Research Article

Fast and highly efficient one-pot synthesis of polyoxadiazole/carbon nanotube nanocomposites in mild acid

Marcio R Loos,[a]* Volker Abetz[a] and Karl Schulte[b]

Abstract

Sulfonated poly(4,4'-diphenylether-1,3,4-oxadiazole) (POD) composites have been successfully prepared through solution polycondensation of 4,4'-diphenylether dicarboxylic acid and hydrazine sulfate. The reactions were performed in the presence of various types of pristine carbon nanotubes, i.e. single-, double- and multi-walled carbon nanotubes, using mild poly(phosphoric acid) as a condensing agent. The POD composites with high molecular weight (of the order of 10^5 g mol^{-1}) were highly soluble in polar aprotic solvents and thermally stable at temperatures as high as 475 °C. The synthesis method used guaranteed an improved interaction between filler and matrix, thus allowing an enhanced load transfer. The overall performance of the composites was enhanced due to a synergistic reinforcement effect. The nanocomposites exhibited an increase of +33% in storage modulus, +56% in tensile strength and +245% in tensile energy to break.
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Keywords: polyoxadiazoles; *in situ* polymerization; carbon nanotubes; nanocomposites; mechanical properties; high-performance polymers

INTRODUCTION

The electrical, mechanical and physical properties of polymeric materials can be improved by incorporating small amounts of carbon nanotubes (CNTs).[1,2] The dispersion of CNTs, however, has been problematic for these applications because CNTs are present in the form of bundles and ropes due to long-range van der Waals interactions.[3] Several approaches, such as chemical functionalization, wrapping, etc., have been used to obtain homogeneous dispersions.[3] Therefore, chemical modification approaches have become popular, with the introduction of organic pendant groups as molecular wedges onto the surface of CNTs promoting homogeneous dispersion of CNTs in, and chemical affinity to, organic matrices such as solvents and/or polymers. However, covalent modification of CNTs requires treatment in strong acids such as nitric acid, hydrochloric acid or nitric acid/sulfuric acid mixtures, which is known to significantly damage CNTs.[4] To overcome this issue, a less destructive but yet effective medium for chemical modification of CNTs would be the best option. Substantial developments have been made during the last few years in this regard, by using poly(phosphoric acid) (PPA) as a reaction medium. Some of these latter works are briefly reviewed in the following.

Kumar *et al.*[5] synthesized poly(*p*-phenylene benzobisoxazole) (PBO) in the presence of single-walled carbon nanotubes (SWCNTs; 5 and 10 wt%) in PPA using typical PBO polymerization conditions. The polymerization reaction applied was very long and involved various time/temperature stages as follows: 65 °C for 16h, 80 °C for 4 h, 100 °C for 16 h, 80 °C for 2 h, 160 °C for 16 h and 190 °C for 4 h. The PBO composites obtained were spun into fibers using dry-jet wet spinning. An increase of 50% in tensile strength was observed for the composites reinforced with 10 wt% of SWCNTs.

In addition, the DC conductivity did not change significantly. The authors explained the observed results in terms of well-dispersed SWCNTs; however, only inconclusive optical micrographs were shown.

A study by Li *et al.*[6] concentrated on the dispersion of multi-walled carbon nanotubes (MWCNTs) in PBO. *In situ* synthesis in PPA was composed of stages of 100 °C for 20 h, 140 °C for 4 h, 160 °C for 24 h and 200 °C for 6 h. The CNTs were treated using concentrated sulfuric and nitric acids and additionally treated with PPA before use. Results from SEM and AFM showed that PBO was grafted on the surface of MWCNTs treated with PPA and therefore they could be uniformly dispersed in the PBO matrix.

Recently, Eo *et al.*[7] prepared poly(2,5-benzoxazole) (ABPBO)/CNT composites via *in situ* polycondensation in PPA medium. The synthesis was realized using the stages of room temperature for 48 h, 60 °C for 24 h and a stepwise increasing of the temperature at 100, 120, 150 and 175 °C for 24, 24, 8 and 72 h, respectively. SEM and transmission electron microscopy (TEM) results showed that individual MWCNTs and bundles of SWCNTs were homogeneously dispersed in the ABPBO matrix.

In a study by Zhou *et al.*,[8] MWCNTs were covalently functionalized with oligo-hydroxyamide (oHA) via surface grafting.

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PBO/MWCNT–oHA composites were prepared through *in situ* polymerization in PPA during more than 20 h at temperatures of up to 180 °C. Fibers were drawn from the PBO/MWCNT composites and their modulus, tensile strength, thermal stability and conductivity were enhanced. The authors attributed the improvement to good dispersion and alignment of MWCNTs in PBO as well as enhanced interfacial interaction between the two components. However, no morphological evidences of a homogeneous dispersion were given.

The functionalization of vapor-grown carbon nanofibers (VGC-NFs) via Friedel–Crafts acylation with 2,4,6-trimethylphenoxy-benzoic acid in PPA/phosphorus pentoxide (P_2O_5) medium was studied by Baek *et al.*[9] The synthesis was performed during more than 80 h at 130 °C. SEM results revealed that the VGCNFs were decorated with moieties. The functionalized VGCNFs were marginally soluble in N-methylpyrrolidone (NMP). The same group described the grafting of poly(oxy-1,3-phenylenecarbonyl-1,4-phenylene) (mPEK) onto VGCNFs via a polycondensation reaction in a PPA/P_2O_5 medium.[10] The synthesis was performed at temperatures of up to 130 °C for 51 h using various amounts of VGCNF (1, 2, 5, 10, 20, 30 wt%). A uniform grafting of linear polymer onto VGCNFs was achieved affording 'hairy tubes'. However, these materials were found to be more soluble in strong acids than in common organic solvents. Estimated molecular weights of up to 33 000 g mol^{-1} have been predicted but not measured.

Lee *et al.*[11] functionalized MWCNTs with 4-methoxybenzoic acid (MeO) and 4-ethoxybenzoic acid (EtO) via a Friedel–Crafts reaction in PPA/P_2O_5 medium to afford MeO–MWCNTs and EtO–MWCNTs, respectively. The functionalization was realized during 48 h at 130 °C. Afterwards, poly(ethylene terephthalate) (PET) was synthesized via a polycondensation reaction of ethylene glycol and terephthalic acid in the presence of pristine and modified CNTs. It was found that the EtO–MWCNTs were most homogeneously dispersed in and showed good interfacial interaction with the PET matrix, thus enhancing the thermal properties of the nanocomposites.

In a study by Oh *et al.*,[12] mPEK and poly(oxy-1,4-phenylene-carbonyl-1,4-phenylene) were directly covalently attached onto the surface of MWCNTs and VGCNFs. The synthesis was carried out in a PPA/P_2O_5 medium using temperatures of up to 130 °C for 48 h. Results from TEM and SEM confirmed that the PPA/P_2O_5 medium is indeed benign, yet effective in covalently connecting an appropriate polymer onto the surfaces and open ends of electron-deficient carbon nanotubes and nanofibers.

Choi *et al.*[13] polymerized *in situ* trimesic acid and phenyl ether as A_3 and B_2 monomers, respectively, in the presence of 10 wt% of MWCNTs affording hyperbranched poly(ether ketone) (HPEK)/MWCNT composites. The polymerization was carried out in PPA/P_2O_5 using steps of 12 h at 100 °C and 6 h at 130 °C. The MWCNTs remained structurally intact under the polymerization and workup conditions and the HPEK-*g*-MWCNT nanocomposites were soluble in polar aprotic solvents. The same group reported the grafting of carboxylic acid-terminated HPEKs onto the surfaces of SWCNTs and MWCNTs affording grafted (HPEK-*g*-SWCNT and HPEK-*g*-MWCNT) nanocomposites.[14] The synthesis was carried out in PPA/P_2O_5 medium during more than 32 h using temperatures of up to 130 °C. The efficiency of PPA in decomposing amorphous carbon and metallic catalysts keeping the structure of the CNTs intact was shown. HPEKs were also polymerized in the presence of various amounts of VGCNFs (1, 2, 5, 10, 20, 30 and 40 wt%) in PPA/P_2O_5 by Wang *et al.*[15] The reaction was performed at 130 °C for 52 h. The nanofibers obtained were highly coated by

HPEKs and soluble in polar aprotic solvents such as NMP, N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA). An increase of 21 °C in the glass transition temperature (T_g) of the composites with 40 wt% of VGCNFs as well as an improvement in thermal stability were observed.

In another study by Tan *et al.*,[16] linear PEK- and HPEK-grafted MWCNTs (PEK-*g*-MWCNT) were prepared by direct Friedel–Crafts acylation in a PPA/P_2O_5 medium. The synthesis was performed during 11 h. SEM and TEM images showed that the polymer was uniformly grafted onto the MWCNTs. However, the nanocomposites were soluble only in strong acids. TGA studies in air showed that the composites displayed improved thermo-oxidative stability when compared with corresponding PEK homopolymers.

Jeong and co-workers[17] functionalized MWCNTs with 4-chlorobenzoic acid via Friedel–Crafts acylation in PPA/P_2O_5 medium. The reaction was conducted during more than 3 days at temperatures of up to 130 °C. The functionalized MWCNTs were soluble in chlorinated solvents and were used to reinforce Nylon 610 via an *in situ* interfacial polymerization.

Recently Saeed *et al.*[18] functionalized MWCNTs with p-aminobenzoic acid in PPA/P_2O_5 medium during 15 h at 130 °C. The modified MWCNTs were used to reinforce Nylon 6 via *in situ* polymerization. The composites were electrospun into fibers. The MWCNTs were found to be well dispersed and oriented in the direction of the composite fibers. Improvements of the mechanical properties of the fibers were found.

The discussion above shows the potential of using PPA as a mild medium to purify and functionalize CNTs. Unlike the treatment in strong acids such as nitric acid, sulfuric acid/nitric acid mixtures and hydrochloric acid, PPA can selectively remove tenacious carbonaceous and metallic impurities with little or no damage to the basic frameworks of CNTs and crystalline carbon materials.

Since PPA is known as an efficient reaction medium for the synthesis of polyoxadiazole-based polymers,[19–21] it provides the advantage of allowing the combination of both purification and functionalization steps into a one-pot process in manufacturing functionalized nanocomposites. It is possible to avoid pre-steps of purification and functionalization of fillers prior to the synthesis. In addition, compared to the studies described in the literature, the synthesis of sulfonated poly(4,4'-diphenylether-1,3,4-oxadiazole) (POD), the polymer chosen for the present study, is much faster and thus attractive from an industrial point of view. In fact, to the best of our knowledge, the method of synthesis described in the present work is the fastest reported up to now to afford polymer/CNT composites via polycondensation in a PPA medium.

EXPERIMENTAL
Materials
The materials used were 4,4'-diphenylether dicarboxylic acid (DPE; 99%, Aldrich), dimethylsulfoxide (DMSO; >99%, Aldrich), NMP (99%, Aldrich), DMA (99%, Aldrich), DMF (99%, Aldrich), hydrazine sulfate (HS; >99%, Aldrich), sodium hydroxide (NaOH; 99%, Vetec), PPA (115% H_3PO_4, Aldrich). Three types of CNTs were used: SWCNTs (S4402, Heji Inc.), double-walled carbon nanotubes (DWCNTs; Nanocyl-2100, Nanocyl) and MWCNTs (CNT-MW, Future Carbon). All chemicals were used as received. Some of the characteristics of the nanoparticles used in this study are described in Table 1.

The density of the CNTs (ρ_{NT}) was calculated by assuming the graphitic layers of the tube shells have the density of fully dense

Table 1. Characteristics of the nanoparticles used in this study

Filler	Diameter[a] (nm)	Length[a] (μm)	l/d[b]	SSA[a] ($m^2\,g^{-1}$)	C purity[c] (%)	ρ_{NT} ($g\,cm^{-3}$)	Production method	Price (€ g^{-1})
SWCNTs	1–2	50	$3.8 \times 10^{4\,d}$	>407	> 90	1.61	Chemical vapor deposition (CVD)	135
DWCNTs	3.5	1–10	$1.6 \times 10^{3\,d}$	>500	>90[e]	1.44[f]	chemical catalytic vapor deposition (CCVD)	160
MWCNTs	15	10–50	$2.0 \times 10^{3\,d}$	250	>97	2.0	CVD	35

[a] Data from supplier.
[b] Aspect ratio (length/diameter).
[c] Determined by elemental analysis.
[d] Average.
[e] SWCNTs purity > 90 wt%, CNTs purity > 95 wt%.
[f] Assuming an internal diameter of 2.1 nm.

graphite ($\rho_g = 2.25\,g\,cm^{-3}$), as suggested by Thostenson and Chou[22]

$$\rho_{NT} = \rho_g \frac{d^2 - d_i^2}{d^2}$$

where d_i is the inner diameter and d the outer diameter of the nanotubes.

Representative *in situ* polymerization of POD with 0.1 wt% CNT load

The reaction conditions for the synthesis of POD were selected based on previous studies and on our patented method.[19] Reactions were carried out in a 250 mL three-necked flask equipped with a dry nitrogen inlet tube. Initially PPA and CNTs (0.02 g) were added to the flask and heated to 80 °C under sonication and simultaneous mechanical stirring during 1 h. The PPA/CNT solution was then stirred at 160 °C for an additional 2 h. HS (0.031 mol) and DPE (0.013 mol) were then separately added to the mixture and reacted under mechanical stirring at 160 °C for 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.

Instrumentation

The polymer and nanocomposite structures and morphologies were characterized using elemental analysis, SEC, TGA and TEM. Elemental analysis was conducted using a Carlo Erba model 1108 elemental analyzer.

A Viscotek SEC apparatus equipped with Eurogel columns (SEC 10.000 and PSS Gram 100 and 1000, with serial numbers HC286 and 1515161 and size 8 × 300 mm) was employed to evaluate the weight-average molecular weights (M_w) of polymer and nanocomposite samples. The equipment was calibrated using polystyrene standards (Merck) with M_w ranging from 309 to 944 000 g mol^{-1}. A solution of 0.05 mol L^{-1} lithium bromide in DMA (≥99.9%, Aldrich) was used as the carrier. Solutions with 0.5 wt% of the polyoxadiazole composite were prepared, centrifuged, filtered through a 0.2 μm filter and injected into the chromatograph.

Film morphology was observed using SEM (LEO 1550VP). TEM images were obtained using a Tecnai G2 F20 field emission electron microscope at an acceleration voltage of 200 kV. The samples were cut into slices of 80 nm thickness using an ultracut microtome with diamond knife.

TGA experiments were carried out using a Netzsch 209 TG, equipped with a TASC 414/3 thermal analysis controller. Bulk samples, under argon and air atmosphere, were heated from 100 to 900 °C at 10 °C min^{-1}.
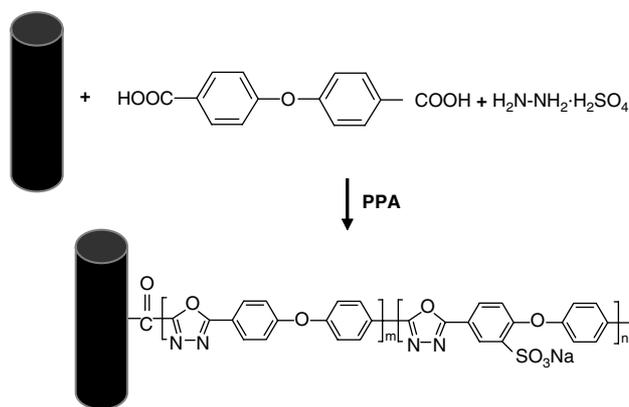
Scheme 1. Synthesis of POD/CNT composites via *in situ* polymerization of dicarboxylic acid and hydrazine sulfate in a PPA medium.

Dynamic mechanical thermal analysis (DMTA) was used to determine the storage modulus (E'), loss modulus (E'') and loss tangent (tan δ) of the composite films. DMTA was performed using a TA Instruments RSA 2 with film tension mode at a frequency of 1 Hz and 0.1 N initial static force. The temperature was varied from 25 to 500 °C at a heating rate of 2 °C min^{-1} and at a constant strain of 0.05%. Tensile tests were performed according to ASTM D882-00 using a Zwick-Roell equipment with a 500 N load cell. From the stress–strain curve the tensile strength of the samples was estimated and the elastic modulus calculated. At least 10 independent specimens from different films were investigated. The tensile energy to break (TEB), i.e. the total energy absorbed per unit of volume of the specimen up to the point of rupture, was also determined.

RESULTS AND DISCUSSION

POD composites containing various concentrations (0.1, 0.5 and 1.0 wt%) of SWCNTs, DWCNTs and MWCNTs were successfully prepared via *in situ* polymerization as shown schematically in Scheme 1. Covalent attachment of POD onto the filler surface should be expected to occur by condensation of *in situ* COOH groups generated on the surface of the CNTs with the hydrazine monomer, leading to the formation of arylcarbonyl and CONHNH$_2$, respectively. The growing POD chains on the filler surfaces are expected to promote physical contact between the CNTs and the polymer matrix, allowing an efficient load transfer from the reinforcement phase to the matrix phase in the nanocomposites.
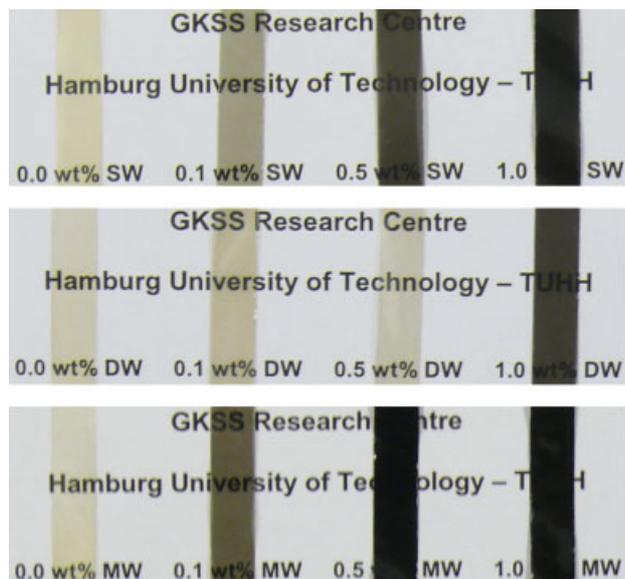
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Figure 1. Digital photographs of the neat polyoxadiazole and nanocomposites films. The composites shown are reinforced with various concentrations of SWCNTs (SW), DWCNTs (DW) and MWCNTs (MW).

During the synthesis, the initial color of all the reaction mixtures is black because of the filler dispersion. In all cases, the reaction mixtures are homogeneous with a marked increase in viscosity at the end of polymerization. The viscosity reaches a level such that the dope sticks to the stirring rod. This provides a visual signal that high-molecular-weight polymers are obtained. Solution behaviors of final reaction mixtures are different. In some cases the composites can be poured into water to spin fibers simply by force of gravity. In other cases, where the viscosity is even higher, water has to be added into the reaction vessel and large pieces of product are isolated. The yields are close to estimated values even after complete workup procedures.

Because of the structure of the POD, one expects to obtain amorphous nanocomposites displaying good solubility.[21] As a consequence, the nanocomposites reinforced with various amounts of different CNTs are highly soluble in polar aprotic solvents such as DMSO, NMP, DMA and DMF. Such solubility

allows further processing of the nanocomposites using solvent-casting technology[23] and the spinning of fibers with the potential to be used as reinforcing agents in polymer matrix composites.

Figure 1 shows the appearance of the POD/CNT composites. The composites films were placed on paper printed with the words 'GKSS Research Centre, Hamburg University of Technology – TUHH'. The composites become darker in color with increasing CNT content. All samples containing 0.1 wt% CNTs and 0.5 wt% SWCNTs and DWCNTs possess good optical clarity.

Elemental analysis (C, H, N and S) was carried out for the composites containing SWCNTs, DWCNTs and MWCNTs. The results are summarized in Table 2. As the N/C ratio expected for POD is equal to 0.17 (by weight) and the values obtained experimentally are in agreement, it is concluded that the polymerization had taken place. Elemental analysis data for the POD composites obtained in this study are in agreement with the range for sulfonated polyoxadiazoles. The polyoxadiazole sulfonation level (S/C) has been shown to be dependent on the reaction time,[19–21] reaching values in the range 0.063–0.12 (33–60%) for synthesis performed between 2 and 7 h. Here, the sulfonation level decreases for all contents of the different fillers. The presence of 1.0 wt% of DWCNTs causes a maximum decrease (−35%) in the sulfonation level of nanocomposites whereas the minimum decrease occurs for samples with 0.5 wt% of MWCNTs (−9%). Another interesting observation from Table 2 is that the sulfonation level is the same for the composites reinforced with 0.1 wt% of DWCNTs and 0.5 wt% of SWCNTs. These results are explained as follows. The sulfonation of polyoxadiazoles synthesized in PPA occurs by dint of the presence of sulfuric acid in the solution of HS salt ($NH_2 NH_2 \cdot H_2SO_4$). This reaction involves an electrophilic substitution reaction of the eletrophilic agent (SO_3) coming from the sulfuric acid and is activated by electron-donating groups, in this case the ether group attached to the aromatic ring.[21] According to the synthesis route used in our study, after the dispersion of the CNTs in the PPA, the HS is added to the reactor. We believe that, during this step, still before the addition of DPE, part of the sulfuric acid, which later participates in the sulfonation reaction, is consumed for the oxidation of the CNTs. Thus, as part of this process, the sulfuric acid releases free oxygen atoms and can make the carbon atoms of the nanotubes become active. Therefore the free oxygen atoms and active carbon atoms can form –COOH groups on the surface of the nanotubes.

Table 2. Elemental analysis data for the sulfonated polyoxadiazole nanocomposites

Filler	Concentration (wt%)	S/C[a] Calculated	S/C[a] Found	N/C[a] Calculated	N/C[a] Found	SL[b] (%)
None	0	0.099	0.088 ± 0.004	0.17	0.17 ± 0.003	46
SWCNTs	0.1	0.099	$0.073 \pm 9 \times 10^{-5}$	0.17	0.17 ± 0.0001	38
SWCNTs	0.5	0.099	0.071 ± 0.0006	0.17	0.16 ± 0.0009	37
SWCNTs	1.0	0.10	0.068 ± 0.001	0.17	0.16 ± 0.0006	36
DWCNTs	0.1	0.099	0.071 ± 0.0003	0.17	0.17 ± 0.001	37
DWCNTs	0.5	0.099	0.067 ± 0.0006	0.17	0.17 ± 0.0002	35
DWCNTs	1.0	0.10	0.058 ± 0.0004	0.17	0.17 ± 0.0004	30
MWCNTs	0.1	0.099	0.065 ± 0.0004	0.17	0.17 ± 0.0002	34
MWCNTs	0.5	0.099	0.079 ± 0.004	0.17	0.17 ± 0.0009	42
MWCNTs	1.0	0.10	0.059 ± 0.0002	0.17	0.17 ± 0.001	31

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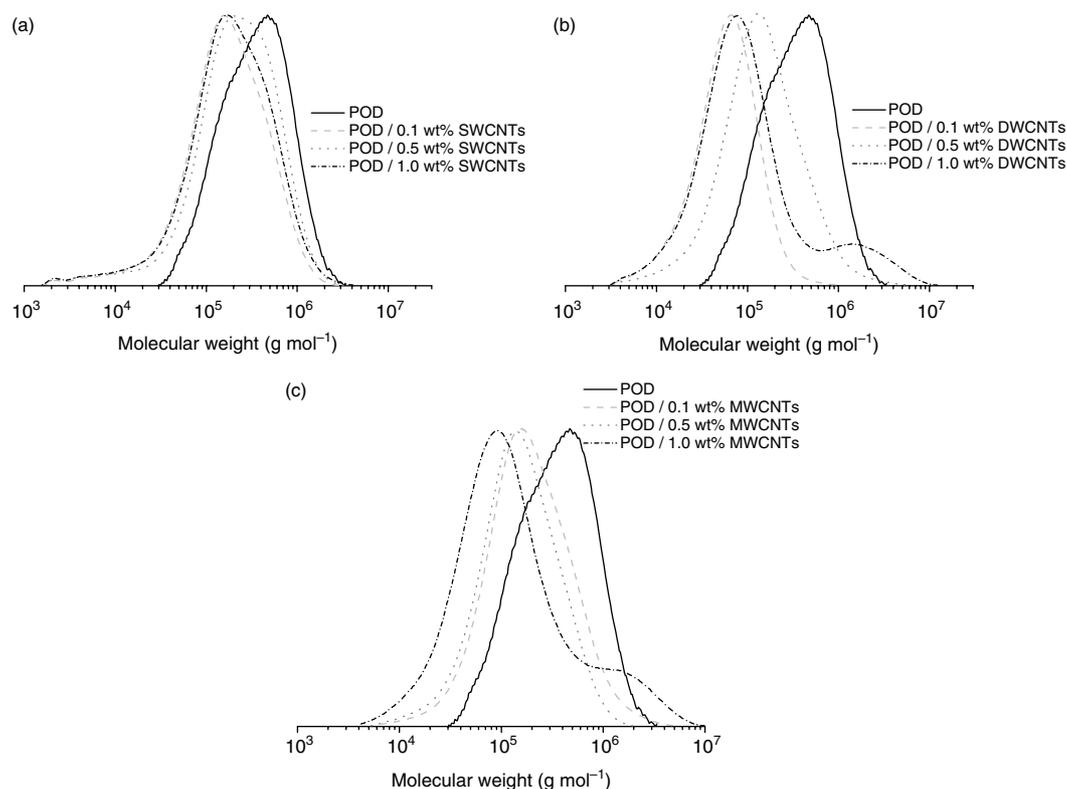[b] Sulfonation level assuming 100% sulfonated when $m = 0$ (S/C = 0.19).

Figure 2. Molecular weight distribution curves of the neat polyoxadiazole and composites reinforced with various concentrations of (a) SWCNTs, (b) DWCNTs and (c) MWCNTs.

Filler	Concentration (wt%)	M_w [a] (kg mol^{-1})	Dispersity	DP
None	0	420	2.0	724
SWCNTs	0.1	220	3.4	236
SWCNTs	0.5	280	4.1	253
SWCNTs	1.0	250	4.1	226
DWCNTs	0.1	74	1.9	140
DWCNTs	0.5	200	2.8	264
DWCNTs[b]	1.0	260	5.6	175
MWCNTs	0.1	252	2.4	390
MWCNTs	0.5	187	2.1	313
MWCNTs[b]	1.0	274	4.8	216

Table 3. Molecular weight, dispersity and degree of polymerization for the POD nanocomposites

[a] Determined by SEC.
[b] Gel formation observed.

Because of a decrease of the amount of sulfuric acid in the reaction media, the sulfonation level of the POD matrix decreases.

There are several works in the literature about thermoplastic nanocomposites prepared via *in situ* polymerization. However, the effect of the addition of nanoparticles on the structural properties of polymers, like molecular weight, dispersity, degree of polymerization or even sulfonation level, has not been reported.[24–26] In the present work we measured the molecular weights of POD with various CNTs and concentrations in order to examine the effect of the fillers on the polymerization. The results of SEC analysis are summarized in Fig. 2 and Table 3. High

molecular weights were obtained of the order of 10^5 g mol^{-1} for the nanocomposites. As is evident from Table 3, M_w obtained for all nanocomposites is below that obtained for the homopolymer. The lowest M_w is obtained for the polyoxadiazoles reinforced with 0.1 wt% of DWCNTs (74 kg mol^{-1}) and the highest with 0.5 wt% SWCNTs (280 kg mol^{-1}). The rest of the composites showed M_w in the range 190–270 kg mol^{-1}. The dispersity is 2.0 for the neat polymer and in the range 1.9–4.1 for the composites reinforced with the various fillers and concentrations. The highest dispersity is achieved with SWCNTs (Table 3). Overall the presence of fillers implies an increase in dispersity. Such increase means that species with lower molecular weights, in the region of 10^3 g mol^{-1}, start to be formed due the presence of the nanofillers in the reaction medium.

The degree of polymerization (DP) is the number of monomer units that polymerize to form the polymer. One can say that it is the number of mer units in a chain. Table 3 summarizes the DP obtained for the homopolymer and all nanocomposites. Among the samples, nanocomposites with 0.1 wt% of DWCNTs have shorter chains whereas nanocomposites with 0.1 wt% of MWCNTs have longer chains. Nevertheless, all the composites have a DP lower than that of the neat polyoxadiazole. In addition, it can be seen from Table 3 that the use of MWCNTs tends to result in nanocomposites with longer chains compared to the nanocomposites reinforced with SWCNTs and DWCNTs. This may be because of the difference in reactivity of the fillers, since, besides higher purity, MWCNTs have a specific surface area (SSA) lower than that of SWCNTs and DWCNTs.

The observed changes in molecular weight, dispersity, DP and sulfonation level can be explained by the presence of the fillers in the reaction medium, which may influence the synthesis
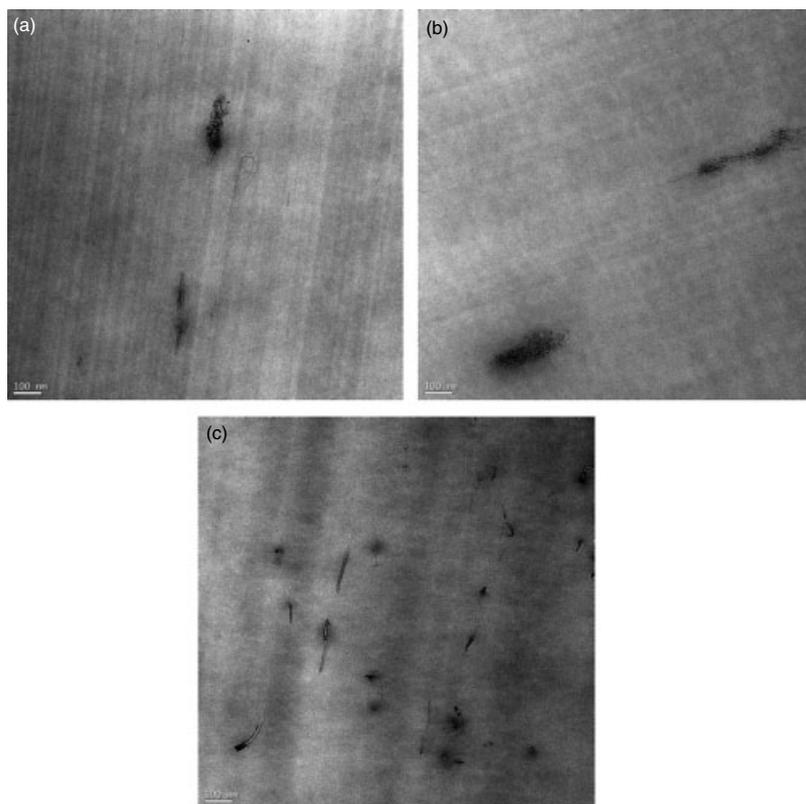
Figure 3. TEM images of POD composites reinforced with 0.5 wt% of (a) SWCNTs, (b) DWCNTs and (c) MWCNTs. Scale bar of 100 nm.

chemically as well as physically. Several parameters, crucial for the synthesis of sulfonated polyoxadiazoles, such as the viscosity of the reaction medium as well as micro-mixing effects, may change due to the addition CNTs. In the case of a polymerization via polycondensation, the polymerization occurs by a continuous reaction between the functional groups of the multi-functional molecules (monomers). The basic characteristics of these reactions include the continuous growth of the average molecular weight with time and release of condensation byproducts, which can be influenced by the presence of fillers. In the case of the POD nanocomposites generated using *in situ* polymerization, the fillers participate in the polymerization reaction and consume HS after the pre-dispersion stage (Scheme 1). Therefore, the increase in dispersity and consequent presence of species with lower molecular weight can also be ascribed to the resultant decrease of amide groups at the end of the growing POD chains. In other words, the generation of $CONHNH_2$ groups on filler surfaces (Scheme 1) triggers the growth of the polyoxadiazole chains, tethered on the filler surfaces, obstructing the growth of longer polymer chains. This kind of end-tethered POD on CNT surfaces promotes physical contact with the polymer matrix, allowing in the nanocomposites an efficient load transfer from the reinforcement phase to the matrix phase. In addition, the results show that the SSA and purity of fillers play a role by means of the reactivity with monomers.

Therefore, the comparison of the composites with the pristine sulfonated polyoxadiazole is difficult since the polymer shows different sulfonation levels (S/C), which influence the dipole–dipole interactions between the sulfonated groups.[27] The introduction of sulfonic groups increases the intermolecular interactions and consequently increases T_g and enhances mechanical properties.[21] It is important to point out that the changes in the polymer properties

are directly correlated to the presence of nanofillers in the reaction medium. Furthermore, the observed changes in structural properties of POD, such as molecular weight, dispersity and sulfonation level, influence the other properties of the nanocomposites, as will be further discussed.

In order to obtain information about the dispersion state of the fillers in the polyoxadiazole matrix, TEM analysis was carried out. Figure 3 shows the state of dispersion achieved for the various fillers. The TEM micrograph in Fig. 3(a) shows a mixture of separated SWCNTs and small agglomerates with a size of *ca* 50–100 nm. The presence of agglomerates in this case is expected due to the large SSA of the SWCNTs used here (SSA > 400 m^2 g^{-1}). This effect is also observed for the DWCNTs (Fig. 3(b)). Most of the DWCNTs are in the form of small aggregates of 50–100 nm in diameter. MWCNTs have an SSA of 250 m^2 g^{-1}, which is the lowest SSA among the fillers used in this investigation. Therefore less agglomeration is expected in this case. And in fact MWCNTs exhibit a good dispersion in the POD matrix (Fig. 3(c)). The analysis of several other images results in the observation of few agglomerates. The state of dispersion of the CNTs observed in the POD matrix, as well as the POD chains growing on the filler surfaces, are expected to enhance the mechanical properties of the nanocomposites.

The composites containing SWCNTs, DWCNTs and MWCNTs were subjected to an investigation of their thermo-oxidative stability by TGA of bulk samples in argon and air. The results are depicted in Fig. 4 and summarized in Table 4. The thermal stability of the nanocomposites in argon is slightly increased, but not significantly. Neat POD and nanocomposites show (in argon) a 5 wt% loss temperature (T_{d5}) in the range 466–475 °C, 10 wt% loss temperature (T_{d10}) in the range 482–488 °C and residue at 500 °C of *ca* 78–83 wt%. The results obtained under air atmosphere are
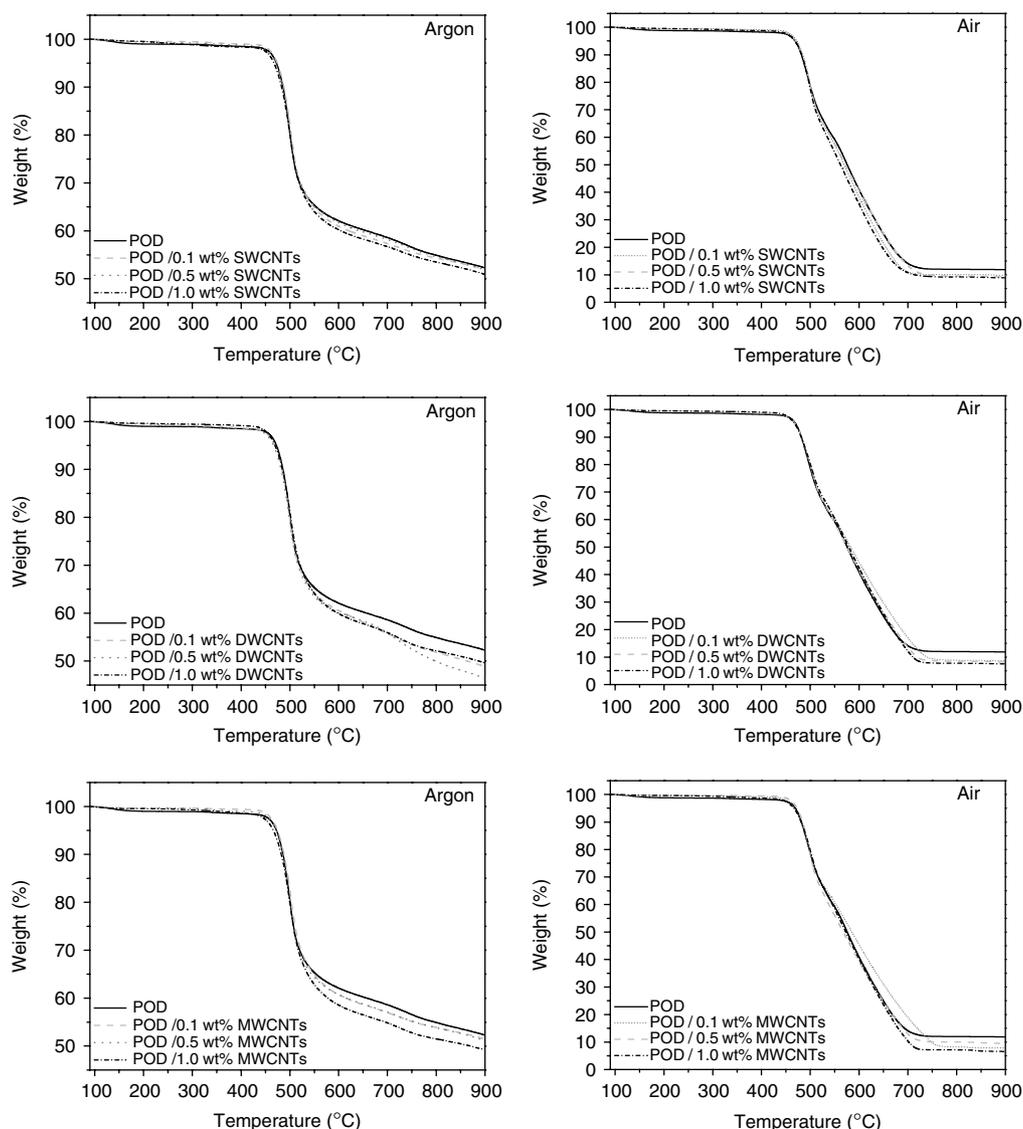
Figure 4. TGA thermograms for the neat POD and composites reinforced with various concentrations of SWCNTs, DWCNTs and MWCNTs.

Table 4. Thermal stability of the POD nanocomposites

Filler	Concentration (wt%)	T_{d5}[a] (°C)		T_{d10}[b] (°C)		Char at 500 °C (%)	
		In argon	In air	In argon	In air	In argon	In air
None	0	466	469	482	483	79	80
SWCNTs	0.1	474	473	488	485	82	79
SWCNTs	0.5	471	470	485	483	81	79
SWCNTs	1.0	467	468	483	482	80	78
DWCNTs	0.1	469	467	483	482	80	80
DWCNTs	0.5	466	468	482	482	79	80
DWCNTs	1.0	470	467	484	481	81	80
MWCNTs	0.1	475	467	488	481	83	79
MWCNTs	0.5	472	473	486	484	80	78
MWCNTs	1.0	466	466	482	481	78	80

[a] 5% weight loss temperature measured by TGA.
[b] 10% weight loss temperature measured by TGA.

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much the same as those obtained in argon, emphasizing the high thermal stability of sulfonated polyoxadiazoles even under an oxidative environment. Such high thermal stability is attributed to the polyoxadiazole ring and the overall structure of the POD.[28] Considering the already discussed decrease in sulfonation level and molecular weight as well as the increase in the dispersity of the composites, the thermal stability of the composites remaining similar to that of the neat POD can be considered a good result.

DMTA of the POD composites was carried out to monitor the effect of the SWCNTs, DWCNTs and MWCNTs on thermomechanical properties and T_g. Values of T_g and storage modulus (E', at 100 and 300 °C) are given in Table 5. The variation of E' for various types and contents of fillers is plotted against temperature in Fig. 5. The values of E', which are correlated with the elastic modulus of the material, for the neat POD and the composites are in the range 3.18–4.24 GPa at 100 °C and 2.39–2.84 GPa at 300 °C. The use of only 0.1 wt% of SWCNTs (Fig. 5(a)) increases E' up to 33% at 100 °C. Overall, the addition of fillers at the various concentrations increases E', as can be seen from Table 5. Even at 300 °C the nanocomposites maintain a high stiffness, suggesting the use of these composites in applications at high temperatures. The increase in E' reflects the interaction between the fillers and the POD as well as their homogeneous dispersion.[29]

Values of T_g are summarized in Table 5. T_g of the neat POD is affected by the sulfonation level and molecular weight.[20,21,27] Indeed, recently we have shown that the higher the sulfonation level, the higher is T_g.[21] Therefore the analysis of the influence of concentration of SWCNTs, DWCNTs and MWCNTs on T_g of the synthesized composites is not simple. Considering T_g obtained from the peaks of curves of tan δ as a function of temperature

Table 5. T_g and dynamic mechanical properties of the POD nanocomposites

| Filler | Concentration (wt%) | $T_g{}^a$ (°C) | | Storage modulus (GPa) | |
		E''	Tan δ	At 100 °C	At 300 °C
None	0.0	430	447	3.18	2.48
SWCNTs	0.1	395	419	4.24	2.84
SWCNTs	0.5	395	425	3.96	2.70
SWCNTs	1.0	375	410	3.98	2.80
DWCNTs	0.1	380	415	3.92	2.67
DWCNTs	0.5	380	410	4.10	2.70
DWCNTs	1.0	370	400	3.72	2.47
MWCNTs	0.1	380	410	3.36	2.45
MWCNTs	0.5	395	430	3.73	2.63
MWCNTs	1.0	365	400	3.65	2.39

^{a} Measured by DMTA.

(Fig. 6; Table 5), it can be seen that T_g decreases from 447 °C for the neat polymer down to 400 °C with the addition of 1.0 wt% of DWCNTs or MWCNTs. A similar tendency is observed for T_g obtained from the loss modulus (E''), as shown in Table 5. When fillers are homogeneously distributed in a polymeric matrix, T_g of the composites should increase with filler content.[27] For the composites prepared in the present study, the sulfonation level decreases upto 35% for all contents of the various fillers. The decrease observed here in T_g might be attributed to the variation of the sulfonation level and average molecular weight.
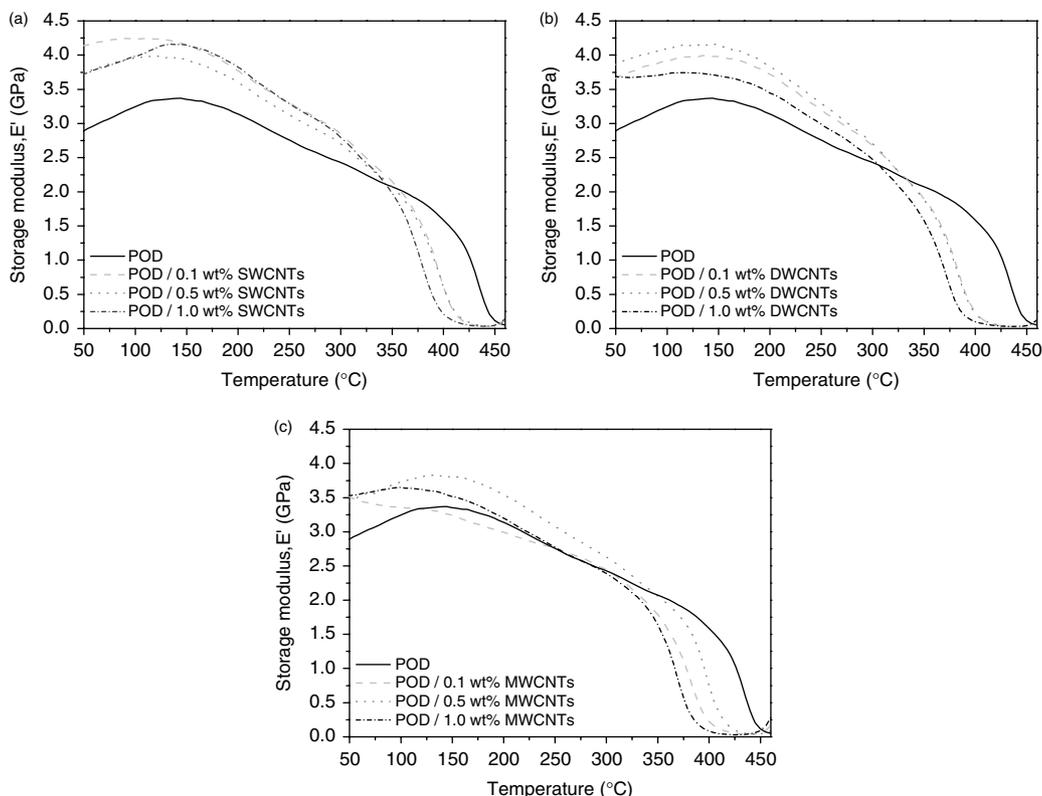

Figure 5. Storage modulus as a function of temperature for the neat POD and composites reinforced with various concentrations of (a) SWCNTs, (b) DWCNTs and (c) MWCNTs.
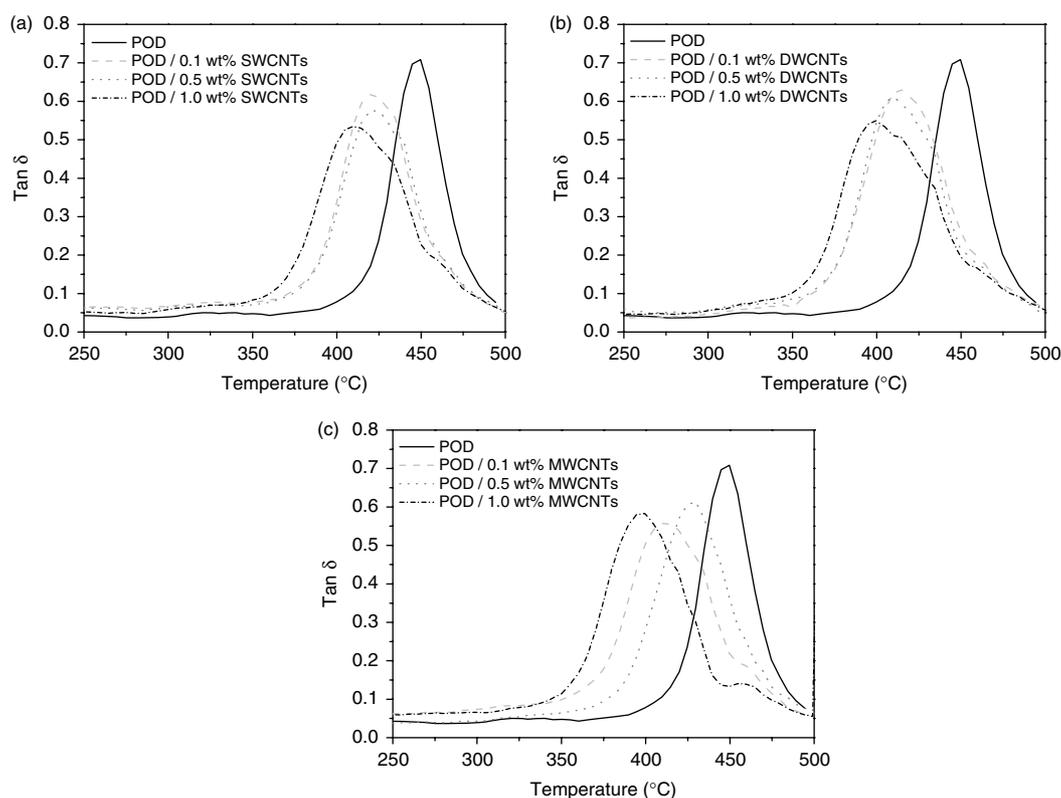
Figure 6. Tan δ as a function of temperature for the neat POD and composites reinforced with various concentrations of (a) SWCNTs, (b) DWCNTs and (c) MWCNTs.

Table 6. Tensile properties of the POD nanocomposites

Filler	Concentration (wt%)	E^a (MPa)	$\sigma_M{}^b$ (MPa)	ε^c (%)	TEB (MJ m^{-3})
None	0.0	2690 ± 42	153 ± 8	45.7 ± 6.8	53 ± 10
SWCNTs	0.1	2880 ± 146	214 ± 11	101 ± 6	155 ± 16
SWCNTs	0.5	2850 ± 75	238 ± 6	109 ± 3	183 ± 7
SWCNTs	1.0	2930 ± 174	213 ± 2	86 ± 9	121 ± 8
DWCNTs	0.1	2610 ± 76	205 ± 12	80 ± 7	120 ± 16
DWCNTs	0.5	2440 ± 140	219 ± 12	72 ± 10	113 ± 21
DWCNTs	1.0	2290 ± 181	221 ± 11	82 ± 10	129 ± 20
MWCNTs	0.1	3330 ± 145	226 ± 19	64 ± 9	101 ± 22
MWCNTs	0.5	2780 ± 206	197 ± 7	65 ± 6	92 ± 11
MWCNTs	1.0	3120 ± 330	198 ± 16	49 ± 11	72 ± 19

[a] Young's modulus.
[b] Tensile strength.
[c] Elongation at break.

In fact, the composites with lower T_g (1.0 wt% of DWCNTs and MWCNTs) have the lowest sulfonation level among all the composites. Therefore, even with a homogeneous dispersion and good interaction between filler and matrix phase, as confirmed by morphological characterization, T_g decreases.

The magnitude of tan δ indicates the relative amount of mechanical energy dissipated during cyclic stress in DMTA testing.[30] As shown in Fig. 6, the value of tan δ decreases from 0.71 to 0.54 when 1.0 wt% of SWCNTs is added to the POD matrix. The tan δ values for all the nanocomposites, in the range 0.55–0.63, are below that observed for the neat polymer. The interaction between filler and polyoxadiazole matrix reduces the

free volume in the nanocomposites, making them behave more elastically, thus leading to the observed decrease in the intensity of the tan δ peak.[31–33] This result further indicates that the fillers reinforce the POD matrix by virtue of their good dispersion and interaction.

Despite the good mechanical properties of CNTs, their potential as a reinforcing material can only be achieved if an interfacial interaction between filler and polymer and an appropriate dispersion of filler in polymer matrix are guaranteed. The high surface area of nanotubes means they can act as interfaces for stress transfer; however, undesirably, it induces strong attractive forces between the CNTs themselves, leading to excessive
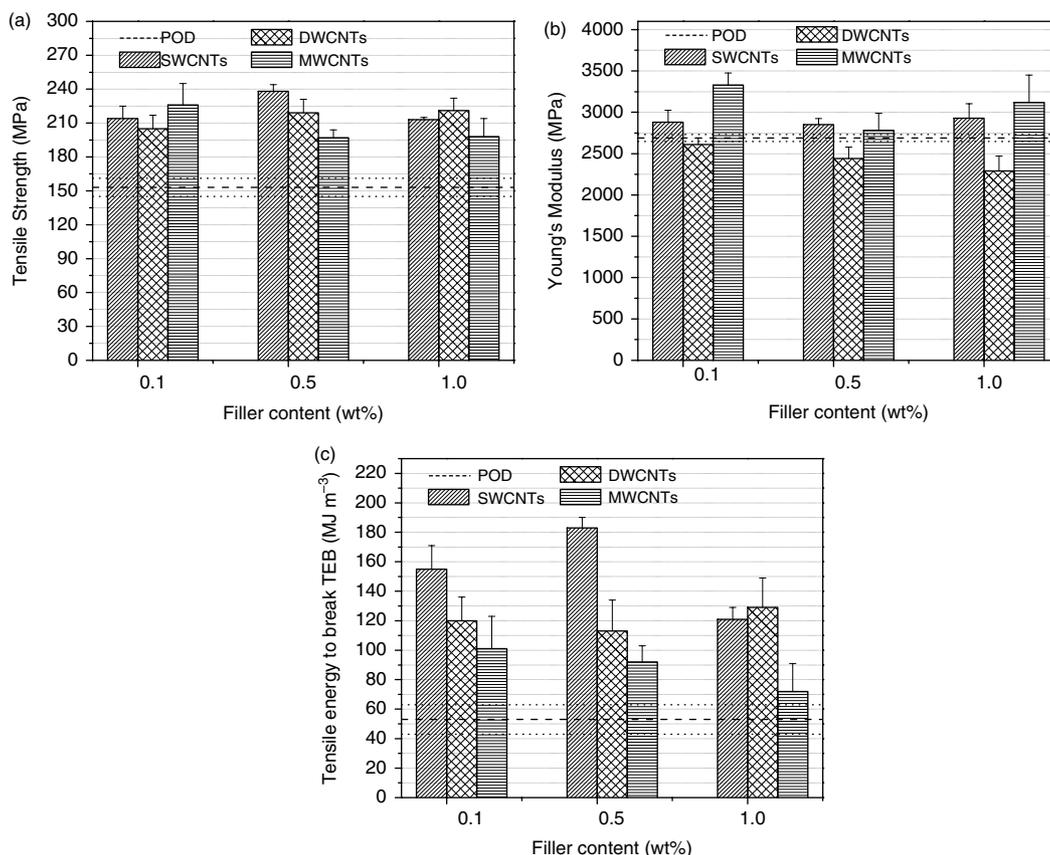
Figure 7. (a) Tensile strength, (b), Young's modulus and (c) TEB for nanocomposites with various CNTs and concentrations. The TS, Young's modulus and TEB of the neat POD are shown as dashed lines.

agglomeration. The synthesis method applied in the present study enhances the interfacial interaction between the various types of CNTs and the POD matrix.[18] Therefore we expect an improvement in the tensile properties of the composites. Table 6 summarizes the tensile properties of all nanocomposites analyzed.

The tensile strength (TS) of the nanocomposites containing SWCNTs, DWCNTs and MWCNTs is shown in Fig. 7(a) as a function of the filler concentration. For comparison, the TS of neat POD is shown as a dashed line. All composites have higher TS than POD. For higher concentrations (0.5 and 1.0 wt%), MWCNTs are less effective in improving TS. The opposite happens at lower concentration (0.1 wt%). A possible explanation for this behavior could be the fact that in MWCNTs only the outermost layer contributes to the mechanical reinforcement. Furthermore, an increase in concentration of fillers can be reflected in an increase of undesirable agglomerates. Such agglomerates are responsible for the concentration of stress and consequently the composites may have an early failure in this case.

The use of 0.5 wt% of SWCNTs leads to an increase in TS from 153 to 238 MPa (+56%). In comparison to the others fillers used in this study, SWCNTs have the highest potential to improve the TS of polymers. This is a consequence of the good specific mechanical properties and high aspect ratio. However, MWCNTs do not agglomerate as much as SWCNTs. The effect of the various fillers on the tensile properties of sulfonated polyoxadiazoles becomes clearer by comparing the representative stress–strain curves of the nanocomposites (Fig. 8).

The strong interaction between the *in situ* functionalized fillers and the POD matrix greatly enhances the dispersion as well as the interfacial adhesion, thus improving the overall mechanical performance of the composites. Figure 7(b) shows the Young's modulus of the nanocomposites containing various CNTs as a function of concentration. For all the composites reinforced with DWCNTs, a decrease in stiffness is observed. The strongest improvement in Young's modulus occurs with the addition of 0.1 wt% of MWCNTs where an increase from 2690 to 3330 MPa (+24%) is observed. It is found that generally the use of MWCNTs is more effective in increasing the stiffness of POD.

Due to dimensional differences, we can expect a much smaller number of MWCNTs in the composites reinforced with the same concentration of CNTs. Therefore the effect of agglomeration is totally dependent of the filler considered. In addition, MWCNTs have a diameter of 15 nm, SSA of 250 m^2 g^{-1} and purity >97% (Table 1). The SWCNTs and DWCNTs have the highest SSA among the fillers considered (>400 m^2 g^{-1}) but a lower purity (>90%). Moreover, among the CNTs used, DWCNTs are the shortest ones (1–10 µm). Due to all these differences in filler purity and reactivity, different effects in the reaction medium are expected and, as a consequence, changes in all the properties of the composites from sulfonation level and molecular weight to mechanical behavior are observed.

The TEB is the total energy absorbed per unit of volume of specimen tested up to the point of rupture.[34] Fig. 7(c) shows the TEB for the composites reinforced with various fillers and concentrations. As can be seen, all the composites display an
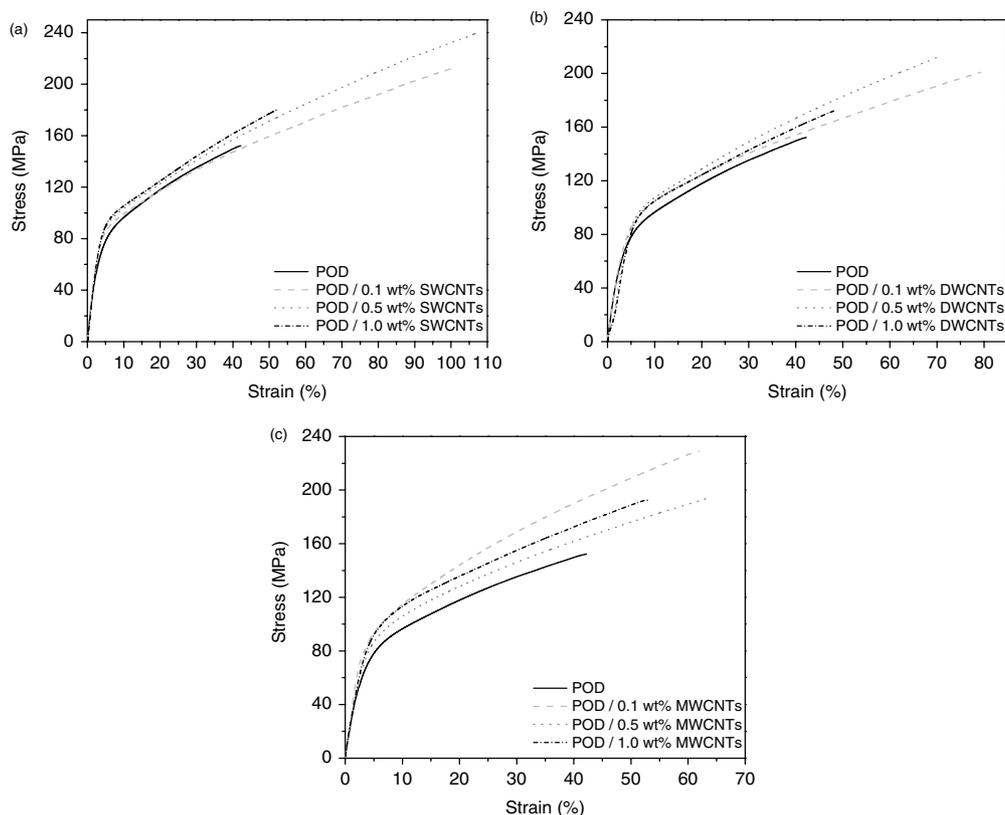
Figure 8. Representative stress–strain curves for the neat POD and composites reinforced with various concentrations of (a) SWCNTs, (b) DWCNTs and (c) MWCNTs.

increase in TEB. The best enhancement occurs with the addition of 0.5 wt% of SWCNTs where TEB increases from 53 to 183 MJ m^{-3} (+245%). Figure 9 shows the macroscopic changes observed in tensile specimens reinforced with 0.5 wt% SWCNTs, after extension up to the point of rupture. It is observed that the elongation at break significantly increases. CNTs represent a great potential to improve the TEB of materials when compared to micro-sized fillers. Large surface areas tend to be more efficient in improving TEB. As a consequence, it is found that SWCNTs and DWCNTs are more effective in enhancing TEB of POD. In addition, the stress–strain curves (Fig. 8) clearly show the increases obtained in elongation at break for the composites. Despite all of results observed relating to tensile properties, in the case of nanocomposites prepared via *in situ* polymerization, the enhancements observed in mechanical and other properties may be a result of several factors and not only a result of the reinforcement effect of the nanofillers. Of course, changes observed in the polymer structure are a consequence of filler addition, which changes the conditions of the reaction medium during synthesis and the morphology.[27,35] In the case of POD, for example, several properties such as mechanical behavior are improved with the increase of molecular weight and sulfonation level.[21]

Figure 9. Morphological changes in length of elongated specimens of POD upon addition of 0.5 wt% SWCNTs.

CONCLUSIONS

Polyoxadiazole composites containing various contents of SWCNTs, DWCNTs and MWCNTs were successfully prepared through polycondensation of DPE and HS using a mild PPA as a reaction medium. The effect of the CNTs in the structural, morphological, thermal and mechanical properties of the POD-based composites has been investigated.

The nanocomposites reinforced with the various CNTs were highly soluble in polar aprotic solvents such as DMSO, NMP, DMA and DMF. High molecular weights, of the order of 10^5 g mol^{-1},
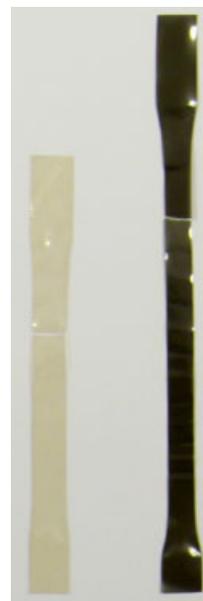
were obtained. Overall, the presence of fillers led to an increase in dispersity. We found that the use of MWCNTs tends in result in nanocomposites with longer chains cpmared to the use of SWCNTs and DWCNTs. This result was attributed to the difference in reactivity of the fillers, since, besides higher purity, MWCNTs have a lower SSA than SWCNTs and DWCNTs.

TEM studies showed that separated SWCNTs and DWCNTs could be found in the POD matrix, as well as small agglomerates, with a size of ca 50–100 nm. The presence of some small aggregates was attributed to the large SSA of the SWCNTs and DWCNTs. Nevertheless, MWCNTs exhibit a good dispersion in the POD matrix. The POD composites are thermally stable at temperatures as high as 475 °C even in an oxidative environment.

We found that the storage modulus increased generally for all the fillers in various concentrations. With only 0.1 wt% of SWCNTs, E' increased up to 33% at 100 °C. Even at 300 °C the nanocomposites maintained their high stiffness. T_g decreased for all the composites due to a decrease in sulfonation level. All the composites exhibited improvement on TS. The use of 0.5 wt% of SWCNTs led to an increase in TS from 153 to 238 MPa (+56%). On the other hand, the Young's modulus showed better improvement with MWCNTs, displaying an increase of 24% at a low content (0.1 wt%). The TEB was found to increase independently of the filler concentration. The best enhancement occurred with the addition of 0.5 wt% of SWCNTs where the TEB increased from 53 to 183 MJ m^{-3} (+245%). SWCNTs and DWCNTs were more effective in enhancing TEB of POD. The strong interactions between the *in situ* functionalized fillers and the POD matrix greatly enhanced the dispersion as well as the interfacial adhesion, thus strengthening the overall mechanical performance of the composites.

In this study, the final properties of the nanocomposites were found to depend on the following factors:

- different reactivity of the fillers, i.e. SSA, purity and aspect ratio;
- homogeneous dispersion of fillers in the POD matrix;
- strong interfacial interaction between fillers and POD;
- variations in molecular weight and sulfonation level of the matrix;
- filler content; and
- changes in morphology.

The final composites may be useful candidates for developing new sensor materials, membranes or coatings for high-performance applications.

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