



Microstructure–property relationships of organo-montmorillonite/polyurethane nanocomposites: Influence of hard segment content



Shahed Taheri^a, Gity Mir Mohamad Sadeghi^{b,*}

^a Department of Biomedical Engineering, Amirkabir University of Technology, Tehran, Iran

^b Department of Polymer Engineering & Color Technology, Amirkabir University of Technology, P.O. Box 15875/4413, Tehran, Iran

ARTICLE INFO

Article history:

Received 18 January 2015

Received in revised form 17 June 2015

Accepted 27 June 2015

Available online 6 July 2015

Keywords:

Polyurethane nanocomposite

Nucleating effect

Organo-montmorillonite

Crystallinity

Hard segment content

ABSTRACT

A comprehensive study was made to correlate the microstructural nucleating effect of an organically-modified montmorillonite with morphology, crystallinity, degree of phase separation and mechanical properties of organo-montmorillonite/polyurethane (PU) nanocomposites. Constituents with the symmetrical chemical structure were chosen to ensure that polyurethane contains sufficient crystallinity in order to expose the nucleating effect of organo-clays. Polyurethane was prepared by in situ polymerization of poly(tetrahydrofuran), 1,6-hexamethylene diisocyanate (HDI) and butanediol in three sets of hard segment contents and nanocomposites were attained by the incorporation of 1 wt.% Cloisite® 30B for each of these three sets. X-ray diffraction patterns revealed exfoliation of clay layers in PU matrix as well as sharp crystalline reflections related to the soft and hard segment domains. Mid-IR spectra displayed the significant role of organo-clays on hydrogen bonding and micro-phase separation, largely in lower hard segment contents. The degree of crystallinity was measured through DSC analysis and the additional crystallization caused by the incorporation of organo-clay, as well as the higher melting point of nanocomposites compared to their PU counterparts were accurately demonstrated; which further confirmed that Cloisite® 30B functioned partly as a nucleating agent. A rare co-continuous structure as well as a spherulitic coarse structure was observed in medium and high-magnification FESEM micrographs, respectively. EDS elemental mapping showed highly-uniform clay distribution for all nanocomposite samples. The incorporation of organo-clay increased the tensile modulus in higher hard segment contents. Additionally, strain-induced crystallization was found as a prominent phenomenon in stress–strain curves, which diminished elongation at break in all nanocomposite specimens.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The use of inorganic fillers in polymer industry is known to be widely economical due to their low cost, while introducing efficient advantages of both polymer materials and inorganic compounds (Toro et al., 2007; Zhao et al., 2012). Furthermore, incorporating finely distributed solid particles into semicrystalline polymers such as polyolefins and polyamides can provoke nucleation which is essential in industrial applications to control the polymer structure via crystallization and also to shorten the cycle time of crystallization (Göschel et al., 2007). Minerals such as talc (Fiorentino et al., 2015), mica (Velten et al., 1999; Lapčík et al., 2015), kaolinite (Saw et al., 2015), calcite (Zhu et al., 2014) and glass fibers (Iroh and Berry, 1993) are among the most frequently employed fillers which also serve as nucleating additives. However, due to their incompatible chemical nature with the polymer matrix, the required uniform dispersion of small particles to acquire

the anticipated fine crystalline structure remains a challenge (Cao and Jana, 2007). Consequently, the incorporation of inorganic fillers usually leads to the formation of microcomposites which significantly limits the enhancement of mechanical properties (Wu et al., 2002; Zhao et al., 2012; Zhu et al., 2014).

In order to combine the high in-plane strength, innate heat durability, immense stiffness and the natural nucleating function of inorganic fillers with chemical compatibility, organically modified clays (e.g., montmorillonite) seem to be excellent materials to be used in polymer systems. Organo-montmorillonites are particularly gaining widespread interest due to their large aspect ratio and huge specific surface as much as 700 m²/g (Wu et al., 2002), which are important factors in the significant improvement of the mechanical properties, as well as in avoiding the deterioration of impact strength, generally observed in microcomposites.

The use of montmorillonite as nanofillers for the preparation of nanocomposites has been recently studied for various prominent types of polymer networks including polypyrrole (Setshedi et al., 2013), polypropylene (Silvano et al., 2013) and polyamide-6 (Yebrá-Rodríguez et al., 2009). Polyurethane (PU) is a polymeric material, which is extraordinarily versatile and has been widely used in this

* Corresponding author at: Amirkabir University of Technology, Department of Polymer Engineering, 424 Hafez Ave, Tehran, Iran.

E-mail addresses: shahed_taheri@aut.ac.ir (S. Taheri), gsadeghi@aut.ac.ir (G.M.M. Sadeghi).

field since the first introduction of organically treated clays/PU by Wang and Pinnavaia (1998). Since then, numerous efforts (Moon et al., 2004; Chavarría and Paul, 2006; Barick and Tripathy, 2010, 2011; Bayer et al., 2010; Yusoh et al., 2010) have been made to investigate the effects of organo-clays on mechanical properties of PU nanocomposites. Research (Jeong et al., 2007; Meng et al., 2008, 2009) has shown that the level of enhancement in properties is extremely dependent on the dispersion level achieved by the nanoparticles in the polymer matrix. In intercalated nanocomposites, the layers of the clay structure are separated by the incorporation of the polymer into the interlayer space while the periodicity of the clay structure is maintained. In exfoliated nanocomposites, the crystal structure of the clay is completely lost by breaking up of the large aggregates into smaller particles. Xia et al. (2005) have shown that intercalated organo-clay/PU nanocomposites exhibited outstanding mechanical properties, in particular a 120% increase in the tensile strength, a 100% increase in the elongation at break and a 300% increase in the fatigue durability, when only 3 wt.% organo-clay had been introduced (Jin et al., 2006, 2009). With the increase of exfoliation level, clay/PU nanocomposites exhibited an improvement in tensile strength and modulus with a reduction in elongation at break and fatigue durability (Xia et al., 2005). Although these investigations suggest that the difference in microphase morphology of intercalated/exfoliated nanocomposites could alter the physical properties of the specimen, few studies have addressed the nucleating effect of organo-clays on clay/PU nanocomposites and merely sufficed to report the existence of such phenomenon (Barick and Tripathy, 2010, 2011; Salahuddin et al., 2010). To the extent of the researchers' knowledge, there has yet to be made a comprehensive study to significantly correlate the nucleating effect of organo-clays with microstructural interactions, crystallinity, degree of phase separation, morphology and how it consequently affects the mechanical properties of clay/PU nanocomposites. This is most likely due to the fact that unlike polypropylene and polyamide-6, polyurethane is not generally categorized under the semicrystalline polymer matrices, making it complex to evaluate the effect of clay incorporation on the crystallinity of polyurethane chain segments. However, it was assumed that choosing synthesis constituents with symmetrical structure could lead to PUs with a considerable crystallinity.

In this work, monomeric units with alternative spatial configurations were selected, which led to semicrystalline PU structures. Polyurethanes were synthesized through in situ polymerization method and with three different hard segment contents (20, 30 and 40 wt.%). Organo-montmorillonite/PU nanocomposites were obtained by incorporating 1 wt.% organo-clay for each set of hard segment contents. The nucleating effect of the organo-clay was initially detected through X-ray diffraction and ATR-IR analysis and further confirmed by DSC thermograms and FESEM micrographs. The nucleating effect of the organo-clay (comparison between nanocomposite specimens and their PU counterparts) on the degree of crystallinity, intermolecular hydrogen bonding, degree of phase separation and surface morphology was evaluated. The analyses were synchronously taken into account by assessing the hard segment content factor, while aiming to establish a meaningful relationship between the mechanical properties obtained from tensile testing and previous observations of the nanocomposite microstructures. No alteration in clay content was made because it would further complicate the subject, making it impenetrable.

2. Experimental

2.1. Materials

The soft segments of polyurethane were based on a polyether-type polyol, poly(tetrahydrofuran) (PTHF; average molecular weight 2000 g/mol, see Fig. 1a for chemical structure) which was purchased from Sigma-Aldrich Chemie GmbH. The hard segments were synthesized from 1,6-hexamethylene diisocyanate (HDI), an aliphatic diisocyanate with a symmetrical molecule structure (Fig. 1b) and two isocyanate

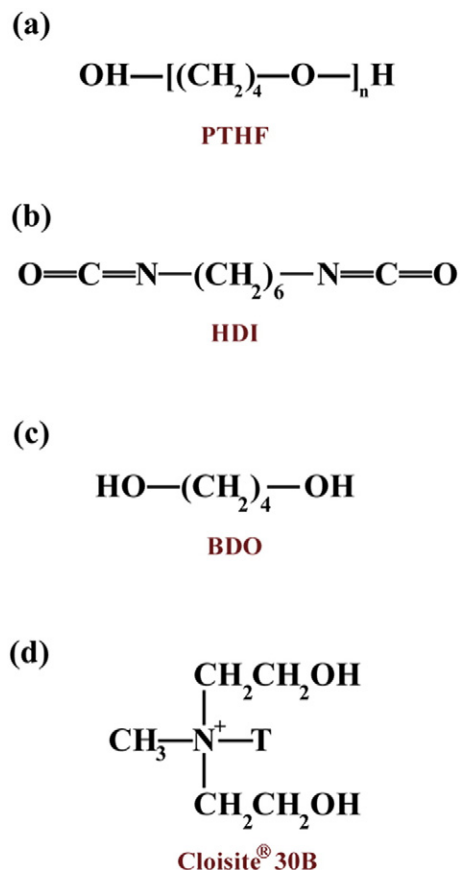


Fig. 1. Chemical structures of components used in the synthesis of clay/PU nanocomposites: (a) poly(tetrahydrofuran); (b) hexamethylene diisocyanate; (c) butanediol; and (d) the surfactant molecule of Cloisite® 30B.

groups of equal reactivity, and 1,4-butanediol (BDO) obtained from Aldrich and Merck Chemicals, respectively.

The commercial organically modified clay used in this study was Cloisite® 30B obtained from Southern Clay Products. The Cloisite® 30B is an organo-clay based on a natural montmorillonite having density = 1.98 g/cm³, d₀₀₁-value = 18.5 Å, and cation exchange capacity (CEC) = 0.9 meq/g with methyl, tallow, bis-2-hydroxyethyl ammonium modifier (MT2EtOH), of tallow composition as ~65% C18; ~30% C16; and ~5% C14 (Fig. 1d).

2.2. Preparation of PU and its nanocomposites

Pristine polyurethane was synthesized through a two-step in situ polymerization method in three sets of samples containing 20, 30 and 40 wt.% hard segments. The prepolymer was prepared from the reaction of a desired amount of poly(tetrahydrofuran) and HDI (Table 1) at 85 °C for 2.5 h in a three-neck flask, equipped with nitrogen inlet and a mechanical stirrer system. The synthesis of thermoplastic polyurethane was then completed by the chain extension reaction between 1 mol

Table 1

Molar ratio of various components used in the synthesis of polyurethane chains and its clay nanocomposites.

Sample	Organoclay content (wt.%)	Molar ratio of HDI/PTHF/BDO
PU20	0	2.284/1/1.284
NC20	1	2.284/1/1.284
PU30	0	3.667/1/2.667
NC30	1	3.667/1/2.667
PU40	0	5.510/1/4.510
NC40	1	5.510/1/4.510

Download English Version:

<https://daneshyari.com/en/article/1694393>

Download Persian Version:

<https://daneshyari.com/article/1694393>

[Daneshyari.com](https://daneshyari.com)