



# In situ-polymerization of fluorinated polyoxadiazole with carbon nanotubes in poly(phosphoric acid)

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## ABSTRACT

In the present work, in-situ polymerizations of fluorinated polyoxadiazole through a polycondensation reaction of A–A (hydrazine sulphate) and B–B (aromatic dicarboxylic acid) monomers with multiwalled carbon nanotubes (MWCNT) in poly(phosphoric acid) were performed in the frame of time 3 to 48 h. The effect of acid treatment in polyphosphoric acid on the CNT structure was analyzed by SEM, TGA and FTIR. Fluorinated polyoxadiazole/MWCNTs soluble in organic solvents with high molecular weights (around 200 000 g/mol) could be synthesized in 3 h. The fluorinated polyoxadiazole/MWCNTs exhibits high thermal stability with degradation temperature at about 460 °C.

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## 1. Introduction

Carbon nanotubes (CNTs) have been the subject of considerable attention because of their exceptional unique electronic, physical, mechanical and optical properties [1,2]. Although the addition of CNT into polymeric materials exhibits a high potential of application in different research fields, there are still many limitations and challenges to be met such as the manufacturing route and surface properties of nanoparticles, which influence the resulting degree of dispersion and interfacial adhesion with the polymer matrix. Various physical, chemical, or combined approaches have been reported to afford homogeneous dispersion of CNTs in polymer solution or melt [1–5]. Functionalization of fillers has been shown to reduce agglomeration and to improve the interaction between the fillers and the polymeric matrix [3,4].

Recently, Oh et al. [4] described a grafting of polyetherketone onto multi-walled carbon nanotube (MWCNT) by in-situ polycondensation of the AB monomers, 3- and 4-phenoxybenzoic acids in viscous PPA at 130 °C for 48 h. In the present work, in-situ polymerizations of fluorinated polyoxadiazole through a polycondensation reaction of A–A (hydrazine sulphate) and B–B (aromatic dicarboxylic acid) monomers with MWCNT in polyphosphoric acid were performed in the frame of time 3 to 48 h. For that, the effect of acid treatment in polyphosphoric acid on the CNT structure was analyzed. Polyoxadiazoles have a great potential as structural material because of their superior thermal, chemical and mechanical properties [6–8]. It has been shown that fluorinated

polyoxadiazole/MWCNTs soluble in organic solvents with high molecular weights (around 200 000 g/mol) can be synthesized in 3 h.

## 2. Experimental section

### 2.1. Materials

4,4'-dicarboxyphenyl-hexafluoropropane, HF (99%, Aldrich), hydrazine sulfate, HS (>99%, Aldrich), sodium hydroxide, NaOH (99%, Vetec), poly(phosphoric acid), PPA (115% H<sub>3</sub>PO<sub>4</sub>, Aldrich), multiwalled carbon nanotubes, MWCNTs (>95%, Bayer MaterialScience). All chemicals were used as received.

### 2.2. In-situ polymerization of fluorinated polyoxadiazole/carbon nanotube composites

Initially polyphosphoric acid, PPA, was added to the flask and heated up to 60 °C under dry nitrogen atmosphere. Then, 1 wt.% multiwalled carbon nanotube, MWCNT, was added to the polyphosphoric acid and homogenized through stirring and heating up to 160 °C. After 0.5–48 h for CNT functionalization, hydrazine sulfate salt, HS, was added to this mixture. After dissolving the HS, 4,4'-dicarboxyphenyl-hexafluoropropane, HF, was added to the flask. The molar dilution rate (PPA/HS) and the molar monomer rate (HS/HF) were kept constant and equal to 10 and 1.2, respectively. After reacting the mixture for 3–48 h, the reaction medium was poured into water containing 5% w/v of sodium hydroxide, for precipitation of the polymer composite. The pH of this suspension was controlled according to literature [9]. Composite polyoxadiazoles soluble in the solvents NMP, DMAc, DMSO, THF and chloroform were obtained (Yield: 97–99%).

(C<sub>16.9</sub>H<sub>8</sub>N<sub>2</sub>O<sub>1</sub>F<sub>6</sub>) (367): Calcd. N/C 0.137; Found N/C 0.130.

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(D. Gomes).

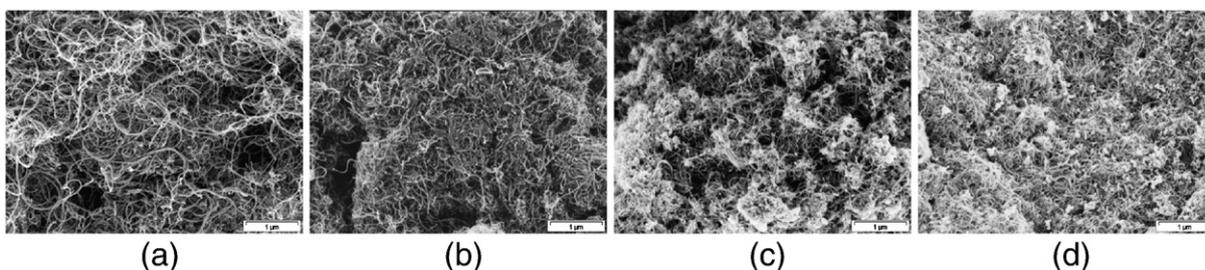


Fig. 1. SEM images of pristine MWCNTs (a) and functionalized after acid treatment at 160 °C for 30 min (b), 3 h (c) and 48 h (d).

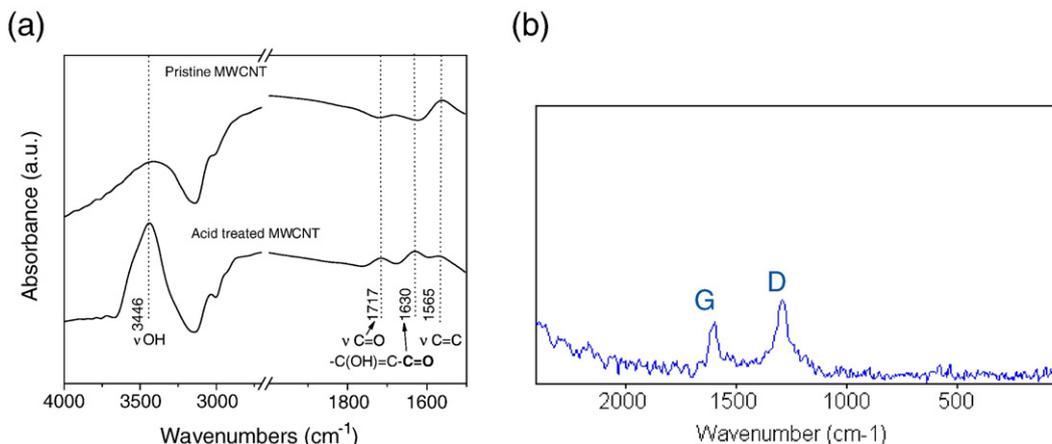


Fig. 2. (a) FTIR spectra of the pristine and of the acid treated MWCNT for 30 min, respectively; (b) Raman spectrum of the pristine MWCNT.

### 2.3. Polymer composite characterization

The polymer composite structures were characterized by elemental analysis, infrared and Raman spectroscopy. Elemental analysis was conducted on a Carlo Erba Elemental Analyzer-Mod 1108. Infrared spectra were recorded on a Bruker Equinox IFS 55 spectrophotometer. Raman spectra were recorded on a FT-Raman Modul RAMIII using a Nd:YAG laser excited at 1064 nm. A Viscotek SEC apparatus was employed to evaluate the weight average molecular weights of the polymer composite samples. A solution with 0.05 M lithium bromide in DMAc was used as carrier. Solutions with 0.5% (w/w) of the composite polyoxadiazoles were prepared, filtered through 0.2  $\mu\text{m}$  and injected into the chromatograph. The polyoxadiazole composite morphology was observed by scanning electron microscopy (SEM) type LEO 1550VP. Thermogravimetric analysis (TGA) experiment was carried out in a Netzsch 209 TG. The samples were heated from 100 to 700 °C at 10 °C/min under nitrogen atmosphere.

### 3. Results and discussion

In order to select the synthesis conditions, the MWCNTs were first treated at 160 °C in poly(phosphoric acid). The reaction temperature was selected based on a previous work for the optimization of polyoxadiazole synthesis based on an experimental design of experiments [10]. Fig. 1 shows the SEM images of pristine MWCNTs and functionalized at 160 °C with different reaction times. The analysis of Fig. 1 indicates an increase of a homogeneous cover on the surface of the MWCNT walls with the increase of the reaction time. Incorporation of hydroxyl and carboxyl groups onto the CNT surface was qualitatively confirmed by FTIR. As no significant difference could be observed for the CNTs treated in poly(phosphoric acid) in the range of time of 30 min to 48 h, only a representative FTIR spectrum of the acid treated CNT for 30 min is shown in Fig. 2 (a). In addition to the peak at ca. 1565  $\text{cm}^{-1}$  arising from C=C stretching observed in all spectra, peaks placed at 1717  $\text{cm}^{-1}$  and 1630  $\text{cm}^{-1}$  related to the C=O stretches, are observed for the acid treated MWCNTs. The C=O stretches at 1717  $\text{cm}^{-1}$  and 1630  $\text{cm}^{-1}$  are related to carbonyl groups in acid (–COOH) and ceto-enolic structures (–C(OH)=C=O), respectively [11]. An increase in the peak at 3446  $\text{cm}^{-1}$  is related to the absorbed water and assigned to the O–H stretch of the hydrogen-bonded groups. The analysis of the Raman spectra indicates no significant changes in the D-band intensity of the acid treated MWCNTs when compared to the Raman spectrum of the pristine MWCNT (Fig. 2 (b)), which shows D- and G-bands at about

1300  $\text{cm}^{-1}$  and 1600  $\text{cm}^{-1}$ , attributed respectively to the disorder and graphite modes. This result maybe attributed to the relative high intensity of the D-band in the pristine MWCNT.

The poly(phosphoric acid) has been reported to be a mild reactive acid medium [4] and after acid treatment in the range of time 3 to 48 h only a small decrease in the thermal stability is observed for the MWCNTs. The treated CNTs for 30 min were quite stable at temperatures up to 700 °C with a residue of 98% while the MWCNT treated for 48 h showed a residue of 93% at the same temperature (Fig. 3). This result is indicative that the CNTs treated for 48 h have more physical defect sites, mainly due to bonding losses on the surface as well as end-capping losses [12]. Taking into account that the thermal stability of the acid treated MWCNTs for 30 min is kept unchanged and that acid groups are already incorporated in this condition, the CNTs were pre-heated at 160 °C for 30 min before adding the monomers for the in-situ polymerization.

The thermal stability of the fluorinated polyoxadiazole (POD) and of the fluorinated polyoxadiazole with 1 wt.% MWCNTs (PODCNT) was analyzed by thermogravimetric analysis (TGA), as shown in Fig. 3. The thermal stability of PODCNT is slightly better than

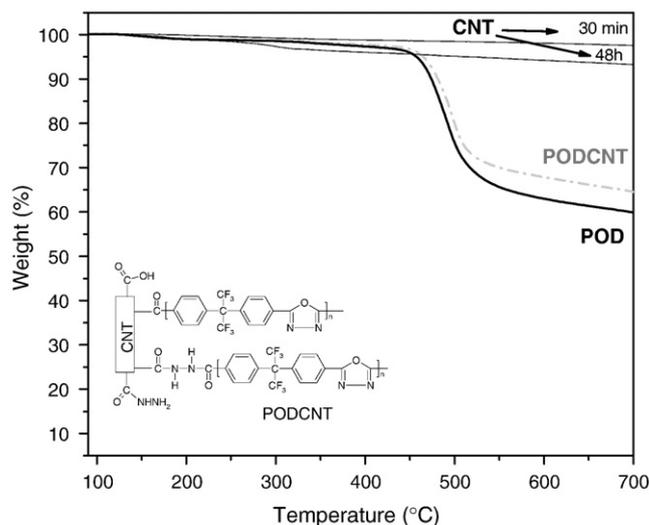
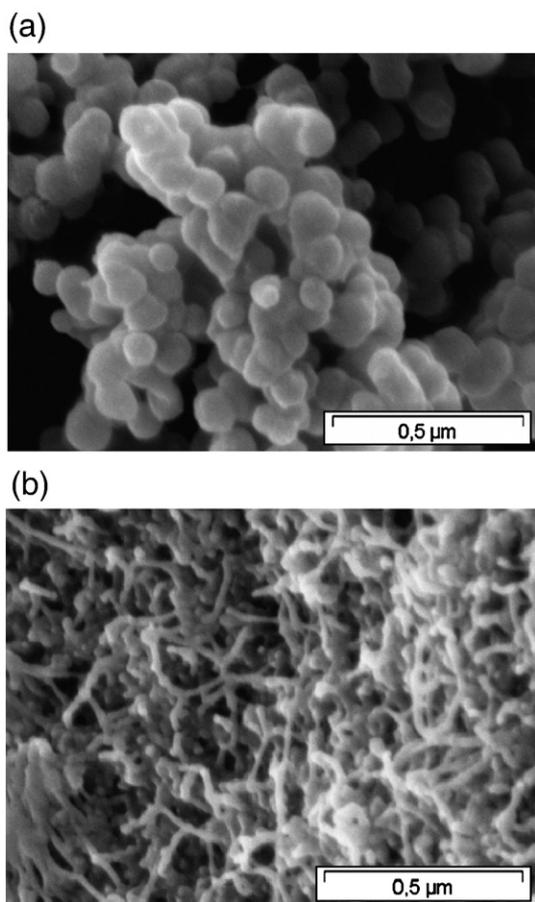


Fig. 3. TGA spectra of acid treated CNTs, fluorinated polyoxadiazole (POD) and fluorinated polyoxadiazole with 1 wt.% MWCNTs (PODCNT).



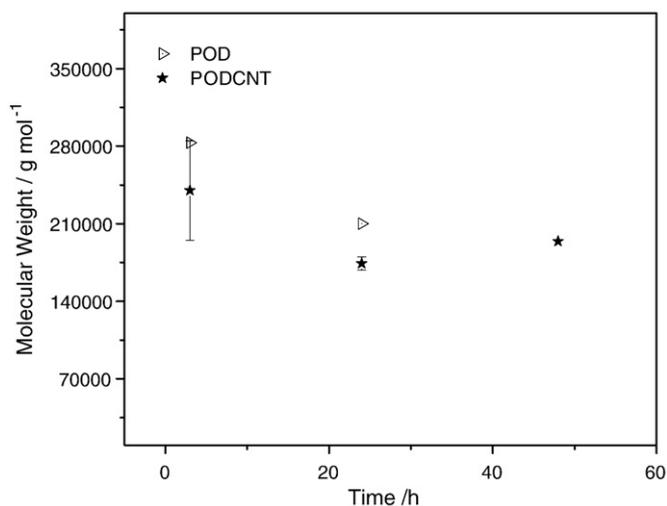
**Fig. 4.** SEM images of the pristine fluorinated polyoxadiazole (a) and of the composite polyoxadiazole (b).

the pristine POD with a 5% weight loss observed at 464 °C in contrast to 457 °C for the POD. As reported in a previous work [13], this polymer additionally shows very high chemical stability with no changes in the molecular weight even after exposed for 19 days at 45 °C to mixtures of sulphuric acid and oleum.

A proposed structure for the PODCNT is also shown in Fig. 3. Covalent attachment of POD on the MWCNT surfaces should be expected to occur both by Friedel–Craft acylation between C=O groups of the acid monomer and C=C of the CNTs [4] as well as condensation reaction of in-situ COOH groups generated on the surface of the CNTs 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. However, no significant difference could be observed in the FTIR spectra of the POD and PODCNT and no C=O stretches in the PODCNT spectrum were observed to confirm the covalent attachment. This result may be attributed to the very low surface amount of C=O groups compared with the other groups present in the main polymer chain. For the same reason explained above, the presence of hydrazide groups were not confirmed in the TGA spectrum of PODCNT (no loss of water which could result from conversion of hydrazide groups to oxadiazole [14] in the range of temperatures between 275 and 375 °C was observed).

Fig. 4 shows the SEM images of the pristine fluorinated polyoxadiazole (a) and of the composite polyoxadiazole (b). It can be seen that the original structure of the highly hydrophobic fluorinated polyoxadiazole formed of spherical particles with diameter of approximately 70 nm was lost as a result of the polymer grafting on the surface of the CNT.

The effect of the in-situ polymerization time on the average molecular weight ( $M_w$ ) of the POD and PODCNT samples was studied (Fig. 5). The analysis of Fig. 5 indicates that for a reaction time of 3 h high molecular weight is already achieved. The high chemical stability



**Fig. 5.** Average molecular weight ( $M_w$ ) of POD and PODCNT samples as a function of the reaction time.

of the fluorinated polyoxadiazole is confirmed once more by the high molecular weight obtained even after exposition to poly(phosphoric acid) for 48 h at 160 °C.

#### 4. Conclusions

In-situ polymerizations of fluorinated polyoxadiazole through a polycondensation reaction of A–A (hydrazine sulphate) and B–B (aromatic dicarboxylic acid) monomers with MWCNT in poly(phosphoric acid) were successfully performed in the frame of time 3 to 48 h. Fluorinated polyoxadiazole/MWCNTs soluble in organic solvents with high molecular weights (around 200 000 g/mol) can be synthesized in 3 h. The fluorinated polyoxadiazole/MWCNTs exhibits high thermal stability with degradation temperature at about 460 °C.

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#### References

- [1] Tasis D, Tagmatarchis N, Bianco A, et al. *Chem Rev* 2006;106:1105–36.
- [2] Moniruzzaman M, Winey KI. *Macromolecules* 2006;39:5194–205.
- [3] Yang Z, Pu H, Yin J. *Mater Lett* 2005;59:2838–41.
- [4] Oh S-J, Lee H-J, Keum D-K, et al. *Polymer* 2006;47:1132–40.
- [5] Laachachi A, Vivet A, Nouet G, et al. *Mater Lett* 2008;62:394–7.
- [6] Yang HH. *Aromatic high-strength fibers*. New York: Wiley; 1989.
- [7] Cassidy PE. *Thermally stable polymers: synthesis and properties*. New York: Marcel Dekker Inc.; 1980.
- [8] Nanjan MJ. *Encyclopedia of polymer science and engineering*. New York: Wiley; 1987.
- [9] Gomes D, Borges CP, Pinto JC. *Polymer* 2004;45:4997–5004.
- [10] Gomes D, Borges CP, Pinto JC. *Polymer* 2001;42:851–65.
- [11] Socrates G. *Infrared and Raman characteristic group frequencies tables and charts*. Chichester: John Wiley & Sons; 2001.
- [12] Najafi E, Kim J-Y, Han S-H, et al. *Colloids and Surf A* 2006;284:373–8.
- [13] Gomes D, Nunes SP. *J Membr Sci* 2008;321:114–22.
- [14] Gomes D, Pinto JC, Borges C. *Polymer* 2003;44:6223–33.