



Application of silane grafted titanate nanotubes in reinforcing of polyamide 11 composites



Lidija Mancic^{a,b,*}, Patricia I. Pontón^a, Sonia Letichevsky^a, Antonio M. Costa^a,
Bojan A. Marinkovic^a, Fernando C. Rizzo^a

^a Department of Chemical and Materials Engineering, Pontifical Catholic University of Rio de Janeiro, CP 38008, 22453-900 Rio de Janeiro RJ, Brazil

^b Institute of Technical Sciences of Serbian Academy of Sciences and Arts, Knez Mihailova 35/IV, 11000 Belgrade, Serbia

ARTICLE INFO

Article history:

Received 17 December 2015

Received in revised form

16 February 2016

Accepted 11 March 2016

Available online 21 March 2016

Keywords:

A. Polymer-matrix composites (PMCs)

B. Mechanical properties

B. Thermal properties

E. Injection moulding

ABSTRACT

Polyamide 11 (PA11) composites reinforced with pristine and silanized titanate nanotubes (TTNT) were prepared using twin-screw melt compounding. A better dispersion of silanized TTNT in PA11 caused increase of crystallinity and decrease of the long period of PA11 lamellar structure. The increase of glass transition (~33%) and decomposition temperature (~3%), as well as, the improvement of Young's, storage and loss modulus (of 17, 27 and 17% respectively) was achieved in the composites loaded with the highest content (2 wt%) of nanofiller silanized by 3-aminopropyltriethoxysilane (APTES), owing to a chemical interaction established at the silanized TTNT-PA11 interface. Contrary to it, lack of compatibility at the pristine TTNT-PA11 interface led to drop (up to 20%) in the strength at break in these composites.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Polyamides (PA) are frequently used today in the production of advanced composite materials due to their excellent properties, including good dimensional and chemical stability, durability, low gas permeability and favorable dielectric properties. The first of such composites, developed by Toyota's Central Research and Development Laboratories, has widespread commercial use nowadays in the automotive industry [1]. The as-suggested concept of montmorillonite clay incorporation in polyamide 6 matrix was intensively explored in the following years resulting in the variety of composites with unique properties [2]. It was shown that the extent of property enhancement depends on the nature of both constituents, interactions on their interface, content of filler and its dispersion state. Apart from clays, which could be intercalated or exfoliated in a polymer matrix, diverse inorganic nanomaterials (broadly classified by their geometries as particles, layered and fibrous materials) were also utilized in nanocomposites due their attractive functionalities [3]. Although the vast number of desired

properties was achieved based on the gathered knowledge, there is no "universal rule" for assessing all of their outstanding values, especially in large scale production. Several approaches have been developed to predict the mechanical properties of nanocomposites. A stochastic multiscale method to quantify the correlated key-input parameters of nanofillers dimensional characteristics, agglomeration degree and volume fraction was used to test the variations of parameters at nano-, micro-, meso- and macro-scales in epoxy – carbon nanotube composites [4]. Furthermore, a stochastic framework based on sensitivity analysis methods to quantify the key-input parameters influencing the Young's modulus of polymer (epoxy) – clay nanocomposites is presented in literature [5]. These methods predict that the key parameters for the Young's modulus are the filler volume fraction and epoxy stiffness. Also, sensitivity analysis has been conducted to examine the influence of uncertain input parameters on the fracture toughness of polymeric clay nanocomposites [6].

Due to their huge specific surface area for a given volume, nanofillers tend to agglomerate into bundles, hindering homogeneous dispersion in polymer matrix. Weak interfacial adhesion is another issue that needs to be overcome in traditional compounding processes. Currently, many efforts are devoted to silane grafting of nanofillers, i.e. forming an intermediate layer of organic molecules attached onto the surface of inorganic nanoparticles prior to mixing with polymers [7]. Thanks to the unique capability

* Corresponding author. Institute of Technical Sciences of Serbian Academy of Sciences and Arts, Knez Mihailova 35/IV, 11000 Belgrade, Serbia. Tel.: +381 112636994, +55 2135271954; fax: +381 112185263, +55 2135271248.

E-mail address: lidija.mancic@itn.sanu.ac.rs (L. Mancic).

of organosilane to form primary covalent bonding between inorganic and organic compounds those molecules might provide multiple benefits in the synthesis of hybrid and nanocomposite materials. It was already shown that silane-treated nanoparticles of Al [8], Fe₂O₃ [9], SiO₂ [10], ZrO₂ [11], ZnO [12] and TiO₂ [13]; carbon nanotubes [14], as well as titanate nanotubes [15] contribute more in reinforcing of epoxy based nanocomposites than their pristine counterparts. Nevertheless, the number of publications related to polyamides is restricted to nanocomposites comprising silanized organoclays [16,17]. Apart from these, only one study related to reinforcing of polyamide 6 (PA6) with silanized hallosite nanotubes has been published up to now [18].

Recently, we reported an efficient silanization of titanate nanotubes (TTNT) synthesized by a simple hydrothermal route [19]. In this work, we investigate their capability in reinforcing of polyamide 11 (PA11) bio-based plastic, which is commercially used for fabrication of internal layer/pressure barrier of flexible pipelines and riser construction in offshore applications. To the best of our knowledge, this is a first report related to the application of silane grafted TTNT in reinforcing of polyamides in general. Up to now, only pristine TTNT have been employed in the fabrication of PA6 [20] and recycled PA11 based composites [21]. The beneficial effect of their elongated geometry (i.e. high specific surface) on boosting interface contact in composites had as a result an increase of 35% on the Young's modulus of PA6 when it was reinforced with 5 wt% of TTNT [20]. However, a less encouraging trend of improvement was revealed when recycled PA11 was used, since that composites filled with 1wt% of TTNT showed poorer mechanical performance than equivalent ones with TiO₂ nanoparticles. In the frame of our previous study of the influence that CTAB (cetyltrimethylammonium bromide) and SDS (sodium dodecyl sulfate) surface modified TTNT have on thermal and mechanical properties of corresponding PA11 composites, we also employed pristine TTNT to emphasize the effect that surface modification has on interfacial contact between a nanofiller and PA11 matrix [22]. Apart from this, Byrne et al. [23] report that TTNT silanization with allyltriethoxysilane and propyltriethoxysilane enhances TTNT dispersibility in polystyrene composite films and led to the increase of Young's modulus and tensile strength for 18% and 30%, respectively. Similarly, it was reported that the utilization of 3-aminopropyltrimethoxy silane grafted TTNT in epoxy raises glass transition temperature and the storage modulus in the rubbery state [15]. A neglecting effect of sodium titanate nanoribbons (NaTiNRs) silanized by four different silane coupling agents on the mechanical properties was reported for corresponding epoxy composites which are characterized by improved thermal stability due to addition of NaTiNRs [24].

Although non consistent in achieving goals, aforementioned studies imply that using the TTNT could be an alternative way to accomplish comparable outcomes with the one established by carbon nanotubes, since that some of their mechanical characteristics (ex. Young's modulus) are similar. At the same time, the synthesis of the TTNT is less complex and more economically justified for large-scale production. The present study indicates that silanized TTNT has beneficial effect on thermal and mechanical properties of PA11 based composites produced through melt compounding. In order to distinguish the effect of TTNT silane grafting, another set of PA11 composites comprising pristine TTNT were prepared and tested under the identical conditions.

2. Materials and methods

2.1. Materials

Pristine TTNT with two different sodium contents of 0.24 wt% (low – TTNT/L) and 8.45 wt% (high – TTNT/H), and consequently

different specific surface areas (S) of 283 and 224 m²/g, respectively, were synthesized by a standard alkaline hydrothermal treatment. The details about their synthesis and posterior silanization by 3-aminopropyltriethoxysilane (APTES) are reported elsewhere [19]. A comprehensive characterization of the silanized TTNT revealed slightly more efficient silane grafting of TTNT/L in comparison to TTNT/H due to the higher density of –OH groups on the surface of the former. After grafting, TTNT maintained their typical morphological characteristic, but their specific surface area decreased unevenly. In order to exclude the influence of this parameter, two lots of powders with similar specific surface areas were chosen for composites production: silane grafted TTNT/L, S = 161 m²/g (F2) and silane grafted TTNT/H, S = 159 m²/g (F3). PA11 was kindly provided by Arkema. It was produced from a renewable source (Castrol oil) and was designed for extrusion (Rilsan® 11G BESNO TL).

2.2. Composites preparation

The composites comprising up to 2 wt% of TTNT (pristine and silanized) were prepared by a conventional melt compounding technique using a twin-screw extruder (DSM Xplore, model 5-08-20) followed by injection molding (DSM Xplore, model 4-11-10). Before processing, PA11, pristine and silane grafted TTNT were dried at 80 °C (4 h) in order to remove moisture. Extrusion was performed using micro compounder that consists of a vertical barrel with two conical co-rotating twin screws and six independently regulated heating zones divided in three sections. Temperatures of sections were set to be 275, 260 and 260 °C (from top to bottom) while the screw speed was 100 rpm. Total time of mixing was 5 min. Temperatures of melt and mould were set to 255 and 60 °C respectively, while the injection pressure was set to 7 bar. The specimens produced were in accordance to ASTM D638-10. Their compositions and labels are given in Table 1.

2.3. Composites characterization

In order to detect possible interactions between TTNT and polyamide matrix Fourier transform infrared (FTIR) spectroscopy was performed using a Perkin–Elmer 400 FTIR spectrometer. Powdered composites were dried at 80 °C for 12 h, mixed with IR-grade KBr and pressed as a wafer that was kept in vacuum prior to analysis. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) were used for the analysis of composite thermal stability and homogeneity of TTNT distribution. In order to erase previous thermal history of polyamide processing prior to DSC data acquisition at TA DSC Q1000, ~5 mg of each specimen has been heated to 280 °C (20 °C/min), kept for 1 min at this temperature and quenched to –80 °C. In the second cycle, heating from –80 to 280 °C at 20 °C/min and cooling down (annealing) to –80 °C at defined rate of 10 °C/min were used to determine sample crystallization temperature. A standard heating scan of 10 °C/min was applied within the same temperature range during the third heating cycle in order to obtain enthalpy of fusion. TG analyses were performed on TA Q500 and Perkin–Elmer STA-6000 instruments. X-ray powder diffraction (XRPD) data were collected on a Bruker D8 Discover diffractometer, operating with Cu K_α radiation at 40 kV and 40 mA. The diffraction patterns were acquired using an angular step size of 0.02 (2 Theta) and acquisition time of 5 s per step. Topas 4.2 software was used for peak deconvolution and crystallinity determination. Small angle X-ray scattering (SAXS) was performed under vacuum on Bruker Nanostar equipped with Vantec 2000 detector and conventional X-ray tube using Cu K_α radiation operating at 40 kV and 35 mA. The SAXS data recorded during 6 h were analyzed using Sasview software. The TTNT

Download English Version:

<https://daneshyari.com/en/article/816850>

Download Persian Version:

<https://daneshyari.com/article/816850>

[Daneshyari.com](https://daneshyari.com)