



Contents lists available at ScienceDirect

European Polymer Journal

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

Macromolecular Nanotechnology

Tensile properties, thermal and morphological analysis of thermoplastic polyurethane films reinforced with multiwalled carbon nanotubes

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ARTICLE INFO

Article history:

Received 15 March 2013

Received in revised form 15 June 2013

Accepted 1 July 2013

Available online xxx

Keywords:

Polyurethanes

Composites

Thermal properties

Mechanical properties

Atomic force microscopy (AFM)

ABSTRACT

The paper reports on thermal, tensile and morphological properties of thermoplastic polyurethane (TPU) based films obtained by melt-compounding and chill-roll extrusion. Composite films containing up to 1 wt% of multiwalled carbon nanotubes (MWNTs) are characterized in terms of thermal properties, tensile behavior and morphological issues taking the neat TPU film as the reference material.

The filler content does not alter the melting temperatures of the hard and soft phases of the matrix but it influences, as the tensile strain, their degree of crystallinity. Mechanical results have highlighted that the tensile behavior of composite films is strongly related to structural changes induced by the process and testing on the complex morphology of the hosting matrix.

In this context, all results, collected on as produced and tensile strained films, are interpreted by assumptions based on the mutual organization of hard and soft phases of the matrix induced by the filming process and strain-crystallization phenomena coming from the included filler and deformations as confirmed by tapping mode atomic force microscopy (AFM) observations.

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1. Introduction

Thermoplastic polyurethanes (TPUs) are linear randomly segmented copolymers consisting of alternating flexible soft segments (SS) and more rigid urethane-containing hard segments (HS). Their unique properties are directly related to their hierarchical morphology and highly dependent on the degree of microphase separation. This degree, in turn, is a function of several parameters as the system thermodynamics, the ability of hard segments to pack correctly to form hydrogen bonds, the chemical struc-

ture and composition of the copolymer, the synthesis conditions and so on [1–5].

At room temperature, soft domains, being above their glass transition temperature, impart to the material its rubber-like behavior while hard domains, below their glass transition temperature, act as physical crosslinking points and are thought to govern mechanical hysteresis, permanent deformation, high modulus and tensile strength.

In this complex structure, the ratio SS/HS content plays a key role in defining the mechanical behavior. For example, TPUs with low HS contents show high elongation at break and low tenacity. Moreover, the elongation at break tends to increase with the increase of SS molecular weight and the decrease of HS content presumably because, in

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these cases, the influence of hard domains on soft ones is ever more reduced.

Numerous characterization techniques have been used so far to study structural changes during deformation of polyurethanes.

Infrared spectroscopy measurements, for example, have shown that the orientation of the SS increases continuously with the draw ratio but the orientation function of hard segments often decreases at low draw ratio even assuming negative values [6–8]. This behavior has been ascribed to connections between soft and hard segments that cause the rotation of hard domains into the strain direction with shear yielding phenomena at a critical strain. In particular, if the long axis (perpendicular to the lamella surface) of a hard domain is oriented along the deformation direction, hard segments that are generally oriented perpendicularly to the lamella surface tend to orient perpendicularly to the deformation direction, resulting in a negative orientation value especially for highly stable hard domains.

At larger elongation strains, the stress transfer can lead to the destruction of the lamellar HS domains into small fragments of HS aggregates with their long axes oriented perpendicular to the chain direction.

As already reported from Bonart et al. [9] at the end of Sixties and recently reported by Waletzko et al. [10], the tensile alignment of initially randomly oriented soft segment chains exerts a local torque force that orients the hard domains perpendicular to the direction up to 300% strain [9,10]. Above 300% strain, the nature of the hard segment (crystalline or paracrystalline) strongly influence the deformation behavior. In particular, for paracrystalline hard segments, further elongation resulted in the reorientation and restructuring of the hard domains along the stretch direction. In crystalline hard domains, instead, the hard segments within the hard domains orient along the equator up to 400% strain, suggesting that crystalline hard segments behave as inert fillers during deformation.

Taking into account that the addition of nanofillers, significantly influences rheological behavior and, in our case, the intrinsic morphology of the matrix, it is necessary to deepen relationships between filming process and both structure and properties of nanocomposite films.

At this regard, Garofalo et al. [11,12] reported about effects of elongational flows on morphology and properties of polyamides based nanocomposites. The attention was focused on systems filled with different amounts of lamellar clays. Structural changes induced in the matrix by the inclusion of layered silicates and final properties of fibers and films were investigated in response of uniaxial and biaxial elongational deformation imposed. In both cases, results highlighted a remarkable increase of the extensional viscosity of the nanocomposite systems, with respect to the neat matrix. Combined effects of filler content and drawing extent on the morphology of crystalline regions are discussed and correlated with mechanical properties of products. In particular, the presence of silicates increases the stiffness of both polyamide 6 fibers obtained by melt-spinning and copolyamide-based films prepared by single bubble film extrusion. Structural analysis of fibers demonstrated that the presence of silicate and

the drawing promote different crystal phases and, consequently, tensile behavior of composite fibers is strictly related to the process conditions. Analogously, detected improvements of oxygen barrier and mechanical properties of films were shown to be dependent on the achieved degree of clay exfoliation/orientation and crystalline morphology of the matrix.

Specifically, about the influence of processing on the structure and mechanical properties of films analyzed in this contribute, previous investigations have shown that the processing technology, in addition to influencing the dispersion of included nanotubes, also affects the mutual arrangement of hard and soft domains characterizing the matrix and, therefore, the potential applications of produced films [13]. The authors, comparing chill-roll extrusion and film blowing technologies, demonstrated that the former filming process produces films with a better distribution of the filler and characterized by smaller hard domains dispersed throughout the amorphous soft phase. Moreover, in both cases, the size of hard domains increases with the carbon nanotubes content.

Among the different experimental approach to investigate TPU structural changes, nowadays tapping mode atomic force microscopy has gained a specific interest for soft materials due to the lower forces involved, and the fact that there is only intermittent contact between the sample and the tip in this mode, unlike for example in contact-mode AFM [14,15]. This technique allows simultaneous detection of height and phase information, which provide insight on the variations in topography and local stiffness, respectively. Therefore the phase image can be used to distinguish between crystalline and amorphous regions [16]. Moreover, since each AFM images is essentially a three dimensional plot of data points, this technique also enables semi-quantitative analysis of the images via surface roughness and power spectral density calculations [17]. AFM tapping mode is indeed a very well established technique to monitor the phase separation of hard and soft TPU segments in real space [18] and, more recently, also to quantify the surface elastic modulus TPU [19]. For these reasons AFM has been widely employed to obtain semi-quantitative information on the phase separation behavior of TPU samples as a function of composition [19,20], molecular weight [21] and post-synthesis treatments [22]. Finally AFM provides informative data in view to understand the mixing process and the interactions involved in the formation of polyurethane composites with many different compounds such as natural polymers [23], synthetic polymers [24], carbon nanotubes [25] and inorganic nanoparticles [26].

In light of the above considerations, this paper reports some results obtained within a project aimed to investigate how the process influence structure–property relationships in composite films based on thermoplastic polyurethane resins. In details, TPU film samples filled with relatively low amounts of multiwalled carbon nanotubes were obtained by extrusion and casting from the melt and systematically analyzed by thermal and tensile tests. Specimens, as produced and stretched at different strains, were investigated by atomic force microscopy in order to study the influence of filler contents and tensile deformations on the complex morphology of the matrix.

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