Polyurethane Elastomers Made from Linear Polybutadiene Diols

MILENA ŠPÍRKOVÁ*

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

ABSTRACT: Segmented polyurethane elastomers made from linear polybutadiene diols terminated with primary (Krasol LBH-P) or secondary (Krasol LBH) hydroxy groups, alicyclic diisocyanate, and aliphatic chain extender were prepared and tested. The system was chemically crosslinked either through isocyanurate, that is, hexahydro-1,3,5-triazine-2,4,6-trione groups (formed by catalyzed cyclotrimerization of isocyanate groups), or by low molecular weight triols. The best balance of stress–strain properties and reasonable thermal stability was obtained for systems in which only a small amount of chemical crosslinks was present in predominantly physically crosslinked networks. The influence of the type of polymer diol, chemical crosslinking, diisocyanate, and technique of preparation on mechanical, thermal, and swelling properties is discussed. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 84–91, 2002

Key words: polyurethanes; polybutadiene diol; isocyanurate groups; mechanical properties; networks; crosslinking

INTRODUCTION

Polybutadiene-based polyurethanes (PBd-PURs) are important industrial polymeric materials. The range of their application has been growing rapidly because of their water-resistant properties (hydrolytic stability, low moisture permeability), good low-temperature characteristics, insulation properties, high elasticity, and superior chemical resistance.[1–4] It was found that PBd-PUR elastomers exhibit outstanding resistance to aggressive aqueous media (acidic and alkaline solutions) as well.[5]

Products of Kaučuk, a.s., Czech Republic are polybutadiene diols containing primary or secondary hydroxy groups marketed under the trademarks Krasol LBH-P and Krasol LBH. They are prepared by a special anionic polymerization technology and differ from most commercially available (radical-polymerized) polybutadiene diols by a narrow molecular weight distribution, purely linear chains with average OH functionality close to but below 2.0. Krasol LBH diols can thus be advantageously used for the manufacture of various isocyanate-terminated polybutadiene prepolymers with good storage stability. The prepolymers can be applied as high-quality binders for waste rubber crumb (e.g., from disposed tires) or in diamine-cured cast elastomers.[6] Krasol LBH-P, which contains more reactive primary hydroxy end groups (compared to the secondary hydroxy end groups of Krasol LBH), offers the possibility of preparing PUR by a simpler, one-step technique.

We recently tested PUR elastomer systems composed of Krasol LBH, aromatic diisocyanates [mixtures of toluene 2,4- and 2,6-diisocyanate (Desmodur T 80) or diphenylmethane 2,4'- and 4,4'-diisocyanate (Baymidur KL 3–5002)], and 2-ethylhexane-1,3-diol as a chain extender.[7] The

influence of the type and amount of crosslink sites on mechanical, thermal, and swelling properties was studied and the microphase structure of the elastomers was examined by small-angle X-ray scattering (SAXS). Two series of PUR elastomers at a constant hard segment content (by the two-step prepolymerization procedure) were prepared. The nature of crosslink sites varied from purely physical to purely chemical, including the so-called combined crosslinks. The physical crosslinking was achieved by addition of a low molecular weight diol, whereas the chemical crosslink sites were built by *in situ* cyclotrimerization (CT) of isocyanate groups catalyzed with an organic salt.

The best balance between stress at break and strain at break was achieved for networks in which the physical junction points strongly predominate over the chemical crosslinks. These systems also exhibit improved thermal stability, compared with those based on physical networks only. SAXS measurements confirmed the two-phase structure with the periodicity of 6–8 nm.

This contribution extends the knowledge concerning PBd-PUR industrial products. We studied the structural–functional properties relationship for products made from linear polybutadiene diols and an alicyclic diisocyanate. Influences of (1) the type of chemical crosslinking (with triols or isocyanurate groups), (2) the type of the OH groups of the polymer diol (primary, secondary), and (3) the way of preparation (one- or two-step processes) on thermal, mechanical, and swelling properties are tested and discussed.

EXPERIMENTAL

Materials

α,ω-Di(2-hydroxypropyl)-polybutadiene [Krasol LBH 2000 (LBH)] and α,ω-di(2-hydroxyethyl)-polybutadiene [Krasol LBH-P 2000 (LBH-P)] are products of Kaučuk Kralupy, a.s. (Czech Republic). They differ in the type of hydroxy end groups. Batches of both diols were chosen such that they had similar molecular parameters (all the data were kindly provided by the supplier): for LBH and LBH-P, respectively, number-average molecular weight (M_n) values of 2100 and 2097; weight-average to number-average molecular weight (M_w/M_n) ratios of 1.23 and 1.16; number-average functionalities (f_n) of 1.94 [f_2 (94.1%); f_1 (5.5%); f_0 (0.4%)] and 1.88 [f_2 (89.4%); f_1 (9.7%); f_0 (0.9%)]; and concentration of secondary OH 0.9 mequiv/g

and primary OH groups 0.89 mequiv/g. (The values of f_2 and f_1 represent the fractions of bifunctional and monofunctional oligomers and values of f_0 are the fractions of polybutadiene chains without functional, that is, hydroxy groups.) The same isomer content ($\sim$ 60 wt % of 1,2-*cis*, 15 wt % of 1,4-*cis*, and 25 wt % of 1,4-*trans*) was found in both cases. Before use, the polymer diols were dried *in vacuo* at 50°C to achieve the water content < 0.03 wt %.

The chain extender 2-ethylhexane-1,3-diol (EHD; Degussa-Hüls, Germany), as well as low molecular weight triols 1,1′,1″-nitrilotripropan-2-ol [triisopropanolamine (TIPA); Degussa-Hüls, Germany] and glycerol (GLY; Lachema, Brno, Czech Republic) were dried *in vacuo* to reach a moisture content < 0.005 wt %.

5-Isocyanatomethyl-3,3,5-trimethyl-cyclohexyl isocyanate [isophorone diisocyanate (IPDI); Fluka Chemie, Buchs, Switzerland] was used as received; the content of isocyanate groups found was 99.1% that of theory.

Dibutyltin dilaurate (DBTDL; Fluka Chemie) was used as a catalyst for the reaction of hydroxy groups with isocyanates ("urethane" catalyst); potassium 2-ethylhexanoate [DABCO K15 catalyst (K15); Air Products and Chemical, Inc., USA] was used to form isocyanurate groups[8,9] ("cyclotrimerization" catalyst).

n-Heptane, xylene (Lachema), and 1,4-dioxane (Penta, Czech Republic), all analytical grade, were used as received. Standard testing oils STO1 to STO3 (the details are given in ČSN ISO 1817) are identical to reference oils 1, 2, and 3, according to ASTM D 471. They are defined mixtures of oils differing in the swelling power (STO1 should cause "little" swelling, whereas STO3 causes "great" swelling).

Sample Preparation

The details of reaction condition optimization are published elsewhere.[7,10]

Samples were prepared by one-step (LBH-P products) or two-step prepolymerization (LBH products) techniques. A soft-segment content, that is, the content of polymer diol (65 wt %) was kept constant in the preparation of all PUR samples. The ratio of the concentration of NCO and total OH groups, $r = [NCO]/[OH]_{total}$, varied in the case of isocyanurate-cured samples. It was kept constant for the triol-cured samples; $r = 1.05$ for Krasol LBH-P products.

One-Step Technique

Polymer diol (LBH-P), chain extender, triol, and catalyst (DBTDL) were mixed at laboratory temperature under nitrogen. The diisocyanate was added as the last component immediately before degassing the reaction mixture. The networks were prepared in Teflon molds at 90°C for 24 h and at 130°C for 1 h.

Two-Step (Prepolymerization) Technique

In the first step, the isocyanate-terminated prepolymer was made from the diisocyanate and LBH in the presence of DBTDL (0.006 wt %) by mixing at 25°C under nitrogen. The reaction mixture was degassed and left to react at 60°C for 2 h.

In the second step, the prepolymer was mixed with a chain extender and triol at 25°C under nitrogen and degassed. When isocyanurate-cured, chemical, and "combined" networks were to be prepared, the cyclotrimerization catalyst K15 (0.18 wt %) was added after 15-min homogenization of all substances. The networks were prepared in Teflon molds by the following sequence of heating: at 25°C for 3 h, then 90°C for 24 h, and finally at 130°C for 1 h in the case of isocyanurate curing, or at 90°C for 24 h and at 130°C for 1 h in the other cases.

Test Conditions

Ultimate mechanical properties were measured on an Instron model 6025 (Instron Limited, England). Specimens (25 × 4 × 1.5 mm) were tested at room temperature and a test speed of 0.33 mm/s. All presented values are averages from five specimens.

Dynamic mechanical properties were studied using a Rheometrics System Four apparatus (Rheometrics, Inc., USA). Rectangular samples (45 × 10 × 1.5 mm) were measured by oscillatory shear deformation at a constant frequency 1 Hz and the rate of heating 3°C/min to obtain temperature dependencies of storage and loss shear moduli (G' and G'', respectively) in the range from −70 to 280°C (or to the temperature of softening).

For swelling measurements, PUR networks were swollen at room temperature in n-heptane, 1,4-dioxane (LBH and LBH-P products), xylene, and standard testing oils (LBH-P products) until equilibrium was established. Extracts were determined after drying the swollen samples to constant weight.

RESULTS AND DISCUSSION

Two series of PUR samples were prepared and tested. The composition and properties of the two-step products (LBH products) are listed in Table Ia and Table Ib, whereas those of the one-step products (LBH-P products) are given in Table IIa and Table IIb. According to the type of network, the samples may be classified as follows: (1) systems containing only physical crosslinks (physical networks, samples 1 and 13); (2) samples containing only chemical crosslinks (chemical networks, samples 2–4 and 14–15); and (3) products with both chemical and physical crosslinks ("combined" networks, samples 5–12 and 16–21).

All polyurethane products made from IPDI exhibited good optical homogeneity; they were either transparent (1–14, 16–19) or opalescent (15, 20, and 21).

Composition

The main possible reactions occurring during PUR preparation are summarized in Scheme I of the previous report.[7]

The completion of both the hydroxy–isocyanate reaction and the isocyanurate formation was verified by FTIR analysis (at 2270 cm^{-1}) for samples 7, 9, and 18. Although sample 9 did not contain isocyanate groups at all, samples 7 and 18 included traces of isocyanates. On the other hand, the final contents of groups did not extend 1% of their initial concentration. It is then possible to consider the isocyanate reactions as complete.

The concentration of trifunctional chemical crosslinks (isocyanurate groups or triol junctions) C was estimated under the following simplifying assumptions: (1) the reaction of hydroxy with isocyanate groups is complete and (2) excess isocyanate groups react quantitatively, to yield the cyclic trimer in the case of isocyanurate curing.

Relations $C = c_T/3$ and $C = c_I(r - 1)/3r$ hold for the systems crosslinked with triols and for the systems crosslinked with isocyanurates, respectively. Here, c_T is the initial concentration of triol (mol/m^3) and c_I is the initial concentration of isocyanate groups (mol/m^3), respectively.

The molar mass of polymer chains between chemical crosslinks M_c was calculated from the relation $M_c = \rho/1.5C$, where for ρ, a value of 10^3 kg/m^3 was used, which is very close to that found experimentally.[11] Possible changes of ρ with the system composition were not taken into account. (For further details, see Špírková et al.[7])

Table I   Composition and Properties of Polyurethane Networks Made from Krasol LBH

Ia

Sample	Network Type	LBH : IPDI : EHD : Triol	r	C (mol/m^3)	M_c (kg/mol)	Q_{dioxane}
1	Physical	65.2 : 23.8 : 11.0 : 0	1.0	0	—	Dissolved
2	Chemical	65.0 : 35.0 : 0 : 0	5.38 (CT)	846	0.79	2.57
3	Chemical	65.0 : 24.7 : 0 : 10.3 (T)	1.0	540	1.23	2.91
4	Chemical	65.0 : 28.9 : 0 : 6.1 (G)	1.0	665	1	3.42
5	Combined	65.0 : 24.7 : 10.3 : 0	1.10 (CT)	67	10	4.66
6	Combined	64.6 : 26.8 : 8.6 : 0	1.36 (CT)	210	3.17	3.38
7	Combined	65.0 : 28.5 : 6.5 : 0	1.72 (CT)	354	1.88	2.96
8	Combined	64.8 : 30.9 : 4.3 : 0	2.34 (CT)	525	1.27	2.75
9	Combined	65.2 : 24.0 : 9.9 : 0.9 (T)	1.0	46	14.5	13.8
10	Combined	65.0 : 24.4 : 4.25 : 6.35 (T)	1.0	328	2.03	3.47
11	Combined	64.9 : 24.3 : 10.3 : 0.5 (G)	1.0	54	12.3	10.9
12	Combined	64.9 : 24.3 : 4.35 : 3.85 (G)	1.0	432	1.54	3.69

Ib

Sample	ε_b (%)	σ_b (MPa)	E (MPa)	G'_{100} (MPa)	G'_{150} (MPa)	M_{100} (MPa)
1	1020	3.4	4.3	<0.01	<0.01	1.25
2	220	8.1	9.4	0.7	0.6	7.2
3	171	10.9	10.9	1.7	1.5	6.6
4	222	8.8	7.4	0.5	0.4	4.9
5	610	12.3	3.8	0.52	0.5	1.85
6	265	11.1	17.8	0.7	0.6	4.8
7	232	10.8	16.7	1.2	1.1	5.35
8	218	11.9	20.3	1.8	1.7	6.0
9	941	9.3	1.8	0.35	0.2	1.65
10	356	12.6	13.4	1.3	1.25	4.6
11	867	6.1	2.1	0.12	0.03	1.75
12	305	10.4	6.6	0.9	0.75	4.4

CT, chemically crosslinked by cyclotrimerization; T, triisopropanolamine; G, glycerol.

Values of r, C, and M_c are summarized in Tables Ia and IIa.

Tensile Properties

Elongation at break ϵ_b, stress at break σ_b, and Young's modulus E are summarized in Table Ib (LBH products) and Table IIb (LBH-P products). Stress–strain curves for some PBd-PURs are shown in Figures 1 (LBH products) and 2 (LBH-P products).

The comparison of stress–strain dependencies of samples 1 to 21 with other PBd-PURs[1–3,5,7,12–14] revealed that these elastomers (in particular, samples 5, 10, 16, 18–20) are products with good tensile properties regarding this type of polyurethanes.

The optimum ultimate properties were obtained mainly for samples with the concentration of trifunctional chemical crosslinks C in the range of 50 to 100 mol/m^3, with M_c ranging from 6 to 14 kg/mol

for both types of polymer diol functional groups and both types of crosslinking procedures (by cyclotrimerization or with triols). The obtained values fit very well with our previous results.[7]

The stress at 100% elongation M_{100} versus concentration of chemical crosslinks C is plotted in Figure 3 for the series described and summarized in Table III. Linear dependencies of the type $M_{100} = a + bC$ are obtained, where a and b are constants.

Experimental dependencies of M_{100} on C have been compared with the classic rubber elasticity theory, which predicts that for a perfect network with trifunctional network junctions, the equilibrium stress σ depends on the extension ratio λ according to the relation: $\sigma = 1.5CRT(\lambda - 1/\lambda^2)$, where R is the gas constant and T is absolute temperature. (For further details, see Špírková et al.[7]) At 296 K and $\lambda = 2$ (100% elongation): $\sigma_{\lambda=2} \equiv M_{100} = 6460C$ (in Pa). The ratio $k = b/b_{th}$

Table II Composition and Properties of Polyurethane Networks Made from Krasol LBH-P

IIa

Sample	Network Type	LBH-P : IPDI : EHD : Triol	C (mol/m^3)	M_c (kg/mol)	$Q_{heptane}$	$Q_{dioxane}$	Q_{xylene}	Q_{STO3}
13	Physical	65.0 : 24.2 : 10.8 : 0	0	—	3.27	Dissolved	Dissolved	1.11
14	Chemical	65.0 : 25.2 : 0 : 9.8 (T)	511	1.3	1.52	2.85	2.79	1.10
15	Chemical	65.0 : 29.2 : 0 : 5.8 (G)	626	1.06	1.46	2.79	2.48	1.09
16	Combined	65.0 : 24.4 : 8.5 : 2.1 (T)	111	6.05	1.85	4.82	5.19	1.17
17	Combined	65.0 : 24.7 : 4.2 : 6.1 (T)	316	2.11	1.65	3.35	3.28	1.13
18	Combined	65.0 : 24.7 : 9.7 : 0.6 (G)	64	10.4	2.0	9.25	8.64	1.18
19	Combined	65.0 : 25.3 : 8.5 : 1.2 (G)	134	4.97	1.84	4.06	4.5	1.18
20	Combined	65.0 : 26.2 : 6.4 : 2.4 (G)	257	2.59	1.63	3.9	3.71	1.11
21	Combined	65.0 : 27.2 : 4.3 : 3.5 (G)	386	1.73	1.51	3.32	3.01	1.10

IIb

Sample	ε_b (%)	σ_b (MPa)	E (MPa)	G'_{100} (MPa)	G'_{150} (MPa)	M_{100} (MPa)
13	833	3.48	4.28	0.11	<0.01	1.54
14	154	8.21	18.8	2.0	1.8	6.0
15	160	12.8	19.7	3.0	2.1	10.0
16	600	11.0	5.26	1.0	0.9	3.2
17	298	10.6	12.3	1.3	1.2	4.55
18	647	15.1	5.2	0.3	0.2	3.5
19	598	13.3	7.1	0.7	0.45	3.65
20	385	16.4	16.2	1.0	0.9	6.15
21	221	12.9	16.4	1.3	1.2	7.45

T, triisopropanolamine; G, glycerol.

(where b and b_{th} are values of the experimental and the theoretical slope, respectively) is given in Table III. A comparison of experimental dependencies of M_{100} on C (Fig. 3) with theoretical values calculated for $\lambda = 2$ and $T = 296$ K (Table III) yields a conclusion that can be simplified as
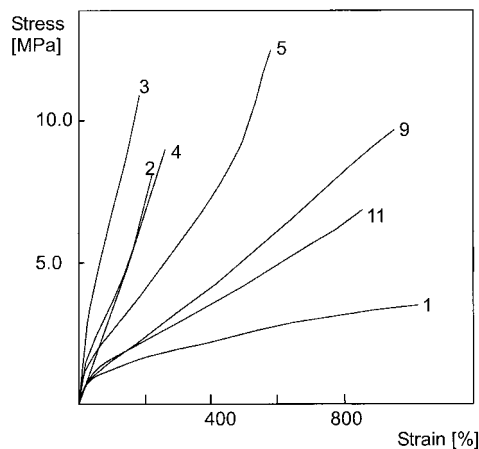

Figure 1 Stress–strain dependencies of polyurethanes prepared from LBH and isophorone diisocyanate: physical network (1), chemical networks (2–4), and combined networks (5, 9, and 11). The composition is given in Table Ia.
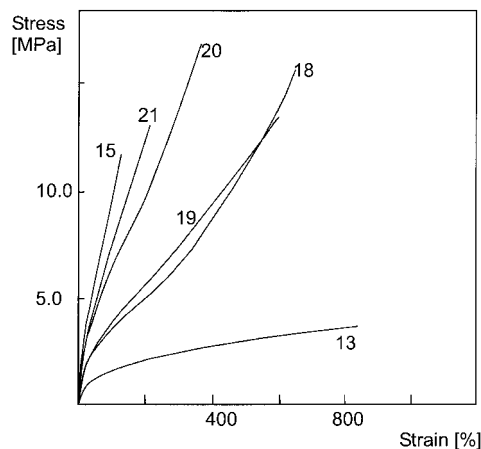

Figure 2 Stress–strain dependencies of polyurethanes prepared from LBH-P, isophorone diisocyanate, and glycerol: physical (13), chemical (15), and combined networks (18–21). The composition is given in Table IIa.
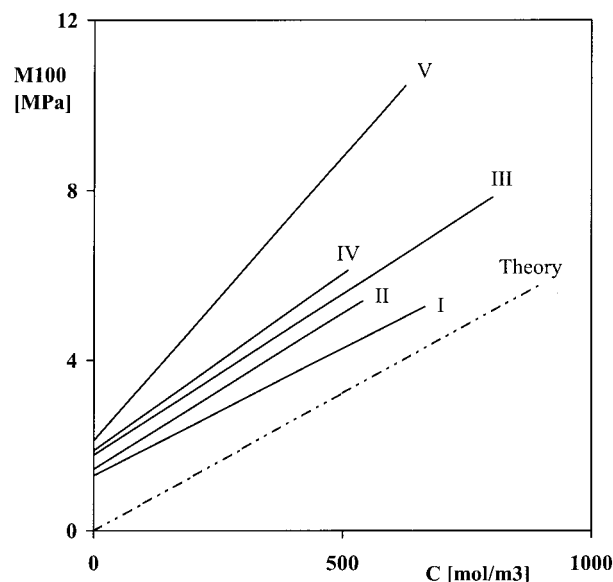
Figure 3 M_{100} modulus versus concentration of chemical crosslinks C. Series I: LBH–IPDI–GLY; series II: LBH–IPDI–TIPA; series III: LBH–IPDI–CT; series IV: LBH-P–IPDI–TIPA; series V: LBH-P–IPDI–TIPA systems. Theory: theoretical dependency.
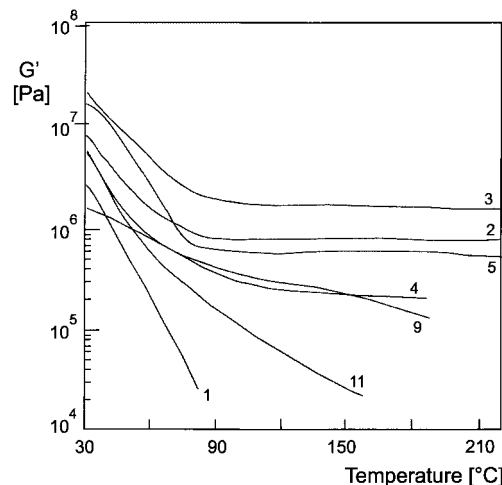

Figure 4 Temperature dependencies of storage shear modulus G' of polyurethanes prepared from LBH and isophorone diisocyanate: physical (1), chemical (2–4), and combined networks (5, 9, and 11). The composition is given in Table Ia.

follows: the experimental dependency of M_{100} on C fits the theory of rubber elasticity if the zero position is shifted vertically by a factor of $(M_{100})_{C=0}$, corresponding to the M_{100} values for pure physical networks (i.e., the systems not composed of chemical crosslinks). The agreement between individual values of M_{100} of samples 1 and 13, on the one hand, and a as well between b and b_{th} (i.e., $k \sim 1.0$), on the other hand, is acceptable for all systems, with the exception of PURs made from LBH-P, IPDI, and GLY (i.e., Series V). On the other hand, the M_{100}, a, b, and k values of Series V are similar to those of the LBH and

L-MDI (Baymidur KL 3-5002) system crosslinked with isocyanurates, studied previously.[7]

Dynamic Mechanical Thermal Analysis (DMTA)

Figures 4 and 5 show temperature dependencies of the storage shear modulus G' for chemical, physical, and several combined networks from IPDI and polymer diols with secondary (Fig. 4) and primary (Fig. 5) hydroxy groups.

The effect of thermal stability of chemical networks compared with physical junctions can be observed mainly at elevated temperatures, at which melting of physical hard domains takes place: the differences in G' at 30°C do not exceed one order of magnitude for all networks, whereas

Table III   Parameter Values of *a*, *b*, and *k*

Series	PUR Made From	Samples[a]	a (MPa)	b (Pa m^{-3} mol^{-1})	$k = b/b_{th}$[b]
I	(LBH + IPDI + GLY)[c]	1, 4, 9, 11	1.29	6000	0.93
II	(LBH + IPDI + TIPA)[c]	1, 3, 10, 12	1.44	7300	1.13
III	(LBH + IPDI + CT)[c]	1, 2, 5–8	1.85	7200	1.11
IV	(LBH-P + IPDI + TIPA)[c]	13, 14, 16, 17	1.87	8300	1.28
V	(LBH-P + IPDI + GLY)[c]	3, 15, 18–21	2.12	13,400	2.07
B	(LBH + L-MDI + CT)[d]		2.4	13,540	2.1
B	(LBH + M − TDI + CT)[d]		3.7	14,800	2.3

[a] M_{100} values for physical networks: sample 1, $M_{100} = 1.25$ MPa; sample 13, $M_{100} = 1.54$ MPa.
[b] $b_{th} = 6460$ Pa m^{-3} mol^{-1} (296 K).
[c] For composition, see Tables Ia and IIa.
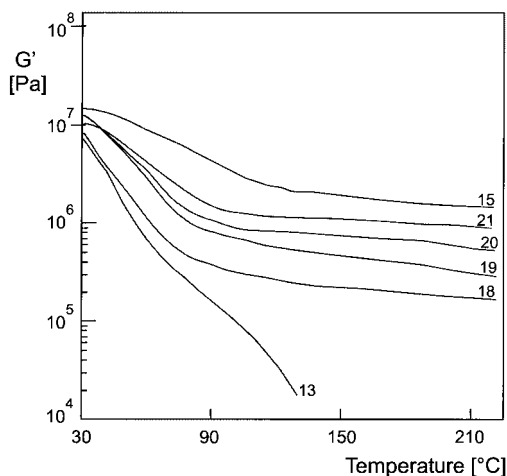[d] Data taken from Spírková et al.[7]

Figure 5 Temperature dependencies of storage shear modulus G' of polyurethanes prepared from LBH-P, isophorone diisocyanate, and glycerol: physical (13), chemical (15), and combined networks (18–21). The composition is given in Table IIa.

at 100°C, and especially at 150°C, the differences in G' were three orders of magnitude or more.

These networks, prepared from isophorone diisocyanate, exhibit very good thermal stability because alicyclic–NHCOO–aliphatic units, in contrast to aromatic–NHCOO–aliphatic units, are stable at higher temperatures.

The values of G' at 100°C (G'_{100}) and at 150°C (G'_{150}) are summarized in Table Ib (LBH products) and IIb (LBH-P products), respectively.

The glass-transition temperature of soft segments ($T_g)_s$, determined as a maximum of loss modulus G'' (at frequency $\omega = 1$ Hz), was found to be independent of the type of functional groups of polymer diol and of the composition, equal to −28°C in all cases. The values of $(T_g)_s$, determined as the maxima of tan δ (tan δ = G''/G'), were always found to be −22°C. We were unable to precisely determine $(T_g)_h$, the glass-transition temperature of hard segment domains (HSD), for most samples. Almost all of them (containing 35 wt % of HSD) exhibited only the plateau region of the second phase without reaching any maximum; the only systems with the second maximum of tan δ were the networks crosslinked with TIPA. In these cases, $(T_g)_h$ varied from 40 to 80°C (increasing with growing amount of TIPA in the samples).

Swelling

All PUR networks were swollen in n-heptane and 1,4-dioxane; in addition, networks prepared from

LBH-P were swollen also in xylene and standard testing oils.

The experimental values of equilibrium degree of swelling Q are given in Tables Ia and IIa (Q = mass of equilibrium-swollen sample/mass of original dry sample). Although the swelling in a nonpolar solvent (n-heptane) is moderate, the swelling in polar (1,4-dioxane) [and similarly in an aromatic solvent (xylene)] is pronounced. The values of Q for standard testing oils STO1 and STO2 did not exceed 1.02 (STO1) and 1.04 (STO2) for all PURs. Values of extract e [(1 − e) = mass of sample dried after extraction/mass of original dry sample] in n-heptane were always <2%. In 1,4-dioxane and xylene, the values of e did not exceed 0.25, with the exception of physical networks.

Small-Angle X-ray Scattering

Several selected samples (5, 9, 11, 16, and 18) were tested by SAXS (for further details, see Špírková et al.[7]). As before, the typical two-phase structure was confirmed by the fact that the intersegmental correlation length ξ, characterizing the periodicity of the network supermolecular structure, assumed a value of 6–8 nm.

CONCLUSIONS

Polybutadiene-based polyurethanes prepared from isophorone diisocyanate exhibit very good elastic properties (even for pure chemical networks). The oil resistance of these polyurethanes is very good; their optical homogeneity is better than that of the products based on aromatic diisocyanates.[7]

When polybutadiene diols (containing primary or secondary hydroxy end groups) of similar molecular characteristics and the same concentrations of diisocyanates, diol, triol, and so forth are used, products with almost identical tensile, thermal, and swelling properties are obtained, provided that either one-step (polymer diol with primary hydroxy groups) or two-step prepolymerization procedures (polymer diol with secondary hydroxy groups) are used. If some differences exist, the following general trend of properties can be found:

1. The networks made from LBH-P prepared by the one-step technique have a somewhat lower strain at break ϵ_b, but higher strength σ_b, as well as Young's, M_{100}, and G' moduli, compared with those of LBH

products prepared by the prepolymeriza-
tion technique.

2. If Q values are different, lower Q values are achieved for one-step LBH-P products.

The results presented here combined with those published recently[7] lead to the conclusion that the type of the diisocyanate used (alicyclic, aromatic) and the nature of chemical crosslinking (isocyanate- or hydroxy-based trifunctional junctions) affect the final properties of polyurethanes only partially.

The main factor influencing tensile (but also thermal and swelling) properties of polyurethane elastomers is the ratio of the concentration of chemical to physical crosslink points. Networks having the best balance of stress–strain dependencies and reasonable thermal stability are obtained for "combined" networks (i.e., the systems containing both crosslinking junctions) at the concentration of chemical crosslinks between 50 and 100 mol/m^3. This region was found to be independent of the type of diisocyanate (alicyclic, aromatic[7]), the nature of crosslinking (with triols or trifunctional isocyanate-based structures), and the procedure (one- or two-step technique).

REFERENCES

1. Bengtson, B.; Feger, C.; MacKnight, W. J.; Schneider, N. S. Polymer 1985, 26, 895.
2. Brunette, C. M.; Hsu, S. L.; Rossman, M.; MacKnight, W. J.; Schneider, N. S. Polym Eng Sci 1981, 21, 668.
3. Brunette, C. M.; Hsu, S. L.; MacKnight, W. J.; Schneider, N. S. Polym Eng Sci 1981, 21, 163.
4. Hepburn, C. Polyurethane Elastomers; Elsevier Science: London, 1992.
5. Pytela, J.; Sufčák, M. in Proceedings of the International Polyurethane Industry Conference, UTECH 2000, The Hague, 2000, Paper 9.
6. Pytela, J.; Sufčák, M.; Čermák, J.; Drobny, J. in Polyurethanes, EXPO '98, Dallas, TX, 1998; p 563.
7. Špírková, M.; Matějka, L.; Hlavatá, D.; Meissner, B.; Pytela, J. J Appl Polym Sci 2000, 77, 381.
8. Špírková, M.; Kubín, M.; Špaček, P.; Krakovský, I.; Dušek, K. J Appl Polym Sci 1994, 52, 895.
9. Špírková, M.; Kubín, M.; Špaček, P.; Krakovský, I.; Dušek, K. J Appl Polym Sci 1994, 52, 1435.
10. Pytela, J. Chem Listy 1999, 93, 441.
11. Dang Thi, A. T.; Camberlin, Y.; Lam, T. M.; Pascault, J. P. Angew Makromol Chem 1983, 111, 29.
12. Ryan, P. W. Br Polym J 1971, 3, 145.
13. Ono, K.; Shimada, H.; Nishimura, T.; Yamashita, S.; Okamoto, H.; Minoura, Y. J Appl Polym Sci 1977, 21, 3223.
14. Frisch, K. C.; Sendirajević, A.; Sendirajević, V.; Yokelson, H. B.; Nubel, P. O. in Proceedings of the International Polyurethane Industry Conference, UTECH '96, The Hague, 1996; Paper 42.