



Thermal and mechanical properties of polyamide 11 based composites reinforced with surface modified titanate nanotubes



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ABSTRACT

The preparation of polyamide 11 (PA11) based composites reinforced with pristine and surface-modified titanate nanotubes (TTNT) is reported. Twin-screw melt compounding was used to produce composites with up to 2 wt% of TTNT. To enhance dispersion and TTNT compatibility with the thermoplastic, these were modified with cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulphate (SDS). Fourier transform infrared spectroscopy and thermogravimetry were used to demonstrate that surface modification prior to composite processing was successful, while scanning transmission electron microscopy combined with energy-dispersive X-ray analysis confirmed the retention of surfactants on TTNT in composites. Nevertheless, scanning and transmission electron microscopy revealed incomplete dispersion of TTNT inside polyamide. The improved wettability on the TTNT–PA11 interface was observed for composites comprising surface-modified TTNT. Consequently, these composites exhibited better thermal and mechanical properties than those containing pristine TTNT. A significant rise of the decomposition temperature was detected in composites containing TTNT modified with CTAB, while the uppermost increment of the storage and Young's modulus (of about 35% and 26%, respectively) was achieved in the composite comprising 0.5 wt% of TTNT modified with SDS. The increase of the nanofiller content improved the yield strength and led to the drop in the strain at break.

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1. Introduction

Polymer-based composites containing a low fraction of nano-sized inorganic particles represent a new class of engineering materials that are currently in the focus of scientific interest. The synergy of the functionalities of an organic matrix and an inorganic nanofiller leads to the creation of novel high-performance materials [1]. The improvement of a polymer's targeted properties (mechanical, thermal, electrical, magnetic or optical) depends on the type and quantity of the inorganic filler in the composite, its agglomeration degree and the dispersion homogeneity, as well as, on the level of interactions established at the nanofiller–matrix interface. Nanoclays are a common and a widely studied example of nanofiller that could reinforce a polymer matrix, although other nanoparticles, nanotubes, nanosheets, nanofibers and fullerenes

have been also used [2]. Since that inorganic nanoparticles have a strong tendency to agglomerate, the formation of macroscopic defects in the polymer is possible and could result in the deterioration of the final properties of the composite. The processing route is one of the important factors which determine the reproducibility and enhancement of the composite's performance [3]. It is known that *in-situ* processing results in a more uniform dispersion of the nanofiller in the polymer matrix than melt compounding but is generally limited to the lab-scale and it is not suitable for industrial production [4]. Therefore, various strategies for the incorporation of nanofiller properties into the macroscopic functions of composite materials produced by twin-screw melt compounding have been reported in the recent years [5]. Surface modification, including silanization, polymer grafting and ligand exchange, is a common approach for the improvement of nanofiller dispersion and its interaction with a polymer [6]. The choice of the surfactant is usually guided by its thermal stability and compatibility with the polymer matrix.

Polyamides and polyesters have been frequently investigated in the context of composites' processing. Polyamide 11 (PA11) is one of the promising engineering bioplastics that can be produced from

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renewable resources, such as castor oil. It is widely used in automotive and offshore oilfield industries due to its good oil and salt water resistance, as well as, excellent piezoelectric and cryogenic properties. Many efforts have been made to improve the mechanical properties of PA11 through preparation of blends with organoclay minerals [7,8]. In these cases, advanced composite properties are commonly associated with full exfoliation of clays (≤ 2 wt%) in polymer matrix [8,9]. More recently, the effects of multi-walled carbon nanotubes (MWCNT) and nanofibers (CNF), nanosilica (NS), halloysite nanotubes (HNT) and BaTiO₃ nanoparticles on the thermal and mechanical properties of PA11-based composites have also been reported and discussed [10–13]. The obtained results show that the composite's thermal stability improves by about 20 °C when the concentration of MWCNT is 1 wt%, whereas the gradual increase of the storage modulus by about 54% is noticed with the rise of the MWCNT content up to 2 wt% [10]. Contrary to the expectations, the addition of CNF (5 wt%) affects the thermal stability of PA11 insignificantly; a better enhancement of the decomposition and heat deflection temperature is reached when a combination of a fire retardant (25 wt%) and CNF (5 wt%) is used [11]. The same study demonstrates a negligible effect of nanosilica on the thermal and flammability features of PA11. The increase of the mechanical strength, stiffness and toughness was achieved for PA11 composite reinforced with 10 wt% of HNT [12]. An improvement of the shear modulus in the glassy and rubbery plateau, as well as a change from ductile to fragile behaviour has been reported for a composite with 12 vol% of BaTiO₃ nanoparticles [13].

To the best of our knowledge, there is no literature on TTNT addition to PA11. Since these have a high specific surface area and an elongated morphology, TTNT are expected to provide an effect comparable to that achieved through the incorporation of MWCNT. Moreover, the synthesis of TTNT by a simple hydrothermal route [14–16] is more adequate for large-scale production. A recent investigation of the PA6 composite containing 5 wt% of freeze-dried pristine TTNT has revealed an increase in the elastic modulus of about 35%, which is twice higher than in the analogue composite reinforced with a commercial TiO₂ nanopowder [17]. Taking into account this report, but also some previous studies on polystyrene/pristine TTNT composite that presented evidence of weak interfacial interactions [18] and a positive effect of silanization [19], TTNT used in the present study have been modified with cetyltrimethylammonium bromide (CTAB) or sodium dodecyl sulfate (SDS) in order to promote their de-agglomeration and to achieve stronger interfacial interaction with PA11. To evaluate the influence of the TTNT surface modification onto the final thermal and mechanical properties of composites, an additional set of composites containing pristine TTNT have also been prepared and analysed.

2. Materials and methods

2.1. Materials

TTNT were synthesised by a standard alkaline hydrothermal treatment of a commercial TiO₂ anatase powder (Vetec Química Fina Ltda Brazil) according to the previously published procedure [20]. In brief, 8.75 g of the TiO₂ anatase powder were dispersed in 350 mL of 10 M NaOH (solid-to-liquid ratio: 2.5%; autoclave filling factor: 70%) and treated hydrothermally at 120 °C for 24 h with constant stirring at 320 rpm. After cooling, the resulting solid phase was filtered and washed either with deionized water (1000 ml) or with a 1 M HCl solution (600 ml) to obtain TTNT with a high (TTNT/H) and low (TTNT/L) sodium content, respectively. The sodium content of 8.45 wt% (TTNT/H) and 0.24 wt% (TTNT/L), detected by flame photometry [20], implicated different

protonation degrees of the layered Na_{2-x}H_xTi₃O_{2n+1} compound and a slight increase of the specific surface area from 224 to 283 m²/g in the latter one. CTAB–C₁₉H₄₂BrN and SDS–C₁₂H₂₅NaO₄S surfactants were purchased from Vetec Química Fina Ltda, while Rilsan® PA11 G BESNO TL was kindly provided by Arkema.

2.2. TTNT surface modification

CTAB and SDS were used as received. Their effects on the TTNT dispersibility were tested in water and butanol as follows: 0.02 g of TTNT were dispersed in 100 ml of an aqueous or butanol solution of the surfactants with the help of an Ultra Turrax Ika T25 dispenser under the frequency of 5000 min⁻¹ for 15, 30 and 60 min. The amount of the surfactants was determined so as to avoid micelle formation based on the critical micelle concentration (CMC) data for these compounds [21,22]. Taking into account different ionic natures of the surfactants and the isoelectric point of TTNT, TTNT/H were modified with CTAB at pH 8 (adjusted by NH₄OH), while TTNT/L were modified with SDS at pH 1.5 (adjusted by HCl). Judging from the scanning electron microscopy analysis (Fig. S1, Supplement file), the best TTNT dispersion was reached after 60 min when either 0.5CMC of CTAB or 1CMC of SDS aqueous solutions were used. Therefore, these samples were used for composite fabrication.

2.3. Composites preparation

The composites were prepared by melt compounding using a micro twin-screw extruder (DSC Xplore, model 5-08-20) followed by injection moulding (DSC Xplore, model 4-11-10) to obtain ASTM D638-10 tensile specimens. PA11, pristine and surface modified TTNT were dried at 80 °C (4 h) prior to mixing in order to remove moisture. Extrusion was performed at 275 °C for 5 min using the screw speed of 100 rpm, while the temperatures of melt and mould were set to the values of 255 and 60 °C, respectively. The compositions and labels of the as-obtained composites are listed in Table 1.

2.4. Characterisation

Zeta potential measurements were performed using a Malvern Zetasizer Nano ZS instrument. An amount of 150 mg of TTNT was dispersed in 100 mL of distilled water and the pH value was settled to be 10 by the addition of 0.1 M NaOH. The dispersion was then titrated with 0.1 M HCl, while the zeta potential was measured at pH steps of 0.5 until pH 1 was reached. In order to study interactions between the surfactants and TTNT, Fourier transform infrared (FTIR) spectroscopy was applied. The analyses were performed on a Perkin-Elmer 400 FTIR spectrometer. Prior to analyses the samples were dried at 80 °C for 12 h, mixed with dried IR-grade KBr and pressed in vacuum. Differential scanning calorimetry (DSC) and thermogravimetric analyses (TG) were used for the analysis of surface modifications, thermal stability and homogeneity of the TTNT distribution in the composite specimens. Standard DSC experiments were systematically carried out under nitrogen atmosphere using a TA Q1000 instrument. In order to erase the thermal

Table 1
Composite specimens.

Specimen	Nanofiller content (wt%)	Label
Polyamide 11 + TTNT/H	0.5; 1; 2	PA-NT/H-wt%
Polyamide 11 + TTNT/L	0.5; 1; 2	PA-NT/L-wt%
Polyamide 11 + TTNT/H-CTAB	0.5; 2	PA-NT/CTAB-wt%
Polyamide 11 + TTNT/L-SDS	0.5; 2	PA-NT/SDS-wt%

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