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The influence of hard segment crosslinking on the morphology and mechanical properties of segmented poly(ester-urethanes)

Summary — The morphology and mechanical properties of uncrosslinked (PUR-unc) and hard segment crosslinked (PUR-c) segmented polyester-urethanes (PUR) obtained with DABCO catalyst were investigated. The crosslinking was introduced by using 60 wt. % of trimethylol propane (TMP) in the mixture with butanediol. The morphology of bulk samples was studied with the use of AFM. Uncrosslinked PUR was characterized by a morphology in which hard-segment domains were inhomogeneously distributed in the whole sample. They created hard-segment rich aggregates (in the range of 70—380 nm diameter) which were connected to each other. Hard-segment crosslinked PUR showed spherical domains in the range of 20 nm diameter. They were homogeneously distributed in a soft-segment rich matrix and no other aggregates were present. The mechanical properties such as stress at 100 % of elongation, tensile strength, elongation at break, permanent set and tensile hysteresis percent (H_t) were compared. All studied parameters changed clearly after crosslinking excluding H_t, which only changed slightly.
Key words: segmented crosslinked polyester-urethanes, atomic force microscopy, morphology, mechanical properties, polyurethanes.

Segmented polyurethanes (PURs) are block copolymers built up of alternating soft and hard blocks. A wide range of their properties can be attributed to the large variations in morphologies that can be obtained, which are partly controlled by the presence of physical or chemical crosslinking. Physical crosslinking is mainly derived from the phase separation of the hard-segment domains, while chemical crosslinking can be introduced into PUR system in many ways but the most common methods use a triol as chain extender or substrate. Different chemically crosslinked polyurethanes are of interest for many applications such as non-linear optics [1], membranes [2], coatings [3] or medical materials [4].

Various studies on PURs have examined the effects of chemical crosslinking on mechanical and thermal properties [5—14], swelling [5, 7] and degradation [15]. 4,4'-diphenylmethane diisocyanate (MDI) based crosslinked poly(ether-urethanes) obtained without a catalyst, were systematically studied by Petrovic *et al.* [8, 9]. They observed a decrease in tensile strength and elongation at break of PURs when up to 50 wt. % of chain extender mixture based on trimethylol propane (TMP) was used as a crosslinking agent.

Konthandaraman *et al.* [6] studied tolylene diisocyanate (TDI) based PUR crosslinked by TMP, and reported an increase in tensile strength with increasing TMP content. Chiou and Schoen [13] reported that TDI based PURs showing higher crosslinking densities exhibited much larger elastic moduli at temperature above glass transition one. Varying the triol (trimethylol propane propoxylate) concentration or NCO/OH ratio also contributed to the controlling of crosslinking density.

Tsai *et al.* [10] used glycerol as a hard segment crosslinking agent for poly(ester-urethanes) and they found an optimum concentration of glycerol necessary to obtain good mechanical properties of PUR.

Desai [11] studied hard segment PURs crosslinked by TMP, that were produced from two different macroglycols and two different diisocyanates, using dibutyl tin dilaurate as a catalyst. Namely, polypropylene glycol (PPG) and hydroxy terminated polybutadiene (HTPB) were used with TDI or MDI. HTPB/TDI system showed the highest tensile strength whereas PPG/MDI system exhibited the highest elongation at break.

In another paper Desai [12] compared the properties of poly(ether-urethanes) crosslinked by TMP or by modified multifunctional starch. Starch-based PURs showed better mechanical properties, moreover they exhibited two glass transition temperatures (T_g), whereas TMP-based PURs showed only one T_g.

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The morphology and phase separation of chemically crosslinked PURs were studied to a much lesser extent. In uncrosslinked polyurethanes the presence of domains of the order of a few nanometers has been reported [16]. Apart from nanodomains, large-scale morphology is developed in PURs obtained by cast or injection molding [17, 18]. It is especially true in the case of PUR systems based on 4,4′-diphenylmethane diisocyanate/butane diol (MDI/BDO), made without a catalyst. Authors of [19—21] studied the phase separation of hard segment crosslinked PURs, obtained without a catalyst. In [19] the decay of phase separation was reported, while Thomas group [20, 21] have observed globules and spherulites, using transmission electron microscope.

Small-angle X-Ray scattering experiments failed to reveal discrete Bragg peaks in crosslinked PURs, explained by the absence of well-defined phase-separated domains. X-ray diffraction and DSC studies have shown the decay of crystallinity when only TMP (instead of mixture) was used as chain extender [9].

The introduction of glycerol to PURs resulted in decrease in H-bonded formation, a decrease in the ordering of hard-segment domains and an increase in the degree of segment mixing [10].

Desai *at al.* [11, 12] have studied the morphology of tensile fractured films by the use of scanning electron microscopy (SEM) and they found the wrinkles or some cracks with or without some irregular grains called by the authors "gel balls". They suggested that some observed "gel balls" could be artefacts due to overheating when the samples were gold plated but it cannot be ascertained that they are not due to disintegrated PUR particles appearing during the fracture process used to prepare the samples. Thus it is rather difficult to draw conclusions about the true morphology of the PURs reported in the paper [11].

The present study was undertaken to investigate both the morphology and mechanical properties of MDI based segmented poly(ester-urethane) elastomers, showing chemical crosslinking coming from TMP, in the hard-segments. The details of bulk morphology at micro/nano scale and mechanical properties are compared for PURs uncrosslinked and crosslinked, both being catalysed with 1,4-diazabicyclo[2,2,2]-octane (DABCO) catalyst. The morphology has been studied by Atomic Force Microscopy (AFM) and according to our knowledge this is the first paper describing AFM results for PURs crosslinked by TMP.

EXPERIMENTAL

Materials

Two samples of cast segmented poly(ester-urethanes) with a hard-segment content of 50 wt. % were investigated. One sample was uncrosslinked and the other was hard-segment crosslinked by TMP. The soft-segment in PUR was derived from α,ω-dihydroxy(buthylene-*co*-ethylene) adipate (PEBA) and modified 4,4′-diphenylmethane diisocyanate (MDI^* — Isonate 143L). The hard-segments in the uncrosslinked PUR are the products of reaction of modified MDI and 1,4-butanediol (BDO) while in the crosslinked PUR they come from modified MDI, BDO and TMP (60 wt. % of TMP was added to BDO chain extender). Isocyanate prepolymer was synthesized by reaction of MDI and PEBA (6:1 mol/mol) at temperature of 70 °C. The prepolymer (1 mole) was cooled to room temperature and the chain extender(s) (1.1 mole) plus DABCO catalyst (0.1 wt. %) were added. After initial curing at 70 °C the samples were annealed at 110 °C for 24 hours. Both sets of 2 mm thick samples (sheets) were made in the same way (casting method) and at a constant NCO/OH ratio of 1.10.

Methods

Morphology

The morphology of the samples was studied using AFM apparatus with Tapping Mode and Phase Imaging [AFM Nanoscope IIIa Digital Instruments (Santa Barbara)]. The smooth surface required for observation in AFM was prepared by cryo-microtoming of bulk PURs samples at temperature about -100 °C. More details about the sample preparation method can be found in our previous paper devoted to AFM studies on uncrosslinked poly(ether-urethanes) [22]. AFM equipment operated in the range of 0.5—1 Hz frequency and 3—6 V of cantilever vibration air amplitude, while 70—80 % of free amplitude was adjusted as set point amplitude. Soft segments were anticipated to give dark contrast, while hard segments should appear as bright areas.

Mechanical properties

Mechanical properties namely stress at 100 % of elongation (M_{100}), tensile strength (R_r), elongation at break (ε_r), permanent set (ε_t) and tensile hysteresis percent (H_t) were measured using Zwick Z020 universal testing device. Tensile hysteresis (one cycle) was examined after the sample stretching to 50 % of deformation (see Fig. 3). H_t was calculated from the ratio of the area bounded by the loading-unloading curves to the total area under the loading curve [23]. Standard dumbbell shaped specimens were cut out from 2 mm thick PUR sheets for all mechanical tests.

RESULTS AND DISCUSSION

Morphology

The hard-segment rich, quasi-spherical areas (light areas in Fig. 1a) connected to each other by many narrow bridges are observed in 5×5 μm size AFM scan of uncrosslinked sample (PUR-unc). The sizes of the spherical globules are in the range of 70—380 nm. Between the

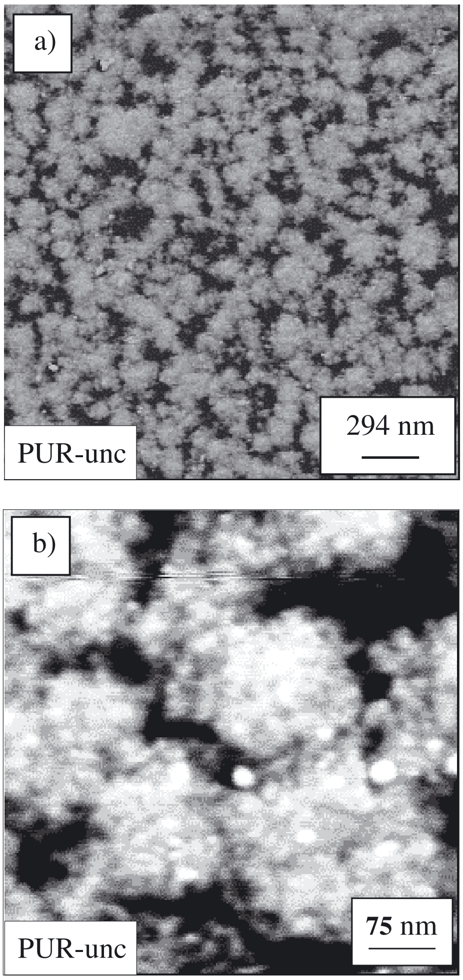

Fig. 1. The morphology (AFM) of uncrosslinked poly(ester-urethanes) (PUR-unc) observed in 5×5 μm (a) and 1×1 μm (b) size scan (phase image); pictures illustrate the fragments of images obtained

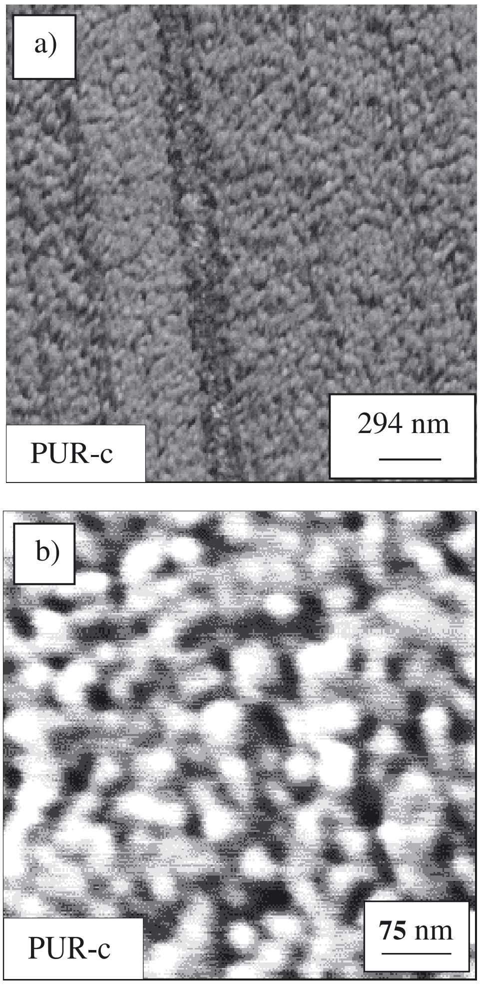

Fig. 2. The morphology (AFM) of crosslinked poly(ester-urethanes) (PUR-c) observed in 5x5 μm (a) and 1×1 μm (b) size scan (phase image); pictures illustrate the fragments of images obtained

hard segment rich globules there are soft-segment rich irregular areas (black areas in Fig. 1a). Having taken all this together it gives a morphology in which the hard-segment rich globules form a continuous phase in a 5×5 μm size scan. Careful analysis of 1×1 μm size scan (Fig. 1b) shows the substructures present in those globules, which can be interpreted as agglomerations of fine domains of hard-segments. The domains' diameters inside the globules are of 11—15 nm in size. To summarise, one can say that PUR-unc is built up of fine nano-domains inhomogeneously distributed in the whole sample.

The morphology of the PUR sample obtained with TMP as the crosslinking agent (PUR-c) is clearly seen in 1×1 μm size scan (Fig. 2b). The hard segment domains of diameters in the range of 15—20 nm can be recognized. They are homogeneously scattered in the soft-segment rich phase and no hard-segment rich globules are present in 5×5 μm size scan (Fig. 2a). The above findings show that the crosslinking influences the way that hard-segment domains are distributed in PUR-c.

Mechanical properties

The values of measured mechanical properties are presented in Table 1.

Table 1. The results of mechanical properties' measurements for uncrosslinked and crosslinked PUR

PUR type	M_{100}, MPa	R_r, MPa	ε_r, MPa	ε_t, MPa	H_t, %
PUR-unc	13.9	41	400	32	0.44
PUR-c	28.9	28.9	100	0	0.51

A decrease in R_r and ε_r is observed after crosslinking with TMP. It can be explained by the reduced slippage and extensibility of hard-segment crosslinked domains and goes along with Smith's studies [24] founding that crosslinked domains are less effective crack propagation stoppers than uncrosslinked ones. The increase in M_{100} after crosslinking can be explained if one takes the type of morphology into account. If PUR-c is treated as a network with hard-segments as inextensible entities, then the complete extension will come from the soft-segments uncoiling. In case the domains are partly connected, they suppress the mobility of soft-segments; at least in the beginning of elongation. After breaking the connection between the domains, the hard-segments are responsible for farther strength. In the case of uncrosslinked samples chain slippage is possible what is the reason of mentioned phenomenon consisting in that R_r and ε_r are higher than in PUR-c. Occurring of permanent set in PUR-unc can be explained by the fact that uncrosslinked hard-segment domains did not interfere the reversibility of elongation after the plastic deformation of uncrosslinked soft-segments. In PUR-c the hard-segments mean that the sample is not only elongated to a lesser extent but that it comes back to the previous size as well. Tensile hysteresis behavior (Fig. 3), representing the storage of energy in the sample during loading-unloading cycle is comparable for both PUR samples. Thus crosslinking does not prevent the heating of the sample during dynamic performance.

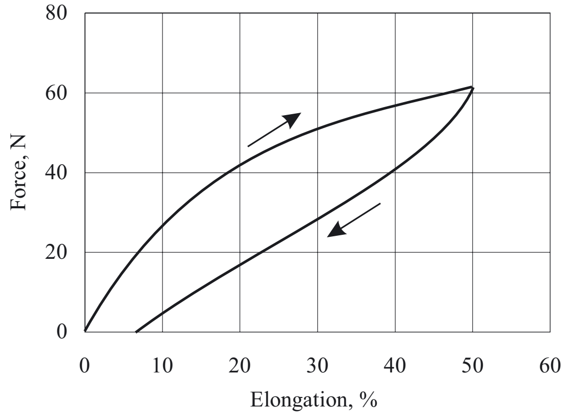

Fig. 3. Tensile hysteresis measurement (the loop represents the loss of energy during one cycle of loading-unloading)

CONCLUSIONS

The properties studied were shown to be sensitive to crosslinking. Crosslinking of hard-segments by TMP influences the domains' distribution, the morphology type and mechanical properties. In the case of mechanical properties the least sensitive is tensile hysteresis. Hard-segment domains are homogeneously distributed in the whole sample of crosslinked PUR, while uncrosslinked PUR exhibit a two-step architecture of the morphology with both domains and the bigger aggregates of globular type being present.

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