



The effects of the chemical composition of titanate nanotubes and solvent type on 3-aminopropyltriethoxysilane grafting efficiency



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ABSTRACT

One of the major challenges in the development of nanocomposites based on a polymer matrix and highly polar ceramic nanofillers is the lack of the compatibility between these two components. In order to improve the chemical interaction between titanate nanotubes (TTNT) and polymer matrix, such as nylon 11, 3-aminopropyltriethoxysilane (APTES) was grafted onto TTNT. The effects of the TTNT chemical composition i.e. sodium content and solvent type on the grafting silane efficiency were thoroughly studied through CHN elemental analysis, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), surface area and zeta potential measurements. The present study brings evidences supporting aqueous ethanol as more efficient reaction medium for TTNT functionalization with APTES, independent of the sodium content of nanotubes, when compared with pure water. It is also worth noting that within aqueous ethanol medium, TTNT with low sodium content are more efficiently grafted than TTNT with high sodium content. Successful APTES grafting decreases concentration of the hydroxyl groups on TTNT surfaces and enables its future application for the fabrication of nylon 11 nanocomposites.

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Introduction

In recent years, polymer nanocomposites have received large attention, in both scientific and industrial areas, due to their potentially advanced properties in comparison to the conventional composites, including mechanical, thermal, optical and barrier properties [1–3]. Polyamide 11 (nylon 11) is an important engineering polymer used in a vast range of industrial fields from automotive to offshore applications, due to its high mechanical properties and barrier resistance against oil and water [4]. It is used as an internal layer or pressure barrier of flexible pipelines for riser construction in offshore applications. Different studies have been performed with the aim to improve mechanical and thermal properties of nylon 11 by the incorporation of organoclays and

carbon nanotubes (CNT) [1,5,6]. TTNT synthesized by a simple alkaline hydrothermal treatment, could be also considered as potential candidates for this purpose, since they have already been used as nanofillers for polystyrene and nylon 6 nanocomposites [7–9].

However, due to their high specific surface area and polarity, TTNT tend to strongly agglomerate during synthesis. They are usually randomly assembled or well aligned into secondary micron sized bundles. Moreover, TTNT show hydrophilic properties as a result of the high concentration of hydroxyl groups (–OH) on the surface [10]. Hence, it is extremely difficult to achieve their homogeneous distribution and a strong interface interaction within hydrophobic polymer matrix by the conventional composite manufacturing processes without a previous treatment of these nanofillers or polymers. To overcome these drawbacks, chemical functionalization of TTNT with silane coupling agents is presented as an attractive alternative to enhance the interfacial interaction between inorganic nanofiller and polymer matrix [3,11,12].

The surface chemistry of TTNT is more versatile compared to the relatively inert chemistry of CNT, which require special treatments under severe conditions for activation of their surface [10]. One can

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take advantage of the existence of –OH groups onto TTNT surface, since these enable primary bonding with silane molecules. On the other hand, an eventual reduction of the number of –OH groups on surfaces could decrease the attractive forces among TTNT and, therefore, the agglomeration process [11,13].

In contrast with the widely studied surface modification of CNT, the number of publications about TTNT functionalization is still restricted. Allyltriethoxysilane, propyltriethoxysilane [8], octadecyltrimethoxysilane [14], 3-aminopropyltrimethoxysilane [14–17], APTES [18] and octadecyltrichlorosilane [19] have been reported in literature as chemical modifiers of TTNT surface. The applications of silanized TTNT focused on absorbent materials, enzyme immobilization for biosensors, coating films for polymer matrix composites, electrolyte polymer membranes, biodegradable polymers and thermoplastic matrix nanocomposites. Regarding to the latter application, Byrne et al. [8] functionalized TTNT with allyltriethoxysilane and propyltriethoxysilane in tetrahydrofuran under argon atmosphere. The formation of Ti–O–Si primary bonding was confirmed by FTIR and Raman spectroscopy. As-silanized TTNT were used as reinforcement of polystyrene films. Shi et al. [18] performed the first work of surface modification of TTNT destined to a biodegradable polymer. Transformation of the hydroxyl inorganic groups of TTNT surface into hydroxyl organic groups was carried out with the aid of APTES and glycidol. Nuclear magnetic resonance and FTIR showed that an anchorage of organic groups on TTNT surface was successfully achieved. Afterward, the organic hydroxyl groups were used as initiators of poly- ϵ -caprolactone (PCL) ring opening polymerization during the synthesis of PCL grafted TTNT.

In the present work, APTES was used for TTNT functionalization. Each APTES molecule possesses two functional groups: (a) three ethoxyl (–O–CH₂–CH₃) and (b) one aminopropyl group (–CH₂–CH₂–CH₂–NH₂). The ethoxyl groups are available to react with –OH on TTNT surface. Since they are not reactive enough to be coupled spontaneously with –OH groups from inorganic surfaces, without a previous hydrolysis, the reaction requires a partially aqueous environment as a minimum condition [20]. This is the so-called hydrolyzation mechanism proposed by Pluedemann [21]. After hydrolysis, the silanol groups and TTNT surface hydroxyl groups are ready to form primary bonds [22]. On the other hand, the aminopropyl groups may increase the compatibility of TTNT with nylon 11 and may connect through primary bonds with this polymer matrix [13,23–25]. Therefore, the aminopropyl functionality will strongly influence the interfacial properties between TTNT and nylon 11 matrix, and consequently, it could affect mechanical and thermal properties of the nanocomposites. For this reason, it is worthy to determine the amount of APTES grafted on TTNT surface in terms of the number of aminopropyl groups on the nanofiller surface per nm² (N_R).

Although the functionalization of TTNT with APTES was previously conducted by Shi et al. [18], this silanization was not studied in detail, since it was performed as an intermediate step for achieving other reactions. To the best of our knowledge, there is no published study related to silanization of TTNT, which includes chemistry of TTNT surface prior and after chemical functionalization. It is already shown that TTNT, obtained through simple hydrothermal treatment, are layered structures with easily exchangeable cations exhibiting a variety of chemical compositions as a result of different washing procedures [10]. Morgado Jr. et al. [26] identified three types of TTNT with the general formula Na_xH_{2–x}Ti₃O₇·*n*H₂O, where 0 < *x* < 2 and *n* < 1.2. Samples graded as TTNT/H (high), TTNT/M (medium) and TTNT/L (low), were obtained after the washing of precipitate up to different pH values (7–8; 5–7 and 1.5), resulting in the sodium contents of 9.87 wt%, 6.39 wt% and 1.22 wt%, respectively. Sodium content is closely related to the amount of the interlayer water (*n*) and influences TTNT chemistry

and thermal stability to a great extent. Another important aspect of functionalization that ought to be taken into account is the appropriate choice of the solvent as a reaction medium.

Therefore, the effects of TTNT chemical composition and solvent type were studied in order to determine the APTES functionalization methodology with the best grafting efficiency, based on N_R values, as the first step for future application of TTNT in the fabrication of nylon 11 nanocomposites.

Experimental methods

Materials

TTNT were synthesized by standard alkaline hydrothermal treatment of the commercial TiO₂ anatase powder precursor (Vetec Química Fina Ltda) according to previously published procedure [26]. The synthesis was carried out in a sealed reactor equipped with a Teflon vessel with inner temperature control (Berghof), where 8.75 g of the precursor were dispersed in 350 mL of 10 M NaOH. Hydrothermal treatment was performed at 120 °C for 24 h with constant stirring of 320 rpm. After cooling, the precipitated material was filtered and washed either with deionized water or 1 M HCl solution to obtain TTNT with high (TTNT/H) and low (TTNT/L) sodium content, and finally dried overnight in an air-circulating oven at 120 °C. The sodium content of TTNT/H and TTNT/L was 8.45 wt% and 0.24 wt%, respectively, as measured by flame photometry. APTES and anhydrous ethanol were purchased from Sigma Aldrich and used as obtained.

Functionalization of TTNT

The amount of APTES used for TTNT functionalization was estimated with Eq. (1) [22,27].

$$X = \left(\frac{A}{w} \right) f \quad (1)$$

where *X* is the required amount of APTES to form a monolayer on TTNT surface (g); *f* is the amount of TTNT to be silanized (g); *A* is the specific surface area of TTNT (m²/g) and *w* is the wetting surface of APTES (353 m²/g). Considering the specific surface areas of high and low sodium TTNT determined as 224 m²/g and 283 m²/g, respectively, APTES to TTNT mass ratios of 0.635 and 0.802 were used for TTNT/H and TTNT/L functionalization, respectively.

Two solvents were employed as reaction medium for APTES silanization: distilled water and aqueous ethanol (95% v/v). The volume of the solvent was estimated based on the amount of APTES (*X*) computed with Eq. (1), for obtaining a silane concentration of 2% v/v. 1 g of TTNT previously ground into a fine powder was added to the reaction medium. The suspension was stirred for 10 min and pH was adjusted in the range 4.5–5.5 by the addition of 1 M acetic acid for TTNT/H and 1 M NaOH for TTNT/L. Suspension was ultrasonicated for 1 h and pH was adjusted again. Afterward, APTES was added dropwise to the mixture that was mechanical stirred at a frequency of 5000 min^{–1} (Ultra Turrax Ika T25 disperser) during 2 h and then placed in an ultrasonic bath for a further 1 h. Surface treated TTNT were washed out three times by the same solvent, filtered and dried in an air-circulating oven at 110 °C for 2 h.

The functionalized TTNT samples were marked as shown in Table 1. APTES to TTNT mass ratio was also expressed in mmol of APTES per gram of TTNT (*C_o*).

Characterization

The sodium content of TTNT was measured on as-such (dried) basis by flame photometry after dissolving TTNT samples in

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