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The effect of ultra-thin graphite on the morphology and physical properties of thermoplastic polyurethane elastomer composites

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ABSTRACT

Composites of thermoplastic polyurethane (TPU) and ultra-thin graphite (UTG) with concentrations ranging from 0.5 wt.% to 3 wt.% were prepared using a solution compounding strategy. Substantial reinforcing effects with increased loadings are achieved. Compared to neat TPU, values for storage modulus and shear viscosity are enhanced by 300% and 150%, respectively, for UTG concentrations of 3 wt.%. Additionally, an enhancement of thermal properties is accomplished. The crystallization temperature and thermal stability increased by 30 °C and 10 °C, respectively, compared to neat TPU. Furthermore, the use of oxidized UTG (UTGO) with its added functional oxygen groups suggests the presence of chemical interactions between UTG and TPU, which additionally impact on the thermal properties of the corresponding composites. Controlling the oxidation degree, thus offers further possibilities to obtain composites with tailored properties. The presented approach is straightforward, leads to homogeneous TPU-UTG composites with improved materials properties and is especially suitable for commercial UTG materials and further up-scaled production.

1. Introduction

Fillers are important to enhance the properties of polymers and can therefore be used for the development of a new generation of composite materials with improved or new functionalities [1]. In the last few decades, carbon-based nanomaterials, especially carbon nanotubes have attracted great attention as nanofiller material [2]. Transferring their exceptional electrical, thermal and mechanical properties to polymer matrices leads to substantial multifunctional property enhancement, achieved at much lower loading fractions than polymer composites with conventional micron-scale fillers [2,3]. Graphene [4,5], a single atomic layer of graphite, is a direct parent of carbon nanotubes with equal if not superior performance, and thus considered as the ultimate carbon nanofiller material [6]. The fact that graphene can be easily fabricated by different kinds of exfoliation methods applied to inexpensive graphite even at larger scales and already is commercially offered by various companies has renewed enthusiasm in the field of polymer nanocomposite research [7]. Although commercial graphene produced by exfoliation of graphite at industrial scale frequently is not fully exfoliated, this type of graphene material, probably better described as ultra-thin graphite (UTG), retains its importance as nanofiller for achieving improved performance and price advantages, essential for new applications of polymers.

A polymer of great technological interest is thermoplastic polyurethane. It is one of the most versatile materials for applications that demand high flexibility and elasticity [8,9]. However, this polymer shows low mechanical strength and poor thermal stability hampering its use in high-temperature applications. The incorporation of carbon nanotubes [10–15] and nanoclays [16–18] has lead to significant improvements of these polymer characteristics. First publications on graphene-based materials (graphene, functionalized graphene, graphene oxide) also report on reinforcing effects in TPU [19–25]. Various compounding approaches were taken: Melt mixing [25], solution mixing [20–25], and *in situ* polymerization [19,25]. From an industrial point of view, the most economically viable method is melt mixing. However, it is prone to re-aggregation of graphene and thermal degradation of the TPU matrix [25]. On the other hand, highest degree of dispersion is achieved by *in situ* polymerization, followed by solution mixing [25]. While *in situ* polymerization if based on the use of polymer precursors, solution mixing is the approach of choice when it

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comes to the use of already prefabricated TPU matrices, especially those available from shelf.

In this work we describe the effect of commercial UTG materials on the physical properties in TPU. To this end, TPU composites with different amounts of UTG were prepared by solution compounding followed by subsequent coagulation process. Morphology, structure, thermal and mechanical properties were probed by scanning electron microscopy, X-ray diffraction, infrared and Raman spectroscopy, differential scanning calorimetry, thermal gravimetric analysis, dynamic mechanical analysis and rheological measurements. Increasing the amount of UTG in TPU leads to significant enhancement of the storage modules up to 300% and the viscosity up to 150% compared to neat TPU. Crystallization temperature and thermal stability increased by 30 °C and 10 °C, respectively. Furthermore, the use of oxidized UTG material (UTGO) leads to chemical interactions between filler and the matrix, positively affecting thermal and processing behavior. The applied approach is straightforward, suitable for commercially available UTG and TPU materials, and leads to reinforced TPU-UTG composites.

2. Experimental

2.1. Materials

Commercial grade, low density ultra-thin graphite (UTG) with a particle size of 1–1.5 μm and 15–20 nm of thickness was purchased from Avanzare S.L. (La Rioja, Spain). Thermoplastic polyurethane elastomer PEARLTHANE® 11T85E (TPU) with a density of 1.16 g/cm^3 (at 20 °C) and a melt flow index of 10 g/10 min (190 °C, 21.6 kg) was kindly provided by Merquinsa (Merquinsa, Barcelona, Spain) and used as received. N,N-dimethylformamide (DMF; Scharlau, Barcelona S.L., Spain), methanol (MeOH; Gilca S.C., Spain), H_2SO_4, 65% (Sigma–Aldrich Co.) and fuming HNO_3, 37% (Sigma–Aldrich Co.) were used as received.

2.2. Preparation of ultra-thin graphite oxide (UTGO)

Commercial UTG material was refluxed in a mixture of HNO_3 and H_2SO_4 3 M (1/3 v/v) for 24 h at 110 °C. The resulting material was filtered and washed with distilled water until pH was neutral. Subsequently, the residue was dried under vacuum overnight at 80 °C. The commercial (UTG) and modified UTG materials (UTGO) were quantitatively analyzed by titration to determine the COOH content on their surface [26]. In a typical experiment, 100 mg of UTGO were dispersed into a 15 ml solution of 0.1 N NaOH, bath sonicated for 30 min, and then stirred for 2 days at room temperature to allow the graphite material to equilibrate with the NaOH solution. The obtained dispersion was filtered under vacuum and the filtrate titrated with a 15 ml solution of 0.1 N HCl to determine the excess of NaOH present in the filtrate and therefore the concentration of COOH groups on the materials. Concentration of carboxylic groups of UTG and UTGO materials amounts to 6 mmol/g and 12 mmol/g, respectively.

2.3. Preparation of TPU composites

Different TPU-UTG composites with increased UTG loadings were prepared. Samples were labeled as TPU, TPU-UTG0.5, TPU-UTG1, TPU-UTG2.5, and TPU-UTG3 for a UTG content of 0, 0.5, 1, 2.5, and 3 wt.% respectively. A TPU-UTGO2.5 composite with a load of 2.5 wt.% of UTGO was also prepared. In a typical experiment 3 g of TPU were completely dissolved in 30 ml of DMF at 35 °C. On the other hand, the required quantity of UTG or UTGO was dispersed in 25 mL of DMF and sonicated in an ultrasound bath for 3 h to obtain homogeneous dispersion of both materials. Subsequently, the UTG dispersion was added dropwise to the TPU solution, and the mixture was stirred for 10 more min in order to get a homogeneous solution. Finally, the mixture was slowly poured into 250 ml of MeOH and the precipitated TPU-UTG(O) composites were washed several times with MeOH. The resulting material was dried overnight at 65 °C in a vacuum oven. For neat TPU, the polymer was dissolved in the total volume of DMF (55 mL) following the same preparation procedure in absence of UTG.

2.4. Characterization

The morphology of the UTG starting material was examined by scanning electron microscopy (SEM) with a Hitachi S3400 N microscope. The polymer-based samples were fractured, and the fractured surfaces were studied by field emission scanning electron microscopy (FE-SEM) with a JEOL JSM-7001F. The samples for FE-SEM were previously sputtered with platinum and afterwards with a conductive wire of colloidal Ag.

ATR-FTIR measurements were performed on a Perkin–Elmer System 2000 FTIR spectrometer incorporating an Attenuated Total Reflectance system (ATR). The spectra were recorded in the range from 500 to 4000 cm^{-1}.

Raman spectra were recorded with a Horiba Jobin Yvon HR800 UV spectrometer using an excitation wavelength of 532 nm. Scans were recorded in the range from 500 to 3000 cm^{-1}.

Powder X-ray diffraction (XRD) measurements were carried out at room temperature on a Bruker D8 Advance diffractometer using a Cu Kα X-ray radiation.

Differential scanning calorimetry (DSC) experiments were performed in a Mettler DSC-823e equipment at a scan rate of ±20 °C min^{-1} over a temperature range of −60 to 300 °C under a nitrogen flow of 100 mL/min. Indium was used as standard for the temperature and heat flow calibration. Different scans of dynamic heating at a rate of 10 and 20 °C/min were performed using a standard 100 μL aluminum pan containing 17 mg on average weight. A heating from room temperature up to 200 °C was applied at a rate of 20 °C/min to eliminate the processing thermal history of the samples. Subsequently, the samples were cooled to −60 °C at 20 °C/min to observe the crystallization transitions, and finally reheated up to 300 °C at 10 °C/min to analyze the melting behavior.

Thermogravimetric analyses were carried out using a Setaram Setsys Evolution 16/18. The measurements were made from 20 °C to 900 °C at a heating rate of 10 °C/min under N_2 atmosphere (100 mL/min) in order to evaluate the effect on TPU degradation.

Dynamic mechanical analysis (DMA) tests were carried out on a TA Instruments DMA 2980 equipment with a 3 point-bending mode applying at a heating rate of 3 °C/min in the interval of −60 to 220 °C, a frequency of 1 Hz, a strain amplitude of 20 μm and a preload of 0.01 N. For this purpose, composite test specimens of 35 mm × 13 mm × 1.5 mm in size were prepared by a compression process at 180 °C applying a pressure of 2 metric tons for 10 min.

Rheological properties were measured using a rotational Rheometer AR-G2 TA Instruments. Shear viscosities were tested by means of parallel plate geometry with 25 mm diameter and 1000 mm gap under nitrogen atmosphere. The temperature applied was 190 °C and the shear rates ranged from 0,001 s^{-1} to 100 s^{-1}.

3. Results and discussion

3.1. UTG and UTGO materials

Morphology and structure of UTG was characterized by SEM and XRD techniques. SEM micrograph (Fig. 1a) reveals a flake-like