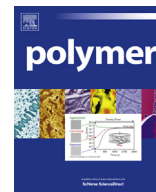




Contents lists available at ScienceDirect

Polymer

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

Strain-induced molecular aggregation states around a crack tip in a segmented polyurethane film under uniaxial stretching

Yuji Higaki ^{a, b, c}, Ken Suzuki ^a, Noboru Ohta ^d, Atsushi Takahara ^{a, b, c, *}

^a Graduate School of Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

^b Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

^c International Institute for Carbon-Neutral Energy Research (WPI-I²CNER), Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

^d Japan Synchrotron Radiation Research Institute / SPring-8, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

ARTICLE INFO

Article history:

Received 13 November 2016

Received in revised form

8 December 2016

Accepted 11 December 2016

Available online xxx

Keywords:

Segmented polyurethane

Deformation

Crack

Toughening

X-ray scattering

ABSTRACT

The development of molecular aggregation structures during stretching deformation and local structure mapping around a crack tip of a segmented polyurethane elastomer film were investigated by *in situ* simultaneous small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) and by micro-beam WAXD, respectively. Both the hard segment (HS) domain orientation and the strain-induced crystallization of poly(ϵ -caprolactone) chains were tracked by the WAXD pattern due to the high crystallinity of the symmetric non-bulky aliphatic HS structure. Strain-induced crystallization occurred locally at the vicinity of the crack tip, and the crystallinity immediately decayed in the exterior, whereas the HS domain orientation was observed throughout the stretched film. The mechanisms underlying crack arrest and the mechanical strength of polyurethane elastomer films are associated with the local strain-induced crystallization at the crack tip, the mechanical stability of the HS domains, and the avoidance of local stress concentration through the HS domain orientation.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Segmented polyurethane (SPU) and segmented polyurethane-urea (SPU(U)) elastomers are an important class of industrial elastic materials applied in general elastic products and cutting-edge applications, including medical products [1]. The elastomeric properties are associated with microphase separation, in which the hard segments (HSs) provide domains of physical cross-linkers and the soft segments (SSs) provide an elastic continuum. Chemical structure and composition play important roles in the aggregation structure [2–4]. The aromatic diisocyanates 2,4- and 2,6-toluene diisocyanate (TDI) and 4,4-diphenylmethane diisocyanate (MDI) are widely used in commercial SPU(U) elastomers, and the evolution of the microscopic structure in the stretching process of aromatic diisocyanate-based SPU(U)s have been elaborated [5–12]. Aliphatic diisocyanates, such as 1,4-butane diisocyanate (BDI), are seldom used for commercial polyurethane products due to cost considerations, but polyurethanes consisting of BDI exhibit mechanical advantages such as elastic modulus, fracture toughness,

tear strength, and weather resistance [13,14]. BDI is also considered a non-toxic alternative for aromatic diisocyanates because the degradation product is the non-toxic 1,4-butanediamine, which occurs in the human body. However, the molecular aggregation structure of BDI-based SPUs has been neglected, despite its importance for developing more refined microscopic models for the design of novel elastic materials with improved mechanical performance.

The first systematic studies of the morphology development of SPUs under stretching deformation were reported by Bonart et al. in the late 1960s [5–7]. Structure analysis by small-angle X-ray scattering (SAXS) indicated that the morphology of the HS domain is diverse and that anisotropic orientation develops under applied strain. Cooper et al. reported the chain orientation in the stretching state using polarized infrared spectroscopy [12]. Kimura et al. investigated the anisotropic HS domain orientation by static laser light scattering [8]. These pioneering studies stimulated investigation of the complex microphase separation and anisotropic HS domain orientation in SPU(U) elastomers under stretching state. *In situ* real-time measurements of molecular aggregation structures in the deformation process and microscopic local structure mapping remained challenging due to the weak X-ray beam power and the

* Corresponding author. Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan.

lower collimation associated with large beam size. An ultra-bright synchrotron radiation X-ray source and highly sensitive two-dimensional (2D) detectors permitted *in situ* rapid measurement and local structure analysis. *In situ* simultaneous SAXS/wide-angle X-ray diffraction (WAXD) is a powerful tool for the capture of the molecular aggregation structure in polymer articles under deformation [15–19]. Hsiao et al. reported real-time molecular aggregation structure tracking of aromatic diisocyanate-based SPU(U)s in the stretching process [17]. A high-flux synchrotron radiation X-ray source and well-designed optical systems provide a highly collimated fine beam with a diameter of less than ten microns and sufficient flux. Micro-beam X-ray WAXD records high-quality diffraction patterns with fine spatial resolution and is a powerful tool for the investigation of local crystalline ordered structure. Micro-beam WAXD has been used for local structure characterization of numerous polymer materials, including fibers [20,21], injection mold products [22,23], spherulites [24–26], polymer/inorganic hybrid materials [27], and precursor of polymer crystallites [28].

In this paper, we elaborate the microscopic structure development of an aliphatic diisocyanate BDI-based SPU elastomer consisting of crystalline HSs in the stretching process and local structure mapping around the crack tip to obtain an insight for the mechanical strength and crack arrest performance that are commonly observed in polyurethane elastomers. We performed *in situ* simultaneous SAXS/WAXD and micro-beam WAXD to capture the molecular aggregation structure.

2. Experimental section

2.1. Materials

1,4-Butane diisocyanate (BDI; Aldrich) and 1,4-butanediol (BDO; Wako Pure Chemicals) were purified by vacuum distillation. Poly(ϵ -caprolactone) diol (PCL; $M_w = 1250$ g/mol, Daicel Chemical Industries, Ltd.) was placed in a vacuum oven at 353 K for 6 h before use to remove residual water. Dibutyltin dilaurate (DBTDL; Wako Pure Chemicals), anhydrous *N,N*-dimethylformamide (DMF; 99.5%, Wako Pure Chemicals), and anhydrous *N,N*-dimethylacetamide (DMAc; 99.5%, Wako Pure Chemicals) were used without further purification. SPU was prepared by a standard one-shot method [29]. The molar ratio of PCL-diol/BDI/BDO was 1/5/4, and the weight fraction of the HS component was 46 wt%. The weight average molecular weight (M_w) and molecular weight distribution (M_n/M_w) were determined by size-exclusion chromatography as 39,000 g/mol and 1.71 [30]. The polyurethane elastomer consisted of a multiblock repeating structure of HS and SS. Scheme 1 shows the abbreviation and chemical structure of the SPU (BDI-BDO).

2.2. Preparation of SPU films

A 10 wt% DMAc solution of SPU (BDI-BDO) elastomer was cast on a Petri dish and dried at 333 K under vacuum overnight. The film was further dried at 393 K in a vacuum oven overnight. The film was removed by immersion in water and dried at 353 K in a vacuum

oven for 5 h. Dumbbell-shaped films with a gauge length of 16 mm (JIS K6251, 4.0 mm width and 16 mm length) were stamped out. The film thickness was measured with a micrometer as approximately 200 μm . The films were annealed at 393 K for 12 h before measurements.

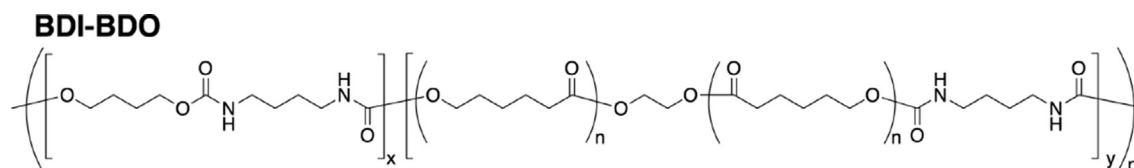
2.3. Measurement

2.3.1. *In situ* simultaneous SAXS/WAXD measurements during stretching

In situ simultaneous SAXS/WAXD measurements were performed at the BL40B2 beam line of SPring-8 (Japan Synchrotron Radiation Research Institute, Hyogo, Japan). The scattering data were recorded with a 1344×1024 pixels charge-coupled device (C4880-50-24A, Hamamatsu Photonics Co., Ltd., Japan) with an X-ray imaging intensifier (V4554P, Hamamatsu Photonics Co., Ltd., Japan) (II-CCD) for SAXS and a 1032×1032 pixel CMOS flat panel (FP) detector (C9728DK, Hamamatsu Photonics Co., Ltd., Japan) for WAXD. The pixel resolutions of the detectors for SAXS and WAXD were 97.5 μm and 50 μm , respectively. The scattering vector q ($= 4\pi\sin\theta/\lambda$), where λ and θ are the wavelength of the X-ray beam and scattering angle, respectively, was calibrated using the peak positions of silver behenate for SAXS and cerium oxide for WAXD. The wavelength of the X-ray beam was 0.1 nm. The camera lengths were 1791 mm for SAXS and 73 mm for WAXD. A SPU film was clamped at both ends with a customized tensile testing apparatus, model OZ501 (Sentech Co., Ltd., Japan), equipped with a 50 N load cell installed on the sample stage. The apparatus allows a film to be stretched symmetrically in the lateral direction, thus ensuring that the X-ray beam always irradiates the same position during stretching. The data collection timing was controlled by an external trigger that synchronized the II-CCD and FP detectors. 2D SAXS and 2D WAXD patterns were accumulated for every acquisition period of 2 s (exposure time = 1 s, interval = 1 s) during the stretching with a stretching rate of 1.0 strain/min. Every data point was an averaged structure during stretching deformation in 1 s. Data processing was performed with FIT2D software. The stress-strain curve was obtained simultaneously with the SAXS/WAXD measurements.

2.3.2. Micro-beam WAXD

Micro-beam WAXD measurements were performed at the BL40XU beam line of SPring-8. The X-ray beam was focused to $2.9 \mu\text{m} \times 3.5 \mu\text{m}$ (full-width at half maximum: FWHM) at a sample position, and the wavelength of the X-ray beam was set at 0.08256 nm. A 1344×1024 pixels CCD (C4880-50-24A) with an X-ray imaging intensifier (V4554P) was used to record the 2D WAXD images. The pixel resolution of the detector was 97.5 μm . The camera length was 131 mm. The scattering vector was calibrated using the peak positions of cerium oxide. The center position of the SPU film (0.2 mm width, 10 mm length, 0.2 mm thickness) was marked with a notch by a trimming knife. The SPU film was elongated using a manually operated tensile apparatus to a strain of 2.0 and fixed on a sample holder. The sample holder was installed in the beam line, and WAXD mapping data were obtained by moving



Scheme 1. Chemical structure of the SPU (BDI-BDO) elastomer examined in this study.

Download English Version:

<https://daneshyari.com/en/article/5178159>

Download Persian Version:

<https://daneshyari.com/article/5178159>

[Daneshyari.com](https://daneshyari.com)