

Elastic and Viscoelastic Behavior of Ethylene-Propylene Copolymers

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Synopsis

The viscoelastic behavior of an ethylene-propylene copolymer is analyzed. Two different vulcanization procedures were followed; in the first a binary mixture of initiator-polymer was used, while in the second the polymer was diluted by a solvent. The networks thus obtained show a different viscoelastic behavior depending on the different vulcanization procedure used. Results, analyzed in terms of supramolecular organization being present in the amorphous material, give some important information about the molecular nature of the C_2 coefficient of the Mooney-Rivlin equation, and therefore about the well-known deviations from the Gaussian theory shown by all rubber-like networks.

INTRODUCTION

It is well known that in monodirectional extension, the isothermal stress-strain behavior of rubber-like materials follows, at moderate deformations, the Mooney-Rivlin phenomenologic equation¹

$$\tau = 2C_1(\alpha - \alpha^{-2}) + 2C_2(\alpha - \alpha^{-2}) \frac{1}{\alpha} \quad (1)$$

where τ is the stress on the unit of undeformed cross-sectional area, α is the strain ratio defined as L/L_0 , where L and L_0 are the deformed and undeformed sample length, and C_1 and C_2 are two coefficients without any apparent molecular significance. The experimental behavior, however, well described by eq. (1), is at variance with the Gaussian theory of rubber elasticity that, on the other hand, gives for the stress the following expression^{1,2}:

$$\tau = nkT \frac{\langle r_i^2 \rangle}{\langle r_0^2 \rangle} (\alpha - \alpha^{-2}) \quad (2)$$

where n is the number of elastic effective chains in the volume unit, k is the Boltzmann constant, T is the absolute temperature, and $\langle r_i^2 \rangle$ and $\langle r_0^2 \rangle$ are the mean-square end-to-end distances for a network chain and a free chain, respectively. Writing

$$G = nkT \frac{\langle r_i^2 \rangle}{\langle r_0^2 \rangle}$$

we have

$$\tau = G (\alpha - \alpha^{-2}) \quad (2a)$$

where G is the Gaussian theoretical modulus.

While in eq. (2a), stress and strain are related by a structural and molecular parameter, very little is known about the molecular significance of the C_1 and C_2 terms of eq. (1). However, the data of Mullins,³ supported by recent experimental results,^{4,5,6} clearly indicate that for highly swollen systems $2C_1$ can be identified with the Gaussian modulus G . For the C_2 term, on the other hand, at present it is possible only to suggest some hypothesis.

Recently, great attention has been given to the possibility that the observed deviations from eq. (2) could be correlated to some kind of supra-molecular organization in the amorphous material. This hypothesis, first given by Kargin,⁷ has been more recently reported by Prins and others,^{8,9} who suggest the presence of chain "bundles" in the elastomeric networks. This interesting hypothesis is supported also by our recent results.^{5,6,10}

Moreover, some interesting information can be obtained from the stress-strain behavior observed on natural rubber and *cis*-polybutadiene vulcanized in the swollen state.^{6,11,12} These kinds of networks follow very closely the relation of eq. (2). The ideality of behavior is of course correlated with the particular topology of the preswollen networks. The first topologic feature has to do with the number of permanent entanglements,^{11,12,6} and the second, with the degree of supramolecular organization.⁶ In the present paper, the elastic and viscoelastic behavior of two samples of ethylene-propylene copolymer has been analyzed. The two samples differ in the vulcanization procedure, which was carried out in the presence and absence of a solvent. The experimental data explained in terms of supra-molecular organizations indicate that the organization phenomena play an important role in the elastic behavior.

EXPERIMENTAL

Material

The ethylene-propylene copolymer studied in the present paper was prepared using the catalytic system $VCl_4-Al(C_2H_5)_2Cl$ at $-78^\circ C$ as reported in the literature.¹⁵

This catalytic system, under our conditions, gives rise to a product with a reactivity ratio $r_1 r_2 \simeq 0.26$. Sample composition (molar amount of ethylene 60%) and distribution index were determined by infrared spectroscopy, following an analytical method as reported in the literature.^{16,17}

The catalytic system used, the high ethylenic content, the infrared data [$(CH_2)_2 = 4.4\%$ weight; $(CH_2)_3 = 18.6\%$; $(CH_2)_{\geq 5} = 30.9\%$] indicate the presence in the chain of long sequences of ethylenic units with a block-like distribution.

Vulcanization Procedure

A vulcanizate (A) sample was prepared following a method previously described,¹³ using 5 phr of a mixture of dicumyl peroxide and CaCO₃, with a 40% peroxide content. The vulcanization was carried out at 160°C for 30 min. A second vulcanizate (B) was prepared using a mixture of the following composition: polymer, 40%; chlorobenzene, 60%; dicumyl peroxide, 6% of polymer weight. The mixture was vulcanized in the manner previously described¹¹ at 140°C for 120 min. The solvent was removed under vacuum at 50°C. The weight of the dry sample did not give evidence of solvent grafting.

Stress-Strain Measurements

The stress-strain measurements were carried out using a Tensilon tensile tester of the Toyo Measuring Instruments Co. Ltd. The strain rate was 2 mm/min. The data were obtained at room temperature ($\approx 20^\circ\text{C}$).

RESULTS

Figure 1 shows the hysteresis cycles obtained with an unswollen sample of vulcanizate A. The sample is indicated as A₁. Three cycles were carried out using a gradually increasing strain ratio of 2, 2.5, and 3, respectively.

Figure 2 shows the same kind of measurements obtained with a swollen sample of vulcanizate A. The swelling degree was $V_s = 0.549$, where V_s is the polymer fraction in the swollen sample. The solvent used was *n*-hexadecane. The sample is indicated as A₂.

The hysteresis cycles carried out with vulcanizate B are shown in Figure 3. The strain rate and the maximum strain ratio were the same in Figures 1 and 2.

From the data of Figures 1, 2, and 3 it is possible to calculate the amount of free energy that is dissipated in every hysteresis cycle. In fact, the area contained in the increasing and decreasing stress-strain curve is a direct measurement of the dissipation energy. Such data are reported in Figure 4.

The data of Figures 1, 2, 3, and 4 clearly indicate that the swelling of sample A and the preswelling treatment of sample B strongly decrease the hysteresis phenomenon. Table I shows the two Mooney-Rivlin constants

TABLE I
Mooney-Rivlin Constants

Sample	$2C_1$, kg/cm ²	$2C_2$, kg/cm ²	C_2/C_1
A ₁	0.80	5.40	6.75
A ₂	0.90	1.65	1.83
B	1.05	1.95	1.86

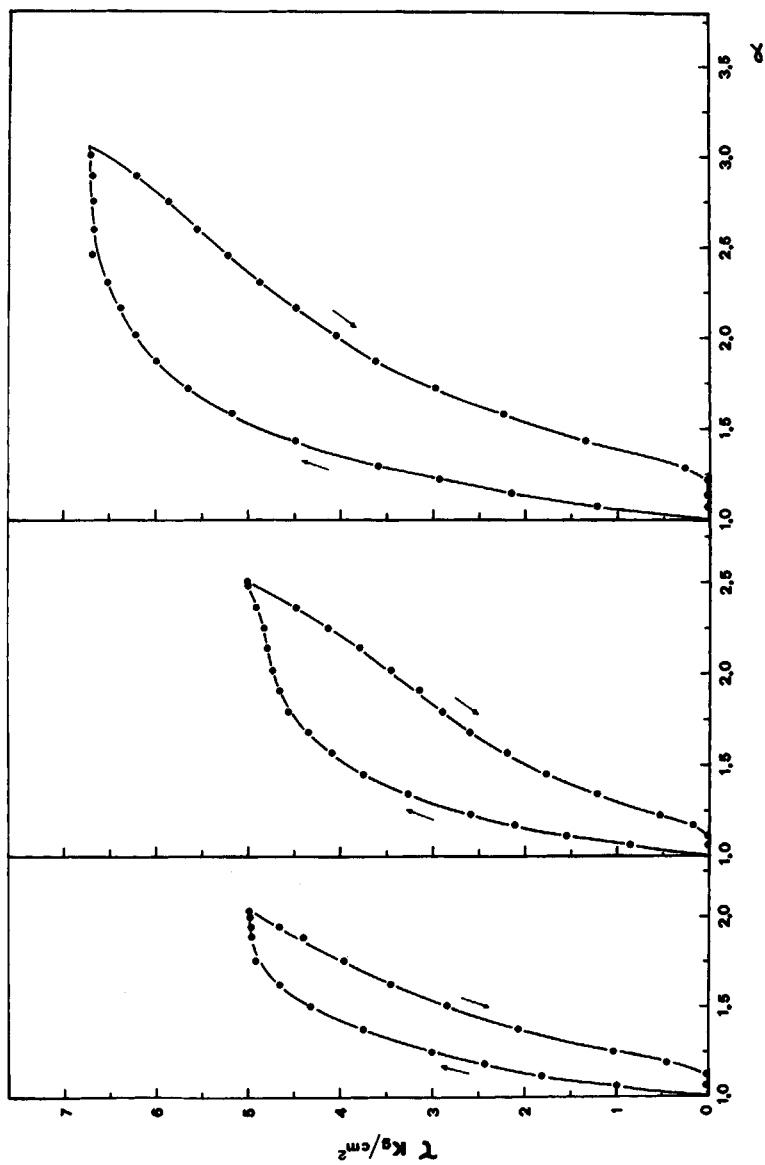


Fig. 1. Hysteresis cycles obtained on vulcanizate A. The maximum strain was gradually increased, and the values were $\alpha = 2, 2.5, \text{ and } 3$. Strain rate was 2 mm/min; sample length, 2 cm; temperature $\approx 20^\circ\text{C}$. The sample is indicated as A_1 .

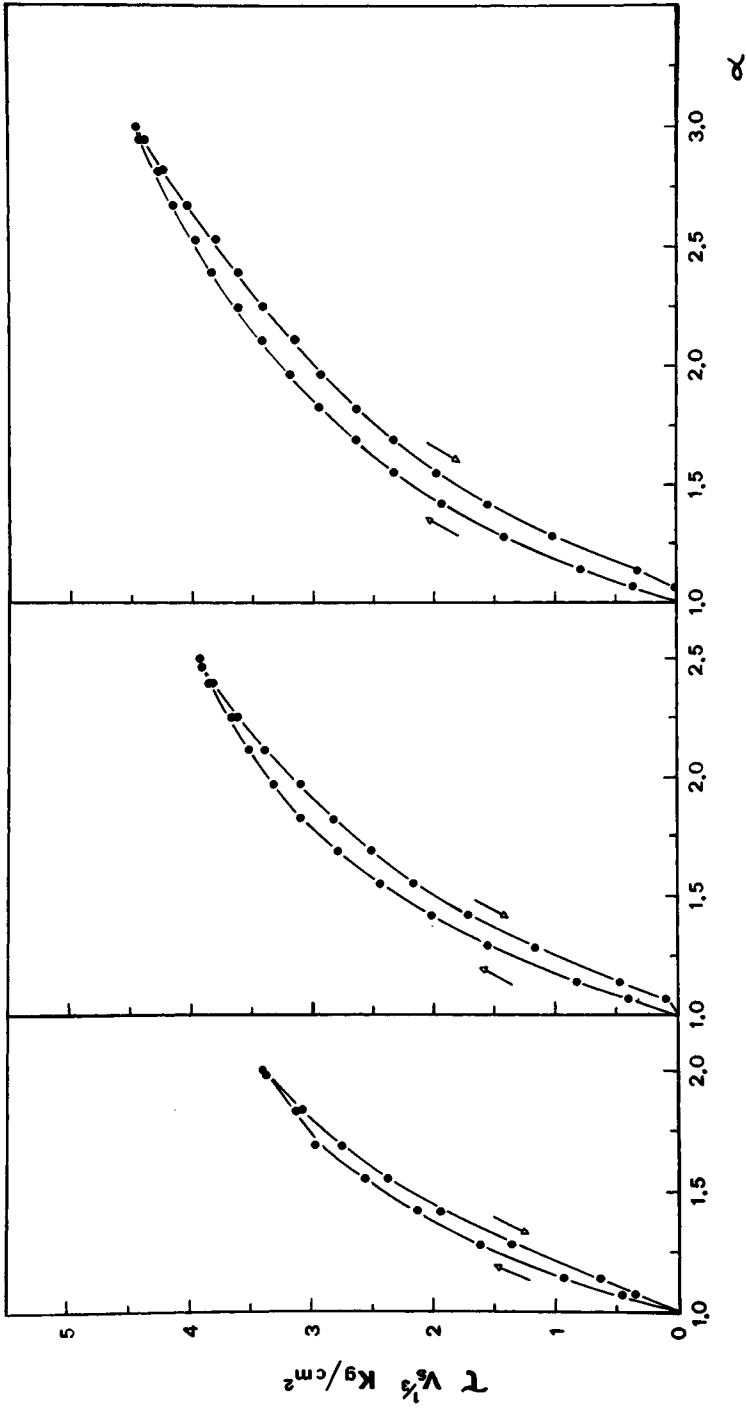


Fig. 2. Hysteresis cycles obtained on a swollen sample of vulcanizate A. Volume polymer fraction in the swollen sample was 0.549, solvent was *n*-hexadecane. Other conditions were as in Fig. 1. The sample is indicated as A₃.

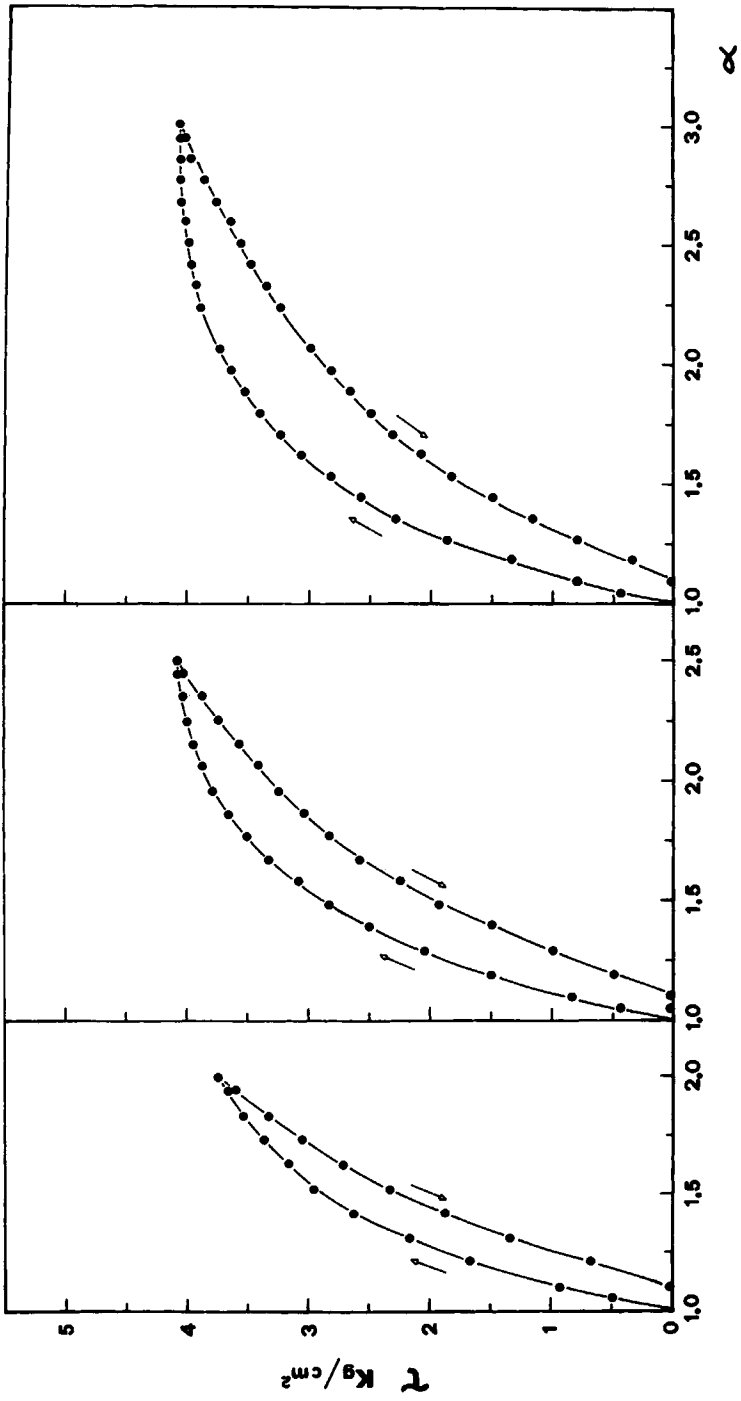


Fig. 3. Hysteresis cycles obtained on vulcanizate B. Experimental conditions were as in Fig. 1. The sample is indicated as B.

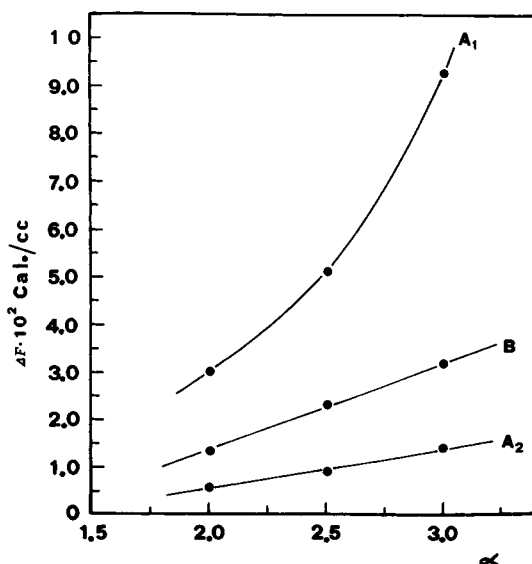


Fig. 4. Energy dissipated in every hysteresis cycles, reported as a function of the maximum strain. Data were obtained by graphic integration of the plots in Figs. 1, 2, and 3 and refer to the samples A₁, A₂, and B.

obtained on samples A₁, A₂, and B, carrying out stress-strain measurements step by step. The stress detection at different strain values was done at 20-min intervals.

DISCUSSION

The purpose of this work was to provide some experimental evidence for the hypothesis that the deviations from the Gaussian theory of rubber elasticity are related to phenomena of supramolecular organization. At the same time, if this hypothesis is correct, the second purpose was to demonstrate that the ideality of elastic behavior previously observed on networks vulcanized in the swollen state^{6,11,12} is due to a smaller tendency of these materials to give rise to organization phenomena. In order to obtain this evidence, we have analyzed the behavior of an ethylene-propylene copolymer, in which the high ethylene content and the long sequences of ethylenic units, observed by infrared analysis, are sufficient conditions to support the presence of chain-chain interactions. In fact there is a tendency of ethylene-propylene copolymers to give aggregates also in dilute solutions.¹⁴ Therefore, for a polymer in the bulk state, and with long ethylenic sequences, this tendency is certainly stronger and favored by the interactions of polyethylenic segments. This picture is supported by the experimental results of Figures 1 and 2, where the very strong hysteresis that is observed in sample A₁ disappears in sample A₂.

As a matter of fact, the stress induces irreversible aggregates, and from this follows a continuous creep that is the direct cause of the hysteresis

phenomenon. This is further supported by the increase in the undeformed sample length observed after every hysteresis cycle. In Figure 2, the solvent, by increasing the mean chain-chain distances, strongly decreases the possibility of interchain aggregations, and then the hysteresis phenomenon practically disappears. On the other hand, the stress-strain cycle carried out on sample B clearly indicates that the viscoelastic behavior of this sample is similar to that observed on swollen sample A₂. Therefore, if the hysteresis phenomena, as suggested, are connected with interchain aggregations, it seems possible to conclude that the presence of a solvent in the vulcanization mixture partially decreases the aggregation, with a mechanism similar to that previously described.⁶ In fact, we believe that the vulcanization reaction interferes with the topology of a polymer diluted by the solvent. Solvent removal allows an approach to the cross-link points, with consequent supercoiling of the network chains. It is less probable, then, that parallel segments of adjacent chains can participate in bundle formation, owing to the supercoiled state of the networks chains.

Results of Figures 1, 2, and 3 are further supported by the data of Figure 4, where the energy dissipated in every hysteresis cycle is given as a function of α . In Figure 4, in fact, the energy observed for sample A₁, at $\alpha = 3$, is about three to six times larger than the values given by samples B and A₂. Coming now to the results of Table I, it is clearly shown that the ratio C_2/C_1 follows very nearly the trend observed in Figure 4. From Table I, therefore, we can conclude that the strong decrease observed in the hysteresis phenomena is correlated with a strong decrease in the relative C_2 value.

In other words, these results indicate that the C_2 value depends directly on chain-chain aggregates present before or induced by the sample stretching. This agrees well with the observation that ethylene-propylene copolymers, with a tendency to give aggregates, also give C_2 values larger than these usually obtained for other elastomers. If, as appears reasonable, we wish to consider the C_2 coefficient as a measure of the nonideality of an elastic network, we can conclude that the observed deviations from eqs. (2) and (2a) are generally correlated to chain-chain interactions or, in other words, to supramolecular organizations present in the amorphous materials.

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