

Investigation of Temperature Dependency of Morphological Properties of Thermoplastic Polyurethane using WAXS and SAXS Monitoring

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Abstract: Polyether and polyether/ester based TPU (thermoplastic polyurethanes) were investigated with wide-angle XRD (X-ray diffraction) and SAXS (small angle X-ray scattering). Furthermore, SAXS measurements were performed in the temperature range of 30 °C to 130 °C. Polyether based polymers exhibit only one broad diffraction signal in a region of 2θ 15° to 25°. In case of polyurethanes with ether/ester modification, the broad diffraction signal arises with small sharp diffraction signals. SAXS measurements of polymers reveal the size and shape of the crystalline zones of the polymer. Between 30 °C and 130 °C the size of the crystalline zone changes significantly. The size decreases in most of investigated TPU. In the case of Desmopan 9365D an increase of the particle size was observed.

Key words: Thermoplastic polyurethanes, morphology, mechanical properties, SAXS, WAXS, temperature influence, crystallinity.

1. Introduction

Polyurethanes achieved an exceptional position among the most important organic polymers due to their highly specific technological application areas. Polyurethanes represent a polyaddition product of isocyanate and diols. In terms of their enormous industrial importance, the chemistry of isocyanates has been extensively studied.

In polyurethane polymerization, a compound containing two or more isocyanate groups per molecule reacts with a diol or a polyfunctional alcohol. Stribeck et al., summarized that isocyanates and a short-chain diol form a rigid or hard segment; these hard segments are linked through the polyol soft block to form a statistical block copolymer. When all the components of the polyurethane are bifunctional, a linear thermoplastic polymer is obtained. As the hard and soft chain segments are thermodynamically

incompatible, the resulting domains are rich in either soft or hard segments [1].

Segmented PU (polyurethane) copolymers are extensively used in applications ranging from foams and coatings, to applications in life science and biomedical devices. These polymers can be synthesized from a wide variety of diisocyanates, diol or diamine chain extenders, and polyols, using convenient addition polymerization methods.

Due to the nature of the polyaddition process, hard segments with a rather broad distribution of sequence lengths are usually generated [2]. This creates complexity in understanding segmented PU microphase separation compared to diblock and triblock copolymers, that often exhibit blocks of well-defined lengths and narrow polydispersity. PUs having different soft segment chemistries commonly exhibit rather incomplete hard/soft demixing when polymerized in bulk or cast from solution, and the extent of segment segregation (and resulting hard domain morphology) is particularly important in determining mechanical and other physical properties [2]. Thus, hard

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segments having short sequence lengths (as well as so-called “lone” isocyanates [3], more prevalent at lower hard segment contents), show higher solubility in the soft phase than longer sequences for entropic reasons. In addition, similarity in cohesive energy density and/or the possibility of hydrogen bonding between hard and soft repeating units also encourages mixing processes [2].

The bulk properties of the polymer that correspond to the cohesion of the polymer are considered as the terms of crystallinity and crosslink density, whereas the interfacial features are determined by roughness, surface energy, and other specific morphology [4]. Understanding the regular arrangement of polymeric materials is essential for the prediction of new processing methods and new technological applications.

Thermoplastic polyurethanes have been extensively investigated with XRD (X-ray diffraction) and SAXS (small-angle X-ray scattering) for detailed structural information [2-7].

XRD patterns of polyurethanes were used to extract the structural information of cell parameters and to obtain crystallite size and texture. Small-angle X-ray scattering was used to determine the size, shape and domain structure of the scattered particles. The WAXS (wide-angle X-ray diffraction) and SAXS investigations discovered structural change during processing and application in a temperature range of 30 °C to 150 °C.

Trovati, et al. [3] analyzed PU resins using X-ray analysis and showed significant differences of rigid and semi-rigid PU. He observed in the case of ester urethane a typical peak at 2-theta of 11° which was indexed as (006). This peak was used for the calculation of the number of rigid parts. The 2-theta of 20° corresponds to the indices (-1, 1, 1).

Prisac [7] observed broad peaks at 2-theta of 20° with small sharp peaks at the top in case of ester homourethanes based on EG (ethylene glycol) and DBDI (di-buthyl di-isocyanate).

2. Experiments

2.1 WAXS Set Up

WAXS measurements were performed on a Bruker D8 Endeavor system with Cu μ -source from Incoatec Micro source ($I_{\mu S}$) of 50 W and spot size diameter of 100 μ m. Exposure time of 60 s was used, while the scattering intensity was registered using a 2D-Vantec 500 detector. One-dimensional curves were obtained by integrating the 2D data with Bruker Evaluation software.

2.2 SAXS Set Up

SAXS measurements were performed at a Bruker D8 SAXS beamline with Cu μ -source from Incoatec Micro source ($I_{\mu S}$) of 50 W and spot size diameter of 100 μ m. An exposure time of 120 s was used while the scattering intensity was registered using a 2D-Vantec 500 detector with a detector window of 140 mm, a resolution of 2,048 by 2,048 pixel and a sample-detector distance of 300 mm. The measurement was performed in transmission mode with the help of a beam stop.

The sample films (1 × 2 cm) were mounted on a capillary sample holder and heated from 30 °C to 130 °C at a rate of 6 °C/min with a precision of \pm 1 °C.

The SAXS data were analyzed using the program NanoFit version 1.2.1.2 (Bruker AXS (Advanced X-ray Solutions) GmbH). Background correction was done for all measurements. It was found that the structure of the particles could be deduced by fitting the SAXS peak with the equation from a theoretical model.

In this case the ZP (Zernike-Prins) model was used to analyze the SAXS data of the TPUs (thermoplastic polyurethanes) [8]. For spherically symmetric particles the scattering intensity can be written as:

$$I(q) = I_0 N \Delta\rho^2 V^2 P(q) \quad (1)$$

where, N is the number density of particles, $\Delta\rho$ is the difference in scattering length density between the particles and the solvent/matrix, V is the volume of the

particles, $P(q)$ is the particle form factor.

$$P(q) = F^2(q) \quad (2)$$

$$F(q, R) = \frac{3[\sin(qR) - qR \cos(qR)]}{(qR)^3} \quad (3)$$

The particle form factor $P(q)$ describes the structure where $F(q)$ is the amplitude of the form factor. The form factor amplitude of a homogeneous sphere of a radius (R) is given by Eq. (3). The average particle size is calculated from the particle volume.

3. Results and Discussions

3.1 Results of WAXS Measurements

Three thermoplastic polyurethanes from BASF (Desmopan 9370, 588L and 9365D) and three thermoplastic polyurethanes from Bayer (Elastollan 1075, 1170A and L11600) were investigated. These TPUs diverge in tensile strength and elongation at break (Tables 1 and 2). The backbone is a linear polymer chain that consists of alternating flexible, elastic segments and rigid crystalline segments. The modification of these phases creates the differences in physical properties; tensile strength, elasticity and cold-flexibility.

The WAXS results of the TPU show a difference in the observed 2-theta-value, the calculated crystal size and the FWHM (Full Width at Half Maximum) of the peak. The results of three different TPU Elastollan types are summarized in Table 1, the results of the Desmopan types are presented in Table 2. The results of tensile strength and elongation at break origin from datasheet [9, 10].

The results of the WAXS measurements are summarized in Fig. 1. Desmopan 588 and Elastollan 1075, which are ether/ester based TPU, unveil sharp peaks at the top of the broad peak.

The ether based Desmopan types 9370 and 9365D and the ether based Elastollans 1170A and 11600 exhibit no sharp peaks at the top of the 2-theta of 20°.

This observation corresponds with the investigations of Prisacariu [7]. He observed broad peaks at 2-theta of 20° with small sharp peaks at the top in the case of

ester homourethanes based on EG and DBDI.

Table 1 Results of mechanical investigations, results of the molecular weight data: Mn (Number average of molecular weight), Mw (weight average of molecular weight) via Size Exclusion Chromatography and 2 θ , FWHM data from X-ray diffraction investigations of Elastollan TPU types.

	TPU E 1075	TPU E 1170A	TPU E L11600
Tensile strength (MPa)	15	30	30
Elongation at break (%)	900	850	400
Mn (Da)	70000	50000	20000
Mw (Da)	205000	115000	40000
Density (g/cm ³)	1.13	1.08	1.05
2 θ (°)	19.59	20.17	18.97
FWHM (°)	6.7	6.4	8.2

Table 2 Results of mechanical investigations, results of the molecular weight data Mn, Mw via Size Exclusion Chromatography and 2 θ , FWHM data from X-ray diffraction investigations of Desmopan TPU types.

	TPU D 9370	TPU D 588L	TPU D 9365D
Tensile strength (MPa)	26	40	58
Elongation at break (%)	740	570	340
Mn (Da)	50000	44000	50000
Mw (Da)	110000	106000	106000
Density (g/cm ³)	1.06	1.15	1.2
2 θ (°)	20.14	20.67	20.59
FWHM (°)	6.3	7.7	7.6

Stribeck, et al. [1] also observed broad peaks in the case of ether based TPU.

Precise WAXS measurements make it possible to determine the exact 2-theta values and FWHM of the peak. Further correlations between these parameters and the SEC (Size Exclusion chromatography) results or mechanical properties have not yet been observed.

3.2 Results of SAXS Measurements

SAXS measurements of polymers reveal the size and shape of the crystalline zones of the polymer. The measurements were taken in transmission mode with beamstop. Further calculations were done after integration and background subtraction. The integration of the 2D-SAXS measurements led to 1D-data. These data were used for the calculation of the particle size using ZP-model. Fig. 2 exhibits Desmopan 9370 at

30 °C with a comparable large particle size of 2.6 nm.

In Fig. 3 the result of the 2D-SAXS investigation of

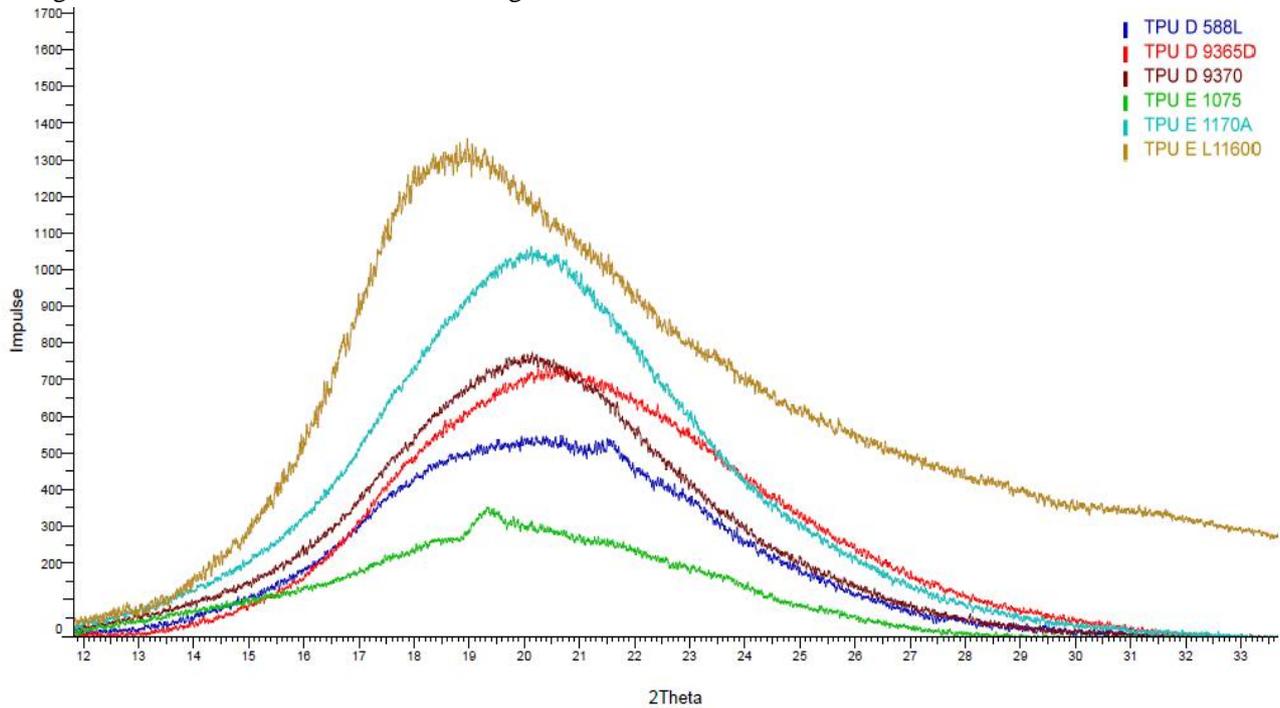


Fig. 1 WAXS measurements of ether based and ether/ester based TPU.

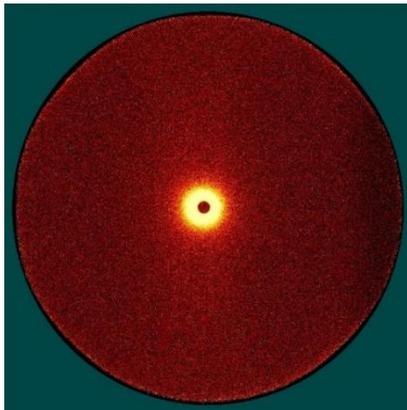


Fig. 2 2D-SAXS measurement of Desmopan 9370.

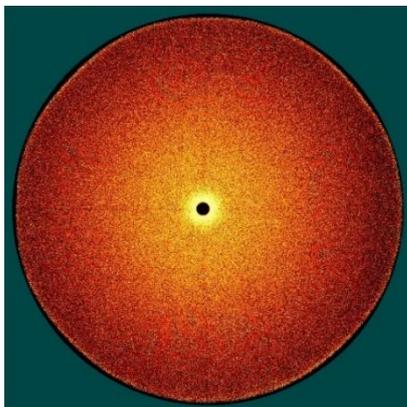


Fig. 3 2D SAXS measurements of Elastollan 1075.

Elastollan 1075 at 30 °C is presented. The particle size is determined as 1.8 nm. Compared to Fig. 2, intensive scattering corona can be observed around the beamstop in the center.

9365D (Figs. 4-6) offers closer structural details which indicate different laminar domain structures [11, 12]. The Desmopan 9370D (ether/ester-type) exhibits a sharp signal. The Desmopan 588L and 9365D (ether-type) offer a broader scattering.

Based on the SAXS data, the particle radius can be calculated using a spherical model. It was observed that the increase in temperature also has a significant influence on the particle radius. The five polyurethanes TPU D 588L, TPU D9370, TPU E 1075, TPU 1170A and TPU E L1160, exhibit a decreasing particle radius at increasing temperatures as shown in Fig. 7.

TPU D9370 and TPU E L11600 in particular manifest a strong decrease in particle radiuses with

increasing temperatures. In contrast, the particle radius of the TPU D 9365D increases with increasing temperatures as seen in Fig. 8.

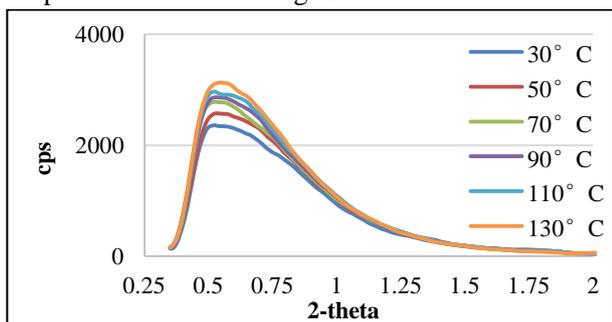


Fig. 4 Integrated SAXS measurements of Desmopan 588L.

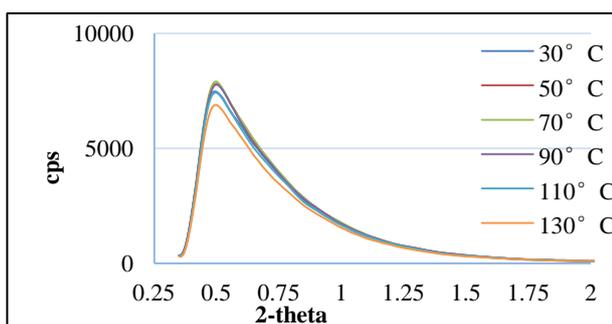


Fig. 5 Integrated SAXS measurements of Desmopan 9370.

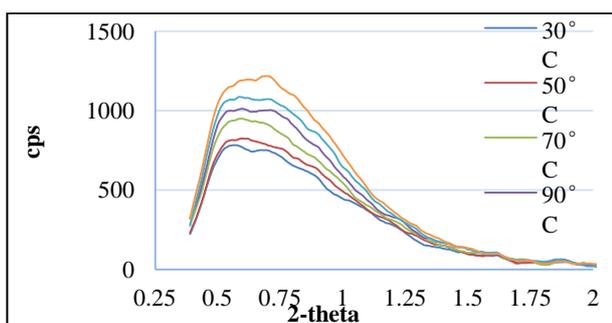


Fig. 6 Integration of SAXS measurements of Desmopan 9365D.

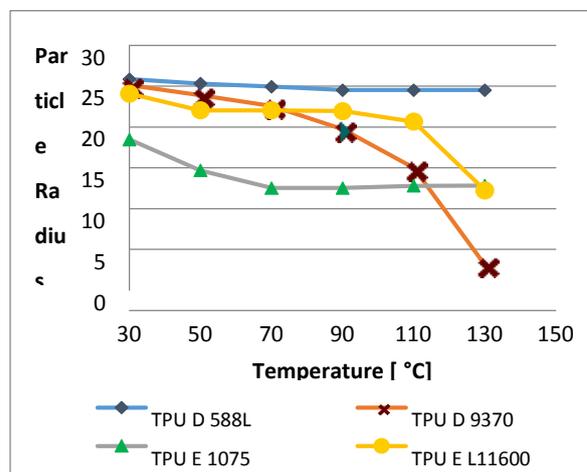


Fig. 7 Particle size in the temperature range of 30 °C to 130 °C of Desmopan 588L, Desmopan 9370, Elastollan 1075 and Elastollan 11600.

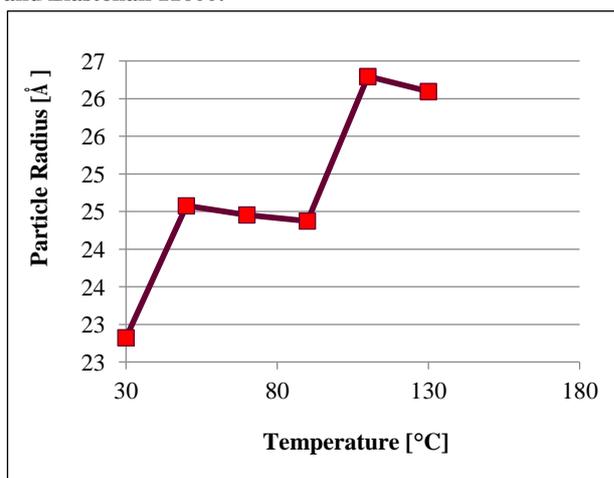


Fig. 8 Particle size in the temperature range of 30 °C to 130 °C of Desmopan 9365D.

The change of the particle radius in the temperature range 50 °C to 90 °C is very small. The same behavior can be observed in the temperature range of 110 °C to 130 °C. The particle radius increases strongly from 30 °C to 50 °C and from 90 °C to 110 °C.

4. Conclusions

In wide-angle XRD, polyether based polyurethanes exhibit only one broad diffraction signal in the region of 2θ 15° to 25°. In case of polyurethanes with ether/ester modification, the broad diffraction signal offers small sharp diffraction signals.

SAXS measurements reveal a significant change in the size of the crystalline zone in the temperature

range between 30 °C and 130 °C. The size decreases in five of the six TPUs investigated (Fig. 9). In the case of Desmopan 9365D, an increase of the particle size was observed which indicates different lamellar domain structures that need to be studied in more detail.

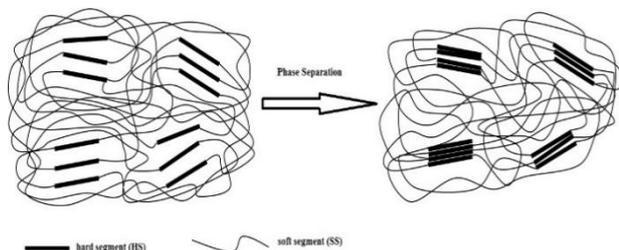


Fig. 9 Particle size change during temperature increase.

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