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Thermal, Mechanical, and Morphological Properties of DPU/Titanate Nanotubes Nanocomposites

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Nanocomposites of Titanates Nanotubes (TNTs) and waterborne polyurethane were prepared by physical mixture using ultra turrax disperser. TNTs were synthesized by hydrothermal method and added in different contents: 1, 3, and 5% w/w in relation to polymer weight. Films were prepared and characterized by DSC, TGA, DMA and SEM. The increase of fillers content reduced the thermal stability of DPU nanocomposites compared to pure DPU and did not modify the glass transition temperature. To mechanical properties, the addition of 3% and 5% of TNT increased the Young's modulus when compared with pure DPU, but nanocomposite with 1% of TNT presented a decrease in Young's modulus. The stress × strain curves of DPU/TNT 5% presented characteristic behavior of rigid material, with low deformation, unlike other nanocomposites and pure DPU. SEM and TGA analysis proves that the preparation method used promoted the incorporation and good filler dispersion in the polymer matrix.

1. Introduction

Polyurethane resins (PU) production from the dispersion of this polymer in water (DPU) is an alternative to minimize the environmental impacts generated by the release of common volatile organic compounds (VOCs) in solvent-based PU systems, as well as the decomposition of resin after its useful life.[1] The search for DPU synthesis methods aiming to improve its properties has received great attention in the past few years. Among the examples there are works exploring the development of high solid content waterborne polyurethane,[2] self-dispersing polyurethane prepolymers,[3] or evaluating the use of different vegetable oils as castor, soybean, linseed, among others.[4,5]

DPU based nanocomposites have been of great interest, since the added particles (inorganic/organic), besides approaching the DPU properties with conventional PU, add inherent properties to the fillers.[6,7] Recent publications of PU nanocomposites development using gold and silver nanoparticles,[8] cellulose nanofibers,[9] silica nanoparticles,[10] silica-titania core-shell nanoparticles,[11] silver, and copper nanoparticles[12] are some examples of importance of these theme in the literature.

Nanostructured fillers such as titanate nanotubes (TNT) obtained by hydrothermal method[13] present high specific surface area and hydrophilic behavior due to the OH groups concentration on their surface.[14] This may favor the interaction with water-dispersed polyurethane micelles in the DPU leading to an improvement in thermal and mechanical properties of the nanocomposites formed by these components. TNTs have already been used as fillers in polymers for example being modified with cetyltrimethylammonium bromide and sodium dodecyl sulfate and applied as filler in polyamide 11 matrices, resulting in increased thermal and mechanical properties using 2% filler.[15] As well as the use of this nanostructure in poly (vinylidene fluoride-*co*-trifluoroethylene-*co*-chlorofluoroethylene) matrices suggests a nucleating action of the nanostructure increasing the polymer crystallization temperature.[16] In a previous study, our group evaluated the influence of the TNT functionalized with tetraethoxy orthosilicate (TEOS) addition in a solvent based PU matrix.[17] The amount of 1% w/w of charge led to a significant increase in the polymer thermal stability. In this context, the present work aims the preparation of DPU/TNT nanocomposites and the evaluation of the influence of the amount of filler on the morphological, thermal and mechanical properties of the polyurethane.

2. Experimental Section

2.1. Materials and Methods

The aqueous polyurethane dispersion obtained from the reaction of a linear polyester polyol with isophorone diisocyanate (IPDI)
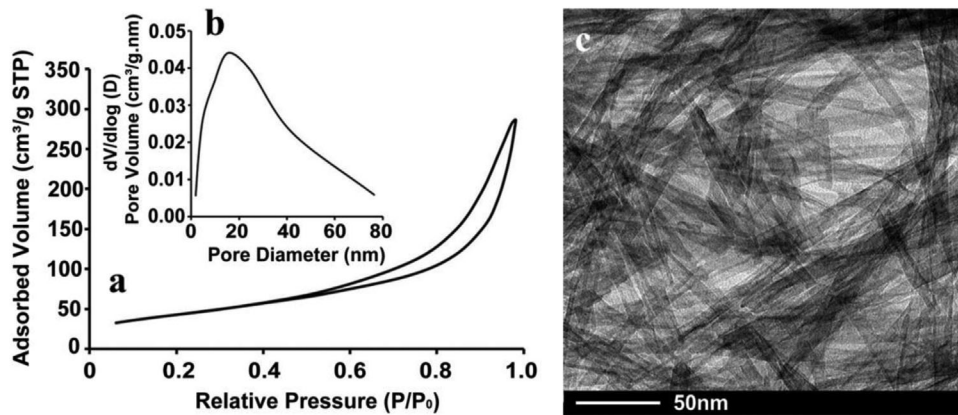
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Figure 1. TNT results obtained by a) N_2 adsorption–desorption isotherms, b) pore size distribution, and c) TEM micrographs, magnification of 180 k.

(solids content of 35% w/w) was donated by NokXeller Micro-dispersions and used as received. Titanate nanotubes were synthesized by the hydrothermal method adapted from literature.[13,17,18] In a typical procedure, 1.5 g of TiO_2 (anatase phase) were added in 120 mL of 10 mol L^{-1} NaOH aqueous solution while stirring for 1 h at room temperature. Afterwards, the mixture was transferred to an autoclave-type stainless steel reactor with Teflon cup remaining in an oven at 135 °C for 72 h. After this period, the precipitate was washed and centrifuged to pH = 8 and then dried in an oven at 80 °C for 8 h. The DPU/TNT nanocomposites were prepared by adding 1, 3, and 5% w/w (based on the prepolymer mass) of TNT in the aqueous commercial PU dispersion with the aid of an ultra turrax disperser (IKA®T25, 11,800 rpm) by 30 min. After the end of reaction, the films of nanocomposite (thickness ≈ 700 μm) were prepared by casting method under controlled temperature and humidity (25 °C and 40%).

2.2. Characterization

For morphological characterization of TNT, transmission electron microscopy (TEM, FEI Tecnai G2 T20) analyzes were performed and all measures were performed by *Image J* software. The N_2 adsorption-desorption isotherms technique was used to determine the specific area using volumetric method at 77 K (−196 °C) (Micromeritics Instruments Corporation, model TriStar II 302 V1.03). The isotherms were measured in the absolute N_2 pressure range of 0.010–1.05 atm for 6 h. The specific area was calculated using BET method and the pore diameter using the BHJ method. The morphology of the films was evaluated by field emission scanning electron microscopy (SEM-FEG) using the mode of secondary electrons. For this analysis, films were fractured by cryogenics. In order to evaluate the influence of the amount of charge added on the thermal
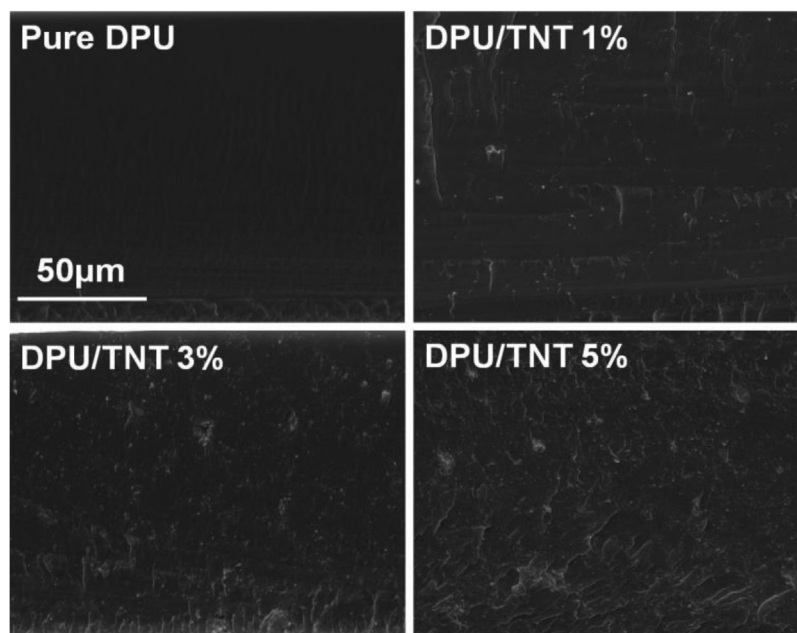

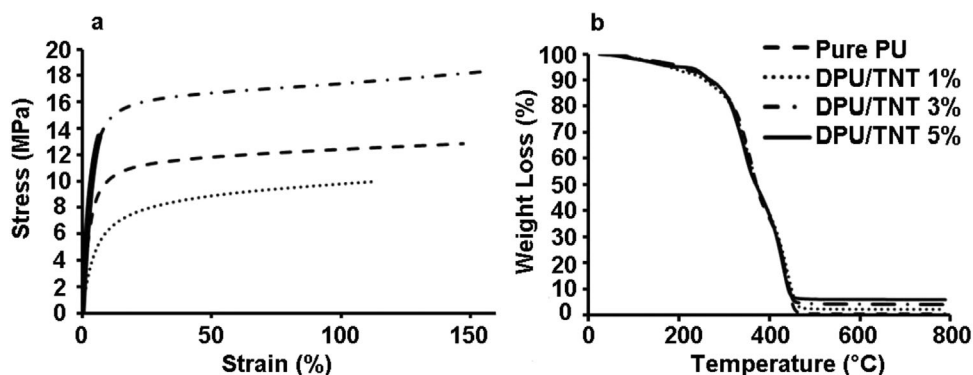**Figure 2.** SEM micrographs of pure DPU and nanocomposites, magnification of 2 k.

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Figure 3. Pure DPU and nanocomposites (a) stress × strain and (b) thermogravimetric analyses.

properties, thermogravimetric analyzes in triplicate (TGA, Q600 – TA Instruments) with $20\,°C\,min^{-1}$ heating ramp starting at $40-800\,°C$ in an atmosphere of nitrogen were performed. To evaluate the mechanical properties, uniaxial tensile tests (DMA equipment, Q800 – TA Instruments) were performed using the ASTM D822 standard. To determinate the loss and storage modulus were performed analyses in the range of temperature between -65 and $30\,°C$ with ramp of $3\,°C\,min^{-1}$.

3. Results and Discussion

For titanate nanotubes, the adsorption-desorption curve of N_2 (**Figure 1**a) shows a type IV isotherm with hysteresis in the range of $P/Po = 0.55-1.0$ indicating the presence of mesopores (2–50 nm) and macropores (>50 nm).[18–20] The TNT presented a specific surface area of $155\,m^2\,g^{-1}$ and a monomodal behavior for the pore diameter distribution with a maximum of 20 nm (Figure 1b). The image obtained by TEM (Figure 1c) shows the presence of tubes with external diameters around 9.2 ± 0.3 nm.

SEM images of pure DPU films and cryogenic fractured nanocomposites are presented in **Figure 2**. It is possible to see that the nanocomposites present white particulates corresponding to the TNTs added. In addition, TNTs are well dispersed throughout the polymer matrix and their amount is proportional to added fillers percentage.

The stress x strain and thermal degradation curves are shown in **Figure 3**a,b, respectively. Pure DPU and DPU/TNT 1 and 3% nanocomposites showed a pseudoplastic material behavior. However, the DPU/TNT 1% had a maximum deformation and tension (113%, 10 MPa) lower than that of pure DPU (147%, 12 MPa), whereas for the 3% DPU/TNT these values (156%, 18 MPa) were higher than pure DPU. This reduction of Young's modulus with a small filler amount was related in the literature.[21] The 5% DPU/TNT nanocomposite presented a behavior of a rigid material with plasticity loss, presenting low deformation (7%) and maximum tension (13 MPa) comparable to pure DPU. As for Young's modulus, pure DPU showed a modulus of 244 ± 20 MPa, superior only to the nanocomposite with 1% of TNT (156 ± 22 MPa). To the other nanocomposites (DPU/TNT 3 and 5%) the Young's modulus were higher with values of 326 ± 18 and 399 ± 35 MPa, respectively. The increase in the Young's modulus with increase in the filler amount is in

concomitance with literature[22] and, besides that, the decrease in the maximum deformation. Improvement in mechanical properties were attributed to the good dispersion of filler in the PU matrix, as well as the strong interfacial interactions between them. These explanations are in according to observed in the SEM images (Figure 2) with filler presenting a good dispersion in the polymer matrix.

In thermal degradation curves it is possible to observe the same behavior in a single step to all nanocomposite samples.

The values of the initial (T_{onset}) and final (T_{endset}) degradation temperatures as well as temperatures where the materials lose 20% ($T_{20\%}$) and 50% ($T_{50\%}$) mass are presented in **Table 1**. The addition of TNT filler promoted a small decrease in DPU thermal stability, where the largest difference ($10\,°C$) was observed for the DPU/TNT 5% nanocomposite. Nanocomposites have a tendency to decrease degradation temperature corresponding to 20% mass loss when compared to pure DPU ($320\,°C$). However, this same behavior is not observed for the temperature corresponding to 50% mass loss. Decreases in thermal properties of polymer matrices are uncommon in literature, but are related to the structural properties of the filler,[23,24] so this decrease in thermal stability as well as in the initial degradation range corresponding to 20% of the mass loss may be related to the high concentration of hydroxyl group on TNT. The values obtained for the residual mass at temperatures above $500\,°C$ are close to the filler values added indicating that the entire amount of filler was incorporated into the polymer matrix and that the blends produced in ultra turrax were efficient for the incorporation of these different amounts of fillers.

From the dynamic-mechanical analysis (**Figure 4**) it is possible to observe that, for all samples, the glass transition

Table 1. Values obtained by mechanical and thermogravimetric analyses.

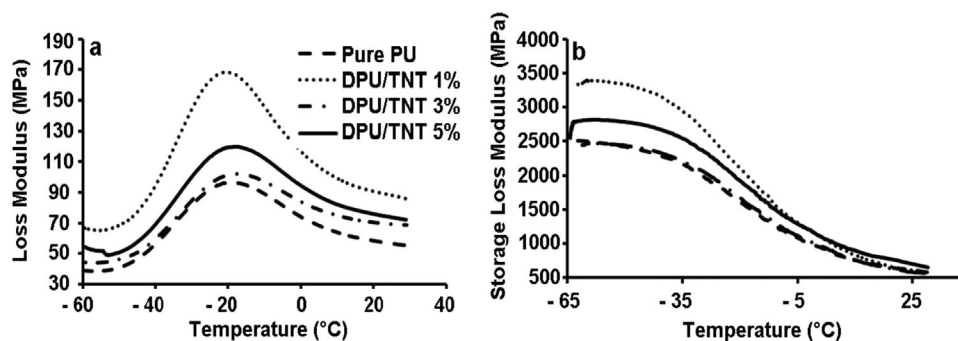|	T_{onset} [°C]	T_{endset} [°C]	$T_{20\%}$ [°C]	$T_{50\%}$ [°C]	Residue [%]
Pure DPU	317 ± 5	456 ± 4	320	371	0.5
DPU/TNT 1%	310 ± 0.3	456 ± 0.5	317	371	2.0
DPU/TNT 3%	309 ± 0.3	449 ± 0.5	317	370	4.0
DPU/TNT 5%	307 ± 3	447 ± 3	315	371	5.7

Figure 4. Pure DPU and nanocomposites (a) loss modulus and (b) storage modulus analyses.

temperatures (Tg) adopted as the highest peak of the loss modulus (Figure 4a) are close ($\approx -21\,°$C), and in addition, maintains the same behavior in vitreous and elastic regions. However, in the glass transition range, the DPU/TNT 1% sample shows a higher loss modulus (170 MPa) when compared to the other samples (103, 106, and 125 MPa for pure DPU, 3% and DPU/TNT 5%, respectively). This result justifies the smaller Young's module presented by the DPU/TNT 1% sample.

In addition, the DPU/TNT 1% sample shows a decrease in the storage modulus (Figure 4b), a fact that corroborates the lower deformation observed when compared with samples with plastic characteristics. For these analyzes, the dynamic-mechanical behavior of DPU/TNT 3 and 5% samples are numerically close to pure DPU.

4. Conclusions

Titanate nanotubes were synthesized by hydrothermal method with high specific area and applied as filler in waterborne polyurethanes using a physical mixing method with percentages of 1, 3, and 5% w/w over the prepolymer mass. As for the thermal analyzes, there was no change in the glass transition temperature value and, in addition, there were no significant reduction in the thermal stability with increase in the filler percentage. The addition of 3 and 5% of TNT increased the Young's modulus, but the DPU/TNT 5% showed to be a rigid material, with decrease in maximum deformation. Beside these, the addition of 1% of filler proved to be the less favorable observed by decrease in the mechanical properties. The obtained values for the degradation residues corroborates the TNTs incorporation in DPU matrix. Yet, evidenced that the synthesis method using ultra turrax disperser allowed the formation of nanocomposites with the dispersed charge even with a higher percentage (5%).

Acknowledgements

Keywords

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