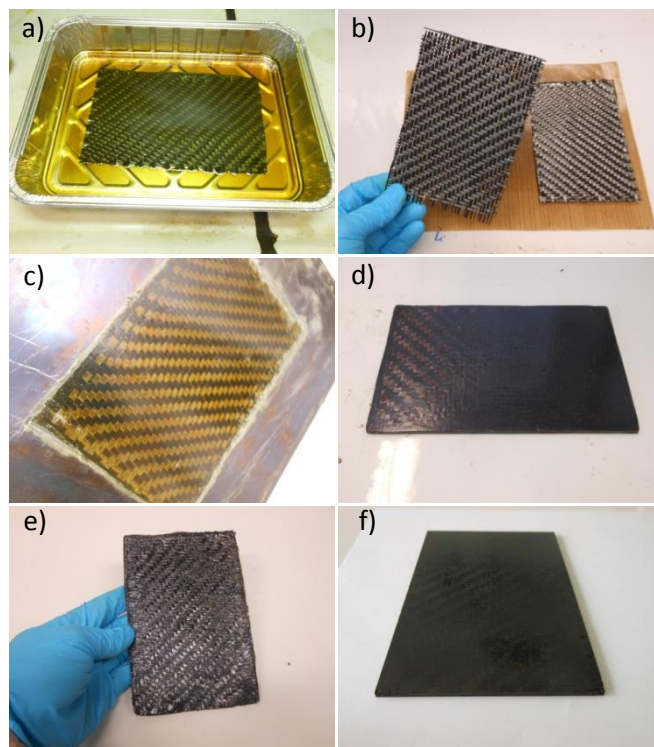
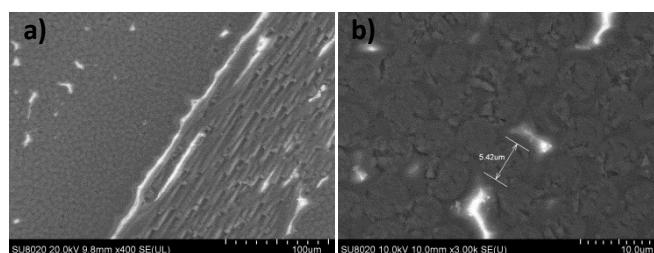


Fig. 1. Elaboration process of (a-d) CF/p(P-pPDA) and (e, f) CF/p(P-pPDA)/CNT composites. a) Impregnation; b) Impregnated carbon fabric after degassing; c) Uncured molded laminate; d) Cured composite; e) Nanoreinforced prepreg after degassing; f) Cured nanoreinforced composite.

The morphology of the composites and the resin distribution in the carbon fabric were investigated by SEM-FEG. SEM-FEG images of cross-sections of CF/p(P-pPDA) and CF/p(P-pPDA)/CNT are shown in Fig. 2. It can be observed that both composites show a good resin distribution and interfacial adhesion between the resin and the fibers. Indeed, the resin is well impregnated into each carbon fiber yarn, even in the case of the nanocomposite. The presence of the nanotubes did not modify the fabric impregnation by the matrix. A zoom on the cross section of a selected yarn (Fig 2. b, e and f) reveals no microscopic void and shows a good interface between each individual fiber and the matrix. Some fibers appear broken but no decohesion is visible on these pictures. The yarns seem to undergo mainly longitudinal cut during the sample preparation (Fig. 2 c and d). This observation stresses again the good fiber/matrices interface with low debonding. In case of the nanocomposite (Fig 2. d), the fibers appear to be cut in a more defined manner (there is no important roughness due to the cutout) which could suggest a stronger interface: the fibers are steadily maintained in the matrix during the cutting. Unfortunately, higher magnification did not allow for evidencing the presence of CNT in the matrix.



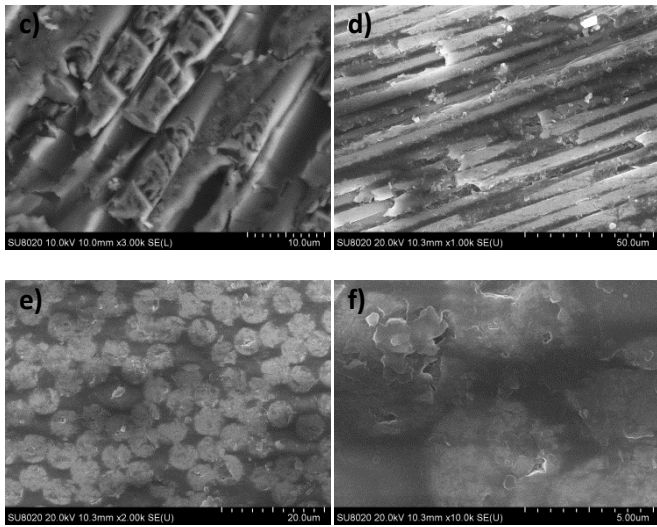


Fig. 2. SEM-FEG images of (a, b, c) CF/p(P-pPDA) and (d, e, f) CF/p(P-pPDA)/CNT composites.

Thermomechanical properties.

The good interfacial adhesion between fiber and matrix is also suggested by the thermomechanical properties of the composite. Fig. 3 shows the variation of the thermomechanical stability of the p(P-pPDA) matrix due to the carbon fabric. The storage modulus is obviously increased from nearly 4 to 25 GPa due to the CF, but more interestingly the thermomechanical stability is also improved as the storage modulus remains almost constant up to 230 °C, 20°C higher than for the pristine p(P-pPDA) suggesting a strong fiber/matrix interface. The thermomechanical transition temperature T_{α} identified by the $\tan \delta$ maximum is around 285°C, which is higher than the 250°C of an equivalent benzoxazine/CF composite prepared with bisphenol-A and 3,5-xylydine (Ba-35X)¹⁷ or to commercial benzoxazine preregs,²⁰ but the differences are due to a better thermomechanical stability of the resin. The properties of the new benzoxazine composite are thus intrinsically very encouraging without the addition of any CNTs.

The presence and the dispersion state of CNTs were then evaluated in an indirect way. Indeed, as it can be clearly seen on Fig. 3. The positive shift of the glass transition temperature due to the CNTs is also observed in case of CF-reinforced composite. The drop of the storage modulus of the composite associated to the T_g is shifted of more than 50 °C and the thermomechanical stability is insured until nearly 300°C for CF/p(P-pPDA)/CNT. This result constitutes an indirect proof that CNTs are well dispersed in the benzoxazine matrix displaying their role leading to nanoreinforcing by constraining the polymer segments around their surface.^{39, 42} The process of preparation of laminates elaborated in this study is thus compatible with nanoreinforcement by CNTs. The CNTs have to keep a sufficient dispersion in the matrix and not severely segregated allowing for effective nanoreinforcement. The storage moduli, in dual cantilever mode, taken at 50°C lie in the range of 25 to 30 GPa for both CF/composites with an apparent little improvement due to the presence of CNTs. This improvement is more visible in the rubbery region, *i.e.* at temperatures higher than 300°C where the difference is more highlighted due to the scale. The effect of CNTs is also evidenced by the evolution of the $\tan \delta$ peak intensities of the

CF/composites. The peak intensity is reduced when the composite contains CNTs traducing a lower number of polymer chains involved in the thermo-mechanical transition at the same temperature. Finally, the $\tan \delta$ peak maximum indicates a thermomechanical transition temperature T_{α} of 305 °C for the CF/p(P-pPDA)/CNT meeting the requirements for high temperature applications.

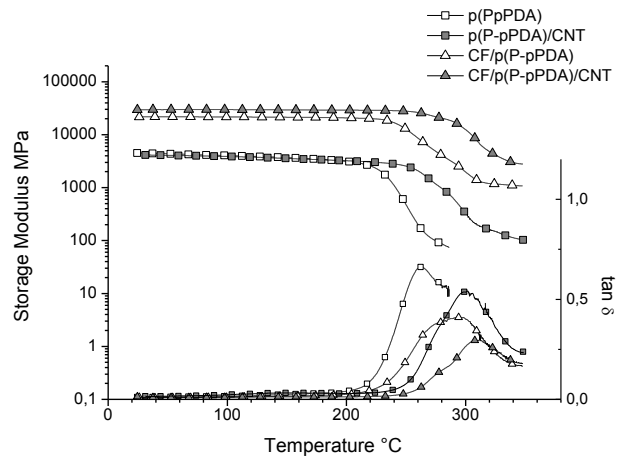


Fig. 3. Evolution of the thermomechanical properties as a function of CNT and CF reinforcement.

Mechanical performances

As a new benzoxazine resin studied in this work which intends to be used as a matrix for high-performance composites, it must have excellent mechanical properties. Representative flexural stress-strain curves of the matrices and composites elaborated are presented in Fig. 3 while the mechanical properties are listed in Table 1, including the flexural strength, elastic modulus and the surface strain at break; and the apparent interlaminar shear strength obtained in 3-point bending mode using small span-to-depth. All the properties presented in this section were average values obtained from at least 5 tests.

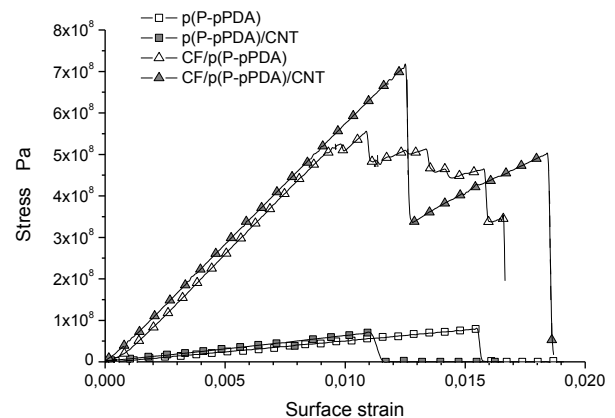


Fig. 4. Stress strain curves obtained in 3-point bending mode for the different matrices and composites.

Table 1. Mechanical properties of the benzoxazine matrices and composites.

	E_r (GPa)	σ_r (MPa)	ϵ_r (%)	τ_{13} (MPa)
p(P-pPDA)	5.5 ± 0.3	85 ± 20	1.5 ± 0.4	9 ± 2

$p(P\text{-}pPDA)/CNT$	6.4 ± 0.5	75 ± 30	1.2 ± 0.5	15 ± 6
$CF/p(P\text{-}pPDA)$	55 ± 6	520 ± 60	1.1 ± 0.1	32 ± 2
$CF/p(P\text{-}pPDA)/CNT$	59 ± 3	700 ± 80	1.3 ± 0.1	35 ± 5

First, the properties of the matrix alone are quite interesting with a flexural modulus E_f of 5.5 GPa and a flexural strength σ_f of 85 MPa. The value of modulus and flexural strength reported for a p(Ba-A) matrix is about 4-4.6 GPa and 75-95 MPa respectively.^{18, 33, 43} The p(P-pPDA) appears thus to be more rigid with a similar mechanical strength. It is well known that these properties are affected by intermolecular packing, free volume, and crosslinking density in the matrix. These results are therefore consistent with a higher crosslinking density and lower free volume for the p(P-pPDA) compared to p(Ba-A) due to its structure. Incorporation of 0.5wt% of CNT has also a positive effect on the modulus which is moderately increased with more than 15 % but no significant change was expected due to their random orientation and the very low content of nanofillers.^{35, 44} An increase of the brittleness of the sample is also observed with a lower strength and elongation at break while the apparent shear stress seems to be increased by more than 66%, however the results are relatively dispersed for the nanocomposite. The influence of CNTs on the matrix mechanical properties is thus relatively moderate but their presence does not degrade them radically.

The CF composites properties are most interesting as high strength and modulus are reached with an E_f of 55 GPa and a σ_f of 520 MPa. Comparison with bibliography is quite difficult as the type of fibers; their content, orientation and sizing are not the same. Kumar *et al.* reported for example an E_f of 32 GPa and σ_f of 320 MPa for a 50 wt% chopped carbon fiber with random orientation.¹⁸ Ishida *et al.* reported a σ_f of 550 to 620 MPa for a benzoxazine Ba-35X reinforced by 60 vol% of CF (plain fabric) depending on the sizing. They show also that the flexural strength can be severely increased up to 830 MPa by applying a coating of amine-terminated-butadiene-acrylonitrile (ATBN) on the fibers.¹⁷ Jubsilp *et al.* obtained a composite made of Ba-A added with pyromellitic dianhydride, reinforced with a fabric of CF (60 wt%).²¹ They reported an E_f of 60 GPa and σ_f of 525 MPa. Our results appear thus to be in a good average and are not so far from the values obtained for equivalent modified epoxy of phenolic with σ_f comprised between 650 and 775 MPa.¹⁷

The incorporation of CNTs impacts significantly the mechanical strength of the composite (Fig 3 and Table 1), with a sharp increase of σ_f from 520 to 700 MPa. The mechanical resistance of the material is thus severely enhanced by only a low amount of nanofillers. The reason of this improvement is not yet well understood, but the comparison of the apparent shear strengths τ_{13} which are comparable for both composites, with or without CNTs, seems to indicate that the fiber/matrix interface is moderately improved. The same behavior was already observed in case of a glass fiber benzoxazine composite reinforced with carboxylic acid functionalized CNTs.²⁶ An explanation given by the authors was that CNTs serve as sites of stress concentration, which would lead to high energy absorption and deflect the micro-cracks during the crack propagation process. In addition, and due to their high aspect ratio and high surface area, the CNTs are also likely to adhere to the surface of fibers which results in an improvement of the interlayer stress transfer. More recently, another

research team used partially reduced graphene oxide to reinforce a benzoxazine/carbon fiber composite.³⁷ The nanofillers were found in this case to increase the adhesion between the matrix and fiber. The mechanical strength was improved of nearly 22 % while the modulus remained almost the same.

Fire properties

To get a rough estimation of the fire resistance potential of the materials elaborated in this study, at least, two samples of each composition were tested by mass loss calorimeter, which is known to be a significant bench scale testing method to study the fire behavior of polymeric based materials. Figure 5 displays the heat release rate curves *versus* time for the composites obtained in the cone calorimeter test, and Table 2 gathers the characteristic data achieved.

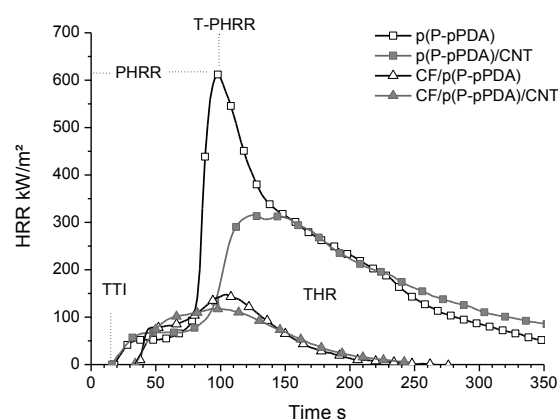


Fig. 5. Cone calorimeter properties of p(P-pPDA)-based composites irradiated with a heat flow of 50 kW/m².

Table 2. Cone calorimeter test results.

	TTI (s)	PHRR (kW/m ²)	T-PHRR (s)	THR (MJ/m ²)
$p(P\text{-}pPDA)$	25	610	98	67.6
$p(P\text{-}pPDA)/CNT$	23	320	132	62.5
$CF/p(P\text{-}pPDA)$	35	135	103	14.8
$CF/p(P\text{-}pPDA)/CNT$	34	113	91	17.4

The heat release rate peak (PHRR) of the unfilled p(P-pPDA) system is around 610 kW/m², in the same range as the values (628 - 751 kW/m²) usually reported for Ba-A resin.^{45, 46} This result is also significantly lower than the 800 kW/m² of a traditional epoxy system, *i.e.*, prepared with tetraglycidyl methylene dianiline and 1,4-butanediol diglycidyl ether with 4, 4'-diaminodiphenyl sulfone as the curing agent, used for aerospace applications^{47, 48}. The T-PHRR and THR of the p(P-pPDA) of 98 s and 67.6 MJ/m² respectively are roughly in the same range as the 80-105 s and 56-77 MJ/m² reported for Ba-A.^{45, 46} A higher T-PHRR indicates that the degradation and volatilization is delayed, while a higher THR shows that the combustion degrades a greater quantity of the sample and liberates more energy. In case of p(P-pPDA), the results are relatively similar to the ones of p(Ba-A) available in literature, expect the lower PHRR.

The addition of CNTs into P-pPDA-based system seems to affect its behavior in two main ways: PHRR is found to be reduced of nearly

half (from 610 to 320 kW/m²) and the time to PHRR appears to be delayed. Fig. 5 illustrates the valuable effect of CNTs with the main decrease of the peak intensity and its shift to longer times. The time-to-ignition and total heat release are not significantly modified by CNTs suggesting that the formed char is not strong enough to interrupt the continuous flame. Moreover, it was also observed that for loadings of CNTs higher than their percolation threshold, the thermal conductivity of CNTs could also be responsible for heat transfer to the degrading polymer below the charring layer. Anyway, the results are in rather good agreement with the ones reported in literature where a thermoplastic was also incorporated in the thermosetting matrix.³⁸

The behavior of the laminates seems quite different. First, the ignition time is delayed from ~25 to 35s, without significant impact of CNTs. The PHRR is also significantly decreased with the presence of carbon fibers which is commonly observed when carbon or glass fiber fabrics are incorporated in a resin because a lower quantity of resin is available for the combustion and the fibers, stable toward fire, may hinder the combustion process.^{25, 38} The value recorded for the CF/p(P-pPDA) composite (135 kW/m²) is lower than the ~ 500 kW/m² reported by Kimura et al.²⁵ for a blend of Ba-A and a bis-oxazoline reinforced by glass fibers and even lower than the ~300 kW/m² of the epoxy/CF system studied by Li et al.³⁸

The T-PHRR and THR of the CF/p(P-pPDA) of 103 s and 14.8 MJ/m² respectively are also improved compared to the ~60 s and 38 MJ/m² reported for a Ba-A/glass fiber system²⁵ suggesting a better fire resistance. Moreover, a comparison of the normalized THR per gram of resin of the p(P-pPDA) and CF/p(P-pPDA), which is of 1.83 and 0.33 MJ.m⁻².g⁻¹, respectively, indicates that all the resin is not consumed in case of CF-based composites. The presence of the carbon fabric does not allow the whole consumption of the matrix. Concerning the addition of CNTs to the composite, a decrease of the PHRR is also observed, but is more moderate (~16%) than in the case of resins without carbon fibers. Both TTI and THR values are not modified by the presence of CNTs whereas the T-PHRR is slightly decreased from 103 s to 91 s.

As a conclusion, the principal effect of CNTs on the fire resistance of the P-pPDA materials is a decrease of the PHRR while the generated heat is released more progressively instead of a sharp exotherm but the combustion is not limited.

Evaluation of the water sensitivity

The effect of water on the thermomechanical properties was evaluated for all samples. The variation of the T_g in dry or wet conditions is indeed a major aspect for high performance matrices especially for aeronautic applications.^{49, 50} The treatment of immersion in boiling water during 24h can be considered as very aggressive compared to the traditional normalized absorption test consisting in an immersion at ambient temperature, but the aim was to exacerbate the possible degradation and evaluate the potential of the resin in drastic conditions.

The impact of water on each sample is depicted in Fig. 6 and 7. An unambiguous plasticization is observed for all samples with a decrease of the thermomechanical transition temperature. For the p(P-pPDA) alone, both the evolution of the storage modulus and tan δ peak reveal a decrease of T_α of around 15°C allowing to still ensure a thermomechanical stability up to 200 °C. In case of p(P-pPDA)/CNT, the decrease of T_α is more pronounced (~30°C) but the

thermomechanical stability remains higher than the one of the dry p(P-pPDA) *i.e.* up to 220°C. No significant variation of the storage modulus value in the glassy state can be noticed.

Concerning the CF/p(P-pPDA) composite (Fig. 7), the plasticization occurs also with the same amplitude: the tan δ maximum is shifted to lower temperatures (~20°C) and the storage modulus remains stable up to 200 °C. However, the shape of tan δ peak is also modified and appears to be composed of two main transitions centered at 260 °C and 290 °C, respectively, resulting in a storage modulus drop in two stages. This irregularity would suggest a heterogeneity of the network due to a partial plasticization of the matrix. For the CF/p(P-pPDA)/CNT composite, a similar behavior is observed. While a severe plasticization leads to a reduction of the thermomechanical stability of nearly 50°C, the storage modulus decreases more progressively after this first transition forming a pseudo plateau before dropping in a significant manner after 260°C. The tan δ peak is also larger and suggests the superimposition of two main transitions centered around 260 and 300°C. By comparing the drop amplitudes of the modulus during the first transition, the presence of CNTs appears to be valuable. Indeed, in the case of CF/p(P-pPDA)/CNT composite, the storage modulus drops from 25 GPa to 15 GPa while for CF/p(P-pPDA), the loss is more pronounced and the modulus value falls from 18 GPa to 3GPa. The reasons of the limitation are not yet totally understood but the presence of CNTs constraining the polymer chains may hinder the water diffusion in the matrix and limit the increase of the free volume associated to the plasticization. Deeper investigations which are out of the scope of the present study are needed to take advantage of this effect in a more valuable way.

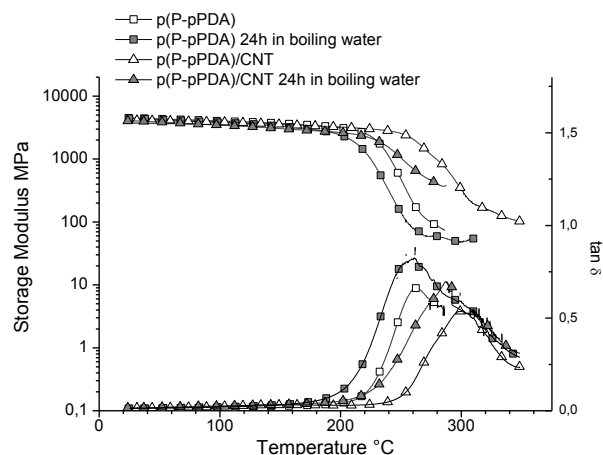


Fig. 6. Evolution of the thermomechanical properties of p(P-pPDA) and p(P-pPDA)/CNT after an aggressive immersion in boiling water during 24h.

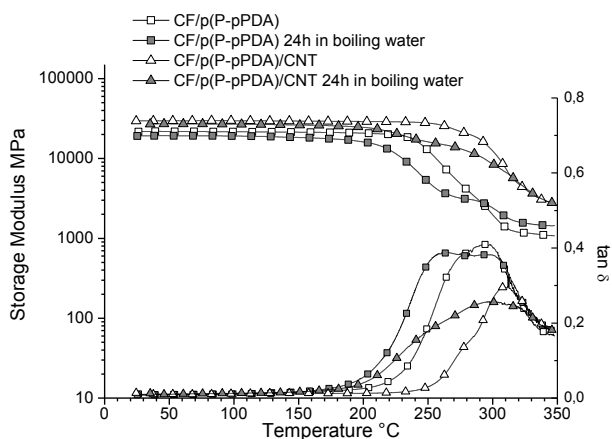


Fig. 7. Evolution of the thermomechanical properties of CF/p(P-pPDA) and CF/p(P-pPDA)/CNT after an aggressive immersion in boiling water during 24h.

Nevertheless, it is of interest to point out that although all the composites elaborated in this study are plasticized by boiling water, the thermomechanical properties of the aged laminate containing CNTs still remain better than these of the unaged composite without CNT. This trend is similar to that of the corresponding matrices and highlights that CNTs are able to bring significant improvements when they develop strong affinities with the matrix.

Conclusions

New benzoxazine/CF laminate composites were successfully elaborated from the synthesis of P-pPDA benzoxazine resin reinforced or not with a small amount of pristine CNTs (0.5wt%) prepreps. Interestingly, the properties of the resulting unfilled CF/P-pPDA composites are very promising with: i) a thermomechanical stability up to 230 and 200°C in dry and wet conditions, respectively; ii) a flexural modulus of 55 GPa and a flexural strength of 520 MPa; and iii) an intrinsic fire resistance. In addition, the study shows also the feasibility of the preparation of a structural composites with prepreps containing a fine dispersion of a small amount of carbon nanotubes (0.5 wt%) which significantly improve the overall set of properties with: i) a thermomechanical stability up to 300°C; ii) a flexural modulus of 59 GPa and an enhanced flexural strength of 700 MPa; iii) an improved fire resistance with a limitation of PHRR; and iv) a valuable effect of CNT toward water sensitivity.

These findings have highly significant implications for the design of new polybenzoxazine-based composites with high performance properties. It is expected that the multi-scale composites reinforced by CNTs exhibiting enhanced thermal, mechanical properties and fire resistance would be further explored for the development of advanced structural composites.

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