

Phase mixing and separation in polyester polyurethane studied by small-angle scattering: A polydisperse hard sphere model analysis



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ARTICLE INFO

Article history:

Received 23 January 2018

Received in revised form

28 April 2018

Accepted 28 May 2018

Available online 29 May 2018

Keywords:

Small-angle scattering

Polyurethane

Phase transition

ABSTRACT

Small-angle scattering was employed to characterize the gradual phase mixing and separation of Estane 5703p, a type of polyester polyurethane, as a function of temperature (20–110 °C) and time (minutes to 80 days). The polymer structure was modelled by polydisperse hard spheres, and microstructure evolution of the material was inferred from the development of the fitting parameters. At temperatures higher than 40 °C, the scattering data indicated the mixing of hard domains (MDI-BDO) with soft matrix (PBA). The hard domain distance showed a sharp increase at 50–60 °C. Between 60 and 90 °C, a newly-observed ordering signalled the formation of a distinct mesophase with a repeat distance of 5.15 nm. Upon heating, the morphology evolution in Estane follows: domain intermixing – mesophase formation – final melting. After cooling, the domain structure partly recovered, but did not reach the original state during storage at room temperature for 80 days.

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1. Introduction

Estane 5703p (hereafter denoted as Estane) is a linear segmented polyurethane (PU) copolymer made of alternating hard urethane segments (HSs) and soft polyester segments (SSs). It is prepared by the reaction of 4,4'-diphenylmethane diisocyanate (MDI) and poly(butylene adipate) (PBA) with 1,4-butanediol (BDO) as the chain extender. The aging behavior of Estane has been extensively studied in the Los Alamos and Lawrence Livermore National Laboratories, because of its use as explosive binder in a number of important propellants and plastic-bonded explosives (PBX) [1]. Estane in these applications slowly degrades in storage, especially at elevated temperatures, which may cause undesirable

degradation in mechanical properties of the composites based on this polymer [2–7]. From both basic and practical viewpoints, it is important to understand how the microstructure is influenced by environmental conditions, such as temperature, stress, and humidity.

As a common characteristic of segmented PUs is that their mechanical performance is not only determined by its chemical composition, but also strongly influenced by the microphase structure. Salazar et al. [5–7] have published a series of articles concerning the degradation of Estane. They identified that ester hydrolysis is the dominant cause of the molecular weight loss of Estane at different temperatures and humidities. Thompson et al. [4] studied the kinetics of phase separation in aged Estane and found that diffusion limited kinetics occurred at a much earlier time for the samples aged in humid conditions at elevated temperature. Recently, we found that Estane kept at 70 °C showed a significant increase of the inter-domain distance and domain size with increasing humidity and aging time [8,9]. Many studies have proved that the microstructure of Estane is very sensitive to the temperature. However, despite extensive studies for over two

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decades, specific knowledge of the morphological evolution of Estane subjected to various temperatures is still limited.

Small-angle scattering (SAS) is a popular technique for determining the domain structure in polymers that can reveal morphology changes in segmented or microphase separated polymers. These changes are reflected in the behavior of certain parameters, such as domain size, inter-domain distance, domain density and volume fraction, as well as the degree of phase separation. Although the influence of temperature on the morphology of MDI-BDO-based segmented PU systems where the HS contents are about 50% has been studied earlier by SAS [10–13], PUs with HS content less than 30 wt % have seldom been investigated. Estane 5703p, having only 23 wt % HS content, has a weak phase segregation of HSs and SSs. Because of the modest scattering contrast between the hard and soft domains, as well as the small content of HSs, it is difficult to observe the domain structure by scattering methods. Mang et al. [14] and Tian et al. [8,9] applied small-angle neutron scattering (SANS) to determine the domain structure of original and aged Estane by swelling the SSs with deuterated toluene in order to increase the contrast. The low contrast between the soft and hard domains makes it very time consuming to measure the domain structure of dry Estane by SANS without using deuterated polymers [15], and limits the possibility of following time-dependent changes. Thanks to the development of synchrotron techniques and high performance laboratory-scale small-angle X-ray scattering (SAXS), monitoring of the time- and temperature-dependent evolution of the morphology of polyurethanes with low hard segment content becomes feasible.

In this study we use the SAXS and SANS techniques to reveal the phase mixing and separation in Estane as a function of temperature. The phase evolution process is slow enough to enable time-resolved scattering experiments to be performed. The poly-disperse hard sphere model, averaging the form factor of hard domains over domain size distribution combined with hard sphere model for the spatial distribution, was used to fit the scattering data. The results reveal how the domains mix together at elevated temperature and how the HSs segregate into domains from the mixed state.

2. Experimental

2.1. Material

Estane 5703p was obtained as pellets from the Lubrizol Advanced Materials, Inc., Westerlo-Ovel, Belgium. The SSs composed of PBA have an average molecular weight in the range from 800 to 1050 Da (Fig. 1). Estane pellets were compression-molded into 1 mm thick film at 20 MPa, 120 °C for 10 min and then cooled to room temperature (RT). The samples were stored at RT in a drying oven for two years before the measurements.

2.2. Small-angle scattering

SAXS experiments were performed on two laboratory

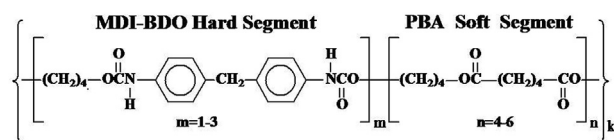


Fig. 1. Chemical structure of the repeating units of Estane 5703p. The part bracketed by m is the hard segment, and the part bracketed by n is the soft segment. In Estane 5703p: $m \approx 1-3$ and $n \approx 4-6$.

instruments and a synchrotron beamline. One is CREDO, commissioned by the Research Centre for Natural Sciences, Hungarian Academy of Sciences [16]. Highly monochromatic Cu K_α radiation with wavelength of 0.154 nm is generated using a GenixX3D Cu ULD integrated beam delivery system (Xenocs SA, Sassenage, France), which consists of a 30 W microfocus X-ray tube and an integrated parabolic multilayer mirror. Scattered X-rays were detected by a Pilatus-300 k CMOS hybrid pixel detector (Dectris Ltd, Baden, Switzerland). The scattering intensity $I(q)$ is measured as a function of scattering vector magnitude $q = 4\pi\sin\theta/\lambda$, where λ is the wavelength of the incident X-rays, and θ is half of the scattering angle. The detector was placed at 416 mm from the sample, resulting in a q range of 0.2–5 nm⁻¹. The scattering cross section in absolute units was determined using a pre-calibrated glassy carbon specimen. Samples were contained in borosilicate glass capillaries, which were inserted in an aluminium sample holder. The temperature of the sample holder block was controlled by water circulation. Measurements were performed at different temperatures. The samples were first heated from 20 °C to 80 °C in 10 °C intervals and then cooled from 80 °C to 20 °C in 20 °C intervals. To confirm the stability of the sample, 10 measurements of 2 min duration were performed at each temperature (Fig. S1 in SI).

The second instrument is SAXSpace manufactured by Anton Paar (Austria) and equipped with a Kratky block-collimation system. The WAXS and SAXS data have been collected simultaneously from $q = 0.8$ to 20 nm⁻¹ by using an image plate detector (Fig. S2 in SI). The X-ray generator was operated at 40 kV and 50 mA. A temperature control unit (Anton-Paar TCS 150) connected with the SAXSpace was used to control the temperature from 20 to 110 °C. An exposure time of 30 min was sufficient to give a good signal-to-noise ratio. All data were normalized to the same incident primary beam intensity and corrected for background scattering from the aluminium foils used as sample cell windows.

The synchrotron SAXS experiments were carried out at the SAXS station (BL16B1) in the Shanghai Synchrotron Radiation Facility (SSRF), China [17]. The radiation from the storage ring is monochromatized using Si(111) double crystal monochromator. Two-dimensional scattering patterns were recorded using an image-intensified charge-coupled device detector. The X-ray wavelength was 0.124 nm, and the distance between the detector and the sample was 2075 mm, covering a q range of 0.15–1.9 nm⁻¹. The samples were first heated at 80 °C for 20 min by a Linkam thermal stage, and then cooled to RT within 10 min with circulating water. The synchrotron SAXS measurements started immediately when the temperature reached RT in order to monitor the phase separation process with time. The data acquisition time for each measurement was 5 min.

The SANS measurements were performed on the small-angle neutron scattering diffractometer at Institute of Nuclear Physics and Chemistry, China Mianyang Research Reactor [18]. With a mean neutron wavelength of 0.53 nm ($\Delta\lambda/\lambda = 0.11$) and sample-detector distance of 5.2 m, the interference peak of the post-heated Estane at RT was monitored over a q range of 0.1–1 nm⁻¹ from several days to 80 days. The scattering data were processed using BerSANS software [19]. Each raw scattering data set was corrected for the sample transmission, thickness, and background scattering.

2.3. Differential scanning calorimetry

The calorimetric measurements were carried out using a DSC8500 apparatus (Perkin–Elmer). Purge gas (nitrogen) was passed through the DSC cell with a flow rate of 20 mL/min. The temperature was calibrated with mercury, water and indium. The

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