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Thermoplastic elastomers by hydrogen bonding

5. Thermorheologically complex behaviour by hydrogen bond clustering

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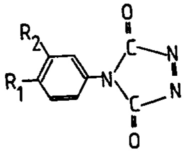
SUMMARY

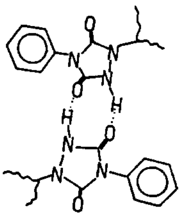
Poly(butadienes) were modified by an 'ene'-reaction using 4-phenyl-1,2,4-triazoline-3,5-dione (**1**), 3'-nitro-4'-hydroxyphenyl-1,2,4-triazoline-3,5-dione (**2**) and 4'-hydroxyphenyl-1,2,4-triazoline-3,5-dione (**3**). The resulting hydrogen bond complexes between urazole groups act as thermoreversible crosslinks and alter the melt rheological behaviour. While dimeric chelate-like complexes are formed in polymers modified with **1** or **2**, a three dimensional structure of hydrogen bond complexes is formed if **3** is used as the modifying agent. The thermorheologically complex behaviour of the latter material is interpreted by structural changes in the three dimensional structure with temperature.

Introduction

The rheological properties of polymer melts are influenced by energetic interactions between chain segments. This is particularly important if the rheology of miscible polymer blends /1,2/ or polymers with few polar units, ionomers/3,4/ for example, is considered. In order to investigate the relationships between specific interactions and flow properties in polymer melts, poly(butadienes) of narrow molecular weight distribution were modified using 4-phenyl-1,2,4-triazoline-3,5-dione (PTD) (**1**)/5,6,7/. The resulting urazole groups, which are randomly distributed along the polymer backbone, form hydrogen bond complexes:



	1	**2**	**3**
R_1	H	OH	OH
R_2	H	NO_2	H



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These hydrogen bond complexes are thermoreversible junctions. The rheological properties of the resulting thermoreversible networks were studied as a function of the primary poly(butadiene) molecular weight and of the number of urazole groups per chain. In this system, one defined complex is formed between two polar groups. In contrast to this "point-like" reversible junction, extended junction zones are present in many biopolymer reversible gels/8,9/. It has been assumed by several authors that such extended junction zones are essential for the formation of reversible gels and that these structures stabilize network structures. The influence of extended, more complex junction structures on the connectivity and thus the properties of reversible networks and gels may also be investigated by a model system based on the modification of an unpolar polymer matrix. Using such an approach the effects on rheological properties arising from different molecular origins can be separated.

In the networks obtained by reaction of poly(butadiene) with **1**, one contact is formed between two urazole groups. If a functional group which is able to form an additional hydrogen bridge with a third functional group is used, a more complex junction structure may result. Again the urazole can be used as the basic structural unit, where one NH-group (hydrogen donor) and two >C=O groups (hydrogen acceptor) are present. Thus, if **1** can be modified in such a way that two hydrogen bond donors are present, the properties should change if more complex junctions are formed.

We have successfully prepared 3'-nitro-4'hydroxy-phenyl-1,2,4-triazoline-3,5-dione (**2**) and 4'-hydroxy-phenyl-1,2,4-triazoline-3,5-dione (**3**)/10/. In these triazolinedione derivatives the additional OH-group may act as an additional H-donor. In the present paper we report on the viscoelastic behaviour of a poly(butadiene) modified with **1**, **2** and **3**.

Materials:

Poly(butadiene) of narrow molecular weight distribution was prepared by anionic polymerization [s-BuLi, cyclohexane, M_n=34900 (osmometry), M_w/M_n=1.05 (GPC)]. 2g of the polymer (0.037 mole of repeating units) were dissolved in dry THF. A solution of 0.37mmole of **1**,**2**, or **3** in the same solvent was added. The red colour of the triazoline-3,5-dione groups disappears within a few minutes. Stirring was continued for 2 h to ensure complete reaction. The polymers were precipitated in methanol, dried, and stored at 0°C in the dark prior to use. Prior to precipitation 2,6-di-tert.-butyl-4-methyl-phenole was added as antioxidant. The samples are designated as PB-35-0, PB-35-1, PB-35-1-NO and PB-35-1-OH (see table1).

Table 1:

sample	modifying agent	degree of modification	$\log(\eta_o)$ η_o [Pa*s]
PB-35-0	-	0%	3.50
PB-35-1	1	1%	4.75
PB-35-1-NO	2	1%	4.75
PB-35-1-OH	3	1%	7.75

Viscoelastic Measurements

The dynamic mechanical experiments were performed in an Instron 3250 rheometer in the oscillating mode (cone-plate geometry). The frequency ranged from 0.04 to 7.5 Hz. The temperature was varied between 223 and 363 K. The isothermal data were reduced and shifted to isothermal master curves according to the time temperature superposition principle/11/ (T^{ref}=273K). No problems occured for samples PB-35-0, PB-35-1 and PB-35-1-NO. As will be discussed below for the sample modified with **3** (PB-35-1-OH), the material evidently loses thermorheological simplicity. Nevertheless, for comparison with the other samples the master curves for G' and η' will be given. The value for the zero shear viscosity must thus be taken as an "apparent zero shear viscosity".

Results and discussion

In figure 1 the storage modulus master curves G'(ω) reduced to 273 K are shown for the 4 samples. For sample PB-35-1 modified with **1**, the transition from rubbery plateau to flow is shifted by 1.5 decades to lower frequencies compared to the unmodified poly(butadiene). This behaviour, which is typical when hydrogen bonds are formed between urazole groups, is also observed for the sample modified with **2**, the 3-nitro-4-hydroxy derivate. Only in the turnover from plateau to flow are slight differences observed. The loss modulus maximum for the transition from rubbery to flow behaviour is also broader and less pronounced for PB-35-1-NO. These small differences between PB-35-1 and PB-35-1-NO indicate that the structures of the reversible networks are very similar, i.e. the type of hydrogen bond linkage is the same.

Very different behaviour is observed for sample PB-35-1-OH, the poly(butadiene) modified with **3**. The master curve given in fig.1 has been obtained by simple horizontal shifting of the reduced G' data. In this sample the transition from the rubbery plateau to the melt is shifted by about 3.5 decades to lower frequencies. In addition, the slope at low frequencies, which is two for polymer melts with narrow molecular weight distribution, approaches this value only at the smallest frequencies (highest temperatures). Smaller slopes are also observed for samples modified with 1 at much higher levels of modification/6,7/. The differences between the different samples are even more pronounced if the dynamic viscosities, calculated from the loss modulus, are considered. The master curves are given in figure 2. At high frequencies, in the Newtonian region, all samples

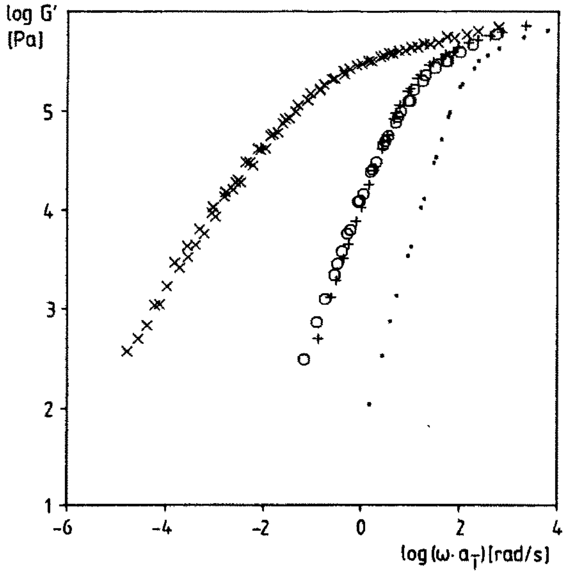

Fig.1: Storage modulus G'(ω*a_T) for samples
· PB-35-0
+ PB-35-1
o PB-35-1-NO
x PB-35-1-OH
T^{ref}=273K

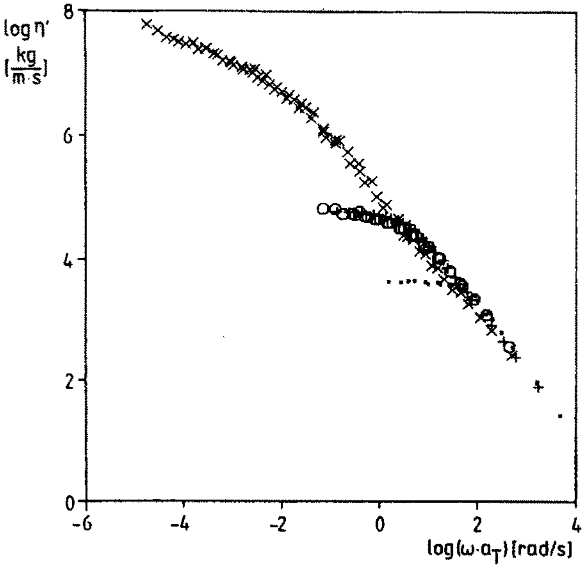

Fig.2: Dynamic viscosities η'(ω*a_T) (for symbols see fig.1)

show similar behaviour. In this region, where short chain rearrangements will be involved, the behaviour is not influenced by the modification. The same conclusion has been drawn for samples with varying degrees of modification. The hydrogen bonds give rise to an apparent increase in the molecular weight, thus increasing the zero shear limit of the viscosity without influencing the rubbery plateau zone. Thus, the plateau modulus G_N^0 changes only slightly with modification7). For PB-35-1 and PB-35-1-NO, very similar behaviour is observed. The viscosity is about 15 times larger compared to the unmodified poly(butadiene) (Table 1). Once again a different behaviour is observed for PB-35-1-OH. From a rough estimation of the zero shear viscosity limit, the increase in the viscosity compared to the poly(butadiene) is calculated to be about 20000.

Since the degree of modification is the same for all samples, the difference must be a consequence of the additional hydroxy group. Recall that two hydrogen bond acceptors and one donor are available in the urazole units. Thus, in phenyl-urazole modified polymers only dimeric chelate-like complexes will form. If an additional hydrogen-bond donor is present, the free carbonyl group may form an additional hydrogen bond. Thus, extended hydrogen bond clusters, or even a three dimensional network structure built from hydrogen bond complexes, may form. Such a situation is shown schematically in figure 3. If the poly(butadiene) is modified with **2**, the additional -OH group is neighbored by the $-NO_2$ group. It is known in organic chemistry that o-nitro-phenols form intramolecular hydrogen bonds. This is the reason for the similar behaviour for samples modified either with **1** or **2**.

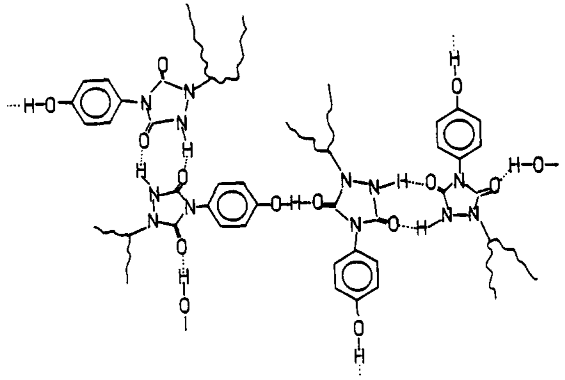

Fig.3: Schematic representation of the extended 3-dimensional cluster of hydrogen bond complexes in sample PB-35-1-OH

The structure proposed in figure 3 is also responsible for the thermorheologically complex behaviour observed for PB-35-1-OH. In thermorheologically simple materials, for which the time temperature superposition is applicable, all molecular processes (with different relaxation times τ) contributing to the viscoelastic relaxation have the same temperature dependence/11/. Thus, the same shift factors a_T can be applied for G' and G", as well as for any other viscoelastic function. A thermorheologically complex system is characterized by a different temperature dependence of the different molecular relaxation processes. Thus, the shift factors are frequency dependent. Such complex behaviour is observed in semicrystalline polymers/11/ or in block copolymers/12/, generally in systems where structure changes with temperature. The master curve for PB-35-1-OH in figure 1 has been obtained by shifting the reduced isothermal G' data. As is discussed in another paper of this series/13/, the poly(butadienes) modified with 1 display thermorheologically simple behaviour, at least in the experimental frequency range, probably due to the fact that the temperature dependence of hydrogen bond formation and breaking is similar to the local activation energy of flow.

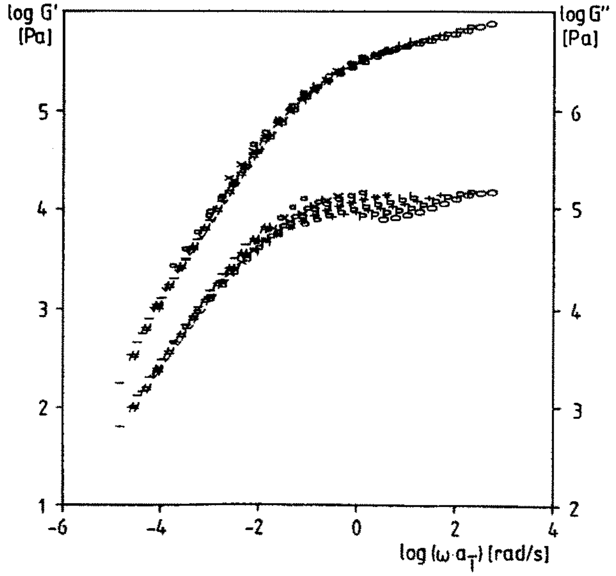

Fig.4: Master curves of G' and G" of sample PB-35-1-OH; shift factors obtained from horizontal shifting of G'^{red} were applied to G''^{red} (T^{ref}=273K)

253K o	;262K p
273K +	;284K b
293K *	;302K q
313K x	;323K d
333K □	;343K v
354K #	;365K -

In figure 4 the storage and the loss modulus master curves of sample PB-35-1-OH are shown. The shift factors used were obtained by shifting the storage modulus data. It is evident that in the plateau region the loss modulus data cannot be represented by a master curve using the same shift factors. In figure 5 the same data are shown, now using the loss modulus data as the reference. Again the failure of the time temperature superposition principle is evident for the storage modulus.

If the storage modulus data are taken as the reference as in figure 4, the loss modulus data, shifted with the same factor along the frequency axes, show a distinct temperature dependence at the higher frequencies. At $\omega*a_T$>-2 the loss modulus decreases with decreasing temperature for the same reduced frequency. The loss modulus represents the intensity of energy dissipating mechanisms in the sample. The decrease with decreasing temperature can be interpreted as a reduction of energy dissipating processes. Correspondingly one may conclude from figure 5, that the storage modulus increases faster with decreasing temperature than expected for a thermorheologically simple material.

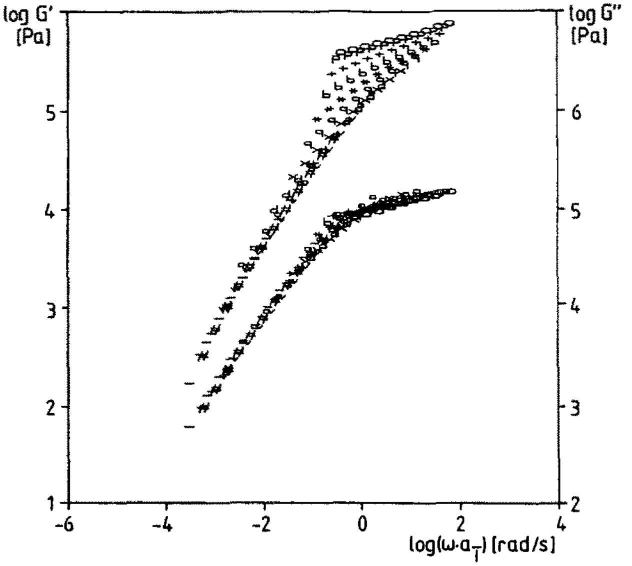

Fig.5: Master curves of G' and G" of sample PB-35-1-OH; shift factors obtained from horizontal shifting of G''^{red} were applied to G'^{red} (T^{ref}=273K)
253K o ;262K p
273K + ;284K b
293K * ;302K q
313K x ;323K d
333K □ ;343K v
354K # ;365K -

It must be noted that the complex behaviour is evident even in the loss modulus curve in figure 5. The data can be classified into two temperature regions: one lasting up to 320K and one for the higher temperatures. In the high temperature region, time temperature superposition is possible and the material is viscoelastically simple. At low temperatures the behaviour is complex.

This behaviour can be interpreted in terms of the three dimensional structure of hydrogen bond complexes proposed in figure 3. Two different types of hydrogen bond links must be discussed: the chelate-like complexes between two urazole groups and complexes between the phenolic -OH and a free >C=O. These different complexes will differ in their association behaviour. The thermorheologically simple behaviour at high temperatures is an indication that in this range the behaviour is similar to PB-35-1 and PB-35-1-NO, i.e. the three dimensional structure is no longer stable. At low temperatures the supermolecular structure reduces molecular relaxations. As result an enhanced storage modulus is observed.

Conclusions

It has been shown in the present paper that, in accordance with biopolymer reversible gels, the stability of synthetic thermoreversible networks is strongly improved if extended "junction zones" are formed instead of point-like linkages. As a consequence of such junction clusters, thermorheologically complex behaviour is observed. This makes the interpretation of rheological data difficult.

The o-nitro-phenole derivate forms hydrogen bond complexes of the same type as the phenyl derivative. On the other hand o-nitro-phenols are highly acidic. Thus, poly(butadienes) modified with **2** can be converted to poly(butadiene) ionomers with properties different from the reversible networks based only on hydrogen bonds/14/.

Acknowledgement

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