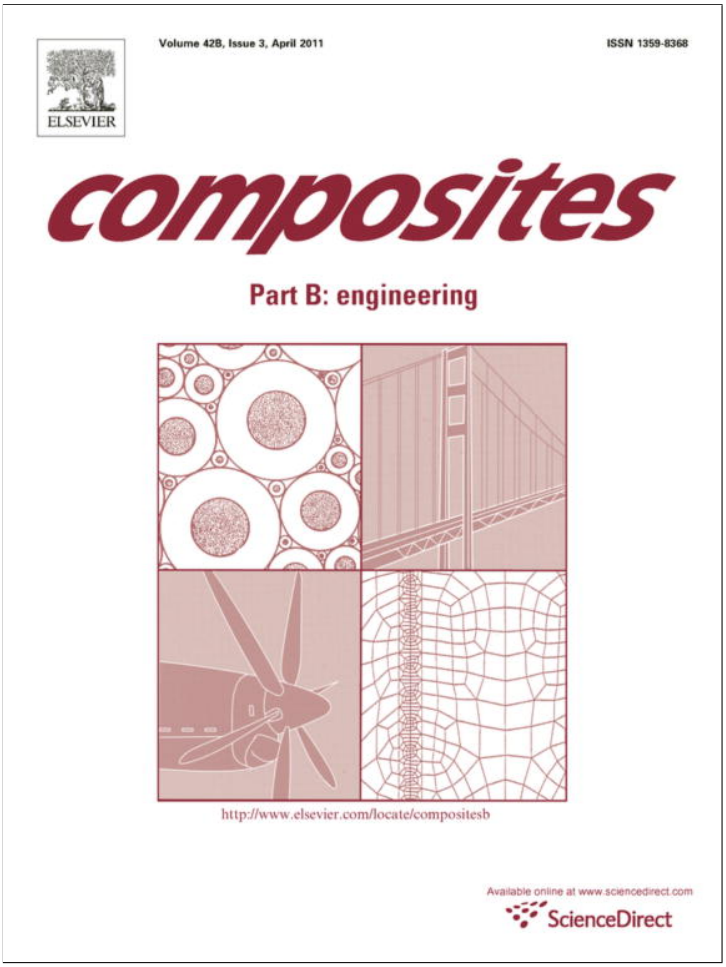

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In situ synthesis of polyoxadiazoles (POD) and carbon black (CB) as an approach to POD/CB nanocomposites

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ABSTRACT

Pristine carbon black was oxidized with poly(phosphoric acid) to produce carboxyl groups. The carboxyl groups were consecutively treated with hydrazine sulfate to introduce arylcarbonyl and $CONHNH_2$ groups. The groups on the CB surface were reacted with dicarboxylic acid to anchor the growing of polyoxadiazole chains. The properties of the bulk POD/CB composites were characterized by elemental analysis (EA), Fourier transform infrared (FTIR) and thermogravimetric analysis (TGA). The final composites were processed in films using a solution method aided by the use of a mini-calendar for final high shear mixing. Transmission electron microscopy (TEM), atomic force microscopy (AFM), dynamic mechanical thermal analysis (DMTA) and tensile tests were used to systemically characterize the high performance composite films. The POD composites with high molecular weight (in the order of magnitude of 10^5 g/mol) were soluble in polar aprotic solvents and stable at temperatures as high as 465 °C. The incorporation of the CB enhanced the overall mechanical properties of the composites at low CB content due to the presence of strong interfacial interaction between the polymer matrix and the filler.

1. Introduction

Nanocomposites are a class of composites in which the dimensions of the reinforcement phase are in the range of 1–100 nm. Because of their nanometer size characteristics, nanocomposites possess superior properties to more conventional composites reinforced with microsized fillers [1–3].

The development of high performance/high temperature polymers has been a demand from the aerospace industries seeking for new materials. Synthesis of polymers containing oxadiazole rings was part of a NASA program on high performance/high temperature polymer for potential use as coatings and composite matrices on aerospace vehicles [4,5]. Particularly, polyoxadiazole (POD) thermoplastic polymers have a great potential as structural material because of their superior thermal, chemical and mechanical properties [6]. POD fibers present a combination of properties (such as good strength and stiffness, good fatigue resistance and low density) that makes these fibers competitive in performance when compared to other reinforcing agents, such as glass, steel, and commercial high temperature fibers (Kevlar, X-500, Cermel, Nomex) [6–8]. Technological applications have also been reported in connection with the basic nitrogen atoms and aromatic character of the oxadiazole heterocyclic ring [9], enabling their use as emissive layers in light-emitting diodes [10–12], electron/proton conducting materials [13,14], electrochemical/acid sensors [15,16], and materials to prevent metal corrosion [17,18].

Recent applications of fiber reinforced polymers in aircraft propulsion systems have resulted in substantial reductions in both engine weight and manufacturing costs [19,20]. A major effort underway in this area is the development of high temperature reinforced polymers, usable up to temperatures as high as 425 °C [21,22]. Continued improvements in the stability of polymer matrices coupled with improvements in polymer/filler interfaces, composite processing, and oxidation-resistant coatings will yield reinforced polymers for use at high temperatures [21,23,24]. In this context, the reinforcement of POD polymer with nanofillers offer a possibility to obtain new light-weight materials suitable to high performance/high temperature applications.

Carbon-based nano-structured fillers include single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), carbon nanofibers (CNFs) and carbon black (CB) and they have attracted great attention due to their unique properties for a wide variety of potential applications such as nanocomposites, electronic devices, field emission display, hydrogen storage, and other fields of materials science [25,26]. When they are used as reinforcing additives for nanocomposites, they could deliver their outstanding properties to support matrices such as polymers [27–33], ceramics [34,35], and even low melting metals [36,37]. The resultant nanocomposites would possibly possess enhanced

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properties providing various potential applications for areas, which require affordable, light-weight and multifunctional materials.

Major problem is the difficult in dispersion of carbon-based fillers in a polymer matrix due to its strong van der Waals interactions. Another issue is the weak interfacial interaction between filler and polymer. The chemical modification is one of the most important approaches to overcome these problems [38,39]. Generally it arises from the functional groups on the surface of the filler, which are derived by the oxidation processes. Other approaches, including the direct dispersion of fillers in the polymer solution via sonication [40–42], surfactant assisted processing of filler-polymer composites [43,44], and in situ polymerization in the presence of the fillers [45,46], have been proposed for obtain polymer composites with homogeneously dispersed fillers.

Compared with carbon-based nano-structured materials as SWCNTs, MWCNTs, CNFs and fullerenes, carbon black nanoparticle is a relatively conductive carbon material composed of 90%–99% elemental carbon, more readily available, and has been widely applied in the industry because of its low price.

In this paper, we demonstrate a fast direct method to obtain POD/CB composites where the CB is in situ functionalized during the synthesis of poly(1,3,4-oxadiazoles) using poly(phosphoric acid) (PPA) as a condensing agent. PPA is a moderate acidic medium and promotes disaggregation to help homogeneous dispersion and purification of CB without or with little damages. Because of the different reactivity of monomers, significant lower synthesis time is required (4 h) to produce the composite polyoxadiazole compared to other composite polymers synthesized via in situ polymerization in PPA [47–50].

2. Experimental

2.1. Materials

All the reagents and solvents were purchased from Aldrich Chemical and used as received. Dicarboxylic acid 4,4′-diphenylether, DPE (99%), dimethyl sulfoxide, DMSO (>99%), hydrazine sulfate, HS (>99%), sodium hydroxide, NaOH (99%), poly(phosphoric acid), PPA (115% H_3PO_4), carbon black (CB, Average particle size: 18 nm, SSA: >250 m^2/g, Evonik/Degussa).

2.2. Instrumentation

Elemental analysis was conducted on a Carlo Erba Elemental Analyzer-Mod 1108. Infrared spectra were recorded on a Bruker Equinox IFS 55 spectrophotometer in the range 4000–400 cm^{-1}. TEM images were obtained using a Tecnai G2 F20 field emission transmission electron microscopy at an acceleration voltage of 200 kV; the samples were cut into slices of 80 nm thickness using a ultracut microtome with diamond knife. Atomic force microscopy of samples was done by using a multi mode scanning probe microscope model with a nanoscope IV controller by Digital Instruments Inc. (Veeco Metrology Group). AFM observations were carried out in air at ambient conditions (25 °C) using tapping mode probes with constant amplitude. Micrographs in topographic and phase contrast modes were obtained. A Viscotek SEC apparatus equipped with Eurogel columns SEC 10.000 and PSS Gram 100, 1000, with serial numbers HC286 and 1515161 and size 8 × 300 mm was employed to evaluate the weight average molecular weights of polymer and nanocomposite samples. The equipment was calibrated using polystyrene standards (Merck) with weight average molecular weights ranging from 309 to 9,44,000 g/mol. A solution with 0.05 M lithium bromide in dimethylacetamide, DMAc ($\geqslant$99.9%, Aldrich) was used as the carrier. Thermogravimetric analysis experiments were carried out in a Netzsch 209 TG, equipped with a TASC 414/3 thermal analysis controller. The bulk sample, under argon and air atmosphere, was heated from 100 °C to 900 °C at 10 °C/min. Dynamic mechanical thermal analysis was performed using a TA instrument RSA 2 with a film tension mode at a frequency of 1 Hz and 0.1 N initial static force. The temperature was varied from 25 °C to 500 °C at a heating rate of 2 °C/min and at a constant strain of 0.05%. Tensile testes were performed according to the ASTM D882-00 using a Zwick–Roell equipment with a 500 N load cell. The reported values correspond to an average of at least eight specimens.

2.3. Representative synthesis of sulfonated poly(1,3,4-oxadiazoles) with 0.1 wt.% CB load

The reaction condition for the synthesis of the POD was selected based on the previous studies [51]. Reactions were carried out in a 250 ml three-necked flask equipped with a dry nitrogen inlet tube, to keep the reaction atmosphere free of oxygen and water. Initially PPA, and carbon black (0.02 g), was added to the flask and heated up to 80 °C under sonication and simultaneous mechanical stirring during 1 h. Afterwards HS (0.031 mol) and DPE (0.013 mol) was added to the mixture and reacted under mechanical stirring at 160 °C during 4 h. At the end of the reaction, the final solution was precipitated in the form of stable fibers into water containing 5% w/v of NaOH. The final polymer yield was always close to 100% in respect to the limiting reactant.

2.4. Fabrication of the POD/CB films

To study the physical properties and morphology of the resultant composites, films were fabricated using a calander (model EXAKT 80E). Solutions with a polymer concentration of 10 wt.% were prepared in DMSO. The solution was magnetically stirred at 60 °C during 3 h. Afterwards the suspension was added to a mini-calander for final high shear mixing. The gap size between the rolls was 5 μm (1st roll), 10 μm (2nd roll) and the speed was set to 50 rpm. The suspension was then collected and re-dissolved in DMSO under stirrer at 60 °C during 3 h. Homogeneous films were cast in glass plates. After casting, the DMSO was evaporated in a vacuum oven at 90 °C for 24 h. For further residual solvent removal, the membranes were immersed in water bath at 50 °C for 24 h and dried in a vacuum oven at 90 °C for 24 h. The final thickness of the films was about 60 μm.

3. Results and discussion

3.1. Synthesis of POD/CB composites

In situ polymerization is one of the most viable rotes to prepare nanocomposites. Sulfonated polyoxadiazole composites containing different concentrations of carbon black (0.1, 0.5 and 1.0 wt.%) were successfully prepared via in situ polymerization. The proposed covalent functionalization of the CB is schematically shown in Fig. 1. Covalent attachment of POD onto the CB surfaces should be expected to occur by condensation reaction of COOH groups generated in situ on the surface of the CB with the NH_2NH_2 hydrazine monomer, leading to the formation of arylcarbonyl and CONHNH$_2$, respectively. The growing POD chains on the CB surface is expected to promote the physical contact with the polymer matrix allowing an efficient load transfer from the reinforcement phase to the matrix phase in the nanocomposites.

During the synthesis, the initial color of all reaction mixtures was black because of the CB dispersion (Fig. 2a). On all cases, the reaction mixtures were homogeneous with drastic increase in viscosity. The viscosity had reached the point that the dope stuck to the stirring rod, and this provided a visual signal that high

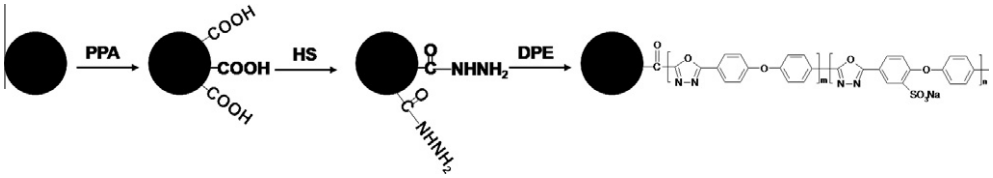

Fig. 1. Proposed route for the oxidation of the CB represented as a black circle and grafting of POD on its surface.

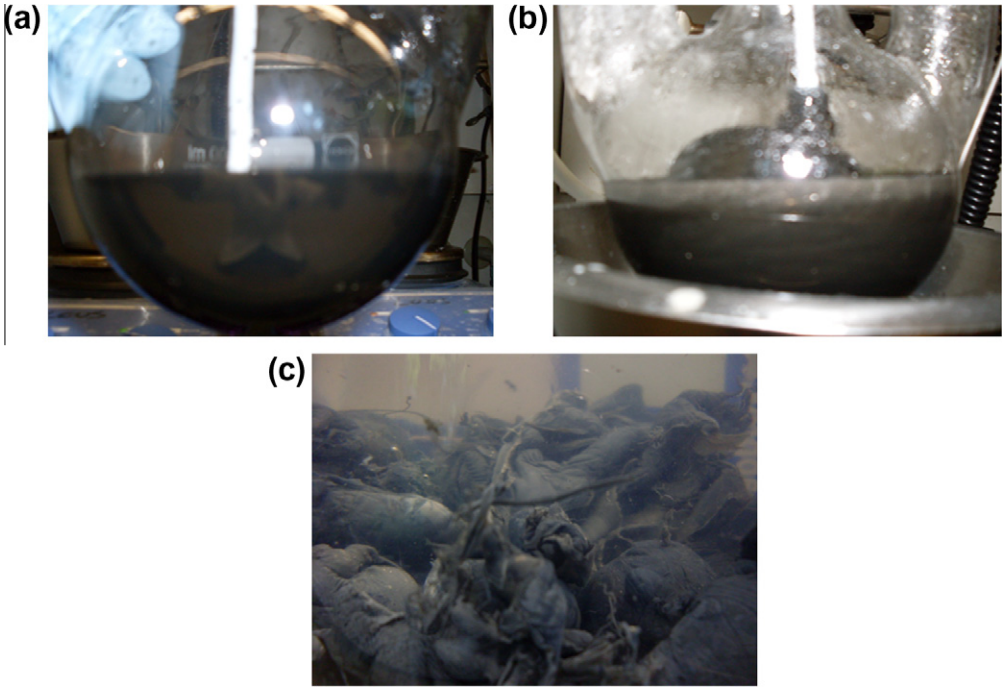

Fig. 2. Digital photographs of the reaction mixture: (a) after the pre-dispersion step, (b) 3 h after starting of the synthesis, and (c) composite precipitated like "noodles".

molecular weight polymers were being synthesized (Fig. 2b). At the end of the synthesis the viscosity was even higher, then water was added into the reaction vessel and big chunk of product was isolated (Fig. 2c).

Elemental analysis data for the sulfonated polyoxadiazole nanocomposites shown in Table 1 are in agreement with the value range for the sulfonated polyoxadiazoles. The polyoxadiazole sulfonation reaction, which occurs during the synthesis due to the presence of sulfuric acid in the solution of hydrazine sulfate has been recently recognized and characterized by Gomes et al. [13]. The polyoxadiazole sulfonation level (S/C) has been shown to be dependent on the reaction time [14], reaching the value range 0.085–0.0998 (44%–51%) for the synthesis performed in 4 h. In this study the sulfonation level has changed for all the used contents of CB (Table 1). The presence of CB causes a decrease of up to 15% in the sulfonation level of nanocomposites reinforced with 0.1–0.5 wt.% and an increase of 19% to the composites reinforced with 1.0 wt.%. An additional factor could be the homogeneity differences of CB concentration in the reaction medium. In regions where the CB concentration is overall or much better distributed, the sulfonation level should proportionally decrease [52]. This explains the lower sulfonation level obtained for the concentrations of 0.1 and 0.5 wt.% CB.

High molecular weights ranging from 2.9 to 3.3×10^5 g/mol with a polydispersity between 2.4 and 4.0 for the CB-based composites were obtained (Table 1). Therefore, the addition of CB implies in a decrease in molecular weight and increase in polydispersity. The observed changes in molecular weight, polydispersity and sulfonation level can be explained by the presence of the CB in the reaction medium, which may influence the synthesis chemically as well as physically. Therefore, the comparison of the composites with the neat sulfonated polyoxadiazole is difficult once the polymer shows different sulfonation levels (S/C), which influence the dipole–dipole interactions between the sulfonated groups

Table 1
Elemental analysis data, average molecular weight and polydispersity (PDI), for the sulfonated polyoxadiazole nanocomposites.

CB (wt.%)	S/C		N/C		SL (%)[a]	M_W (g/mol)	PDI
	Calc.	Found	Calc.	Found			
0	0.099	0.091	0.17	0.17	48	$4.2 \times 10^5 \pm 3 \times 10^3$	2.0 ± 0.1
0.1	0.099	0.080	0.17	0.17	41	$3.1 \times 10^5 \pm 6 \times 10^3$	4.0 ± 0.2
0.5	0.099	0.083	0.17	0.16	43	$2.9 \times 10^5 \pm 3 \times 10^3$	2.4 ± 0.3
1.0	0.10	0.11	0.17	0.17	57	$3.3 \times 10^5 \pm 6 \times 10^3$	2.8 ± 0.4

[a] Sulfonation level assuming 100% sulfonated when $m = 0$ (S/C = 0.19).

[51,52]. The introduction of sulfonic groups increases the intermolecular interaction and consequently increases the T_g and mechanical properties [51].

Fig. 3 shows the appearance of the POD/CB composites. The composites films were placed on a paper printed with the words 'GKSS Research Centre – Institute of Polymer Research, Hamburg University of Technology – TUHH'. The composites become darker in color with increasing of CB content. Samples with CB concentration of 0.1 wt.% posses good optical clarity.

In order to confirm the covalent attachment proposed in Fig. 1, FTIR analysis of the composites were performed. Fig. 4 shows the representative FTIR spectra of neat sulfonated polyoxadiazole, composites and CB. There were no discernable characteristics among samples. Assignments are observed for the pristine polymer at 1603 and 1490 cm^{-1} arising from C=C stretching of the aromatic groups and the assignments placed at 1468 cm^{-1} and 1416 cm^{-1} related to the C=N stretching of oxadiazole ring group [30]. The infrared analysis was also performed on the CB. The two bands at 1690 and 1522 cm^{-1} can be attributed to stretching vibrations of C=O and C=C groups in the carbon material [53].

3.2. Solution properties

The nanocomposites reinforced with different amounts of CB were highly soluble in polar aprotic solvents such as DMSO, *N*-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMA) and N′N-dimethylformamide (DMF). Such solubility allow the further processing of the nanocomposites using the solvent casting technology [54] and the spinning of fibers with potential properties to be used as reinforcing agent in polymer–matrix composites.

3.3. Dynamic mechanical thermal analysis of the POD/CB composites

Fig. 5 shows the DMTA curves of the neat POD and its composites. The values of E', which are correlated with the elastic modulus

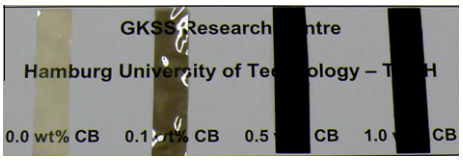

Fig. 3. Digital photographs of POD nanocomposites reinforced with different CB amounts.

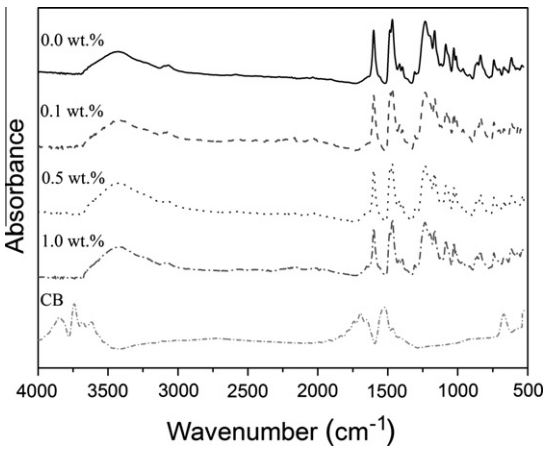

Fig. 4. Representative FTIR spectra of the neat polyoxadiazole, pristine CB and CB/POD composites.

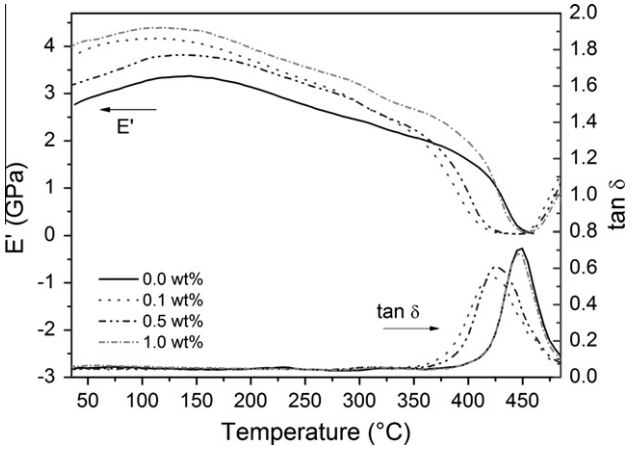

Fig. 5. (a) variation of the storage modulus (E') and tan δ as a function of temperature for the CB/POD nanocomposites.

of the material, for the neat POD and the POD/CB composites containing 0.1, 0.5 and 1.0 wt.% CB at 100 °C are 3.18, 4.16, 3.70 and 3.92 GPa, respectively. The use of only 0.1 wt.% CB increases E' up to 31% at this temperature. It can be still seen that even at 300 °C the nanocomposites maintain a high stiffness. The increase of E' observed in the composites with 0.1–0.5 wt.% CB, despite the lower sulfonation level and molecular weight in comparison to the neat POD, reflects the interaction between the CB and the POD [55,56], and the homogeneous dispersion.

The variation of tan δ among various CB contents is also plotted against temperature in Fig. 5 and values of the T_g are listed in Table 2. The T_g values of the composites are affected by the sulfonation level, molecular weight (M_W), polydispersity and by the CB content. Considering the T_g value obtained from the peak of tan δ as a function of temperature (Fig. 5), it can be seen that the T_g decrease up to 22 °C with the addition of 0.5 wt.% CB. When the filler is homogeneously distributed in a polymeric matrix, the T_g of the composites should increase with filler content [52]. Such decreased observed here in T_g values might be attributed mainly to the variation of the sulfonation level and molecular weight. Comparing Tables 1 and 2, one can see that the composite with the lower T_g (0.1–0.5 wt.% CB) has a lower M_W and sulfonation level that those of the neat polyoxadiazole. Therefore, even with a homogeneous dispersion and good interaction between filler and matrix phase, as confirmed by morphological characterization, the T_g decrease. However, nanocomposites reinforced with 1.0 wt.% CB have not shown changes in the T_g value. Such result is attributed to the increase observed in sulfonation level and polydispersity allied with the decrease on molecular weight, as discussed previously. As depicted in Fig. 5, the value of tan δ decreased from 0.71 to 0.56 when 0.1 wt.% CB was added to the POD matrix. The interaction between the CB and the polyoxadiazole matrix reduce the free volume in the nanocomposites, make then behave more elastically, thus leading to the observed decrease in the intensity of tan δ peak [57–59]. As expected, composites with 1.0 wt.% CB do not show significant changes in the value of tan δ. This result further indicates that the CB reinforces the POD matrix by virtue of their good dispersion and interaction.

3.4. Thermal analysis of the POD/CB composites

In order to study the thermal stability of the composites, TGA characterization has been carried out under dry air and argon atmospheres. The results are depicted in Table 2. Overall, the thermal stabilities of nanocomposites in argon were unchanged as

Table 2
Glass transition temperature, thermal stability and tensile properties of the CB/POD nanocomposites.

CB (wt.%)	T_g (°C)[a]	T_{d5} (°C)[b]		Char at 700 °C (%)		E (MPa)	σ_M (MPa)	ε (%)
		In arg.	In air	In arg.	In air			
0.0	447	466	469	59	14	2690 ± 42	153 ± 8	45.7 ± 6.8
0.1	425	463	467	57	52	2840 ± 100	118 ± 8	21.5 ± 4.0
0.5	425	465	463	57	9	2680 ± 84	161 ± 7	59.0 ± 5.4
1.0	445	468	469	59	18	2270 ± 130	109 ± 7	34.5 ± 1.0

E: Young modulus; σ_M: tensile strength; ε: elongation at break.
[a] Glass transition temperature measured by DMTA (tan δ).
[b] 5% weight loss temperature measured by TGA.

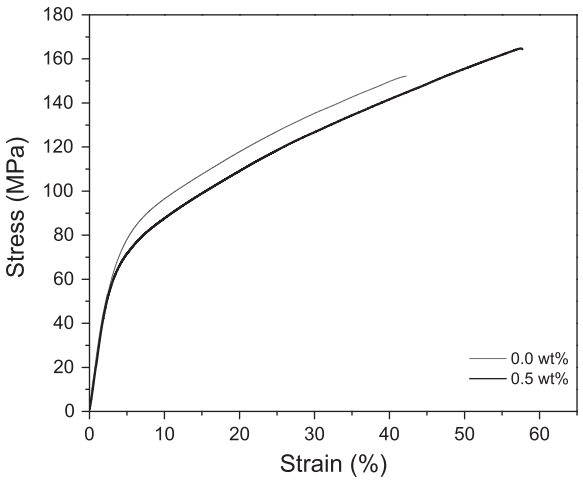

Fig. 6. Representative stress–strain curves of the CB/POD nanocomposites.

indicated by the fact that the temperatures ($T_{d5\%}$) at which a 5% weight loss of the POD/CB composites occurred were in the range of 463–468 °C, while the corresponding homopolymer was at 466 °C. The char yields in argon at 700 °C were 59, 57, 57 and 59% to the neat polymer and composites reinforced with 0.1, 0.5 and 1.0 wt.%, respectively. In air, $T_{d5\%}$s of polymer and composites were in the range of 463–469 °C with chair yield 9%–52% at 700 °C. Surprisingly, the composites with 0.1 wt.% CB show an increase of up to 171% in chair yield at 700 °C under air atmosphere. This increase in thermal stability may result from the decrease of free volume and improved adhesion between CB and surrounding POD matrix. Therefore, the observed thermal properties suggest the potential use of this nanocomposites in engineering applications requiring high thermal stability.

3.5. Tensile properties of the POD/CB composites

Table 2 lists the tensile properties and Fig. 6 shows the stress–strain curves of neat POD and POD containing 0.1, 0.5 and 1.0 wt.% CB. Young's modulus increased slightly when 0.1 wt.% CB is incorporated into the polyoxadiazole but decrease significantly to the samples with 1.0 wt.% CB. The decrease observed in tensile strength to the samples containing 1.0 wt.% CB implies that possibly in that case aggregates in the POD matrix might act as defect sites, where stress concentration points lower the strength. This result is also well corresponding to the tan δ values discussed previously. The best improvement was observed to the composites reinforced with 0.5 wt.% CB where there was an increase of 5% in tensile strength and 29% in elongation at break (Fig. 6). Such increase reflects in a considerable improvement in the toughness of the composites in relation to the neat polymer. In addition, the decrease in the tensile performance of some of the composites may be attributed to the variation observed in M_W, Sulfonation level and PDI, which are responsible for a change in the morphology of the composites as well as their structure. The strong interaction between the functionalized CB and the POD matrix greatly enhanced the dispersion as well as the interfacial adhesion, thus strengthening the overall mechanical performance of the composites containing 0.5 wt.% CB.

3.6. Morphology of the POD/CB composites

After conducting tensile tests of the POD composites reinforced with 0.5 wt.% CB, the fracture surface was observed by the AFM and TEM to investigate the dispersion state of the CB in the polyoxadiazole matrix. As shown by the AFM images (Fig. 7), the CB formed a core–shell structure, in the order of 50–200 nm, wetted by the polymer [26]. Good distribution could be observed. In accordance with the AFM results, the TEM image (Fig. 8) confirms the homogeneous distribution of the CB aggregates (size of up

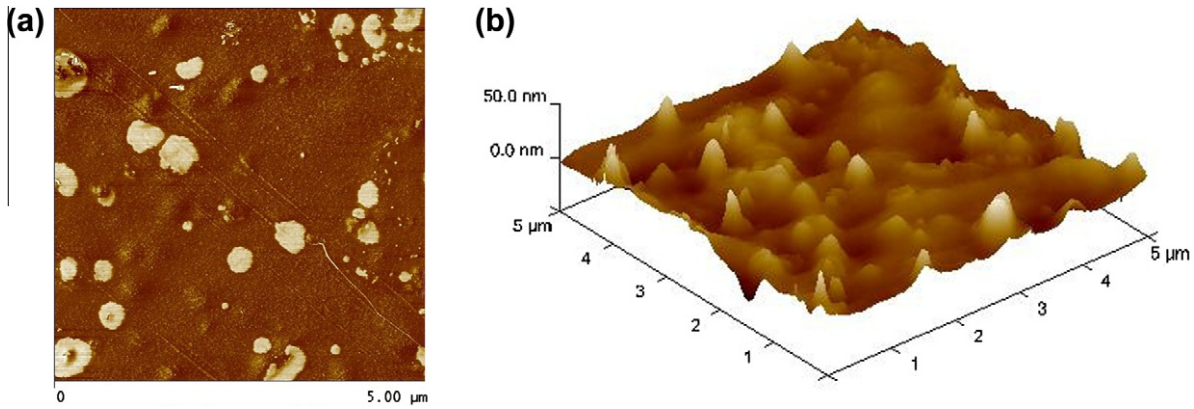

Fig. 7. AFM images of the fracture surface of the POD nanocomposites reinforced with 0.5 wt.% of CB after conducting tensile tests.

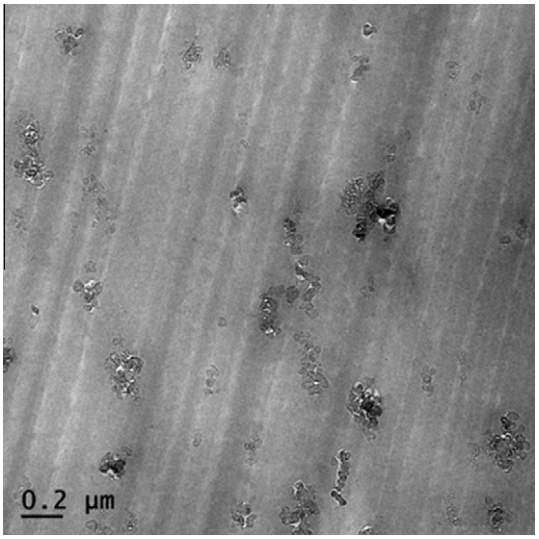

Fig. 8. TEM image of the fracture surface of the POD nanocomposites reinforced with 0.5 wt.% of CB after conducting tensile tests.

0.5 μm) coated by the polyoxadiazole. This might be due to the fact that the carboxyl groups generated on the surface of the CB during the pre-dispersion step effectively anchored the growing of polyoxadiazole chains and improve the interfacial bonding between the CB and the surrounding matrix. The interfacial bonding is expected to enables an effective load transfer between the polymer and filler.

4. Conclusions

In the present work, we demonstrate a fast direct method to obtain POD/CB composites, where the CB is in situ functionalized during the synthesis of poly(1,3,4-oxadiazoles). Sulfonated polyoxadiazole composites containing different concentrations of carbon black (0.1, 0.5 and 1.0 wt.%) were successfully prepared and processed in films using a solution method aided by the use of a mini-calander. The effect of the in situ functionalized CB on the morphological, structural, thermal and mechanical properties of the POD matrix was demonstrated. The presence of CB caused a decrease of up to 15% in the sulfonation level of nanocomposites reinforced with 0.1–0.5 wt.% and an increase of 19% to the composites reinforced with 1.0 wt.%. Composites with high molecular weight (10^5 g/mol) and soluble in polar aprotic solvents were obtained. As a result of the method applied, increase of 31% in storage modulus at 100 °C was observed. The elongation at break shows increases of up to 29% coupled with improvement of tensile strength at low concentration of CB (0.5 wt.%). The increase of E' observed in the composites with 0.1–0.5 wt.% CB, despite the lower sulfonation level and molecular weight in comparison to the neat POD, was attributed to the homogeneous dispersion and interaction between the CB and the POD. The interaction between the CB and the polyoxadiazole matrix reduce the free volume in the nanocomposites making then behave more elastically. The polyoxadiazole/CB exhibits high thermal stability with degradation temperature at about 460 °C. Composites with 0.1 wt.% CB show an increase of up to 171% in chair yield at 700 °C under air atmosphere. TEM results confirmed the homogeneous dispersion of the CB coated by the polyoxadiazole. This might be due to the fact that the carboxyl groups generated on the surface of the CB during the pre-dispersion step effectively anchored the growing of polyoxadiazole chains and improve the interfacial bonding between the CB and the surrounding matrix. The POD films CB concentration of 0.1 wt.% showed good optical clarity. The final composites films may be useful candidate for developing new sensor materials, membranes or coatings for high performance applications.

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