Characterization of the Aging Behavior of Raw Epoxidized Natural Rubber with a Rubber Processing Analyzer

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ABSTRACT: Tests of the strain sweep, frequency sweep, and stress relaxation for raw epoxidized natural rubber were carried out with a rubber processing analyzer. The results showed that the complex viscosity, η^*, decreased with the prolongation of the aging time in the region of Newtonian flow, but in the region of non-Newtonian flow, the decrement of η^* with a rising shear rate decreased with the prolongation of the aging time. The torque (S') response from the strain sweep indicated that aging brought about an obvious decrease in the increment of S' with rising strain in the linear viscoelastic region and a small increase in the slope of the plateau on the curve of the S' response in the nonlinear viscoelastic region. The stress relaxation rate constants k and b, calculated according to the equations $S_t = S_0e^{-kt}$ and $S_t = S_1t^{-b}$ (where S_t, S_0, and S_1 are the stresses at relaxation time t, $t = 0$, and $t = 1$, respectively), increased, and the stress relaxation time obtained directly from the rubber processing analyzer shortened with the prolongation of the aging time. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1277–1281, 2006

Key words: ageing; relaxation; rubber; viscosity

INTRODUCTION

Epoxidized natural rubber (ENR) is a modified natural rubber obtained from the reaction of natural latex with peracetic acid.[1] ENR has unique features, with oil resistance similar to that of acrylonitrile-butadiene rubber with medium acrylonitrite and gas permeability similar to that of butyl rubber as well as good wet-grip characteristics.[2] However, instability and poor aging resistance during storage are defects of ENR. Studies[3,4] on the aging mechanism of ENR have indicated that thermal oxidation occurs not only in the carbon–carbon double bond of ENR but also in the epoxy bond of ENR. Research[5,6] on the aging properties of ENR during storage has shown that the mechanical properties deteriorate seriously. Fourier transform infrared spectrometry, thermal analysis, and tests of the mechanical properties are generally used to characterize the aging behavior of ENR, but only a few reports on the characterization of the effects of thermal oxidative aging on the viscoelastic properties of ENR with a rubber processing analyzer (RPA) are available.

RPA is a dynamic mechanical rheological tester designed to provide dynamic property data on rubber polymers, master batches, uncured compounds, and cured compounds.[7] RPA produces a shear strain to a sample by oscillating the lower die sinusoidally. The lower die can oscillate from ±0.05 to ±90.00° of arc, corresponding to a strain of ±0.7 to ±1256%.The oscillation frequency can be set from 0.1 to 2000 cycles per minute, corresponding to a frequency of 0.0017–33.3333 Hz. Various combinations of strain and frequency can produce shear rate ($\dot{r}$) values of $\leq 30\ s^{-1}$. The test temperature is in the range of 40–230°C. The measurements of the viscoelastic properties of rubber at various strains and frequencies can be performed in one test. A distinct advantage of RPA over a traditional dynamic rheological tester is that no special sample needs to be prepared. Therefore, it is very convenient to apply RPA for research on the viscoelastic properties of raw rubber.

$\dot{r}$ of RPA can be obtained with the following equation:[8]

$$\dot{r} = r_0\omega \sin(\omega t) \quad (1)$$

where r_0 is the maximum strain, ω is the frequency, and t is the time. Equation (1) gives two types of shear rates. The first is produced by the change in strain at a constant frequency, and the second is produced by the change in the frequency at a fixed strain. Hence, the first is defined as the strain shear rate, $\dot{r}_s$, and the second is defined as the frequency shear rate, $\dot{r}_f$, for the purpose of distinction.

This article concerns tests of the strain sweep, frequency sweep, and stress relaxation of raw ENR aged

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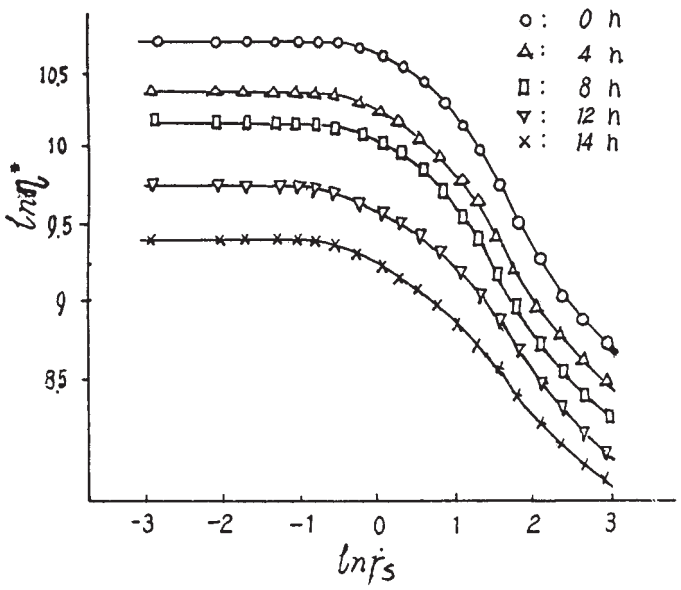

Figure 1 Relation between ln η^* and ln $\acute{r}_s$.

in an oven at 100°C. Our purpose is to obtain a method for the characterization of the aging behavior of ENR with RPA and to determine the effect of aging on the viscoelastic properties of raw ENR.

EXPERIMENTAL

Material

ENR with 47.10 mol % epoxidation, a product from South China Tropical Agricultural Product Processing Research Institute (Guangdong, China), was used.

Sample preparation

Raw ENR were cut into pieces (4 × 4 cm, ca. 5 g). The pieces were put in an oven at 100°C for 4, 8, 12, or 14 h.

Tests

An RPA2000 (Alpha Technologies U.S.L.P., Akron, OH, USA) was used for all tests. The strain sweep was carried out at a frequency of 0.33 Hz and at a temperature of 100°C, and the frequency sweep was carried out at 1° of arc and 100°C. The stress relaxation was measured at 30° of arc (a strain ratio of 5.2) and 55°C, and the test time was 2 min.

RESULTS AND DISCUSSION

Effects of aging on the viscosity of ENR

The relation between the apparent viscosity, η^α, of rubber and $\acute{r}$ can be expressed as follows:[9]

$$\eta^\alpha = k\acute{r}^{n-1} \quad (2)$$

where k and n are constants of rubber. The complex viscosity, η^*, obtained from RPA is used as η^α in our work because η^* corresponds well to the η^α value obtained from a capillary rheometer.[10] A plot of ln η^* versus ln $\acute{r}_s$ according to eq. (2) (see Fig. 1) indicates that in the range of low $\acute{r}_s$ values, the change in ln η^* with ln $\acute{r}_s$ appears as a straight line that is almost parallel to the ln $\acute{r}_s$ axis, and the constant n is approximately 1; this is a feature of Newtonian behavior. In the range of high $\acute{r}_s$ values, ln η^* decreases with rising ln $\acute{r}_s$; this is a phenomenon called shear thinning, a feature of non-Newtonian behavior (pseudoplastic behavior). An obvious effect of aging on the movement behavior of the melt of ENR can also be seen in Figure 1. The value of ln η^* expressed by the straight line drops with the prolongation of the aging time, and the decrement of ln η^* with rising ln $\acute{r}_s$ decreases with the prolongation of the aging time.

A plot of ln η^* versus ln $\acute{r}_f$ (see Fig. 2) illustrates a change in ln η^* that is different from that in Figure 1; that is, the decrease in ln η^* is linearly related to the increase in ln $\acute{r}_f$ over the whole range of $\acute{r}_f$ values, and the slope of the straight line decreases with the prolongation of the aging time.

On the basis of the changes in η^* with $\acute{r}$ shown in Figures 1 and 2, the value of the zero-shear viscosity, η_0, cannot be calculated. However, according to the drop in the value of ln η^* expressed by the straight line in Figure 1 and the decrease in the slope of the straight line in Figure 2, it may be assumed that η_0 of ENR would decrease with the prolongation of the aging time. The decrease in η_0 means a decrease in the molecular weight of ENR, and the decrease in the molecular weight may provide an explanation for why the decrement of η^* of ENR with rising $\acute{r}$ is reduced with the prolongation of the aging time.

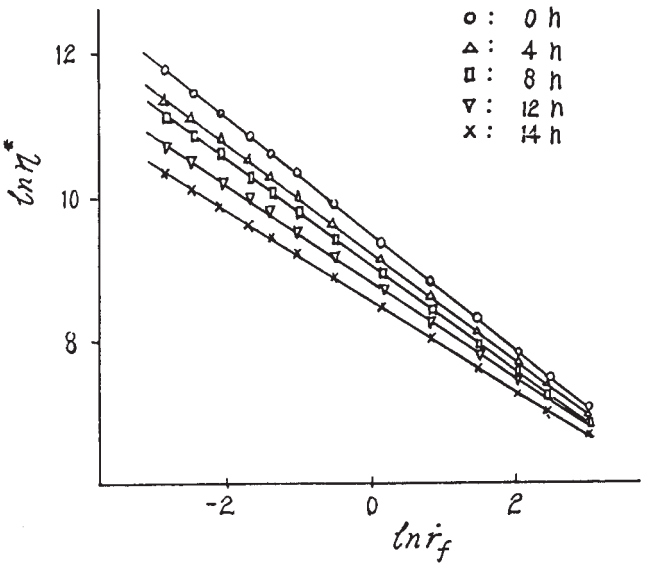

Figure 2 Relation between ln η^* and ln $\acute{r}_f$.

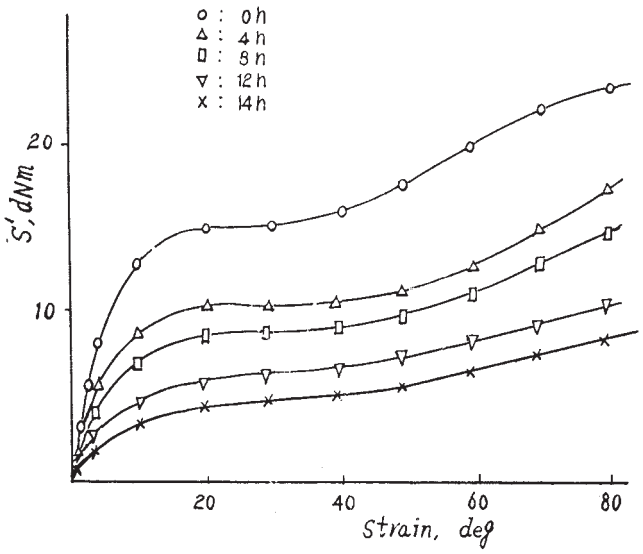

Figure 3 Curve of the S' response from the strain sweep.

Torque (S') response from the strain sweep

The S' response from the strain sweep is sensitive to rheological differences among polymers.[11] Figure 3 shows that the curve of the S' response from strain consists of a linear viscoelastic region and a nonlinear viscoelastic region.[11] In the linear viscoelastic region, the rapid increase in S' with rising strain is related to the elastic property of ENR. Figure 3 shows that the increment of S' with rising strain drops significantly, and this means that the prolongation of the aging time brings about an obvious decrease in the elastic property of ENR. In the nonlinear viscoelastic region, a plateau occurs on the curve of the S' response in which S' does not increase with rising strain because of the irreversible movement of the molecular chain. After passing the plateau, S' increases again with rising strain, and this is the result of strain-induced crystallization.[12] The slope of the plateau in Figure 3 shows a small increase with the prolongation of the aging time. This subtle change in the slope of the plateau can probably provide information about how the rate of strain-induced crystallization increases because of the lower molecular weight caused by the prolongation of the aging time.

Effect of aging on the stress relaxation of ENR

The process of ENR stress relaxation can be treated with the following equation:[13,14]

$$S_t = S_1 t^{-b} \tag{3}$$

where S_t and S_1 are the stresses at relaxation time t and $t = 1$, respectively, and b is the rate constant of stress relaxation. A plot of ln S_t versus ln t according to eq. (3) (see Fig. 4) indicates that eq. (3) can fully describe the process of stress relaxation of ENR after a relaxation time of 0.0006 min, but not the process before 0.0006 min. The process that does not follow eq. (3) is treated with another equation:[15,16]

$$S_t = S_0 e^{-kt} \tag{4}$$

where S_0 is the stress at $t = 0$ and k is the rate constant of stress relaxation. A plot of ln S_t versus t according to eq. (4) (see Fig. 5) indicates that eq. (4) describes well the initial process of stress relaxation of ENR, which cannot be described in eq. (3). Figures 4 and 5 show clearly that the slopes of the straight lines increase with the prolongation of the aging time. The rate constants b and k are calculated by regression. Figure 6 shows that b and k increase with the prolongation of the aging time.

The constant τ in the Maxwell model represents the time for the stress relaxation when S_t/S_0 is equal to 36.79%[15] and can be theoretically related to the specific rate constant of the cleavage reaction.[17] The value of τ can be directly obtained from RPA. Figure 7 shows clearly the effect of the aging time on τ. It is well known that τ is related to the modulus, G, and viscosity, η, as follows:[15]

$$\tau = \eta/G \tag{5}$$

Because the elastic property of ENR decreases with the prolongation of the aging time, as shown in Figure 3, it may be assumed that the shorter value of τ with the prolongation of the aging time means a decrease in η of ENR.

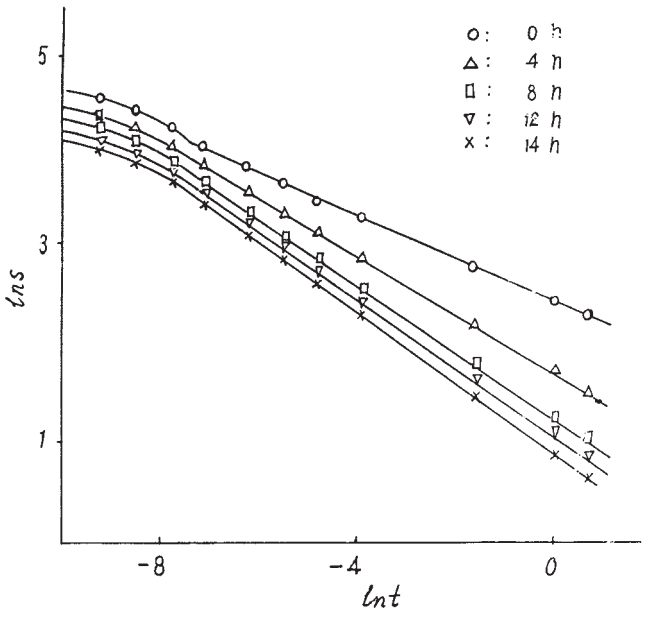

Figure 4 Relation between ln S and ln t.

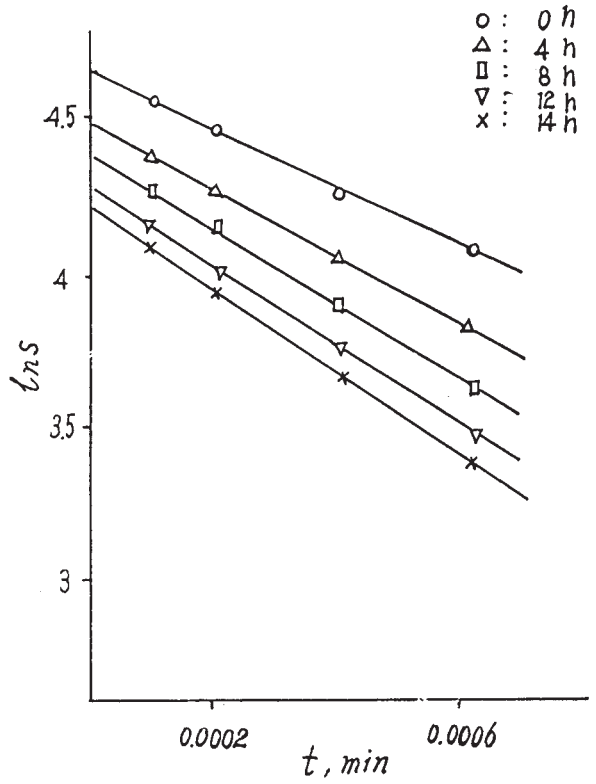

Figure 5 Relation between ln S and t.

CONCLUSIONS

The changes in η^* with $\acute{r}_s$ show that ENR behaves like Newtonian flow in the range of low $\acute{r}$ values and like non-Newtonian flow (pseudoplastic behavior) in the range of high $\acute{r}$ values. η^* in the region of Newtonian flow decreases, and the decrement of η^* with rising $\acute{r}_s$ in the region of non-Newtonian flow decreases with the prolongation of the aging time. The decrement of η^* is linearly related to the increase in $\acute{r}_f$, and the slope of the straight line decreases with the prolongation of the aging time.

The curve of the S' response from strain shows that in the linear viscoelastic region, the increment of S' with rising strain is reduced with the prolongation of the aging time. In the nonlinear viscoelastic region, a plateau occurs on the curve of the S' response from strain, and the slope of the plateau shows a small increase with the prolongation of the aging time.

The test results of the stress relaxation show that whole process of stress relaxation of ENR can be separated into two stages, which are treated by two equations: $S_t = S_0 e^{-kt}$ and $S_t = S_1 t^{-b}$. The rate constants of stress relaxation (k and b) calculated from these equations by regression increase, and the value of τ obtained directly from RPA shortens with the prolongation of the aging time.

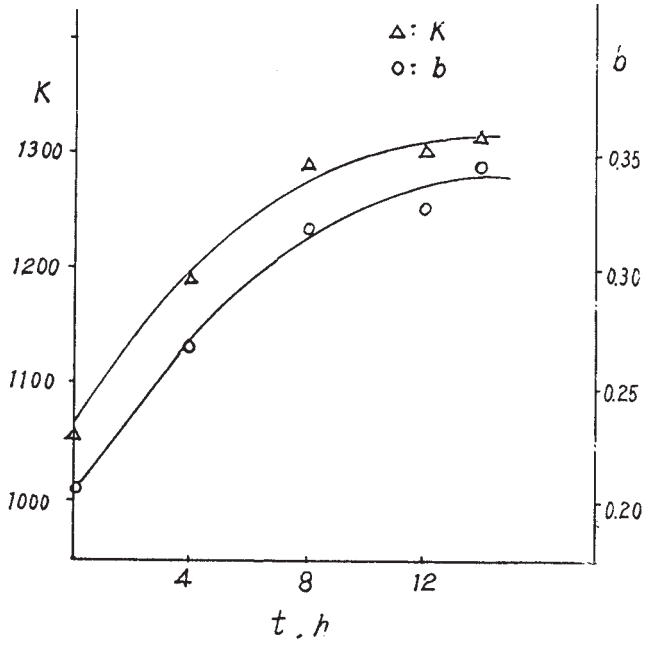

Figure 6 Effect of prolonging aging time t on rate constants k and b.

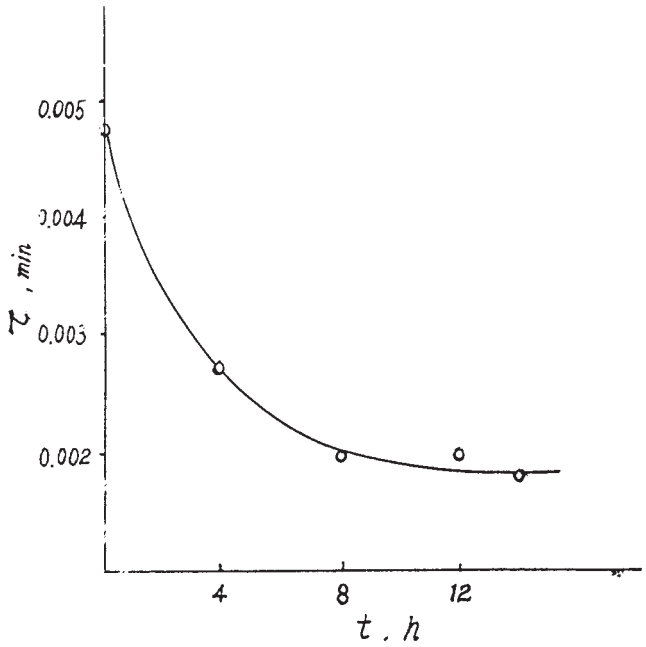

Figure 7 Effect of prolonging aging time t on τ.

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