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Structure and properties of nanocomposites based on PTT-*block*-PTMO copolymer and graphene oxide prepared by *in situ* polymerization

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ABSTRACT

Poly(trimethylene terephthalate-*block*-tetramethylene oxide) (PTT-PTMO) copolymer/graphene oxide nanocomposites were prepared by *in situ* polymerization. From the SEM and TEM images of PTT-PTMO/GO nanocomposite, it can be seen that GO sheets are clearly well-dispersed in the PTT-PTMO matrix. TEM images also showed that graphene was well exfoliated into individual sheets, suggesting that *in situ* polymerization is a highly efficient method for preparing nanocomposites. The influence of GO on the two-phase structure, melt viscosity and mechanical properties of PTT-PTMO block copolymer was examined by using DSC, ARES rheometer and tensile tests. The DSC results imply that the introduction of GO did not affect the glass transition temperature of PTMO-rich soft phase, melting temperature of PTT hard phase and degree of crystallinity of the nanocomposites. As the graphene oxide loading in the nanocomposites increase, the enhanced Young's modulus and yield stress was observed. The tensile strength slightly increased with the increase of GO from 0 to 0.5 wt% when elongation at break was higher or comparable to the value of neat PTT-PTMO copolymer.

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1. Introduction

Polymer composites that display a change in composition and structure over a nanometer length scale have been shown over the last 10 years to present considerable property enhancements relative to conventionally scaled composites. Layered silicates dispersed as a reinforcing phase in an engineering polymer matrix are one of the most important forms of such "hybrid organic–inorganic nanocomposites" with remarkably improved thermal, mechanical (higher modulus, increased strength), optical, barrier and physicochemical parameters [1–3].

Graphene, mostly in the form of graphite, has been experimentally studied for over 40 years [4–7] and measurements of transport properties in micromechanically exfoliated layers [8] of graphene grown on (SiC) [9] large area graphene grown on copper (Cu) substrates [10], as well as a variety of studies involving the use of chemically modified graphene to make new materials [11–13]. Despite the number of methods for its synthesis, as-prepared graphene itself is not soluble and thus cannot be dispersed in water or any organic solvent. Suitably modified graphene nanosheets could display good solution chemistry with properties such as dispersability and solubility in water and organic solvents [14]. Therefore, hydrophilic and organophilic affinities for graphene nanosheets should be achievable through chemical functionalization. Many

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researchers are now focusing on derivatives of graphite, which is inexpensive and available in large quantities. A particularly popular derivatives is graphite oxide (GO), which is hydrophilic and has a larger interlayer distance than graphite. It can readily exfoliate into individual GO sheets in water and forms stable dispersions after sonication. Unlike the bulk graphene sheets – if left unprotected – will spontaneously agglomerate and even restack to form graphite, chemical functionalization or the use of dispersant generally prevents agglomeration [15–17]. The GO synthetic pathway is attractive for stabilizing individual sheets in solutions. The oxygen functional groups that exist in GO provide reactive sites for chemical modification using known carbon surface chemistry. The chemical attachment of appropriate organic groups leads to physical separation of the resultant graphene sheets but also makes it possible to directly form stable graphene dispersion during the synthetic process. The successful dispersion of graphene has enabled the use of low cost solution processing techniques to fabricate various potentially useful graphene-based materials [18,19]. Polymer nanocomposites with GO-derived graphene materials as filler have shown dramatic improvements in properties such as elastic modulus, tensile strength and thermal stability. Moreover, these improvements are often observed at low loadings of filler evidently due to the large interfacial area and high aspect ratio of these materials, requiring small amounts of filler to achieve percolation [20,21]. Furthermore, studies on PANIPAM/GO nanocomposite hydrogels [22] prepared by *in situ* polymerization have shown that introduction of GO has significant influence on the microstructure, mechanical performance and swelling properties of composite hydrogels.

Segmented block copolymers which behave as thermoplastic elastomers are composed of flexible and rigid segments. Due to structural differences, the flexible and rigid segments usually separate into two phases or domains. At room temperature, the segmented block copolymers have multi-phase structures consisting of a continuous soft phase of the flexible segments with a low glass transition temperature and a dispersed hard phase with a high melting temperature [23]. Soft phase provides extensibility, whereas hard domains play the role of physical crosslinks and act as high modulus filler. Crystallization of block copolymer micro-domains exerts tremendous influence on the morphology, properties and applications of these materials. Actually, in polyester-segmented block copolymers, the phase separation occurs mainly by crystallization [23]. Multiblock poly(ether–ester) (PEE) based on poly(butylene terephthalate) (PBT) as rigid segments and poly(tetramethylene oxide) (PTMO) as soft segments have been intensively studied [24,25]. Due to their excellent mechanical properties, like strength and elastic properties in a wide temperature range they are of special interest. The PBT-*block*-PTMO copolymers are available as commercial products (Elitel™, Arnitel, Hytrel®, DSM, etc.). Recently a study on a novel family of polyester thermoplastic elastomers based on PTT has been conducted [26,27]. The influence of organoclay [28] and carbon nanotubes [29] on the structure and physical properties of PTT-*block*-PTMO copolymers has been previously described. These type segmented copolymers based on poly(trimethylene terephthalate) (PTT) rigid segments and polyether flexible segments possess excellent thermoplastic elastomer properties, such as a low-temperature glass transition (T_g), a high melting point (T_m) and a temperature independent rubbery plateau. The excellent properties of this type of polyester block copolymer make it suitable for a number of applications where mechanical strength and durability in a flexible component is required. Similar to standard Hytrel grades, PTT-based block copolymers can be an excellent choice in applications ranging from auto parts and innovative furniture design to sporting goods and filaments.

The presence of carbon nanostructures in PTT-*block*-PTMO matrix can influence the phase separation changing their elastic properties. The purpose of this study was to examine the effect of GO content on the phase structure and physical properties of poly(trimethylene terephthalate-*block*-tetramethylene oxide) (PTT-PTMO) elastomer investigated. A reinforcement by GO has been observed for PTT-PTMO/GO nanocomposites based on the increase in tensile strength and tensile modulus.

2. Experimental section

2.1. Materials

For the poly(trimethylene terephthalate-*block*-tetramethylene oxide) (PTT-PTMO) elastomer synthesis the following chemicals were used: dimethyl terephthalate (DMT, Sigma–Aldrich) and poly(tetramethylene oxide) glycol with molecular weight of 1000 g/mol (PTMG, Terathane 1000, DuPont, USA) were used as received. 1,3-Propanenediol (PDO, Sigma–Aldrich) was distilled before using. Tetrabutyl orthotitaniate (TBT, Fluka) was used as catalyst in transesterification and polycondensation. Irganox 1010 (Ciba-Geigy, Switzerland) was used as antioxidant.

Graphene oxide (GO) with average particle size of 50 μm was obtained from expanded graphite (SLG TECHNOLOGIES GMbH, Germany) by Brodie oxidation method reported in [14]. C1s XPS spectra of GO: sp2-C: 14.97%; sp3-C: 29.47%; C—OH: 39.82%; C═O: 10.75%; COOH: 4.40%; π–π: 0.59%. O1s XPS spectra of GO: C—O: 90.38%; C═O 9.62%.

2.2. Preparation of PTT-PTMO/GO nanocomposites

Preparation method of nanocomposites is presented in Fig. 1. A similar procedure as previously described for PTT-PTMO/Nanofil 32 nanocomposites was used [28]. Before polymerization, a dispersion of GO sheets was prepared by dispersing the desired amount of graphite oxide in PDO through ultrasonication for 15 min using laboratory homogenizer (Sonoplus HD 2200, with frequency of 20 kHz and 75% of power 200 W) and subsequent intensive mixing for 15 min with high-speed stirrer (Ultra-Turax T25). Additionally, to improve the dispersion/exfoliation of GO in PDO an ultra-power lower sonic bath (BANDELIN electronic GMbH & Co. KG, Sonorex Digitec, with frequency of 35 kHz and power 140 W) was applied for 20 h. The

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