

Chemorheology of Crosslinked Polyisoprene / Poly(butadiene co-styrene) Blends

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Synopsis

Physical and chemical properties of IR/SBR blend systems crosslinked by dicumyl peroxide were investigated in detail. In order to study physical structure of cross-linked rubber blends, measurement of birefringence of extended samples and observation by scanning electron microscope (SEM) of ones ruptured in liquid nitrogen were also carried out. In the vicinity of IR/SBR = 30/70 (weight ratio) the phase structure of blends was reversed. The size of domain was in about 0.2 to 0.7 μm dependent on the blend ratio. In preparing the cross-linked rubber blends, cross-linking reaction seemed to occur independently in each rubber phase. The birefringence linearly increased with the blend ratio in the range of IR/SBR = 100/0 to 40/60 and then largely increased in IR/SBR < 30/70. Stress relaxation of rubber blends was observed at 373 K in both air and nitrogen. Chemical stress relaxation of these systems could be represented by a combination of rate constant of stress relaxation and volume fraction of each cross-linked rubber, that is, the degradation of the networks of cross-linked rubber blends occurred independently in each rubber phase.

INTRODUCTION

So far, we have investigated the behavior of chemical stress relaxation of EPDM and natural rubber (NR) having different cross-linking structures, at high temperature¹⁻³. Since an elastomer has characteristic chemical and physical properties, in many cases, it has been used to blend with other elastomers in order to modify the properties. Therefore, it is practically important to investigate the properties of rubber blends. The various physical properties of polymer blends have been studied by many workers.⁴⁻⁹ Study of degradation of rubber blends, however, has been scarcely carried out.¹⁰⁻¹³

In the present paper, physical and chemical properties of cross-linked polyisoprene (IR)/poly(butadiene co-styrene) (SBR) blends were investigated by stress relaxation, birefringence, swelling, and scanning electron microscope (SEM). Chemical stress relaxation at high temperature in air was studied in detail in connection with the blend ratio of rubbers.

EXPERIMENTAL

Samples

Cis-1,4polyisoprene (Nipol 2200, 98.5% *cis*) and poly(butadiene co-styrene) (SBR 1502, 25% styrene) used here were obtained from Nippon Zeon Co., Ltd. Cross-linked rubber blends were prepared as follows. Each raw rubber was milled with 2.5 phr dicumyl peroxide (DCP) and then both milled rubbers were mixed with different weight ratio at 323 K. Thin sheets of these rubber blends were pressed for 20 min at 418 K. All the samples were extracted by hot acetone for 48 h under nitrogen and then dried *in vacuo*.

Stress relaxation. Continuous and intermittent stress relaxation measurements were carried out at 373 K both in air and nitrogen. Extension ratio was about 1.2.

Swelling. Each sample was swollen in *n*-decane for 48 h. Weights of rubber blends, W_0 and W_s were measured before and after swelling, respectively, and volume fractions, v_r , of the blends in the swollen state were estimated.

Estimation of sol fraction. Each degraded sample was immersed in benzene for 48 h at room temperature, the soluble part of rubber (sol) was removed, and the remaining gel was weighed after drying *in vacuo*. The sol fraction was estimated from the weight loss during the degradation. In order to adopt the same initial condition as for the stress relaxation measurement, the sample preheated for 20 min was taken as the undegraded one.

Estimation of relative chain density from sol fraction of degraded samples. According to Kaeriyama, Ono, and Murakami,¹⁵ the intermittent stress-relaxation measurement was connected with sol fraction by the following equation when the random scission along the main chain of the rubber networks occurred;

$$f(t)/f(0) = f_s(t)/f_s(0) = n_{s(t)}/n_s(0) = \left\{ \frac{1 - S(t)^{1/2}}{1 - S(0)^{1/2}} \right\}^2 \quad (1)$$

where, $S(0)$ and $S(t)$ are sol fractions at the degradation time $t = 0$ and $t = t$, respectively, and $f_s(t)/f_s(0)$ and $n_{s(t)}/n_s(0)$ is a relative stress and a relative chain density obtained from the sol fraction measurement, respectively.

Measurement of birefringence. Dependence on the extension ratio, α from 1 to 6.0 of birefringence, Δn of cross-linked rubber blends was observed at room temperature.

Observation of scanning electron microscope of ruptured samples. The sample surface, which was ruptured in liquid nitrogen and was etched by ion beam, was observed by scanning electron microscope (SEM) (Akashi Seisakusho Co., Ltd; ALPH-10).

RESULTS AND DISCUSSION

Characterization of Undegraded Cross-linked Rubber Blends

As the mixtures of different homopolymers have various structural complexities, it is first necessary to investigate the characterization of undegraded rubber blends.

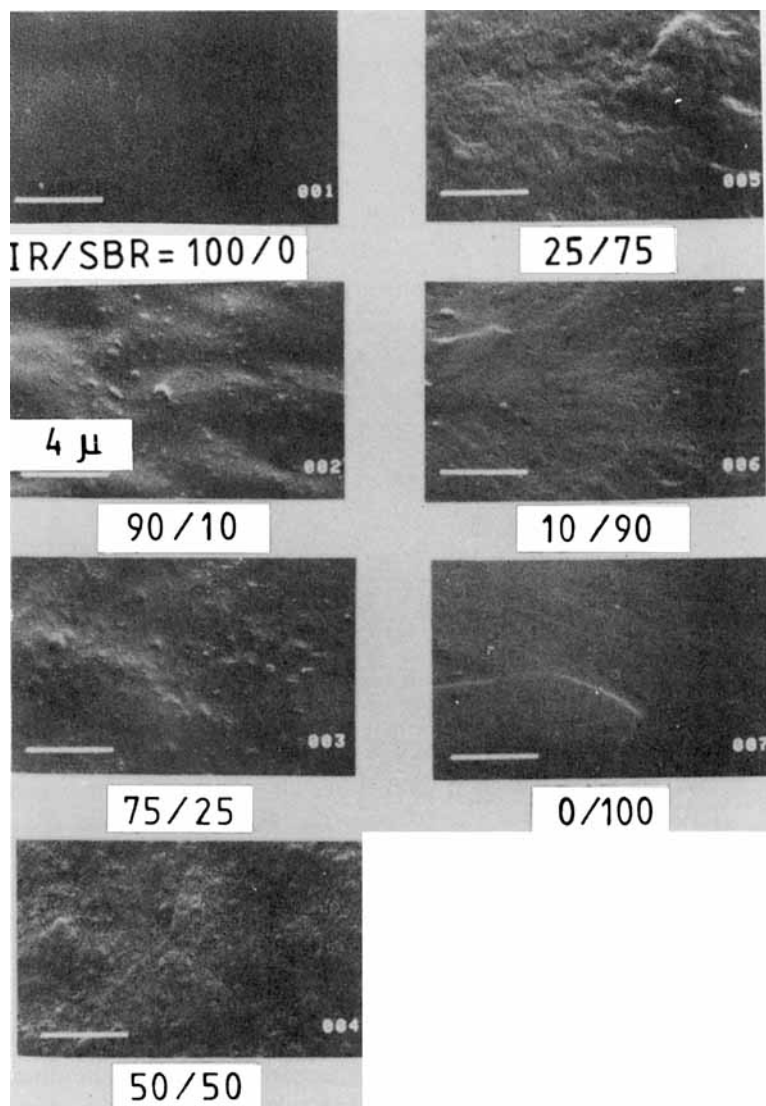


Fig. 1. Scanning electron microscope (SEM) of ruptured samples in liquid nitrogen.

Miscibility of homopolymers. There are several methods to investigate the miscibility of polymers. Firstly, the sample surface ruptured in liquid nitrogen was observed by scanning electron microscope (SEM). Figure 1 is the result. It finds that the miscibility of polyisoprene with SBR is not good in all blend systems. The state of mixture of rubbers changes with blend ratio. The phase structure of mixtures appears to change in the vicinity of IR/SBR = 25/75 (weight ratio), that is, in the range of IR/SBR > 25/75, IR is a continuous phase (matrix) and SBR is a dispersed phase (domain), and in IR/SBR < 25/75, the structure is reversed. This has also been observed by transmission electron microscope.¹⁶ The shape of domain is mostly spherical. The domain size has been reported to be in the range of 1.3 to 2.0 μm .¹⁶ In the

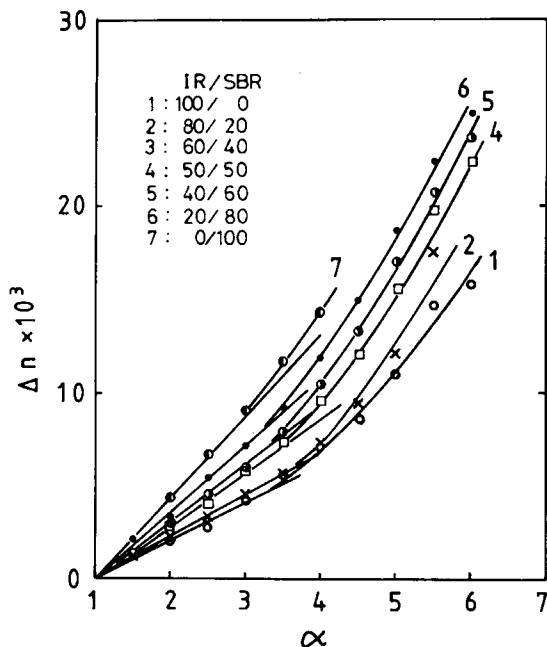


Fig. 2. Relation between birefringence and extension ratio for crosslinked IR/SBR blends.

case of DCP-cured rubber blends used here, however, as can be seen from Figure 1, the domain size is 0.2 to 0.7 μm . The size is approximately a digit smaller than that reported. The domain size appears to become slightly larger with increasing amount of SBR in the mixtures.

Figure 2 shows the relation between the birefringence Δn and the extension ratio, α for all the samples. In the region of small deformation, Δn is proportional to α , that is, the orientation of polymer chains proportionally progresses with increased extension. In the region of large deformation, however, the value of Δn gradually deviates from the linear relationship as α increases. This is thought to be due to the greater increase of the number of polymer chains oriented to the direction of extension, which are attributed to the network chain ruptures caused by large deformation.¹⁷ Figure 3 shows the plots of Δn versus blend ratio related to various values of α . It can be seen from the figure that Δn gradually increases with SBR content in IR/SBR = 100/0 to 40/60 and the pronounced enlargement of Δn is especially presented in IR/SBR < 20/80. This means that the structure of blend systems changes in the vicinity of IR/SBR = 30/70 and this result agrees with the observation of SEM. Thus, we can also see the phase transition of cross-linked rubber blend systems from the measurement of birefringence under the various extension ratios.

Density, ρ , apparent initial chain density, $n(0)$, ratio of sample weights before and after swelling, W_s/W_0 and volume fraction of swollen rubber blends, v_r , for all the samples are given in Table I and Figure 4. As shown in the figure, the density appears to be an additive property for the composition of blends. This is representative in the heterogeneous elastomer blend sys-

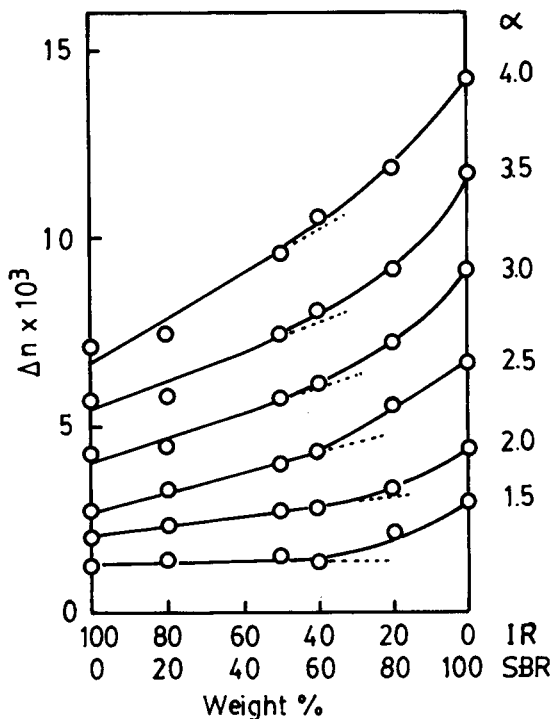


Fig. 3. Relation between birefringence at various deformation and IR/SBR blend ratio.

tems.¹⁸⁻²⁰ From the above results, it has become apparent that the blend systems used here are heterogeneous, the phase transition occurs in the vicinity of IR/SBR = 30/70, and the domain size is in the range of 0.2 to 0.7 μm , that is much smaller than the values (1.3 to 2.0 μm) reported. Although the reason for the discrepancy between the domain sizes is not adequately clear, it may be dependent on the difference of mixing conditions of rubbers.

Apparent Initial Chain Density and Degree of Swelling. Initial chain density of cross-linked rubbers can be easily estimated by several methods (e.g., the stress-stain measurements based on the statistical theory of rubber-

TABLE I
Characteristic Parameters of Cross-linked IR/SBR Blends

No.	IR/SBR	ρ^a kg dm ⁻³	$n(0) \times 10 \text{ mol dm}^{-3}$		W_s/W_0	v_r^b
			Observed	Calculated		
1	100/0	0.921	1.06	(1.06)	2.55	0.228
2	80/20	0.927	1.09	1.20	2.40	0.249
3	60/40	0.939	1.23	1.33	2.00	0.261
4	50/50	0.937	1.31	1.42	1.95	0.310
5	40/60	0.942	1.54	1.53	1.76	0.333
6	20/80	0.946	1.75	1.79	1.56	0.328
7	0/100	0.955	2.18	(2.18)	2.21	0.410

^a ρ : density of rubber blends.

^b v_r : volume fraction of rubbers in the swollen state.

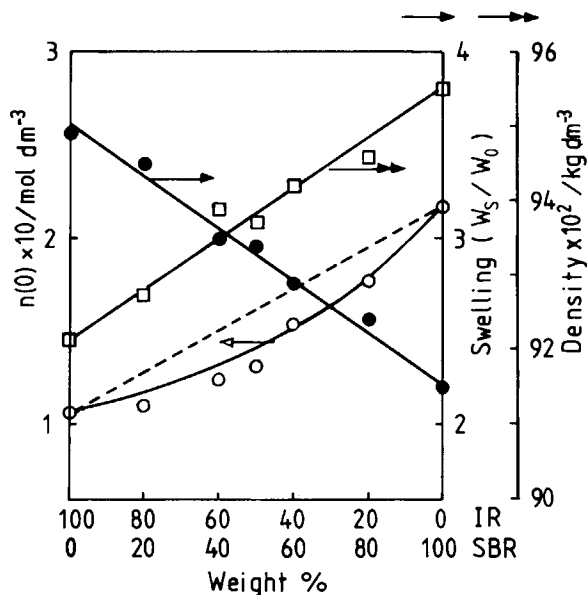


Fig. 4. Relation between density, apparent initial chain density, $n(0)$ and degree of swelling, W_s/W_0 and blend ratio of rubbers. \square : density, \circ : apparent initial chain density [a solid line represents initial chain density calculated from Eq. (4)], \bullet : degree of swelling.

like elasticity and the swelling measurements). In the case of elastomer blends, especially heterogeneous ones, however, the initial chain densities cannot be obtained. In the present paper, apparent initial chain density, $n(0)$ was estimated for convenience, as an average of initial chain density of both rubber phases, by using the theory of rubberlike elasticity. The relation between $n(0)$ and blend ratio is not linear as shown in Figure 4. Now, in order to explain this relation, we assume the series model for two-phase polymer blend systems proposed by Takayanagi.²¹ If the initial moduli of both rubbers (IR and SBR) are $G_A(0)$ and $G_B(0)$, respectively, and the volume fractions of each component of the blends are v_A and v_B , respectively, the modulus of the rubber blends, $G(0)$ may be expressed as:

$$1/G(0) = v_A/G_A(0) + v_B/G_B(0) \quad (2)$$

If the strain is smaller,

$$G(0) = n(0)RT \quad (3)$$

$$1/n(0) = v_A/n_A(0) + v_B/n_B(0) \quad (4)$$

where, $n_A(0)$ and $n_B(0)$ are initial chain densities of both rubbers when they were separately cured.

The results estimated by Eq. (4) is also shown in Figure 4 (a full line). This shows comparatively good agreement with plots of the data. Furthermore, the relation between degree of swelling, W_s/W_0 and blend ratio gives a straight line. These results suggest that the cross-linking reaction of blend systems used in the present study proceeds independently in each rubber.

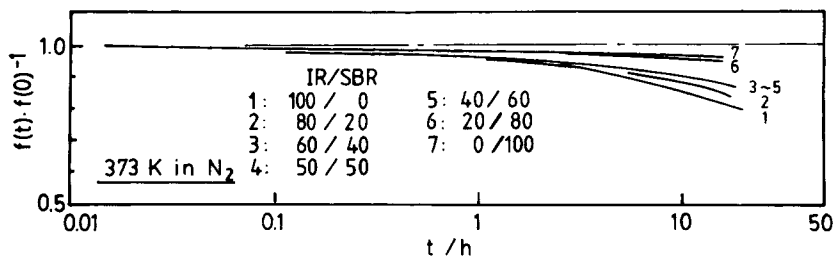


Fig. 5. Stress-relaxation curves of cross-linked IR/SBR blends under nitrogen at 373 K. 1: IR/SBR = 100/0, 2: 80/20, 3: 60/40, 4: 50/50, 5: 40/60, 6: 20/80, 7: 0/100.

Chemical Stress Relaxation of Cross-linked Rubber Blends

Firstly, it is necessary to see how physical stress-relaxation, which is probably based on the physical flow of the polymer chains, occurs in the rubber blends. Figure 5 shows the stress-relaxation curves of blends at 373 K under nitrogen. The rate of stress-relaxation gradually increases with increasing amounts of IR. Here, the effect of the interface between both rubbers should be investigated for the stress-relaxation of the blend systems. This effect will appear in the stress-relaxation curve of rubber blends when it is measured under the different extension ratios. Although the stress-relaxation of PI/SBR = 50/50 (No. 4) was measured under the constant extension ratio in the range of $\alpha = 1.2$ to 2.0 at 373 K in nitrogen, all the stress-relaxation curves were in good agreement with each other. Therefore, it cannot be considered that the complexity of interface of both rubber phases affects the stress-relaxation of these blends.

Figure 6 shows the stress-relaxation curves of all the samples in air at 373 K. The rate of stress-relaxation more remarkably depends on the blend ratio of rubbers compared with the case in nitrogen. In the stress-relaxation in air, the physical relaxation based on the slippage of polymer chains as found in Figure 5 also will be contained. In order to eliminate the effect of slippage from these data, the following approximation was applied by assuming that

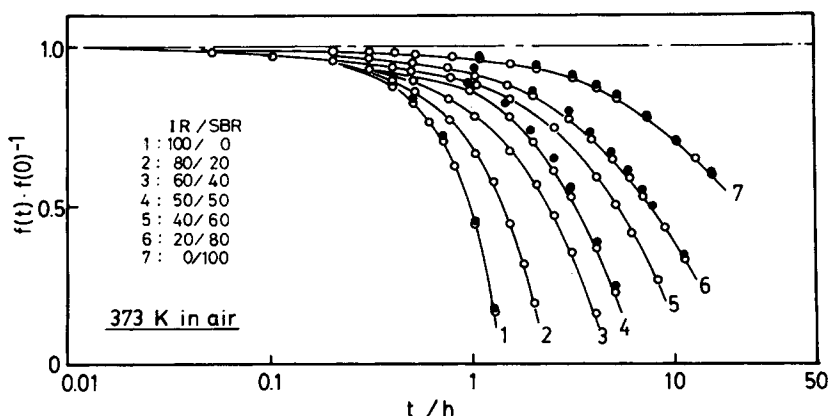


Fig. 6. Stress-relaxation curves of cross-linked IR/SBR blends in air at 373 K. Numbers in the figure are the same as in Figure 5. ○: original data; ●: corrected data by Eq. (5) (real chemical stress relaxations).

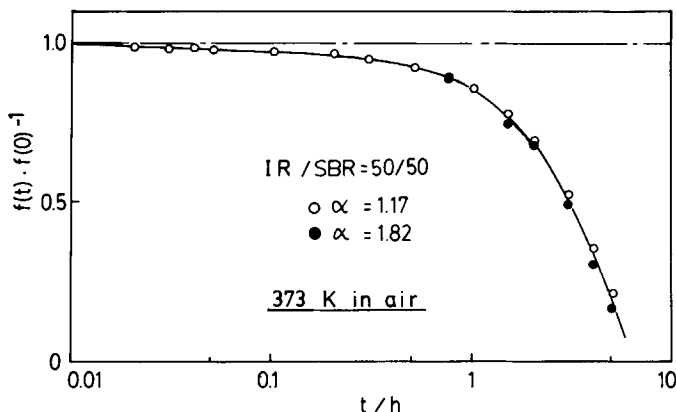


Fig. 7. Stress-relaxation curves of cross-linked IR/SBR = 50/50 blend extended to different elongation in air at 373 K.

the magnitude of physical relaxation occurring in air was the same as that under nitrogen;

$$(f(t)/f(0))_C = (f(t)/f(0))_{\text{air}} / (f(t)/f(0))_N \quad (5)$$

where, $(f(t)/f(0))_C$ is a chemical relative stress owing to the network chain scissions, $(f(t)/f(0))_{\text{air}}$ is an observed relative stress in air and $(f(t)/f(0))_N$ is one under nitrogen at time, t , respectively. Some corrected stress-relaxation curves were also shown in Figure 6. It can be seen from the figure that the effect of physical stress-relaxation is very small over the range of observation time and will be negligible.

Again, we should consider the effect of interface between rubber phases on the chemical stress-relaxation. It is well known that the rate of chemical stress-relaxation of cross-linked simple rubbers is not generally influenced by the extension ratio up to 2.²² Therefore, through the measurement of the chemical stress-relaxation under the different extension ratio in air, we can also investigate the effect of the interface between both rubber phases on the oxidative degradation of the blends. As shown in Figure 7, the stress-relaxation of sample No. 4 (IR/SBR = 50/50) is independent on the extension ratio up to at least $\alpha = 1.8$. It can be thought from this result that the bond strength of the interface of this blend system is, chemically and also physically, compared with that in each cross-linked rubber phase (domain or matrix). If the bond strength of interface were weaker than that in the phases, the rate of stress-relaxation under the different elongations would be distinct from each other; that is, it would become progressively greater as the extension ratio became larger.

Next, each intermittent stress-relaxation curve of all the rubber blends was compared with the relative chain density, $n_s(t)/n_s(0)$ (dashed lines) estimated by Eq. (1) from the measurement of sol fractions. The result is shown in Figure 8. A pair of curves of each sample is in relative agreement with each other. This means again that the consideration of the physical effect at the interface between the rubber phases is not important. In the blend systems containing the greater amount of SBR, however, the large difference between

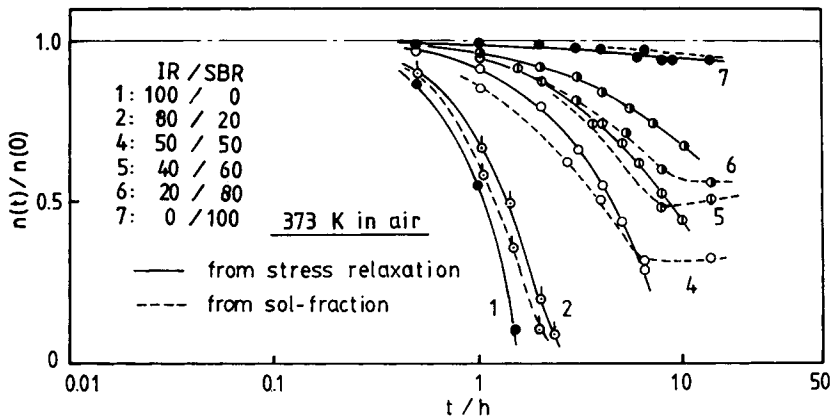


Fig. 8. Comparison of intermittent stress-relaxation curves with relative chain density estimated from sol fraction of crosslinked IR/SBR blends degraded under the same condition. Numbers in the figure are the same as in Figure 5.

both results is observed in the longer time region, that is, the relative effective chain density from the measurement of sol fraction gradually increases with the degradation time. This will be based on the production of a large number of crosslinkages together with the oxidative scission along the main chain.

From above results, we can obtain the following information: (1) The interface between the domain and the matrix of rubber blend systems used here is strongly jointed with each other. Therefore, the bonds at the interface are not easily cleaved by the extension of sample. (2) The oxidative scission reaction independently occurs in each rubber phase and the chemical interaction does not take place.

Although not observed, it is said that in the interface between the different polymers, generally, they are partially mixed with each other.^{4,5} The width of interface has been evaluated to be several nm¹ by the thermodynamic treatment. In the case of IR/SBR = 50/50 (No. 4), if the domain is a spherical particle having a diameter of 0.5 μm and the width of interface is in the range of 2 to 5 nm, the volume of the interface is only in the range of 1.4×10^{-14} to 2.2×10^{-13} m³/m³. Therefore, the degradation occurring in the interface can be substantially neglected.

In order to investigate the chemical stress-relaxation behavior of these blend systems in some detail, the results in Figure 6 were replotted as shown in Figures 9(a) ($\log(f(0)f(t)^{-1})$ versus t) and (b) ($\log \log(f(0)f(t)^{-1})$ versus t).

From the figures, every stress-relaxation curve is represented by the following equations:

at the initial stage;

$$\ln(f(0)f(t)^{-1}) \approx k_1 t \quad (6)$$

at the later stage;

$$\ln \ln(f(0)f(t)^{-1}) \approx k_2 t + C \quad (7)$$

where, k_1 and k_2 are rate constants of stress-relaxation at the initial stage

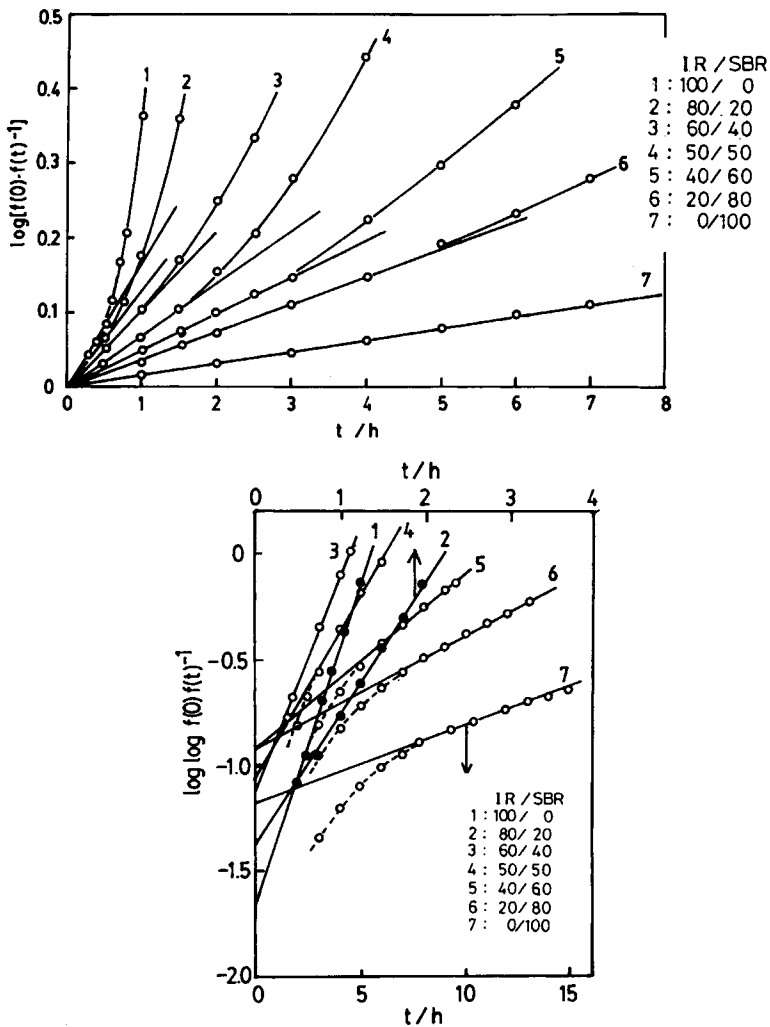


Fig. 9. Replots of Figure 6 ($\log(f(0)f(t)^{-1})$ versus t). (b) Replots of Figure 6 ($\log \log(f(0)f(t)^{-1})$ versus t).

and the later stage, respectively, and C is a constant depending upon the blend ratio. The rate constants, k_1 and $\log k_2$, and the parameter, C obtained from Figures 9(a) and (b) were plotted against the volume fraction of IR, v_A . The result is shown in Figure 10. It is evident that each plot is represented by the straight line. That is to say, at the initial stage;

$$\begin{aligned} \ln(f(0)f(t)^{-1}) &\approx k_1 t \\ &= (k_{1A}v_A + k_{1B}(1 - v_A))t \end{aligned} \tag{8}$$

at the later stage; (i) for the samples of blend ratio, IR/SBR = 100/0 to

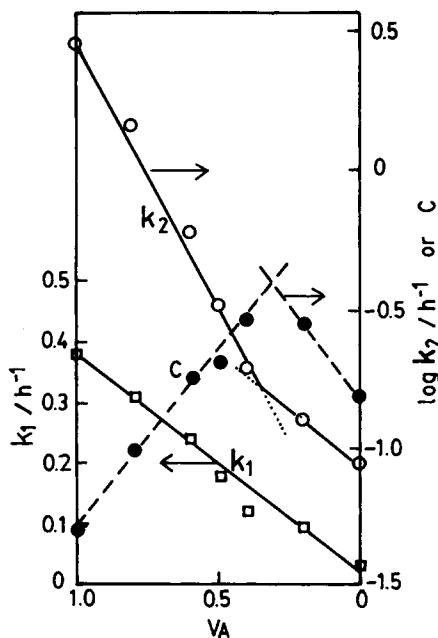


Fig. 10. Plots of k_1 , $\log k_2$ and C against volume fraction of IR, v_A .

30/70,

$$\begin{aligned} \ln \ln(f(0)f(t)^{-1}) &= k_2 t + C \\ &= k_{2A} \exp(a_A(1 - v_A))t + b_A(1 - v_A) + C_A \end{aligned} \quad (9a)$$

(ii) for the samples of blend ratio, IR/SBR = 30/70 to 0/100,

$$\ln \ln(f(0)f(t)^{-1}) = k_{2B} \exp(a_B v_A)t + b_B v_A + C_B \quad (9b)$$

where,

- k_{1A} rate constant of the stress-relaxation at the initial stage for cross-linked IR (sample No. 1)
- k_{2A} rate constant of the stress-relaxation at the later stage for cross-linked IR (sample No. 1)
- k_{1B} rate constant of the stress-relaxation at the initial stage for cross-linked SBR (sample No. 7)
- k_{2B} rate constant of the stress-relaxation at the later stage for cross-linked SBR (sample No. 7)
- a_A slope of straight line in $\ln k_2$ versus v_A plots in the range of $v_A = 0.3$ to 1.0
- a_B slope of straight line in $\ln k_2$ versus v_A plots in the range of $v_A = 0$ to 0.3
- b_A slope of straight line in C versus v_A plots in the range of $v_A = 0.3$ to 1.0
- b_B slope of straight line in C versus v_A plots in the range $v_A = 0$ to 0.3
- C_A constant C in Eq. (7) for sample No. 1
- C_B constant C in Eq. (7) for sample No. 7

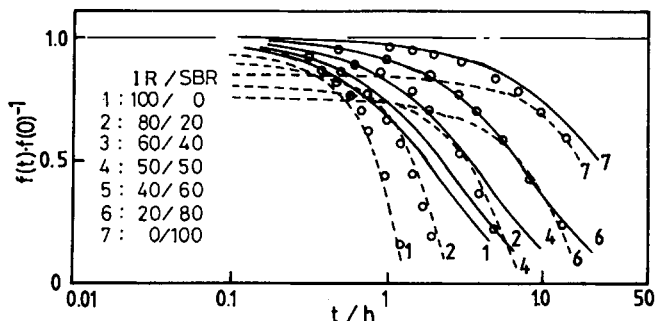


Fig. 11. Comparison of observed stress relaxation curves with calculated ones for cross-linked IR/SBR blends. —: calculated from Eq. (8); ---: calculated from Eqs. (9a) or (9b); ○: observed.

By using the values of $k_{1A} = 0.164$, $k_{2A} = 3.15$, $C_A = -3.00$ for IR (sample No. 1), $k_{2A} = 0.013$, $k_{2B} = 0.080$, and $C_B = -1.83$ for SBR (sample No. 7), and $\alpha_A = -4.30$, $\alpha_B = 2.24$, $b_A = 2.85$, and $b_B = 2.81$ which are obtained from Figures 9(a), 9(b), and 10, respectively, the theoretical stress-relaxation curves for all the rubber blend systems can be drawn. The comparison of the calculated curve with the observed one for each rubber blend are shown in Figure 11. Every pair of curves is comparatively in agreement with each other. This suggests that the rate of chemical stress-relaxation of cross-linked rubber blends is dependent on only the volume fractions. Thus, at the initial degradation stage, at least, the scission reaction in the networks occurs independently in each rubber phase.

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