



Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Montmorillonite/poly(urethane-siloxane) nanocomposites: Morphological, thermal, mechanical and surface properties

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ARTICLE INFO

Keywords:

Polyurethane nanocomposites
Thermal properties
Clay nano-fillers
Surface properties
Microphase separation

ABSTRACT

The aim of this work was to prepare and characterize the series of segmented polyurethane nanocomposites (PUNC) modified with poly(dimethylsiloxane) and based on montmorillonite (Mt) as a nano-filler. α,ω -Dihydroxy-poly(propylene oxide)-*b*-poly(dimethylsiloxane)-*b*-poly(propylene oxide) macrodiol was used as the soft segment component, while 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BD) were selected as the hard segment components. PUNC were synthesized with different ratio of hard/soft segments. PUNC were morphologically, structurally, thermally, mechanically and surface characterized by XRD, TEM, FTIR, AFM, TGA, DMTA, tensile test, XPS, contact angle, surface free energy (SFE) and water absorption measurements. Added Mt (1 wt%) was completely delaminated and well dispersed in the form of mixed exfoliated/intercalated layers in the polymer matrix, and that PUNC have more pronounced microphase separated morphology, higher thermal stability, superior mechanical features, enhanced surface properties, as well as outstanding hydrophobicity. Due to the improved features, developed polymers can be considered as candidates for materials with specific biomedical applications or as waterproof coatings.

1. Introduction

Analyzing the dynamic progress that occurred in past few decades within polymeric materials, the outstanding accomplishments are related to the preparation of new materials that combine different organic and inorganic materials. These new polymer materials should meet requirements for specific applications that were imposed by contemporary disciplines such as biomedicine, electronics or aircraft industry. Example of such materials includes also segmented copolymers, which combine polyurethane and polysiloxane block structures (Choi et al., 2009; Kozakiewicz, 1996; Yilgör et al., 1989). Segmented polyurethanes (PU) are multiblock copolymers consisting of alternating soft segments (SS) and hard segments (HS) (Tang et al., 1994). The features of these PU copolymers can be controlled and adjusted by different nature of SS and HS. A large number of papers that include the preparation of PU based on poly(dimethylsiloxane) (PDMS) macrodiols as a part of SS and various comonomers as a part of HS (Hernandez et al., 2007; Sheth et al., 2004; Simmons et al., 2008; Yeh and Shu, 2010) has been published.

Useful properties of PU copolymers mostly originate from their different composition and appropriate degree of microphase separation. Moreover, polyurethanes on one side have substantial strength, toughness and elasticity, while on the other side PDMS contributes to the excellent thermal and oxidative stability, outstanding hydrophobicity, chemical inertness and good biostability and biocompatibility of the final PU (Adhikari et al., 2000; Hernandez et al., 2007; Roohpour et al., 2009). In spite of the fact that PU combine these useful properties from their SS and HS, there has been a tendency among researchers toward incorporation of inorganic nano-fillers, such as clay minerals, inside these polymers in order to prepare different polyurethane nanocomposites (PUNC) (Lee et al., 2013; Maji et al., 2009; Turri et al., 2008; Wang et al., 2009a,b). Addition of low quantities of clay nano-fillers usually leads to the significant improvement of thermal, mechanical, surface and barrier properties of PU. Due to the large specific surface area (750 g m^{-2}), high aspect ratio (70–150) and high strength and stiffness of the clay mineral nanoparticles, it is an excellent choice for the use as nano-filler for polyurethanes (Ho et al., 2006). However, natural montmorillonite (Mt), which is the most

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<http://dx.doi.org/10.1016/j.clay.2017.08.021>

Received 27 January 2017; Received in revised form 21 August 2017; Accepted 22 August 2017
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commonly used for this purpose, consists of two external silicon tetrahedral sheets and one internal aluminum octahedral sheet that make one layer, while layers are spaced apart by interlayer spaces. Natural Mt has hydrated alkali cations in these interlayer spaces to compensate the negative layer charge resulting from substitution in the tetrahedral and octahedral sheets, resulting in poor compatibility with hydrophobic polymers. Hence, these cations need to be exchanged with hydrophobic surfactants i.e. organomodifiers (for example alkylammonium or alkylphosphonium ions) in order to improve the clay/polymer interactions and to ensure uniform dispersion within the polymer matrix (Ho et al., 2006). In other words, clay mineral modification is necessary to increase the distance between the layers and to enable better incorporation of polymer chains between the stacked layers (to obtain intercalated structure) or to get completely dispersed clay mineral layers (to obtain exfoliated structure) in polymer matrix (Paul and Robeson, 2008).

Recent studies are related to the preparation of the PUNC with different clay minerals and their various mass percentages in order to obtain improved features for the widespread usage. For example, Silvestri et al. (2011) prepared PUNC based on mixed poly(dimethylsiloxane)/polytetramethylene oxide (PDMS/PTMO) macrodiols of different molar ratios and with addition of two different clay minerals. As nano-fillers they have used organically modified Mt (OMt) (Cloisite 30B® and Cloisite 20A®) in an amount of 1 and 3 wt%. They have shown that the application of these clay nano-fillers leads to an increase of water repellency and slightly better mechanical properties of the PUNC, by addition of 1 wt% of OMt. Moreover, Barick and Tripathy (2010a,b) have prepared PUNC based on methylene bis(cyclohexyl) diisocyanate-1,4 butanediol hard segments and PTMO ($M_n = 1000 \text{ g mol}^{-1}$) soft segments with different percentages of incorporated Cloisite 30B® clay mineral (1, 3, 5, 7 and 9 wt%). They have shown that due to the homogenous dispersion of clay nano-fillers and strong interactions of clay layers with polymer chains, the PUNC begin to degrade at ~ 20 to 40°C higher temperature than pure PU copolymers. TEM analysis confirmed the existence of mixed intercalated/exfoliated morphology of OMt nanoparticles inside polymer matrix for PUNC containing 1, 3 and 5 wt% of OMt. Furthermore, in order to achieve better dispersion and exfoliated clay structure, Heidarian et al. (2011) prepared PUNC by *in situ* polymerization using the ultrasonicated-assisted process at different processing times (15, 30 and 60 min). They have shown that application of the ultrasound sonicated process with prolonged times allows better delamination of the clay layers and their homogenous dispersion in polymer matrix, leading to the improved barrier, thermal and mechanical properties of the PUNC.

Besides these studies, Pavličević et al. (2013) prepared PUNC based on aliphatic polycarbonate and 1 wt% of two different OMt and bentonite clay minerals. They have shown that the microphase separation is not influenced by the addition of these two clay minerals, indicating uniform dispersion of silicate layers in the PU matrix. Furthermore, Rueda et al. (2011) synthesized several PUNC based on polycaprolactone-*b*-polytetrahydrofuran-*b*-polycaprolactone ($M_n = 2332 \text{ g mol}^{-1}$) as the SS and 1,6-hexamethylene diisocyanate and 1,4-butanediol as the HS components. These PUNC contained 1 to 4 wt% of well dispersed Cloisite 30B® clay nanoparticles. However, although the PUNC have shown better thermal stability and improved mechanical features with mixed exfoliated/intercalated OMt morphology, they were still not good candidates for application as biomedical devices.

The aim of this study was to prepare PUNC with good thermal and mechanical properties and excellent hydrophobicity using PDMS as soft segment component. In order to do that, different polyurethane nanocomposites based on α,ω -dihydroxy-poly(propylene oxide)-*b*-poly(dimethylsiloxane)-*b*-poly(propylene oxide) (PPO-PDMS-PPO) and OMt nanoparticles (Cloisite 30B®) were synthesized. The effects and dispersion of the OMt nanoreinforcement on the morphological, structural, thermal, thermomechanical, mechanical and surface properties of the

PUNC were investigated by different experimental techniques.

2. Experimental section

2.1. Materials

α,ω -Dihydroxy-poly(propylene oxide)-*b*-poly(dimethylsiloxane)-*b*-poly(propylene oxide) (PPO-PDMS-PPO) was supplied from ABCR (purity 95%) and dried over molecular sieves (0.4 nm) before use. The number average molecular weight of the PPO-PDMS-PPO macrodiol, determined from ^1H NMR spectroscopy was 2970 g mol^{-1} . The molecular weights of the PDMS and PPO blocks were 1020 and 975 g mol^{-1} , respectively. 4,4'-Diphenylmethane diisocyanate (MDI) (from Aldrich, purity 98%) was used as received. 1,4-Butanediol (BD) (from Aldrich, purity 99%) was purified with distillation and dried over molecular sieves before application. *N,N*-Dimethylacetamide (DMAc) (from Acros, purity 99%) was dried over CaH_2 and purified with distillation under reduced pressure. Tetrahydrofuran (THF) (from J. T. Baker, purity 99.99%) was dried over LiAlH_4 and purified with distillation. The catalyst solution ($\text{Sn}(\text{Oct})_2$) (from Aldrich, purity 95%) was prepared by dissolving an appropriate amount of stannous octoate in an anhydrous solvent mixture of THF/DMAc (1/1, v/v). Cloisite 30B® (supplied from Rockwood) was natural Mt organomodified with methyl-tallow-*bis*-2-hydroxyethyl quaternary ammonium salt (from Southern Clay Product Inc.), where tallow represents an alkyl group of $\sim 65\% \text{ C}_{18}\text{H}_{37}$, $\sim 30\% \text{ C}_{16}\text{H}_{33}$ and $\sim 5\% \text{ C}_{14}\text{H}_{29}$. Cloisite 30B® has cation exchange capacity of 90 meq/100 g and d-value of 1.85 nm.

2.2. Synthesis of the PUNC

Complete synthesis procedure and preparation of the PU films based on PPO-PDMS-PPO soft segments are described in the previous paper by Stefanović et al. (2016b).

The PU nanocomposites (PUNC) based on PPO-PDMS-PPO macrodiols and 1 wt% of OMt (relative to the total weight of reactants) are prepared with the *in situ* polymerization technique in solvent mixture. The OMt (Cloisite 30B®) was previously dried in vacuum oven at 30°C for 2 days. Then it was introduced in the mixture DMAc/THF (1/1; v/v) (in amount of 10 wt%) and mixed 10 h at room temperature and then 2 h at 50°C . After that, the swollen OMt was sonicated in ultrasonic bath at room temperature for 1 h. Adequate amount of the so prepared OMt was added in the first phase of the polyaddition reaction. At the end of the synthesis, the polymer solutions were 30 min sonicated at room temperature, before pouring polymer solution into a Teflon dishes. Sonication process was used to ensure a high level of swelling of Mt layers and better incorporation of polymer chains inside the interlayer space. The polymer solutions were dried at 35°C in a force-draft oven for 1 day and then dried in vacuum oven at 40°C for 3 days, until a constant weight. All PUNC were allowed to age at room temperature in desiccators for at least 2 weeks prior the characterization. The PUNC were labeled as PUNC10, PUNC20, PUNC30, PUNC40, PUNC50 and PUNC60 (the last two numbers represent the weight percent of the HS).

2.3. Characterization

Wide angle X-ray diffraction (XRD) analysis was performed on Bruker D8 Advance diffractometer in Bragg-Brentano transmission mode θ/θ , equipped with focusing Ge-crystal primary monochromator of Johansson type, with $\text{CuK}\alpha_1$ radiation ($\lambda = 0.15418 \text{ nm}$) (the step-time and step-width for all measurements were 12 s and 0.05° , respectively). Anodic voltage and anodic current were 40 kV and 30 mA, respectively. The diffraction patterns were collected in the Bragg angle range from 2 to 60° , on the clay powder and PUNC films sizes $20 \times 15 \times 0.5 \text{ mm}$. The degree of crystallinity of the PUNC was calculated by peak deconvolution technique, as the ratio of the area under the crystalline peaks and total (amorphous and crystalline) area.

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