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Publisher *Taylor & Francis*

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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Fujiwara, Shizuo and Fujimoto, Kunihiko(1970) 'NMR Study of Vulcanized Rubber', Journal of Macromolecular Science, Part A, 4: 5, 1119 – 1124

To link to this Article: DOI: 10.1080/00222337008061006

URL: <http://dx.doi.org/10.1080/00222337008061006>

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NMR Study of Vulcanized Rubber

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SUMMARY

It is shown that NMR-linewidth measurements are useful to obtain information about the cross-linkage density and the average distance between the cross-links in vulcanized rubber. Inhomogeneous structure of the rubber phase in carbon-filled rubber is evidenced and the thickness of the rubber layer on carbon is evaluated at 50 Å.

INTRODUCTION

Line widths and spin-lattice relaxation times of magnetic resonance have been measured with respect to rubber, natural and vulcanized. Rubber can be classified into three groups from its NMR linewidth, as it has been shown by the pioneering work by Gutowsky [1]; the first one gives a very broad linewidth which refers to the rigid structure, the second a very narrow line of high resolution, and the third an intermediate linewidth which is responsible for the hindered molecule governed by inter- or intramolecular

forces. In this paper, it is investigated how the linewidths of the second kind or the third kind are affected by the changes in molecular motion in rubber which are produced by the vulcanization or filling by carbon.

EXPERIMENTAL

NMR spectrometer of the type of JEOLCO JNM-3H-60 was used at 60 MHz for the measurement of NMR. The pulse NMR was measured by the pulse spectrometer of NMR specialities, PS-60A.

The composition of the sample is as shown in Table 1.

Table 1. Standard Recipe

Material	Parts by weight
Natural rubber (RSS #3)	100
Pinetar	5
Stearic acid	3
Zinc oxide	5
Antioxidant*	1.5
Sconoc†	0.5
2-Mercaptobenzo thiazole	0.5
Sulfur	3

*Phenyl-naphthylamine.

†N-Nitrosodiphenylamine.

RESULTS AND DISCUSSION

At higher temperatures the rapid molecular motion gives linewidths which are very narrow and almost temperature independent. These narrow and temperature independent linewidths are characteristic with respect to the species of the sample, i.e., these linewidths are determined by a residual local magnetic field after the intra- and intermolecular thermal motions average out, and dependent on the density of cross-links

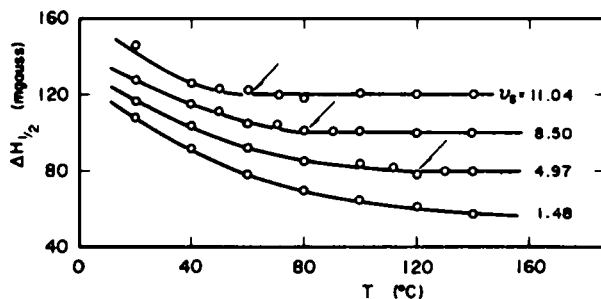


Fig. 1. Temperature dependence of the NMR half maximum linewidth; ν_s (density of cross-links) in 10^{-5} mole/g.

and also on the concentrations of carbon which is used as the filler for the rubber.

Figure 1 shows the temperature dependence of the linewidths of natural rubber vulcanizates with different densities of cross-links. Each curve can be divided into two parts, the temperature-dependent part at low temperature, and the temperature-independent part at high temperature. The temperature dependence of the curve may be interpreted in terms of the decrease in magnitude of the average local field which results from the increase of the free volume. The temperature-independent intrinsic linewidth which is observed at high temperature is responsible to the residual local magnetic field. This intrinsic linewidth will be denoted as H_{eq} hereafter. The results shown in Fig. 1 refers that the magnitude of H_{eq} is increased with the density of cross-links. Moreover, the temperature where the equilibrium linewidth is attained is lowered with temperature.

As we plot H_{eq} as the function of $1/\bar{R}^2$, reciprocal of the square of the distance between the nearest cross-links, a linear relation is obtained as shown in Fig. 2. The \bar{R}^2 value is obtained, according to the treatment of Kuhn [2], from the data of molecular lowering of the freezing point of benzene in the swollen rubber, and directly related to an average size of the molecular space of the rubber molecule.

Detailed discussion of the results shown above will not be given here, being left as a future problem, and it will simply be pointed out that the linear relation of Fig. 2 can be used to estimate the average distance between the nearest cross-links from NMR linewidth. For example, the values of H_{eq} of 60 or 120 mG for a natural rubber corresponds to 10,000 or 150 Å as the average distance of the cross-links, respectively. A similar relation is obtained with respect to the filled rubber vulcanizates.

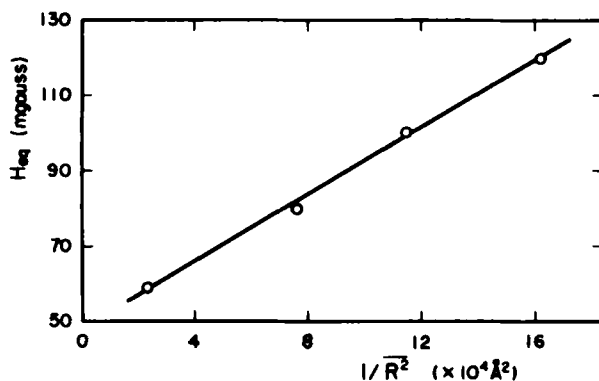


Fig. 2. Linewidth at equilibrium vs $1/\overline{R^2}$, the reciprocal of square average of the distance between nearest cross-links.

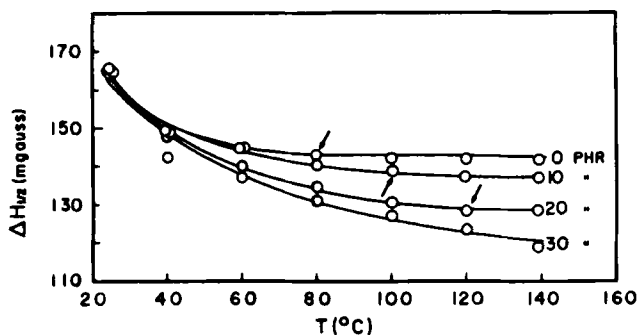


Fig. 3. Temperature dependence of the NMR half maximum linewidth.

Figure 3 shows the presence of the equilibrium linewidth in the latter sample, and the relation between the degrees of filling, namely, the volume fraction of carbon, ϕ , and the critical temperature where this equilibrium linewidth is achieved. As in the case of the natural rubber, we can find a linear relation between H_{eq} or T_{eq} and ϕ as shown in Fig. 3, where T_{eq} refers the temperature over which H_{eq} appears. Figure 3 shows that T_{eq} increases and H_{eq} decreases linearly with ϕ . With the results of the natural rubber in mind, we can conclude that the cross-link density is reduced with filling by carbon. The results which have so far been presented will suggest

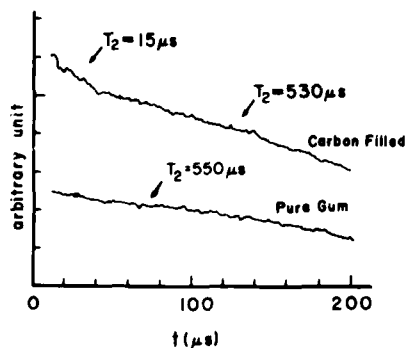


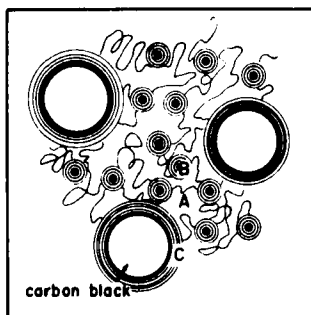
Fig. 4. Decay curves of the pulse NMR signal.

that the linewidth measurement of proton resonance is useful for the evaluation of cross-linkage in natural and vulcanized rubbers.

It will be shown next how the measurement of the relaxation times is useful for the investigation of the heterogeneous structure in carbon-filled gums. Figure 4 shows the decay curves of the pulsed NMR signal. It is observed that the vulcanized rubber shows a single T_2 , whereas the carbon-filled gum exhibits two values of T_2 . From these results we deduce the copresence of two different phases of molecules in the sample; one phase of linewidth of 70 or 150 mG and the other of about 5 G. As the slow sweep NMR spectrum is measured with this sample, the latter has shown a superposition of a narrow and a broad line.

The narrow line can be taken as referring to the liquid phase, and the broad one to the quasi-glassy state. A possible model that can be deduced from these experiments is as follows. The liquid phase refers to the rubber matrix, and the glassy phase to the rubber molecule attached to the carbon black particles. With this model (Fig. 5) in mind, the NMR spectrum of rubbers filled with carbon black has been compared to that filled with silica gel; the latter has been chosen as a filler which is not active (adhesive) to rubber. According to the results of experiment, the intensity of the narrow component is much reduced with the carbon black rubber whereas that of the silica gel rubber, if any, is very small. This finding is not attributed to the reduction of the narrow component as the result of the paramagnetic dipolar broadening effect of carbon because the amount of the observed reduction is linearly proportional to the volume fraction of the rubber phase and not to the surface of the carbon.

With the consideration of the intensities of proton signal and the actual



A: liquid state

B: cross-linked rubber molecules

C: quasi-glassy state

Fig. 5. Model of the inhomogeneous structure of the carbon-filled rubber.

composition of the sample and the size of carbon black particle, we could estimate the thickness of the layer which is attached to the latter as about 50 Å.

The results shown above could be taken as an example of the application of NMR for the nondestructive analysis of rubber.

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- [2] W. Kuhn, *Rubber Chem. Technol.*, **33**, 245 (1960).