

ESR Study of Vulcanizates Under the Deformed State

Junji Funatsu, Ryuichi Takagi, Masayoshi Ito

Department of Chemistry, Tokyo University of Science, Kagurazaka, Shinjuku-ku, Tokyo 162-0826, Japan

Received 15 April 2008; accepted 20 September 2008

DOI 10.1002/app.30340

Published online 1 May 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Electron spin resonance (ESR) measurements under the tensile deformation of cross-linked polyisoprene were examined by the combination of home-built stretching machine with commercially available ESR spectrometer. The changes of radical concentration during tensile deformation were successfully determined by this technique. It was found that the number of radicals produced by the stretching process decreased during the retraction of stretched sample. In addition, at a given strain, the decrease of radical concentration with time was accompanied by the increase of stress. Such changes were more prominent in the cross-linked sample by sulfur PS sample (PS) than by dicumyl peroxide (PCP), PD sample (PD). The

tensile modulus of the samples after the one cyclic deformation increased with increasing the keeping time at room temperature after the cyclic deformation. The increase was larger for the PS than for the PD. These results suggest that the broken cross-linking structure induced by the stretching process was partly reconstructed during and after the retraction with this tendency more prominent in the PS than in the PD. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2791–2795, 2009

Key words: ESR; deformed state; polyisoprene; reconstruction of network structure

INTRODUCTION

Electron spin resonance (ESR) is a powerful technique to study the mechanochemical reactions in deformed polymeric materials including elastomers where mechanically produced free radicals exist. The application of ESR to monitor radical formation during mechanical deformation of elastomers in the glassy state has been reviewed.^{1–4} Mead et al.⁴ studied an oxidation in uniaxially deformed diene rubbers and reported that radicals formed following tensile testing of polybutadiene and polyisoprene at 83 K in predominantly nitrogen atmospheres containing small amounts of oxygen were a peroxy radical and most probably an allyl radical arising from main chain rupture. The radical stability vs. temperature tests showed that the peroxy radical decayed at a temperature approximately 20 K lower than the allyl radical which, in turn, decayed rapidly in the vicinity of the glass transition temperature of the samples. Carstensen^{5,6} reported that the allyl radicals in polybutadiene and polyisoprene formed liquid nitrogen temperature were easily transformed into polyenyl radical during heating. However, the stability of polyenyl radical was uncertain.

We reported the ESR results for the stretched silica filled SBR unvulcanizates and their vulcanizates.^{7–9} In the study, samples for the measurements were

stretched by a tensile tester at room temperature up to a desired strain in the range of 10–200%, followed by a release of tensile stress, subsequently transferred to the precooled ESR cavity (–100°C) to avoid radical decay. By this method, we could obtain information on the radicals produced by the stretching at room temperature. It was found that polyenyl and sulfur radicals were produced by the stretching of the vulcanizates. With increasing the mechanical energy applied to the samples by the stretching, the carbon-sulfur linkages around silica particles were broken first, followed by the breakdown of carbon-sulfur and carbon-carbon linkages in the rubber matrix. When the ESR measurements for the stretched samples were carried out at room temperature, the signal intensity decreased with increasing the keeping time of stretched state, which suggests the occurrence of radical reactions at room temperature.

ESR measurement of vulcanizate under the tensile deformation exactly gives us more detailed information on the radicals with short decay time produced by tensile deformation, which enable us to discuss on the changes in the chemical and physical structures during tensile deformation of vulcanizate. However, in our knowledge, little report has been published concerning the radical reaction of vulcanized elastomer under the tensile deformation.

In this study, a home-built stretching machine was combined with commercially available ESR spectrometer and *in situ*-ESR measurements were carried out for vulcanized polyisoprene under the tensile deformation.

Correspondence to: M. Ito (itma56@rs.kagu.tus.ac.jp).

TABLE I
Compound Formulations (Weight Per Hundred Rubber)

Sample	PS	PD
PIR	100	100
Stearic acid	2	—
Zinc oxide	3	—
Sulfur	1.5	—
Accelerator CZ ^a	1.5	—
DCP ^b	—	2

^a *N*-cyclohexyl-2-benzothiazol-sulfenamide.

^b Dicumyl peroxide.

EXPERIMENTAL

Samples

The raw rubber used was a 1,4-cis polyisoprene rubber (PIR) (Nipole PIR 2200, $M_w = 1.36 \times 10^6$, Nippon Zeon, Japan). PIR was put into a Banbury mixer (Laboplastomill 50MR, Toyo Seiki, Japan) and masticated under 50 rpm at 50°C for 1 min. In this study, two different vulcanization systems were used for the sample preparation. The first was that the masticated PIR was mixed with dicumyl peroxide (DCP) at 50°C for 4 min. The second was that the masticated PIR was mixed with zinc oxide and stearic acid at 50°C for 2 min. Then the master batch was mixed with sulfur and accelerator of *N*-cyclohexyl-2-benzothiazyl-sulfenamide (CZ) under 50 rpm at 50°C for 3 min. The composition for them is listed in Table I.

Both compounds were vulcanized at 160°C for 30 min under a pressure of 400 kg/cm².

Measurements

Measurements of stress–strain curves were carried out on a tensile tester (IM-20ST, Intesco, Japan) at room temperature (24°C). The stretching speed was 10 mm/min which corresponded to the initial strain rate of 1.0 min⁻¹. Tensile properties of the samples are shown in Table II.

The cross-link density (v_e) of the samples were determined by the Flory-Rehner relationship¹⁰

$$v_e = -[\ln(1 - V_{2m}) + \chi V_{2m}^2 + V_{2m}]/V_1 V_{2m}^{1/3}$$

TABLE II
Properties of the Samples

Sample	T_g (°C)	v_e (mol/cm ³)	IM (MPa)	E_B (%)	TS (MPa)
PS	-59.2	1.46×10^{-4}	1.4	717	10.7
PD	-59.9	1.56×10^{-4}	1.6	457	5.5

T_g , glass transition temperature; v_e , cross-link density; IM, initial modulus; E_B , elongation at break; TS, tensile strength.

where V_{2m} is the volume fraction of polymer at equilibrium degree of swelling, V_1 is the molar volume of solvent, χ is the interaction parameter between the polymer and the swelling agent. In this study, swelling tests were carried out by toluene at room temperature by soaking the samples in toluene for 2 days. Thus, $V_1 = 106.5$ (cm³/mol) and $\chi = 0.39$ ¹¹ were used for the calculation. The results obtained are listed in Table II.

Glass transition temperature (T_g) of the samples was evaluated from DSC thermograms by the conventional method by using a Seiko Instrument differential scanning calorimeter (Model SSC-5200, DSC). The results are shown in Table II.

The home-built stretching machine was combined with ESR spectrometer (ES-FA200 X-band, JEOL, Japan). Figure 1 shows a stretching machine installed in the ESR cavity schematically. The size of unstretched sample in the cavity was 40 mm (L) \times 5 mm (W) \times 1 mm (T). The L of 40 mm was large enough to minimize the effect of sample position in the cavity on the signal intensity. The sample volume changed with stretch ratio which influenced on the signal intensity. Thus, the signal intensity was corrected by the volume changes assuming that the poisson ratio of the samples was 0.5. The temperature in the cavity was about -20°C which was controlled by a cooled nitrogen gas flow. The utilization of nitrogen gas was important to minimize the effects of oxygen gas in the air on the ESR spectrum. Also, the temperature was well above the glass transition temperature of the samples where the mobility of radicals was high enough to induce the radical reactions. With increasing the measurement temperature, the life time of the radicals and signal to noise ratio of ESR absorption curve decreased, which made it difficult to carry out a quantitative analysis of ESR curve. Thus, the measurement temperature was chosen to be -20°C.

ESR measurements were carried out under the tensile deformation of the vulcanized samples. The

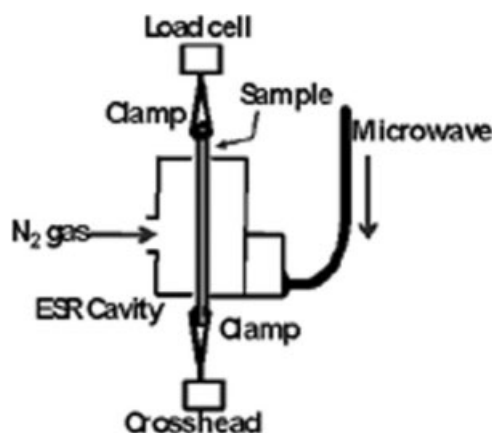


Figure 1 Schematic representation of ESR cavity with stretching machine.

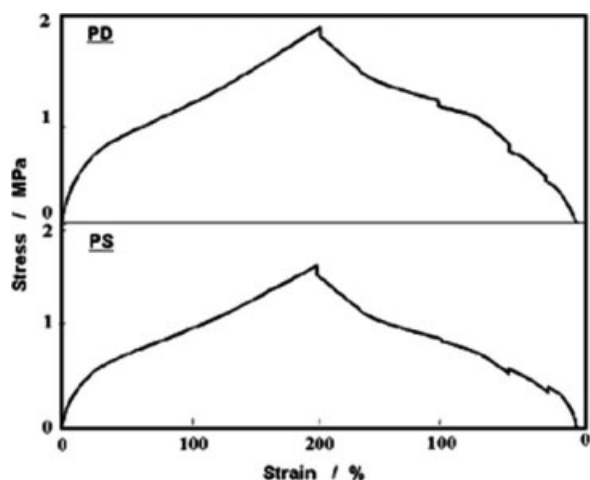


Figure 2 Relation between stress and strain for vulcanizates at room temperature.

samples were stretched under a constant stretching speed of 10 mm/min up to a desired strain and then held at constant strain while ESR measurements were taken. The ESR signals were accumulated to increase the signal to noise ratio (S/N). In this study, two times accumulation was enough to get an ESR absorption curve with high S/N. The strain was increased up to 200% which was the maximum strain due to an instrumental limitation.

The g value and the radical concentration of the samples were determined by the following procedure. First of all, ESR measurement was carried out for the sample at room temperature to determine the magnetic field at the center of resonance line. Then the measurement was done for the external standard involving Mn^{2+} . The Mn^{2+} showed six resonance lines. Among them, the third and fourth resonance lines of which g value were 2.034 and 1.981 were used to determine the g value of the sample. The g values of Mn^{2+} were put into the data processor equipped with ESR spectrometer. The resonance frequency determined by the frequency counter equipped with the spectrometer was also fed into the data processor automatically. Then data processor calculated the g value of the sample. The value of magnetic field at the center of resonance line was almost the same for all samples. In addition, the value was almost constant between room temperature and $-20^{\circ}C$. From these results, the g value for all samples was determined to be 2.004.

A double integration of the first derivative curve of ESR signal at room temperature from benzene solution of 4-hydroxy-2,2,6,6-tetramethyl piperidinoxyl radical (TEMPOL) with a known radical concentration was used as a standard to calculate the radical concentrations of the samples at $-20^{\circ}C$, because the signal intensity from TEMPOL at $-20^{\circ}C$ was too weak to use the quantitative analysis.

RESULTS AND DISCUSSION

Stress-strain behavior

Figure 2 shows stress-strain curves at room temperature for both PS and PD. First of all, both samples were stretched up to 200% with the stretching speed of 10 mm/min. After keeping the strain of 200% for 10 min, the strain of the samples was decreased to 0% with -10 mm/min. During the retraction, the samples were held at a given strain (100 or 50 or 25%) for 10 min.

It is seen that both samples showed a similar stress-strain curve at the stretching process. This is reasonable because both samples had similar cross-link densities as shown in Table II. However, the curves for the retraction process were quite different between the two samples. At a strain of 100%, the stress for both samples decreased with increasing holding time due to the well-known stress relaxation. The PD showed a similar stress relaxation even at a low strain (50 and 25%). On the other hand, the PS exhibited a strange behavior, at a given low strain (50 and 25%), the stress increased with time. The changes of stress at a given strain of 25% are plotted against the holding time in Figure 3. The results again clearly demonstrate that the stress for the PD decreased with increasing the holding time up to 10 min, followed by a saturation. On the other hand, the PS showed an increase of the stress up to around 15 min, followed by a saturation. The changes of stress with time at a given strain suggest the changes of network structure in the vulcanizates.

It is known that the tensile stress at the second stretching of filled vulcanizates is always lower than that for the first stretching.^{12,13} This phenomenon is

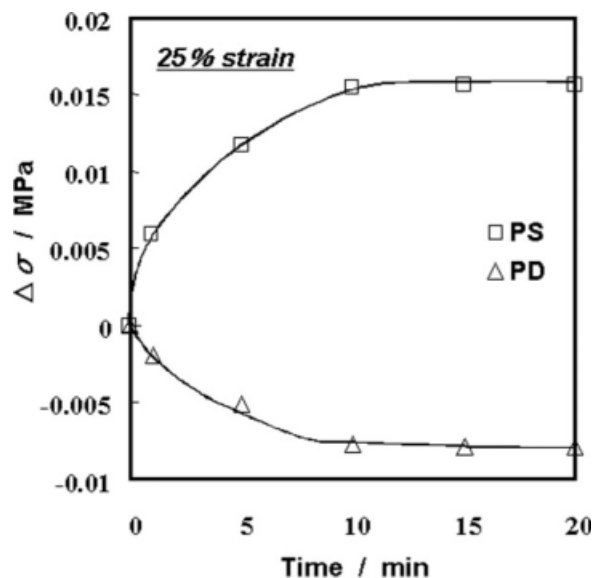


Figure 3 Changes of stress at a given strain of 25% as a function of time at room temperature for vulcanizates.

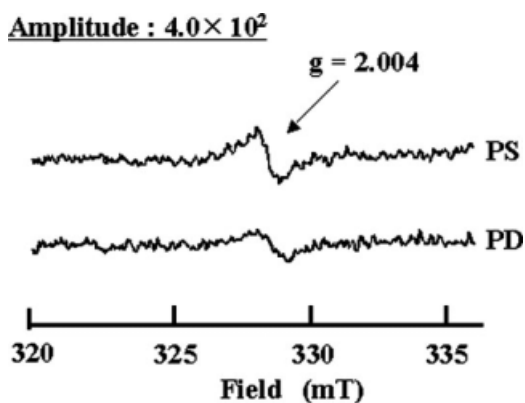


Figure 4 ESR spectra for vulcanized samples with 200% strain.

called Mullins effect, and well recognized to be caused by the following mechanisms;

1. Physical disentanglement of rubber molecules^{14,15}
2. Decrease in the interactions between rubber molecules and fillers^{16,17}
3. Chain scission of rubber molecules¹⁴

Among the three, the chain scission has a possibility to induce radical reactions during cyclic deformation, which might influence on the changes of the network structure. Thus, ESR measurements were carried out under the deformed state.

ESR results under the tensile deformation

ESR data under the deformed states of PS and PD exactly gave us useful information on the behavior of radicals produced by the stretching of the samples.

Figure 4 shows the first derivative ESR curves at -20°C for both PS and PD with the 200% strain. Both samples showed broad absorption curves with the g value of 2.004 and the ΔH msl of 1.55 mT. The spectra are responsible for the breakdowns of C—C linkages for the PD and breakdowns of C—C and sulfur linkages for the PS.^{5–9} It is evident that the signal intensity for the PS is much larger than that for PD. The radical concentration was calculated by using both spectra. The values were 3.8×10^9 and 0.9×10^9 mol/cm³, respectively for the PS and PD. As shown in Figure 2, the stress at 200% strain was slightly smaller for the PS than for the PD. Nevertheless, the radical concentration was higher for the PS than for the PD. The binding energy for carbon-sulfur (C—S—C) and sulfur-sulfur (C—S—S—C) linkages has been estimated to be smaller than that for carbon-carbon (C—C) linkage.¹⁸ Thus, it is reasonable to speculate that during the stretching, the C—S—S—C and/or C—S—C linkages are broken first followed by the breakdown of C—C linkage in the

samples. The PS involves sulfur linkage but the PD does not. Thus, the value of radical concentration for the PS was responsible for both carbon and sulfur radicals. On the other hand, only carbon radicals appeared in the PD, resulted in the difference of radical concentration between the two samples. During the retraction, especially for 200 to 100%, the changes of radical concentration with deformation ratio were minor. However, the changes became remarkable at a small strain below 50% especially for the PS (data not shown). The retention of spin number at 25% strain for the PS and PD is plotted against holding time in Figure 5. The retention for the PD was very high even after 20 min. On the other hand, the PS showed a large decrease of retention with holding time, which suggested an occurrence of radical reaction in the PS. As stated, sulfur radicals, in addition to the carbon radicals were produced during the stretching process of PS. The carbon radicals are actually polyenyl radicals with long allyl chains.^{5,6} Thus, the mobility of polyenyl radicals in rubber matrix might be slow compared with that of small molecules of sulfur radicals. With the recovery of tensile deformation, the mobility of radical species might increase, which enhances the radical reaction especially for sulfur radicals. The radical reaction is an exothermic. Thus, sample temperature was increased by the reaction heats.

It is well known that the elastic modulus increases with increasing temperature. Thus, it is reasonable to speculate that at a constant strain, the increase of stress appeared in the PS (Figs. 2 and 3) was induced by the increase of elastic modulus due to the increase of sample temperature. On the other hand, for the PD, the stress relaxation rather than the increase of elastic

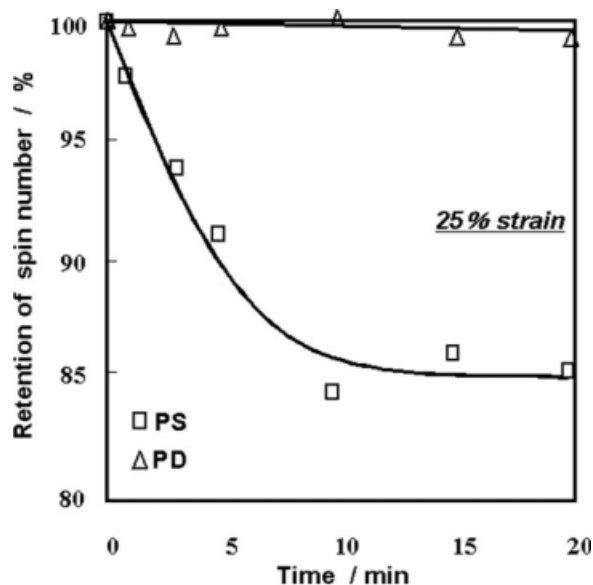


Figure 5 Retention of spin number as a function of time for vulcanizates.

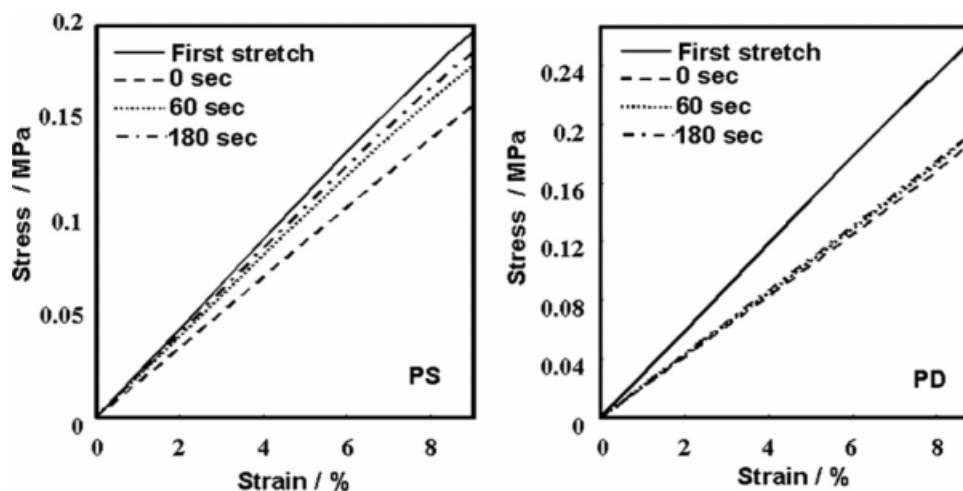


Figure 6 Stress-strain curves at room temperature for the prestretched samples with different holding times.

modulus was observed. In this study, it was difficult to determine the increase of elastic modulus with time at 25% strain directly. Instead, the elastic modulus was determined by using stress-strain curves which were measured at room temperature for the samples with one cyclic deformation. That is, the sample was stretched up to 200% with the speed of 10 mm/min first stretch, then the stretched samples were retracted to 0% strain with the speed of -10 mm/min (prestretched). The second stretch was carried out for the prestretched samples which were kept under a free of stress for a given time. The results are shown in Figure 6.

It is seen that for the PS, the initial slope of stress-strain curve increased with increasing the holding time. This means that elastic modulus of PS increased with increasing holding time. On the other hand, the change of slope with time was minor for the PD. These results suggest that the broken network structure was partly reconstructed in the PS, on the other hand, the reconstruction was minor in the PD, and support our consideration that the increase of stress at a given strain shown in Figure 3 was related to the increase of elastic modulus of the vulcanizates.

CONCLUSIONS

1. ESR measurements under the tensile deformation were successfully carried out for the cross-linked polyisoprene with different cross-linking styles.
2. At the first stretching process, the radical concentration was higher for the sample which was cross-linked by sulfur than for cross-linked by DCP, although both samples had a similar

value of cross-link density. The difference was attributed to the difference in the sort of radicals produced by the stretching.

3. The broken cross-linking structure formed by sulfur in the PS was partly reconstructed during and after the retraction. On the other hand, such behavior was minor in the sample cross-linked by DCP. These were well explained by the changes of radical concentrations during tensile deformation.

References

1. DeVries, K. L.; Rolyance, D. K.; Williams, M. L. *J Polym Sci Part A-2* 1972, 10, 599.
2. Natarajan, R.; Reed, P. E. *J Polym Sci Part A-2: Polym Phys* 1972, 10, 585.
3. Mead, W. T.; Reed, P. E. *Polym Eng Sci* 1974, 14, 22.
4. Mead, W. T.; Porter, R. S.; Reed, P. E. *Macromolecules* 1978, 11, 56.
5. Carstensen, P. *Makromol Chem* 1970, 135, 219.
6. Carstensen, P. *Makromol Chem* 1971, 142, 131.
7. Suzuki, N.; Ito, M. *e-J Soft Mater* 2005, 1, 1.
8. Suzuki, N.; Ito, M.; Yatsuyanagi, F. *Polymer* 2005, 46, 193.
9. Ito, M.; Isago, H.; Suzuki, N. *J Appl Polym Sci* 2008, 108, 1385.
10. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: N. Y., 1953; p 576.
11. Barton, A. F. M. *CRC Handbook of Polymer-Liquid Interaction Parameter and Solubility Parameters*; CRC Press: Boca Raton, Florida, 1990; p 242.
12. Bueche, F. *Reinforcement of Elastomers*; Krau, G., Ed.; Interscience: New York, 1965; Chapter 1.
13. Mullins, L. *Rubber Chem Technol* 1948, 21, 281.
14. Harwood, J. A. C.; Mullins, L.; Payne, A. R. *Rubber Chem Technol* 1966, 39, 814.
15. Roland, C. M. *J Rheol* 1989, 33, 559.
16. Bueche, F. *J Appl Polym Sci* 1960, 4, 107.
17. Kilia, H. G.; Strauss, M.; Hamm, W. *Rubber Chem Technol* 1994, 67, 1.
18. Kruger, F. W. H.; McGill, W. J. *J Appl Polym Sci* 1992, 45, 1545.