



Understanding phase separation and morphology in thermoplastic polyurethanes nanocomposites



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ABSTRACT

Carbon nanotubes (CNTs) can be effective in influencing the hard domain (HD) and soft domain (SD) morphology in thermoplastic polyurethanes (TPU), and their combination with cellulose nanocrystals (CNCs) can maximize these effects in TPU composites. Atomic force microscopy (AFM) indicated that TPU morphology exhibits multi-scale phase separation characterized by heterogeneous morphologies at the micro- and nano- scales. CNTs appear to preferentially aggregate in the HD regions, favoring the nucleation and growth of smaller and more distributed HD spherulites, while thermal analyses confirmed a significant changes in the crystallization behavior of TPU nanocomposites. Scanning electron microscopy (SEM) analyses performed on TPU nanocomposites prepared by in-situ polymerization and compression molding suggested that incorporation of a small amount of CNCs can have a positive effect on CNT dispersion and favor a more homogeneous distribution.

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1. Introduction

Polymer nanocomposites (PNCs) are a recently developed class of composites in which at least one of the dimensions of the reinforcement phase is in the range of 1–100 nm. As nanostructured materials are characterized by a very high surface- to-volume ratio, strong molecular interactions and unconventional material properties may arise when nanofillers are incorporated in polymer matrices. It has been widely proven that the addition of a nanofiller to a polymeric matrix can enhance its mechanical performance [1], degradation and chemical resistance [2,3], gas and solvents barrier properties [4,5]. Moreover, significant improvements in the abovementioned properties can be achieved by incorporating a relatively low amount of filler (generally less than 5 wt %), avoiding the typical drawbacks (embrittlement, loss of transparency, loss of lightness) associated to the usage of traditional organic microfillers [6]. In general, the properties of nanocomposites depend on the level of nanofiller dispersion within the matrix and on the degree of filler-matrix interfacial interactions [7,8]. Therefore, there is a strong need to improve filler dispersion into smaller structures and strengthen the interfacial interactions in order to fully exploit the potential benefits of nanocomposites. Noteworthy, recent studies

have reported how incorporation of nanofillers of different geometrical shape and aspect ratio led to significant improvements in filler dispersion and better properties due to synergistic effects [9–11].

Thermoplastic polyurethanes (TPU) are an important class of polymeric materials presenting remarkable properties such as abrasion resistance, chemical and corrosion resistance, low temperature flexibility and a wide range of mechanical strength and toughness [12,13]. TPU is a block copolymer characterized by alternating soft and rigid segments, which tend to aggregate into soft domains (SDs) and hard domains (HDs) due to their thermodynamic incompatibility. Morphology significantly affects TPU final properties. Specifically, the soft and hard domain size, the nature of domain interface, as well as mixing of hard segments into the soft segment phase influence most of physical properties such as elasticity and toughness [14]. On account of their flexibility in formulation and morphology, TPU properties can be tailored depending on the end-use application, enabling their utilization for a variety of applications including structural foams, coatings, composites and nanocomposites [12,13]. In particular, significant improvements in TPU properties have been recently reported through the incorporation of small amounts of nanostructured materials such as carbon nanotubes (CNTs) [13,15–17], exfoliated graphite and graphite oxide [18,19] and cellulose nanocrystals (CNCs) [20–22] into TPU systems through different techniques, such as in-situ polymerization [15,23–25], melt blending [26,27], solution mixing techniques

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[16,28], and solvent-exchange processing [29]. Interestingly, some nanofillers such as CNTs, CNCs and layered silicates can significantly change the micro-phase domain size and shape of block copolymers, enabling control of the morphology at the nanoscale and consequently altering their properties [21,24,30,31]. In the present work, we investigate the effect of two nanofillers presenting different size, aspect ratio and surface properties, namely CNTs and CNCs, on the morphology and microstructure of TPU nanocomposites. For the first time, phase morphology variations and filler interactions with HDs and SDs have been correlated to the thermal behavior of the TPU nanocomposites.

2. Experimental section

2.1. Materials

The matrix used in this study was prepared from a polyol (mixture of polyether polyols based on polycaprolactone), a *p*-phenylene diisocyanate (PPDI) as isocyanate and 1,4-butanediol (BDO) as chain-extender. The multi-walled carbon nanotubes (MWCNTs) are hydrophobic 1D nanofillers with an average diameter and length of 13 nm and $>1 \mu\text{m}$, respectively, resulting in an aspect ratio in the range of 80–120. Microcrystalline dry cellulose powder (Sigma–Aldrich, Ireland), with 20 μm average particle size, was used as the source raw material for preparing CNCs. Sodium hypochlorite (NaClO) solution, TEMPO ($\text{C}_9\text{H}_{18}\text{ON}$, 98%), sodium bromide (NaBr), anhydrous ethanol, dimethylformamide (DMF) and sodium hydroxide (NaOH) of laboratory grade were provided from Sigma–Aldrich. All materials were used as received.

2.2. Preparation of cellulose nanocrystals (CNC)

TEMPO-mediated oxidation of cellulose microcrystals was performed according to a procedure described in the literature [32,33]. NaBr (400 ml) was mixed with distilled water (400 ml) and stirred for 20 min at 300 rpm. TEMPO (64 mg) was dissolved in the water–NaBr solution with continuous stirring for 10 min. NaClO (7.45 g) solution was added slowly to the suspension to start the oxidizing reaction. The pH condition of the mixture was maintained at 10 by adding 0.5 M NaOH dropwise, while stirring the suspension for 4.5 h at room temperature. After oxidation, the reaction was quenched by addition of ethanol (20 ml). The suspension of oxidized CNCs was washed thoroughly with distilled water several times in order to adjust the pH to 7. Freeze-drying was finally carried out to obtain cellulose nanopowder. The resultant CNCs are hydrophilic 1D nanocrystals of average size in the order of 150–250 nm in length and 10–15 nm in diameter (aspect ratio in the range of 10–25), as observed by transmission electron microscopy (Zeiss Libra 200EF) at an acceleration voltage of 200 kV in bright field mode, Fig. 1.

2.3. Preparation of the liquid suspensions and thermoplastic films

Polyol mixtures containing the selected nanofillers were prepared by ultrasonication for 20 min in a water bath at 85 °C (cycle time of 8 s, duty cycle 50%, power = 30 W, energy ~ 90 kJ) with following degassing in a vacuum oven at 70 °C for 12 h. Nanocomposite TPU films were then obtained by reaction of the polyol mixture with the MDI and chain extender during in-situ polymerization carried out in a lab-size reactor at 105 °C. Specifically, after the polyol mixture was degassed and shear-mixed for 5 min inside the reactor, the MDI was added with concurrent nitrogen purging and shear-mixing for 1 h. The chain-extender was added dropwise using a syringe and the reaction was stopped after 1 min. The liquid TPU was finally cast on aluminum molds and cured in oven at 110 °C

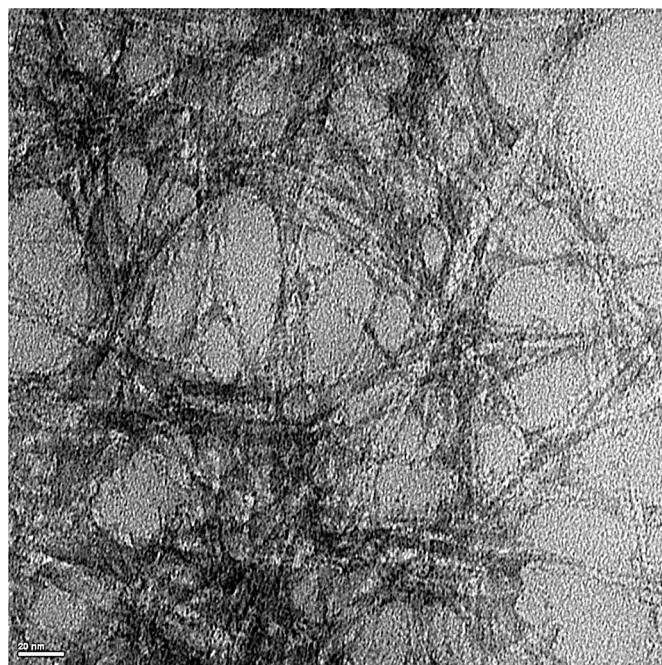


Fig. 1. Transmission electron microscopy of CNCs (scale bar is 20 nm).

for 16 h. Thin (0.50 mm) films were obtained by hot pressing (temperature = 220 °C, pressure = 10.1 MPa, time = 5 min).

Nanocomposite samples containing only CNTs or CNCs were prepared with a filler concentration of 0.05, 0.1, 0.2 and 0.5 wt%. Moreover, different ratios of CNT:CNC were considered for hybrid systems containing a total amount of nanofiller of 0.1 wt% and were designated as CNT_{0.2} CNC_{0.8} (20:80), CNT_{0.4} CNC_{0.6} (40:60), CNT_{0.6} CNC_{0.4} (60:40) and CNT_{0.8} CNC_{0.2} (80:20).

2.4. Experimental techniques

2.4.1. Morphological analyses

Atomic force microscopy (AFM) was used to investigate the nanocomposite morphology and phase separation in TPU nanocomposites, including dimension and arrangement of HDs and SDs, as well as their interphase characteristics. A Veeco AFM (model OMV-NTSC) connected to a Nanoscope V controller was used. AFM was operated in tapping mode using an uncoated silicon cantilever (Nanodevices Inc.) with length of 125 μm , spring constant of 5 N/m, resonance frequency of 150 KHz, tip radius smaller than 10 nm.

Scanning electron microscopy (SEM); (JEOL JSM-6510LV) was used to observe the fracture surfaces of the TPU composites with an operating voltage of 20 kV. The samples were coated with gold prior to observation.

2.4.2. Thermal analyses

Modulated differential scanning calorimetry (MDSC) tests were performed by a DSC Q2000 (TA Instruments, New Castle, DE) under a constant nitrogen flow of 50 ml/min on specimens of about 8–10 mg. Noteworthy, MDSC analyses were performed on TPU samples prior to compression molding in order to avoid introducing further thermal events and limit the material thermal history.

The data regarding melting and crystallization behavior of TPU soft and hard segments was collected by heating the samples from the equilibrated temperature of –80 °C to 200 °C at a rate of 5 °C/min. A temperature modulation of ± 1 °C every 40 s was set

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