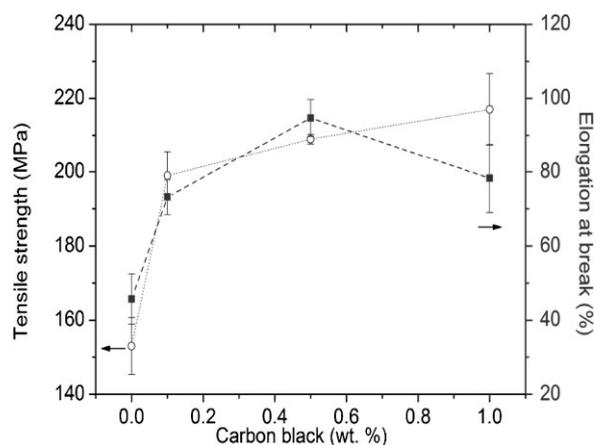


# A Highly Efficient One-Pot Method for the Synthesis of Carbon Black/Poly(4,4'-Diphenylether-1,3,4-Oxadiazoles) Composites

Marcio R. Loos,\* Volker Abetz, Karl Schulte

A series of polyoxadiazoles (PODs) based composites containing carbon black (CB) are prepared through a fast polycondensation reaction of hydrazine sulfate and dicarboxylic acid monomers using poly(phosphoric acid) (PPA) as reaction medium. In order to achieve a homogeneous dispersion of CB, a predispersion step is applied to the CB prior to the synthesis. The moderate acidic nature and high viscosity of the PPA medium promote the oxidation of the CB and suppress reaggregation after dispersion. The carboxylic groups generated on the surface of the CB effectively anchored the growing of POD chains, improving the interfacial interaction between the CB and the surrounding matrix. An increase of 22% in storage modulus at 100 °C is observed. The tensile strength increases up to 48% with the CB addition and the elongation at break increases up to 118% at a low concentration of CB (0.5 wt.-%). The resultant CB/POD composites, which can be cast as dense films, are soluble in several polar aprotic solvents and their POD matrix have molecular weights in the range of  $10^5 \text{ g} \cdot \text{mol}^{-1}$ . The high-performance, high-temperature light-weight materials obtained are thermally stable at temperatures as high as 450 °C.



## Introduction

In the last decades, carbon-based nanostructured materials such as single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), carbon nanofibers (CNFs), and carbon black (CB) have gained increasing

attention. Due to their unique properties, this class of materials have been considered for a wide variety of potential applications such as composites, electronic devices, field emission display, hydrogen storage, and other fields of materials science.<sup>[1,2]</sup> When used as reinforcing additives for composites, they could deliver their outstanding properties to support matrices such as polymers,<sup>[3–8]</sup> ceramics,<sup>[9,10]</sup> and even low melting metals.<sup>[11,12]</sup> The resultant composites would possibly possess enhanced properties providing various potential applications for areas, which require affordable, light-weight, and multi-functional materials.

Most research in this topic has focused on improving the dispensability of CNTs,<sup>[13–18]</sup> CNFs,<sup>[19]</sup> fullerene,<sup>[20,21]</sup> and CB.<sup>[2,22]</sup> Compared with these carbon materials, CB

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nanoparticles are a relatively conductive carbon material composed of 90–99% elemental carbon. It is most readily available and has been widely applied in industry because of its low price.

Due to their large specific surface areas, carbon-based fillers usually exist as agglomerates, hampering their homogeneous dispersion in a multicomponent system. Consequently, their outstanding properties emerging from nanoscale are not effectively transferred to matrix materials. Many efforts have been done to achieve homogeneous dispersion of carbon fillers in various matrix materials, via physical methods aided by sonication,<sup>[23–25]</sup> chemical methods using strong acids such as sulfuric acid and nitric acid,<sup>[26–29]</sup> or combined approaches applying sonication in strong acids.<sup>[30–33]</sup> However, harsh reaction conditions such as power level, exposure time, and temperature usually damage the structure of the filler.<sup>[32,34]</sup> Furthermore, another concern is that the desired material properties of a composite invariably depend on the strength of specific interactions between fillers and matrix polymers. Mechanical properties of CNTs composite via physical mixing depend greatly on the homogeneity of CNTs and interfacial interactions. The same is valid for other carbon-based fillers, such as CB. Introduction of suitable chemical groups to the surface of fillers by chemical methods are a viable approach because they can better prevent agglomeration, enabling higher degree of exfoliation, and allowing better compatibility with matrix components.<sup>[35–40]</sup>

In the light of the above and from an industrial point of view, the in situ process to generate composites seems to be promising.<sup>[41,42]</sup>

Aromatic poly(1,3,4-oxadiazole)s are a class of chemically resistant and thermally stable heterocyclic polymers.<sup>[43,44]</sup> They have been the focus of considerable interest with regard to the production of high-performance materials, particularly owing to their high thermal stability in oxidative atmosphere and specific properties determined by the structure of 1,3,4-oxadiazole ring, which, from the spectral and electronic points of view, is similar to a *p*-phenylene structure.<sup>[45]</sup> Along with their excellent resistance to high temperature, polyoxadiazoles (PODs) have many desirable characteristics such as good hydrolytic stability, high glass transition temperatures, low dielectric constants, and tough mechanical properties. Some PODs have semiconductive properties whereas other structures can be electrochemically doped and thus made conductive, and others have liquid-crystalline properties, which make them very attractive for a wide range of high-performance applications. They exhibit excellent fiber- and film-forming capabilities, thus being considered for use as heat-resistant reinforcing fibers for

advanced composite materials, highly resistant fabrics for the filtration of hot gases, special membranes for gas separation or reverse osmosis, precursors for highly oriented graphite fibers, films, and in the construction of nuclear reactor walls.<sup>[46]</sup>

The present study relates to a fast direct method for the in situ preparation of POD/CB composites. Because of the different reactivity of monomers, significant lower synthesis time is required (4 h) to produce the composite POD compared to other composite polymers synthesized via in situ polymerization in poly(phosphoric acid) (PPA).<sup>[47–49]</sup> Moreover, the viscous PPA is expected to play two important roles for both purification and dispersion of the CB.

## Experimental Section

### Starting Materials

Dicarboxylic acid 4,4'-diphenylether, DPE (99%, Aldrich), dimethyl sulfoxide, DMSO (>99%, Aldrich), hydrazine sulfate, HS (>99%, Aldrich), sodium hydroxide, NaOH (99%, Vetec), CB (average particle size: 18 nm, SSA: >250 m<sup>2</sup>·g<sup>-1</sup>, Evonik Degussa), and PPA (115% H<sub>3</sub>PO<sub>4</sub>, Aldrich). All chemicals were used as received.

### Synthesis of Sulfonated Poly(4,4'-Diphenylether-1,3,4-Oxadiazoles)

The reaction condition for the synthesis of the POD was selected based on the previous studies.<sup>[50]</sup> A typical polycondensation (Figure 1) was run as shown in the following example: polymerizations were carried out in a 500 mL three-necked flask equipped with a mechanical stirrer, with a dry nitrogen inlet tube, to keep the reaction atmosphere free of oxygen and water. Specified amounts of PPA and HS were initially added to the flask and vigorously stirred. The temperature was then increased, in order to reach the desired reaction temperature. After reaching the specified reaction temperature, a specified amount of DPE was added to the flask. The reacting medium was then kept at constant reaction temperature under constant stirring for 4 h.

The final reaction medium is very viscous, which makes precipitation and neutralization of the polymer very difficult. Thus, the final polymer may present high amounts of residual acid, which may cause degradation. To avoid this, the polymer sample was shredded into small fragments using a Retsch Grindomix GM

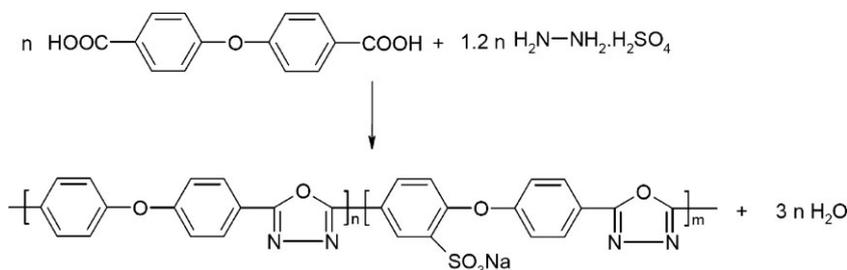


Figure 1. Scheme of synthesis for the poly(4,4'-diphenylether-1,3,4-oxadiazoles).

200 Knife Mill. The reaction medium is first poured into water containing 5% w/v of sodium hydroxide for precipitation of the polymer. Afterwards, the polymer suspension feeds a shredder, where the polymer material is shredded into small fragments. The suspension containing the shredded material was finally transferred to a container, where purification proceeds.<sup>[50]</sup> The final polymer yield was always close to 100% in respect to the limiting reactant. Figure 1 shows a scheme of the reaction synthesis.

### In Situ Polymerization of Sulfonated Poly(4,4'-Diphenylether-1,3,4-Oxadiazoles) With CB Load

In order to prepare composites with homogeneously dispersed fillers a predispersion of the CB in the reaction medium was performed, before the beginning of the synthesis. The predispersion stage is explained as follows: into a 500 mL three-necked flask equipped with a high torque mechanical stirrer, nitrogen inlet, and outlet, PPA and CB were placed and stirred under sonication at 80 °C for 1 h. Afterwards, the PPA/CB solution was stirred at 160 °C during additional 2 h. The rest of reaction sequence and work-up procedure are the same as for the synthesis of POD homopolymer. The initial color of all reaction mixtures was black because of the CB dispersion. At the end of the reaction, the color of the mixture was dark shiny, and the mixture was poured into distilled water to form bundles.

Homogeneous films were cast from solutions with a polymer concentration of 3 wt.-% in DMSO. 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 100 °C for 24 h. The final thickness of the films was about 60 μm.

### Characterization

The polymer and composite structures were characterized by elemental analysis, Raman and infrared spectroscopy. Elemental analysis was conducted on a Carlo Erba Elemental Analyzer-Mod 1108. Raman spectra were recorded on a Jobin Yvon HR800 LabRam spectrometer, using the 633 nm laser line. Infrared spectra were recorded on a Bruker Equinox IFS 55 spectrophotometer in the range 4000–400 cm<sup>-1</sup>. 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<sup>2</sup> was employed to evaluate the weight average molecular weights of polymer and composite matrix. The equipment was calibrated using polystyrene standards (Merck) with weight average molecular weights ranging from 309 to 944 000 g·mol<sup>-1</sup>. A solution with 0.05 M lithium bromide in dimethylacetamide, DMAc (≥99.9%, Aldrich) was used as the eluent. Solutions with 0.5 wt.-% of the composite PODs were prepared, centrifuged, filtered through 0.2 μm, and injected into the chromatograph.

The film morphology was observed by transmission electron microscopy (TEM). The TEM images were obtained using a Tecnai G2

F20 field emission at an acceleration voltage of 200 kV; the samples were cut into slices of 80 nm thickness using an ultracut microtome with diamond knife.

Thermogravimetric analysis (TGA) 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 to 900 °C at 10 °C·min<sup>-1</sup>. Dynamic mechanical thermal analysis (DMTA) was used for determination of the glass transition temperature ( $T_g$ ), storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ). DMTA 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 to 500 °C at a heating rate of 2 °C·min<sup>-1</sup> and at a constant strain of 0.05%. Tensile tests 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.

## Results and Discussion

### Synthesis of POD/CB Composites

Sulfonated POD composites containing different concentrations of CB (0.1, 0.5, and 1.0 wt.-%) have been prepared via in situ polymerization as schematically shown in Figure 2. Covalent attachment of POD onto the CB surface should be expected to occur by condensation reaction of in situ COOH groups generated on the surface of the CB with the NH<sub>2</sub>NH<sub>2</sub> hydrazine monomer, leading to the formation of arylcarbonyl and CONHNH<sub>2</sub>, respectively. Formation of hydrazide groups (CONHNHCO) is expected based on the reaction between CONHNH<sub>2</sub> and C=O groups of the acid monomer.

The initial color of all the reaction mixtures was black as a consequence of the CB dispersion. In all cases, the reaction mixtures were homogeneous with drastic increase in viscosity at the end of polymerization. The viscosity had reached the point that the dope stuck to the stirring rod, and this provided a visual signal that high molecular weight polymers were being synthesized. Solution behaviors of

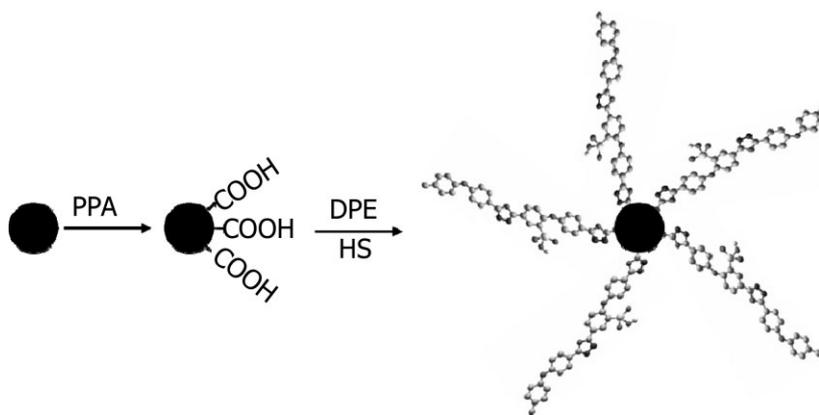


Figure 2. Proposed route for the oxidation of the CB (represented as a black circle) and grafting of POD on its surface.

final reaction mixtures were different. The composite with 0.1 wt.-% CB could be poured into water to spin fiber simply by force of gravity. In the composites with 0.5 and 1.0 wt.-% CB, the viscosity was higher, so water was added into the reaction vessel and a big chunk of product was isolated in each case.

The resultant composites were soluble in various common polar aprotic solvents such as DMSO, *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMA), and *N,N*-dimethylformamide (DMF). Therefore, they are potentially most valuable for further applications.

Against what could be expected, taking into account that polycondensation reactions could be hindered in the presence of CB, which could act as an impurity, sulfonated POD composites containing CB were successfully prepared via in situ polymerization, as observed by SEC measurements, elemental analysis, FTIR, and Raman spectra.<sup>[18]</sup>

Elemental analysis data for the sulfonated POD homopolymers shown in Table 1 are in agreement with the value range for the sulfonated PODs. The POD sulfonation level (S/C) has been shown to be dependent on the reaction time,<sup>[51]</sup> reaching the value range 0.085–0.0998 (44–51%) for the synthesis performed in 4 h. In this work, the sulfonation level has been changed for all the used contents of CB (Table 1). The presence of CB leads to a decrease of up to 26% in the sulfonation level of composites. These results are explained as follow. The sulfonation of PODs synthesized in PPA occurs by the presence of sulfuric acid in the solution of HS salt ( $\text{NH}_2\text{-NH}_2 \cdot \text{H}_2\text{SO}_4$ ). This reaction involves an electrophilic substitution reaction of the electrophilic agent ( $\text{SO}_3$ ) coming from the sulfuric acid and is activated by electron donating groups, in this case the ether group attached to the aromatic ring.<sup>[22]</sup> As a consequence of the synthesis route used in our study, after the dispersion of the CB in the PPA, the HS is added to the reactor. We believe that, during this step, still before the addition of the DPE, part of the sulfuric acid, which would later participate in the sulfonation reaction, is consumed for the oxidation of the CB. Thus, as part of this process, the sulfuric acid releases free oxygen atoms and can make carbon atoms of the CB

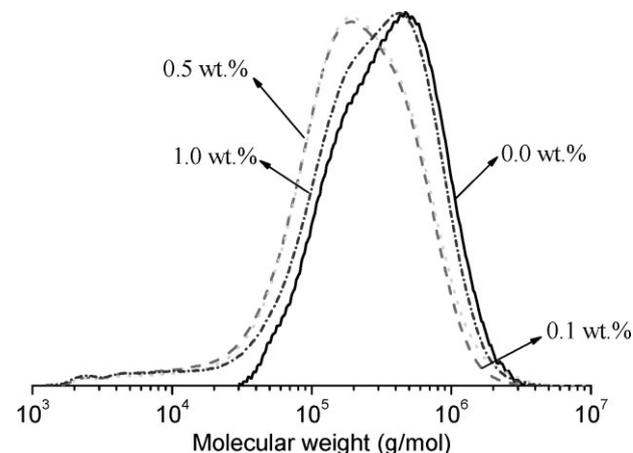


Figure 3. Molecular weight distribution curves of the neat polyoxadiazole and CB/POD composites.

become active. Therefore, the free oxygen atoms and active carbon atoms can form  $\text{-COOH}$  groups on the surface of CB. As a result of the decrease of sulfuric acid in the reaction media, the sulfonation level of the POD matrix decreases.

We measured the molecular weights of POD with different CB concentrations in order to examine the effect of CB in the polymerization. The results of GPC analysis are summarized in Figure 3 and Table 2. High molecular weights in the order of magnitude of  $10^5 \text{ g} \cdot \text{mol}^{-1}$  for the CB-based composites were obtained. As CB contents in POD increased, we found that the molecular weight of POD increases, however, the values are below the obtained for the homopolymer. Moreover, the polydispersity (PDI) measured was 2.0, 3.8, 4.0, and 4.2 for the neat polymer and composites reinforced with 0.1, 0.5, and 1.0 wt.-% CB, respectively. Such increase in PDI implies that species with lower molecular weights in the order of magnitude of  $10^3 \text{ g} \cdot \text{mol}^{-1}$  started to be formed due the presence of the nanofillers in the reaction medium. The degree of polymerization (DP) is the number of monomer units which polymerized to form the polymer, i.e., the number of mer units in a chain. Table 2 reports the DP obtained for the homopolymer and composites. We found that among the samples, nanocomposites with 0.1 wt.-% CB have shorter chains whereas composites with 1.0 wt.-% CB have longer chains. Nevertheless, all the composites have a lower DP than that measured for the neat POD.

Table 1. Elemental analysis data and empirical formulas for the sulfonated polyoxadiazole nanocomposites.

CB [wt.-%]	C [%]	N [%]	S [%]	S/C	SL [%] <sup>a)</sup>
0	54.5	9.2	4.8	$0.088 \pm 0.004$	46
0.1	58.7	9.9	4.4	$0.075 \pm 0.004$	39
0.5	57.9	9.7	3.8	$0.066 \pm 0.0007$	34
1.0	58.0	9.7	4.1	$0.071 \pm 0.0002$	37

<sup>a)</sup>Sulfonation level assuming 100% sulfonated when  $m = 0$  ( $S/C = 0.19$ ).

Table 2. Molecular weight and polydispersity of the POD nanocomposites.

CB [wt.-%]	$\bar{M}_w$ [ $\text{g} \cdot \text{mol}^{-1}$ ]	PDI	DP
0.0	$4.2 \times 10^5 \pm 3.5 \times 10^3$	$2.0 \pm 0.1$	724
0.1	$2.7 \times 10^5 \pm 2.8 \times 10^3$	$3.8 \pm 0.1$	270
0.5	$3.0 \times 10^5 \pm 3.5 \times 10^3$	$4.0 \pm 0.3$	280
1.0	$3.6 \times 10^5 \pm 5.7 \times 10^3$	$4.2 \pm 0.5$	315

The observed changes in molecular weight, PDI, DP, and sulfonation level can be explained by the presence of the fillers in the reaction medium, which may influence the synthesis chemically as well as physically. Several parameters, crucial for the synthesis of sulfonated PODs, as the viscosity of reaction medium as well as the micromixing effects may change due to the addition of CB. In the case of a polymerization via polycondensation, the polymerization occurs by a continuous reaction between the functional groups of the multifunctional molecules (monomers). The basic characteristics of these reactions include the continuous growth of the average molecular weight with time and releasing of condensation byproducts, which can be influenced by the presence of fillers. As discussed previously, the fillers participated in the polymerization reaction and consumed the HS after the predispersion state (Figure 2). Therefore, the increase in PDI 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 POD chains under growing. In other words, the generation of CONHNH<sub>2</sub> groups on the fillers surface (Figure 2) triggers the growing of the POD chains, tethered on the filler surfaces, obstructing the growth of longer polymer chains. This kind of end-tethered POD on CB surfaces promotes the physical contact with the polymer matrix, allowing in the nanocomposites an efficient load transfer from the matrix phase to the reinforcement phase. Due to the mechanism of reaction involved in the synthesis of the composites, it is very complex to control the polymerization conditions. Due to the constant growing of POD chains on the CB surface, we are not able to avoid the formation of low molecular weight polymer fraction. Therefore the evaluation of the extent of the influence of different factors (sulfonation level, MW, PDI, and DP) separately is not possible.

Nevertheless, the comparison of the composites with the pristine sulfonated POD is difficult once the polymer shows different sulfonation levels (S/C), which influence the dipole-dipole interactions between the sulfonated groups.<sup>[18]</sup> The introduction of sulfonic groups increases the intermolecular interaction and consequently increases the  $T_g$  and mechanical properties.<sup>[51]</sup> It is worth noting that the changes in the polymer properties are directly correlated to the presence of nanofillers in the reaction medium. Moreover, the observed change in structural properties of the POD, as molecular weight, PDI, and sulfonation level, influence the other properties of the nanocomposites, as will be further discussed.

Attempts to confirm the proposed route shown in Figure 2 were done by analyzing the FTIR and Raman spectra of the composites. No difference (additional band or shifted band) was observed between the spectra of the neat polymer and composites containing different CB amounts.<sup>[52–55]</sup> Figure 4 shows the Raman spectra of

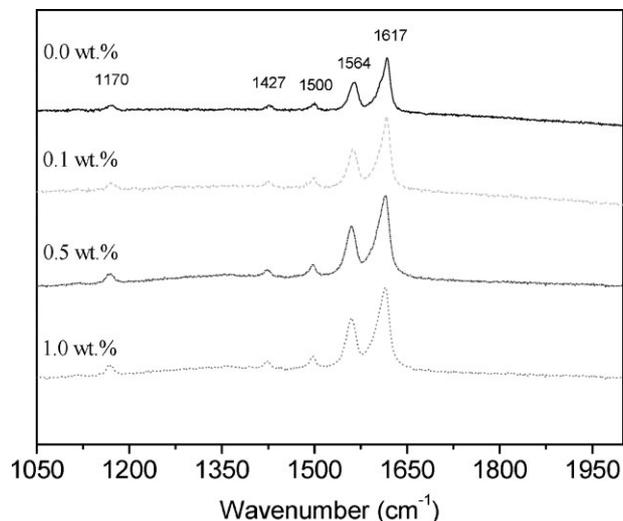


Figure 4. Raman spectra of the neat POD and CB/POD composites.

sulfonated POD composites containing 0.1–1.0 wt.-% of CB. All composites have similar bands as the ones present in the pristine sulfonated POD, at 1 617, 1 564, and 1 427 cm<sup>-1</sup> attributed to the aromatic groups, and at 1 170 cm<sup>-1</sup> relative to sulfonated groups of the main chain of the POD.<sup>[56–58]</sup> Bands at 1 500 cm<sup>-1</sup> due to the oxadiazole ring are also observed. For all the composites the signals of the polymer overcomes completely that of the CB. This is most likely because of the low amount of CB compared to POD.

### Dynamic Mechanical Thermal Analysis of the POD/CB Composites

Dynamic mechanical thermal analyses of the POD/CB composites were carried out to monitor the effect of the CB on thermomechanical properties and glass transition temperature ( $T_g$ ). Values of the  $T_g$  and storage modulus ( $E'$ , at 100 and 300 °C) are listed in Table 3.

Table 3.  $T_g$  and dynamic mechanical properties of the POD nanocomposites.

CB [wt.-%]	$T_g$ [°C] <sup>a)</sup>		Storage modulus [GPa]	
	$E''$	$\tan \delta$	at 100 °C	at 300 °C
0.0	430	447	3.18	2.48
0.1	390	420	3.88	2.58
0.5	390	414	3.75	2.70
1.0	400	425	3.04	2.16

<sup>a)</sup>Glass transition temperature measured by DMTA: loss modulus ( $E''$ ) and  $\tan \delta$ .

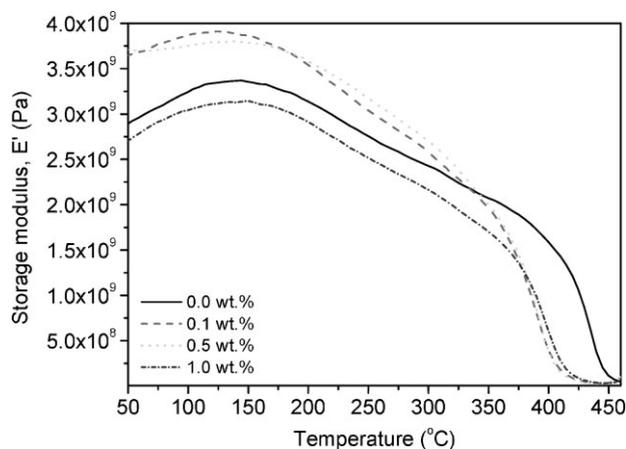


Figure 5. Storage modulus as a function of temperature for the CB/POD nanocomposites.

The variation of  $E'$  and  $\tan \delta$  among different contents are plotted against temperature in Figures 5 and 6. The values of  $E'$ , which are correlated with the elastic modulus 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, 3.88, 3.75, and 3.04 GPa, respectively. The increase in  $E'$  reflects the interaction between the CB and the POD and the homogeneous dispersion. The  $T_g$  values of the composites are affected by the sulfonation level, molecular weight ( $\bar{M}_w$ ), PDI and by the CB content (Tables 1–3). Recently we have shown the effect of the sulfonation level on the  $T_g$  of sulfonated POD: the higher the sulfonation level, the higher the  $T_g$ .<sup>[50]</sup> Considering the  $T_g$  value obtained from the peak of  $\tan \delta$  as a function of temperature (Figure 6), it can be seen that the  $T_g$  decrease up to 33 °C with the addition of 0.5 wt.-% CB. A similar tendency is observed for the  $T_g$  values obtained from the loss modulus ( $E''$ ) (Table 3). Such decrease observed in  $T_g$  values may be attributed mainly to the

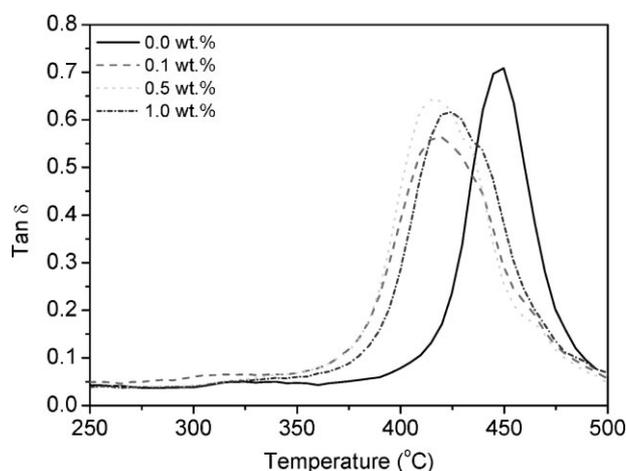


Figure 6.  $\tan \delta$  as a function of temperature for the CB/POD nanocomposites.

variation of the sulfonation level and molecular weight. Comparing Tables 1–3, one can see that the composite with the lower  $T_g$  (0.5 wt.-% CB) have a lower  $\bar{M}_w$  and sulfonation level than those of the neat POD. Therefore, even with a homogeneous dispersion and good interaction between filler and matrix phase, as confirmed by morphological characterization, the  $T_g$  decreases. Moreover, the magnitude of  $\tan \delta$  indicates the relative amount of mechanical energy dissipated during cyclic stress in DMTA testing.<sup>[59]</sup> A material is perfectly elastic if  $\tan \delta$  is 0; perfectly viscous if  $\tan \delta$  is infinity and equally elastic and viscous if  $\tan \delta$  is one. As shown in Figure 6, the value of  $\tan \delta$  decreased from 0.71 to 0.52 when 0.1 wt.-% of CB is added to the POD matrix. This result shows that the composites behave more elastically.<sup>[60–62]</sup>

### Thermal Stability of the POD/CB Composites

The samples were subjected to determine their thermo-oxidative stability by TGA of the bulk samples in argon and air, respectively. The results are depicted in Figure 7.

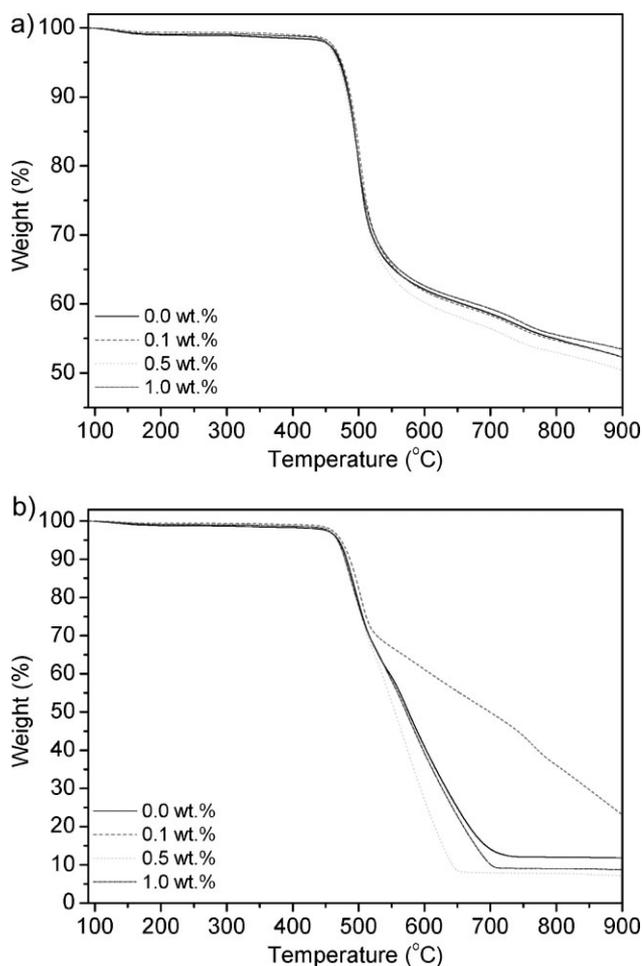


Figure 7. TGA thermograms of neat POD and CB/POD nanocomposites: (a) in argon and (b) in air.

Thermal stabilities of composites in argon were slightly increased, but not significantly. Neat POD and CB-based composites show (under argon) a 5 wt.-% loss ( $T_{d5}$ ) in the range 466–470 °C, 10 wt.-% loss ( $T_{d10}$ ) in the range 482–485 °C and residue at 500 °C around 80%. Such high thermal stability is attributed to the POD ring and the overall rigid structure of the POD.<sup>[46]</sup> Under air atmosphere, the addition of fillers did not have significant effect on the thermal stability of the composites. However, surprisingly the composites with 0.1 wt.-% CB showed an increase of up to 171% in char yield at 700 °C under air atmosphere (Figure 7b). This result was not expected and is still not fully understood.

Considering the previously discussed decrease in sulfonation level and molecular weight as well as the increase of the PDI of the composites, keeping the thermal stability of the composites similar to the neat POD can be considered a good result.

### Tensile Properties of the POD/CB Composites

Table 4 lists the tensile properties and Figure 8 shows the stress–strain curves of neat POD and POD containing 0.1, 0.5, and 1.0 wt.-% CB. The Young's modulus increased slightly (up to 7%) when 0.5 wt.-% CB were incorporated into the POD. The tensile strength increases up to 34, 37, and 48% when the CB concentrations are 0.1, 0.5, and 1.0 wt.-%, respectively. 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. As can be seen in Figure 8, the addition of the CB makes the POD more ductile. The use of only 1.0 wt.-% of CB increased the elongation at break up to 118%. There are several works reporting the increase of tensile strength and Young's modulus of composites by the addition of carbon-based fillers.<sup>[59,63,64]</sup> The increase of elongation at break has been less reported.<sup>[63]</sup> Furthermore, in the case of composites prepared via in situ polymerization, the effect of the addition of nanoparticles in the polymer structural properties, such as molecular weight, PDI, or even sulfonation level has not been considered before.<sup>[41,65–67]</sup> Therefore, in the case of composites prepared via in situ polymerization,

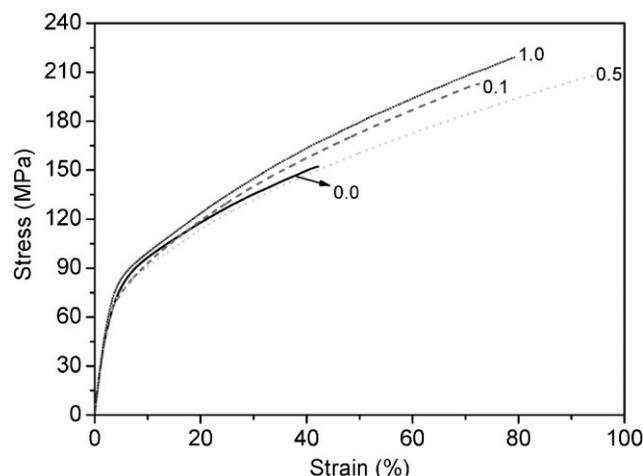


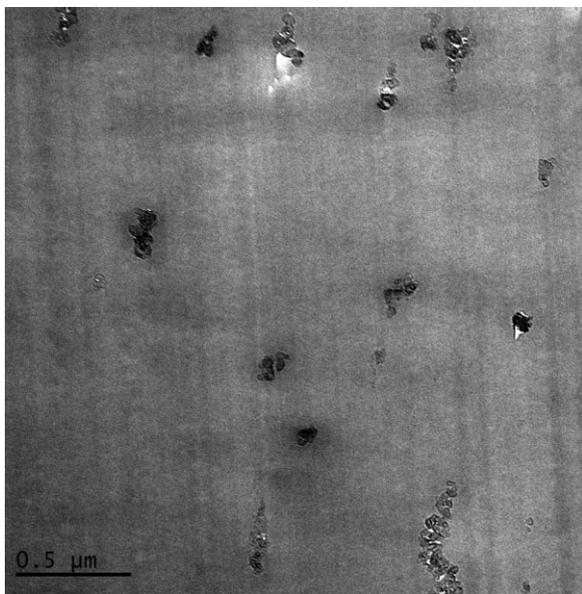
Figure 8. Representative stress–strain curves for the CB/POD nanocomposites.

variations observed in mechanical or any other polymer properties may be a result of several factors and not just a result of the reinforcement played by the nanofillers. Obviously, changes observed in the polymer structure are a consequence of the filler addition, which may change the conditions of the reaction medium.<sup>[18,45]</sup> The influences of the molecular weight in the properties of POD have been recently studied by this author. In the case of POD, for instance, several properties like thermal stability and mechanical behavior are improved with the increase of molecular weight and sulfonation level.<sup>[50]</sup> However, as previously discussed, the addition of CB significantly decreased the  $\bar{M}_w$  and sulfonation level of PODs. In the light of the above, the observed increase of tensile strength and elongation at break observed in this work may be attributed mainly to a homogeneous dispersion of CB and a strong interfacial interaction between CB and the POD matrix. This is probably due to the fact that, the carboxyl groups generated on the surface of the CB during the predispersion step, effectively anchored the growing POD chains, thus improving the interfacial bonding between the CB and the surrounding matrix. The interfacial bonding enables an effective stress transfer from the polymer to the CB phase.

Table 4. Tensile properties of the POD composites.

CB [wt.-%]	$E^a$ [Mpa]	$\sigma_M^b$ [Mpa]	$\sigma_M$ change [%]	$\varepsilon^c$ [%]	$\varepsilon$ Change [%]
0.0	2690 ± 42	153 ± 8	–	45.7 ± 6.8	–
0.1	2540 ± 332	199 ± 7	+30	73.2 ± 4.7	+62
0.5	2830 ± 41	209 ± 1	+37	94.7 ± 5.0	+107
1.0	2770 ± 115	217 ± 10	+42	78.3 ± 9.3	+71

<sup>a</sup>Young's modulus; <sup>b</sup>Tensile strength; <sup>c</sup>Elongation at break.



**Figure 9.** TEM images of the fracture surface of the POD nano-composites reinforced with 0.5 wt.-% CB after conducting tensile tests.

### Morphology of the POD/CB Composites

In order to investigate the dispersion of the CB in the POD matrix, the fracture surface of the POD composites reinforced with 0.5 wt.-% of CB was analyzed by using a TEM. As shown in Figure 9, the CB exists in the form of small aggregates with size in the range of 50–200 nm. However, such aggregates might be coated by the POD polymer improving the interfacial interaction with the POD matrix. Consequently, the CB aggregates tend to be stretched in the direction of the applied stress during the tests and thus imply in resist to crack development, suggesting a synergistic effect of the coated CB during the fracture.

### Conclusion

Different POD/CB composites, with 0.1, 0.5, and 1.0 wt.-% CB content, have been prepared through a fast polycondensation reaction using a new method. A homogeneous dispersion of the CB in the POD matrix was achieved due to a predispersion step applied to the CB previously the synthesis, as revealed by TEM micrographs of fractured films. The carboxyl groups generated on the surface of the CB during the synthesis effectively anchored the growing of POD chains, thus improving the interfacial bonding between the filler and the surrounding matrix. The interfacial interaction enabled an effective stress transfer between the polymer and the CB. The presence of CB led to a decrease of up to 26% in the sulfonation level of composites and increase in the PDI. An increase of 22% in storage modulus at 100 °C was observed. TGA thermograms show a

substantial increase of up to 171% in char yield at 700 °C for the composites with 0.1 wt.-% CB. Improvements of tensile strength with the CB concentration (up to 48%) and elongation at break (up to 118%) within low concentration of CB (0.5 wt.-%) were obtained. 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. Therefore, the observed results reveal the efficiency of our synthesis method.

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