

Thermoplastic elastomers by hydrogen bonding

1. Rheological properties of modified polybutadiene

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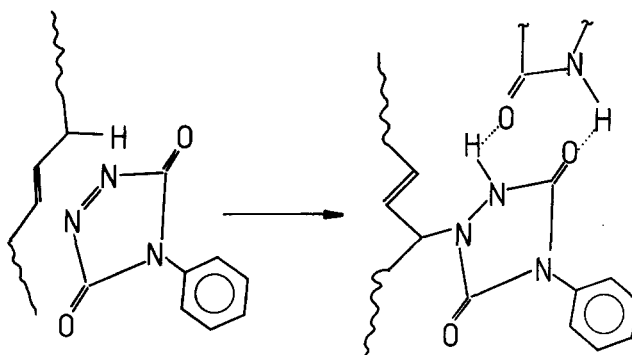
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Abstract: Polybutadiene of narrow molecular weight distribution was modified using 4-phenyl-1,2,4-triazoline-3,5-dione. The degree of modification was 1% and 2% with respect to the repeating units. Hydrogen bonding between the highly polar urazole groups thus incorporated into the polymer gives rise to the formation of a thermoreversible elastomeric network. Dynamic mechanical measurements in the temperature range between 220 and 330 K support the picture of the thermoreversible hydrogen bond interaction. The rubber elastic plateau is shifted to higher temperatures and lower frequencies. The increase in the plateau modulus cannot be attributed solely to the contribution of the network structure but is mainly a consequence of the broadening of the relaxation time spectrum in the modified samples. From the temperature dependence of the shift factors $\log(a_T)$ it is concluded that the general WLF approach fails. The strong temperature dependence of the apparent activation energy of flow is a consequence of the temperature dependence of the hydrogen bond interaction.

Key words: Thermoplastic elastomers, rheological properties, polymer modification, hydrogen bonding.

Introduction

One main approach to develop high performance plastics is based on polymer blending. The properties of different polymers are combined to result in a new material with enhanced mechanical properties [1]. Due to the nonmiscibility of the most polymers phase separation occurs. To avoid a macroscopic phase separation, the microscopic phase dispersion has to be stabilized. One approach to enhance the interfacial adhesion in polymer blends is the use of specifically interacting functional groups in the polymer constituents. Electron donor and acceptor systems [2, 3] as well as hydrogen bonding [4, 5] can serve as compatibilizing functionalities. In a previous study hydrogen bonding has been proposed to obtain a close interfacial adhesion in elastomeric blends [6]. The modification of polydienes using 4-phenyl-1,2,4-triazoline-3,5-dione (PTD) I gives rise to the formation of hydrogen bonds between two urazole groups [6, 7].



From the dilute solution behaviour of modified polybutadienes it was concluded, that hydrogen bonding occurs either intra- or intermolecular. DSC measurements on blends of modified polybutadiene and polyisoprene indicated enhanced mixing between the two components, corresponding to an enhanced interfacial adhesion.

It is evident that hydrogen bonding in a modified elastomer strongly influences the mechanical proper-

ties [7]. Such systems may also be considered as models for ionomers where complicated aggregation phenomena according to the ionic dipole interaction are avoided. In the present paper the first results concerning the bulk rheological properties are presented.

Experimental

Polybutadiene of narrow molecular weight distribution ($M_n = 48500$, $M_w/M_n = 1.06$) prepared via anionic synthesis (cyclohexane, *s-Bu-Li*, room temperature) has been used throughout this study. Characterization was performed by osmometry and GPC. 4-phenyl-1,2,4-triazoline-3,5-dione was prepared according to literature prescriptions [8]. The polybutadiene was dissolved in THF (5 wt-%) and an appropriate amount of a solution of PTD in THF was added. To ensure quantitative reaction the mixture was stirred for 2 hours after the red colour of *I* had vanished. According to kinetic measurements this corresponds to a conversion of > 99.99% [9]. The polymer was precipitated in methanol. The samples were dried and kept under high vacuum for 6 days to remove final traces of solvent. The samples were stored at 0°C in the dark prior to use.

The degree of modification is related to the total number of double bonds available. The characterization of the samples is given in Table 1. Rheological measurements on samples containing 0, 1 and 2 mol% PTD were performed in an Instron 3250 rheogoniometer with cone and plate geometry in the oscillatory mode. Amplitudes were checked to be kept in the linear viscoelastic region. The frequencies used were 0.0443, 0.0787, 0.1396, 0.2484, 0.442, 0.7865, 1.396, 2.484, 4.312 and 7.5 Hz. Temperature was varied between 220 and 330 K in steps of 10 K. In all cases it was possible to obtain smooth isothermal master curves by shifting the reduced modulus G' [10] along the log(frequency) axes (see below). The same shift factors were used for both storage modulus G' and loss modulus G'' . 273 K was chosen as reference temperature.

Results and discussion

A. Frequency dependence of G' and G''

In Figure 1 the master curves of the storage modulus are shown for the unmodified polybutadiene and the samples modified using 1 and 2 mol% of PTD (*I*). The unmodified polymer shows a small rubbery plateau region and the transition to the flow region, typical for

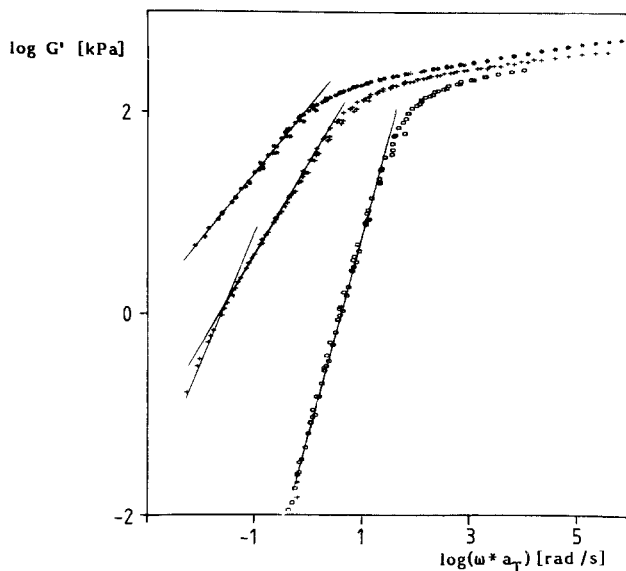


Fig. 1. In phase modulus G' master curves for the samples: \circ = PB 50-0; $+$ = PB 50-1; \times = PB 50-2. Reference temperature: 273 K, slopes in the terminal zone as indicated by the solid lines: PB 50-0 = 2; PB 50-1 = 0.88 and 1.2; PB 50-2 = 0.66

narrow distributed polymers. In the terminal zone the slope of $\log G'$ versus $\log(\omega \cdot a_T)$ is 2 as predicted from theory without hydrodynamic interaction [10]. The modified polymers show a very different behaviour. The rubber elastic plateau is broadened to lower frequencies and the level of the plateau is slightly increased, which may be a consequence of the network structure. A more detailed discussion is given in section B. The broadening of the rubber plateau increases with the degree of modification. This corresponds to an increased effective molecular weight of the sample. In addition the transition to the flow is different from the unmodified polybutadiene. The slope in the terminal zone is 0.88 for the 1% modified sample, indicating an apparently broader molecular weight distribution. For this sample the slope increases with decreasing frequency to 1.2. This suggests a narrowing of the rheologically effective molecular weight distribution. For the 2% modified sample this terminal flow region is characterized by a slope of 0.66 in the experimental accessible temperature range. If higher temperatures are used, problems may occur due to partial cross-linking of the polybutadiene.

In Figure 2 the loss modulus G'' master curves are shown. For the unmodified sample a very distinct maximum is observed at about 40 rad/s, at the onset of the flow region. The slope in the flow region is 1 as

Table 1. Characterization of the samples

Sample	Degree of modification mol%	T_g (K)	T_o (K)	T_u (K)	C1	C2
PB 50-0	0	162	273	127	3.91	146.06
PB 50-1	1	166	274	144	5.34	129.5
PB 50-2	2	170	273	151	5.84	122.37

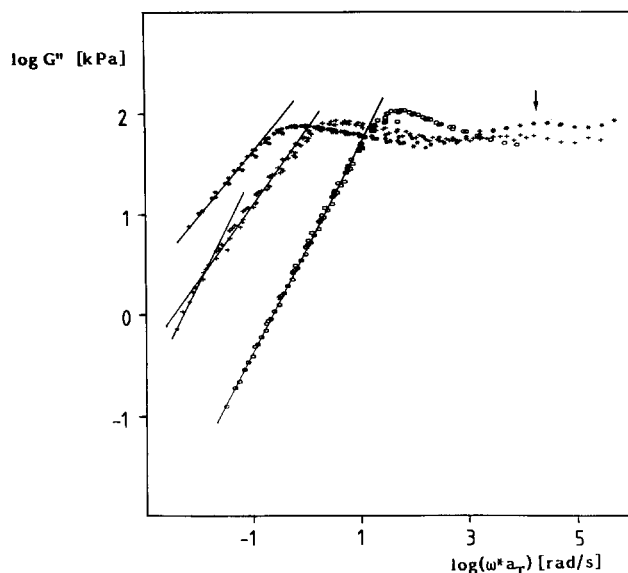


Fig. 2. Out of phase modulus G'' master curves. Symbols as Figure 1, slopes in the terminal zone as indicated by the solid lines: PB 50-0 = 1; PB 50-1 = 0.63 and 1; PB 50-2 = 0.55

predicted by theory and observed commonly for narrow distributed polymers [10]. The modified samples show a dispersion curve which is strongly broadened. The maximum corresponding to the transition from the rubbery to the flow region is less pronounced and shifted to lower frequencies (3.6 rad/s for PB 50-1, 0.46 rad/s for PB 50-2). The slopes left to the dispersion maximum are less than for the unmodified polybutadiene. For the 1% modified sample a change in the slope is observed as in the storage modulus. In addition at rather high frequencies (10^4 rad/s) a second, small dispersion maximum is observed which increases in intensity with degree of modification.

It is evident that the rheological changes observed in the modified samples arise from the incorporation of the urazole functionalities. The hydrogen bond formation is equivalent to an interlinking of different chains. The enthalpy of formation for various types of hydrogen bonds is in the range of 3–6 kcal/mol [11]. Consequently at high temperatures (low frequencies) the hydrogen bonds will break up and a viscoelastic flow similar to the unmodified narrowly distributed sample should be observed. Indeed for the sample modified with 1% of PTD this behaviour is observed in the experimentally accessible temperature range. The broadening of the rubbery plateau indicates a broadening of the relaxation time spectrum or equivalently an increase of the mechanically effective molecular

weight. As can be deduced from the loss modulus master curves, the contribution of long relaxation times to the viscoelastic response increases with degree of modification. According to the principles of viscoelasticity the longest relaxation time (0. mode of motion) is caused by a reptation of the whole molecule [10]. The increase of the long relaxation times reflects the hindrance of long range configurational rearrangements in the modified samples. As will be shown below, not only the long range rearrangements are influenced by the hydrogen bonding but also the mean activation energy of flow. The observed small dispersion maximum at high frequencies could be associated with the onset of dynamic processes involving the hydrogen bonds. Dielectric relaxation measurements should be very sensitive to motions in the highly polar urazole groups and could contribute to clarify this open question.

B) Temperature dependence of G' and G''

A comprehensive description of the influence of modification on the mechanical properties requires the discussion of the temperature dependence. This may be done either directly in comparing G' and G'' for fixed frequencies or by considering the temperature dependence of the logarithmic shift factors (section C).

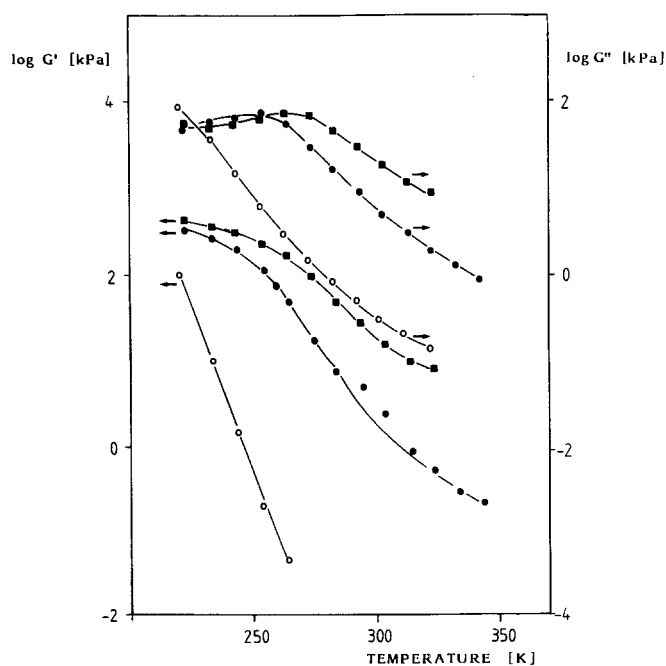


Fig. 3. Temperature dependence of G' and G'' for 0.0443 Hz: \circ = PB 50-0; \bullet = PB 50-1; \blacksquare = PB 50-2

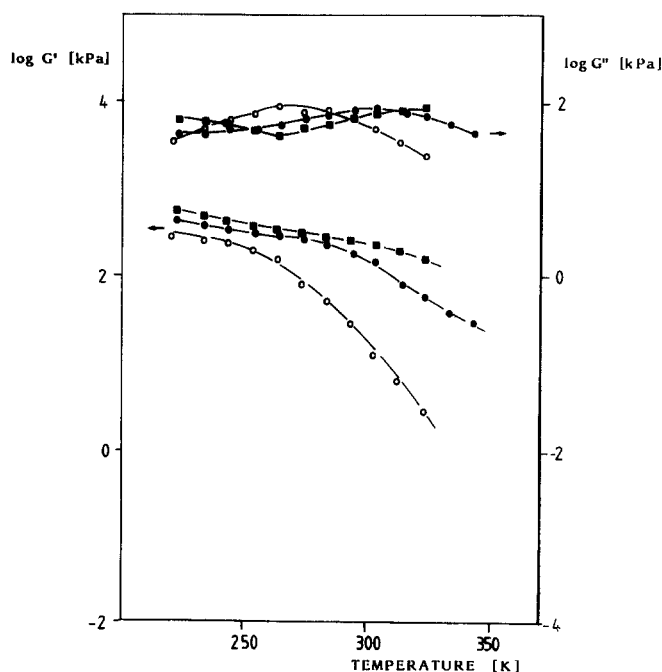


Fig. 4. Temperature dependence of G' and G'' for 7.5 Hz. Symbols as Figure 3

In Figures 3 and 4 the storage modulus G' and the loss modulus G'' are plotted as a function of temperature for the lowest and highest frequency under study.

Similar to Figures 1 and 2 the effect of modification on the mechanical behaviour is evident. The prolonged curvature of the modified samples at low frequency (G' in Fig. 3) indicates the marked effect of hydrogen bonds on the temperature dependent mechanical properties even at high temperatures. In addition the

modulus in the rubbery plateau region increases with modification. This turns out more clearly for the measurement at 7.5 Hz ($\log G'$ in Fig. 4) where both the unmodified and the modified samples are in the rubbery zone. First the assumption has to be checked whether this increase is a consequence of the network structure obtained by the hydrogen bond linkages.

According to rubber elasticity the equilibrium shear modulus of a network G^e is correlated to the number of network chains per unit volume N_c according to

$$G^e = N_c k T \quad (1)$$

where k is the Boltzmann constant and T the temperature. If a real network is formed, its contribution to the modulus should be the difference between the modulus of the modified and unmodified samples at fixed temperature and frequency:

$$\Delta G'_{\omega, T} = G'(\text{PB 50-}x)_{\omega, T} - G'(\text{PB 50-0})_{\omega, T} \quad (2)$$

$$x = 1, 2.$$

This estimation will be valid if the increase in the modulus is mainly due to the thermoreversible cross-linking. The values should be independent of frequency and decrease with increasing temperature with changing hydrogen bond efficiency. In Table 2 the values of $\Delta G'$ are given for the data of Figure 3 and 4. It turns out that the values are strongly dependent on i) temperature and ii) frequency. There appears to be no simple correlation between $\Delta G'$ and temperature for the high frequency measurements.

From this result the assumption has to be rejected that the increase of the rubbery plateau modulus is

Table 2. Differences between the modulus of the modified and unmodified samples

Temperatures (K)	$G'(\text{PB 50-1}) - G'(\text{PB 50-0})$ kPa		$G'(\text{PB 50-2}) - G'(\text{PB 50-0})$ kPa	
	0.0443 Hz	7.5 Hz	0.0443 Hz	7.5 Hz
222	211	145	313	280
233	204	129	301	227
243	169	102	259	227
253	100	109	198	180
263	47	144	137	194
273	14	175	80	215
283	—	184	—	238
293	—	160	—	237
303	—	135	—	216
313	—	75	—	193
323	—	55	—	163

directly correlated to the network density of the thermoreversible network. The increase in the plateau modulus is the consequence of the changes in the overall relaxation behaviour of the system. It has been pointed out in section A that the introduction of the urazole groups has a marked effect on the relaxation time spectrum. The contribution of slow relaxation processes to the viscoelastic response is enhanced. This bearing in mind, the difference in the temperature dependence of G' of the two different frequencies may be understood: In the modified samples exist a considerable number of modes of relaxation that contribute to the modulus at low frequencies and high temperatures which are not present in the unmodified samples. At low temperatures and high frequencies the behaviour is more complicated due to the additional relaxation process that is detected for the modified samples at high frequency (see G'' in Fig. 4). This process is responsible for the different temperature dependence of $\Delta G'$ at low and high frequencies. A comparison of values of $\Delta G'$ only will give physically significant information if the states of relaxation of the different systems are comparable. This is not the case for the present system.

C) Application of the time-temperature superposition principle

To obtain the frequency dependent viscoelastic functions from the experimentally accessible frequency region (Figs. 1, 2) the time-temperature superposition principle [10] has been applied. Using the reduced

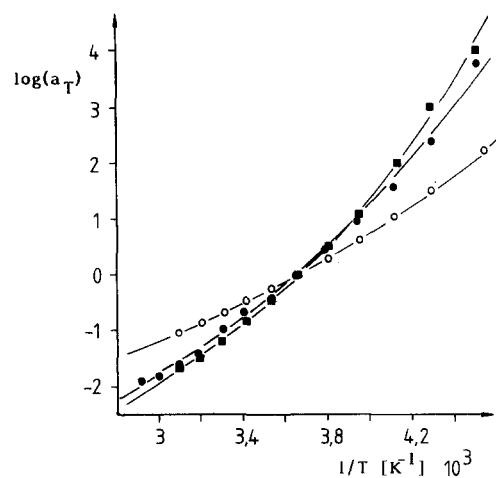


Fig. 5. Shift factors ($\log a_T$) as a function of inverse temperature; solid lines correspond to the WLF equation, using the values given in Table 1; symbols as Figure 3

variables smooth master curves were obtained. In Figure 5 the shift factors $\log a_T$ are plotted as a function of the inverse temperature for the three samples investigated. The solid curves are calculated according to the WLF equation [10]

$$\log a_T = -C1 \cdot (T - T_o)/(C2 + T - T_o) \quad (3)$$

with T_o as reference temperature. $C1$ and $C2$ were obtained using a linear representation of Equation (3) by linear regression, as well as by use of the Vogel equation [10, 12]

$$\log a_T = C1 \cdot (T - T_u)/(T - T_u). \quad (4)$$

The data for $C1$ and $C2$ and the Vogel-temperature T_u are collected in Table 1. The values for PB 50-0 are in very good agreement with those given in the Literature [10], while the values of the modified samples strongly differ.

In our previous work [6] it has been shown that the glass transition temperatures for the 1% and 2% modified samples are only slightly increased by the introduction of the urazole groups. According to the basis of the WLF approach – the free volume concept – the viscoelastic properties of different polymers should be the same if the reference state is chosen at the same distance to the glass transition temperature. As a consequence the product $C1 \cdot C2$ should be a universal constant. A critical review on the WLF approach shows that the simplifications used in the general model are too severe [12]. Generally speaking the influence of the chemical structure on the rheological properties are underestimated in the generalized model. For the modified samples the failure of the general approach is evident. While the glass transition temperatures do not change greatly, the Vogel temperatures which are located at $T_g - 51$ K in the generalized WLF model are strongly shifted to higher temperatures. At this temperature below T_g the molecular motions should freeze in. The observation that modification induces a strong increase in T_u while the influence on T_g is small supports the discussion given by Schneider et al. [12] concerning the significance of the chemical structure on the viscoelastic properties.

The different temperature dependence of the shift factors compared to the unmodified PB 50-0 cannot be explained by a different free volume caused by large differences in the glass transition temperatures. It is more promising to search for an explanation for the experimental finding on the basis of the specific inter-

action between the urazole groups. It has been shown in the case of miscible blends of PS and PVME that the relaxation time spectrum is broadened [13,14]. This has been explained by the existence of specific interactions between the ether linkage and the aromatic ring in PS. In the present case the type of interaction is even more specific and the broadening of the relaxation time spectrum as well as the increased temperature dependence of $\log a_T$ can be discussed in a similar way by the hindrance of local flow processes due to the interaction.

In studies dealing with the deformation mechanism in elastomers it has been shown that near crosslink junctions the restrictions acting on chain segments are enhanced [15]. A similar behaviour should be observed for the chain segments near hydrogen bond sites. The influence of the hydrogen bonds on the local flow processes decreases with increasing distance of a segment along the contour path. The observed increase in the width of the rubbery plateau is consequence of the superposition of different degrees of retardation of molecular motions. The temperature dependence of the shift factors reflects the changes in the apparent activation energy of flow [10]. For the high temperatures where we assume the hydrogen bonds to be less effective, the slopes of the unmodified and modified samples become comparable. Consequently the efficiency of hydrogen bonding is reflected in the apparent energy of flow. A quantitative evaluation of this effect will be given in a subsequent paper [16].

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References

1. Paul DR, Newman S (eds) (1978) *Polymer Blends*, 2 volumes, Academic Press, New York
2. Schneider HA, Cantow H-J, Lutz P, Northfleet Neto H (1984) *Makromol Chem Suppl* 8:89
3. Schneider HA, Cantow H-J, Massen U, Northfleet Neto H (1982) *Polym Bull* 7:263
4. Pearce EM, Kwei TK, Min BY (1984) *J Macromol Sci A-21*:1181
5. Kwei TK, Pearce EM, Min BY (1985) *Macromol* 18:2326
6. Stadler R, Burgert J, *Makromol Chem*, in press
7. Leong KW, Butler GB (1980) *J Macromol Sci A-14*:287
8. Cookson RC, Gupte SS, Stevens IDR, Watts CT (1971) *Org Synth* 51:121
9. Freitas LL, Jacobi MM, Stadler R (1984) *Polym Bull* 11:407
10. Ferry JD (1980) *Viscoelastic properties of polymers*, 3rd ed, Wiley Interscience, New York
11. Pimentel GC, McClellan AC (1960) *The Hydrogen Bond*, WH Freeman and Co, San Francisco
12. Schneider HA, Brekner MJ, Cantow H-J, *Polym Bull*, in press
13. Brekner MJ, Cantow H-J, Schneider HA (1985) *Polym Bull* 14:17
14. Faivre JP, Jasse B, Monnerie L (1985) *Polymer* 26:879
15. Gronski W, Stadler R, Jacobi MM (1984) *Macromol* 14:741
16. Stadler R, Freitas LL, Burgert J, in preparation

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