



Thermal annealing behavior and structure development of crystalline hard segment domain in a melt-quenched thermoplastic polyurethane

Yu Yanagihara^{a,b,*}, Noboru Osaka^{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 Central Research Laboratory, Nippon Polyurethane Industry Co., Ltd., Yokohama, Kanagawa 245-0052, Japan

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ABSTRACT

Thermal annealing behavior and structure development of crystalline hard segment (HS) (43 wt%) domains in a melt-quenched multi-block thermoplastic polyurethane (TPU) have been investigated using differential scanning calorimetry, atomic force microscopy, wide-angle X-ray diffraction (WAXD), and small-angle X-ray scattering (SAXS). A single endothermic peak was observed by annealing the melt-quenched TPU at wide temperature (T_a) region between 25 and 150 °C, while it was not observed in the melt-quenched TPU. Interestingly, the onset temperature of the endothermic peak linearly increased with a slope of unity against T_a and was observed at about 14 °C above T_a . The WAXD peak of the melt-quenched TPU was sharpened and increased by annealing. The quantitative SAXS analysis by fits using the ellipsoidal form factor with the Percus-Yevick equation revealed that the crystalline HS domain largely grew in the preferential direction along the chain axis by annealing the melt-quenched TPU. These results suggest that the endothermic peak is attributed to the HS domain consisting of the fringed micelle-like crystal. On the other hand, the number density of the HS domain decreased with increasing T_a . This growth behavior of the HS domain might be induced from the coarsening driven by phase separation between HS and SS, in which the smaller HS domain disappeared and redeposited onto the larger HS domain.

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1. Introduction

Thermoplastic polyurethanes (TPUs) consist of the sequenced crystalline hard segment (HS) and amorphous soft segment (SS) having sequence length distribution. TPU shows rubber like texture such as deformation recoverability and abrasion resistance. The excellent mechanical properties are attributed to the microphase-separated structures induced by the thermodynamic incompatibility between HS and SS; i.e., the SS provides elastomeric behavior and the HS acts as physical cross-links [1,2]. Owing to these excellent mechanical properties, TPU is now widely used in industry and daily life.

Annealing of TPU significantly improves the mechanical and thermal properties [3–7] and hence the annealing process is conducted in the manufacturing processes of TPU. Changes of their properties should be attributed to the change of the structure in

TPU. Therefore, to understand the change of the structure by annealing is the important key to reveal the improvement of the mechanical and thermal properties of annealed TPU.

The annealed TPU shows the apparent multiple endothermic peaks during the heating process in the DSC experiments. Interestingly, the temperature of an endothermic peak, which is called T_1 peak, shifts to the higher temperature proportional to the annealing temperature (T_a) with a slope of unity and is observed at a few ten degrees above T_a . This specific shift of the endothermic peak against T_a is thought to be ascribed to various phenomenon such as melting of fringed micelle structure of HS [8], or short-range order [9,10] and enthalpy relaxations of a hard micro-domain [5], SS [4], or interfacial materials [3]. However, the appearance of the multiple endothermic peaks in the crystalline TPU and the lack of the detailed insight into the structure change in TPU have prevented the comprehensive understanding about the origin of the specific thermal annealing behavior.

In this study, we aimed to reveal the relationship between the thermal annealing behavior of T_1 peak and the detailed structure change of annealed TPU. For this purpose, we used a melt-quenched TPU consisting of comparatively short and multi-block HS of diphenyl methane diisocyanate with 1,4-butane diol as the

* Corresponding authors. Department of Organic and Polymer Materials Chemistry, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan.

E-mail addresses: 50012832202@st.tuat.ac.jp (Y. Yanagihara), osaka@cc.tuat.ac.jp (N. Osaka).

simple model system. In addition, to prevent crystallization of SS, SS having the smaller number average molecular weight of ca. 1000 was used [10]. This TPU shows only the single T_1 peak in the DSC measurements by annealing and hence enables us to easily discuss the origin of the T_1 peak from the viewpoint of the HS structure change.

The detailed structure change in TPU was investigated by using AFM, wide-angle X-ray diffraction (WAXD), and SAXS. So far, a number of characterization techniques have been used to understand the structures in TPU [1,2]. Transmission electron microscopy [11,12] and atomic force microscopy (AFM) [13] were used to visually investigate the structure in numerous polyurethane materials. On the other hand, small-angle X-ray scattering (SAXS) has the advantage that the bulk sample can be measured with the better statistics and the ease multiple measurements for differently prepared samples. SAXS has been used mainly to evaluate the inter-domain distance, degree of microphase separation and interfacial thickness between the hard domain [14–17]. Only a few authors reported structure parameters of the phase separated structure such as size or volume fraction depending of the content of the hard segment by using the curve fitting technique [6,18].

In order to understand the thermal annealing behavior of T_1 peak on the basis of HS structure in detail, we discussed quantitative structure parameters such as HS domain size or volume fraction obtained by fitting SAXS curves with the sum of the ellipsoidal form factor multiplied by the Percus-Yevick equation and the Debye-Bueche equation at various T_a 's. As a result, the structure change in TPU was discussed on the basis of the obtained structure parameters such as the semimajor axis, the semiminor axis, the volume fraction, and the number density of the ellipsoidal domain.

2. Experimental

2.1. Sample preparation

A thermoplastic polyurethane elastomer (TPU) used in this work was synthesized through so-called the prepolymer method. The prepolymer was prepared through the mixing of 739.0 g of a polyester glycol (N-164; Nippon Polyurethane Industry Co., Japan) and 454.5 g of 4,4'-diphenyl methane diisocyanate (MDI) (Millionate-MT; Nippon Polyurethane Industry Co.) in a separable flask at 100 rpm at 80 °C for 1 h with a molar ratio of 0.28 and 0.72, respectively. The polyester glycol was constructed from adipic acid and 1,6-hexane diol. The number average molecular weight of the polyester glycol was 1031 determined from hydroxyl value and the molecular weight distribution was 2.0 determined from gel permeation chromatography. The termination of the reaction was confirmed by measuring an isocyanate value of the prepolymer by means of standard di-n-butylamine back titration method [19]. The isocyanate value (1.84 mmol/g) corresponded to theoretical value (1.84 mmol/g). Therefore, side reaction of the extra isocyanate groups did not occur in the preparation of the prepolymer. 190.0 g of the synthesized prepolymer and 15.0 g of the curing agent of 1,4-butane diol (1,4-BD) (Mitsubishi Chemical, Co., Japan) were mixed with NCO and OH with a molar ratio of 0.51 and 0.49, respectively, for 90 s by hand mixing. Then, about 130 g of the mixture was poured into a centrifugal mold and reacted to obtain the TPU at 120 °C at 1000 rpm for 1 h.

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 curing agent of 1,4-BD having sequence length distributions. Weight fraction of the HS in the TPU was 43 wt%.

The repeating unit distribution of HS was calculated according to the method proposed by Peebles [20,21]. The normalized

distribution by the number of MDI residues in the i -mer ($i + 1$) was then multiplied by the weight. The TPU with 43 wt % HS has almost the same predominant polydispersity ranging between 1-mer and 6-mer of HS shown in Fig. 2 in Ref. [15]. The obtained weight averaged repeating unit was 2.0.

2.2. Cold-crystallization procedure

In order to erase memory of preexisting structure, the sample was melted at 225 °C for 10 min. The melted sample was rapidly quenched into ice water at 0 °C. For the cold-crystallization procedure, the quenched sample was immediately transferred into an oven and then annealed at the aimed temperature (25–160 °C) for 16 h. Note here that the aimed temperature is sufficiently above the glass transition temperature of SS (ca. –25 °C). 16 h was enough time for annealing because the melting behavior was not changed by further annealing. The melt-quenched sample is designated as MQ. The annealed samples are designated as the nomenclature: T_aXX where XX indicates the annealing temperature on degree Celsius.

2.3. Differential scanning calorimetry measurement

Differential scanning calorimetry (DSC) measurements were conducted to reveal the thermal behavior of TPU annealed at various temperatures. A 8.5 (± 2.0) mg of the TPU was put into an aluminum pan. The DSC measurements were carried out using a DSC6200 (SII Nanotechnology Co., Japan) from –70–240 °C at a heating rate of 10 °C/min.

2.4. Atomic force microscopy observation

Tapping-mode atomic force microscopy (AFM) observations were performed by SPM-9600 (Shimadzu Co., Japan) attached with a PP-NCHR-20 (NanoWorld AG, Switzerland) cantilever having 204–497 kHz of resonant frequency and 10–130 N/m of spring constant. The TPUs were cut with a sample slicer and then the sliced surface was observed.

2.5. Wide-angle X-ray diffraction and small-angle X-ray scattering measurement

WAXD and SAXS measurements were performed by using NANO-Viewer system (Rigaku Co., Japan). A Cu-K α radiation (46 kV, 60 mA) was generated and collimated by a confocal max-flux mirror system. The wavelength was 0.154 nm. The sample to detector distances were 15 mm for WAXD and 700 mm for SAXS, respectively. An imaging plate (IP) (Fujifilm BAS-SR 127) was used as a two-dimensional detector and the IP reading device (R-AXIS Ds3, Rigaku Co.) was used to transform the obtained image into the text data. The exposure times were 15 min for WAXD and 3–6 h for SAXS, respectively. The thickness of the specimens was about 1 mm. The scattering intensities were corrected with respect to the exposure time, the sample thickness and the transmittance.

3. Results and discussion

Fig. 1 shows the DSC thermograms of the melt-quenched (MQ) and the annealed TPUs at various T_a 's. The thermogram of MQ did not show the clear endothermic peak while a small exothermic peak suggesting the recrystallization of HS was observed at around 40 °C during the heating process. On the other hand, a clear endothermic peak was observed in the each thermogram of the TPU annealed at T_a from 40 °C to 150 °C. They largely shifted toward higher temperature as T_a increased. The endothermic peak was

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