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Facile preparation of a novel high performance benzoxazine–CNT based nano-hybrid network exhibiting outstanding thermo-mechanical properties

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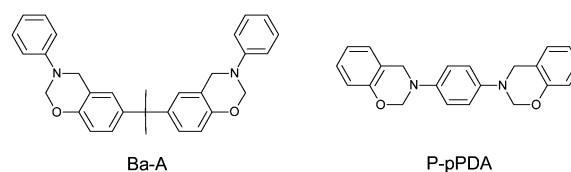
Untreated multi-walled carbon nanotubes (MWCNTs) have been dispersed in two benzoxazine precursors following an easy procedure. The strong intrinsic interactions of CNTs with a selected precursor give rise to the formation of a reinforced network with outstanding thermo-mechanical properties.

Due to their excellent intrinsic properties, carbon nanotubes have received much attention for applications in a wide range of fields and more particularly as reinforcement fillers in polymer composites.¹ Their exceptional mechanical properties combined with additional excellent thermal and electrical conductivities make them a filler of choice in the polymer nanocomposite field. However, to fully exploit the potential of such nano-fillers, the control of their interactions with the matrix has to be achieved.² Several approaches have been developed to enhance the interactions of CNTs with polymer matrices and can be classified into two main categories: the covalent attachment of reactive chemical groups and the noncovalent supramolecular adsorption of functional molecules onto the nanotubes.³ While the first method allows the establishment of strong linkages to the matrix, the number of covalent bonds generated is relatively low. Moreover, the modification of the CNT skeleton is also known to disrupt its electrical properties. Conversely, the noncovalent approach not only maintains the intrinsic properties of CNTs 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 have a naturally strong interaction between the CNT and the matrix.

Recently, benzoxazine resins have attracted extensive interest due to their potential 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 higher than the curing temperature.⁴ Other interesting features are the great versatility of the monomer molecular design with the incorporation of additional functionalities,⁵ and also the emergence of recently developed fully bio-based monomers,⁶ making these new resins of prime interest to prepare high performance thermosets. Moreover, only a few studies have been conducted to improve the properties of polybenzoxazines by incorporating nanofillers such as CNTs, and it is worth noting that the few studies reported in the literature mainly emphasise covalent binding.⁷ More precisely, the moderate improvements of mechanical and thermal properties that have been obtained are closely dependent on the kind of functionalization of the CNTs generating additional cross-link points. Non-covalent functionalization with hyperbranched polyborate has also been investigated in the literature.⁸ Both the dispersity and the thermal properties were found to be enhanced, but it is mainly due to a synergistic effect of the functionalizing agent and CNTs. To the best of our knowledge, the dispersion of untreated CNTs into a benzoxazine resin without the help of any kind of functionalization has not been achieved yet.

In this study, we report the first facile and efficient dispersion of neat CNTs within a polybenzoxazine matrix leading to a nano-composite hybrid network exhibiting outstanding thermo-mechanical properties. For this purpose, two benzoxazine monomers were used (Scheme 1). The first one is the most common commercial bifunctional monomer, *i.e.* the bisphenol A based benzoxazine (Ba-A). However, recent studies have shown that the thermal polymerization of this kind of monomer is accompanied by an irreversible degradation with the release of volatile imino species.⁹ In order to tackle this problem, *p*-phenylenediamine based benzoxazine



Scheme 1 Benzoxazine structures.

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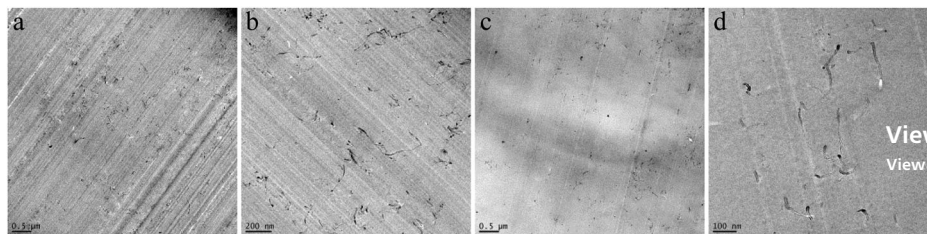


Fig. 1 Representative TEM images of cross-linked thermosets containing 0.5 wt% of CNT. (a and b) p(Ba-A); (c and d) p(P-pPDA).

(P-pPDA) was synthesized for the first time using a solventless method adapted from the well known classical procedure detailed elsewhere.¹⁰ The reaction can be summarized as follows: a fine mixing of *p*-phenylene diamine, paraformaldehyde and phenol in a stoichiometric ratio of 1 : 4.4 : 2 followed by reaction at 140 °C for 30 min. The as-synthesized P-pPDA precursor was then dissolved in CHCl₃ and filtrated in order to remove residual insoluble parts (weight yield >90%).

The incorporation and dispersion of 0.5 wt% MWCNTs were achieved by an ultrasonication step using a finger tip sonifier. Sonication was carried out on the filtrated mixture for P-pPDA, and directly in the melted resin for Ba-A for 10 and 2 min, respectively.

In both cases, a huge increase of viscosity was observed suggesting a fine dispersion state according to rheological theory.¹¹ However, since rheology in melt cannot be properly used in the case of the P-pPDA precursor due to its thermal reactivity, TEM analysis remains the most common way to characterize the dispersion quality of CNTs in such systems. Both nanocomposite resins were degassed under vacuum to remove solvent or entrapped air, and step cured until the maximum cross-linking degree is reached. Cross-linked nanocomposite thermosets p(Ba-A) and p(P-pPDA) were then subjected to further analysis. The distribution of CNTs into the matrices is shown in Fig. 1. From large scale images (a and c), a uniform and random dispersion with small agglomerates or clusters can still be observed in both matrices. Higher magnification images (b and d) showed evidence of effective disentanglement of CNT bundles and their individualization within the matrices. So without the help of any kind of external functionalization, the CNTs are dispersed into the two benzoxazine monomers and the dispersion is preserved during the curing process.

Interestingly, the two insulating thermosets became electrically conductive with a sharp jump of the volume conductivity from around 10⁻¹³ S cm⁻¹ (ref. 7c) to 10⁻⁴ S cm⁻¹ for both nanocomposites. These conductive properties indicated the formation of an electrical percolating network. Moreover, the conductivities were actually two orders of magnitude higher than those reported for a similar matrix for CNT contents 5 times higher (2.5 wt%).^{7c} Therefore the excellent electrical properties of pristine CNTs were preserved because of their non-functionalization.

Additionally, thermomechanical properties were investigated in dual cantilever mode on both nanocomposites and their respective reference matrices without nanotubes.

Fig. 2 highlights the spectacular change of thermomechanical behaviour of the p(P-pPDA) nanocomposite. Indeed, while both the storage modulus G' and $\tan \delta$ remain unchanged for p(Ba-A),

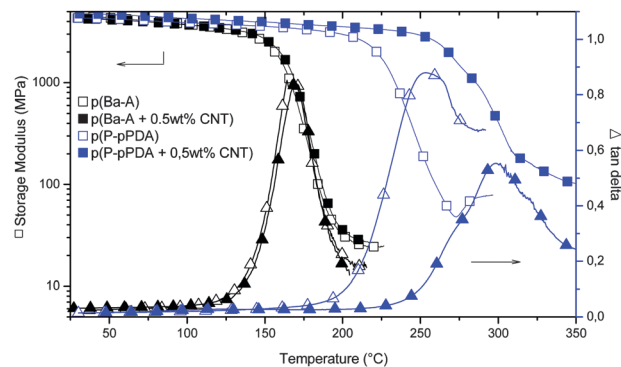


Fig. 2 Influence of CNTs on the thermomechanical behaviour of p(Ba-A) (black) and p(P-pPDA) (blue). Open symbols stand for reference samples and closed symbols stand for nanocomposites containing 0.5 wt% CNT. Frequency: 1 Hz, temp ramp rate: 3° min⁻¹.

the presence of CNTs in p(P-pPDA) leads to a significant improvement of the thermomechanical stability. The drop of the storage modulus associated to the glass transition was shifted by nearly 50 °C towards higher temperatures. The improvement of thermomechanical stability is so pronounced that the transition temperature T_g was in this case superimposed with the onset of thermal degradation which cannot be neglected at 300 °C. Such improvement represents an unprecedented achievement in the benzoxazine research field and may be correlated to the presence of interfacial constraints as described in the case of epoxy-carbon black nanocomposites.¹² This result implies a strong interfacial filler-matrix interaction which could be supramolecular. Indeed, it is well known that both carbon nanotubes and benzoxazines are able to form π - π stacking with other media.^{3d,13} Surprisingly, no effect has been found in the case of p(Ba-A) while the dispersion state was similar. This difference indicates that interactions between CNT and Ba-A are sufficient to promote a fine dispersion but are not as strong as in the case of P-pPDA to allow a subsequent modification of the material behaviour.

The binding affinity of CNTs and benzoxazine thermosets was supported by thermogravimetric analysis performed under nitrogen (Fig. 3). Despite the much higher char yield of p(P-pPDA), no effect of CNTs was firstly evidenced by the comparison of each TGA curve. Indeed, TGA profiles are not significantly modified by the presence of CNTs. However, the comparison of residue consistencies was unequivocal (photographs in Fig. 3). Indeed, for p(P-pPDA) containing CNTs, the shape of the sample was preserved during the pyrolysis, although a weight loss of nearly 50% was recorded. The same sample without nanotubes lost its physical integrity and no drastic variation was observed in the

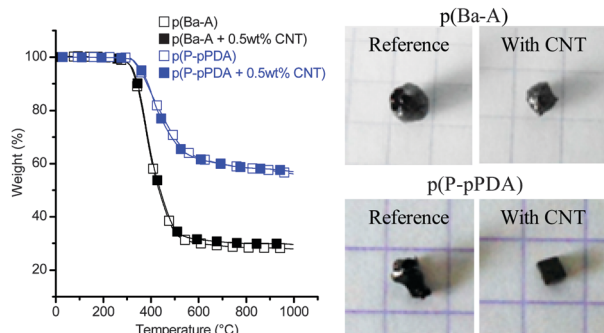


Fig. 3 TGA analyses of p(Ba-A) and p(P-pPDA) and their respective nano-composites containing 0.5 wt% of CNT. Under N_2 , $10^\circ C\ min^{-1}$. Pictures of char obtained after TGA analysis up to $1000^\circ C$ under N_2 .

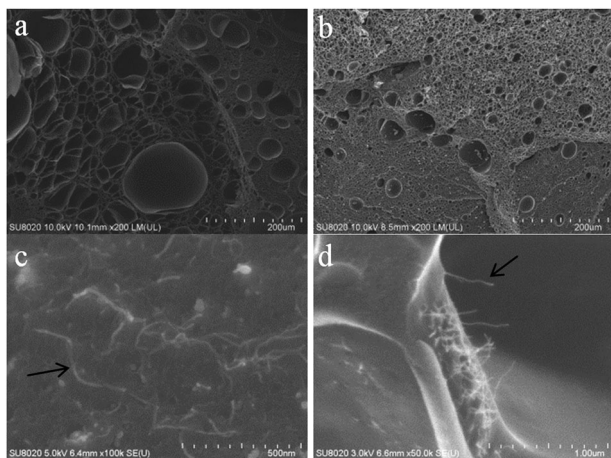


Fig. 4 SEM-FEG images of char residues of (a) p(P-pPDA) and (b–d) p(P-pPDA) containing 0.5 wt% of CNT. (c) Top surface, (d) the fractured cell wall (CNTs are shown by the arrows).

case of the p(Ba-A) matrix. The cohesion of the p(P-pPDA) nanocomposite char was quite unexpected and its mechanical resistance under a manually applied pressure was relatively high compared to the easy disintegration of p(P-pPDA) char. Based on these experimental observations, subsequent interest in char residue characterization has been awakened.

Fig. 4a and b show the different structures of the p(P-pPDA) char residues observed using SEM-FEG. A refinement of the foam structure (decrease of average alveolus size and dispersity) was obtained in the case of nanocomposites, which could explain its greater resistance.¹⁴ Indeed, the location of CNTs was observed both at the surface of the char (Fig. 4c) and inside alveolus walls (Fig. 4d). In addition, the strong cohesion of the structure and the limited volume modification of the sample during its thermal degradation could also be explained by the presence of special interactions between CNTs and the p(P-pPDA) matrix network.

In summary, preliminary experiments have shown that benzoxazine precursors (Ba-A and P-PDA) exhibit an excellent intrinsic affinity with pristine MWCNTs. Their dispersion could be achieved easily and further functionalization of CNTs or any chemical modification was not required. The strength of the interactions generated between CNTs and the polybenzoxazine

network seemed to be closely dependent on the chemical structure of the precursor and led, in the case of P-pPDA benzoxazine, to the establishment of unique properties. More specifically, the char cohesion and the remarkable thermo-mechanical reinforcement suggest the formation of a nanohybrid composite with an effective participation of nanotubes in the network. The development of new nano-hybrids presenting such outstanding properties is very promising especially within the framework of the increasing demand from industries such as Aerospace and Micro-electronics.¹⁵

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