Applied Clay Science 146 (2017) 468–474

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Effect of nanoparticle on the mechanical and gas barrier properties of thermoplastic polyurethane

Shruti Pandey[a], Karun K. Jana[a], Vinod K. Aswal[b], Dipak Rana[c], Pralay Maiti[a,*]

[a] School of Materials Science and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi 221 005, India
[b] Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India
[c] Industrial Membrane Research Institute, Department of Chemical and Biological Engineering, University of Ottawa, 161 Louis Pasteur St., Ottawa, ON KIN 6N5, Canada

ARTICLE INFO

Keywords:
Thermoplastic polyurethane
Nanohybrid
Structure
Mechanical properties and gas permeability

ABSTRACT

Thermoplastic polyurethane (TPU) nanohybrids have been prepared through melt extrusion using ester type PU and different concentrations of Indian origin organically modified nanoclay as filler. The level of dispersion of nanoclay in TPU is found to be good and considerable intercalation occurs due to strong interaction between polymer matrix and filler. The interaction is shown through spectroscopic measurement from the shifting of peak position in FTIR and UV–vis. absorption spectra. Nanoclay induces crystallization in polymer while the blob size, as measured through small angle neutron scattering, decreases in nanohybrid (1.5 nm) as compared to pure TPU (1.7 nm) obtained after fitting the initial data point to Debye-Bueche model. Mechanical responses are much superior in nanohybrid as compared to pure TPU and stiffness values continue to increase with nanoclay concentration while the toughness reach ata maximum value at an optimum concentration of 4 wt% of nanoclay. Uniaxial stretching lead to the crystallization of segments and ordering of hard segments as verified through sharp melting points in stretched TPU vis-à-vis predominant amorphous nature before stretching. Nanohybrid membranes are prepared to investigate the gas permeation across the membranes and very high gas barrier of nanohybrid (449 Barrer) is found as opposed to pure TPU barrier of 169 Barrer. Critical assessment of permeability is performed in presence of nanoclay in different concentrations with a plausible mechanism of gas barrier.

1. Introduction

During past decades, the development of nanohybrids is customized with different fillers and it has been the basis of production of many superior products. Polymers with inorganic clay particles with high aspect ratio with nanoscale dimension have yielded improved chemical and physical properties including thermal, mechanical, flame-retardant, electrical, biodegradability and barrier properties (Wang and Pinnavaia, 1998; Shah et al., 2004; Jana et al., 2012; Jana et al., 2013; Jana et al., 2015a, Jana et al., 2015b). Clays are layered silicate materials commonly used as reinforcing filler for the preparation of nanohybrids due to their easy availability, natural abundance and low cost (Barick and Tripathy, 2010). Indian origin NK75 is a montmorillonite (Mt) clay and has planar octahedral alumina layer sandwiched between two tetrahedral silicate layers (Nguyen and Baird, 2006). The structure repeats itself with a characteristic distance. Mt. clay has high cation exchange capacity (CEC), aspect ratio, surface area, surface reactivity and adsorptive properties (Salahuddin et al., 2010). Higher percentage of iron in nanoclay (NK75) helps in improving the biocompatibility and, therefore, NK75 is used as a filler in biomedical applications as well (Kapusetti et al., 2014). The properties of nanohybrids improve when the silicate layers (inorganic phase) exfoliate or considerable intercalation occurs (Lebaron et al., 1999; Kim et al., 2003; Song et al., 2005). Improved nanohybrid preparation is very much reliant on the structural aspects of the polymer in addition to the compatibility of the clay with the matrix. Isomorphic substitution within the silicate layers generates negative charges which are counter balanced by Ca^{++} and Na^{+} cations (residing in interlayer gallery) resulting better miscibility between silicate layer and matrix and overall good dispersion of the silicate layers (Corcione and Maffezzoli, 2009). There are two fundamental processes to prepare nanohybrids (1) direct intercalation of polymer chain into layered clay, and (2) intercalation of monomer onto clay interlayer and consequent heat treatment for polymerization (Rehab and Salahuddin, 2005; Joulazadeha and Navarchiana, 2010a,Joulazadeha and Navarchiana, 2010b). The nanohybrid with large surface area can be used in a variety of applications such as food packaging (Qian et al., 2011), biotechnology (Singh et al., 2011), devices (Mitra et al., 2011) and fuel cell membrane (Jana et al.,

* Corresponding author.
E-mail address: pmaiti.mst@itbhu.ac.in (P. Maiti).

http://dx.doi.org/10.1016/j.clay.2017.07.001
Received 4 March 2017; Received in revised form 3 July 2017; Accepted 3 July 2017

2015a,b). Thermoplastic polyurethane (TPU) is a thermoplastic block copolymer characterized by a wide range of properties consisting of blinking soft segments (which is high molar mass polyether or polyester macro-diol) and hard segments (which is self-possessed of diisocyanate and chain-extender molecules that are either diol and diamine) (Koerner et al., 2008; Mishra et al., 2012). TPU bridges the gap between flexible rubber and rigid plastics and offers exceptional benefits. Unlike other thermoplastic elastomers, TPU provides numerous physical properties which makes it extremely flexible material adaptable to various uses. Polymer nanohybrids obtained from a polyurethane matrix and the adequate nanofillers offer a chance to produce new materials (Finnigan et al., 2004), where the properties of polyurethanes can be improved. Polyurethane elastomers have massive challenge in modern time as TPU possess good properties like high hardness, abrasion resistance, excellent mechanical properties and flexibility and it has a variety of universal applications caused by its distinctive properties, e.g. biotechnology, adhesives and packaging etc. (Osman et al., 2003; Choi et al., 2011; Mahanta et al., 2015). This work has been carried out to study the properties of elastomeric TPU with clay (NK75) with significantly improved properties as compared to pure polymer and the effect of varying concentration of fillers in the nanohybrids properties. Mechanical, morphological, thermal, gas barrier properties are used to study the structure and the performance of the nanohybrids.

2. Experimental segment

2.1. Materials

Thermoplastic polyurethane (TPU) was obtained from Bayer Material Science AG: polyester based TPU (Desmopan 385S) having the shore hardness of 86A. A typical nanoclay (NK75; Indian origin high iron content Mt., ion-exchanged with dimethyl dihydrogenated tallow ammonium; CEC = 70 meq/100 g) was used as a filler for nanohybrid preparation (Kapusetti et al., 2014). Tallow contains ~65% C_{18}, ~30% $C_{16\ and}$ ~ 5% C_{14} alkyl chains.

2.2. Preparation of nanohybrid

Melt extrusion technique was used for the preparation of nanohybrid (Dan et al., 2006; Grande and Pessan, 2017). Nanoclay (NK75) was mixed with TPU in a Haake twin-screw extruder (Hakke Mini Lab) for 10 min excluding the feeding time at 220 °C with the shear rate of 100 rpm. Henceforth, the nanohybrid of TPU will be termed as "NH" with 4 wt% of nanoclay in the pristine polymer. Nanohybrids containing 2, 6 and 10 wt% of nanoclay were also prepared to understand the effect of nanoclay loading. Films (~120 μm thick) of pristine polymer (TPU) and extruded nanohybrids (NHs) were prepared using a compression molding machine (S. D. Scientific Ltd.).

3. Characterization

3.1. TEM

Bright field images of nanohybrid specimens were obtained using TEM (Technai G^2) operated at an accelerating voltage of 100 kV. A thin layer, around 70 nm thick, from the sample was sectioned at − 85 °C using a Leica ultra-microtome equipped with a sharp diamond knife.

3.2. XRD

The change in *d*-value of silicate layers of the nanoclay was determined using Bruker AXS D8 Advance wide-angle X-ray diffractometer with Cu-Kα radiation with a graphite monochromator (λ = 0.154 nm). The samples were scanned at 1°/min in 1 to 10° range and at 3°/min for 10 to 40° 2θ range. The basal spacing of the nanoclay, d_{001} was calculated using Bragg's law.

3.3. Small-angle neutron scattering

Small angle neutron scattering experiments were performed on the spectrometer at the Dhruva reactor at Bhabha Atomic Research Centre in Mumbai, India. The data was collected for the scattering vector (q) range from 0.17 to 3.6 nm^{-1}. The scattering from the samples was modified after background correction. The characteristics length (Λ_c) was calculated using the equation:

$$\Lambda c = \frac{2\pi}{q_m} \quad (1)$$

where, q_m is the scattering vector q consequent to the peak position of shoulder in the scattering patterns of the samples. The temperature was kept constant and stable at 30 °C during each measurement.

3.4. FTIR

Fourier transform infrared (FTIR) spectroscopy was performed on a Thermo Scientific FTIR (NICOLET-6700) in the ATR mode in the wavenumber range of 650–4000 cm^{-1}. Each spectrum was recorded by accumulating 100 scans with a peak resolution of 4 cm^{-1}in reflectance mode.

3.5. UV–Vis spectroscopy

The UV–visible absorbance spectra of neat polymer and nanohybrid films were taken using Shimadzu 17,001 in the range of 200–800 nm wavelengths of light.

3.6. TGA

Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA under nitrogen atmosphere. Thermal degradation of TPU and NH specimens were studied with a heating rate of 20°/min in the measurement range of 40to 600 °C and the sample weight of nearly 5 mg was used for TGA experiments.

3.7. DSC measurement

Differential scanning calorimetry (DSC) measurements were performed on a Mettler832 instrument. The DSC was calibrated with indium and zinc before actual experiment. The heat of fusion and melting temperature were evaluated from the melting endotherms using a software and computer attached to the instrument. Weight of the samples was in the range from 3 to 10 mg range and a10°/min heating rate was employed for all experiments.

3.8. Mechanical properties

Tensile tests were carried out on a universal testing machine (Instron 3369). The strain rate was 5 mm/min at room temperature. Dog bone shaped specimens with gauge length 20 mm, thickness 2.12 mm and width 4 mm were prepared using Haake micro-injector.

3.9. Measurement of gas Permeability

Gas permeability of the specimens (neat TPU and NH) was examined at a constant pressure using three parallel cells method (Savoji et al., 2012). A spherical film of 11.044 cm^2 area and 0.003 cm thick sample was placed in the cell and was fixed using aluminum foil, glue and cello tape. The feed pressure was set at 80 psi while permeate side was maintained at the atmospheric pressure. The calculation of gas permeation rate was resolved using soap bubble flow meter (Rana et al., 2012). Each experiment was performed triplicate for reproducibility and the averages of those results are reported. The gas permeability was calculated from the following Eq. (2);