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Rubber

Unusual Stress-Strain Properties of Natural Rubber Vulcanizates with High Primary Molecular Weight

K. Ono (1), A. Kato, and K. Murakami

Chemical Research Institute of Non-Aqueous Solutions,
Tohoku University, Katahira, Sendai 980, Japan

Summary

Natural rubber vulcanizates with high primary molecular weight were prepared by mixing raw rubber and dicumyl peroxide in benzene followed by freeze-drying. The stress-strain properties of these vulcanizates were quite different from those prepared by conventional mastication method. The important characteristics of these vulcanizates is high tensile modulus, high tensile strength, large hysteresis loss, and higher degree of strain-induced crystallization. The difference in the stress-strain behavior between these rubbers and conventional vulcanizates are discussed from the standpoint of the network structure.

Introduction

According to the classical theory of rubber elasticity, the tensile stress of uniaxial elongation σ for a tetrafunctional network is represented by,

$$\sigma = \nu RT(\lambda - 1/\lambda^2)(1 - Mc/M) \qquad [1]$$

where, σ is the nominal tensile stress of the rubber, λ is the extension ratio, ν is the twice of the number of closs-links, R is the gas constant, T is the absolute temperature, Mc is the number average molecular weight of network chains, and M is the number average molecular weight of primary macromolecules, respectively. The last term (1 - Mc/M) was introduced by Flory (2) to correct the effect of dangling chains which is attached to the network gel at only one end. Equation [1] predicts the linear relationship between the modulus and reciprocal M, which was actually observed for loosely cross-linked butyl rubbers (2). The validity of equation [1] in the range of high primary molecular weight M, however, has not been fully examined, since the usual mastication process of rubbers reduces the molecular weight to less than $3X10^5$.

This paper describes the structure and stress-strain properties of natural rubber vulcanizates which have very high primary molecular weight. Samples were prepared by solution mixing followed by freeze-drying prior to vulcanization.

Experimental

Natural rubber (Smoked Sheet) was dissolved in benzene and the gel fraction was filtered off. The curing agent, 1.5 phr dicumyl peroxide (DCP), was then introduced in the filtrate and thoroughly dissolved. The mixture was freeze-dried and cured at 145°C for 20 minutes. The viscosity average molecular weight of this sample prior to curing was determined to be 1.33X10^6 by the use of following viscosity equation (3).

$$[\eta] = 5.02 \mathrm{X} 10^{-4} M_v^{0.667} \quad (\mathrm{ml/g}) \quad (\text{in toluene}) \qquad [2]$$

The vulcanizate was designated as D-133.

A conventional natural rubber vulcanizate was prepared by compounding raw rubber and 1.5 phr DCP with a laboratory mill, and then cured under the same condition as that of D-133. The viscosity average molecular weight of this sample prior to curing was 3.1X10^5 and it was designated as D-31.

In order to check the effect of mixing method, a part of the D-31 compound was dissolved in benzene, freeze-dried, and vulcanized under the same condition. This sample was designated as D-31F.

All the samples were extracted with an acetone-chloroform-methanol azeotropic mixture and then dried under vacuum. The network chain density of these samples were estimated from the equilibrium degree of swelling in benzene with the use of familiar Flory-Rehner equation (4). Determined values for D-133 and D-31 were 0.103 and 0.096 mol/dm^3 . Thus Mc of these vulcanizates are calculated to be ca. 8900 and 9500, respectively. The network chain density for the D-31F was essentially the same as that of the D-31.

Stress-strain measurements were carried out with the aid of an Instron type tensile tester (Shimadzu Autograph DCS-100). The rate of extension was fixed to 10 mm/min. Infrared dichroism of stretched samples was measured on a Fourier-transform infrared (FT-IR) spectrometer (JEOL JIR-100) equipped with a polarizer. X-ray diffraction (XRD) studies of stretched samples was carried out on a Shimadzu VD-1 diffractometer with Ni-filtered CuK$_\alpha$ radiation.

Results and Discussion

Typical stress-strain curves for the D-133 and the D-31 vulcanizates are shown in Fig. 1. The tensile modulus and tensile strength of the D-133 were surprisingly higher than those of the D-31. The stress at 200% elongation and the tensile strength of the D-133 were about 1.4 and 1.5 times greater than conventional vulcanizates. According to equation [1], the difference in tensile moduli between the D-133 and the D-31 should be less than 5%, provided that the network chain densities of these rubbers are the same. Moreover, considering that the molecular weight of these vulcanizates employed for the above estimation is the viscosity average one, the difference should be further reduced. Therefore, the observed large difference in tensile modulus cannot accounted for the effect of the chain end.

In order to examine the effect of the

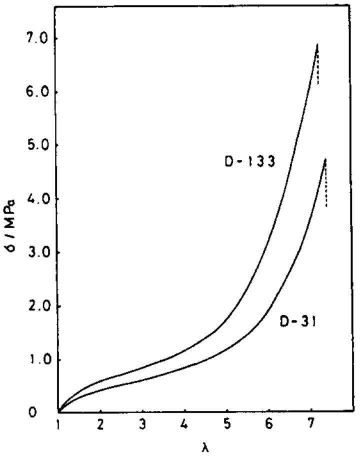

Fig. 1. Stress-strain curves for the D-133 and the D-31 vulcanizates.

compounding method, the stress-strain properties of D-31F vulcanizate which was prepared by freeze-drying was compared with those of D-31. It was found that the stress-strain behavior of both rubbers essentially agreed each other. Hence, the unusual high tensile modulus of the D-133 vulcanizate which has a high primary molecular weight is not due to the mixing by freeze-drying, but to a certain fundamental difference in the network structure between this rubber and the conventional vulcanizate obtained by mastication. It is also noted in Fig. 1 that although the elongation at break for the D-133 was slightly reduced than that of the D-31, the fracture energy for the D-133 was also very large. It should be emphasized that these unusual properties of the high primary molecular weight vulcanizate was also observed in the case of sulfur cured natural rubbers (5).

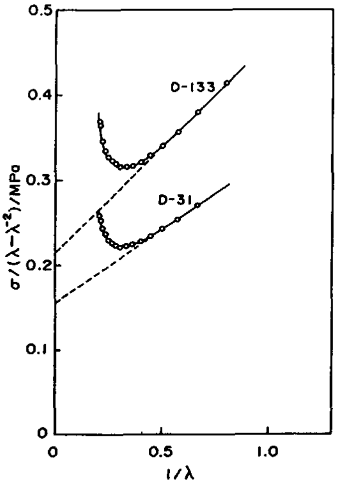

Fig. 2. Mooney-Rivlin plots for the D-133 and the D-31 vulcanizates.

As has been well known, the stress-strain curves of rubber vulcanizates are well represented by the semiempirical Mooney-Rivlin equation (6).

$$\sigma = (\lambda - 1/\lambda^2)(2C_1 + 2C_2) \qquad [3]$$

where, $2C_1$ and $2C_2$ are constants characterizing the network structure. Fig. 2 shows the Mooney-Rivlin plots for the D-133 and the D-31 vulcanizates. It can be seen from the figure, both $2C_1$ and $2C_2$ were greater for the D-133. Although there have been serious controversies with respect to the molecular origin of these constants in recent years (7.8), the greater values of $2C_2$ and $2C_1+2C_2$ for the D-133 are no doubt ascribed to the greater contribution of entanglement effect of this rubber. Since both D-133 and D-31 were prepared under the same condition, there is no reason that the probability of entanglement coupling becomes different in these rubbers, so long as the network structure is homogeneous. It can be therefore presumed that some network heterogeneity is present in the D-31 vulcanizates resulting in the reduction of the formation of entanglements.

Fig. 3 shows the first hysteresis cycles of the D-133 and the D-31 vulcanizates. An extremely large hysteresis loss was observed for the D-133. One of the probable cause of the large hysteresis loss is the strain-induced crystallization. As shown in Mooney-Rivlin plots

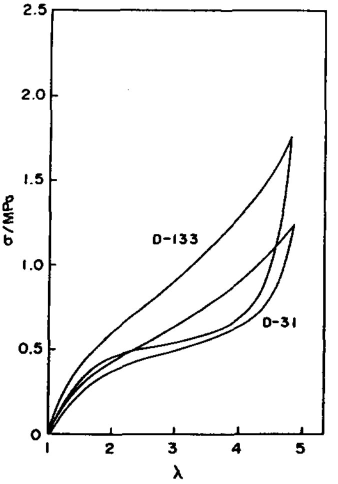

Fig. 3. First stress-strain cycles for the D-133 and the D-31 vulcanizates.

(fig. 2), the extension ratio where the upturn is evident is lower for the D-133 than for the D-31, indicating that the crystallization occurs at lower elongation in the case of D-133 vulcanizate. The crystallization of the stretched D-133 was apparent even by the visual observations, since the sample becomes opaque above 300% elongation.

In order to examine the contribution of the strain-induced crystallization in further detail, FT-IR and XRD studies were carried out for both vulcanizates. Fig. 4 shows typical FT-IR spectra of stretched vulcanizates obtained with the light polarized parallel and perpendicular to the stretching direction. The 1126 cm^{-1} absorption band which was assigned to a C-CH$_3$ in-plane deformation vibration was able to be used to monitor the degree of crystallization (9). The dichroic ratio (DR) of this band was calculated using the 1090 cm^{-1} band as a reference one, and plotted in Fig. 5 against the stretch ratio. A significant enhancement of the dichroic effect was observed for the D-133 vulcanizate.

The higher degree of strain-induced crystallization for D-133 can be more directly checked by the X-ray diffraction studies. In Fig. 6, the equatorial XRD patterns are shown for stretched vulcanizates. For D-133, two diffraction peaks which are characteristic of (200) and (120) reflections were apparently observed even at 300% elongation, whereas D-31 vulcanizate showed only amorphous halo. At 350% elongation, where the crystallization of the D-31 sets in, XRD peaks for D-133 becomes already prominent. These results clearly shows that the degree of crystallization of high primary molecular weight D-133 vulcanizate is much larger than that obtained by mastication. This is probably the main cause of the large hysteresis loss observed for D-133 (Fig. 3).

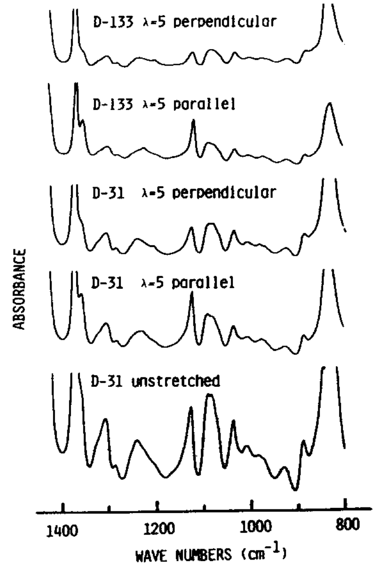

Fig. 4. FT-IR spectra for the stretched D-133 and D-31 vulcanizates.

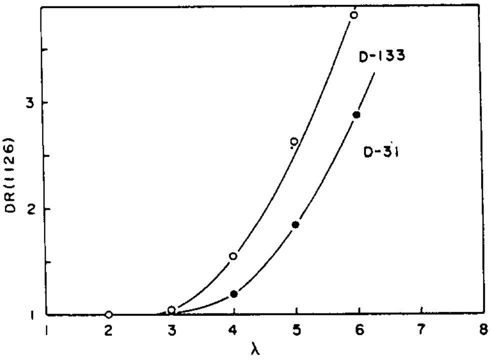

Fig. 5. Dichroic ratio (DR) at 1126 cm^{-1} plotted as a function of stretch ratio.

Crystallization would depend on the average orientation of network chains. Thus the more homogeneous the network structure, the greater the degree of crystallization becomes. Some kind of network inhomogeneity, for instance the inhomogeneity of the network chain density, would contribute to reduce the crystallinity of conventional D-31 vulcanizate.

Recently, we have observed a microblock structure with an average size of 200 Å for stretched D-31 samples in terms of the high resolution scanning electron microscopy (5). For D-133 vulcanizate, no such structures were observed up to as high as 600% elongation. This result also supports the idea that the origin of the difference between the stress-strain properties of the D-133 and the D-31 vulcanizates is due to the difference in the higher order network structure.

In conclusion, high modulus, high strength, and higher degree of strain-induced crystallization of high primary molecular weight vulcanizates may be ascribed to the homogeneous network structure of these rubbers.

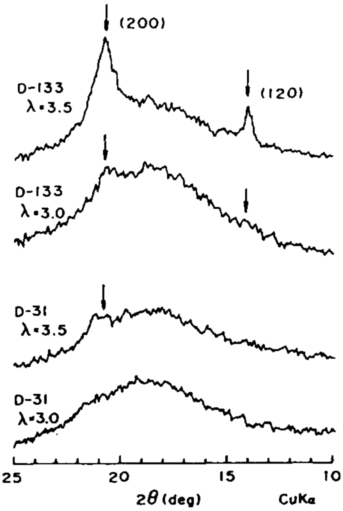

Fig. 6. Equatorial XRD patterns of the stretched D-133 and D-31 vulcanizates.

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