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Relationship between modulus and structure of annealed thermoplastic polyurethane

Yu Yanagihara[a,b,*], Noboru Osaka[a], Sohgo Iimori[a], Satoshi Murayama[b], Hiromu Saito[a]

[a] Department of Organic and Polymer Materials Chemistry, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan
[b] Polyurethane Research Laboratory, Tosoh Corporation, Yokohama, Kanagawa 245-0052, Japan

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ABSTRACT

Relationship between elastic modulus and structure of an annealed thermoplastic polyurethane (TPU) has been investigated by small-angle X-ray scattering (SAXS), tensile testing, and dynamic mechanical thermal analysis (DMTA). With increasing annealing temperature (T_a) up to 125 °C, volume fraction of hard segment (HS)-rich domain increased, which is usually expected to increase elastic modulus. However, the elastic modulus at 25 °C decreased with increasing T_a. Due to the decrease in number density of the HS-rich domain acting as the cross-links, the glass transition temperature (T_g) of the soft segment (SS)-rich matrix decreased with increasing T_a. Nevertheless, the change in the T_g contributed only slightly on the change in the elastic modulus at 25 °C. On the other hand, the electron density difference between the HS-rich domain and the SS-rich matrix decreased with increasing T_a, suggesting that the densification in the HS-rich domain decreased with T_a. The modulus of the HS-rich domain calculated by the micromechanical approach with parallel model using the structural parameters obtained from SAXS analysis decreased with T_a. Thus the decrease of the modulus with increasing T_a is mainly ascribed to the decrease in the modulus of the HS-rich domain due to the decrease in the densification in the HS-rich domain.

1. Introduction

Thermoplastic polyurethanes (TPUs) are rubber like materials consisting of sequenced amorphous soft segment (SS) and crystalline hard segment (HS). Due to a poor compatibility between SS and HS, phase separation occurs in nanometer scale. It is well known that HS-rich domain acts as a physical cross-link and excellent mechanical properties are exhibited in TPU [1]. Mechanical properties of TPU have been discussed by micromechanical approach such as parallel model with thermodynamic consideration [2] or logarithmic model [3], and by phenomenological approach based on Mooney–Rivlin model without considering structure definition [4,5]. However, most of the studies are focused on the mechanical properties by means of chemical structure [6–8] and the composition [9–11].

Since the mechanical properties can be changed by annealing [12–14], the annealing of TPU is an important industrial process to obtain the desired properties. However, the structure change by annealing is difficult to understand because of its complexity; e.g., the annealed TPU often exhibits the multiple endothermic peaks in the differential scanning calorimetry (DSC) measurements [15–17]. Therefore, only a few authors reported the relationship between the mechanical properties and the structural change with annealing temperature (T_a) of annealed TPU [12–14]. Nallicheri et al. found that the mechanical properties of solvent-cast TPU having the long-range crystalline HS domain was improved due to the increase of the cohesive forces [13]. On the other hand, the decrease in the mechanical properties by annealing was reported by Prisacariu et al. [14] and Laity et al. [12]. The decrease in the mechanical properties was suggested to be attributed to the reduction in the mesophase interactions by change of the copolymeric order [14] and to the de-mixing of SS and HS [12]. So far, the thermal annealing effect on the mechanical properties of TPU has not been well elucidated due to the lack of comprehensive understanding for the detail of the structural changes.

To prevent the complexity of the structural change with T_a, we prepared a TPU as a simple model, which shows no crystallinity in the melt-quenched specimen and only a single endothermic peak was seen in the DSC measurements by annealing [18]. Hence, we could easily discuss quantitative structure parameters such as HS-rich domain size or volume fraction obtained by fitting SAXS curves.

* Corresponding author at: Polyurethane Research Laboratory, Tosoh Corporation, Yokohama, Kanagawa 245-0052, Japan. Tel.: +81 45 812 1516.
E-mail address: yuu-yanagihara-am@tosoh.co.jp (Y. Yanagihara).

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The previous SAXS study revealed that the volume fraction (ϕ_{HS}) and the size of the HS-rich domain increased while the number density decreased with increasing T_a due to the coarsening induced by phase separation [18].

Recently, we found that elastic modulus decreased with increase in T_a despite the increase in ϕ_{HS}. In this study, to clarify the origin of the characteristic T_a dependence of the mechanical property, we investigated the relationship between the elastic modulus and the structural changes by annealing the melt-quenched TPU at various T_a's, as the subsequent paper of our previous study [18]. The mechanical properties of the annealed TPU obtained at various T_a's were discussed based on the glass transition temperature (T_g) of SS-rich matrix, structural parameters obtained by fitting the SAXS profiles, and elastic modulus of the HS-rich domain estimated by micromechanical parallel model. The neat SS polymer (NSS) was also prepared as the model system of the SS-rich matrix, to compare T_g and elastic modulus with those of the SS-rich matrix of TPU.

2. Experimental

2.1. Sample preparation

2.1.1. Thermoplastic polyurethane elastomer

A thermoplastic polyurethane elastomer (TPU) used in this work was synthesized through so-called prepolymer method. The prepolymer consists of a polyester glycol (Nippon Polyurethane Industry Co., Japan) and 4,4′-diphenylmethane diisocyanate (MDI) (Nippon Polyurethane Industry Co., Japan). The polyester glycol having the number average molecular weight of ca. 1000 was constructed from adipic acid and 1,6-hexane diol. The experimental detail to synthesize the prepolymer was described in our previous paper [18]. The synthesized prepolymer and the chain extender of 1,4-butane diol (1,4-BD) (Mitsubishi Chemical, Co., Japan) were mixed on a molar ratio of NCO group and OH group to be 0.495 and 0.505, respectively. Then, about 130 g of the mixture was poured into a centrifugal mold rotated continuously on its axis at 1000 rpm and was reacted at 165 °C for 10 min.

The synthesized TPU consisted of amorphous soft segment (SS) blocks made of the polyester glycol, and crystalline hard segment (HS) blocks made of MDI and chain extender 1,4-BD having sequence length distributions. Weight fraction of HS in the TPU was 43 wt%. The repeating unit distribution of HS was calculated to be 2.0 according to the method by Peebles [19].

2.1.2. Neat soft segment elastomer

A neat soft segment elastomer (NSS) was synthesized by the similar method of the TPU without using 1,4-BD. MDI (70 °C) and the polyester glycol (80 °C) were mixed by hand for 120 s on the same molar ratio of NCO group and OH one with that of the TPU mentioned above. About 200 g of the mixture was poured into an aluminum tray and was reacted to obtain NSS at 80 °C for 10 h.

2.2. Cold-crystallization procedure

The TPU and NSS were hot-pressed at 185 °C and at 120 °C for 5 min, respectively. Then, they were rapidly quenched by ice water at 0 °C and the melt-quenched specimens were obtained. The melt-quenched TPU is designated as MQ. MQ was transferred into an oven immediately after quenching and annealed at the aimed temperature (25–145 °C) for 16 h. Change of the melting temperature obtained by differential scanning calorimetry was finished within the annealing time of 16 h. The annealed TPUs thus obtained are designated as the nomenclature: T_aXX where XX indicates the annealing temperature on degree Celsius. The annealed TPUs were used for the subsequent measurements after storing at the room temperature over 7 days to terminate any relaxation after annealing, while MQ was used for the measurements immediately within 1 h after quenching.

2.3. Small-angle X-ray scattering measurement

SAXS measurements were performed by using NANO-Viewer system (Rigaku Co., Japan). Cu-Kα radiation (wavelength 0.154 nm) was generated (at 46 kV, 60 mA) and collimated by a confocal max-flux mirror system. The sample to detector distance was 700 mm. An imaging plate (IP) (BAS-SR 127, Fujifilm Co., Japan) was used as a two-dimensional detector and the IP reading device (R-AXIS Ds3, Rigaku Co., Japan) was used to transform the obtained image into the text data. The exposure time for the annealed TPU was 16 h and for MQ was 1.5 h. To improve the signal-noise ratio on the SAXS profile of MQ, the SAXS measurement for MQ was conducted three times and then the obtained three profiles were merged as one profile. The thickness of the specimens was about 0.8 mm. The scattering intensities were corrected with respect to the exposure time, the sample thickness and the transmittance.

2.4. Tensile testing

Tensile-deformation measurements of the dumbbell-shaped specimens were performed at 25 °C at a crosshead speed of 300 mm/min using an Instron-type tensile-testing machine (STROGRAPH 05D, Toyo Seiki Seisakusho Ltd., Japan). Dumbbell-shaped specimen with a gauge length of 12 mm, a width of 5 mm and a thickness of 0.7 mm was cut from the TPU or NSS film.

2.5. Dynamic mechanical thermal analysis

Dynamic mechanical analyses were performed using a dynamic mechanical spectrometer (DMS 6100, Seiko Instruments, Co., Japan). Rectangular-shaped specimen with dimensions of 5.0 mm × 20.0 mm × 0.8 mm was used for the measurement. The temperature scan was conducted at a heating rate of 10 °C/min from −80 to 160 °C. The imposed strain and frequency were set at 5 μm and 10 Hz, respectively.

3. Results and discussion

Fig. 1 shows the stress–strain properties of the melt-quenched TPU (MQ) and the annealed TPUs obtained at various annealing temperatures T_a's. Here the stress–strain behavior was measured at 25 °C. All the annealed TPUs showed much higher tensile stress than that of MQ (Fig. 1a). The Young's modulus estimated from the initial slope shown in Fig. 1b of the stress–strain curve below a strain of 0.08 of the annealed TPU was much higher than that of MQ (Table 1). These results indicate that the melt-quenched TPU strengthens by annealing. Our previous SAXS studies revealed that the hard segment (HS)-rich domain grows largely by annealing; i.e., the radius and the volume fraction of the HS-rich domain in the annealed TPUs are much larger than those of MQ [18]. The structural parameters were obtained by the same procedure of the SAXS fits mentioned in our previous paper [18] and the previous results were confirmed as shown in Table 1. Thus the tensile stress and Young's modulus of MQ increase due to the growth of the HS-rich domain by annealing. As shown in Table 1, the volume fraction (ϕ_{HS}) and the radius of HS-rich domain (R) increase with increasing T_a. Hence, the tensile stress and the Young's modulus are expected to increase with increasing T_a. However, the tensile stress and the Young's modulus monotonically decreased with increasing T_a. This result seemingly contradicts to the widely accepted idea that incorporation of hard component such as filler into soft matrix causes