JOURNAL OF POLYMER SCIENCE: PART A VOL. 1, PP. 3569–3580 (1963)

Thermodynamic Interpretations of the Elastic Properties of Rubbers Obtained from Ethylene–Propylene Copolymers

G. NATTA, G. CRESPI, and U. FLISI, *Istituto Chimica Industriale del Politecnico di Milano* and *Istituto Ricerche Divisione Petrolchimica, Società Montecatini, Milan, Italy*

Synopsis

Stress–temperature coefficients have been measured for a high-molecular-weight ethylene–propylene copolymer, containing 45 mole-% of ethylene, chlorinated and vulcanized with a cure system based on sulphur and accelerators. From the relationships:

$$f = \left[\frac{\partial E}{\partial l}\right]_T - T\left[\frac{\partial S}{\partial l}\right]_T \text{ and } \left[\frac{\partial S}{\partial l}\right]_T = -\left[\frac{\partial f}{\partial T}\right]$$

the thermodynamic functions $[\partial E/\partial L]_T$ and $-T\,[\partial S/\partial L]_T$ have been determined in a range of the extension ratio up to $\alpha = 6.9$. A good agreement has been found between the experimental data and the stress–strain theoretical curve obtained for a non-Gaussian type network.

Introduction

Extensive research work on the production of linear, amorphous, high molecular weight copolymers of ethylene with α-olefins and on their use in the field of elastomers has been carried out in this laboratory for several years.[1] Beside studying the most suitable catalysts for obtaining copolymers with a random distribution of monomeric units, vulcanization was studied as well as the properties of the vulcanizates.[2]

The considerable interest aroused by these new rubbers, which are already being produced on a commercial scale, is not only due to the low cost of the olefinic monomers, as compared with that of the diolefinic used for the production of the unsaturated rubbers, but also to their peculiar properties.

Unlike natural rubber and many other synthetic rubbers, these elastomers do not contain unsaturation in the macromolecules; as a consequence of this their resistance to oxidation and to aging is far higher than that of unsaturated rubbers. These properties, as well as the good mechanical and elastic properties, make these copolymers of particular interest.

The copolymers with a fairly high ethylene content, even if prevailingly amorphous, show stress–strain curves which are similar to those of natural

rubber; in fact, an increase of the elastic moduli versus the degree of stretching follows the rather low initial moduli.

We had previously attributed these properties both to the presence of polymethylenic chain segments, even if rather short, and to their parallelization under stretching that causes an association of these chain segments with an effect comparable to a crystallization.

In order to interpret better the shape of such stress–strain diagrams and the other properties of the rubbers based on ethylene–propylene copolymers, we have carried out researches in two directions: (*1*) we tried to produce copolymers with a higher ethylene content, and such that the presence of longer methylenic chains might be foreseen, so as to favor crystallization under stretching; (*2*) we have prepared copolymers as much as possible amorphous and lacking regular chain segments, which will favor crystallization under stretching.

The runs carried out according to (*1*) for the amorphous copolymers showed that the increase in ethylene content causes a decrease of the temperature of the second order transition, but only a slight increase, at room temperature, of resilience with respect to the copolymers with an ethylene content of 50%. Copolymers containing more than 80 mole-% of ethylene show a crystallinity of the ethylenic type also in the unstretched state with a slight increase of the equatorial lattice constants, but have poorer elastomeric properties. Those copolymers of such ethylene contents that they yield a clear crystallinity by x-rays show an increase of the initial elastic modulus and on the whole less valuable elastomeric properties of the amorphous copolymers.

In research carried out according to (*2*) we tried to prepare definitely amorphous copolymers; for this purpose, we studied copolymers with a content of 50 mole-% of ethylene prepared with the aid of homogeneous catalyst systems that favor the random distribution of the monomeric units. The stress–strain curve of these copolymers shows only a slight decrease in mechanical properties, with respect to that of copolymers with a higher ethylene content. Such a decrease may be attributed to the more irregular structure of the chain. Consequently, and in order to study its effect devices have been adopted to increase the disorder in the structure of the macromolecules. Therefore, amorphous copolymers have been chlorinated, taking into account that chlorination causes, also in crystalline polymers such as polyethylene, an amorphization that is higher, the higher the chlorine content introduced.

The lack of unsaturation in the ethylene–propylene copolymers makes their vulcanization with the ingredients normally used for unsaturated rubber impossible; in fact, these rubbers are usually vulcanized with the aid of organic peroxides as crosslinking agents.[3] However, other crosslinking systems have been investigated in order to study the properties of these elastomers.[2]

In particular, we wish to refer here to the crosslinking system based on the dehydrochlorination reaction of chlorinated copolymers,[4] which

allows the use in the vulcanization of those ingredients normally used for unsaturated rubbers. In fact, this paper describes the results obtained from investigations on the mechanical properties of amorphous ethylene–propylene copolymers previously chlorinated up to a chlorine content of 15 wt.-%. Chlorination was performed in solution in order that the introduction of the chlorine atoms might be as much disordered as possible. Since the stress–strain curves of these chlorinated and vulcanized copolymers show behavior very similar to that of the rubbers crystallizable under stretching, we have started a thermodynamic study of such elastomers in order to understand better the nature of the phenomenon and to interpret it.

A chlorine content of 15% corresponds to 8 chlorine atoms for 100 carbon atoms. Also considering that in the subsequent vulcanization a part of chlorine is removed from the polymeric chains by dehydrochlorination, it must be assumed that no more than 6–7 chlorine atoms per 100 carbon atoms are bound to the polymeric chain. Such an amount can influence the completion of the amorphization of the polymer, but practically it exerts little influence on the mobility of the chain itself.

Obviously, chlorination causes an increase in the transition temperature, which could be foreseen on the basis of the Cl content: the nonchlorinated copolymer has a transition temperature of about −60°C., that of polyvinyl chloride is +77°C. The calculated value (−25°C.) corresponds to that found experimentally.

For rubbers crystallizing under stretching, some relationships exist between mechanical properties and crystallization phenomena:[5] the latter can be studied by means of stress–temperature measurements at constant length.[6,7]

In rubbers, crystallization under stretching is accompanied by a strong negative variation of internal energy; this variation, added to that of entropy, gives rise to a considerable increase in the retractive force, thus contributing to increase the tensile strength of the elastomer. In rubbers that do not crystallize under stretching, the variation of internal energy at high stretching ratios can be hardly determined because test pieces in general break before reaching the equilibrium conditions; therefore, it is impossible to determine the values of stress versus temperature within a wide range of the stretching ratio.

The thermodynamic properties versus the stretching ratio of a chlorinated and vulcanized ethylene–propylene copolymer are examined in this paper. For this rubber, unlike those rubbers that do not crystallize under stretching, it is possible to perform the stress–temperature measurements at high elongation values also.

Experimental

A high molecular weight ethylene–propylene copolymer containing 45 mole-% of ethylene and prepared with the aid of homogeneous catalysts based on soluble vanadium compounds and aluminum alkyls, was used

for these runs.[8] This copolymer was subsequently chlorinated by addition of chlorine to a solution of the copolymer in carbon tetrachloride under the conditions described in a previous paper,[9] until in the final product, a chlorine content of 15 wt.-% was attained.

The chlorinated ethylene–propylene copolymer was then mixed, in a laboratory roll mixer, with the vulcanization ingredients reported in Table I. The amount of zinc oxide is higher than that normally used for recipes of this type; however, it allows regular crosslinking to be obtained, the hydrochloric acid evolved being absorbed by the chlorinated polymer on vulcanization.

TABLE I
Recipe Used for Vulcanization of the Chlorinated Ethylene–Propylene Copolymer

Component	Parts
Polymer	100
Stearic acid	2
Zinc oxide	10
2-Mercaptobenzathiazole (MBT)	1
Tetramethylthiuram disulfide (TMT)	2
Sulfur	2

The recipe was then vulcanized in a parallel plate press at 150°C. for 30 min, and the vulcanized product thus obtained had the properties reported in Table II.

TABLE II
Properties of the Vulcanizates

Property	
Tensile strength, kg./cm.^{2}	148
Elongation at break, %	840
300% Modulus, kg./cm.^{2}	10
700% Modulus, kg./cm.^{2}	38
Resilience at 20°C., %	31
Degree of swelling at equilibrium	5.71
Degree of crosslinking, moles/cc.	0.55×10^{-4}

The degree of crosslinking was determined by measuring the retractive force at equilibrium on test pieces swollen in benzene at 30°C. For these runs test pieces of the type described in ASTM D 412 type C were used. The apparatus used was the same as that adopted by us to perform analogous measurements on cured *cis*-1,4-polybutadiene; it has been described in a previous paper.[7]

Temperature control was obtained by circulating ethyl alcohol in the tube containing the test piece; this allowed temperatures lower than

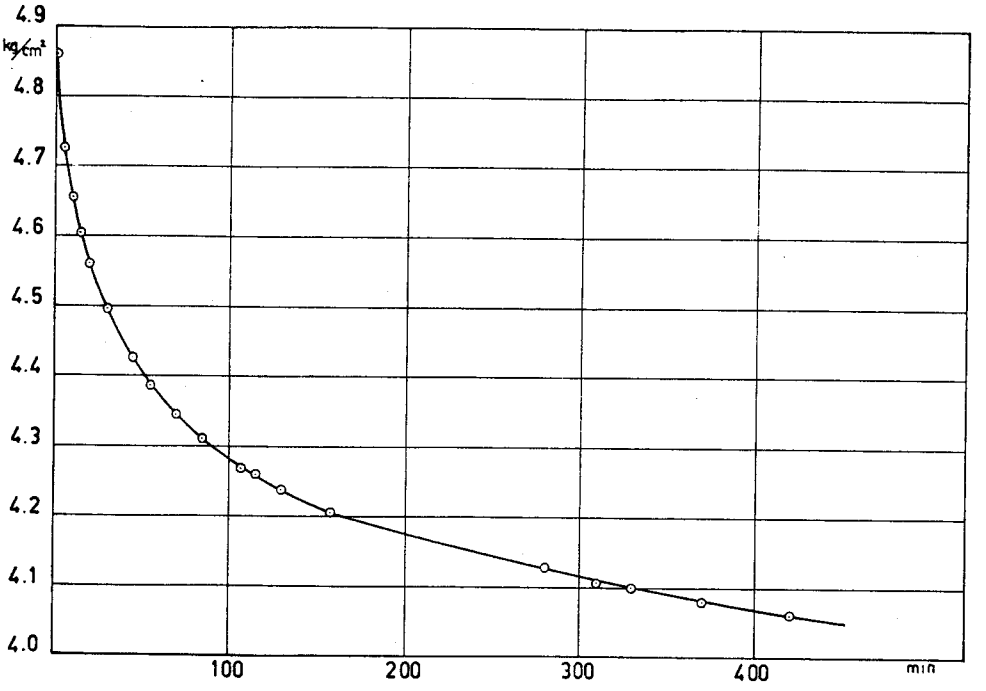

Fig. 1. Relaxation curve at 40°C. with $\alpha = 1.82$.

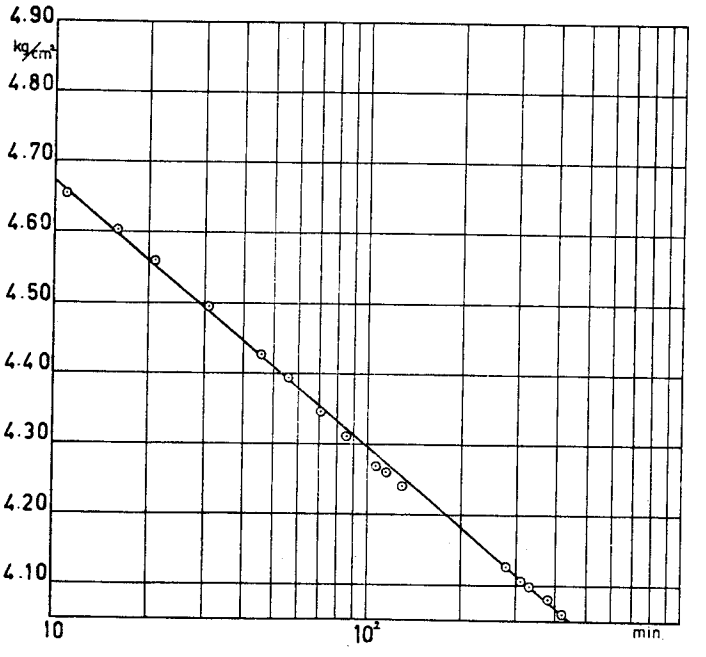

Fig. 2. Relaxation curve at 40°C. with $\alpha = 1.82$ (logarithmic scale of time).

0°C. to be attained. For these measurements the temperature was kept constant within ±0.3°C. The technique used for these runs was the same as that used by us for *cis*-1,4 polybutadiene. The test piece was stretched at the highest test temperature and left under these conditions until the stress did not appreciably decrease any longer with time (generally 3–5 hr. was enough); after that the temperature was lowered at intervals. Figures 1 and 2 show two relaxation curves obtained at the highest test

temperature. In the two figures the time scale is linear and logarithmic, respectively.

It has been observed that, after prestretching, stress at the lower temperatures remained constant also for times higher than the test time. It was also observed that, on increasing the elongation of test pieces, the relaxation temperature had to be decreased in order to avoid the breaking of test pieces before the equilibrium was reached.

Stress–Temperature Curves

The stress–temperature curves obtained as reported above are shown in Figure 3. It can be observed from it that, contrary to what was observed by us[7] for *cis*-1,4-polybutadiene, stress is directly proportional to temperature, at least in the range of temperature considered here, for all elongations examined. Therefore, the stress–temperature curves are straight lines and do not show curvature with variations in slope as in the case of *cis*-1,4-polybutadiene and natural rubber, when crystallization phenomena under stretching occur.[7]

At high stretching ratios, the slope of the stress–temperature lines are very steep; this indicates a strong variation of entropy with respect to the elongation.

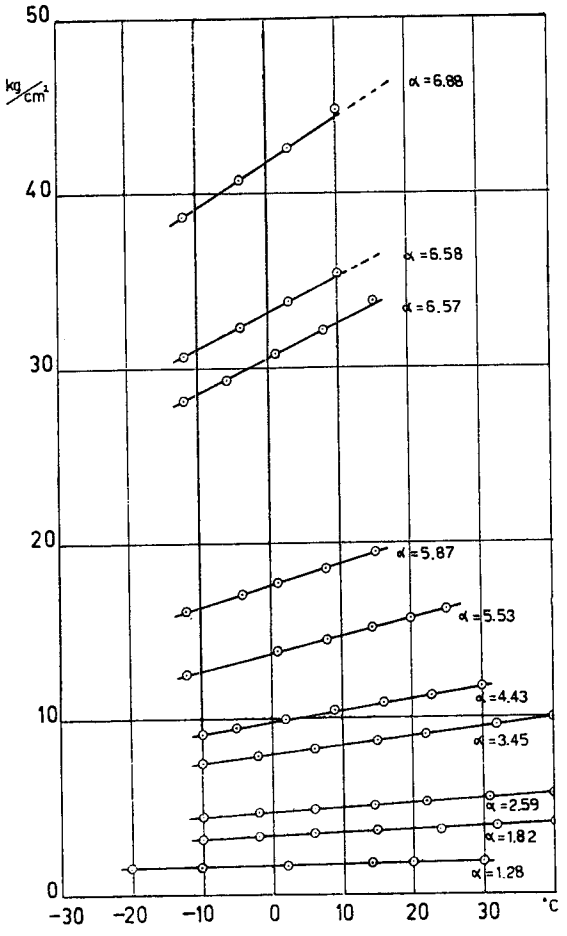

Fig. 3. Stress–temperature curves at constant length.

By extrapolating these lines to absolute zero, negative values are obtained also for low elongation values; from this point of view, the chlorinated copolymer behaves in an analogous way to crosslinked polyethylene,[10] whereas SBR shows rather low positive values, which however change their sign rapidly[11] with the increase of the stretching ratio.

Variation of the Internal Energy and of Entropy

As known, the relationships that permit the thermodynamic functions to be drawn from the stress–temperature measurements are

$$f = (\partial E/\partial l)_{T,V} - T\,(\partial S/\partial l)_{T,V} \tag{1}$$

$$-(\partial S/\partial l)_{T,V} = (\partial f/\partial T)_{l,V} \tag{2}$$

$$f = (\partial E/\partial l)_{T,V} + T(\partial f/\partial T)_{l,V} \tag{3}$$

where f is the stress exerted on the test piece in order to maintain it at a constant length, E is the internal energy, S is the entropy, l is the length, and T is the absolute temperature.

By using relation (3) it is possible to obtain the term $(\partial E/\partial l)_{T,V}$ from the stress–temperature plots by extrapolation to absolute zero. Figures 4 and 5 report the values of $(\partial E/\partial l)$ $(\partial S/\partial l)$ and of f versus the stretching ratio at the temperatures of 15 and 0°C., respectively.

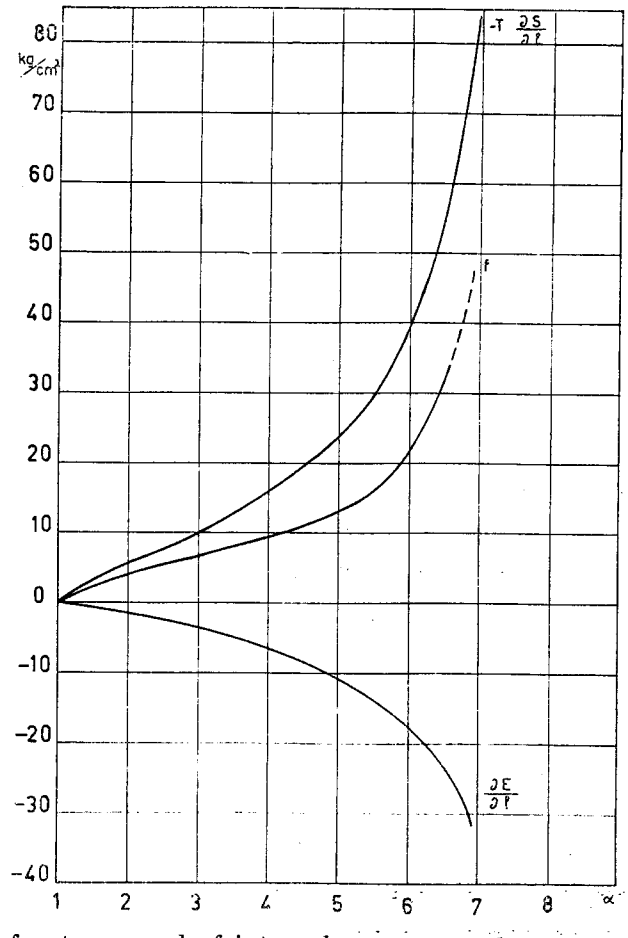

Fig. 4. Variation of entropy and of internal energy vs. elongation (values at 15°C.).

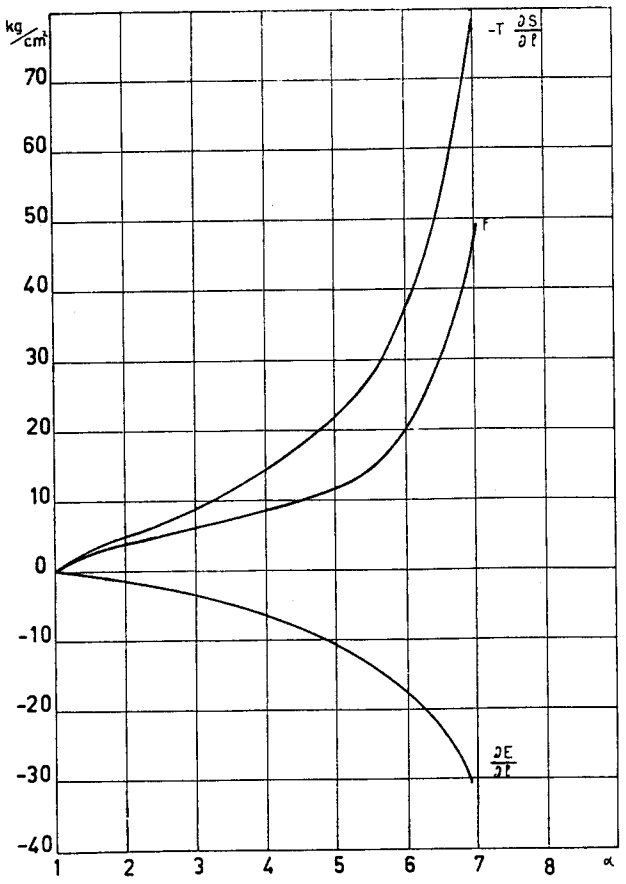

Fig. 5. Variation of entropy and of internal energy vs. elongation (values at 0°C.).

In order to study the properties of the polymeric network, the most important term to be examined is $(\partial E/\partial l)_{T,V}$.

It has already been noticed how, from this term, it is possible to obtain $d \ln \bar{r}_0^2/dT$,[12] within the limits of validity of the kinetic theory of elasticity, based on a Gaussian distribution, and also how it is possible to evaluate, to a good approximation, the degree of crystallization of the rubbers crystallizing during stretching.[7]

For chlorinated ethylene–propylene copolymer, it can be observed in Figures 4 and 5 how this term is always negative and assumes high absolute values at high stretching ratios.

If the possible occurrence of crystallization phenomena is excluded, as is seen from the x-ray analysis of samples stretched up to $\alpha = 7$, the strong variations of internal energy that were observed must be attributed to the interaction arising between the chains when they are parallelized owing to stretching; this interaction is such that it can be compared to a change of state, from the energetic point of view; probably an association of the polar groups present contributes to it.

The linearity of chains in the absence of bulky substituents favors the associations between the chains, parallelized by stretching. These associations can be compared, with regard to their effect, to a crystallization of lower degree, which cannot be detected by x-ray analysis.

Theoretical Stress–Strain Curves and Comparision between Them and the Experimental Data

It is known that the theory of elasticity based on the Gaussian network is valid only for a narrow range of the stretching ratio, and that the theoretical curves are quite different from the experimental ones for values of α higher than $^1/_3\ R_{max}/\bar{r}_0^2$, where R_{max} is the length of the chain fully extended and $\bar{r}_0^2$ is the mean-square length of the unstretched chain.

A theoretical stress–strain relation that does not introduce the approximations assumed for the Gaussian network was obtained independently by Kuhn and Grün[13] and by James and Guth[14] treating the non-Gaussian network, and is given in eq. (5):

$$f = \frac{NKT}{3} n^{1/2}[\mathcal{L}^{-1}(\alpha n^{-1/2}) - \alpha^{-3/2}\,\mathcal{L}^{-1}(\alpha^{-1/2} n^{-1/2})] \tag{5}$$

In this equation N is the total number of chains, K is the Boltzmann constant, T is the absolute temperature, n is the number of links of the chains, α is the stretching ratio, and $\mathcal{L}^{-1}$ is the inverse Langevin function.

If the contribution to stress of the internal pressure is small, eq. (5) can be simplified to:

$$f = \frac{NKT}{3k} [\mathcal{L}^{-1}(\alpha k) - (3k/\alpha^2)] \tag{6}$$

where $k = n^{-1/2}$.

By indicating by G the NKT product, which is constant at a given temperature, eq. (6) becomes the simple equation:

$$f = \frac{G}{3k} [\mathcal{L}^{-1}(\alpha k) - (3k/\alpha^2)] \tag{7}$$

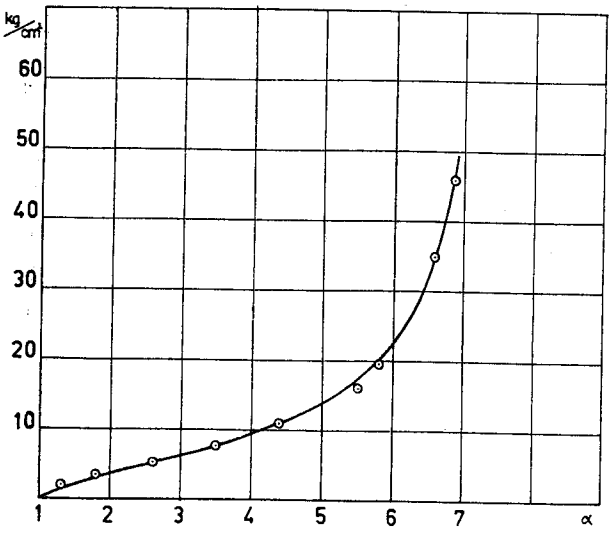

Fig. 6. Curve obtained from eq. (7) for $G = 1.95$ and $k = 0.13$ and stress values (⊙) obtained from Fig. 3.

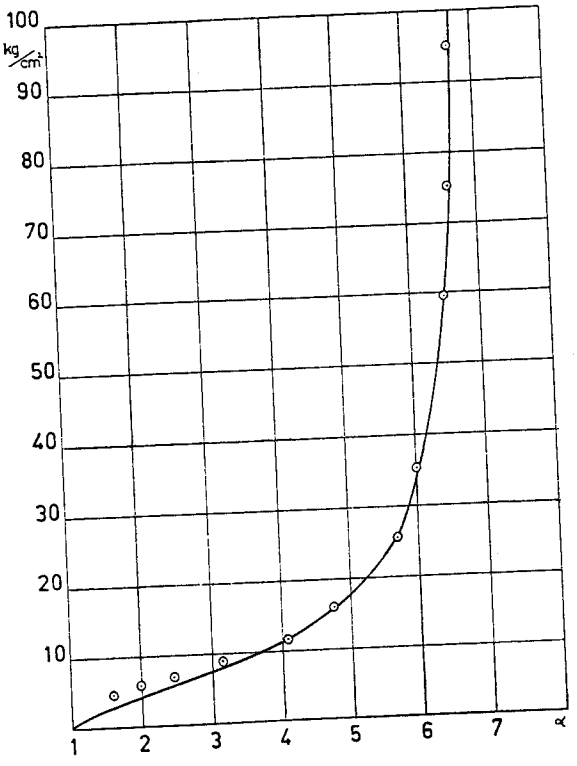

Fig. 7. Curve obtained from eq. (7) or $G = 2.25$ and $k = 0.14$ and values of the stress (⊙) obtained on the dynamometer.

In Figure 6, relation (7), calculated for the values $G = 1.95$ kg./cm.^{2} and $k = 0.13$, is compared with the experimental values of stress at equilibrium versus elongation, obtained from the diagram of Figure 3, at a temperature of 15°C.

The perfect agreement between the actual values of stress measured at equilibrium conditions and the theoretical curve demonstrates the validity of eq. (7) for the whole elongation range. In Figure 7 a comparison is also made between relation (7) and the stress–elongation curve obtained at 15°C. on an Amsler-type dynamometer, after several cycles when conditions near to equilibrium are reached, as revealed by the superposition of curves obtained at subsequent cycles. In this case, in order to obtain a good agreement between the experimental values and the theoretical curve, the value of G and k were to be varied to 2.25 and 0.14 respectively. In fact, under these conditions, equilibrium for low values of the stretching ratio is not reached.

Conclusions

The stress–temperature curves for a chlorinated ethylene–propylene copolymer have been examined, and the variations of the thermodynamic functions with respect to the extension ratio have been deduced.

It has been observed that these rubbers give a strong variation of the internal energy, of the same order as that of rubbers that crystallize during stretching. This notwithstanding that the stress–temperature relations

are linear and that the copolymer used has a composition excluding the crystallization under stretching.

On the contrary it was observed that the stress–elongation curves at equilibrium can be represented with excellent agreement, by the theoretical relation between stress and elongation derived for the non-Gaussian network. This relation foresees a strong upward curvature of the stress–elongation curve for values of the stretching ratio which are near the highest extensibility of the chains. This phenomenon, observed here under equilibrium conditions, was difficult to be appreciated in rubbers that do not crystallize under stretching and is masked by the effect of crystallization for rubbers with structure regularity.

References

1. Natta, G., *Rubber Plastics Age*, **39**, 493 (1957); G. Natta, G. Mazzanti, A. Valvassori, and G. Pajaro, *Chim. Ind. (Milan)*, **39**, 733 (1957).
2. Natta, G., and G. Crespi, *Chim. Ind. (Milan)*, **41**, 123 (1959); G. Natta, G. Crespi, and M. Bruzzone, *Kautschuk Gummi*, **14**, 3, 54 (1961).
3. Natta, G., G. Crespi, E. DiGiulo, G. Ballini, and M. Bruzzone, *Rubber Plastics Age*, **42**, 43 (1961).
4. Crespi, G., and M. Bruzzone, *Chim. Ind. (Milan)*, **43**, 137 (1961).
5. Treloar, L. R. G., *The Physics of Rubber Elasticity*, Clarendon, Oxford, 1958, p. 270.
6. Boonstra, B. B. S. T., *Ind. Eng. Chem.*, **43**, 361 (1951).
7. Crespi, G., and U. Flisi, *Chim. Ind. (Milan)*, **43**, 993 (1961).
8. Mazzanti, G., A. Valvassori, and G. Pajaro, *Chim. Ind. (Milan)*, **39**, 743 (1957); G. Mazzanti, A. Valvassori, and G. Pajaro, *ibid.*, **39**, 825 (1957); G. Natta, A. Valvassori, G. Mazzanti, and G. Sartori, *ibid.*, **40**, 717 (1958).
9. Bruzzone, M., and G. Crespi, *Chim. Ind. (Milan)*, **42**, 1226 (1960).
10. Ciferri, A., C. A. J. Hoeve, and P. J. Flory, *J. Am. Chem. Soc.*, **83**, 1015 (1961).
11. Roth, F. L., and L. A. Wood, *J. Appl. Phys.*, **15**, 749 (1944).
12. Flory, P. J., A. Ciferri, and C. A. Hoeve, *J. Polymer Sci.*, **45**, 235 (1960).
13. Kuhn, W., and F. Grün, *Kolloid-Z.*, **101**, 248 (1942).
14. James, H. M., and E. Guth, *J. Chem. Phys.*, **11**, 455 (1943).

Résumé

On a mesuré les coefficients thermiques de tension d'un copolymère éthylène–propylène de poids moléculaire élevé, contenant 45 mole-%, d'éthylène, chloré et vulcanisé au moyen d'un système basé sur du soufre et des accélérateurs. Les fonctions thermodynamiques $[\partial E/\partial l]_T - T[\partial S/\partial l]_T$ et sont déterminés en partant des relations

$$f = [\partial E/\partial l]_T - T[\partial S/\partial l]_T \text{ et } [\partial S/\partial l]_T = -(\partial f/\partial T)_l$$

dans un domaine de rapports d'extension jusqu' à $\alpha = 6.9$. On constate un bon accord entre les courbes de tension-élongation théoriques obtenues pour un réseau d'un type non-Gaussien.

Zusammenfassung

Es wurden die Spannungs-Temperatur-Koeffizienten eines Äthylen–Propylen-Copolymeren hohen Molekulargewichtes mit einem Äthylengehalt von 45 Mol% gemessen, das chloriert und mit einem aus Schwefel und Beschleuniger bestehenden Vulkanisationssystem vulkanisiert wurde. Aus den Gleichungen

$$f = [\partial E/\partial l]_T - T[\partial S/\partial l]_T \text{ und } [\partial S/\partial l]_T = -[\partial f/\partial T]_l$$

wurden die thermodynamischen Funktionen $[\partial E/\partial l]_T$ und $-[\partial S/\partial l]_T$ in einem Bereich des Dehnungsverhältnisses bis hinauf zu $\alpha = 6{,}9$ berechnet. Die Ergebnisse stimmen mit den für ein Netzwerk vom Nicht-Gauss'schen Typ berechneten theoretischen Spannungs-Dehnungs-Kurven gut überein.

Received June 10, 1963