Stress Relaxation of Reptating Chains of Acrylonitrile–Butadiene Copolymer in End-linked Acrylonitrile–Butadiene Copolymer Networks*

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Synopsis

Stress relaxation of unattached chains of acrylonitrile–butadiene copolymer in TDI end-linked acrylonitrile–butadiene copolymer has been studied. The advantage of this system is that the polar nature of the TDI crosslinking agent in end-linked acrylonitrile–butadiene copolymer can be compensated if an unattached acrylonitrile–butadiene copolymer with moderate acrylonitrile content is selected. It was found that with increasing unattached chain content, the position of the relaxation spectra transitions shifted to shorter times. The frictional resistance for the relaxation of networks containing unattached chains was proportional to the amount of crosslinked components. This means that crosslinked components not only bear load but also resist the relaxation of unattached chains. The relaxation moduli contribution from unattached chains first increased and then decreased with increasing amount of crosslinked components. This can be explained by the presence of two kinds of entanglements, i.e., those between unattached chains themselves and those between unattached chains and crosslinked components, which in turn depend on the amount of unattached chains. At lower concentrations of unattached chains, relaxation of unattached chains requires that molecules pass only through obstacles formed by one kind of entanglement; this results in lower relaxation modulus. With increasing unattached chain content, the relaxation of those chains require molecular reptation through both kinds of entanglements, which results in higher relaxation modulus. Therefore, the enhancement of mechanical properties for networks containing unattached chains originates not only from load-bearing of crosslinked components but also from the relaxation of unattached chains.

INTRODUCTION

The mobility of unattached chains in a network influences the elastic component of viscoelastic properties[1] as well as the ultimate properties of elastomers.[2] Thus, studying the relaxation process of unattached chains in a network is helpful to understanding the failure mechanism of polymers. Although fracture of the chain backbone is the primary cause of failure of polymers,[3] the contribution of chain slippage to failure is not negligible, especially for failure at elevated temperatures and/or long times and for highly entangled systems. The effect of a large amount of unattached chains, up to 90 wt %, on the ultimate properties of crosslinked networks has been reported.[2] On the other hand, the unattached-chain-dependent viscoelastic properties have been reported only for networks containing up to 50 wt % unattached chains.[4,5] This

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work studies the relaxation process of unattached chains in networks containing a large amount of these moieties.

The study of the relaxation of unattached chains in a network has been reported for many systems.[1,6,7] The system used here is an end-linked acrylonitrile–butadiene copolymer blended with unattached linear acrylonitrile–butadiene copolymer. The advantage of this system is that the effect of the polar nature of the diisocyanate crosslinking agent in an end-linked acrylonitrile-butadiene copolymer can be diminished if an unattached acrylonitrile–butadiene copolymer with moderate acrylonitrile content is selected. The content of unattached acrylonitrile–butadiene copolymer in the present system ranged from 20 to 80 wt %. Young's modulus and relaxation spectra were determined and the relaxation process of unattached chains in the networks is discussed.

EXPERIMENTAL

The hydroxyl-terminated acrylonitrile–butadiene (HTNB) is of $\bar{M}_n = 2000$ g/mol, acrylonitrile content of 15 wt %, and hydroxyl end group content of 1.1 $\times 10^{-3}$ g eq. The content of acrylonitrile in the unattached acrylonitrile–butadiene copolymer (ULNB) is 19 wt %. Weight-average molecular weight and molecular weight distributions of ULNB were, respectively, 3.8×10^5 g/mol and 3.1. ULNB was first dissolved in toluene for several days and then mixed with HTNB at weight percents of 80, 55, 40, and 20. The mixtures were then reacted with a stoichiometric amount of toluene diisocyanate (TDI) in an open Teflon dish. The reaction was carried out at room temperature while the solvent was slowly evaporated.

The solubility parameters at 25°C, δ, for ULNB and TDI-linked HTNB were calculated as follows[8–10]:

ULNB

$$\delta = \rho[10.7934 W_N + W_B(9.2394 W_c + 9.1215 W_t + 8.6215 W_v)] \quad (1)$$

TDI-linked HTNB

$$\delta = \rho[8.7150 W_U + 10.7934 W_N + W_B(9.2394 W_c + 9.1215 W_t + 8.6215 W_v)] \quad (2)$$

where ρ is the density, W_N, W_B, and W_U are weight fraction of acrylonitrile, butadiene, and urethane composition in the system, respectively. The subscripts c, t, and v refer to *cis*-1,4, *trans*-1,4, and vinyl structures in the butadiene composition. The resulting δ values for ULNB and TDI-linked HTNB were 8.985 and 8.875, respectively, indicating that the two components are compatible.

A Rheovibron Dynamic Viscoelastometer Model DDV-II-EA was used to determine Young's storage modulus E'. Details of the measurement have been reported previously.[11] Stress relaxation measurements were made between 25 and 70°C and under a stretch ratio of 1.25 by using a laboratory-made instrument. The data were calculated as the apparent Young's modulus:

$$E_a(t) = 3f(t)/A_0(\lambda - \lambda^{-2}) \tag{3}$$

where $f(t)$ is the time-dependent force, A_0 the original cross-sectional area of specimens, and λ the stretch ratio.

RESULTS AND DISCUSSION

Relaxation moduli $E_a(t)$ for the networks containing various amounts of unattached chains measured at different temperature superposed quite well to form the master curve (Fig. 1). However, the shift factors were not the same for all master curves, analoqous to results reported by Ferry et al. for a poly-butadiene network containing linear polybutadiene.[6] It is thus evident that the temperature dependence for relaxation of the networks containing various amount of unattached chains is different.

As with ultimate properties,[2] the modulus of a network containing unattached chains is controlled not only by the number of load-bearing chains but also by the ability of the materials upon being stressed to dissipate mechanical energy into heat through molecular friction. The former is proportional to the fraction of crosslinked components and the latter is determined by the number of un-attached chains and the magnitude of their frictional resistance. The effect of load-bearing chains is seen in Fig. 1, as the moduli of the networks containing larger proportions of crosslinked components are higher. On the other hand,
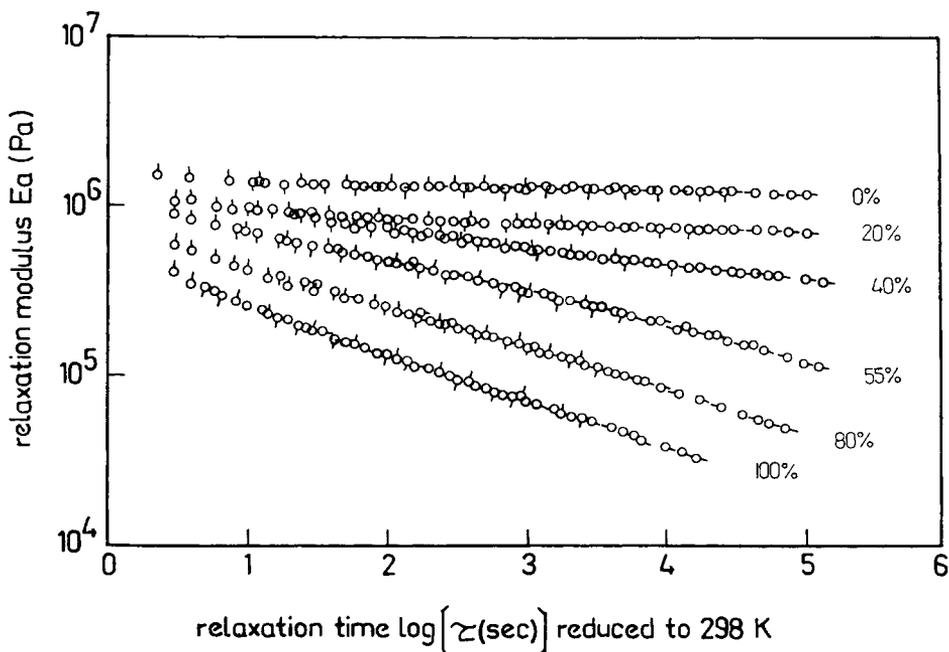

Fig. 1. Time-dependent relaxation modulus for end-linked acrylonitrile–butadiene copolymer containing unattached acrylonitrile–butadiene copolymer. The figures refer to weight percent of unattached acrylonitrile–butadiene copolymer.

discussion of the effect of molecular friction on the modulus requires one to know the frictional resistance of the molecules.

The general method of determining the monomeric friction coefficient from Young's modulus has been reported elsewhere.[11,12] Briefly, friction coefficient, ζ_0, can be determined from the theoretical slope of $-\frac{1}{2}$ on a double logarithmic plot of the relaxation spectrum vs. relaxation time:

$$\log \zeta_0 = 2 \log H + \log \tau + \log(6/kT) + 2 \log(2M_0\pi/a\rho N_A) \qquad (4)$$

Because information on a in Eq. (4), the root-mean-square end-to-end distance per square root of the number of monomer units, is uncertain in the case of our copolymer, the product of $a^2\zeta_0$ was used here as a measure of frictional resistance, as commonly seen in the literature.[12,13]

The relaxation spectra for the end-linked HTNB containing various amount of ULNB chains are shown in Figure 2. With increasing amount of unattached chains, the position of the transition shifts to shorter time, although for some systems the shift is not prominent. The relaxation spectra in Figure 2 are matched to the theoretical slope of $-\frac{1}{2}$ by drawing a tangent. Table I lists the values of $\log a^2\zeta_0$. Increasing the crosslinked component results in a higher value of $\log a^2\zeta_0$. Figure 3 shows that the value of $\log a^2\zeta_0$ is proportional to the weight fraction of crosslinked components, suggesting that the crosslinked
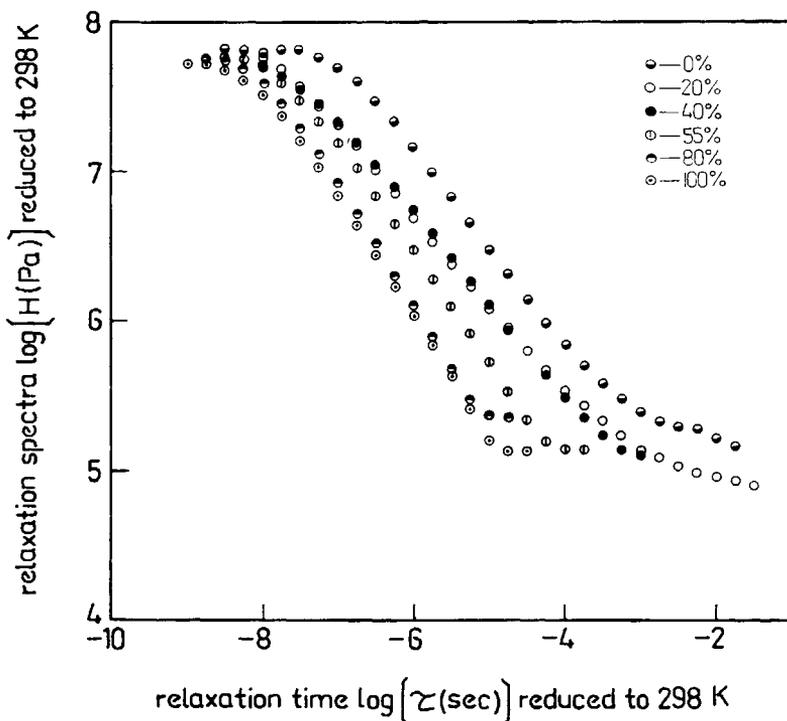

Fig. 2.   Relaxation spectra of end-linked acrylonitrile–butadiene copolymer containing unattached acrylonitrile–butadiene copolymer. The figures are weight percent of unattached acrylonitrile–butadiene copolymer.

TABLE I

Properties of End-linked Acrylonitrile–Butadiene Copolymer Containing Unattached
Acrylonitrile–Butadiene Copolymer

Weight percent of unattached chains	80	55	40	20
$\log a^2 \rho_0$	−22.605	−22.175	−21.335	−21.205
$E_e \times 10^{-5}$ (Pa)	0.565	1.52	3.15	6.58
E_e/E_e^0	0.0491	0.132	0.274	0.572
V_2^2	0.0441	0.223	0.396	0.704
H_η (kcal/mol)	12.44	15.37	15.08	12.11

components not only bear load but also resist the relaxation of unattached chains.

The contribution $E_1(t)$ of the unattached chains to the relaxation modulus $E_a(t)$ of networks containing them is usually calculated by Eq. (5)[6]:

$$E_1(t) = E_a(t) - (E_e/E_e^0)E^0(t) \tag{5}$$

where $E^0(t)$ is the relaxation modulus of the networks with no unattached chains, E_e^0 and E_e are, respectively, the equilibrium moduli of the networks without and with unattached chains. In this work E_e^0 and E_e were taken as the relaxation moduli at the relaxation time of 10^5 s, since it has been reported that at the relaxation time of 10^4 s the unattached chains contribution to the network was quite small.[5] The values of E_e are listed in Table I.
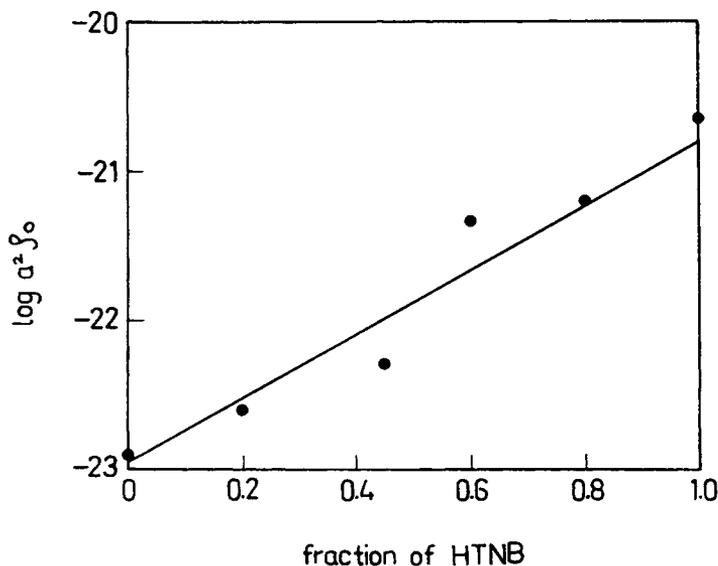

Fig. 3.   Friction resistance for the end-linked acrylonitrile–butadiene copolymer containing various amount of unattached acrylonitrile–butadiene copolymer.

To compare the relaxation modulus $E_1(t)$ for the networks containing various amount of unattached chains, it is necessary to normalize the magnitude of $E_1(t)$ to take into account the dilution of the unattached chains by the networks.[6] This has been done by the factor $(1 - \nu_2^2)^{-1}$, where ν_2^2 can be taken as either the volume fraction of the crosslinked component V_2^2 or the ratio of E_e/E_e^0.[1] Both values of V_2^2 and E_e/E_e^0 for the system studied here are listed in Table I. It is found that at large proportions of crosslinked components, the difference between V_2^2 and E_e/E_e^0 is significant. In this work ν_2^2 was taken as E_e/E_e^0.

From Figure 4, a plot of $E_1(t)/(1 - \nu_2^2)$ vs. τ, there is apparently no significant change in relaxation rate since the curves are parallel. It is interesting that throughout the whole relaxation time range in Figure 4, the magnitude of moduli contributed from unattached chains increases first and then decreases, as these chains are diluted by crosslinked components. It is further shown in Figure 4, that the system with 60 wt % crosslinked components is of higher normalized modulus $E_1(t)$ than that with 80 wt % crosslinked components. The same tendency has been reported for the tearing energy at 25°C of butyl rubber containing reptating polyisobutylene chains,[2] where the system with 45–60 wt % reptating polyisobutylene chains, i.e., with 40–55 wt % crosslinked butyl rubber, showed the highest tearing energy.

Dilution of unattached chains of acrylonitrile–butadiene copolymer by end-linked acrylonitrile–butadiene copolymer can be classified in three ways. In case I, i.e., dilution by 20% crosslinked components, the unattached chains are mostly self-entangled. The unattached chains in case II, i.e., dilution by 45–
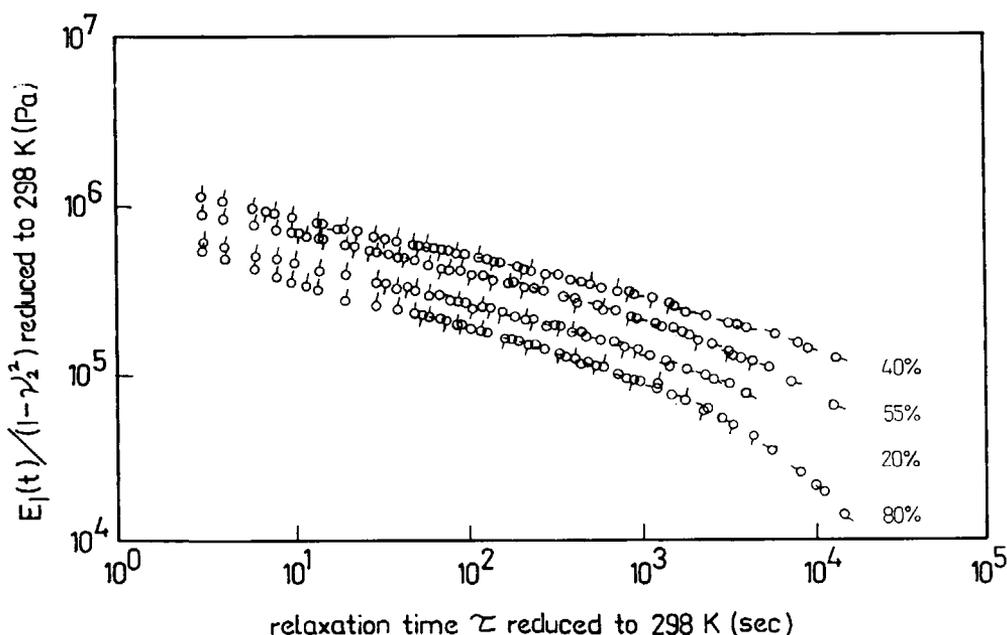

Fig. 4.   Normalized relaxation moduli contributed from unattached acrylonitrile–butadiene copolymer in end-linked acrylonitrile–butadiene copolymer. Figures are weight percent of unattached acrylonitrile–butadiene copolymer in the networks.

60% crosslinked components, are self-entangled as well as entangled with crosslinked components; and case III, wherein unattached chains are diluted by 80% crosslinked components, exhibits unattached chains that are generally entangled with crosslinked components only, similar to a swollen network where unattached chains are separated and in contact with the crosslinked components. Since moduli in Figure 4 are determined only by unattached chains that relax through a network, these values are controlled by a relaxation process of unattached chains.

It has been known that the relaxation process can be characterized by the activation energy of relaxation of unattached chains. By using the shift factors forming the master curves in Figure 4, the activation energy of relaxation of unattached chains can be calculated as follows:

$$H_\eta = 2.303 Rd \log \alpha_T / d(1/T) \tag{6}$$

where R is the gas constant, α_T the shift factor, and T the temperature in Kelvin. Values of H_η are listed in Table I. It is not unexpected that the activation energy of relaxation for unattached chains in case II, i.e., unattached chains diluted by 45–60% crosslinked components, is highest since the frictional resistance of relaxation for unattached chains in case II is highest due to the existence of two kinds of entanglements, i.e., between unattached chains themselves and between unattached chains and crosslinked components. In this work no significant discrepancy was found in the activation energy of relaxation for unattached chains in cases I and III. This suggests that there may be no difference in the nature of the relaxation processes for unattached chains passing through themselves and/or passing through crosslinked components.

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