



Characterization of hard-segment crystalline phase of thermoplastic polyurethane in the presence of butane and glycerol monosterate and its impact on mechanical property and microcellular morphology



N. Hossieny, V. Shaayegan, A. Ameli, M. Saniei, C.B. Park*

Microcellular Plastics Manufacturing Laboratory, Department of Mechanical & Industrial Engineering, University of Toronto, 5 King's College Road, Toronto, Ontario M5S 3G8, Canada

ARTICLE INFO

Article history:

Received 12 January 2016

Received in revised form

26 January 2017

Accepted 4 February 2017

Available online 7 February 2017

Keywords:

Thermoplastic polyurethane

Hard segment

Crystallization

Phase separation

Heterogeneous nucleation

ABSTRACT

The effects of glycerol monosterate (GMS) and high-pressure butane on the phase-separation and crystallization of the hard segment (HS) of thermoplastic polyurethane (TPU) were investigated. Small and wide angle x-ray diffraction, polarized optical microscopy and atomic force microscopy were used to characterize the crystalline morphology of TPU under various conditions. Overall, 60% higher HS crystallinity was observed in TPU-GMS samples annealed with butane compared to the neat-TPU samples. The toughness and Young Modulus in the TPU-GMS samples were increased due to the higher HS crystallinity compared to the neat-TPU samples. The HS crystallites were effectively utilized as heterogeneous bubble nucleation sites to induce microcellular morphologies in the TPU microstructure. Compared to neat-TPU, the TPU-GMS microcellular morphology showed higher cell density over the wide saturation temperature of 150–170 °C due to the increased HS phase separation and crystallization mechanism in the presence of GMS and dissolved butane.

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1. Introduction

Thermoplastic polyurethanes (TPUs) are multi-block copolymers that exhibit a unique combination of strength, flexibility and processability due to their phase-separated microstructure [1,2]. These properties result from a molecular structure with rigid HS domains dispersed in the soft segment (SS) matrix. The SS is a polyol with an ester or ether group in the main chain having a low glass transition temperature and is viscous at service temperature, imparting flexibility to TPU. The HS is formed by the reaction of diisocyanate and short-chain diols, which crystallizes and influences the mechanical properties in TPU such as hardness and tear strength. As a result of this unique microstructure, TPUs exhibit very good impact properties at low temperature, excellent chemical resistance and great flexibility over a broad service temperature, which make them suitable for a wide range of demanding applications such as automobile parts, construction materials, sports equipment, and medical instruments [3].

TPU's phase separation strongly depends on the hydrogen

bonding between the HSs and its crystallization kinetics [4,5]. Generally, the extent of phase separation is incomplete and the microstructure of TPU consists of mixed HS and SS segmental chains. The presence of inter-segmental mixing affects the morphology, the thermal and the mechanical properties of TPUs. The incorporation of HSs within the SSs elevates the glass transition temperature and degrades the TPUs elastic properties [6]. On the other hand; the inclusion of SS within the HS domains reduces its crystallinity. Due to its high commercial value, the HS phase-separation and crystallization behavior in TPUs based on the reaction of 4,4'-methylenediphenyl 1,1'-diisocyanate (MDI) and butanediol (BDO) have been extensively studied [7,8]. A detailed morphological analysis using SAXS for a series of MDI/BDO based TPUs showed that the HS phase-separated domain structure was in agreement with a model proposed by Koberstein and Stein [6]. The basis of this model is that HS chains shorter than the critical length for microphase separation are presumed to remain dissolved within the SS microphase, while longer segments aggregate into lamellar HS crystalline domains.

The multiple endotherms, size, and melting peak temperatures in TPUs have been studied by numerous authors in the past, and the changes in such characteristics have been attributed to the changes in the HS and SS ratio, thermal annealing, thermal history,

* Corresponding author.

E-mail address: park@mie.utoronto.ca (C.B. Park).

processing condition, and mechanical deformation [4,5,9–11]. Thermal annealing of TPUs leads to rearrangement of hydrogen bonds and thus improves the formation of HS domains and their crystallization kinetics [6,12,13]. The crystalline HS domains are important to the mechanical properties of TPUs. The HSs act as physical crosslinks, and since they are stiffer than the SS, they function as effective nano-scale fillers strengthening the material. Annealing TPU at elevated temperatures also improves the tensile properties of the material due to an increase in the HS crystallinity within the HS domains. The thermal studies on TPU have been conducted at atmospheric pressure [6–8,12–14]. There is, however, very limited study on the effects of high pressure gas on the phase-separation and crystallization behavior of HS in the TPU microstructure and the corresponding influence on the mechanical properties of TPU. Some studies have investigated the diffusion of gases such as oxygen, carbon dioxide and hydrogen through TPUs at high pressures; however, none have discussed the phase-separation and/or crystallization of HSs in the presence of the dissolved gas [15,16]. In our recent study, we demonstrated the effect of butane gas on the phase separation and crystallization behaviors of HSs in TPU [17]. The dissolved butane acted as a plasticizer and assisted the HS chains to phase-separate and significantly increased the overall heat of fusion of the TPU. Although, the previous work provided some clarification on the effect of butane on the crystallization behavior of TPU, the TPU crystallization behavior in the presence of dissolved butane and GMS is much more complicated, and there are still numerous uncertainties and ambiguities, which require investigation. It would also be particularly interesting to correlate the mechanical properties of the TPU material such as elasticity, toughness and strength to the changes in the HS crystallization achieved due to the dissolved gas, which would also be addressed in the present study.

The concept of utilizing dissolved gas to improve the phase separation and crystallization of HS chains can be effectively used to develop a number of interesting technologies for TPU. One of the technologies is to introduce cellular morphology, which would lead to density and hardness reduction and consequently decrease the cost. The heterogeneous cell nucleation rate during foam processing can be significantly promoted through local pressure variations [18–20], around the HS domains and crystallites [21–23]. In addition, the surrounding areas of newly formed (or growing) HS domains and crystals have an increased amount of gas due to gas exertion from the phase-separated and crystallized region, which is further favorable for heterogeneous cell nucleation [24]. It is well known that the crystallization behavior of polymers under dissolved gas is expected to be fundamentally different from that under air at ambient pressure [25]. Dissolved gas causes swelling of the polymer matrix which increases the molecular chain mobility [25,26]. This affects the surface tension [27–31], the viscosities [32–34], and the thermal behaviors including the crystallization kinetics [35–38]. Overall the varying crystallization kinetics at various pressures can significantly influence the final foam morphology.

Recently, expanded TPU bead foams (E-TPU) that can be molded into complex three-dimensional products have been developed [39]. At the present, industry utilizes soft grade TPUs to process E-TPU beads in order to make sintering of the beads more effective and easier during the steam-chest molding process. However, softer grade TPUs have less concentration of HS (i.e. crystallinity) and hence suffer from lower mechanical properties and lower service temperatures. Further, the soft TPUs may suffer from severe dimensional instability from exposure to high temperature steam during the steam-chest molding process [40]. The expanded TPU beads can also suffer from a high degree of shrinkage after foaming due to the loss of gas. Glycerol esters are predominant additives

used commercially which provides anti-collapse protection by forming a barrier on the surface of the foam, slowing the egress of the blowing agent. This allows time for air to enter the cells, replace the blowing agent, and prevent collapse of the foam. After acting as a plasticizer, GMS eventually migrates to the surface of the bubbles within the polymer matrix. Hence the amount of GMS collected on the skin of the foams is minimal. The use of glycerol esters may also affect the crystallization kinetics of a polymer. Naguib et al. reported increase in the crystallization temperature and the degree of crystallinity of linear and branched polypropylene in presence of GMS [36]. The crystals generated during the foaming process can lead to the production of high quality foams with fine cell size and high cell density. The crystals can also be effectively used in the sintering of beads during the steam-chest molding process [41–44]. In this context, investigating the crystallization behavior of TPU with the presence of GMS and butane can provide new strategies on the processing and molding of E-TPU bead foams and their products.

This paper presents the phase-separation and crystallization behavior of TPU in the presence of GMS and dissolved butane and its effect on the tensile properties of TPU. The study also investigated the influence of the HS crystalline domains on the cell nucleation/growth during the microcellular foaming process. The TPU samples containing 0–2 wt% GMS were melt compounded using a twin-screw extruder. The annealing study with butane and the foaming of the samples were conducted in a high-pressure chamber. The microstructure was characterized using differential scanning calorimetry (DSC), small and wide angle x-ray diffraction (SAXS and WAXS), and atomic force microscopy (AFM). Overall, the presence of GMS improved the phase-separation and crystallization of HSs and the foaming ability of TPU over a wide range of the processing temperature.

2. Experimental procedure

2.1. Materials and sample preparation

The TPU used in this study was Elastollan (1190A) manufactured by BASF with a melting temperature of 171 °C, a specific density of 1.13 g/cm³, and a hardness of Shore 90A. Elastollan 1190A was uncolored and supplied in a pellet form. The HSs are composed of reaction between MDI and BDO. The SSs are polyether diols, with a high hydrolysis resistance tendency. The GMS was Pationic 915. The N-butane, supplied by Linde Gas Canada, was used as the blowing agent.

The “as-received” TPU and GMS were dry blended and then compounded in a twin screw extruder (DSM Microcompounder). Prior to compounding, the “as-received” TPU was dried in a CONAIR drier at 105 °C for 4 h to remove moisture. The compounding was implemented at a processing temperature of 190 °C for 3 min and a screw speed of 50 rpm. A series of TPU-GMS samples with GMS contents of 0.5, 1 and 2 wt%, named as TPU-0.5GMS, TPU-1GMS and TPU-2GMS, respectively, were prepared. For reference, the “as-received” TPU without any GMS was also melt compounded with the same thermal history as discussed above and designated as “neat-TPU”.

2.2. Atomic force microscopy

The AFM experiment was performed on both neat-TPU and TPU-GMS samples using a Nanoscope IIIA Multimode AFM machine. The data was collected in air in tapping mode using a diving board TESP cantilever. The data were recorded as 512 × 512 pixel data sets at a scanning rate of 1 Hz. Prior to the AFM experiment, the samples were cryo-microtomed with a Leica UltraCut UCT microtome

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