



Structure/transport property relationships within nanoclay-filled polyurethane materials using polycaprolactone-based masterbatches



Samira Benali^{a,*}, Giuliana Gorrasi^b, Leila Bonnaud^a, Philippe Dubois^{a,*}

^a Centre d'Innovation et de Recherche en MATériaux Polymères CIRMAP, Service des Matériaux Polymères et Composites, Université de Mons – UMONS and MATERIA NAOVA Research Center, Place du Parc 20, B-7000 Mons, Belgium

^b Department of Industrial Engineering, University of Salerno, Via Ponte don Melillo, 84084 Fisciano, Salerno, Italy

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ABSTRACT

The lamellar structure of montmorillonite (MMT) clays exhibits an interesting potential to improve the barrier properties of thermoplastic polyurethanes (TPU). However direct melt blending of an ester-based TPU and functional organoclays, despite showing good filler dispersion, did not allowed for improving neither barrier properties (i.e., sorption and diffusion to water vapor) not mechanical performances with respect to the unfilled TPU. Therefore, two alternative strategies involving poly(ϵ -caprolactone) (PCL)/organoclay masterbatches were explored to investigate the possibility to prepare materials with improved mechanical and barrier properties. In the first strategy, a PCL/organoclay masterbatch with high inorganic content was obtained by melt-blending (coined “free PCL” masterbatch), whereas in the second strategy PCL-grafted organoclay nanohybrids, also with high inorganic content were synthesized by *in situ* intercalative grafting/ring-opening polymerization of ϵ -caprolactone (CL). Purposely, ROP of CL was initiated from hydroxyl groups available onto the MMT surface actually organo-modified by alkylammonium cations bearing hydroxyl functions (coined “nanohybrid PCL” masterbatch). These highly-filled PCL masterbatches (with ca. 25 wt% in inorganics) were then added into the ester-based TPU to prepare nanoclay/polyurethane nanocomposites by melt-blending. The morphology and dispersion of the resulting materials were characterized by X-ray diffraction and transmission electron microscopy. Improved sorption and diffusion properties towards water vapor as well as mechanical properties were measured. Herein, these results are discussed as a function of both clay dispersion and matrix/organoclay interaction.

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1. Introduction

The research concerning polymer–clay nanocomposites [1–6] has highlighted the interest for organo-modified layered silicates such as montmorillonite (MMT) not only for increasing polymer stiffness [4] but also for enhancing other properties like thermal resistance [6], flame retardancy [6] and gas barrier properties [7,8].

The possibility of reaching large enhancement of polymer properties lies upon reaching a high level of nanoplatelet dissociation and ultimate clay exfoliation throughout the polymer matrix [1,2,5]. Lightweight and economic competitiveness using a minimal amount of reinforcing materials, usually below 5 wt%, represent other key-advantages of polymer–clay nanocomposites, which make them suitable for a broad variety of applications such as in automotive, electronic, food packaging, biotechnology, biomedical field, and tissue engineering [9].

The wide applicability of polyurethane (PU) coatings is owing to versatility in selection of monomeric materials from a long list of macrodiols, diisocyanates and chain extenders [10]. With the development of low-cost polyols, PU coatings based on layered silicate-filled nanocomposites, for instance, are expected to display higher permeation-barrier properties towards water and oxygen molecules owing to the tortuous path created by the fine dispersion of the impermeable clay nanoplatelets [11]. Many studies have been reported often employing traditional methods known for preparing nanocomposites such as (i) *in situ* polymerization of diisocyanates, macrodiols and chain extenders (CE), that are initially intercalated between silicate layers [12–23] and (ii) melt intercalation and further dispersion/exfoliation of thermoplastic PU [9,24–28]. However, it is difficult to compare these different results from literature because the monomers or polymers studied differ from one study to the other. Reported *in situ* polymerization methods lead to exfoliated structures, but no drastic changes of properties are observed.

The preparation of PU nanocomposites based on an organosilicate, e.g., a commercially available organo-modified MMT like Cloi-

* Corresponding authors. Tel.: +32 (0)65 373480; fax: +32 (0)65 373484.

E-mail addresses: samira.benali@umons.ac.be (S. Benali), philippe.dubois@umons.ac.be (P. Dubois).

sit[®]30B (from Southern Clay Products, US), hereafter reported as MMT–OH₂, through melt compounding technique was first reported by Finnigan et al. [24], who achieved a large increase in stiffness while tensile strength and ultimate elongation were not substantially affected. This result also illustrates that the MMT–OH₂ nanoplatelets could be dispersed and delaminated to some extent in the segmented PU matrix via melt processing route where molecular diffusion and shear stress played a good driving force for intercalation between the polymer chains and nanofillers [24]. Other authors have reported nanoclay-based TPU nanocomposites also prepared by melt intercalation technique [26,27,29–39]. Overall, the best organoclay particle dispersion and highest matrix reinforcement were obtained using hydroxylated alkyl ammonium cations as surfactants as confirmed by morphology analysis and mechanical testing. More recently, Barick et al. [9,33,34] have investigated the use of a dimethyl dehydrogenated tallow ammonium organoclay with TPU matrix using melt-blending. With a complete study, i.e. morphology, thermal stability, rheological and mechanical properties, authors explained the structure–property relationships.

In parallel, another approach has been investigated by some of us to enhance the clay nanoplatelet delamination within the nanocomposite materials, the so-called “PCL-clay masterbatch” process [5,40–48]. In such a process, a highly filled (organo-modified) clay/PCL is first prepared by melt intercalation or by *in situ* polymerization of ϵ -caprolactone (CL), followed by its addition as a masterbatch that is blended with the molten polyester matrix. Essentially it consists in using PCL chains known to be miscible with the selected polymer matrix. The PCL chains are present onto the clay nanoplatelets in order to compatibilize the clay/matrix interface and to facilitate the homogeneous dispersion of the nanofillers. When the masterbatch is obtained by melt-blending, the so-called “free PCL” masterbatch is then used with a commercial matrix by melt-blending. On the other hand, when the masterbatch is obtained by “grafting–from” intercalative polymerization, the resulting polymer surface-treated/grafted clay or “nanohybrid PCL” masterbatch is also dispersed in the polymer matrix via conventional melt-mixing processes. This technique has already successfully led to a large improvement of clay dispersion within PCL matrix [46] and poly(styrene-co-acrylonitrile) matrix, thus miscible with PCL [44,45,49,50].

On the other hand, the studies of chlorinated polyethylene (CPE) nanocomposites using PCL/clay nanohybrid [42,43,48] have highlighted a synergistic effect in mechanical reinforcement of CPE through partial crystallization of PCL.

The present work focuses on the potential of PCL/clay masterbatches within TPU matrix to prepare new materials with enhanced mechanical and gas barrier resistance properties. The TPU is a very versatile matrix with a complex system including hard segments immiscible with PCL matrix and soft segments potentially miscible with PCL. This first study aims to compare the different PCL masterbatches, i.e. ‘free-PCL’ or ‘nanohybrid-PCL’. The relationships between the clay dispersion and properties are discussed. Three methods to manufacture TPU/clay materials have been investigated: (i) a direct melt intercalation method (TPU/MMT–OH₂), (ii) a “free PCL” masterbatch method (TPU/(MMT–OH₂/PCL)), (iii) a “nanohybrid PCL” masterbatch method (TPU/(MMT–OH₂–g–PCL)). For sake of comparison, a TPU/PCL blend is also prepared.

2. Experimental part

2.1. Materials

Thermoplastic polyurethane (TPU) based on polyester (DESMO-PAN[®] DP 2786 A) is provided by Bayer (Germany). ϵ -Caprolactone

(CL, from Fluka, Switzerland) was dried over CaH₂ and distilled under reduced pressure prior to use. Tin(II) bis(2-ethylhexanoate), also known as tin(octoate) (Sn(Oct)₂), diluted with dried toluene and stored under nitrogen atmosphere was purchased from Fluka (Switzerland).

CAPA[®]2402, a PCL oligomer (OH value = 27.62 mgKOH/g, M_n = 4000 g mol^{−1}) were obtained from Solvay Interlox (United Kingdom). Cloisite[®]30B (MMT–OH₂), a montmorillonite organo-modified by 23.4 wt% of methyl bis(2-hydroxyethyl)tallowalkyl ammonium cations was supplied by Southern Clay Products (USA).

2.2. Characterization

Unless specified, the analyses were carried out on the compression-molded samples. The morphology of the nanocomposites was analyzed by wide-angle X-ray diffraction (WAXD) and transmission electronic microscopy (TEM). WAXD patterns were recorded between 1.65° and 30° (by steps of 0.04°) with a Siemens D5000 diffractometer (Germany) operating with Cu K α radiation (λ = 1.5406 Å). For recording TEM images, the samples were cryomicrotomed at −100 °C with an Ultracut FC4E microtome from Reichert–Jung. A truncated pyramid was cut in the sample. Ultrathin sections of the pyramid were removed for TEM experiments. The TEM images were recorded with a Philips CM100 microscope with an acceleration voltage of 100 kV.

DSC Q2000 from TA instrument was used for Differential Scanning Calorimetry (DSC) analysis. Samples (weighing ~10 mg) were sealed in aluminum DSC pans and placed in the DSC cell. The DSC was calibrated with indium. Samples were heated from −80 °C to 200 °C with a heating rate of 3 °C/min. Dynamic mechanical thermal analyses (DMTA) were performed with a DMA2980 from TA Instrument from −70 °C to 100 °C on compression molded (0.5-mm thick and 5-mm wide) sheets of either unfilled PU or PU/layered silicates nanocomposites. Measurements were carried out in tensile mode at 1 Hz with a deformation amplitude of 20 μ m. The heating rate was 3 °C/min. DSC and DMTA analyses were performed 1 week after preparation and were realized on three specimens for each formulation in order to check the reproducibility.

Transport properties experiments were performed using a conventional McBain spring balance system, which consists of a glass water-jacketed chamber serviced by a high vacuum line for sample degassing and permeant removal [51]. Inside the chamber samples were suspended from a helical quartz spring supplied by Ruska Industries, Inc. (Houston, TX) with a spring constant of 1.892 cm/mg. The temperature was controlled to 30 ± 0.1 °C by a constant temperature water bath. Before beginning the sorption experiments, the sample was exposed to vacuum for at least 24 h in order to remove previously sorbed air gas and water. Sorption was measured as a function of the relative pressure, $a = P/P_0$, where P is the actual pressure (in mm Hg) of the experiment, and P_0 the saturation pressure at 30 °C for water. The samples were exposed to the penetrants at fixed pressures, and the spring position was recorded as a function of time using a cathetometer. The spring position data were converted to mass uptake data using the spring constant. Diffusion coefficients and equilibrium mass uptake were extracted from these kinetic sorption data. Data were averaged on three samples.

2.3. Preparation of PCL/clay masterbatches

Fig. 1 (insert) represents the ammonium cation used in this work for organo-modifying MMT. Quaternary ammonium ion of MMT–OH₂ is derived from tallow amine. This ammonium was used as received with commercial organoclay.

A non-grafted PCL/MMT–OH₂ (nano)composite (highly filled, i.e., containing 25 wt% inorganics) was prepared by melt mixing

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