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ORIGINAL CONTRIBUTION

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Molecular dynamics of elastomers investigated by DMTA and the NMR-MOUSE®

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Abstract A series of elastomers, consisting of different polymers and crosslink densities, is investigated by dynamic-mechanical thermal analysis (DMTA) and NMR relaxation in an inhomogeneous field by the NMR-MOUSE®. A broad range of molecular mobilities and therefore variation in the glass transition temperature is covered by use of polymers with different side groups. The molecular mobility of every system is also investigated by the frequency-temperature superposition principle. Reduced variables are deduced from analysis of the DMTA results. Comparison of both DMTA and NMR results leads to consistent conclusions. The temperature dependence of the transverse relaxation time can be predicted by the use of an empirical power law presented in this paper and the WLF-equation.

Keywords Molecular motion · Relaxation · Free volume theory · WLF-equation

Introduction

Because many of the elastomeric products are in use in a dynamical way, the dynamic-mechanical properties are important for most rubber products like tires or shock absorbers. Molecular parameters determine the bulk behavior of elastomers and the time of macroscopic mechanical response of excited polymeric samples. For many years the well established way to measure these properties in the rubber industry has been dynamic-mechanical thermal analysis (DMTA) [1]. By this method, many important characteristics, e.g., the glass transition temperature and frequency-temperature characteristics, which are expressed in terms of master curves, can be obtained. These curves characterize the molecular motion of the polymeric chains. On the other hand the NMR relaxation accounts for the molecular mobility as well [2]. It has been shown that the transverse relaxation time T_2 decreases with increasing crosslink density of elastomers [3, 4, 5, 6]. By the help of a non-invasive, *mo*bile *u*niversal *s*urface *e*xplorer, called NMR-MOUSE® [3] measurements, e.g., on the surface of tires of the transverse relaxation time T_2 can be performed easily. Therefore the interpretation of the molecular mobility in terms of DMTA and NMR are of high practical interest. In the present study model elastomeric systems are investigated by both methods. The results obtained are compared with particular attention to molecular mobility.

Interpretation of the molecular mobility

The molecular mobility is interpreted in terms of the free volume theory according to Doolittle [7]. Due to the thermal energy of the polymer chain, a segment of the chain performs a movement from one equilibrium position to another. The conditions for the realization of such a jump are: 1) enough free volume for the segment to fit in; 2) the segment has enough energy to break off from its surroundings and move into the free volume space; and 3) movement of the segment in the proper direction at just the right time [8]. The molecular motion results in a viscosity η for the system which can be described by Eq. (1), often called the "Doolittle equation":

$$\eta = k_1 \cdot e^{k_2 \cdot \frac{v^*}{v_f}}, \tag{1}$$

where v_f is the free volume of the polymer, v^* the required free volume to perform a jump, and k_1 and k_2 are constants. Therefore Doolittle's equation describes the viscosity in terms of free and required volumes without regarding temperature. However, the temperature dependence of the viscosity is introduced by the dependence of the free volume v_f on temperature T according to Eq. (2):

$$v_f = v_g + v_m \Delta\alpha \left(T - T_g\right), \tag{2}$$

where v_g is the free volume at the glass transition temperature T_g, v_m is a fictive volume of the molecule at absolute zero without free volume, and $\Delta\alpha$ the difference of the thermal expansion coefficients in the glassy and the liquid phases, respectively. Assuming that v_m is independent of temperature, and regarding Eqs. (1) and (2) for two different temperatures, leads to Eq. (3) following rearrangement of terms:

$$\log \frac{\eta_g}{\eta} = \frac{\overbrace{\left(v^*/v_g\right)}^{C_1}\left(T - T_g\right)}{\underbrace{\left(v_g/v_m\Delta\alpha\right)}_{C_2} + \left(T - T_g\right)}. \tag{3}$$

Using the results of many different authors, Williams et al. [9] could empirically show that $C_1 \approx 17{,}44$ and $C_2 \approx 51{,}6$, which nowadays are well recognized as the WLF-parameters. Therefore the WLF-parameters are not only empirical constants but have a physical meaning as stated above. As mentioned by Ferry, these "universal" values should be considered as a first approximation, obtained as an average for a large number of different polymers [10]. In the present study the specific C_1 and C_2 values for every single system were evaluated according to the second method of Ferry ([10], p 305). Interpretation of the viscosity of the system in terms of molecular mobility leads to the formulation of a so-called "molecular jump frequency" ϕ, which can be described by Eq. (4) [11]:

$$\log \frac{\phi}{\phi_g} = \frac{C_1\left(T - T_g\right)}{C_2 + \left(T - T_g\right)}, \tag{4}$$

where ϕ_g is the jump frequency in the glassy state. From dielectrical measurements a reasonable number of $\phi_g = 0.1$ Hz is obtained [8], which means in general a lower limit for ϕ. That means, in the sense of the present interpretation, a polymeric chain segment performs one jump every 10 s in the glassy state. An upper limit is set by the vibration frequency of molecules at $\phi = 10^{12}$–10^{14} Hz [8, 12]. Frequencies at 10^{13} Hz, for example, are typical for molecular vibrations which can be detected, e.g., by IR spectroscopy.

By the relation $2\pi\phi = \tau^{-1}$ the frequency scale can be turned into the time scale where τ means a mechanical relaxation time. The main relaxation time determines the time dependence of a mechanically excited rubber sample and can be obtained by dynamic-mechanical thermal analysis (DMTA). For example, by the approximation of Tobolsky [13] the "relaxation time spectrum" $H(\tau)$ can be obtained according to Eq. (5):

$$E''(\omega) \approx \frac{\pi}{2}\left[H(\tau)\right]_{\tau = 1/\omega}, \tag{5}$$

where E'' displays the loss modulus.

With respect to the different time scales of motion one has to regard a whole time spectrum of mechanical relaxation times. Note that the mechanical relaxation time τ must not be confused with the transverse relaxation time T_2.

Experimental

Sample formulation and preparation. The systems investigated consist of unfilled rubber types, which cover a broad range of molecular mobility; see Fig. 1. All polymers are free of oil, which can be regarded as a low molecular weight impurity leading to a further contribution in T_2. All samples are sulfur crosslinked and a crosslink series within every polymer was available for measurements. For the particular formulation of the samples see Table 1. All samples were mixed in a laboratory Brabender Banburymixer according to Table 1 and sheeted out through a mill afterwards. The samples were vulcanized in a laboratory press at 160 °C to maximum crosslink density according to a Monsanto MDR2000E vulcameter.

DMTA and NMR-measurements. The DMTA investigations were performed by an "Iwamoto"-viscoelastic spectrometer in tensile mode. The dimensions of the samples were (l×w×t) 20×4×2 mm. The measurements were carried out under 10% prestrain with a dynamical amplitude of ±0.15%. This condition was chosen with respect to the force limit and the force resolution of the spectrometer at low and high temperatures. With these parameters the maintenance of constant strain amplitude over the whole range of temperature was assured. The investigated temperature range started at least 20 °C below the respective glass

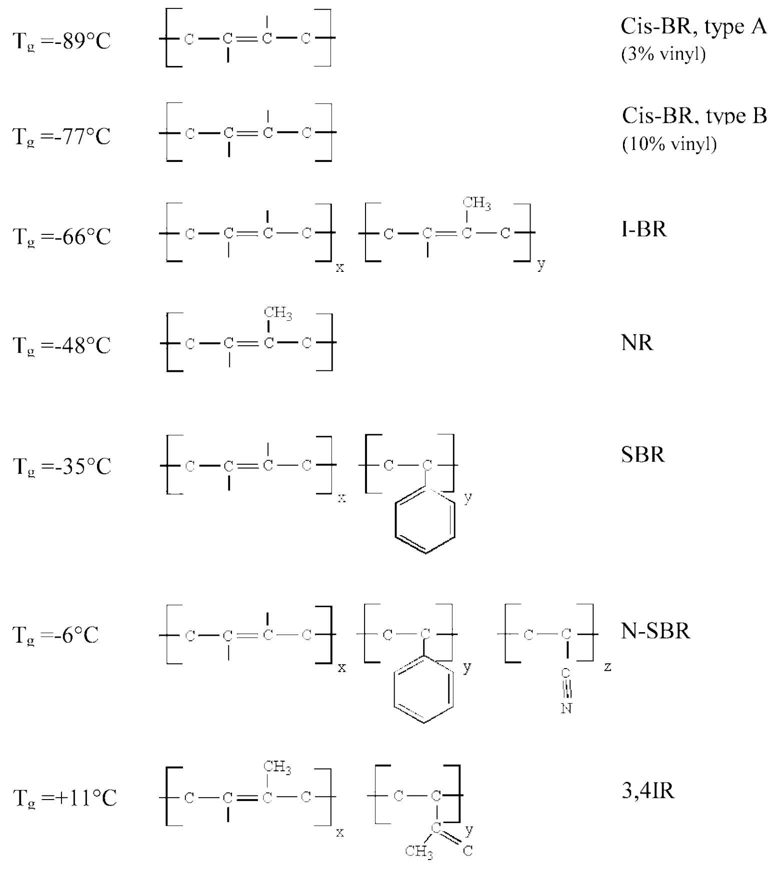

Fig. 1 Microstructure of the polymers investigated and glass transition temperatures at 10 Hz

Table 1 Compound formulation and mixing data

Polymer	100 phr
ZnO3000	3 phr
Stearic acid	2 phr
Sulfur	1,2,3,4,5 phr
TBBS	1,2,3,4,5 phr
Mixing process:	
0′ Polymer	
8′ Zinc oxide + Stearic acid + TBBS + Sulfur	
18′ dump	

Table 2 Test parameters for NMR relaxation measurements

Recycling delay/s	0.25
Number of scans	1250
Frequency/MHz	19.5
Receiver gain	95
Pulse attenuation	10
Min. echo time/ms	0.075
Increment	1.15
Max. echo time/ms	20
Pulse lengths/µs:	
Cis-BR (A)	5.2
Cis-BR (B)	5.0
I-BR	4.8
NR	5.0
SBR	4.4
N-SBR	4.2
3,4 IR	2.4

transition temperature and went up to 100 °C for all samples. The measurements were performed at frequencies of 1, 10, and 50 Hz.

The NMR-investigations were carried out with an NMR-MOUSE® [3] at room temperature (23 ± 2 °C). The samples were cylindrical in shape with a diameter of 20 mm and a thickness of 2 mm. To improve the signal-to-noise ratio, two samples, one on top of the other, were investigated together. The ^1H spin-spin relaxation time T_2 was investigated by Hahn echo experiments [2]. The magnetization decay was fitted by a single exponential curve using the program Table Curve 2D v5.00. For all samples the same range of echo times was chosen independent of the glass transition temperature (Table 2). For every polymer system the optimum pulse length was determined and kept constant within the crosslink series of the polymer. Care was taken to avoid heating of the samples by the pulse sequence, therefore the measurement of one sample took 24 h. The specific parameters used are listed in Table 2.

Results

Table 3 displays the glass transition temperatures obtained for the three frequencies investigated and the transverse relaxation time T_2. The specific WLF-constants C_1 and C_2 for every system, obtained by the shift-procedure according to Ferry [10], are displayed in Table 3 as well as the “molecular jump frequency”, calculated by Eq. (4) for $T = 23$ °C. The mechanical

Table 3 Results of DMTA and NMR relaxation measurements

Sample	C_1	C_2/°C	T_2/ms	log(τ_0/s)	ϕ/Hz	T_g/°C 1 Hz	T_g/°C 10 Hz	T_g/°C 50 Hz
Cis-BR (A)1/1	12.32	50.3	2.306	Not poss.	4.6E+07	–92.4	–89.2	–85.7
Cis-BR (A)2/2	12.90	45.7	1.760	Not poss.	1.9E+08	–89.9	–85.0	–81.8
Cis-BR (A)3/3	13.41	50.2	1.406	–11.095	2.3E+08	–87.7	–82.5	–78.6
Cis-BR (A)4/4	13.04	51.9	1.163	–10.619	8.4E+07	–84.6	–78.8	–75.1
Cis-BR (A)5/5	12.92	48.3	0.999	–9.822	9.5E+07	–81.3	–74.5	–70.1
Cis-BR (B)1/1	13.86	38.3	1.660	–11.064	2E+09	–83.1	–76.6	–73.4
Cis-BR (B)2/2	14.83	50.6	1.383	–9.960	1.2E+09	–79.1	–73.9	–70.2
Cis-BR (B)3/3	13.32	48.2	1.157	Not poss.	1.3E+08	–75.6	–71.2	–66.5
Cis-BR (B)4/4	12.84	59.4	1.000	–9.106	1.1E+07	–71.0	–65.8	–61.6
Cis-BR (B)5/5	13.12	56.0	0.865	–9.925	1.8E+07	–66.7	–61.3	–57.2
I-BR 1/1	13.03	46.2	1.706	–9.531	7.4E+07	–70.7	–65.9	–62.2
I-BR 2/2	12.50	50.0	1.406	–9.696	1.4E+07	–66.3	–62.2	–58.3
I-BR 3/3	12.65	63.5	1.160	–8.973	2942701	–63.7	–58.1	–54.8
I-BR 4/4	12.38	46.6	0.965	–9.983	1.1E+07	–59.2	–54.3	–51.3
I-BR 5/5	12.69	50.1	0.840	–10.740	1E+07	–57.0	–51.6	–46.6
NR 1/1	11.80	57.3	1.604	–9.081	754693	–52.3	–47.6	–43.8
NR 2/2	11.08	61.5	1.202	–8.644	141961	–49.3	–44.4	–41.1
NR 3/3	12.38	53.5	0.909	–7.935	1659847	–46.9	–41.9	–37.9
NR 4/4	12.05	56.3	0.803	–8.503	555039	–43.8	–39.2	–35.0
NR 5/5	12.07	51.9	0.625	–8.637	838453	–41.8	–37.0	–32.9
SBR 1/1	11.47	50.6	0.555	–8.175	381010	–39.9	–34.8	–30.7
SBR 2/2	11.74	63.6	0.443	–7.977	79054.3	–35.9	–30.3	–26.2
SBR 3/3	11.01	59.0	0.378	–7.907	38751.5	–32.2	–26.3	–21.9
SBR 4/4	8.88	37.6	0.304	–8.770	21778.8	–28.9	–24.1	–20.2
SBR 5/5	8.54	46.0	0.219	–8.696	3856.85	–25.2	–19.7	–15.8
N-SBR 1/1	8.53	43.5	0.130	–7.740	1083.26	–10.7	–5.8	–1.3
N-SBR 2/2	12.67	55.2	0.100	–7.116	8336.35	–6.8	–1.7	2.5
N-SBR 3/3	11.01	51.8	0.073	–6.945	2023.46	–4.3	2.1	6.6
N-SBR 4/4	11.21	59.3	0.064	–6.391	452.279	–0.8	4.4	8.2
N-SBR 5/5	11.60	59.4	0.050	–6.099	275.574	3.3	8.5	12.8
3,4 IR 1/1	12.94	48.8	0.038	–5.408	2599.31	4.0	10.9	15.5
3,4 IR 2/2	11.51	51.3	0.036	–4.967	87.3312	10.4	15.0	19.2
3,4 IR 3/3	11.23	64.1	0.036	–4.205	9.49479	14.5	18.4	23.4
3,4 IR 4/4	12.05	66.1	0.036	–3.360	2.30567	19.8	25.4	29.2
3,4 IR 5/5	12.69	62.5	0.036	–2.692	2.70715	21.7	27.8	33.6
Measurement of repeatability:								
Cis-BR (B)1/1 (I)	11.76	47.8	1.648	–7.826	12897250	–79.1	–76.7	–72.4
Cis-BR (B)1/1 (II)	12.90	49.1	1.587	–10.22	75820517	–80.9	–76.2	–72.5
Cis-BR (B)1/1 (III)	11.16	50.9	1.636	–9.104	3486204.4	–79.7	–77.8	–74.1
Cis-BR (B)1/1 (IV)	12.65	50.7	1.479	–9.894	46115993	–81.9	–76.4	–72.3

relaxation time given in Table 3 is the respective "main" relaxation time τ_0 (relaxation time at the maximum of the spectrum; see, for example, Fig. 2) for the spectrum at the reference temperature of 23 °C, which was the measurement temperature of T_2. Figure 3 shows the damping curves obtained by DMTA for the 1/1 crosslinked systems as well as T_2 as a function of the glass transition temperatures of all systems at 1 Hz. In general, T_2 decreases as T_g increases [14]. This is a result of the molecular mobility and steric hindrance of the segments due to increasing crosslinking and the microstructure of the polymers. One can see the background signal of the NMR-MOUSE of 0.039 ms of the NMR measurement at room temperature indicated in the figure with a horizontal line. Figure 4, top displays the relationship between mechanical and transverse relaxation times T_2. For hard samples one obtains a short T_2 and long mechanical relaxation times. Because the mechanical relaxation time and the "molecular jump frequency" are related to each other, the latter increases as T_2 increases; see Fig. 4, bottom. In order to obtain the limits of experimental error, four additional measurements of the Cis-BR (B) 1/1 sample were performed. The results are shown in Table 3. The percentage of error of log T_2 is in the region of approximately 2%, whilst those of log τ_0 and log ϕ are both in the region of 13%. Therefore it appears that the greater part of the experimental error apparent in Fig. 4, i.e., log τ_0 and log ϕ are due to the construction of the master curves.

Discussion

By the variation of the microstructure of the polymers (see Fig. 1) a wide range of molecular mobilities is achieved.

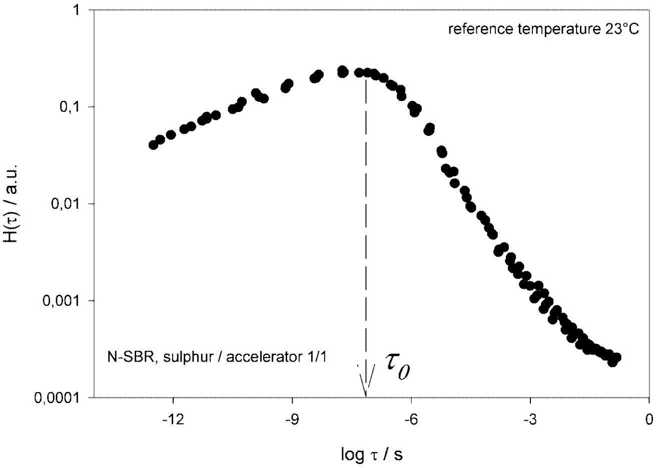

Fig. 2 Relaxation time spectrum of N-SBR according to Tobolsky [13], obtained by DMTA

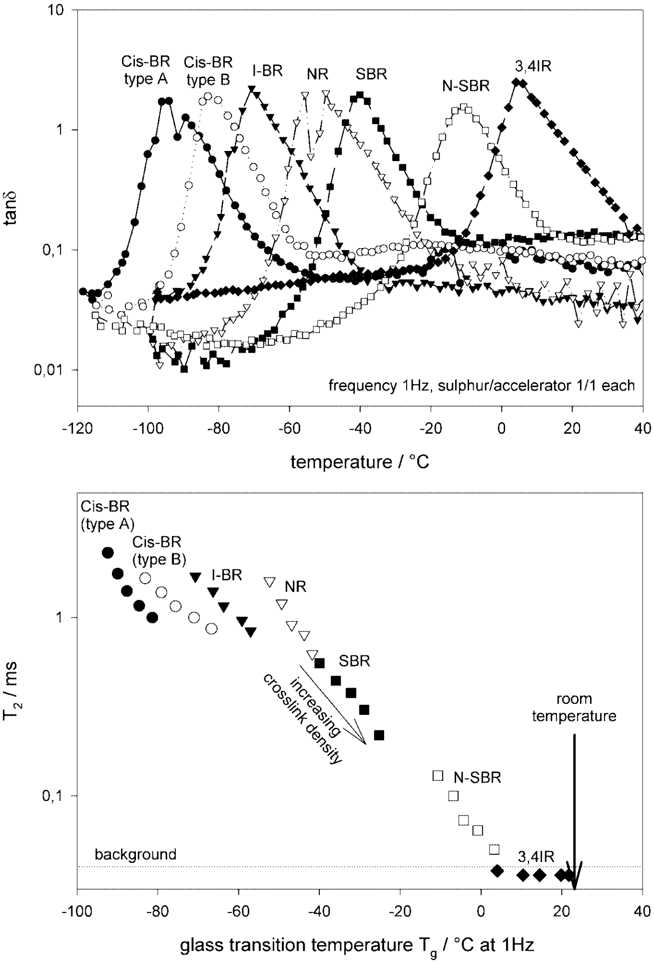

Fig. 3 Damping curves by DMTA of the polymers used (*top*) and T_2 over T_g for the polymer- and crosslink series (*bottom*)

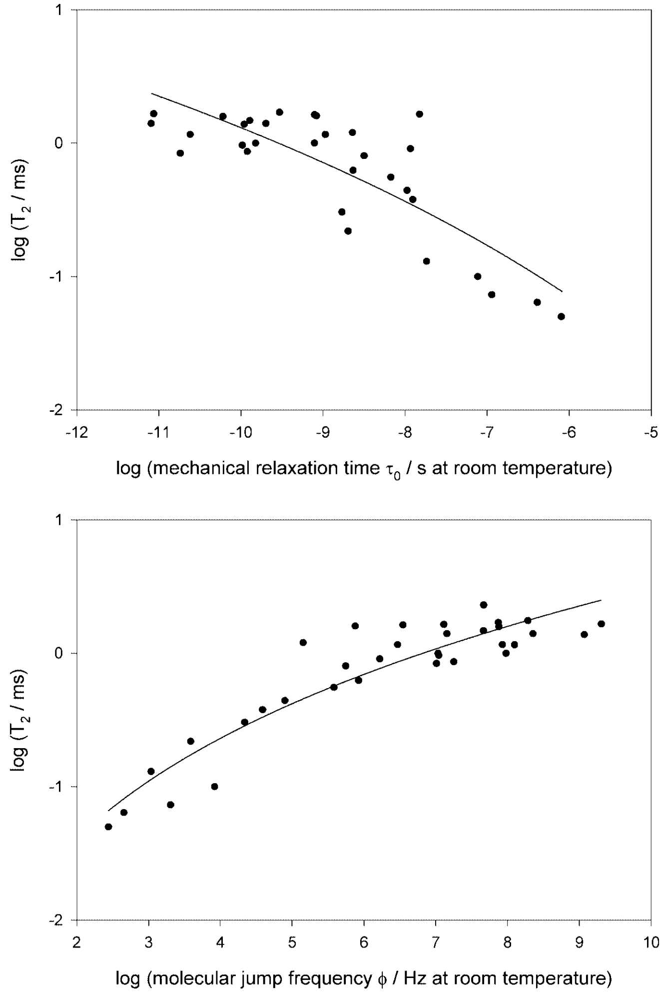

Fig. 4 Relationship between T_2 and molecular parameters obtained by DMTA. Mechanical relaxation time (*top*) and molecular jump frequency (*bottom*). Samples consisting of 3,4 IR are not included because of the short T_2

The polymers investigated in this study vary in amount and size of the side groups respectively, which affects the glass transition [15]. Further variation in molecular mobility was achieved by variation of the crosslink density, which affects the glass transition as well. The variation in crosslink density influences the glass transition in a different way than the sterical hindrance of the side groups of the polymers does. This becomes obvious in Fig. 3, bottom, where the different polymers do not fall on one line, whereas the crosslink density within each polymer does. With increasing glass transition temperature the material appears harder and the transverse relaxation time T_2 becomes smaller. Note the technical limit of the NMR-MOUSE® used: the determination of T_2 is currently limited to the temperature range $T_{measurement} > \approx T_g + 20$ °C. The horizontal line indicated in Fig. 3, bottom is due to a measurement without sample, where the signal obtained arises from the resin inside the probe. With the help of master curves, and mechanical relaxation time spectra according to Eq. (5), respectively, one is able to characterize the whole spectrum of molecular dynamics. The relation of the "main" mechanical relaxation time τ_0 and the transverse relaxation time T_2 is shown in Fig. 4, top. Due to molecular restrictions of the mobility of the chain, a mechanically excited sample with high T_g reacts slowly. Therefore, with high mechanical relaxation times the material appears hard, which results in a short T_2. On the other hand for high mobility systems, the "molecular jump frequency" is high, which correlates with large T_2, due to the averaging of the nuclear dipolar coupling for rapid molecular motion (Fig. 4, bottom). Apparently, by the help of the DMTA, reduced variables in terms of τ_0 or ϕ can be deduced, which relate to the transverse relaxation time because both methods reflect the molecular mobility of the systems. Note, that in Fig. 4, the variation of τ_0, resp. ϕ is achieved by both, microstructure of the polymer and crosslink density variation. Whereas in Fig. 3, bottom, one can still discriminate between the two influences, no difference can be identified in Fig. 4. This is also a result of the use of the specific WLF constants for each system. After Williams et al. introduced their work [9], soon NMR and dynamic-mechanical measurements were compared [16, 17]. In particular it could even be shown that NMR results can be shifted according to the WLF theory. Because the WLF constants have physical meaning (see previous section) it seems reasonable that each system has to be treated with its own WLF constants. The inaccuracies in Fig. 4, top may result from low molecular weight parts, e.g., dangling chain ends, sol molecules, or solvents which deliver contributions in T_2 [18, 19, 20, 21]. These would not affect the peak of the relaxation time spectrum significantly, but rather influence the left side of the spectrum. This might also be the case for NR polymers, which sometimes contain impurities such as proteins [22]. Further deviations might arise from crystallinity especially for NR and Cis-BR [23, 24]. In the case of the latter, for some samples presented here no proper relaxation time spectra for room temperature could be constructed. Therefore no main relaxation times τ_0 could be evaluated for these Cis-BR samples (see Table 3). Evaluation of Fig. 4, bottom leads to an empirical fit according to Eq. (6):

$$\log T_2 = a + b \cdot (\log \phi)^c, \qquad (6)$$

where $a = -7.58$, $b = 5.53$, and $c = 0.165$. The regression coefficient is $r = 0.93\%$.

It can be seen that T_2 is more sensitive to the mobility for slow than to that for rapid motion, which is already known and could be shown in earlier investigations [2, 21, 25]. It is of interest, if the parameters a, b, and c according to Eq. (6) change for different pulse sequences. In any case for a given relation of the kind of Eq. (6) one is able to calculate the temperature dependence of T_2 by the help of the WLF equation. This seems to be a matter of interest. Another influence on T_2 to be mentioned here is the restriction in molecular motion due to strain. As could be shown [3, 21], T_2 decreases with increasing strain because of the lower degree of freedom of the segments. According to the former argumentation the interesting question arises if the glass transition of an amorphous elastomer measured with the DMTA at higher prestrain is shifted to higher temperatures. Another interesting matter is to relate the main relaxation time τ_0 to the NMR correlation time, which contains information about molecular dynamics and can be obtained, e.g., by the field cycling technique [26].

Conclusion

The molecular mobility of elastomers can be characterized by dynamic-mechanical thermal analysis and NMR relaxation. Whereas the glass transition temperature T_g is influenced by the microstructure of the polymers and the crosslink density in a different manner, reduced variables like the mechanical relaxation time or the molecular jump frequency reflect the molecular mobility in general, when compared with the NMR relaxation time T_2. An empirical power law was found to describe the relationship between log T_2 and log ϕ. By the use of this equation (Eq. 6), the WLF equation, and the specific WLF constants, it should be possible to confirm the temperature dependence of T_2, which will be verified in future work.

There is supposed to be an influence from strain on the molecular parameters τ_0 or ϕ because of the strain dependence of T_2 due to molecular hindrance. Therefore a variation in the WLF constants, and a shift of the glass transition temperature to higher temperatures with higher prestrain, is expected.

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