Mechanical Properties of Crosslinked Polyurethanes

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Synopsis

Stress–strain and stress–relaxation behavior of polyurethane elastomers based on poly(ethylene adipate), poly(ethylene maleate), polyethylene glycol, and 4,4′-diphenylmethane diisocyanate (MDI) have been studied. The elastomers were crosslinked by an excess of MDI and by dicumyl peroxide (DiCup); the latter was supposed to form additional crosslinks on the unsaturated bonds. The determined values of Young's modulus, Mooney-Rivlin elastic parameters C_1 and C_2, relaxation moduli $E(10$ sec$)$ and $E(100$ sec$)$, as well as relaxation speed were used to estimate the effect of MDI- and DiCup-formed crosslinks on the mechanical behavior of polyurethanes. It was found that while the elastomers crosslinked by MDI only apparently displayed viscoelastic properties, the polyurethanes additionally crosslinked by DiCup exhibited more elastic behavior. The results obtained were explained on the basis of changes in the amount of secondary bonding due to the additional network junctions formed by DiCup at nonpolar groups.

INTRODUCTION

For years polyurethane elastomers have been the subject of research and continue to find everwidening applications in various fields, for their properties can be extensively controlled using components of different structure. They are usually formed by polyaddition of diisocyanates with hydroxyl-terminated polyesters or polyethers as well as with low molecular diols or diamines.

One may consider polyurethane elastomers to be crosslinked block copolymers, consisting of moderately flexible long, linear polyester or polyether segments and relatively stiff segments of aromatic and urethane groups.

The mechanical properties of polyurethane elastomers are the result of a combination of segment flexibility, crosslinking, chain entanglement, orientation of segments, rigidity of aromatic units, hydrogen bonding, and other van der Waals forces.[1] As hydrogen bonding and other secondary attractive forces contribute much to the mechanical properties of polyurethanes, their mechanical behavior strongly depends on temperature. With increasing temperature, rapid deterioration of the mechanical properties takes place, which is caused by breaking of hydrogen and other secondary bonds as well as by the presence of relatively weak crosslinks that make up their network. In order to render the mechanical properties of polyurethanes more stable and improved, one can form stronger crosslinks in addition to the typical weak ones. Some efforts concerning this problem have been reported.[2–5]

The aim of the present study was to examine the effect of additional peroxide-formed crosslinks on the stress relaxation and tensile properties of a polyurethane having unsaturated polyester blocks.

The elastomers studied were based on two hydroxyl-terminated polyesters: poly(ethylene adipate) (PEA) and poly(ethylene maleate) (PEM) as well as of

low molecular polyethylene glycol (PEG). The molar ratio of the diols was constant: PEA:PEM:PEG = 5:1:5. The polyaddition was carried out in the presence of 4,4′-diphenylmethane diisocyanate (MDI), whose varied excess in relation to hydroxyl endgroups was to form a number of allophanate crosslinks besides urethane groups, linking randomly distributed PEA and PEM longer segments and PEG shorter segments. The PEM segments having unsaturated bonds were assumed to be the sites where additional crosslinks could be formed. For this purpose, dicumyl peroxide (DiCup) was used, as it had been found to be an effective curing agent of polyurethanes.[6]

EXPERIMENTAL

Materials

Poly(ethylene adipate) was a commercial product (Zakłady Chemiczne w Bydgoszczy, Poland) whose hydroxyl number was 58.5 and water content 0.18%. The number-average molecular weight, 1900, of the polyester was determined by the endgroup method.

Poly(ethylene maleate) was prepared by polycondensation of maleic anhydride with ethylene glycol in the presence of p-toluenesulphonic acid as a catalyst and hydroquinone as crosslinking inhibitor, according to the procedure described elsewhere.[7] The hydroxyl number of the product was 114.7, and water content was 0.12%. The molecular weight of PEM, found analytically by the endgroup method, was 960.

Polyethylene glycol 200 (Carl Roth OHG) was used as received. Its hydroxyl number was 547, water content 0.09%, and molecular weight 205, found analytically.

4,4′-Diphenylmethane diisocyanate was a commercial product (Desmodur 44-v, Bayer). It was purified by distillation under reduced pressure in the atmosphere of dry nitrogen, just before use for synthesis. The content of NCO groups found analytically was 33.23 wt %.

Dicumyl peroxide was extracted with acetone from DiCup-40 (a commercial product received from Stomil, Grudziądz), and the solvent was then removed by evaporation.

Polymerization and Preparation of Samples

The polyaddition was carried out by the one-step cast technique. A mixture of all the components was poured into Teflon molds, heated at 80°C under reduced pressure for 8 hr, and then cured at 155°C for 1 hr; the procedure has been described in detail elsewhere.[8] The sheets of elastomers produced were about 12 × 9 × 0.25 cm in size and were cut into samples for measurements. Two series of samples (A and B) were obtained. The samples belonging to a given series had a constant molar ratio of the components PEA, PEM, PEG, and different amounts of MDI or DiCup, as shown in Table I.

In order to evaluate the changes of crosslinking density with amount of crosslinker used, the sol/gel ratio and the equilibrium volume fraction v_r of the polymer in toluene-swollen samples were determined at 25°C. The results are given in Table II.

TABLE I
Components of the Elastomers Prepared

Sample	Molar ratio of main components PEA:PEM:PEG-200:MDI	DiCup crosslinker concentration $c \times 10^4$, moles/cm^3
A1	5:1:5:11.22	—
A2	5:1:5:11.33	—
A3	5:1:5:11.55	—
A4	5:1:5:11.77	—
A5	5:1:5:12.10	—
A6	5:1:5:12.65	—
A7	5:1:5:13.20	—
A8	5:1:5:13.75	—
A9	5:1:5:14.30	—
B1	5:1:5:12.10	—
B2	5:1:5:12.10	0.256
B3	5:1:5:12.10	0.512
B4	5:1:5:12.10	0.769
B5	5:1:5:12.10	1.28
B6	5:1:5:12.10	2.05
B7	5:1:5:12.10	3.08
B8	5:1:5:12.10	4.10

Measurements of Mechanical Properties

The measurements of mechanical properties were carried out using an Instron tensile testing instrument Type 1026, equipped with a thermostating jacket connected to a thermostat.

Extensional Stress–Strain Measurements

Strips of samples of approximate dimensions $110 \times 7.4 \times 2$ mm were continuously extended at low constant cross-head speed of 0.5 cm/min up to an elongation of about 200%. The increasing value of tensile forces was recorded on the moving chart. The measurements were carried out at 50° and 75°C. During the experiments the temperature of the samples was controlled within an accuracy of 0.2°C. The test was started when the temperature became stabilized at the required value, but not sooner than 1 hr after maintaining the thermostating jacket.

The results were expressed as plots of stress σ, related to the initial cross-sectional area of a specimen, versus strain ϵ. The values of Young's modulus E were calculated from the slopes of plots $\sigma\alpha$ versus ϵ, where α is the principal extension ratio, which equals $\epsilon + 1$. The results were also plotted as $\sigma/(\alpha - \alpha^{-2})$ versus α^{-1} to find the values of the elastic parameters C_1 and C_2 of the Mooney-Rivlin equation[9]:

$$\sigma = (C_1 + C_2\alpha^{-1})(\alpha - \alpha^{-2}) \tag{1}$$

TABLE II
Swelling Characteristics of the Elastomers in Toluene

Sample	MDI cross-linker concentration $c \times 10^4$, moles/cm^3	DiCup-cross-linker concentration $c \times 10^4$, moles/cm^3	Sol/gel ratio	v_r
A1	0.193	—	—	—
A2	0.289	—	0.316	0.088
A3	0.479	—	0.190	0.128
A4	0.668	—	0.143	0.156
A5	0.949	—	0.101	0.190
A6	1.41	—	0.069	0.294
A7	1.86	—	0.0526	0.341
A8	2.31	—	0.0417	0.406
A9	2.74	—	0.0307	0.469
B1	0.949	—	0.0638	0.231
B2	0.949	0.256	0.0549	0.329
B3	0.949	0.513	0.0493	0.361
B4	0.949	0.769	0.0449	0.425
B5	0.949	1.28	0.0419	0.458
B6	0.949	2.05	0.0395	0.527
B7	0.949	3.08	0.0373	0.580
B8	0.949	4.10	0.0363	0.614

Stress–Relaxation Experiments

Samples of approximate dimensions 110 × 7.4 × 2 mm were rapidly extended at a cross-head speed of 50 cm/min to an elongation of 20%. The strain was maintained constant throughout the experiment, lasting for about 3 hr. The changing value of tensile force was recorded on a moving chart. The stress-relaxation behavior was investigated at a temperature of 75°C, which was controlled within an accuracy of 0.2°C. The relaxation moduli $E(t)$ were calculated using

$$E(t) = \sigma(t) \, \epsilon^{-1} \qquad (2)$$

where $\sigma(t)$ is stress at the time t, related to the initial cross-sectional area, and ϵ is the deformation. The results were plotted in terms of log $E(t)$ versus log t.

RESULTS AND DISCUSSION

Extensional Stress–Strain Behavior

In both series of samples, which differed in the amount of MDI and DiCup crosslinking agents, the stress σ relating to a given strain ϵ increased with increasing amount of crosslinker, as expected (see some examples in Fig. 1). Simple stress–strain plots were nonlinear, like those of most rubbers. In order to obtain Young's modulus values E, $\sigma\alpha$ was plotted versus ϵ, yielding good linear relationships (see Fig. 2). Moduli E, defined as slopes of these plots, are given in Table III.
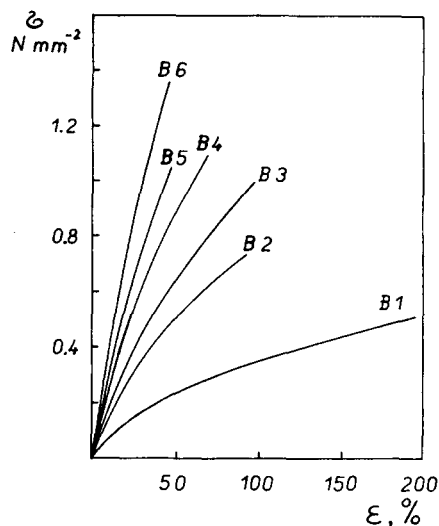
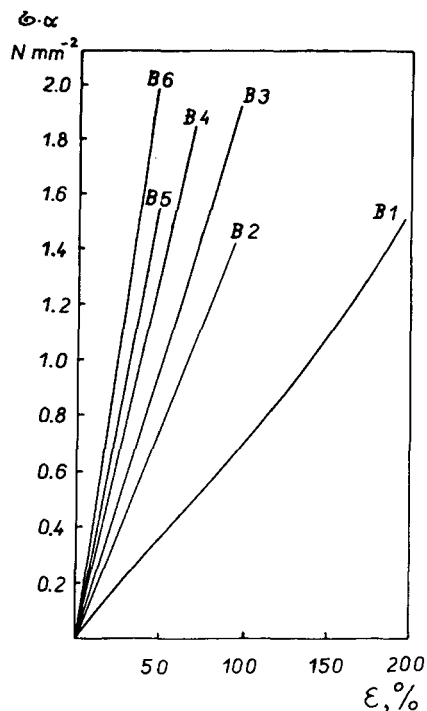Fig. 1. Stress–strain dependence for samples B1 to B6. Temperature 75°C.

Fig. 2. Stress–strain dependence in terms of $\sigma\alpha$ vs ϵ for samples B1 to B6. Temperature 75°C.

For samples A1 to A9, modulus E increased with increasing amount of MDI. At 75°C, however, all the E values but one were smaller than those measured at 50°C. Polyurethanes are known to contain a high degree of hydrogen bonding[10] formed by urethane NH groups, acting as donors, and urethane carbonyl or macroglycol ester carbonyl, which act as acceptors. Hydrogen and other secondary bonds present in polyurethanes readily dissociate when the temperature increases above 40°–50°C,[11,12] and van der Waals attractive forces disap-

TABLE III

Mechanical Properties of Polyurethane Rubbers Measured at 50° and 75°C. Dependence of Moduli on Concentration of MDI and DiCup Crosslinking Agents

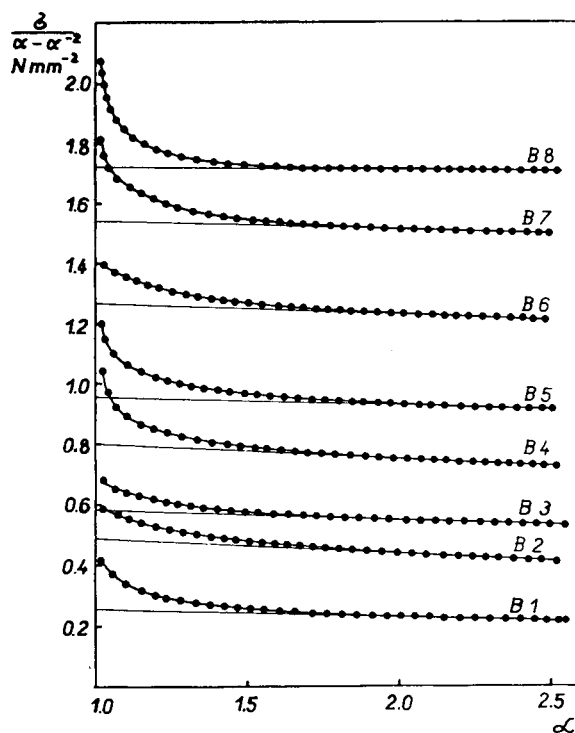| Sample	MDI cross-linker concentration $c \times 10^4$, moles/cm^3	DiCup-cross-linker concentration $c \times 10^4$, moles/cm^3	50°C			75°C		
			E, N/mm^2	E^*, N/mm^2	$3(C_1 + C_2)$, N/mm^2	E, N/mm^2	E^*, N/mm^2	$3(C_1 + C_2)$, N/mm^2
A1	0.193	—	0.088	0.081	—	0.060	0.060	0.060
A2	0.289	—	0.112	0.108	—	0.088	0.081	0.126
A3	0.479	—	0.220	0.210	—	0.160	0.150	0.189
A4	0.668	—	0.351	0.330	—	0.350	0.323	0.426
A5	0.949	—	0.524	0.510	—	0.600	0.582	0.720
A6	1.41	—	1.22	1.18	—	1.10	1.01	1.33
A7	1.86	—	1.68	1.60	—	1.72	1.64	2.12
A8	2.31	—	2.31	2.30	—	2.36	2.36	2.90
A9	2.74	—	3.11	2.99	—	3.18	3.05	3.90
B1	0.949	—	0.770	0.765	1.00	0.700	0.675	0.846
B2	0.949	0.256	1.52	1.47	1.71	1.55	1.47	1.70
B3	0.949	0.513	1.88	1.74	2.02	2.03	1.88	2.11
B4	0.949	0.769	2.61	2.40	2.70	2.70	2.63	2.92
B5	0.949	1.28	3.00	2.87	3.23	3.31	3.24	3.47
B6	0.949	2.05	4.01	3.81	4.16	4.30	4.23	4.46
B7	0.949	3.08	4.91	4.62	5.00	5.01	4.92	5.22
B8	0.949	4.10	5.39	5.16	5.55	5.48	5.39	5.71

Fig. 3. Stress–strain dependence in terms of $\sigma/(\alpha - \alpha^{-2})$ vs α for samples B1 to B8. Temperature 50°C.

pear first at a temperature of about 20°C lower than that of the rupture of hydrogen bonds.[13] Lower E values at higher temperatures for samples A1 to A9 indicated that these values did not represent equilibrium. Presumably this was caused by the fact that in elastomers A1 to A9, which were crosslinked with an excess of MDI only, the contribution of hydrogen bonding and other van der Waals attractive forces to the modulus was considerable. As the temperature increases, those secondary bonds disappear, causing the drop in E values. Such a behavior of lightly crosslinked polyurethanes has already been reported.[14]

Samples B2 to B8, on the other hand, having increasing amounts of DiCup crosslinker, showed higher E values at higher temperatures (Table III), as the theory predicts. These results might suggest that the presence of DiCup, which formed additional network junctions besides the constant concentration of allophanate crosslinks, reduced the amount of secondary bonding in the elastomers tested.

To illustrate how the extensional behavior of these elastomers deviates from the predictions of the theory of rubber elasticity, expressed by the equation[15]

$$\sigma = RT\frac{\nu_e}{V}(\alpha - \alpha^{-2}) \tag{3}$$

(where R is gas constant, T is absolute temperature, and ν_e/V is the elastically effective crosslinking density), $\sigma/(\alpha - \alpha^{-2})$ versus α was plotted. According to the theory one should obtain a straight line, parallel to the α axis. The plots obtained, however, start with a rapid nonlinear decrease of $\sigma/(\alpha - \alpha^{-2})$ values.

As α increases, the decline in $\sigma/(\alpha - \alpha^{-2})$ is smaller, and the plots become linear, with slight slopes (Fig. 3). When the linear part of these plots was extrapolated to $\alpha = 1$, the shear modulus $G^* = RT\,\nu_e/V$ was obtained and then converted to E^* values using the expression $E = 3G$. The results listed, in Table III, show that the E^* moduli obtained from extrapolation were in good agreement with E values determined from the slopes of $\sigma\alpha$-versus-ϵ plots. Moduli E^* were a few per cent smaller than E moduli.

From the tensile testing at 50° and 75°C, Mooney-Rivlin plots were done. Elastomers of the series A1 to A9 at 75°C and B1 to B8 at 50° and 75°C yielded good Mooney-Rivlin plots (see some examples in Fig. 4), from which the elastic parameters C_1 and C_2 could be determined. Both C_1 and C_2 increased with increasing crosslinker concentration (Table IV). For samples A1 to A9 at 50°C, no part of the $\sigma/(\alpha - \alpha^{-2})$-versus-$\alpha^{-1}$ plots was a straight line, indicating that viscoelastic properties still predominated. It might suggest that these elastomers, at 50°C, still have a considerable amount of secondary bonding.

Equations (1) and (3) can be combined to form the well-known expression $G = C_1 + C_2$, and hence $E = 3(C_1 + C_2)$. Comparing the values of $3(C_1 + C_2)$ with those of E and E^* (see Table III), one can notice that for the samples A1 to A9, at 75°C, the $3(C_1 + C_2)$ values are about 20% larger than the E values. On the other hand, far better agreement of $3(C_1 + C_2)$ values with E moduli was found for samples B1 to B8. Their $3(C_1 + C_2)$ values deviate from those of E by about 5% only.

The elastomers A1 to A9, crosslinked with increasing excess of MDI, did not show any apparent dependence of the C_2/C_1 ratio on the amount of the crosslinker. The C_2/C_1 values ranged from 1.1 to 1.9 and are much higher than those reported by Blokland.[16] On the other hand, the elastomers B1 to B8 display an
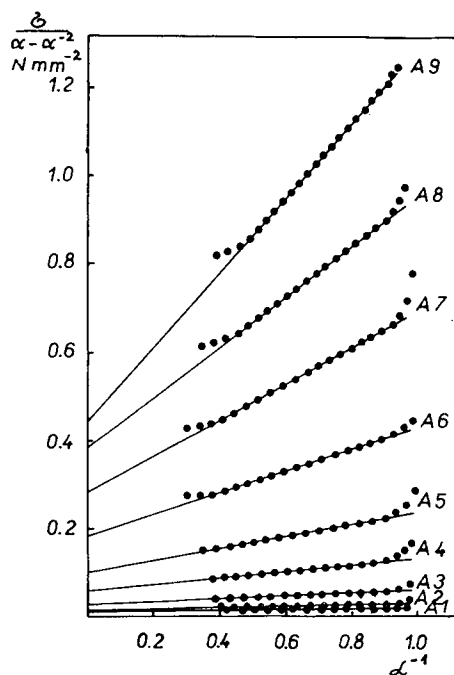

Fig. 4. Mooney-Rivlin plots for samples A1 to A9. Temperature 75°C.

TABLE IV
Mooney-Rivlin Elastic Parameters Measured at 50° and 75°C. Dependence of C_1 and C_2 Constants on Concentration of MDI and DiCup Crosslinking Agents

Sample	MDI crosslinker concentration $c \times 10^4$, moles/cm³	DiCup-crosslinker concentration $c \times 10^4$, moles/cm³	50°C			75°C		
			C_1, N/mm²	C_2, N/mm²	C_2/C_1	C_1, N/mm²	C_2, N/mm²	C_2/C_1
A1	0.193	—	—	—	—	0.009	0.011	1.22
A2	0.289	—	—	—	—	0.017	0.025	1.47
A3	0.479	—	—	—	—	0.030	0.033	1.10
A4	0.668	—	—	—	—	0.057	0.085	1.49
A5	0.949	—	—	—	—	0.100	0.140	1.40
A6	1.41	—	—	—	—	0.187	0.255	1.36
A7	1.86	—	—	—	—	0.280	0.425	1.52
A8	2.31	—	—	—	—	0.380	0.585	1.54
A9	2.74	—	—	—	—	0.450	0.850	1.89
B1	0.949	—	0.110	0.224	2.04	0.117	0.165	1.41
B2	0.949	0.256	0.295	0.275	0.93	0.310	0.255	0.82
B3	0.949	0.513	0.390	0.284	0.73	0.433	0.270	0.62
B4	0.949	0.769	0.570	0.330	0.58	0.633	0.340	0.54
B5	0.949	1.28	0.730	0.348	0.48	0.796	0.360	0.45
B6	0.949	2.05	1.03	0.355	0.34	1.12	0.365	0.33
B7	0.949	3.08	1.29	0.375	0.29	1.37	0.369	0.27
B8	0.949	4.10	1.48	0.375	0.25	1.53	0.372	0.24

TABLE V
Stress–Relaxation Properties of Polyurethane Rubbers

Sample	MDI cross-linker concentration $c \times 10^4$, moles/cm^3	DiCup-cross-linker concentration $c \times 10^4$, moles/cm^3	$E(10\,\text{s})$, N/mm^2	$E(100\,\text{s})$, N/mm^2	$|E(10\,\text{s}) - E(100\,\text{s})|/E(10\,\text{s})$	E_∞, N/mm^2
A1	0.193	—	0.102	0.061	0.402	—
A2	0.289	—	0.154	0.098	0.356	—
A3	0.479	—	0.235	0.156	0.336	—
A4	0.668	—	0.348	0.230	0.334	—
A5	0.949	—	0.668	0.519	0.223	—
A6	1.41	—	1.36	1.15	0.154	—
A7	1.86	—	1.73	1.54	0.109	—
A8	2.31	—	2.44	2.26	0.074	—
A9	2.74	—	3.19	3.02	0.056	—
B1	0.949	—	0.773	0.678	0.123	—
B2	0.949	0.256	1.52	1.40	0.073	1.29
B3	0.949	0.513	1.67	1.56	0.066	1.51
B4	0.949	0.769	2.28	2.18	0.044	2.07
B5	0.949	1.28	2.73	2.65	0.029	2.57
B6	0.949	2.05	3.50	3.44	0.017	3.38
B7	0.949	3.08	4.35	4.32	0.007	4.09
B8	0.949	4.10	4.85	4.82	0.006	4.30

explicit decrease in C_2/C_1 ratio as DiCup amount increases at constant MDI concentration (see Table IV). The C_2/C_1 ratio is known to be strongly dependent on the character of a network and is influenced by the previous history of the elastomer, its preparation, and the measurement conditions. Since the C_2/C_1 ratio is often taken as an important variable characterizing departures from ideal elasticity, as well as a relative measure of intermolecular interaction, one might conclude that the peroxide-formed additional crosslinks changed the properties of the polyurethane networks tested toward more elastic behavior, diminishing simultaneously the intermolecular attractive forces.

Stress–Relaxation Behavior

Stress–relaxation measurements of the polyurethanes investigated showed that their viscoelastic properties strongly depended on the kind and amount of crosslinker. For the samples A1 to A9, crosslinked with MDI only, log $E(t)$-versus-log(t) plots did not give any equilibrium values of the relaxation moduli. Such a behavior of polyurethanes has already been reported[14,17–21] and has been attributed to the relative instability of urethane and allophanate groups, which can break and, perhaps, reform as a result of stress. In addition to the breaking of primary bonds, stress relaxation of polyurethanes is known to be effected by the breaking of hydrogen bonds and other van der Waals attractive forces.[22,23] From the tensile stress–relaxation plots, the 10- and 100-sec moduli $E(10$ sec$)$ and $E(100$ sec$)$ were estimated, and the values of $[E(10$ sec$) - E(100$ sec$)]/E(10$ sec$)$, which can be taken as a qualitative measure of the relaxation speed, were calculated (Table V). The elastomers B1 to B8 behaved differently from elastomers A1 to A9, showing that the presence of DiCup crosslinker improved their relaxation properties. Samples B2 to B8, with increasing amount of DiCup, had much smaller relaxation speeds, and the relaxation moduli $E(t)$ attained equilibrium values, $E_\infty(t)$ (Table V). In all cases, $E_\infty(t)$ moduli were smaller than E values determined from tensile stress–strain measurements.

Both tensile stress–strain and stress–relaxation results proved that additional DiCup-formed crosslinks considerably changed the mechanical properties of polyurethane elastomers. While the elastomers crosslinked by MDI only apparently show viscoelastic behavior, polyurethanes additionally crosslinked by DiCup become more elastic. The presence of DiCup, on the one hand, increases crosslinking density of the elastomers, forming additional network junctions at nonpolar groups; and on the other hand, it decreases the amount of hydrogen bonding as well as supermolecular structuring. All these structural changes shift the mechanical properties of polyurethanes toward rubber-like elastic behavior.

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