Effect of addition of montmorillonite and carbon nanotubes on a thermoplastic polyurethane: High temperature thermomechanical properties

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ABSTRACT

Thermoplastic polyurethane (TPU) and thermoplastic polyurethane/polyamide 11 (TPU/PA) nanocomposites were prepared via melt compounding, incorporating Cloisite®30B (Cl) and multi-walled carbon nanotubes (MWNT). Morphological characterization of all samples was conducted using X-ray diffraction, transmission electron microscopy, differential scanning calorimetry, and Fourier transform infrared spectroscopy. Thermophysical properties were characterized using dynamic mechanical analysis and thermogravimetric analysis at 500 °C/min. A correlation was drawn between addition of nanoparticles and degree of phase separation (DPS), and further between DPS and the thermomechanical property termed the "reinforcement gap." This gap has been associated with TPU dripping behavior at high temperatures. It is postulated that only polar-type reinforcing nanoparticles will reduce DPS. Rate of chemical degradation of TPU was reduced by both Cl and MWNT.

1. Introduction

Polyurethane is one of the most interesting polymers used today, exhibiting a widely tunable range of properties arising from the complexity of microdomains possible when composites are formed. Markets include automobile interiors, adhesives, coatings, and battery cables. Incorporation of nanofillers, such as organoclays, multi-walled carbon nanotubes and iron—silica (core—shell) nanoparticles into the thermoplastic polyurethane (TPU) matrix can result in an improved balance of mechanical, thermal and electrical properties including greater modulus and improved fire/thermal performance [1–6]. However, these improvements from a structure—property perspective can have quite complex morphological roots. TPU is a pseudo-block copolymer where at least two microstates exist based on chemical composition, the hard segment domain and soft segment domain. The hard segments often consist of a short chain extender diol and aromatic or aliphatic diisocyanates, while the soft segments typically consist of long chain diols (usually polyethers, polyesters, or polycaprolactones.) Hard segments and soft segments phase separate due to thermodynamic incompatibility. The polymer chains in the hard segments have a tendency to hydrogen bond, one driver of phase separation, and a feature which can be detected by FTIR spectroscopy. The hard segments function as physical crosslinks, mechanically reinforcing the material. The soft segments primarily contribute elasticity to the TPU. If the sizes of the two domains or the volume ratio of the two domains are changed, the physical properties of the TPU will change.

The addition of a nanofiller, such as an organoclay represents a second type of domain formation, special in that it has the potential to alter the hard/soft segment domain structure. The presence of the nanofiller alone can affect composite mechanical properties and thermal/fire properties. Additionally, if the baseline polymer domain morphology also changes on forming the nanocomposite, the mechanical performance can be altered synergistically.

The existence of a synergistic effect has been documented for TPU nanocomposites. Finnigan et al. have demonstrated that varying the processing method (solvent cast versus melt processed)

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for TPU organoclay nanocomposites affected polymer microphase separation [7,8]. Barick et al. studied the same organoclay in a TPU and described how filler loading affected rheology, also suggesting that microstructure changed with increased filler loading. The same authors have described composites with multi-walled carbon nanotubes and carbon nanofibers [9–11]. Chavvaria et al. investigated how incorporating different organically modified clays affects the morphology and the mechanical properties of TPU, and a polar surfactant on the organoclay was shown to provide the greatest modulus enhancement (similar to trends for the analogous polyamide nanocomposites) [12].

Polyamide mixtures with organoclays (as opposed to TPU mixtures with organoclays) have produced the most exfoliated (highly mechanically reinforced) of the many polymer/organoclay nanocomposites reported in recent years. Thus, the most robust structure−property database in the literature to date is for polyamide nanocomposites. If one wishes to study structure/property optimization for TPU nanocomposites, it is compelling to ask if the addition of a polyamide into the already complex TPU system could increase dispersion and ultimately have a positive effect on mechanical or thermal/fire performance. If that is the case, it would be interesting to determine which polyamide could perform that function.

Polyamides have been found in some cases to form blends with TPUs. Kim et al. reported compatibility between TPU and polyamide 11 (PA) which also resulted in increased tensile strength with increasing concentration of PA in TPU [13]. Li et al. reported compatibility between TPU and PA12,12 [14]. He et al. used EVA-g-MAH as a compatibilizer for blends of TPU with PA6. An increase in tensile strength was reported with increasing concentration of EVA-g-MAH [15]. Pesetskii et al. showed compatibility between a polyether-based TPU and PA12 [16]. These previous reports show that particular polyamide/TPU pairs have a window of compatibility; we further postulate that polyamides can be used to alter nanoparticle dispersion in TPUs, which may in turn lead to improved thermomechanical properties. However, adding the polyamide or dispersing the filler better may clearly alter microphase domain structure and/or PA crystallinity. An early effort at understanding this complex morphological system, e.g. a TPU blended with a variety of nanoparticles in the presence of a polyamide compatibilizer, is therefore, the subject of this paper. Particular attention is paid to structural roles and thermal properties associated with fire and extreme temperature performance.

2. Experimental

2.1. Materials

Table 1 describes all the materials used in this study. Previous studies indicated that a loading of 7.5wt% exhibited the best combination of flammability and mechanical properties [6]. Therefore, TPU and TPU/PA blends were reinforced with loadings of 7.5 wt% throughout the study. All materials were used as received.

Table 1
Material designations.

Polymer	Nanoparticle	Nanoparticle loading (wt%)	Material designation used
TPU/PA (90/10)	MWNT	7.5	TPU/PA/MWNT
TPU/PA (90/10)	Cloisite 30B	7.5	TPU/PA/Cl
TPU/PA (90/10)	MWNT and Cloisite 30B	3.5 and 3.5	TPU/PA/MWNT/Cl
TPU	MWNT	7.5	TPU/MWNT
TPU	Cloisite 30B	7.5	TPU/Cl

The TPU used in this study was DESMOPAN® 6065A, which is an aromatic polyether-based TPU manufactured by Bayer Material Science. The soft polyether in Desmopan 6065A is a C3 ether-based segment whereas the hard segment is based on methylene diphenyl diisocyanate (MDI) [17]. The polyamide used in this research was a polyamide 11 (PA), Rilsan®, from Arkema.

Two different types of fillers were used in this study. Montmorillonite (MMT) nanoclay Cloisite® 30B (Cl) was manufactured by Southern Clay Products. The modifier used to surface treat Cl was a methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium ion at 90 meq/100 g exchange ratio. The hydroxyl group lends some polarity to the organic end of this surfactant. The d-spacing (001) for Cl is reported as 1.74 nm [18]. Multi-walled carbon nanotubes (MWNT) were obtained from Arkema. MWNTs under the trade name of Graphistrength® C100 were produced by chemical vapor deposition at elevated temperature of ethylene on a metal/ceramic catalyst. Typical dimensions for the MWNT are 10−15 nm in diameter for 5−15 concentric tubes while the length ranges from 1 to 10 μm.

2.2. Processing

Extrusion was carried out at The University of Texas at Austin using a Haake co-rotating, intermeshing twin screw extruder (diameter = 30.5 mm, $L/D = 10$) with a barrel temperature of 170 °C and at 270 rpm. Injection molding was carried out at the same facility using an Arburg Allrounder 305-210-700 with 50 ton clamp capacity. Gardner impact discs, tensile bars (ASTM D638), and Izod bars (ASTM D256) were fabricated. For injection molding the barrel temperature was approximately 180 °C with a mold temperature of 51 °C.

Four injection molded Gardener impact discs were placed on top of each other, in a circular mold to form a thicker disc which would be used for dynamic mechanical analysis. The utility of using pre-injection molded disks was that the shear history and therefore, filler alignment in the parts would be more reproducible. This mold (with samples) and plunger were heated in vacuum oven at 145 °C for 18 min. The mold was then transferred to a Carver press for compression molding at 170 °C. The samples were kept under pressure for 5 min and then allowed to cool down under ambient conditions. The dimensions of each sample were 25.6 mm in diameter and 2.6 mm in thickness.

2.3. Characterization

Wide angle X-ray diffraction (XRD) was carried out using Rigaku Ultima IV X-ray diffractometer. All samples were tested using parallel beam mode from $2° \leq 2\theta \leq 40°$ with a scintillation counter and a monochromator.

Transmission electron microscopy (TEM) was performed on sections from tensile bars. Samples were cryogenically sectioned using an RMC Products Powertome microtome with a diamond blade at −25 °C. Thin slices were floated from the diamond knife using a dimethyl sulfoxide (DMSO)/water mix and then deposited on a Cu TEM grid. The samples were taken from the centered cross section of injection molded tensile bars as shown in Fig. 1, such that the reader is viewing along the axis of flow. The sections were imaged using a Hitachi-H-7650-600 series microscope operating at 100 kV.

DSC experiments were carried out using a TA Instruments DSC Q1000. All the samples were heated to 200 °C (first heat) to erase the thermal history and then cooled back to −75 °C and heated again to 200 °C. All steps were performed using a ramp rate of 10 °C/min and in presence of nitrogen.