Polybutadiene-Based Polyurethanes with Controlled Properties: Preparation and Characterization

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ABSTRACT: A series of segmented polyurethanes was prepared from the new commercial product KRASOL LBH (linear liquid polybutadiene terminated with secondary hydroxy groups), aromatic diisocyanates, and an aliphatic low-molecular-weight diol. Three types of networks were prepared, with the nature of the crosslinks varied from purely chemical to physical, with a continuous transition to "combined" networks containing both crosslink types. Potassium 2-ethyl hexanoate was used as a catalyst of the *in situ* formation of trifunctional isocyanurate groups (by cyclotrimerization of isocyanate groups). It was confirmed that mechanical, thermal, and swelling properties are considerably influenced by the ratio of chemical to physical crosslink concentration. The best balance of stress–strain properties was obtained for "combined" networks at a NCO–OH molar ratio of 1.10 when only a few chemical crosslinks are present in predominantly physically crosslinked networks. The presence of thermally stable isocyanurate groups mainly influences the storage shear modulus at elevated temperatures. Small-angle X-ray scattering confirmed the two-phase structure of polyurethanes with a periodicity of 6–8 nm. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 381–389, 2000

Key words: polyurethanes; polybutadiene diol; isocyanurate groups; mechanical properties; SAXS

INTRODUCTION

Segmented polyurethanes (PURs) are important commercial materials distinguished for the incompatibility of their soft (macrodiol) and hard (diisocyanate and chain extender, i.e., low-molecular-weight diol or diamine) segments. The hard segments aggregate to form glassy or crystalline hard-segment domains in the soft matrix.[1] The main factors influencing the phase separation include the type and segment length, crystallizability, tendency for soft segment–hard segment hydrogen bonding, sample composition, and history of the sample preparation.[2–4]

Hard-segment domains act as physical junction points, greatly improving mechanical properties of PUR networks.[3] The tensile strength varies with the content of the hard segments and mainly grows up to the optimum.[3,5–7]

Chemically crosslinked polyurethanes are formed if a tri- or higher-functional compound is present in the system. Compared to physical networks, they are distinguished for better shape memory and better thermal stability (they do not flow at elevated temperature unless chemical degradation occurs), but their ultimate mechanical properties are limited (an increase in modulus and often stress at break are accompanied by a considerable decrease in elongation at break, as the reorganization of chains is reduced because of covalent bonds). Triols are mostly used as crosslinking agents, but it is also possible to utilize a tri- or higher-functional isocyanate component, for instance, to cyclotrimerize the isocyanate groups

under formation of isocyanurate (hexahydro-1,3,5-triazine-2,4,6-trione) groups. Isocyanurate groups take advantage of an increased thermal and hydrolytic stability compared to other groups present in a PUR system.[2,8,9]

A combination of physical and chemical crosslinking offers the possibility of obtaining materials with reasonable tensile properties (high strength at sufficient elongation at break). This has been demonstrated on polyester-based PURs containing trifunctional allophanate (biuret) groups[4,10] or isocyanurate groups.[11]

Polybutadiene-based PURs generally have lower mechanical strength compared to conventional polyether or polyester analogues.[2] For polybutadiene-based PURs (1,2- and *cis, trans*-1,4-polybutadiene isomers), tensile strength of 10–20 MPa and elongation at break of 200–600% are considered good mechanical properties.[3,5–7,9,12] However, exceptional tensile properties (strength of 25.8 MPa vs. 992% of elongation at break) have been recently documented for purely bifunctional 1,4-polybutadiene diol (DIFOL 2000).[13]

PURs prepared from hydroxy-terminated polybutadienes exhibit[2,3,6,7] superior water-resistant properties (excellent hydrolytic stability, low moisture permeability), high elasticity, very good low-temperature characteristics (a low glass transition temperature, flexibility), excellent insulation characteristics, and superior chemical resistance compared with conventional (polyether- or polyester-based) PURs. No change of a considerable nature was observed in the mechanical properties of polybutadiene-based PURs over a wide range of temperatures.[3,6,7] For all these purposes, they are useful mainly in special applications, for example, in encapsulation of electronic components.

New polyol products of Kaučuk, a.s., Czech Republic are commercial polybutadiene diols containing secondary hydroxy groups with the trademark KRASOL LBH. They are prepared by a special anionic polymerization technology. The key features of these products in comparison with most of other commercially produced (free-radical-polymerized) polybutadiene diols are: a narrow molecular-weight distribution and a purely linear chain character with average functionality close to (below) 2.0. KRASOL LBH diols can thus be advantageously used for the manufacture of various isocyanate polybutadiene prepolymers with good storage stability. The prepolymers find their applications in diamine-cured cast elas-

tomers or as high-quality binders for waste rubber crumb (e.g., from old tires).[14]

In this study, we tested PUR elastomer systems composed of KRASOL LBH diol, aromatic diisocyanates, and 2-ethylhexane-1,3-diol as a chain extender, studying the influence of the type and amount of crosslink sites on mechanical, thermal, and swelling properties. The microphase structure of the elastomers was studied by SAXS. The choice of diisocyanate types, a short chain diol and hard-segment content, was done according to recently published data for KRASOL LBH–based PURs.[15] Two series of PUR elastomers at a constant hard-segment content were prepared, with the nature of crosslink sites varied from the purely physical to the purely chemical, with a continuous transition of "combined" crosslinks. The physical crosslinking was achieved by an addition of low-molecular-weight diol, and the chemical crosslink sites were built up by the organic-salt-catalyzed cyclotrimerization of isocyanate groups.

EXPERIMENTAL

Materials

Hydroxy Components

α,ω-Di(2-hydroxypropyl)-polybutadiene KRASOL LBH2000 (experimental product of Kaučuk Kralupy, Czech Republic) has the following characteristics: molecular-weight averages M_n (1730) and M_w (2020); molecular-weight distribution M_w/M_n (1.17); number-average functionality (f_n, 1.86; f_2, 87%; f_1, 11.5%; f_0, 1.5%); concentration of hydroxy groups (1.021 meq.g^{-1}); and isomer content (60 wt % of 1,2-; 15 wt % of 1,4-*cis,* and 25 wt % of 1,4-*trans*). Before using, the macrodiol was dried in a vacuum at 50°C to achieve the content of water < 0.03 wt %.

The chain extender, 2-ethylhexane-1,3-diol (Hüls; EHD), was dried in vacuum at 50°C to reach the moisture content < 0.005 wt %.

Isocyanate Components

BAYMIDUR KL 3-5002 (Bayer) (L-MDI) is a mixture of 2,4'- and 4,4'-disocyanato-diphenylmethane (50–60/40–50 wt %). DESMODUR T 80 (Bayer) (M-TDI) is a mixture of 2,4- and 2,6-toluene diisocyanate (80/20 wt %).

Catalysts

Dibutyltin dilaurate (DBTDL) (Fluka) was used as a catalyst for the reaction of hydroxy groups

with isocyanates (a "urethane" catalyst); the DABCO K15 (K15) catalyst, potassium 2-ethyl hexanoate (Air Products) was utilized in order to form the isocyanurate groups[16,17] (a "cyclotrimerization" catalyst).

Solvents

n-Heptane (Lachema, Czech Republic) and 1,4-dioxane (Penta, Czech Republic), both analytical grade, were used as received.

Reaction Conditions

The samples were prepared using a two-stage a prepolymerization technique. A hard segment content of 35 wt % was kept constant in the preparation of all PUR networks.

In the first stage the isocyanate-terminated prepolymer was made from diisocyanate and LBH2000 in the presence of DBTDL (0.006 wt %) by mixing at 25°C under nitrogen. The prepolymer was degassed and reacted for 2 h at 60°C.

In the second step the prepolymer was mixed with a chain extender (EHD) at 25°C under nitrogen and degassed. The cyclotrimerization catalyst, K15 (0.18 wt %), was added (in chemical and "combined" networks) 15 min after homogenization of all substances.

The networks were prepared in Teflon molds at 25°C for 3 h and 90°C for 24 h.

This technique was chosen as a result of tests optimizing PUR network preparation. It was also experimentally confirmed that the efficiency of one catalyst used was not influenced by the other.

Test Conditions

Ultimate Mechanical Properties were measured on an Instron model 6025. Specimens of the size $25 \times 4 \times 1.5$ mm were tested at laboratory temperature at a test speed of 0.33 mm/s. All reported values are averages from five specimens.

Dynamic Mechanical Properties were followed using a Rheometrics System Four apparatus. Rectangular samples of size $45 \times 10 \times 1.5$ mm were measured by oscillatory shear deformation at a constant frequency of 1 Hz and at the rate of heating 3°C/min to obtain temperature dependences of storage and loss shear modulus G', G'' from −70 to 200°C (or to the temperature of softening).

Small-Angle X-Ray Scattering: SAXS curves were taken with a Kratky camera. CuKα radiation was registered using a position-sensitive de-

tector[18] (Joint Institute for Nuclear Research, Dubna, Russia). The measured intensities were put to an absolute scale using a standard Lupolene sample.[19,20] The intensities were taken in the range of the scattering vector $q = (4\pi/\lambda)\sin \theta$ from 0.1 to 4.0 nm^{-1} (where λ is the wavelength and 2θ is the scattering angle). The scattering curves were not corrected for the primary beam profile.

Swelling Measurements: PUR networks were swollen at laboratory temperature in *n*-heptane and 1,4-dioxane up to equilibrium. The amount of sol was determined by repeated extraction; the swollen samples were dried (50°C/1330 Pa) to a constant weight.

RESULTS AND DISCUSSION

Three types of PUR networks made from L-MDI (nos. 1–8) and M-TDI (nos. 9–17) were prepared [Table I(a)]: (1) networks containing only chemical crosslinks called chemical networks—numbers 1 and 9; (2) networks comprising only physical crosslinks denoted as physical networks—numbers 7, 8, 16, and 17; and (3) networks with both chemical and physical crosslinks called "combined" networks—numbers 2–6 and 10–15.

The networks numbers 6 versus 7 and 14 versus 16 have an almost identical composition; the only difference is the presence (nos. 6 and 14) or absence (nos. 7 and 16) of cyclotrimerization (K15) catalyst.

All networks were slightly yellow transparent materials with the exception of opaque samples 9 and 16.

Analysis of Composition

The main possible reactions occurring during PUR preparation are summarized in Scheme I.

The concentration of urea groups formed from traces of water and isocyanates is approximately two orders of magnitude lower compared with the concentration of urethane groups (arising from isocyanate and both diols), and hence it is not considered later.

According to model reactions,[16,17] trifunctional allophanate, biuret, and isocyanurate groups are formed in a catalyzed cyclotrimerization of isocyanates in the presence of K15 catalyst. As allophanate and biuret groups were found to be only intermediate products, we assume that isocyanurate groups are the only stable trifunctional cen-

Table I   Composition and Properties of Polyurethane Networks

Sample No.	Network Type	LBH2000 : L-MDI : (M-TDI) : EHD (wt %)	$r = c_I/c_{OH}$	C (mol/m³)	M_c (kg/mol)	w_s	v_2	ξ (nm)
1	chemical	66.9 : 33.1 : (0) : 0	4.14	540	1.23	0.013	0.503	6.0
2	combined	66.4 : 31.1 : (0) : 2.5	2.37	425	1.57	0.016	0.447	6.0
3	combined	65.1 : 30.0 : (0) : 4.9	1.77	315	2.12	0.024	0.380	6.6
4	combined	64.8 : 27.9 : (0) : 7.3	1.31	173	3.85	0.050	0.260	8.0
5	combined	65.2 : 26.2 : (0) : 0.6	1.12	72	9.32	0.142	0.129	6.3
6	combined	64.9 : 26.0 : (0) : 9.1	1.07	48	14.0	0.179	0.115	6.3
7	physical	64.9 : 26.0 : (0) : 9.1	1.07	0	—	1.0	—	6.6
8	physical	64.8 : 25.5 : (0) : 9.7	1.00	0	—	1.0	—	6.9
9	chemical	66.3 : 0 : (33.7) : 0	6.04	800	0.83	0.001	0.553	7.6
10	combined	64.8 : 0 : (30.4) : 4.9	2.76	600	1.11	0.020	0.509	5.2
11	combined	64.8 : 0 : (27.7) : 7.5	1.88	452	1.47	0.022	0.403	6.6
12	combined	64.8 : 0 : (25.5) : 9.7	1.47	306	2.18	0.012	0.392	5.2
13	combined	64.9 : 0 : (23.4) : 11.7	1.19	146	4.55	0.050	0.346	5.3
14	combined	64.8 : 0 : (22.8) : 12.4	1.10	81	8.2	0.118	0.174	6.0
15	combined	64.8 : 0 : (22.5) : 12.7	1.06	62	10.8	0.178	0.108	6.3
16	physical	64.6 : 0 : (22.9) : 12.5	1.10	0	—	1.0	—	6.0
17	physical	64.9 : 0 : (21.6) : 13.5	1.00	0	—	1.0	—	6.6

Sample No.	ε_b (%)	σ_b (MPa)	E (MPa)	G'_{100} (MPa)	M_{100} (MPa)
1	85	6.6	21.8	10.5	(7.9)
2	75	7.1	20.2	9.62	(8.8)
3	130	8.4	13.7	4.72	6.4
4	260	8.5	6.2	1.42	4.1
5	500	13.1	3.6	0.56	3.6
6	660	14.3	3.6	0.52	3.0
7	710	11.0	3.5	0.06	2.4
8	600	7.4	3.1	0.028	1.7
9	85	8.2	29	14.2	—
10	65	6.9	31.5	14.0	—
11	70	7.8	36.5	12.4	—
12	90	8.2	28.5	7.5	(9.6)
13	290	13.4	9.4	1.0	5.7
14	550	17.6	6.3	0.82	4.5
15	620	15.6	6.0	0.27	4.2
16	585	9.5	6.7	0.10	3.8
17	610	6.5	6.1	0.013	2.0

Comments: r: initial molar isocyanate/OH ratio.
C: concentration of chemical crosslinks calculated using eq. (1).
M_c: molar mass of polymer chains between chemical crosslinks, calculated using eq. (2).
w_s: fraction of sol (1,4-dioxane extract).
v_2: volume fraction of polymer gel in the gel–1,4-dioxane system in swelling equilibrium.
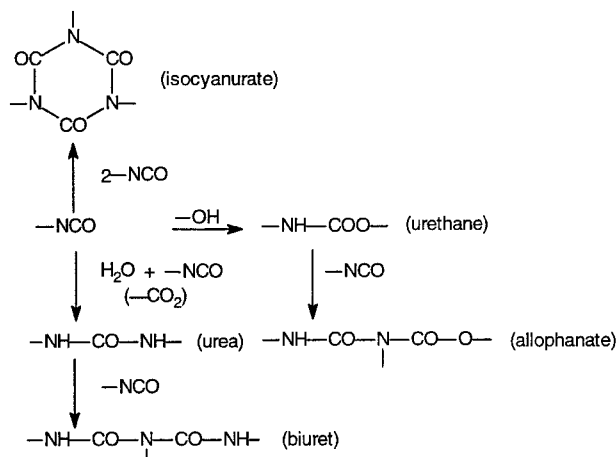ξ: intersegmental correlation length.
ε_b: elongation at break.
σ_b: stress at break.
E: Young's modulus (initial slope of the stress–strain curve; strain rate 0.33 mm/s).
G'_{100}: storage shear modulus (1 Hz) at 100°C.
M_{100}: stress at 100% elongation (extrapolated values in parentheses).

Scheme 1 Isocyanate reactions.

ters present in the (chemical and combined) PUR networks.

In the second step of the PUR preparation, competitive reactions—the "urethane" and "cyclotrimerization" reactions—occur. In order to promote the reaction of isocyanate with the chain extender (the "urethane" reaction) to proceed first, a stepwise addition of the chain extender (EHD) and cyclotrimerization catalyst (K15) and a low temperature at the beginning of the network preparation were used (see Reaction Conditions, above).

The concentration of trifunctional chemical crosslinks (isocyanurate groups), C, was estimated using these simplifying assumptions: (1) the reaction of hydroxy with isocyanate groups is complete; (2) the excess isocyanate groups react quantitatively to form isocyanurate groups:

$$C = c_I(r - 1)/3r \qquad (1)$$

where c_I and c_{OH} are initial concentrations of isocyanate and (total) hydroxy groups (mol/m^3); $r = c_I/c_{OH}$ is the initial NCO/OH ratio.

The molar mass of polymer chains between chemical crosslinks, M_c, was calculated from the relation

$$M_c = \rho/1.5 \ C \qquad (2)$$

As the density of polybutadiene-based PURs, ρ, was found[9] to be very close to 103 kg/m^3, we used this value for simplicity in calculating M_c. Possible changes in ρ with the system composition were not taken into account.

The calculated values of r, C, and M_c are summarized in Table I(a) (columns 4 to 6).

Static Mechanical Properties

The tensile properties—elongation at break (ε_b), stress at break (σ_b), Young's modulus (E), and stress at 100% elongation (M_{100})—are summarized in Table I(b), columns 2–4 and 6.

The stress–strain curves for some L-MDI- and M-TDI-based PURs (chemical, physical, and combined networks with optimum ultimate properties) are shown in Figure 1.

A comparison of stress–strain dependences of our samples with other polybutadiene-based PURs[3,5–7,9,12–14]—revealed that our elastomers (samples nos. 6, 14, and 15) rank among products with better tensile properties in this group.

The optimum ultimate properties have been obtained in the region of C of about 50–80 mol m^{-3}, with M_c ranging from 14 to 8 kg mol^{-1}. This is approximately the same crosslinking degree range where optimum ultimate properties of filler-reinforced general-purpose (natural, butadiene, and styrene–butadiene) rubbers are obtained.[21] The optimum weight concentration of carbon black or silica filler (around 33 wt %) is similar to the content of hard segments that we
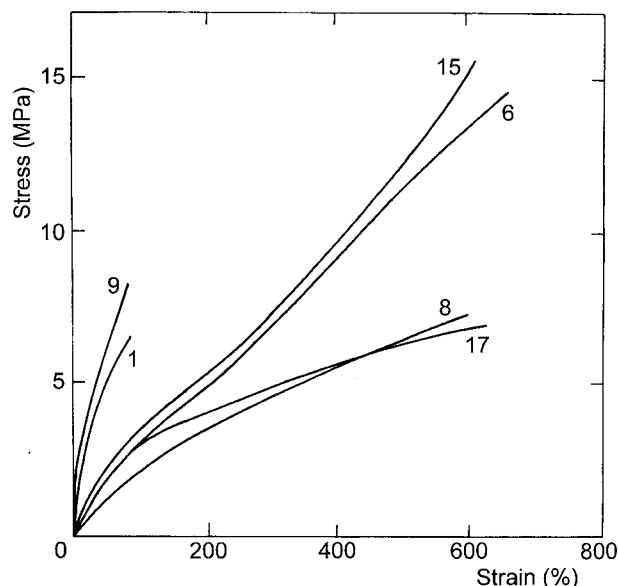

Figure 1 Stress–strain dependences of chemical networks (nos. 1 and 9), physical networks (nos. 8 and 17), and combined networks with optimum tensile properties (nos. 6 and 15). The composition of L-MDI- and M-TDI-based networks is given in Table I(a).

used. On the other hand, the volume fraction of filler is lower (ca. 20%) since the filler density is much higher than that of hard domains.

The dependences of the stress at 100% elongation, M_{100}, on the concentration of chemical crosslinks, C, are plotted in Figure 2. A linear dependence is obtained:

$$M_{100} = a + bC \qquad (3)$$

where the parameters a and b obtained for the M-TDI series data are somewhat higher than those for L-MDI series (Table II). The latter phenomenon may be ascribed to a lower molar mass of M-TDI in comparison to L-MDI. This leads to a high-polarity material since the proportion of polar urethane groups in the hard domains of M-TDI networks is somewhat higher than those in L-MDI networks.

In Figure 2 we compare our data with the data published by Barikani[11] on chemically (isocyanurate) crosslinked polyester-based PURs (PES–PURs) [the product of poly(caprolactonediol) (M_w 2000), *trans*-cyclohexane-1,4-diisocyanate, butane-1,4-diol, and cyclohexane-1,4-dimethanol]). The C
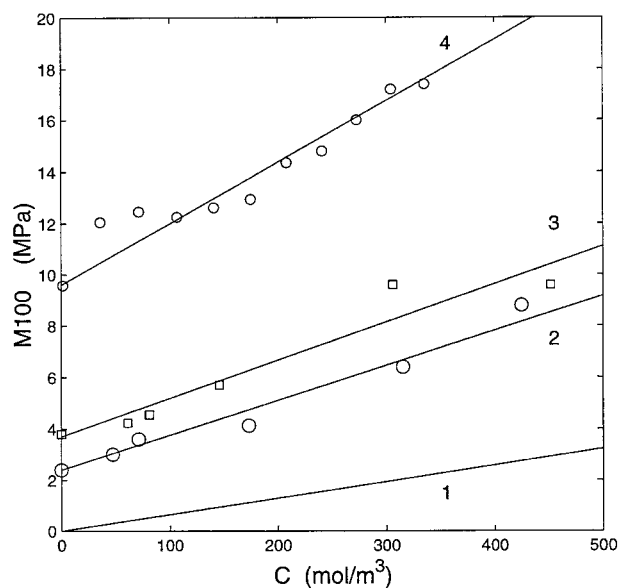

Figure 2 M_{100} modulus versus concentration of isocyanurate crosslinks (C): Series 1—theoretical dependence; Series 2—L-MDI-based polybutadiene PURs; Series 3—M-TDI based polybutadiene PURs; Series 4—polyester PURs crosslinked by isocyanurate groups[11] (Series A in Table II).[2] For a more detailed description, see eq. (3), eq. (4), and Table II.

Table II   Parameter Values of Eq. (3)

Series	a (MPa)	b (Pa m^3 mol^{-1})	$k = b/b_{th}$
L-MDI, 23°C	2.4	13540	2.1
M-TDI, 23°C	3.7	14830	2.3
A, 23°C	8.5	19350	3.0
A, 180°C	4.0	13160	1.33
B, 23°C	9.6	23860	3.7

A, Data of Barikani[11] (taken from Reference[2], p 93–94, Table 3.27) for system polycaprolactone : diol : diisocyanate = 1 : 1 : 2 r.

B, Data of Barikani[11] (taken from Reference[2], p 95, Table 3.28) for system polycaprolactone : diol : diisocyanate = 1 : 2 : 3 r (r is initial molar NCO/OH ratio).

b_{th}, theoretical value of $b = (d\sigma/dC)_{\lambda=2}$ calculated from eq. (4); 23°C, $b_{th} = 6450$ Pa m^3 mol^{-1}; 180°C, $b_{th} = 9886$ Pa m^3 mol^{-1}.

values of the networks[11] were estimated from the material composition using eq. (1).

The higher polarity of PES–PURs (and, presumably, the presence of crystallinity) is assumed responsible for the higher modulus (higher a) of PES–PURs and, at the same time, for a higher rate of the modulus increase with the crosslink concentration (higher b) in comparison with that of polybutadiene-based PURs. A second factor contributing to the higher value of b is a gradual increase in the hard segment content with increasing r in the PES–PUR series where the weight of the polyester and extender was kept constant while the weight of isocyanate was increased. The values of modulus were found to decrease with increasing temperature of measurement, with the values of a and b decrease in parallel (see Table II). Partial melting of hard domains may be responsible for this effect.

The experimental dependence of M_{100} on C can be compared with the result of the classic rubber elasticity theory. The latter predicts the following dependence of the equilibrium stress, σ, on the extension ratio, λ, for a perfect network with trifunctional network junctions:

$$\sigma = 1.5 \, CRT(\lambda - 1/\lambda^2) \qquad (4)$$

where R is the gas constant and T is absolute temperature.

For room temperature and $\lambda = 2$ (100% elongation) it affords $\sigma_{\lambda=2} = 6450 \, C$ (Pa).

The ratio k of the experimental (b) and theoretical slope (b_{th}) = 6450 is also given in Table II. For polar PES–PURs, k is significantly higher

than unity. With decreasing polarity (higher temperature of measurement and replacement of polyester by polybutadiene segments), k decreases and approaches unity.

Dynamic Mechanical Properties

Figure 3 shows temperature dependences of storage shear modulus, G', for chemical, physical, and some combined networks.

Higher values of G' of the chemical networks are the result of the reinforcing nature and higher thermal stability of chemical crosslinks compared with physical ones. The curves of G' for particular types of networks show a similar shape for both isocyanates; the small differences in G' temperature dependences may the result of differences in thermal stability of M-TDI and L-TDI and differences in the isocyanurate group concentration [(Table I(a)].

A beneficial effect of thermally stable isocyanurate groups can be seen mainly at elevated temperatures, where the melting of physical hard domains takes place: for example, the differences in storage shear modulus G' at 30°C do not exceed an order of magnitude for all networks, while at 100°C the differences in G' were three orders of magnitude or more. The values of G' for all samples at 100°C, G'_{100}, are summarized in Table I(b).

Figure 4 SAXS intensities of selected samples typical of chemical (nos. 1 and 9), physical (nos. 8 and 17), and combined PUR (nos. 6 and 15) networks.
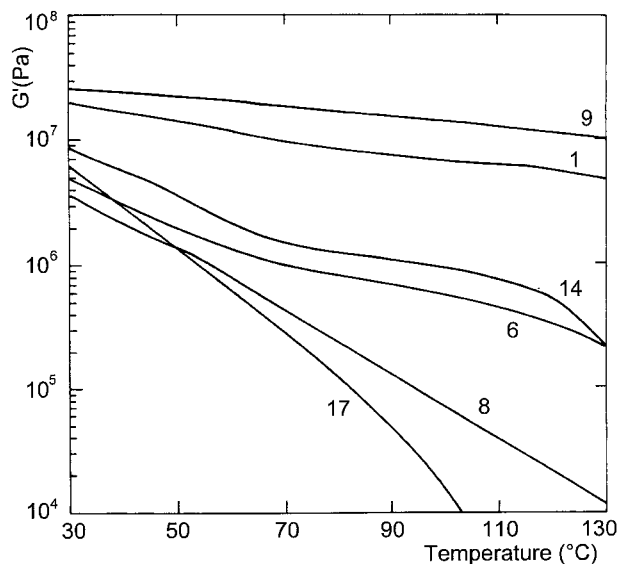

Figure 3 Temperature dependences of storage shear modulus, G', of chemical networks (nos. 1 and 9), physical networks (nos. 8 and 17), and combined networks (nos. 6 and 14). The composition of individual networks is described in Table I(a).
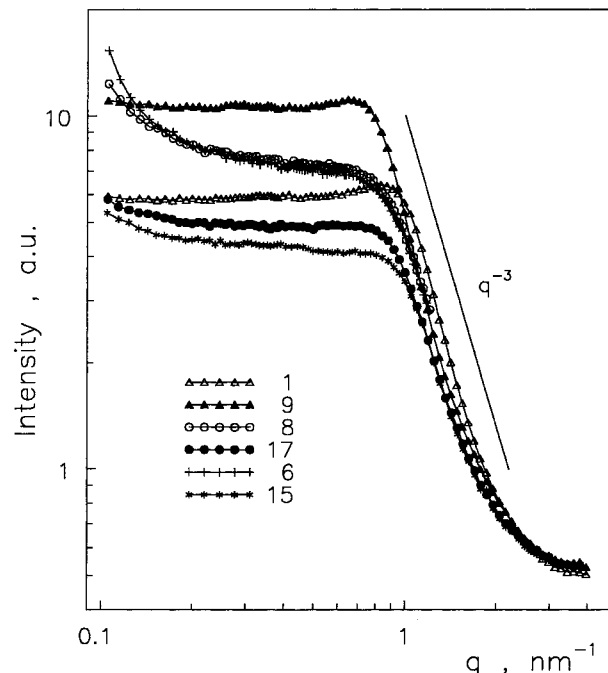
The values of G'_{100} gradually increase with r, that is, with the isocyanurate concentration, C.

The glass transition temperature (T_g) of soft segments determined as a maximum of loss modulus G'' (at frequency $\omega = 1$ Hz) was found to be independent of the composition, that is, on the type of crosslinks being -28°C in all cases. The higher the r, the higher and more distinct the maximum.

On the other hand, we were unable to determine precisely the glass transition temperature of hard segment domains [HSD; $(T_g)_h$]. All samples (containing 35 wt % HSD) exhibited only the plateau region of the second phase without reaching any maximum. Similar results were obtained for polybutadiene-based PURs containing less than 40 wt % of HSD.[3,6,7]

SAXS

Unlike some types of hybrid organic–inorganic networks, the structure of which can be described in fractal terms,[22,23] the polybutadiene–based polyurethane networks exhibit a pronounced compact two-phase structure. As follows from Figure 4, for virtually all samples, the tail of the SAXS curves obeys Porod's law,[24]—the scattered
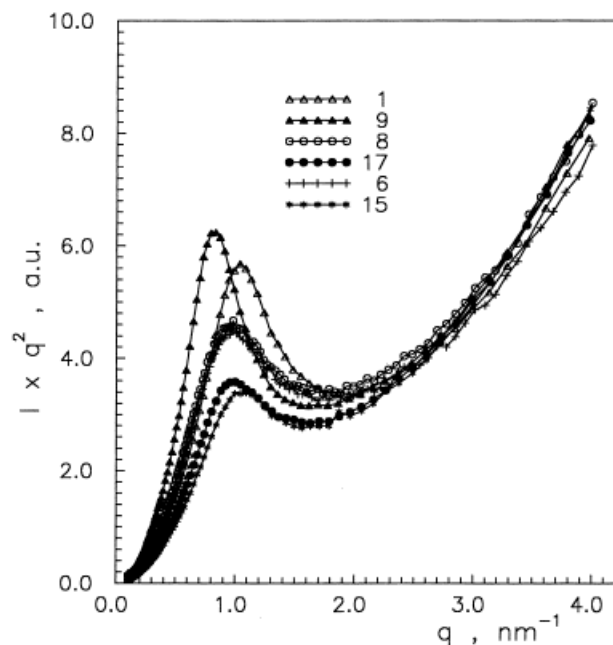
Figure 5 Lorentz-corrected SAXS curves (Iq^2 versus q) of the same samples as in Figure 4.

intensities are proportional to q^{-3}. In addition, an interference maximum in the scattering vector range $q = 0.80–1.05$ nm^{-1} is observed on each of these SAXS curves.

This type of SAXS curve can be attributed to a two-phase system with sharp boundaries. One phase, the soft one, is formed by the butadiene component of the network, while isocyanates and the chain extender are phase-separated as hard segments. This structure model for polybutadiene-based PUR networks (physically and chemically crosslinked elastomers), studied, for example, by Lagasse,[1] can explain well mechanical properties of these materials.

For the precise determination of the maximum position, q_m, corresponding to the intersegmental correlation length, ξ, that characterizes the periodicity of the network supermolecular structure, Lorentz-corrected desmeared SAXS curves (Iq^2 versus q) were used (Fig. 5). On the basis of the q_m values deduced from these curves, ξ values were calculated according to the Bragg equation ($\xi = 2\pi/q_m$) to be 6.0–7.7 nm [Table I(a)].

The SAXS results show that the two-phase structure of physical networks is not affected by chemical crosslinking.

Swelling Experiments

All PUR networks were swollen in n-heptane and 1,4-dioxane.

n-Heptane is a poor solvent for these materials because it doesn't dissolve physical networks, and the extract does not exceed 3%.

For 1,4-dioxane, an experimental modulus, degree-of-swelling correlation is shown in Figure 6 where M_{100} is plotted versus the volume fraction of polymer gel at swelling equilibrium, v_2. The values of v_2 (together with the values of the sol fraction, w_s) are summarized in Table I(a).

A theoretical correlation between the equilibrium stress, σ, and v_2 is offered by the Flory equation:

$$\sigma/(\lambda - 1/\lambda^2)RT = -1/V_1[\ln(1 - v_2) + v_2 + \chi v_2^2]$$
$$/(v_2^{1/3}v_0^{2/3} - 2v_2/f) \quad (5)$$

where V_1 is the molar volume of the solvent (1,4-dioxane), v_0 is the volume fraction of the polymer during crosslinking, f is the functionality of crosslinks, χ is the polymer–solvent interaction parameter.

The experimental M_{100} versus v_2 dependence is compared with eq. (5) in Figure 6 using the following assumptions: First, the contribution σ of the chemical crosslinks to the experimental values of M_{100} are given by the difference between the respective M_{100} values measured at a given C and the extrapolated M_{100} at $C = 0$. The latter extrapolated values are close to the parameter a
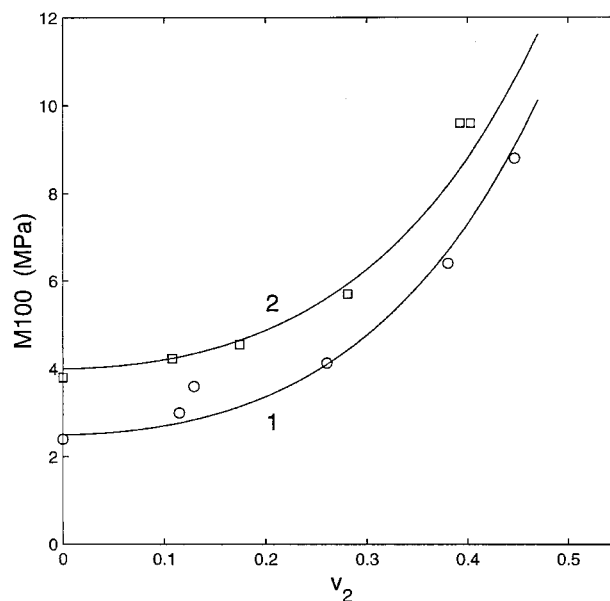

Figure 6 M_{100} modulus versus volume fraction of polymer in the swollen gel, v_2: Series 1—L-MDI-based PURs; Series 2—M-TDI-based PURs.

(see Table II), that is, 2.5 and 4.0 MPa for the L-MDI and M-TDI series, respectively. Second, the volume fraction v_0 is unity. And finally the interaction parameter is adjusted to obtain an optimum fit to the data.

Curves in Figure 6 are drawn according to eq. (5), with $\chi = 0.36$ the value indicating a thermodynamically good solvent. No quantitative significance should be associated with this result, which is intended merely to demonstrate the basic structure–property relationship for polybutadiene-based PUR networks.

CONCLUSIONS

Polybutadiene-based PUR networks prepared without using the cyclotrimerization catalyst (physical networks) are soluble in 1,4-dioxane, they have rather low tensile properties, and their storage shear modulus, G', decreases rapidly above room temperature.

On the other hand, the products prepared with the addition of the cyclotrimerization catalyst (potassium 2-ethyl hexanoate) show the usual signs of the presence of chemical crosslinks. With an increasing degree of chemical crosslinking, the amount of the sol fraction (in 1,4-dioxane) decreases and eventually drops almost to zero; the equilibrium degree of swelling decreases; the moduli (M_{100}, E, G') increase monotonically, with this effect especially pronounced at elevated temperatures. The elongation at break decreases with decreasing length of chains between crosslinks in the chemical networks, the tensile strength goes through a maximum, and the level of storage shear modulus, G', is retained at elevated temperatures (100°C or even higher). These effects are similar in the two series of networks prepared using L-MDI and M-TDI.

The best balance of stress–strain properties was found for slightly chemically crosslinked combined networks preferably containing physical junction points. The optimum tensile strength of polybutadiene-based PURs has been achieved in the same range of degree of crosslinking where the optimum ultimate properties of filler-reinforced general-purpose rubbers are obtained.

Small-angle X-ray scattering confirmed a compact two-phase structure with the periodicity 6.0–8.0 nm. The intersegmental correlation length was independent of the composition of networks and the type and concentration of crosslinks.

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