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ORIGINAL CONTRIBUTION

Interrelationship between ultimate mechanical properties of variously structured polyurethanes and poly(urethane urea)s and stretching rate thereof

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Abstract The ultimate mechanical properties of polyurethane determine their possible applications under various conditions of mechanical action. The mechanical properties of nine polyurethane and polyurethane urea samples were investigated in a range of stretching rates 0.56÷0.002 s^{-1}. A part of experiments was performed at several temperature values under conditions of stepwise variable stretching rates. The interrelationship between rate dependence of strength–strain properties of polyurethane compositions and the structure thereof was ascertained. The influence of molecular structure's variations, of physical network density and of segmented polyurethane and polyurethane urea morphology on said interrelationship was examined on samples subjected to large strain values. The structure of some samples was radically distorted by plasticizers oppositely influencing micro-phase segregation of soft and hard segments. Multiple kinds of dependency (direct, inverse, moderate and strong) of elastomers' strength versus stretching rate were demonstrated. Produced data and ascertained regularities are useful to perceive reasons for diversity of mechanical behavior of polyurethane materials and to control properties thereof.

Keywords Polyurethanes · Poly(urethane urea)s · Mechanical properties · Structure · Strength

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Introduction

Polyurethanes are a unique class of polymers structure and properties of which are controlled in wide limits due to using various polyols, diisocyanates and chain extenders during synthesis. Depending on chemical structure and quantity of components, polyurethane materials with various combinations of properties can be produced [1–6]. Many polyurethane block-copolymers are featured by such properties as high tensile strength, relative elongation at rupture, abrasive resistance, elasticity in a wide range of negative and positive temperatures [2, 4, 7, 8].

Segmented polyurethanes (SPUs) consist of alternating soft and hard segments (blocks) of various chemical structure and polarity. The chemical structure of SPU soft segments is determined by structure of oligomers used for their synthesis [1, 5, 9–11]. Hard segments are formed during reaction of diisocyanate with low-molecular bi-functional compounds, e.g., diols or diamines.

The difference in polarity of soft and hard segments leads to micro-phase separation with subsequent formation of hard segments' domains. Hydrogen bonds in micro-domains play an important role in stabilization of hard phase structure [9, 12–14]. In SPUs, hard domains appear to be strengthening fillers and also physical cross-linking points in specific physical network which is stable in a wide temperature range [15, 16].

Smith [16] had proposed the following mechanism explaining strengthening effect of heterogeneous elastomers by hard domains: increased dissipation of energy, deflection and bifurcation of cracks, cavitation and plastic deformation of domains. The following strengthening processes take place in a soft polymer matrix: viscoelastic dissipation of energy inside a crack's tip, possible strain-induced crystallization, and high deformability.

Comparison of tensile strength for three samples of heterogeneous polyurethanes and poly(urethane urea) has been performed at various temperatures and strain rates. It has been demonstrated that the time–temperature superposition principle is not appropriate for these materials as opposed to single-phase polyurethanes [16, 17].

No doubt that temperature, degree of micro-phase separation between hard and soft segments, glassing temperature of soft phase and its chemical structure are important factors influencing strength of SPUs.

Two different structures of hard domains, namely, fibril and lamellar, have been ascertained to influence the strain mechanism of polyurethanes [18, 19]. Alterations in elastomers' structure with urethane and urethane urea hard segments and with polyether soft segments of various molecular mass were investigated most thoroughly including rheooptical technique [18, 20]. Obtained results allowed marking out reorganization elements of SPUs structure contributing to their strengthening under strain: predominant orientation of not only soft but also hard segments under relative strain value 400–600%, crystallization of soft segments disposed to crystallization in the strain process.

Earlier, Bonart et al. [19, 21] had proposed conception of molecular orientation and inhomogeneous transfer of force throughout a polymer matrix under strain. According to this conception, certain chains bear high local stresses under first strain of block-copolymer. Pre-stretching of chains causes pulling of hard segments out of some domains until the stress gets leveled. Pulling of hard segments takes place under high loading (model crystallizing systems were used to evidence). In our opinion, this factor also influences significantly mechanical properties of SPUs.

Alteration of elastic properties of polyurethanes under various strain conditions was investigated sufficiently enough including compression conditions in a wide range of strain rates [1–3, 16, 23, 24]. Strain–stress dependences for some types of polyurethane at various stretching rates and temperatures, as well as regularities of elastic behavior for such type of materials, have been investigated in some works [1, 15, 20, 22–26].

The ultimate strength–strain properties of elastomers while under strain are important criteria of a material's ability to withstand loading and strain. This paper represents research results in strength and relative critical strain of polyurethanes and poly(urethane urea)s in a wide range of stretching rate values. The objective of this study is to ascertain regularities of ultimate mechanical properties' variation in polyurethane materials under various strain conditions and to identify certain important relations between these properties and the structure of elastomers with urethane and urethane urea hard segments. Six poly(urethane urea) samples and three polyurethane ones have been investigated. The structure of poly(urethane urea) with poly(propylene oxide) soft segments was regulated by plasticizers, chemical composition of polymers being the same or similar.

Experimental section

Materials

The synthesis of poly(urethane urea) was performed on the base of oligoetherdiols' prepolymers and 4,4′-methylene-bis-(2-chloraniline) (MOCA). Prepolymers were produced from 2,4-toluene diisocyanate (TDI) and oligoether diol. 2,4-Toluene diisocyanate Scuranate T100 (99% purity) was provided by Lyondell Basell Co. (Netherlands). The following oligoetherdiols were used: oligo(propylene oxide) diol (PPO) Voranol 1010L (average molecular weight M_n= 1,000 gmol^{-1}) from Dow Plastics (Belgium); oligo(tetramethylene oxide) diol (PTMO) from BASF (M_n=1,000 and 2,000 gmol^{-1}) and from Invista Co. (M_n=1,380 g mol^{-1}). MOCA (99% purity) was obtained from Mitsubishi International Corp. (Japan).

Prepolymer produced by interaction of PTMO (M_n= 2,000 gmol^{-1}) and 4,4′-diphenylmethane diisocyanate was used for synthesis of SPU. 4,4′-Diphenylmethane diisocyanate was purchased from the BASF. 1,4-Butanediol (BD) was used as chain extender. 1,1,1-Trimethylol propane (TMP) was used as the cross-linking agent in a polyurethane composition. BD and TMP as well as tributyl phosphate (TBP) and di-2(ethylhexyl) phthalate (DEHP) plasticizers were provided by Sigma-Aldrich.

Water from oligoethers, BD and TMP was removed at 90 °C while stirred for 7 h under a vacuum (0.2 kPa). Prepolymers were produced via reaction of oligoether diols with TDI (NCO/OH=2.02) and PTMO with MDI (NCO/OH=2.2) while stirred at 60–70 °C for 6–8 h. The content of NCO groups in oligomers was determined using the ASTM D2572-80 standard method (Table 1).

Poly(urethane urea) samples with poly(propylene oxide) soft segments were produced by hardening the mix of respective prepolymer with MOCA. Prepolymers were previously stirred for 30 min at 60 °C under a vacuum (0.2 kPa).

Table 1 Prepolymers on the base of olygoetherdiols

Prepolymer	Molar ratios	M_n of olygoetherdiol	NCO (%)
POTT-1	PTMO/TDI=2.02	1,000	6.21±0.03
POTT-2	PTMO/TDI=2.02	1,380	4.83±0.03
POTT-3	PTMO/TDI=2.02	2,000	3.55±0.03
POTM-3	PTMO/MDI=2.2	2,000	3.95±0.02
POPT-1	PPO/TDI=2.02	1,000	6.26±0.04

Next, MOCA melt was added into reactor (production of samples without plasticizer). In the opposite case, solutions of this diamine into respective plasticizers were added. The mix of prepolymer and hardener was stirred for 3 min at 60 °C in vacuum and then cast into special molds of 2-mm thickness. Curing was carried out for 2 days at 90 °C. Conversion completeness of NCO groups was controlled using the FTIR spectroscopy method.

The synthesis of polyurethane with low content C_{h} of urethane urea segments differed in the preliminary preparation of the MOCA solution in PTMO (M_{n}=1,000 $\mathrm{g mol^{-1}}$) at 80 °C. Then, the prepared solution was added to the POTT-1 prepolymer (Table 1).

An SPU with urethane segments was produced using the POTM-3 prepolymer and BD under conditions discussed above.

In addition, a polyurethane elastomer without low-molecular-mass chain extender was prepared. The POTT-1 prepolymer was mixed with TMP solution in PTMO (M_{n}= 1,000 $\mathrm{g mol^{-1}}$) at 60 °C in vacuum. All samples were kept at room temperature for at least 20 days before tests.

Samples for FTIR spectroscopy (10- to 15-μm-thick films) were prepared by curing a reactionary mix without volatile solvents between glass plates at 90 °C. Glass plates were preliminary covered by polytetrafluorethylene 10-μm-thick films. Earlier, it was shown that this fluor-containing polymer did not influence the investigated area of carbonyl absorption spectrum (Amide I).

Methods

The glass temperature ($T_{\mathrm{g}}^{\mathrm{s}}$) of soft phase and melting temperature of crystalline part of the soft segments' matrix were determined by DSC method using the DSC 822$^{\mathrm{e}}$ calorimeter (Mettler Toledo) at a scanning rate of 0.08 $\mathrm{K s^{-1}}$; the softening temperature T_{h} of hard phase was determined by means of thermo-mechanical measurements using the SDTA 841$^{\mathrm{e}}$ device (Mettler Toledo) at the scanning rate of 0.05 K $\mathrm{s^{-1}}$ under load 0.015 MPa.

The density of the cured samples was determined by hydrostatic method using the OHAUS balance with an accuracy of 0.0001 g.

FTIR spectra in area of carbonyl valence vibrations (diapason of wave numbers ν=1,600–1,760 $\mathrm{cm^{-1}}$) of initial samples were recorded using the IFS-66/S spectrometer (Bruker, Germany) with spectral resolution 1 $\mathrm{cm^{-1}}$. For convenient comparison, spectral curves were normalized on the 1,600 $\mathrm{cm^{-1}}$ band typical for C–C valence vibrations of the aril ring.

IR spectra of samples' surfaces were registered by the multiple attenuated total reflectance (MATR) method using the IFS-66/S spectrometer and specially designed MATR accessories with 45° KRS-5 trapezoid as internal reflection element (operating number of reflections=1,000). Tests were conducted using samples cut according to crystal size 20×40 $\mathrm{mm^2}$, thickness 2 mm before and after stretching up to the given strain value. The 20×80 $\mathrm{mm^2}$ sheets were stretched, then samples for spectra registration were cut off from working parts of sheets.

Mechanical tests were conducted on the Instron 3365 universal stretching machine using the Standard Video-Extenziometer to reliably measure the strain values of samples. Tests were performed in υ=0.56–0.002 $\mathrm{s^{-1}}$ range at a constant rate, with stepwise variable load, according to a prescribed program with automatic rate switching. First, a sample was stretched at 0.056 $\mathrm{s^{-1}}$ up to ordered strain value. Then, stretching rate was automatically 10-fold increased and the sample was stretched up to complete disruption. Tensile strength σ_k (maximal stress value calculated for initial cross-sectional area of samples), relative critical strain value ε_k (%), and true tensile strength $f_r = \sigma_k \cdot \lambda_k$, where λ_k=(ε_k+100)/100 , were determined under various conditions.

The effective density of spatial network conditioned by hard segments' domains and by chemical cross-linkage $N_{\mathrm{d}x}$ was determined using the Cluff–Gladding–Pariser method [27] on equilibrium samples swollen in toluene which did not affect the hard domains [14, 15] and on samples swollen in TBP. Equilibrium swelling in TBP completely destroys the domain structure of polymers [15]. The total effective density $N_{\mathrm{d}x}$ of the network was calculated from results of equilibrium compression modulus values obtained under low strain values (up to 5%) for samples swollen in toluene to equilibrium state. The effective density N_x of the chemical network was calculated from results for samples swollen in TBP to equilibrium state. Thus, the value of network density conditioned by hard domains was $N_{\mathrm{d}} = N_{\mathrm{d}x} - N_x$.

Characteristics of materials

Experiments were carried out on samples of two-phase poly (urethane urea)s with hard segments' concentration 9–38% (PUU-1–PUU-3, PUE-1, PUUP-1 without plasticizer, PUUP-1D with 20 wt.%. DEHP, PUUP-1T with 20% wt. TBP) and PU-3 polyurethane (molecular mass of soft polyether segments was 1,000, 1,380, and 2,000 $\mathrm{g mol^{-1}}$, respectively). The PUE-2 polyurethane was prepared using oligomeric diol and triol. This polymer was supposed to be a single-phase one. Five out of nine materials under investigation had been thermoplastics soluble in TBP and dioxane. Three elastomers, namely, PUE-1, PU-3, PUUP-1T (Table 2), had low density N_x of chemical network.

Physical cross-linking points of specific spatial network of materials under investigation are hard segments domains ($N_{\mathrm{d}x} = N_{\mathrm{d}}$) or predominantly hard domains ($NN_{\mathrm{d}x} >> N_x$), as is apparent from $N_{\mathrm{d}x}$ values. An exception is the PUE-2 cross-linked polyurethane with high effective chemical

Table 2 Properties of investigated polyurethanes and polyurethane ureas

Sample	Molar ratios	C_h (%)	ρ (g cm^{-3})	N_{dx} (10^{-3} mol cm^{-3})	N_x (10^{-3} mol cm^{-3})	T_g^s (°C)	T_h (°C)
PUU-1	POTT-1/MOCA=0.98:1.00	38	1.131	1.77	0	−50	204
PUU-2	POTT-2/MOCA=0.98:1.00	31	1.112	1.37	0	−64	204
PUU-3	POTT-3/MOCA=0.98:1.00	24	1.085	0.77	0	−72	205
PU-3	POTM-3/BD=1.04:1.00	24	1.063	0.56	0.02	−65	170
PUE-1	POTT-1/OTD-1/MOCA=1.02:0.7:0.3	9	1.064	0.19	0.01	−56	182
PUE-2	POTT-1/OTD-1/TMP=1.14:0.7:0.3	–	1.038	0.15	0.15	−63	–
PUUP-1	POPT-1/MOCA=0.98:1.00	38	1.153	1.30	0	−10	184
PUUP-1D	POPT-1/MOCA=0.98:1.00	38^a	1.113	1.36	0	−40	183
PUUP-1T	POPT-1/MOCA=1.03:1.00	38^a	1.111	0.73	0.03	−29	142

network density $N_x=1.5\times10^{-4}$ mol cm^{-3} and N_{dx}. The N_{dx} value decreases with the decrease in concentration of urethane urea hard segments in materials with poly(tetramethylene oxide) soft segments (PUU-1–PUU-3, PUE-1).

As evidenced by the comparison of DSC curves, heating of samples with molecular mass of soft segments 2,000 g mol^{-1} and preliminarily cooled down to −130 °C leads to partial crystallization of poly(tetramethylene oxide) soft segments with subsequent melting. Melting peak was observed at 8 °C for PU-3 and at 6 °C for PUU-3, melting diapason was −8.8÷8 °C and −12.6÷6 °C, respectively (Fig. 1a). Soft phase of PUU samples does not crystallize at M_n of poly(tetramethylene oxide) soft segments equaling to 1,380 or 1,000 gmol^{-1}, as is the case for soft phase of PUUP samples with poly (propylene oxide) soft segments (Fig. 1b).

The presence of characteristic bands in the carbonyl area of the FTIR spectrum of the investigated elastomers enables us to recognize important features of their structural organization and their influence on the properties of the said polymers.

The position of absorption bands for carbonyl in FTIR spectra of poly(urethane urea)s and polyurethanes can be shifted to some extent for compositions with various diisocyanates, diamines and low-molecular-mass diols. Identification of C=O absorption bands was made using the results of spectral investigations of real and model compositions with urethane urea and urethane groups [12, 18, 28–33]. The band at wave number $\nu=1{,}640$ cm^{-1} relates to the absorption of ordered hydrogen-bonded urea carbonyl [18, 29, 30, 32]. Urea groups are bonded by H bonds (self-associates of urea-groups) and localized in hard segments domains. The intensity of this band can be used for comparative evaluation of micro-phase separation degree of hard and soft domains [18, 34]. The band at 1,692–1,693 cm^{-1} in spectra of poly(urethane urea) can be related to the absorption of hydrogen-bonded ordered C=O urethane and of free urea carbonyl [28–30]. The band at 1,698 cm^{-1} selected on model compositions and appropriate for hydrogen bonding between urethane carbonyl and N–H group of urea [29] does not appear in FTIR spectra of poly(urethane urea)s under investigation (Figs. 2 and 3).

In the FTIR spectrum of PU-3 SPU, the band at 1,703 cm^{-1} is related to the absorption of hydrogen-bonded, ordered

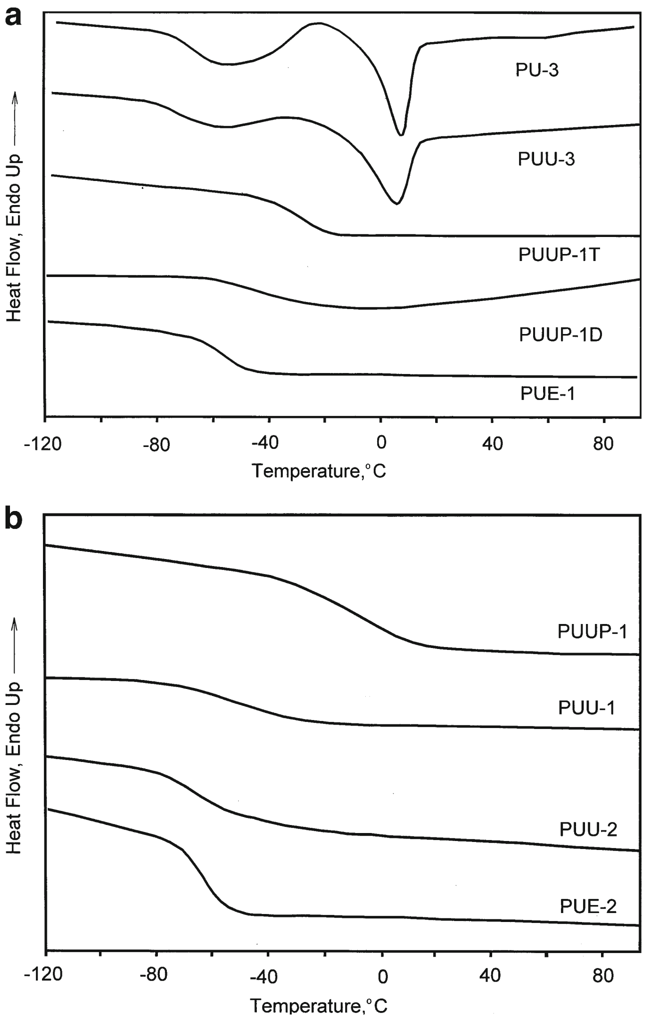

Fig. 1 DSC curves for polyurethanes and poly(urethane urea)s

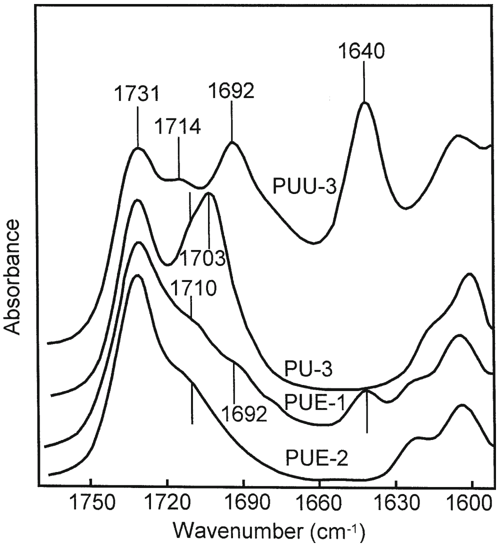

Fig. 2 FTIR spectra for polyurethanes and poly(urethane urea)s

urethane carbonyl (C=O associated [31, 34]) localized in hard phase of polymer. The band at 1,729–1,731 cm^{-1} is related to the absorption of free urethane carbonyl, and the band at 1,710–1,711 cm^{-1} is related to absorption of hydrogen-bonded urethane carbonyl in the soft phase of the polymer [18, 28, 29]. The band at 1,666 cm^{-1} is related to the absorption of the hydrogen-bonded, disordered urea carbonyl [28]. This band appears, e.g., in the FTIR spectra of poly(urethane urea) with poly(propylene oxide) soft segments (Fig. 3).

Significant differences in the structure organization of materials under investigation after analysis of FTIR spectra (Figs. 2 and 3) can be highlighted. There are two absorption bands of carbonyl or urethane groups at 1,730 and 1,731 cm^{-1}. The band at 1,703 cm^{-1} is not observable. This indicates the absence of hard phase in the material, thus corresponding to existing ideas on single-phase structure of such polyurethanes [1, 35]. Partial micro-phase separation of hard and soft segments is observed at low content of MOCA mixed with oligoether diol. Intensity of carbonyl absorption band at 1,640 cm^{-1} in the FTIR spectrum of PUE-1 is low. Intensity of bands at 1,692 and 1,640 cm^{-1} increases significantly on curing prepolymer based on oligo(tetramethylene oxide) diol with terminal NCO groups by solely MOCA (PUU-1, PUU-3). Accordingly, the network density $N_{dx} = N_x$ increases many times, with the softening temperature T_h of hard phase increasing by 23 °C (Table 2), thus indicating more ordered domain structure. The T_h value for poly(tetramethylene oxide urethane urea) practically does not depend on molecular mass of oligoether segments.

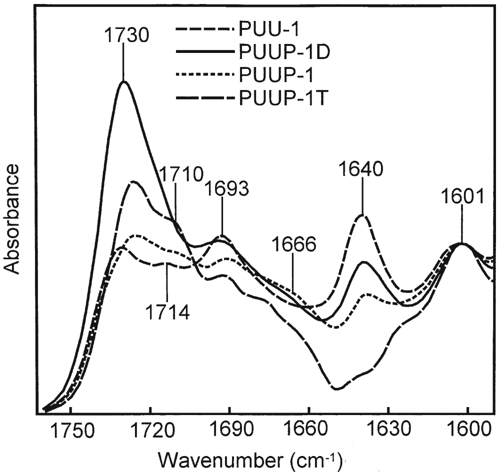

Fig. 3 FTIR spectra for initial poly(urethane urea)s and plasticized ones

Earlier, we had shown that the degree of micro-phase separation of hard and soft segments in poly(urethane urea) with poly(propylene oxide) soft segments PUUP-1 (M_n~1,000 gmol^{-1}) is 3-fold lower than that of poly (tetramethylene oxide urethane urea) PUU-1[34]. The presence of a large quantity of urethane urea segments in soft phase (the band at 1,666 cm^{-1}) leads to the increase in glassing temperature.

As evidenced by comparison of FTIR spectra (Fig. 3) of non-plasticized sample (PUUP-1) and plasticized ones of poly(urethane urea) (PUUP-1T, PUUP-1D), the intensity of band at 1,640 cm^{-1} decreases significantly in the presence of 20% TBP (a solvent for hard segments). The decrease in glass temperature T_g^s of the soft phase of a polymer is accompanied by the decrease in softening temperature T_h of the hard phase by 40 °C (Table 2). Hence, plasticization takes place not only in the soft phase but also in the hard phase. Plasticization of hard phase results in partial disruption of interchain hydrogen bonds.

Evaluation of effective density N_{dx} of the spatial network of PUUP-1T in this case is insufficiently correct. The swelling of plasticized poly(urethane urea) in toluene leads to the transfer of TBP from hard and soft phases into toluene, thus leading to modification of the material's structure. In this case, the N_{dx} value can be overestimated.

Replacement of TBP by 20% DEHP in composition of poly(propylene oxide urethane urea) (PUUP-1D) leads to a significant decrease in the glass temperature of polymer's soft phase (Fig. 1a, Table 2). The DEHP plasticizer with higher glass temperature (−89 °C) influences glass temperature of soft the phase of polymer more than TBP does with lower glass temperature (−131 °C). The reason for this effect is the decrease in solubility of hard segments with high glass temperature in the soft phase of poly(urethane urea) in the presence of DEHP that is distinctly evidenced by the increase in intensity of the band at 1,640 cm^{-1} in FTIR spectrum of poly(propylene oxide urethane urea).

The softening temperature of hard phase of poly(urethane urea) does not vary on addition of DEHP. Hence, plasticizer is localized in the soft phase of the polymer. Spatial network density of material on plasticization does not decrease (Table 2).

Thus, synthesized elastomers vary greatly in structural organization. This allows revealing of regularities and features of the influence of structural factors on the mechanical behavior of various types of polyurethanes in a wide range of strain rates.

Materials for the study were chosen so that there were elastomers among them, which changes in morphology at different strains (PU-3 and PUU-3), had already been studied in detail [20] and therefore do not require repetition.

Results and discussion

Typical strain–stress plots for poly(tetramethylene oxide urethane urea) (PUU-2) at various temperatures and stretching rates are represented in Fig. 4. Diagrams have been plotted in conventional σ–ε coordinates, where ε stands for relative strain (%) and σ stands for stress calculated on the initial cross-sectional area of a sample.

Results of mechanical tests for poly(urethane urea) at 25 °C show the unusual influence of stretching rate on the engineering tensile strength σ_k of a material. The least value of tensile strength σ_k of poly(urethane urea) was reached at a high stretching rate. Triplicate deceleration of stretching leads to a significant increase in tensile strength of material. At that, relative critical strain value does not alter much. Strengthening of elastomer at the last stages of strain is most distinctly marked out at low rates and at 25 °C. The increase in temperature up to 90 °C or its decrease to −20 °C leads to intensive decrease in strengthening of elastomer under high strains. The same regularity will be observed in f_r–ε coordinates (true strength–strain).

The dependence true strength of poly(tetramethylene oxide urethane urea) versus ln$v$ is consistent in the given range of v values at −20 °C, but it has extremum at positive temperatures (Fig. 5). The increase in temperature leads to the shift of strength extremum position towards the increase in strain rate i.e., decrease in values of −ln(v, s^{-1}). The K_f ratio (maximum strength at any rate: strength value at v= 0.56 s^{-1}; ln v=−0.58) allows us to evaluate the maximal degree of strength increase of polymer while decreasing the stretching rate at various temperatures. The obtained results show that true strength at −20 °C depends strongly on the stretching rate (K_f=2.1). This dependence weakens significantly upon heating the poly(urethane urea) up to 90 °C (K_f=1.3).

Mechanical tests of variously structured materials at 25 °C have shown that significant increase in strength upon decreasing the stretching rate was observed in the range 0.56–0.028 s^{-1} (ln v from −0.58 to −3.57) for PU-3 segmented polyurethane and poly(urethane urea)s PUU-1–PUU-3 with various molecular mass of soft segments (1,000, 1,380 and 2,000 gmol^{-1}). Significant reduction of strength at v> 0.056 s^{-1} (ln v<−2.88) was typical for PUE-1 compositions with a low concentration of hard segments (9%). True strength of single-phase polyurethane decreases monotonically on increasing the stretching rate (Figs. 5 and 6).

Plasticization of poly(propylene oxide urethane urea) by TBP leads to radical variation in the material's mechanical behavior. The true strength of the PUUP-1T poly(urethane urea) in the range 0.56–0.003 s^{-1} decreases approximately 8-fold. The true strength of PUUP-1D with 20% DEHP alters little under the same conditions (Fig. 7).

Thus, various types of dependence of strength f_r on the stretching rates for a whole class of polyurethanes have been revealed while using a wide range of this investigation's objects: a monotonic dependence with significant increase in strength, extreme one with predominant effect of increase in strength, extreme one with weak effect of increase in

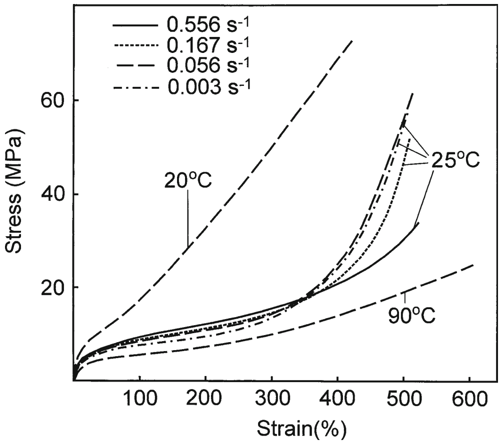

Fig. 4 Stress–strain plots for poly(urethane urea) PUU-2 under various temperatures and stretching rates

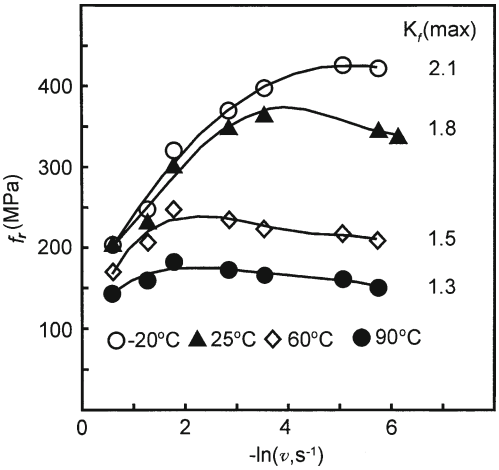

Fig. 5 Influence of temperature on the dependence of true tensile strength versus stretching rate for PUU-2

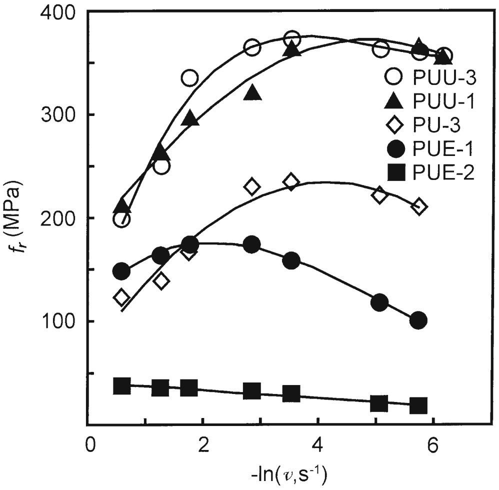

Fig. 6 Dependence of true tensile strength of polyurethanes and poly (urethane urea)s on the stretching rate at 25 °C

strength, and monotonic one with various degrees of decrease in strength on decreasing the stretching rate.

Evaluation of the effective network parameters of polyurethane compositions shows that the network density $N_{dx} = N_x$ of the PUE-2 single-phase polyurethane does not vary on stretching up to disruption. Analogous results were obtained for the PUUP-1T poly(urethane urea) plasticized by TBP. The relative critical strain ε_k of these materials decreases the stretching rate is decreased.

The effective network density N_{dx} of other compositions decreases when decreasing the stretching rates up to disruption. The ε_k value alters little (Table 3). It was shown above that $N_{dx} = N_x$ for thermoplastics, $N_{dx} >> N_x$ for materials with sparse chemical network PU-3, PUE-1 (Table 2).

It has been proven earlier that effective network parameters of polyurethane practically do not vary for a long period after mechanical tests (up to 30 days) at 25 °C [36]. This has allowed us to ascertain the dependence of effective molecular mass of elastically active chains between network cross-linking points ($M_{dx} = \rho N_{dx}^{-1}$) of materials under investigation versus strain values for samples swollen in toluene up to equilibrium.

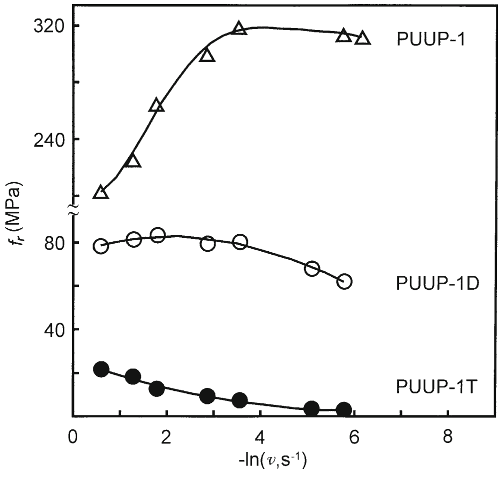

Fig. 7 Influence of plasticizers on the true tensile strength of poly (urethane urea) under various stretching rates

As evidenced by curves in Fig. 8, the M_{dx} value differs little from its initial value under strain up to 200%. The effective molecular mass M_{dx} of elastically active chains increases under large strains (>350%). Accordingly, the effective network density decreases, thus indicating the partial destruction of the domain structure of the elastomer. The M_{dx} value at disruption of elastomer exceeds the M_n value of polyether segments. It has turned out that the effective network parameters of segmented polyurethane and poly (urethane urea) do not really depend on stretching rate in the given range of this parameter (Fig. 8, Table 3). Thus, the disruption degree of the physical network is approximately the same at various rates due to the availability of hard domains.

Differences in spectra of initial poly(urethane urea) samples and samples after stretching up to 400% at v=0.56 and 0.056 s^{-1} were revealed using the FTIR–MATR method. Strain leads to significantly decrease in intensity of absorption band at 1,643 cm^{-1} of hydrogen-bonded, ordered urea carbonyl in hard phase of polymer. The absorption band at 1,666 cm^{-1} is distinctly apparent and relates to the hydrogen-bonded, disordered urea carbonyl [29] in soft the phase of the material. The band at 1,776 cm^{-1} relates to carbonyl absorption in soft phase of block copolymer as well (Fig. 9).

This redistribution of band intensities in FTIR–MATR spectrum indicates partial disruption of poly(urethane urea)'s domain structure. Under large strain values, a part of urethane urea segments passes on from hard domains into soft phase of material, thus strengthening the interchain interaction in this phase including the hydrogen bonds' formation.

Qualitative analysis of FTIR–MATR spectra of PU-3 SPU before strain and after stretching up to 500% shows that strain leads to redistribution of carbonyl absorption bands' intensity. The intensity of carbonyl absorption bands at 1,731 and 1,710 cm^{-1} in soft phase increases (Fig. 10). Obtained results are consistent with results of investigation in strain influence on spatial network of polyurethane and poly(urethane urea) (Table 3, Fig. 8). Partial disruption of spatial network in these materials is due to the decrease in hard phase content under large strains.

Some important aspects and reasons for diversity in polyurethane materials' mechanical behavior under various conditions of strain can be emphasized using the results of previous studies and modern ideas on variations in structure of heterogeneous block copolymers under mechanical load.

Table 3 Values of relative critical strain and network dense for elastomers at stretching up to failure

v (10^2 s^{-1})	N_{dx} (10^{-3} mol cm^{-3})							ε_k (%)						
	PUU-3	PUU-1	PUE-1	PUE-2	PUUP-1	PUUP-1D	PUUP-1T	PUU-3	PUU-1	PUE-1	PUE-2	PUUP-1	PUUP-1D	PUUP-1T
0	0.77	1.77	0.19	0.15	1.30	1.36	0.73	0	0	0	0	0	0	0
55.6	0.38	1.23	0.12	0.15	1.12	1.09	0.73	619	486	795	410	536	625	682
27.7	0.40	1.23	0.12	0.15	1.10	1.09	0.71	615	494	786	406	537	628	650
16.7	0.39	1.24	0.12	0.15	1.12	1.09	0.74	590	476	800	408	526	634	605
5.6	0.38	1.28	0.12	0.15	1.11	1.11	0.71	594	472	770	386	514	627	578
2.8	0.40	1.2	0.11	0.15	1.09	1.09	0.73	588	479	798	375	510	630	471
0.6	0.39	–	0.11	0.15	–	1.12	0.72	600	–	798	347	–	645	390
0.3	0.40	1.28	0.11	0.15	1.12	1.13	0.73	606	492	840	330	511	660	358
0.2	0.38	1.24	–	–	1.13	–	–	605	483	–	–	517	–	–

Investigations on the morphological reorganization of segmented polyurethane and poly(urethane urea)s during stretching (including structurally similar PU-3 and PUU-3 samples) have shown that large (400–600%) strain values lead to orientation of hard segments in domains predominantly along the direction of stretching [18, 20]. Micro-fibril morphology forms as large strain values develop. During partial crystallization of soft segments, micro-fibrils consist of parallel hard and soft segments with small hard nano-sized domains [20]. Hard domains' micro-fibrils form in the absence of crystallization or on low-degree crystallization of soft phase. Such reorganization contributes to the significant strengthening of block copolymer at last stages of strain.

Attention should be drawn to the fact that alterations in morphology of variously strained PU and PUU samples have been studied under fixed relative strain values (microscopy, X-ray measurements) and at low stretching rates (FTIR spectroscopy). For example, FTIR-polarization spectra in [18] were obtained at ~100% min^{-1} rate and at 4 cm^{-1} resolution. In our tests, the highest stretching rate was 3,300% min^{-1}. Under these conditions, it was problematic to produce correct spectral data.

The orientation of hard segments depends not only on the stretching but on time, too [1]. It is reasonable to assume that such a rate value can be found at which hard domains or a part thereof would have no time to become orientated in the line of applied force. Consequently, the tensile strength of the segmented material decreases as the stretching rate increases. After orientation of hard segments in domains under low-rate strain, the following high-rate strain should lead to increased strength of the material as opposed to test conditions at uniform high stretching rate; this phenomenon was actually observed in our experiment (Fig. 11).

Significant strengthening of segmented poly(urethane urea) takes place after its stretching to high strain values (ε=450%) at the rate 0.056 s^{-1} and after following high-rate

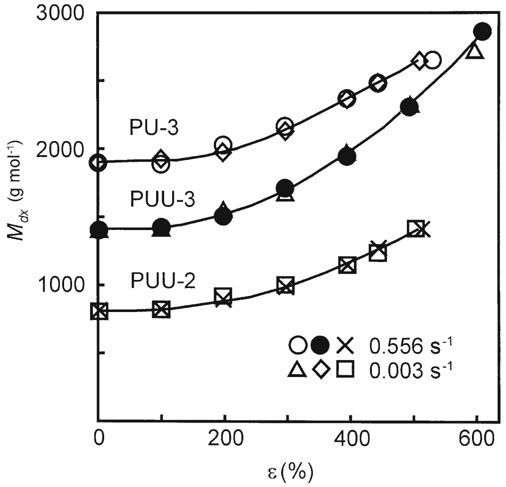

Fig. 8 Dependence of effective network parameter M_{dx} on the relative strain of elastomer.

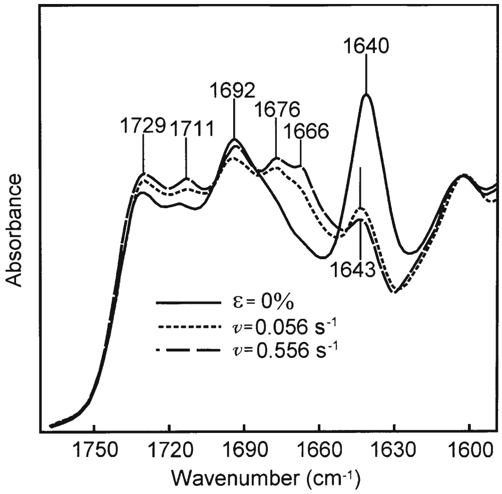

Fig. 9 FTIR–MATR spectra of PUU-1 for initial sample, and for one after stretching to ε=400%

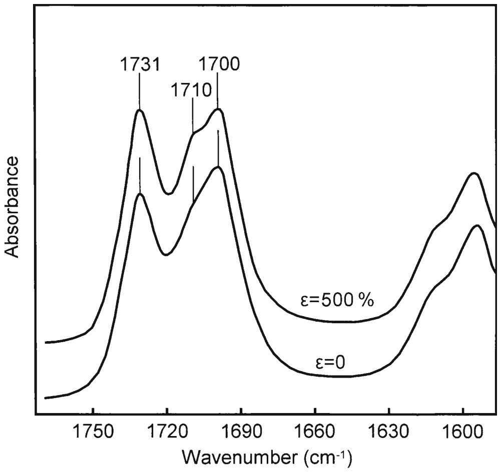

Fig. 10 FTIR–MATR spectra of PU-3 for initial sample, and for one after stretching to ε=500% with v=0.556 s^{-1}

stretching up to disruption (v=0.56 s^{-1}). This effect is weakly marked out at relative strain value 200–300%, at first stage of strain (v=0.056 s^{-1}). Similar results were obtained for PU-3 samples with urethane hard segments. According to the model [20] proposed and proven by experimental data, orientation scope of hard and soft segments in the line of stretching direction is little.

Another important factor influencing strength of elastomer is interchain interaction in the soft phase of elastomer. As a result of relaxation processes during the material's stretching, the more the quantity of loaded interchain linkages (including hydrogen bonds) decreases, the lower is the stretching rate [16]. For this reason, true strength of single-phase polyurethanes with labile physical network should significantly decrease at decelerated stretching as is observed in tests of PUE-2 samples (Fig. 6). The same trend also prevails in certain intervals of stretching rate values for PUE-1 polyurethane with low content of hard segments (9%).

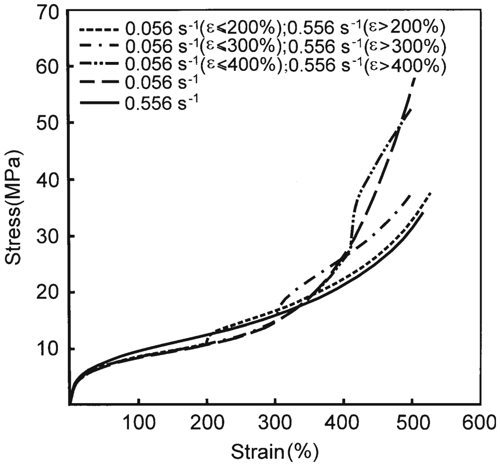

Fig. 11 Stress–strain plots for stepwise stretching of poly(urethane urea) PUU-2

The extreme character of dependence of f_r values on v values for segmented polyurethanes and poly(urethane urea)s is due to superposition of two factors: the increase in orientation degree of hard segments under high strain values on decreasing the stretching rate and the decrease in density of labile physical network in soft matrix. The decrease in density of this network is compensated to some extent by additional increase in interchain interaction value in the soft matrix as a result of the partial disruption of the hard phase during high stretching (Figs. 9 and 10).

Investigations performed at 75 °C and at room temperature have ascertained that the increase in temperature results in the earlier appearance of positive orientation of hard segments [1]. Reduction of time necessary for hard segments' orientation results in the shift of strength maximum on $f_r = f(\upsilon)$ curves towards higher strain rates (Fig. 5). The rise of temperature results in considerable decrease in labile physical network's density [16]. The effect of segmented elastomer's strengthening at 90 °C due to orientation of hard segments is weakened by the negative influence of disruption of labile interchain linkages' network under action not only of decelerated stretching but also of increased temperature.

During plasticization of soft and hard phases of poly(urethane urea) (PUUP-1T), the increase in hard segments' solubility in soft phase of polymer in the presence of TBP leads to strongly pronounced decline of material's strength at decreased stretching rate (Fig. 7). In case of plasticization of soft phase only (PUUP-1D sample), material's strength depends weakly on the stretching rate. Micro-phase segregation degree of hard and soft segments increases in the presence of DEHP (Fig. 3). However, the effect of significantly increased polymer's strength depending on the decrease in stretching rate υ is not observed as opposed to the mechanical behavior of non-plasticized material. The obtained data indicate a considerable influence of soft phase plasticization on the character of true strength's variations in segmented polymer as the stretching rate decreases. This phenomenon will be studied in detail later.

Partial crystallization of soft segments with M_n=2,000 g mol^{-1} content of poly(tetramethylene oxide) urethane urea under conditions of stretching at room temperature has been described by Christenson et al. [20]. Tests of similar PUU-3 poly(urethane urea) and PUUP-1, PUU-1 elastomers with non-crystallizing soft segments did not reveal significant differences in the character of dependence of these materials' strength versus stretching rates.

Conclusions

In this investigation, the direction and degree of variations in strength and strain properties of polyurethanes and poly (urethane urea)s differing in hard segments' concentration, molecular mass of soft segments, degree of micro-phase segregation and spatial network density have been compared in a wide range of stretching rates.

This comparison has allowed us to reveal following types of dependencies of strength versus stretching rates for the class of polyurethanes: monotonic dependence with significant increase in strength at lowered stretching rates, an extreme one with weakly and strongly pronounced effect of the increase in strength, and a monotonic one with a different degree of decrease in strength at stretching rates in the range 0.56–0.002 s^{-1}.

The relative critical strain of heterogeneous elastomers alters weakly in the absence of plasticizers dissolving hard segments. The increase in temperature contributes to the weakening of the dependence of strength on stretching rates for segmented elastomers with micro-phase segregation. Single-phase cross-linked polyurethane is characterized by the decrease in strength and strain properties depending on the decrease in stretching rate. Solvation of hard and soft phases and the increase in solubility of hard segments in the presence of plasticizer lead to a strong decline in strength of segmented poly(urethane urea) as the stretching rate decreases. The critical strain value at a material's disruption decreases as well.

Results of investigations have shown that the effective density of segmented elastomers' network, cross-linking point of which are mainly hard domains, significantly decreases under high strains. Accordingly, effective molecular mass of flexible chains between network cross-linking points increases (at $\varepsilon>350\%$). It has been ascertained using the FTIR–MATR method that partial destruction of the physical network with hard domains playing a role of cross-linking points is related to the decrease in the content of hard phase in polyurethanes and poly(urethane urea)s under large strain values.

Data on morphology of segmented polyurethanes and poly(urethane urea)s under various strains, our earlier data on effect of temperature and stretching rate on density of labile physical network outside hard segments' domains as well as results of investigations represented in this paper have enabled us to reveal the structural factors significantly influencing the character and degree of variations in strength of this class of polymers; these include the following: orientation of hard segments in the stretching direction under high strain values (400–600%); the decrease in density of the physical labile network in soft phase depending on the decrease in stretching rate or on the increase in temperature; the increase in interchain interaction in soft phase as a result of partial destruction of hard phase of segmented polymer under high strains; solvation of soft phase and dissolution of hard phase in the presence of plasticizer.

The increase in orientation degree of hard segments at decelerated stretching rate contributes to the strengthening of elastomers at last strain stages thereof. The increase in interchain interaction in the soft phase under high strains on account of a part of hard segments' transfer from hard phase into soft phase partially compensates for the negative effect of the decrease in density of the labile physical network under conditions of decelerated stretching on the material's strength. The remaining structural factors contribute to the decrease in strength of polyurethanes and poly(urethane urea)s at decelerated stretching rates. The rxtreme character of dependence of strength on the stretching rate of elastomers with micro-phase segregation is related to superposition of structural factors oppositely affecting material's strength.

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