



Experiment title: New multi-block polyurethane thermoplastic elastomers with shape memory effect: in situ study of crystallization kinetics and morphology during tensile deformation

Experiment number:
SC-4900

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Report:

Currently, thermoplastic polyurethanes (TPU) are actively used in biomedicine as patches, sutures, implants, etc. due to the combination of elasticity and strength [1,2]. Such TPUs change their shape under the influence of various factors (temperature, light, magnetic and electric field, etc.) and belong to the class of adaptive, or so-called "smart" polymers [3,4]. TPUs consist of incompatible polyester crystallizable soft block and polyurethane urea amorphous rigid block. The presence of intermolecular interactions and physical network of rigid blocks due to hydrogen bonds provides TPU high strength at room temperature [5]. Mechanical properties of adaptive materials are determined by the physical structure of crystals of the soft block. Varying the type and ratio of polyetherdiols, as well as the nature of the end isocyanate groups of rigid blocks, it is possible to control the crystallization rate and the degree of crystallinity of soft blocks. Recently, there is very few information in the literature on the mutual influence of the processes of phase separation and crystallization. The objective of the experiment was to

study a relationship between chemical composition, semi-crystalline morphology of series of thermoplastic polyurethanes during deformation and heating.

We have synthesized thermoplastic elastomers based on new diblock and triblock polyurethane urea of different composition and ratio of the soft block [6]. Polymers contain poly- ϵ -caprolactone diol (PCL) and polybutylene glycoladipinate diol (PBA) as soft crystallizable blocks and diolurethane and ureaurethane fragments derived from diisocyanates (1.6-hexamethylene diisocyanate, HMDI and 2.4-toluene diisocyanate, TDI) and chain extensions (1.4-butanediol, BD and 2-aminoethanol, EA) as rigid blocks. The soft block contains PBA (TPU-1A), PCL (TPU-1B) or an equimolar mixture (TPU-1AB).

In order to determine the effect of the structure of the interphase boundary on phase separation of TPU, a series of polymers with different terminal diisocyanates was prepared: cycloaliphatic isophorone diisocyanate IPDI (TPU-2A), aliphatic HMDI (TPU-2B), and aromatic TDI (TPU-2C). Small-angle X-ray scattering (SAXS) experiments were carried out on BM26 beamline with photon energy 12 keV ($\lambda = 1.54\text{\AA}$). Two-dimensional diffractograms were recorded using the Pilatus 1M detector. Temperature-resolved experiments were

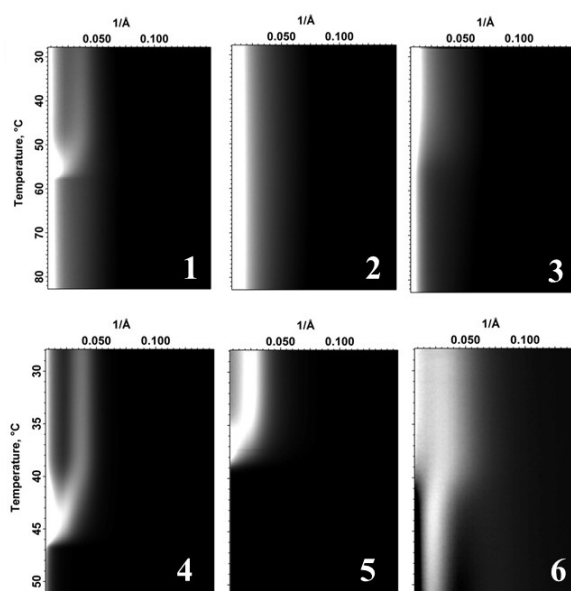


Fig. 1 The curves of DSC (a,b) of the first heating (solid lines), of the second heating (dashed lines) and dependence of and SAXS profile on temperature (c) for samples of TPU-1A (1), TPU-1B (2), TPU-1AB (3), TPU-2B (4), TPU-2A (5) and TPU-2C (6)

performed with Linkam THS stage with heating rate $10 \text{ deg}\cdot\text{min}^{-1}$. In situ deformation experiments were performed on Linkam TST350 with stretching rate 1 mm min^{-1} . The obtained two-dimensional diffractograms were analyzed using the software package created in the Igor Pro (Wavemetrics Inc.) environment.

Evolution of supramolecular structure during heating is shown in Fig.1. It can be seen that the small-angle maximum typical for the morphology of semi-crystalline polymers with regular lamellar stacks of is observed only for the sample TPU-1A, containing PBA as a soft block (Fig. 1, sample 1). The samples with PCL block are characterized by low degree of crystallinity and irregular distribution of lamellae. Thus, the presence of the second soft block completely suppresses crystallization. The high melting point ($52\text{-}53^\circ\text{C}$) of TPU-1A indicates the stabilization of the crystal phase due to the effective phase separation of soft and hard blocks. Thus, a detailed analysis of diffractograms taken during the heating of the samples shows a significant difference between the semi-crystalline structure in the PBA and PCL domains.

Fig. 1, images 3-6 shows SAXS patterns of the samples with PLC as crystallizable block and different diisocyanates as precursor. Difference in the diisocyanate nature results in different driving force for phase separation of rigid and soft segments. Fig. 1, image 6 shows that melting of TPU-2C with aliphatic HMDI begins earlier than TPU-2A (image 1) and TPU-2B (image 2).

The analysis of the SAXS data shows that in the TPU-2C based on HMDI (Fig. 1c, 6) thinner crystals are formed due to the higher rate of crystallization and greater undercooling in comparison with TPU-2A and TPU-2B. Better phase separation between aliphatic soft block and cyclic and aromatic diisocyanates leads to a decrease in the crystallization rate and the formation of thick and regular crystals of TPU-2A and TPU-2B.

Variation of polymer morphology was studied during in-situ stretching experiments on TPU films (Fig.2).

Isotropic film of TPU-1A reveals lamellar structure with long period of 18 nm (Fig. 2a). After stretching at $\varepsilon=300\%$ we see four spot pattern typical for fibrillar morphology (Fig. 2b). The found pattern is kept after release of stress (Fig. 2c).

Heating above PBA block melting point results in preserving of phase separated

structure with long period app. 24 nm (Fig. 2d). During crystallization of amorphous film SAXS peak become more narrow and slowly shifts to wider angles (Fig. 2e). Interesting that stretching of the amorphous TPU-1A does not cause stress-induced crystallization (Fig. 2f). Consequently, the TPU sample has three morphological states: amorphous phase-separated, isotropic semi-crystalline and oriented fibrillar morphology. Transition between those states determines thermal and mechanical properties of the materials.

Difference in crystallization rate and morphology affect mechanical behavior of the samples. Particularly, TPUM-1B based on PCL reveals the elastic state (elongation at break $\varepsilon_r = 1445\%$, Young's modulus $E = 7 \text{ MPa}$). In contrast, TPUM-1A with PBA as soft block shows thermoplastic behavior ($\varepsilon_r = 807\%$, $E = 199 \text{ MPa}$). TPUM-1AB films containing a blend of oligodioles demonstrate an increase in tensile strength and Young's modulus without loss of elasticity. In series of TPU-2A...2C the polymer TPU-2B based on aliphatic HMDI shows optimal physical and mechanical parameters: Young's module - about 39 MPa, ultimate strength $\sigma_r - 33 \text{ MPa}$, and $\varepsilon_r -$ up to 1000 %. Excellent strength of TPU-2B can be explained by the presence of urethane groups and strong intermolecular interactions due to hydrogen bonds. Consequently, variation of mechanical characteristics of the TPU films from soft elastomers to hard plastics depending on the composition of the soft and hard blocks and semi-crystalline morphology gives the possibility of fine tuning of properties of adaptive polymers on the stage of synthesis.

The presented results will be included in coming publication in journal Materials that will be submitted by June, 2020.

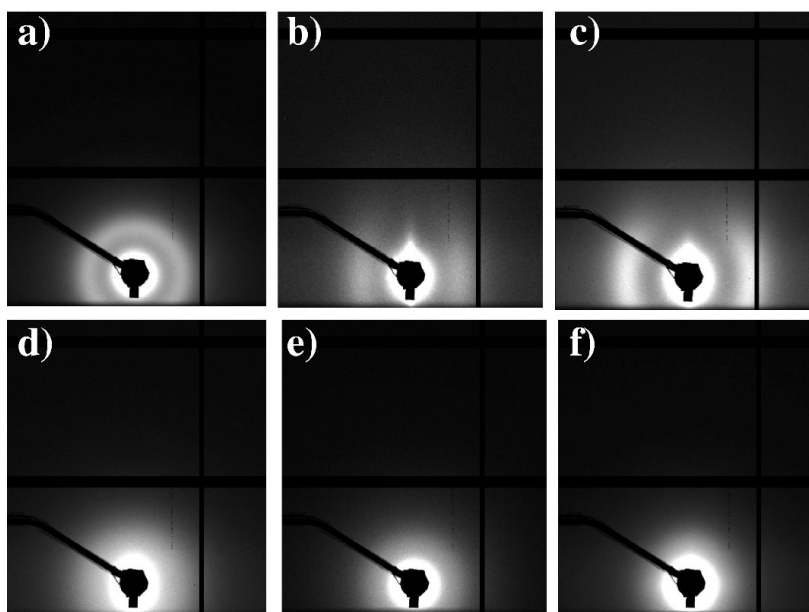


Fig. 2 2D SAXS patterns of TPU-1A: non-oriented (a), at $\varepsilon=300\%$ (b), after release of stress ($\varepsilon\approx 200\%$) (c), after heating to 70°C (d), crystallization at 25°C for 1h (e), second stretching after crystallization (f).

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