

## MISCIBILITY AND CROSSLINKING OF POLYBUTADIENE-BASED POLYURETHANES

Miloslav PEKAŘ<sup>1,\*</sup> and Pavel KOPECKÝ<sup>2</sup>

*Institute of Physical and Applied Chemistry, Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic; e-mail: <sup>1</sup>pekar@fch.vutbr.cz, <sup>2</sup>kopecny@fch.vutbr.cz*

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Rheokinetics of polybutadiene-based polyurethanes was studied. Sixteen mixtures differing in the miscibility of reactive components and hard segments contents were prepared. Regardless of the miscibility of the components, the rheokinetics behaviour is qualitatively very similar. The viscous response part is formed and finished much earlier than the elastic part. The quantitative dissimilarities, caused by cooperative effect of miscibility and differences in reactivity, are described. Using a well miscible initial mixture need not give the best results as a reactive crosslinker can easily react with isocyanate and separate from the rest of the reaction mixture thus impairing the final phase structure.

**Key words:** Crosslinking; Miscibility; Polybutadiene; Polyurethanes; Rheokinetics; Polymers; Macromolecules.

Polybutadiene-based polyurethanes (PBPUR) have been introduced to make elastomers of high hydrolytic resistance which combine properties of conventional rubber materials with the high performance of polyurethanes. Despite the increased degree of phase separation which is generally assumed to improve polyurethane mechanical properties, data seem to indicate that the tensile strength and toughness of PBPUR are inferior compared with conventional, polyether- or polyester-based polyurethanes<sup>1</sup>. Explanation is based usually on premature phase separation during polymerization leading to compositional heterogeneity, especially if the reaction is performed in bulk which is the prevailing method in practice. This behaviour results from the structure of polybutadiene backbone. Compared with conventional polyurethane polymers, polybutadiene is much less polar and much more hydrophobic. Other components of polyurethane composition – isocyanates, chain extenders, crosslinking agents – are usually polar. Structure of the final product may be thus much more dependent on the initial liquid mixture and poor miscibility of initial components may result in deterioration of properties of the cured material.

For example, Bengtson and co-workers<sup>2</sup> tried to restrain poor initial compatibility by preparing polybutadiene-based polyurethanes from solution. The solution-prepared products possessed better mechanical properties than the polymers prepared in bulk. Xu *et al.*<sup>3</sup> found even supramolecular structures formed because of poor miscibility of initial components. They claim these structures to be important for mechanical properties but without further explanations. Speckhard and Cooper<sup>1</sup> analyzed tensile properties of polybutadiene-based polyurethanes in detail and stated that poor miscibility of polybutadienes with other components is one of the causes of the worse tensile properties of these products compared with traditional materials. Siegmann *et al.*<sup>4</sup> stated that the polymerization course of PBPUR and, consequently, properties of the final material are influenced by parameters as follows: polybutadiene diol reactivity, components compatibility, component partition between phases, size and shape of dispersed droplets, *etc.*

A new type of liquid polybutadiene polyol, prepared by anionic polymerization, has been recently introduced by the Kaučuk company<sup>5</sup> under the trade name Krasol LBH. This work aims at the study of relationships between the components miscibility and rheological curing behaviour of the PBPUR based on Krasol. The knowledge of these relationships has important consequences for practical applications of PBPUR, for instance, for selection of components and control of curing process in order to obtain requested final material properties. Standard rheokinetic method, *i.e.* time-sweep oscillations at constant frequency and strain, was used.

Few studies have been published on the polybutadiene-polyurethane rheokinetics. Koike *et al.*<sup>6</sup> measured crosslinking of PBPUR in solution near the gel point. Cohen *et al.*<sup>7</sup> and Varghese *et al.*<sup>8</sup> published data on viscosity and torque rise during PBPUR curing. Dubois *et al.* included in their modelling paper<sup>9</sup> some rheokinetic data for PBPUR but in the form of frequency and not time sweep. All studies used other polybutadiene materials and measurement conditions which do not allow direct comparison with our results.

## EXPERIMENTAL

### Materials

Krasol LBH – dihydroxypolybutadiene, lot C017, supplied by Kaučuk, Inc., with the following specifications:  $M_w = 2\ 610$ ,  $M_n = 2\ 310$ ; OH content 0.765 mmol/g;  $f_2 = 91.4\%$ ,  $f_1 = 7.5\%$ ,  $f_0 = 1.1\%$  (fractions of bi-, mono-, and nonfunctional chains, respectively); Brookfield viscosity 16 Pa s, water contents less than 0.05%. In general, Krasol contains 60% of 1,2 (vi-

nyl), about 25% of 1,4-*trans* and about 15% of 1,4-*cis* structure units. Krasol LBH has one secondary hydroxy group (2-hydroxypropyl group) at each end of the linear chain.

The following substances of various origin were supplied by Kaučuk as samples of the standard products used there: methyl-1,3-phenylene diisocyanate (TDI), mixture of 4-methyl (80%) and 2-methyl (20%) isomer; Suprasec X 2385, liquid form of bis(4-isocyanatophenyl)methan developed by ICI, NCO contents 31%; dibutyltin dilaurate (DBTL), either pure or dissolved in paraffin oil, was used as catalyst. Following crosslinkers were used: glycerol (Onex, Czech Republic), anhydrous; tris(2-hydroxypropan-2-yl)amine ("triisopropanolamine" TIPA; Fluka, Czech Republic), vacuum dried. It should be emphasized that TDI is purely difunctional material, while Suprasec X 2385 has average functionality slightly higher than 2 (viz. 2.06). Glycerol contains both primary and secondary hydroxy groups, while TIPA only secondary groups which are less reactive than the primary ones.

### Procedure

BBPURs were prepared by one-step method at laboratory temperature. All components except catalyst were weighed in a plastic container and thoroughly mixed under vacuum (4–7 min) to remove bubbles. Then catalyst was added and mixed under vacuum (1 min). Mixtures containing TIPA were prepared by first melting TIPA in Krasol at 70 °C. Mixtures of TIPA with Krasol remain liquid and clear even at laboratory temperature, indicating good miscibility<sup>10</sup>.

The reaction mixture was placed into the parallel plates sensor of Haake RS100 rheometer which was maintained at 25 °C during measurement. This relatively low temperature was chosen because of our bad experience with curing of some mixtures at elevated temperature. Increased temperature lowers the viscosity of reacting mixture and may thus cause phase separation of unmiscible component before the network is strong enough to prevent the separation. Measurements were performed in oscillatory regime with frequency of 1 Hz under constant deformation  $\gamma = 0.005$  defined as  $\gamma = \phi R/h$ , where  $\phi$  is the deformation angle,  $R$  is the plate radius (10 mm), and  $h$  is the plate gap (1 mm).

As the zero reaction time, the instant of catalyst addition was taken. Rheokinetic measurements were made continuously for about 8 h and an additional 30-min reading was made the next day, if possible.

### Polyurethane Samples

Sixteen different polybutadiene-based polyurethane compositions were used for rheokinetic study (Tables I, II). All compositions contained the same polyol, Krasol LBH. Glycerol and triisopropanolamine were used as immiscible<sup>10</sup> and miscible (both with polyol and diisocyanates) crosslinking agents, respectively. TDI is much more miscible with Krasol LBH than Suprasec X 2385; miscibility limit of TDI at laboratory temperature is about 20 wt.% and of Suprasec lower than 0.6% (for miscibility tests see ref.<sup>10</sup>).

Thus, the mixtures can be divided into four groups, differing in the initial components miscibility. Group 1 (Table I) contains the least miscible initial components whereas group 4 is formed from the most miscible substances. Within each group, different contents of hard segments is used (Table II).

Molar ratio of functional groups (NCO : OH) was 1.05 in all samples.

Catalyst amount was kept constant in the phr (*i.e.* parts per hundred parts of rubber) units (Table I). Thus, total catalyst concentration decreases with increasing contents of hard

segments. On the other hand, the higher the hard segments contents the bigger the amount of crosslinker which is much more reactive than long dihydroxypolybutadiene molecules. Keeping constant phr catalyst amount can be roughly viewed as keeping constant catalytic acceleration of the slower reaction.

Influence of different catalyst concentration on the measured complex moduli value within each group cannot be excluded. However, we believe that this effect is suppressed by the much more pronounced influence of the hard segments contents.

## RESULTS AND DISCUSSION

The main aim of this work was to study development of moduli (and loss angle) values during crosslinking reaction. Therefore we strongly prefer to present data without usual transformations, *i.e.*,  $\log G'$ ,  $G''$ ,  $\tan \delta$ . These

TABLE I  
Composition of studied mixtures (per 100 g Krasol LBH)

Group	Sample	Crosslinker weight g	Isocyanate weight g	Catalyst <sup>a</sup> wt. %		
1	P1	glycerol	0.5	Suprasec X 2385	13.0	0.00365
	P2		2.0		20.0	0.00340
	P3		8.0		48.0	0.00266
	P4		10.0		57.15	0.00248
2	P5	glycerol	1.0	TDI	10.0	0.00374
	P6		4.5		21.25	0.00330
	P7		12.0		42.67	0.00268
	P8		15.0		51.6	0.00249
3	P9	TIPA	1.04	Suprasec X 2385	13.1	0.00363
	P10		4.15		20.04	0.00333
	P11		16.6		49.87	0.00249
	P12		20.77		57.15	0.00233
4	P13	TIPA	2.08	TDI	9.90	0.00370
	P14		9.30		20.25	0.00320
	P15		24.98		42.74	0.00247
	P16		31.16		51.60	0.00227

<sup>a</sup> Uniform catalyst amount: 0.083 g of 5% solution per 100 g Krasol LBH.

transformations are highly nonlinear functions with different sensitivity to the argument values throughout the definition domain and destroy the shape of measured curves.

Although some samples were not fully cured even after 8 h, it can be stated that the viscoelastic rheokinetic behaviour of all studied compositions is qualitatively very similar, regardless of components miscibility and reactivity. A typical example of measured curves is given in Fig. 1. The viscous modulus grows faster and attains its stationary value much earlier than the elastic modulus. The elastic modulus keeps growing long after the viscous modulus achieved practically constant value. The viscous part of the mechanical response of the sample is evidently constituted much faster and earlier than the elastic part. Both moduli–time curves intersect shortly before the rate of the growth of viscous modulus decreases and viscous

TABLE II  
Hard segments contents and OH groups ratio in studied mixtures

Group	Sample	Hard segments wt. %	$\frac{[\text{OH}]_{\text{LBH}}}{[\text{OH}]_{\text{crosslinker}}}$
1	P1	11.89	1 : 0.21
	P2	18.03	1 : 0.85
	P3	35.9	1 : 3.41
	P4	40.7	1 : 4.26
2	P5	9.91	1 : 0.43
	P6	20.45	1 : 1.92
	P7	35.34	1 : 5.11
	P8	39.98	1 : 6.39
3	P9	12.38	1 : 0.21
	P10	19.48	1 : 0.85
	P11	39.32	1 : 3.40
	P12	43.79	1 : 4.26
4	P13	10.69	1 : 0.43
	P14	21.81	1 : 1.91
	P15	40.38	1 : 5.12
	P16	45.28	1 : 6.39

modulus approaches the stationary value. The same shape of moduli evolution curves was observed in all studied samples.

The end of viscous modulus growth is probably related to the termination of main part of branched macromolecule length growth. After the termination, the network formation predominates through connecting of formed long and branched chains. Sometimes, the point of moduli intersection,  $t_1$  (or, equivalently,  $\tan \delta = 1$ ), is considered a point of gelation<sup>11,12</sup>. However, Winter has shown that this claim has not general validity<sup>13</sup>.

Our results show that differences in miscibility do not affect the general character of moduli responses. In other words, all samples gave similar response shapes. However, responses differed in their position on the time scale, *i.e.*, in the underlying reaction rates. There are two sources of rate differences. The first one is the inherent reactivity of various components. For example, the 2,4 isomer of TDI contains two isocyanate groups of different reactivity, primary hydroxy group is more reactive than secondary, long molecules (polybutadiene polyol) are less reactive than short molecules. The second source is poor miscibility of reacting components.

Influence of miscibility is markedly shown up on the time evolution of the complex modulus (Fig. 2). Additional information can be obtained from analogous curves for the loss angle  $\delta$  (Fig. 3).

It is expected that after an increase in the relative crosslinker contents, *i.e.*, an increase in the hard segment content, the overall reaction rate grows. The small crosslinker molecule is after all more reactive than the long polyol chain. Only the most miscible mixtures in group 4 approach to this behaviour (*cf.* Fig. 2d). Curing rate of P13 is slightly higher than of P14. Sample P13 contains the smallest amount of crosslinker within the group 4,

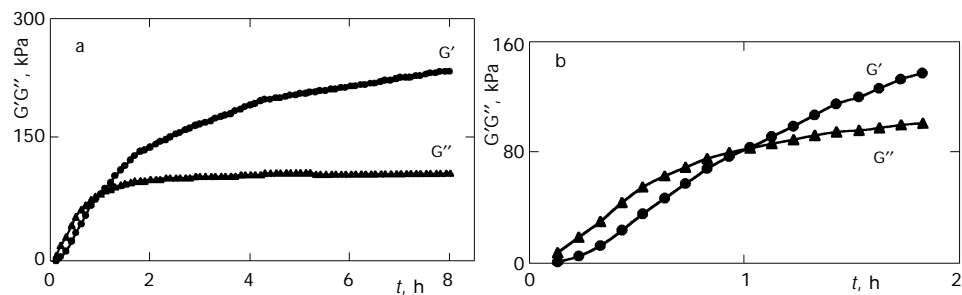


FIG. 1

Moduli responses measured for the sample P9. a overall view, b detailed view

however, the whole mixture is well miscible. Although the crosslinker contents is higher in P14, its curing rate is slower because of poorer miscibility. Initial phase separation hamper the good contact of reacting molecules and separated crosslinker works like a plasticizer lowering the modulus. Concentration of the phase separated crosslinker is so high in samples P15, P16 that it can readily react with free and phase separated isocyanate (which is miscible with the crosslinker) forming high modulus product and, consequently, the curing rate is higher than for the sample P13.

The less miscible mixtures from group 1 give more pronounced break point. The overall curing rate changes as follows: P2 > P1 > P3 ≈ P4 (Fig. 2a). Increasing contents of immiscible compounds cause strong phase separation in mixtures P3 and P4, which prevents good contact of reactive groups. Similar behaviour is observed for group 3 (cf. Fig. 2c).

Mixtures from group 2 are the least reactive and overall curing rate decreases with increasing amount of crosslinker (Fig. 2b). Besides the miscibility problems of glycerol with both the polyol and isocyanate, an additional problem of low and dissimilar reactivity of TDI occurs. Therefore, the

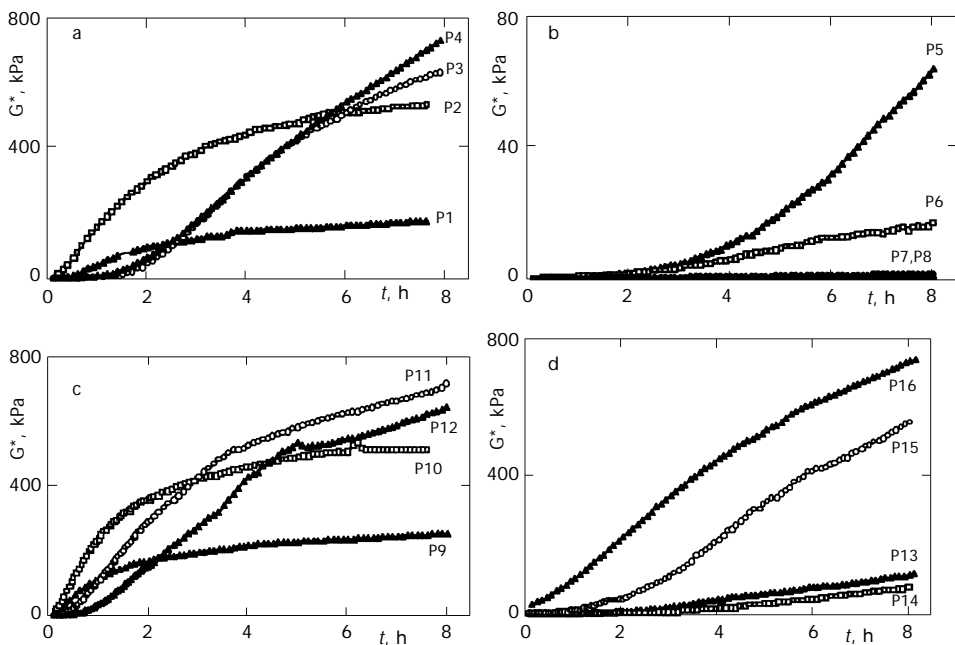


FIG. 2

Time evolution of complex modulus of the samples of group 1 (a), 2 (b), 3 (c), 4 (d)

higher the relative contents of glycerol (and, consequently, the amount of TDI), the lower the overall crosslinking rate. In contrast, TIPA used as a crosslinker in group 4 is much more miscible with both TDI and polyol and the overall rate changes as expected. It was even observed, particularly for the mixture P16, that part of TIPA reacts with TDI already during the mixing phase giving a relatively highly viscous mixture at the very beginning of the reaction (*cf.* the first measured value of complex modulus for this mixture in Fig. 2d).

Miscibility effects on the reaction rate are apparent also from the viscoelastic responses obtained with different amounts of catalyst. Mixtures P3 and P7 were prepared with the same portion of catalyst solutions of various concentrations (Table III). The behaviour of mixture P7 (Fig. 4) corresponds to the expected response to increased absolute amount of catalyst. However, in the case of mixture P3, there is some break point again (Fig. 5). The response obtained with the highest concentration of the catalyst shows the lowest build up of complex modulus. Probably, the catalyst accelerated first the reaction between the crosslinker and isocyanate which resulted in

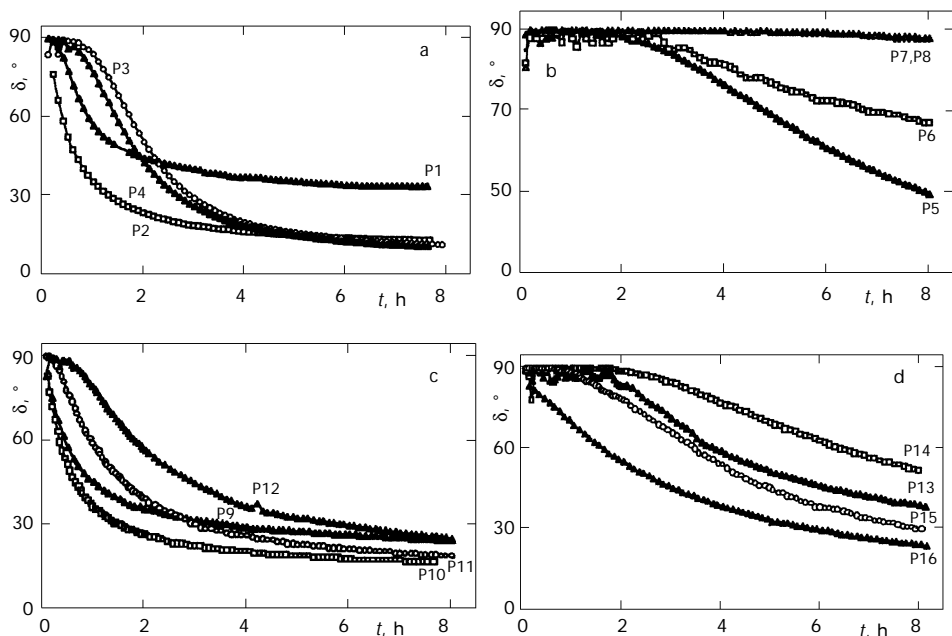


FIG. 3

Time evolution of loss angle of the samples of group 1 (a), 2 (b), 3 (c), 4 (d)



formation and separation of relatively large hard domains impeding good contact of remaining reactive groups. This is supported by the results obtained with 100P3. Mixture 100P3 was unmeasurable because of forming semi-solid product already during mixing. The catalyst did not have such strong accelerating effect on the less reactive TDI used in mixture P7 and this mixture behaves as expected: increasing the absolute catalyst amount results in rise in the overall reaction rate (*cf.* Fig. 4).

No maximum on  $G''(t)$  or  $\delta(t)$ , *i.e.* not on  $\log G''(t)$  or  $\tan \delta(t)$  curves was found on any sample in the measured time domain.

From a comparison of  $t_1$  values, the following conclusions can be derived. The mixtures from groups 1 and 3 show a minimum on the dependence of

TABLE III  
Concentration of catalyst solutions and total catalyst amount used in the reaction rate tests

Sample P3	Catalyst solution wt. %	Catalyst <sup>a</sup> wt. %	Sample P7	Catalyst solution wt. %	Catalyst <sup>a</sup> wt. %
5P3	5	0.00266	5P7	5	0.00268
10P3	10	0.00532	10P7	10	0.00536
20P3	20	0.01064	20P7	20	0.01073
50P3	50	0.02659	50P7	50	0.02682
			100P7	100 <sup>b</sup>	0.05363

<sup>a</sup> 0.083 g of catalyst solution per 100 g Krasol LBH. <sup>b</sup> Undiluted catalyst.

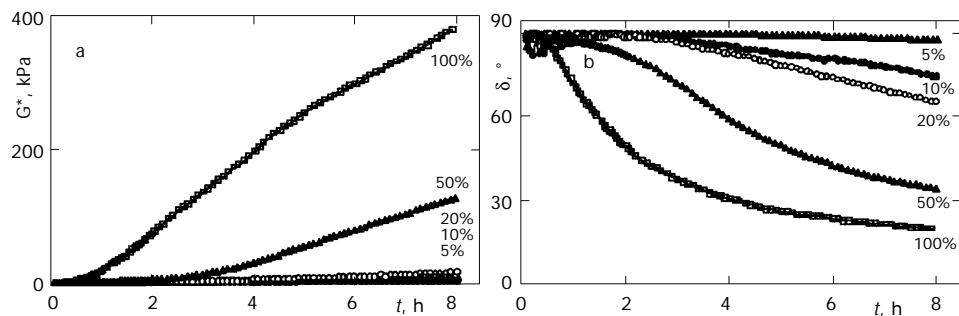


FIG. 4

Effect of the catalyst concentration (see Table III) on the time evolution of complex modulus (a) and loss angle (b) of the sample P7

TABLE IV  
Time of moduli curves intersection and corresponding moduli value

Group	Sample	$t_p$ , min	$G' = G''$ in time $t_p$ , Pa
1	P1	111	64 490
	P2	36	62 750
	P3	128	44 350
	P4	111	38 500
2	P5	537	58 454
	P6	1 375	35 600
	P7	>1 380	-
	P8	>1 380	-
3	P9	57	82 000
	P10	35	113 000
	P11	92	155 500
	P12	171	186 000
4	P13	>480	-
	P14	374	58 600
	P15	298	228 500
	P16	180	243 000

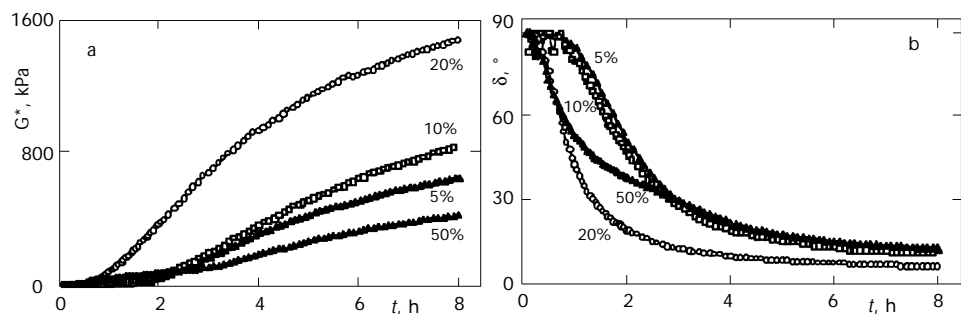


FIG. 5

Effect of the catalyst concentration (see Table III) on the time evolution of complex modulus (a) and loss angle (b) of the sample P3

$t_1$  on the hard segment contents (Table IV). The minimum occurs with the second sample of each group. If the  $t_1$  value is considered to be the gelation point, it can be stated that the second sample gels most rapidly. As the ratio of molar amounts of polyol and crosslinker in both samples (1.77) is close to the ratio for regular network (1.5), *i.e.*, the network containing two trifunctional crosslinker molecules per three polydiol (and six diisocyanate) molecules, it can be speculated that such a specific composition supports fast formation of first gel molecules. Increasing the crosslinker amount probably results in the preferential formation of short, isolated hard segments (probably OH-ended) and gelation delay.

Values of  $t_1$  increase and decrease with the hard segment contents in groups 2 and 4, respectively (Table IV). This can be explained by the effect of miscibility and higher reactivity of crosslinker. Higher concentrations of miscible, more reactive crosslinker (*e.g.* TIPA) accelerate gelation.

TABLE V  
The last measured moduli values

Group	Sample	$t$ , h	$G'$ , Pa	$G''$ , Pa
1	P1	22.0	244 000	112 500
	P2	23.0	633 000	117 000
	P3	23.0	1,057 000	142 600
	P4	–	–	–
2	P5	24.0	274 500	110 000
	P6	22.5	35 100	35 400
	P7	23.5	2 300	5 500
	P8	22.5	2 200	4 280
3	P9	23.5	329 000	107 400
	P10	23.0	753 000	180 500
	P11	25.5	994 140	218 250
	P12	22.5	817 000	270 500
4	P13	24.5	275 000	126 500
	P14	22.5	228 870	100 500
	P15	–	–	–
	P16	23.0	1,078 624	280 350

There are two opposite trends in the changes of moduli values in  $t_1$  with the hard segments contents. The moduli decrease within groups 1 and 2 and increase within the other two groups (Table IV). This is probably the effect of the crosslinker structure and miscibility. The more bulky and miscible TIPA was used in groups 3 and 4. Theoretically, glycerol should be more reactive than TIPA because it contains two primary hydroxy groups. However, miscibility can change these predictions markedly as demonstrated by a very simple experiment. When stoichiometric amounts of glycerol or TIPA with, *e.g.*, TDI are mixed at laboratory temperature, completely different reaction behaviour is observed. Whereas TIPA-TDI mixture reacts within several minutes forming solid product, glycerol-TDI mixture remains liquid, unreacted even after 24 h unless the catalyst is added. Glycerol does not mix with the isocyanate and settles in the form of droplets on the bottom of container. It should be pointed out that TIPA may also act as a catalyst because of its tertiary amine structure.

Regarding the final moduli (including complex modulus) values, only partial conclusions can be made because of very slow curing of some mixtures. Very probably, the higher the hard segments content, the higher the complex modulus values, as expected. From the results obtained with more reactive mixtures from groups 1 and 3, prepared from the fast-reacting isocyanate, it seems that increased hard segment contents raises much more the elastic than the viscous modulus (Table V). This difference is more distinct for the immiscible crosslinker.

## CONCLUSIONS

Although polyurethane formation is very complex process incorporating influence of various miscibility of individual components, different reactivity of both molecules and individual functional groups, influence of using isocyanate mixture *etc.*, some general conclusions can be made.

Regardless of the miscibility and reactivity of polybutadiene polyurethane components, their rheokinetics behaviour is qualitatively very similar. The viscous response part is formed and finished much earlier than the elastic part. Increasing hard segment contents raises much more the elastic than the viscous modulus. Thus, the crosslinking density influences first elastic response and, to a lesser degree, the viscous response.

Quantitative differences in the rheokinetic behaviour of samples were detected. This means that the common shape of moduli responses is spread over different time scales for different mixtures. These dissimilarities are caused not only by miscibility effects but also by differences in reactivity.

Joint effect of miscibility and reactivity on the overall curing rate shows up particularly on the time plot of complex modulus.

Although poor miscibility of initial components is regarded to be one of the main causes of worse properties of polybutadiene polyurethanes, using a well miscible initial mixture need not give the best results. For instance, a well dissolved and more reactive crosslinker can easily react with isocyanate, forming relatively large solid hard segments which separate from the rest of the reaction mixture and impair the final phase structure. On the other hand, less miscible initial mixtures may lead to satisfactory results provided they are well and finely emulsified.

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