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Influence of the Chemical Structure of Flexible Blocks on the Mechanical Properties of Poly(Urethane–Ureas) in a Humid Atmosphere

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Abstract—Sorption of moisture on segmented poly(urethane–ureas) with flexible segments of various chemical structures and the effect of a humid atmosphere on the mechanical properties of these materials were studied. Poly(urethane–urea) prepared from mixtures of oligoethers shows advantages from the viewpoint of preservation of high strength in a humid atmosphere.

Block polyurethane elastomers, so-called segmented polyurethanes (SPUs), are widely used in various branches of industry thanks to their high strength, good deformation characteristics, and resistance to a number of solvents [1]. Depending on the destination, polyurethane items can operate in air or in direct contact with water (e.g., polyurethane coatings of squeeze rolls in paper-making industry).

Published data on the behavior of SPUs in moist media mainly concern the moisture transfer in these materials [2–5] and changes in the structure [2, 5, 6] and glass transition point [5, 6] of moistened polyurethanes. Experiments were performed with thin polyurethane films prepared from solution; in this case, correct estimation of changes in mechanical properties on moistening is complicated by intense moisture exchange with the surrounding medium. Data on the mechanical properties of the films are limited to the results of their mechanical tests before moistening [3]. Therefore, it is unclear to what extent the mechanical characteristics of various SPUs vary on moistening and how the extent of their variation depends on the polymer structure.

Studies in this direction are necessary for understanding how the mechanical characteristics of polyurethanes change on moistening and for choosing formulations of polyurethane materials suitable for operation in moist media.

In this study we examined the influence of the relative air humidity, varied in a wide range, on the mechanical properties of SPUs with various flexible

segments. Our main goal was to reveal what structure of flexible blocks would provide the highest strength of the polyurethane material in a humid atmosphere.

EXPERIMENTAL

We used segmented poly(urethane–ureas) with poly(tetramethylene oxide) flexible blocks (SPUM-1), poly(propylene oxide) segments (SPUM-2), mixed polyether blocks (SPUM-3), and mixed polybutadiene–poly(tetramethylene oxide) flexible segments (SPUM-4). To prepare SPUMs, we took prepolymers based on oligo(tetramethylene oxide)diol ($M \sim 1700$), oligo(propylene oxide)diol Laprol 2102 ($M \sim 1950$), and polybutadienediol ($M \sim 2100$, SKU-DF-2 prepolymer). The molecular weight of the oligomeric diols was estimated from the content of hydroxy groups. The prepolymers were prepared by the reactions of appropriate diols with toluylene-2,4-diisocyanate. The prepolymers and their mixtures (in preparation of SPUMs with mixed flexible segments) were cured with 3,3'-dichloro-4,4'-diaminodiphenylmethane (Diamet Kh) by the procedure described in [7].

The molar ratio of the prepolymers (or their mixture) to Diamet Kh was 1.03, and the molar ratio of the NCO and OH groups in the synthesis of the prepolymers, 2.1.

The isotherms of the moisture sorption by SPUMs were obtained using the kinetic curves of the weight gain of the samples placed in atmospheres of different relative humidities φ (over appropriate solutions of

inorganic salts) at $22 \pm 1.5^\circ\text{C}$. The control samples were kept over freshly calcined calcium chloride. As expected, the sample weights in this case were virtually the same as the initial weights of the samples taken from the molds. The weights of the dry and moistened samples were determined with an Ohaus AR-2140 analytical balance with an accuracy of $\pm 3 \times 10^{-7}$ kg.

For mechanical tests, SPUM samples were kept similarly in a dry or humid atmosphere to attain the equilibrium. The total time of the mechanical tests of a single sample did not exceed 120 s. In this time, the specific moisture content c changed by less than 4% relative to the equilibrium value.

The mechanical characteristics of SPUMs, strength f_b (breaking stress, or maximal stress calculated for actual sample cross section), relative critical strain ε_c , and nominal modulus E_{100} at 100% relative strain, were determined at $22 \pm 1.5^\circ\text{C}$ and an extension rate of 0.3 s^{-1} .

The molecular structures of the dry and moistened SPUM samples were studied by IR spectroscopy on a Bruker IFS-66/S Fourier spectrometer. Samples were prepared as films without solvents, by curing of the reaction mixture placed between two Teflon films. We checked that the Teflon film does not absorb in the range of carbonyl stretching vibrations ($\nu = 1620\text{--}1750 \text{ cm}^{-1}$). At moistening, one of the insulating Teflon films was removed. Before recording the spectrum, the sample surface was again covered with the Teflon film, and the sample was placed between KBr plates. The conversion of the isocyanate groups was also monitored by IR spectroscopy (disappearance of the absorption at $\nu = 2275 \text{ cm}^{-1}$). For the sake of convenient comparison, as in [8], the spectra of different samples were normalized with respect to the band at $\nu = 1575 \text{ cm}^{-1}$.

The results of the experiments showed that the equilibrium moisture content c of the samples was independent of whether it was reached from above (desorption from samples taken from a more humid atmosphere) or from below (sorption).

The reversibility of the moisture sorption and desorption and the shape of the curves in Fig. 1 indicate that the isotherms of the moisture sorption by the examined materials belong to type IV, according to the generally accepted classification. A significant difference in the moisture absorption by SPUM-1 and SPUM-2 (by a factor of 1.67–1.8) at $\varphi \geq 60\%$ may be caused not only by the different polarity of the flexible chains with different content of oxygen atoms.

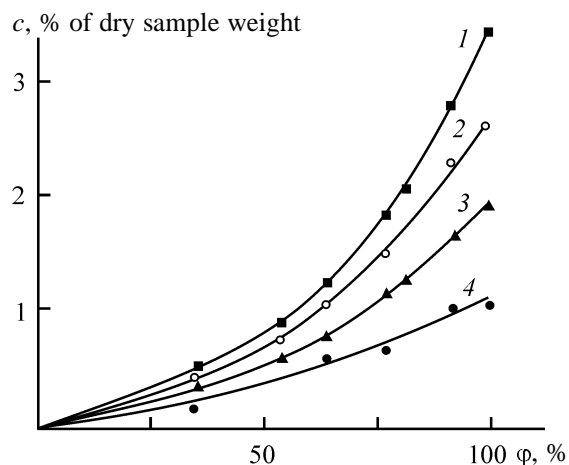


Fig. 1. Isotherms of moisture sorption by (1) SPUM-2, (2) SPUM-3, (3) SPUM-1, and (4) SPUM-4 at 22°C : (c) specific moisture content of the material and (φ) relative air humidity.

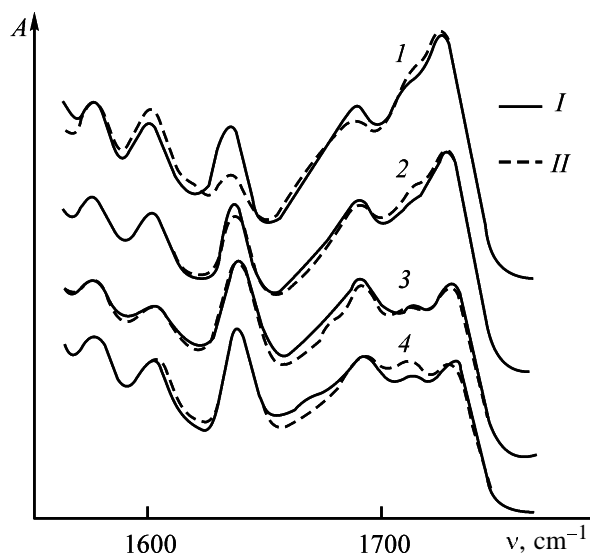


Fig. 2. IR spectra of (I) dry and (II) moistened (at $\varphi = 92\%$) samples: (1) SPUM-2, (2) SPUM-3, (3) SPUM-1, and (4) SPUM-4. (A) Absorption and (ν) wave number.

On replacement of poly(tetramethylene oxide) flexible blocks by poly(propylene oxide) blocks, the degree of microphase segregation in poly(ether–urethane–urea) decreases; correspondingly, the amount of rigid polar blocks dissolved in the flexible phase of the polymer increases, and the volume of this phase grows [8]. Furthermore, the sorbed moisture breaks a part of self-associates of the urea groups localized in domains of rigid urethane–urea blocks. This is clearly seen from comparison of the intensities of the urea carbonyl absorption band ($\nu = 1640 \text{ cm}^{-1}$) in the IR spectra of the initial and moistened samples (Fig. 2, spectra I, dashed and solid lines). As shown in [2], an increase

Mechanical characteristics of dry and moistened SPUM samples

φ , %	SPUM-1		SPUM-2		SPUM-3		SPUM-4	
	E_{100} , MPa	ε_c , %	E_{100} , MPa	ε_c , %	E_{100} , MPa	ε_c , %	E_{100} , MPa	ε_c , %
0	7.7	700	3.6	1070	4.7	1060	7.3	680
35	7.6	710	3.4	1050	4.4	1040	7.1	680
54	7.3	700	2.9	1060	–	–	–	–
64	6.9	700	–	–	3.9	1080	6.6	–
77	6.7	700	2.4	1080	3.6	1090	6.3	660
82	6.6	690	–	–	–	–	–	–
92	6.5	680	2.0	1060	3.3	1080	5.9	680
100	6.3	670	1.8	1070	3.0	1080	5.9	680

in the volume accessible to water molecules and in the amount of polar groups capable of H bonding should increase the moisture absorption of the polyurethane material.

The structure of the rigid domains of the material with poly(tetramethylene oxide) flexible segments is less defective than that of SPUM-2 domains [8]. On

moistening of SPUM-1, the amount of the strongest structural formations, self-associates of urea groups, remains essentially unchanged (Fig. 2, spectra 3). As expected, the isotherm of moisture sorption by SPUM-3 containing mixed oligoether flexible blocks is intermediate between the isotherms of the moisture sorption by SPUM-1 and SPUM-2, and the specific moisture content of poly(urethane–urea) drastically decreases on partial replacement of polyether blocks by nonpolar polybutadiene flexible segments (Fig. 1, curve 4).

The mechanical tests of SPUMs showed that the moistening exerted virtually no effect on the critical strain ε_c (see table). SPUM-2 sample with propylene oxide flexible segments is characterized by the lowest values of f_b and E_{100} and by their most pronounced decrease on moistening (by a factor of 2 at $\varphi = 100\%$; Fig. 3, curves 4). In the material containing 50% nonpolar flexible blocks, the decrease in the strength and nominal modulus was the least pronounced (Fig. 3, curves 3). The curves of the relative change in the breaking stress upon SPUM moistening (Fig. 3b) are arranged in the order opposite to the sorption isotherms in Fig. 1.

The observed pattern of the mechanical behavior of SPUMs in a humid atmosphere is apparently caused by significant differences between the materials in the extent to which the domain structure and interchain interactions affect their density. The results of previous studies [8, 9] suggest that an increase in the intensity of the carbonyl absorption band belonging to urea self-associates ($\nu = 1640 \text{ cm}^{-1}$), observed in going from SPUM-2 to SPUM-3, SPUM-1, and SPUM-4, is indicative of an increase in the degree of segregation of rigid blocks in the same order. As the polarity of flexible chains decreases (and, as a result, the microphase segregation of rigid and flexible blocks in the polymer increases), the effect of the reinforcing filler

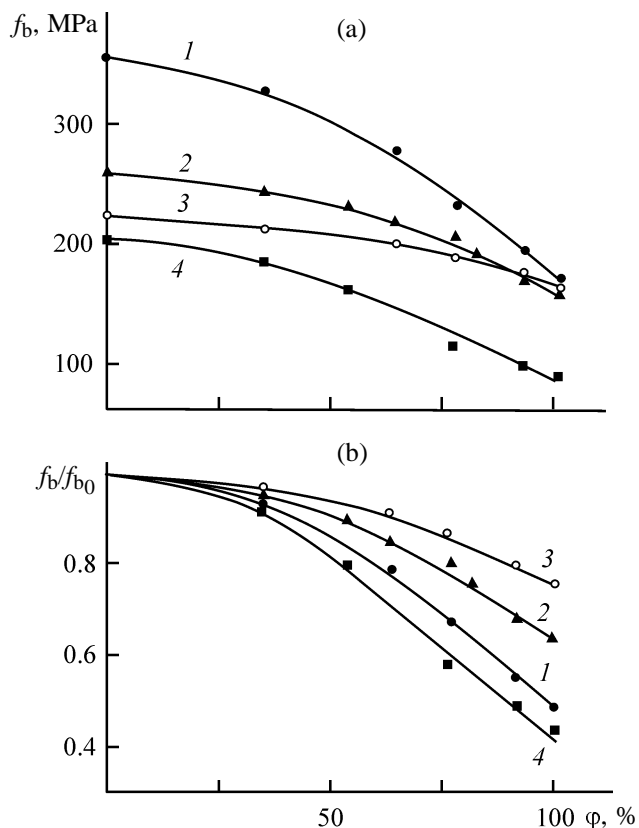


Fig. 3. (a) Strength f_b and (b) its relative change f_b/f_{b0} on moistening of (1) SPUM-3, (2) SPUM-1, (3) SPUM-4, and (4) SPUM-2 samples, as functions of the relative air humidity φ .

on the material strength (SPUM-1, SPUM-4) becomes stronger.

With an increase in the polarity of the flexible blocks and the corresponding increase in the solubility of the rigid segments in the SPUM flexible phase, the effect of the interchain interaction in the polymer matrix on the material strength is enhanced [1]. Correspondingly, weakening of this interaction upon water sorption should substantially decrease the strength of poly(ether-urethanes), which is the case. Partial break of urea self-associates in the presence of moisture also leads to a decrease in the elastomer strength (Fig. 3b, curve 4).

It is noteworthy that, owing to high initial f_b of SPUM-3 (before moistening), the strength of the material with mixed flexible segments in a humid atmosphere is higher than f_b of the other materials, especially at moderate humidity ($\varphi = 50-75\%$) typical of industrial premises.

The fact that the strength properties of the SPUM containing nonpolar flexible segments are not significantly deteriorated in a humid atmosphere is of interest for developing materials preserving high strength in a moist medium.

CONCLUSIONS

(1) The dependence of the moisture absorption of poly(urethane-ureas) with various flexible blocks on the structural organization of the materials was elucidated.

(2) A correlation between the capability of poly(urethane-ureas) to sorb moisture and the decrease in their strength in a humid atmosphere was revealed.

(3) Moisture only weakly affects the mechanical characteristics of the material with mixed polyether and nonpolar polybutadiene flexible segments. The decisive effect on the properties of this material is

exerted by the microdispersed rigid phase, which is not altered upon moistening of the polymer.

(4) To ensure high strength of poly(ether-urethane-urea) in a moist medium, it is appropriate to use for its synthesis a mixture or prepolymers derived from oligo(tetramethylene oxide)diol and oligo(propylene oxide)diol.

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