Introduction

Mechanical properties of polymer condensed system are characterized by viscoelasticity and remarkable nonlinearity in large deformation and/or high deformation rate\(^1\). In nonlinear viscoelasticity of well entangled polymers, there may be two possible origins, the change in entanglement density and the anisotropic configuration of the chain molecule.

The contribution of the former factor has been proved to be acceptable from the experimental results that the height of rubbery plateau, which is a measure of entanglement network, really changes in high strain and high strain rate\(^2\)–6\). The latter contribution may be plausible, but experimental evidences are not so enough. Stress in polymers is considered to appear due to chain anisotropy. Therefore, relaxation of stress corresponds to the transient process from anisotropic to isotropic chain configuration. In the previous papers\(^2\)–6\), it was found by measuring the differential dynamic modulus during stress relaxation processes in single-step large shearing deformations that differential storage modulus \(G'(\omega, \gamma; t)\) showed initial drop from the original value measured before straining followed by gradual increase, and differential loss tangent \(\tan \delta(\omega, \gamma; t)\) did initial rise followed by gradual decrease to attain the original value at a time scale of the longest relaxation time. It has been discussed that such initial drop in \(G'\) and initial rise in \(\tan \delta\) appeared due to the effect of chain anisotropy. However, effect of entanglement network rupture may be included. Similar results on \(G'/\eta^{\alpha}\) were observed again in the coarsely cross-linked polymer where no loss of entanglement was expected\(^8\)–9\). These results were all taken during the stress decay processes. We could expect more direct experimental evidence, if we could keep the high anisotropic chain configuration in polymeric materials. In the previous papers\(^8\)–9\), chemical cross-linking was introduced in no deformation. To keep the anisotropic chain configuration, it should be introduced in a deformed state. However, even if it could be done in deformation, polymer chains will relax to equilibrium before completion of cross-linking reaction because the molecular chains can move quickly to recover to equilibrium at high temperature required for chemical cross-linking process. However, if the polymeric materials are fairly cross-linked partly in no deformation followed by the second cross-linking in large deformation, the polymer chains are expected to take desirable anisotropic configuration. We call this process “two-step cure method”.

The purpose of this work is to clarify the effect of chain anisotropy on nonlinear viscoelasticity of polymers by using the polymer specimens prepared by two-step cure method.
Experimental

Materials

The rubber used was polybutadiene BR-1220 (cis-content; 96%, Zeon Cooperation). The average molecular weights and heterogeneity index were estimated to be $M_n = 1.7, \times 10^5$, $M_w = 5.0, \times 10^5$, and $M_w/M_n = 2.9$, on the basis of polystyrene standards with the use of high-speed liquid chromatography HLC-803 (Tosho Ltd.). The agent and the co-agent for cross-linking were 1,1-di(3,5-trimethylcyclohexane) (abbreviated as 3M, half-periods in 0.1 mol/L benzene solution are 1 h at 375 K and 10 h at 365 K, Arkema Yoshitomi Ltd.) and ethylene glycol dimethacrylate (abbreviated as EG, Sanshin Chemical Industry Ltd.), respectively. Sample formulation is shown in Table 1.

Specimens

Sample films were prepared by a solvent casting method. That is, the solution-mixtures of the rubber BR-1220 and necessary amounts of cross-linking agent and co-agent were cast into film of ca. 1 mm thickness on plate-like vessel by evaporating the solvent gradually from benzene solution of about 2.5 wt% of the rubber for one week at room temperature. The film thus formed was further dried in a vacuum oven for three days. The sample films in which cross-linking agent and co-agent distributed homogeneously were cross-linked in various conditions. The conditions for cross-linking reactions were determined by optimization explained later. The one-step cure was performed at elevated temperature in no deformation. The two-step cure was performed in the next procedures as explained schematically in Figure 1; firstly the sample was pre-cured at temperature $T_1$ in no deformation up to a time $t_1$, and then the specimen was deformed in extension at the ratio of $l_1$ at $T_1$, and after being released, it was provided for measurements of specimen length and viscoelastometry. After releasing, the sample shrunk partly due to equilibration. So the residual extension ratio was observed by measuring the distance between fiducial marks with a traveling microscope. In all measurements, the shrinkage reached to equilibrium after 20 h elapsed. The values shown later as extensional strain $\varepsilon$ are not the extensional strain set in the second cure process in two-step cure but that obtained after shrinkage equilibrium.

Measurements

The storage ($G'$) and loss ($G''$) moduli were measured in oscillatory shear with a VES-S (Iwamoto Seisakusho) viscoelastic spectrometer. The measured frequency ranged from $3.14 \times 10^{-2}$ to $1.25 \times 10^2$ rad/s. The strain amplitude and temperature were 3.0 $\times 10^{-2}$ or lower and 303 K, respectively. The strain amplitude used was confirmed to be in linear viscoelasticity.

Results and Discussion

Optimization for cross-linking condition

The cross-linking reaction should be performed carefully to avoid sample degradation and/or gelation. It is known that thermal gelation of polybutadiene takes place more easily than thermal chain scission. So, change in frequency dependent curves of $G'$ of the sample after being kept at elevated temperature was tested as shown in Figure 2. The increase in $G'$ at lower frequencies was observed after 1.5 h at 433 K, and 2 h at 423 K. However, no substantial change in $G'$ curves was observed up to 2.5 h at 413 K. It is desirable for us to finish the first and the second cures within 2.5 h at 413 K at longest.

Figure 3 shows the change in $G'$ of BRs cured at various temperatures ranged from 383 to 413 K. The curve shows almost no progress in cross-linking at 383 K, but development at higher temperatures. The cure rate

Table 1. Sample formulation

| Ingredient          | Amount (phr) |
|---------------------|--------------|
| SBR (BR1220)        | 100          |
| Cure agent (3M)     | 0.2          |
| Co-agent (EG)       | 2            |

a) 1,1-Di(3,5-trimethylcyclohexane.
b) Ethylene glycol dimethacrylate.
increased with temperature. The results show that the cure will finish after 100 min, 50 min, and 30 min at 393, 403, and 413 K, respectively. In order to perform the two-step cure, the first cure must be stopped at moderate cross-linking density at a controllable time. The cross-linking rate at 413 K was too high. Taking the degree of progress and rate in cross-linking reaction into account, the conditions of the first cure in 10 min at 403 K and the second cure in 30 min at 413 K may be suitable for the two-step cure process. Figure 4 shows the change in $G'/H_{11032}$ and $\tan \delta$ of various BR samples, uncured, cured for 10 min at 403 K, and cured for additional 30 min at 413 K. Here all samples were processed in no deformations. The uncured sample shows rubber-to-flow transition. While the samples cures at 403 and 413 K show moderate and developed cross-linking network behaviors as expected. Thus we have determined the optimum cross-linking conditions for the two-step cure method that pre-cure should be made for 10 min at 403 K followed by imposition of large extensional deformation and post-cure for 30 min at 413 K. In case of the one-step cure process, no deformation has been given throughout the process.

**Reversible change in $G'$ and tan$\delta$ of the samples by one-step cure**

The dynamic modulus and loss tangent for the rubber sample cross-linked at equilibrium state should show deviation from the equilibrium ones in large deformation, but complete recovery after the deformation has been eliminated. Figure 5 shows the change in $G'$ and tan$\delta$ in reversing double-step large deformations for the BR samples prepared by one-step cure method. In extensional deformation, it is not easy to give perfectly reversible deformation and to measure dynamic modulus in...
deformation. So we have chosen reversing double-step shear deformations as the deformation history.

Dynamic modulus and loss tangent values measured before shearing are denoted by broken lines. After large shearing at strain $\gamma=0.5$ and 1.0, decrease in $G'$ and increase in $\tan\delta$ were observed, but complete recovery was observed both in $G'$ and $\tan\delta$. They are consistent with the results for the cross-linked SBRs measured for revering double-step compression experiments. The results mean clearly that dynamic modulus and loss tangent are functions of chain configuration as discussed preliminarily in the introduction.

Chain anisotropy has effects to lower the storage modulus and to raise loss tangent. When the deformation recovers to the original state, that is, chain configuration recovers to be isotropic, however, both $G'$ and $\tan\delta$ take the original values reversibly. Therefore, the sample prepared by one-step cure method shows no nonlinearity at the state of recovery in shape.

Two-step cure

Figure 6 shows the storage modulus and loss tangent curves of the samples prepared by two-step cure method. They can be compared with the curves of the sample prepared by one-step cure. The former curves for storage modulus are lower than the corresponding latter one, and those for loss tangent are higher than as expected. The deviations from the curve of one-step cure sample increases with the residual extensional strain. In the sample through the two-step cure, coarse cross-linking was introduced to the chains in the pre-cure process. When the coarsely cross-linked sample was deformed in extension, the chains are also expected to be extended. Then the dense cross-linking was introduced to the extended chains in the post-cure process. At the state of extension, chains should take anisotropic configuration. After being released, the sample shows shrinkage due to rubber elasticity along the extensional axis. However, if we take the post-cure state as a new standard, relative extension of some transversal chains occurs in the normal direction. So the shrinkage should stop at certain extensional state where shrinkage and expansion stresses are balanced. In fact, the residual extensional strains observed were not zero but...
finite. The values were 0.085, 0.153, and 0.275 for the samples extended to $\lambda = 1.25, 1.5$ and 2.0, respectively. Therefore, the chains still keep the anisotropic configuration even after the stress free condition was attained.

In the sample prepared by the one-step cure, chain configuration must be isotropic, because all cross-linking points were introduced at the state of no deformation. Therefore, the difference between the two-step cure and one-step cure curves in Figure 6 should be attributed to that in chain anisotropy. In other words, Figure 6 shows clearly that chain anisotropy is one of the origins for nonlinear viscoelasticity of polymers.

Figure 7 shows comparison of storage modulus and loss tangent values measured in different directions, that is, along the extensional axis and along another axis perpendicular to the extensional direction. For a usual rubber cross-linked at no deformation, the residual extensional strain of 0.27 would correspond to compressive strain of 0.11 in the normal direction under the condition of incompressibility of rubber, suggesting increase in $G'$ from the value taken at equilibrium state, if we refer the data reported previously on $G'$ of compressed vulcanizate. However, significant difference cannot be found between the two curves observed in parallel and perpendicular directions to the extensional axis. The present cross-linking points in the two-step cure method have been introduced at the highly extended state. If we look at the chain of the sample after post-cure was made in extension followed by release, its shape is considered to extend in both directions parallel and normal to the extensional axis as was already discussed. This may be the reason why no substantial difference was observed in the curves denoted by open symbols. This point may be important for industrial application.

**Summary**

Nonlinear dynamic modulus was measured on the polybutadiene samples having anisotropic chain configuration, and compared with that of the polymers having isotropic configuration. Chain anisotropy effect was confirmed to lower the energy storage term and to raise the energy loss term. Such effect may be useful for process control of loss energy.
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