

Dynamic Properties of PBNA-Natural Rubber Vulcanizates

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Synopsis

Some crystalline organic compounds containing a β -naphthyl group stiffen rubbers considerably. This paper discusses the dynamic behavior of these systems when subjected to oscillatory strain of increasing amplitude. Modulus-strain amplitude plots similar to that in carbon black-natural rubber systems are obtained. The implication of these results to reinforcement theory is discussed.

Introduction

Incorporation of some crystalline organic compounds containing a β -naphthyl group has been found to produce a pronounced stiffening of rubber vulcanizates under certain conditions. This has been reported by Linnig et al.,¹ who also noted that when the organic material is removed from the rubber by extraction, the stiffening effect vanishes. Stiffening by the most effective of the materials they examined, phenyl- β -naphthylamine, was obtained in vulcanizates made from various elastomers and having different vulcanizing agents and was essentially independent of the state of cure. In some instances about 5% PBNA produced the same initial stiffness as 30-40% carbon black, but the stiffness was markedly reduced by flexing. Less than 3% crystalline PBNA produced an isotropic Young's modulus of about 20 kg./cm.² at room temperature. At higher concentrations of PBNA, anisotropic effects were observed. The temperature coefficient of Young's modulus was negative,¹ analogous to that of vulcanizates containing carbon black.²⁻⁷ The addition of PBNA to a rubber vulcanizate did not affect significantly the glass transition temperature.¹

The apparent similarity between the effects of a few per cent of PBNA and 30-40% of carbon black was surprising, and it was thought that light would be thrown on the PBNA effect by dynamic measurements of the same type which has been found useful in the study of carbon black-elastomer systems, that is, by studying the change in dynamic modulus with the strain amplitude.

Experimental

PBNA was added to vulcanized specimens of a natural rubber tetramethylthiuram disulfide compound by the procedure described by Linnig et al.¹ Two test strips were bonded between a central metal plate, which applied the oscillating force, and restraining plates at either side.^{2,3} It was convenient to apply a chosen stress and to record the strain produced in the range of displacements between 0.1 to 100 μ ; for greater displacements measurements were made at selected strains. The frequency was 0.1 cps.^{2,3}

After setting up and resting overnight, the specimens were tested at increasing sinusoidal strain amplitudes. The maximum straining force, the strain amplitude, and the phase angle between the stress and strain were measured. From these results, the components of the in-phase modulus with the strain G' , the out-of-phase modulus G'' , and the loss tangent $\tan \delta = G''/G'$, were calculated; δ is the phase angle in degrees.^{2,3}

Dynamic Results

Figure 1 shows the dynamic shear modulus G' for five vulcanizates plotted against the total dynamic amplitude. It can be seen that the modulus-dynamic strain plots are typical of those found by the author for carbon black-elastomer systems. The phase angles were very low, about 1.5°, and the accuracy of measurement was not sufficient to trace any systematic change with the amplitude of oscillation.

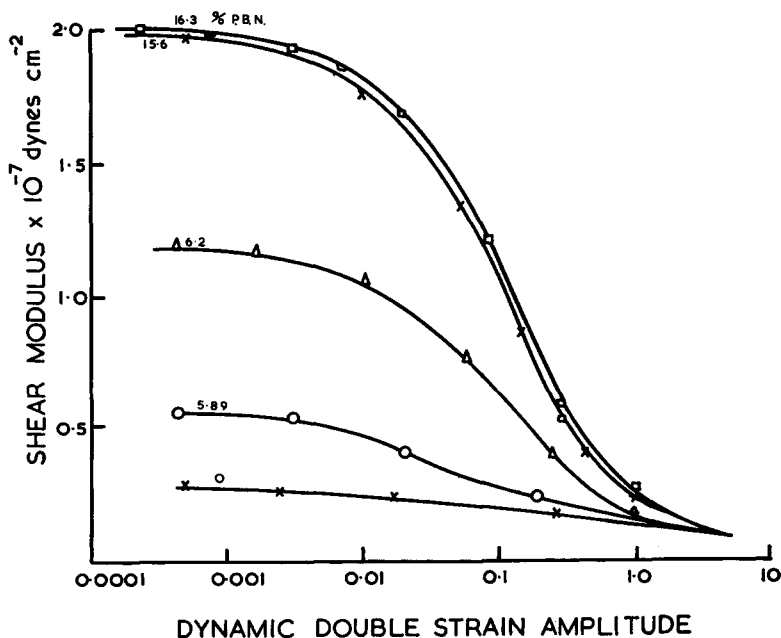


Fig. 1. Dynamic shear modulus G' vs. total dynamic amplitude.

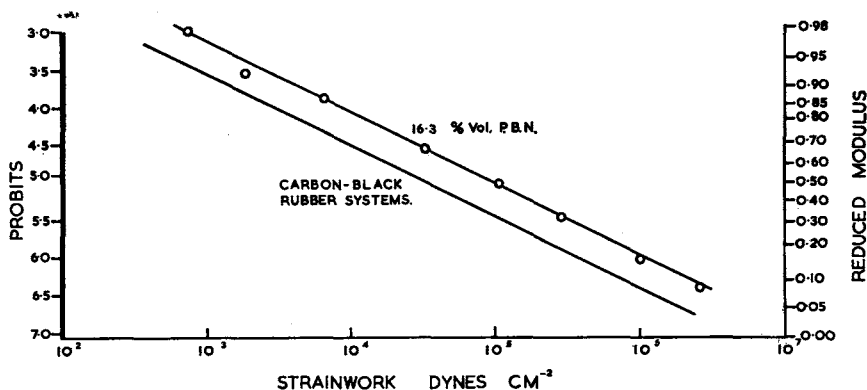


Fig. 2. Plots of reduced modulus vs. the energy of oscillation for a specimen containing 16.3% PBNA and a carbon black-rubber system.

Various empirical relationships have been suggested by different authors²⁻⁷ for the dependence of the dynamic modulus on the strain amplitude. It is proposed here, in line with previous studies²⁻⁷ on carbon black-elastic systems, to use a method of presentation which emphasizes the similarity between the modulus breakdown curves of PBNA and carbon black vulcanizates. The method involves normalizing the data obtained between very high and very low strains. Let G'_0 be the value of G' at strains approaching zero, and G'_∞ its value at very high strains, where there is not further change in G' with increase of strain. The reduced or normalized modulus is given by:

$$Z = (G' - G'_\infty) / (G'_0 - G'_\infty)$$

and is shown in Figure 2 plotted on probability paper against the energy of oscillation or strain work for a specimen containing 16.3% PBNA (by weight) with $G'_0 = 2 \times 10^7$ dyne/cm.² and G'_∞ is 1.0×10^6 dyne/cm.². It will be appreciated that there is some latitude in fixing a value for G'_∞ , but the variation is too small to influence the position of the plot on probability paper.

It has been shown in previous papers²⁻⁷ that neither stress nor strain are the independent parameters which govern the variation of the dynamic modulus with strain, but that the strainwork is the determining factor. Strainwork being defined as total stress amplitude times total strain amplitude.

The linearity of the plot of the normalized modulus against the logarithm of the strainwork implies a relationship of the type

$$\begin{aligned} Z &= (G' - G'_\infty) / (G'_0 - G'_\infty) \\ &= (1/\sigma\sqrt{2\pi}) \int_{-\infty}^x \exp \{ -(1/2\sigma^2)(x - \mu)^2 \} dx \end{aligned} \quad (1)$$

where

$$x = \ln X, \text{ where } X \text{ is the strainwork}$$

and

μ is the mean value of $\ln X$

Equation (1) suggests that the dynamic modulus Z at a strainwork X is the result of the breakdown of normally distributed breakdown mechanisms with the spread σ .

As described in statistical text books, the mean value of μ occurs at $Z = 0.5$ and is equal to 1×10^5 dyne-cm.². This value is higher than that for carbon black-elastomer systems which varies from 2.8 to 4.8×10^4 dyne/cm.² with an average value of about 3.57. A typical plot of a carbon black-elastomer system is shown in Figure 2.

The "width" in log units between $Z = 0.10$ and $Z = 0.90$ is about 2.57 and $\sigma^2 = 1.0$ for both the PBNA and the carbon black results; the distributions are therefore similar but the characteristic energy of the structure breakdown in the specimen containing 16.3 vol.-% PBNA is about two to three times larger than that for carbon black vulcanizates.

Discussion

Microscopic examination of the crystals of PBNA in the rubber vulcanizate shows a typical dendritic network, with the crystals radiating in a fernlike manner. The dynamic strain breaks down the crystal structure, but the nature of the breakdown resembles remarkably that of the continuous structure which is assumed to be formed by carbon black particles. The energy required to break the structure is higher than with carbon black filler.

The implication of this work to reinforcement theory is that as the results obtained with PBNA and carbon black systems are similar, it confirms the hypothesis suggested in earlier papers²⁻⁷ that the carbon black forms rigid, three-dimensional structures in the rubber and therefore behaves similarly to a rigid crystalline network.

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Résumé

Certains composés organiques cristallins contenant un groupe β -naphthyl-lique durcissent considérablement les caoutchoucs. Cet article discute le comportement dynamique de ces systèmes lorsqu'ils sont soumis à une tension oscillatoire d'amplitude croissante. Les diagrammes module-amplitude tension sont semblables à ceux obtenus pour le noir de carbone et le caoutchouc naturel. La conséquence de ces résultats en ce qui concerne la théorie de renforcement est soumise à discussion.

Zusammenfassung

Durch gewisse kristalline organische Verbindungen mit einer β -Naphthylgruppe werden Kautschuke beträchtlich versteift. In der vorliegenden Mitteilung wird das dynamische Verhalten dieser Systeme bei Schwingungsbeanspruchung mit steigender Amplitude diskutiert. Es werden Modul-Verformungsamplitude-Diagramme ähnlich denjenigen bei Russ-Naturkautschuksystemen erhalten. Die Bedeutung der Ergebnisse für die Theorie der Verstärkung wird diskutiert.

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