The Influence of Precure Dilation on the Stress-Strain Properties of Ethylene–Propylene Terpolymer Networks

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Synopsis

A study has been made of the influence of a dilating liquid, present during vulcanization, on the stress–strain behavior of EPT vulcanizates. Stress–strain measurements performed on the vulcanizates after extraction of the dilating liquid, taken over a range of strain rates, indicate the effective absence of time-dependent behavior and suggest that a close approach to equilibrium has been achieved. From the experimental data, values of the C_1 and C_2 constants of the empirical Mooney-Rivlin equation were derived. It was found that both C_1 and C_2 decreased with increased precure dilation, C_2 decreasing more rapidly than C_1. The observed decrease in C_1 is less than would be predicted by simple analogy with the Gaussian modulus; it is suggested that this difference might be explained by changes in network configuration and topology associated with the precure dilation.

INTRODUCTION

The classical statistical theory of rubber-like elasticity leads to a stress–strain relationship for simple elongation which may be written as[1,2]

$$f = NkT(\lambda - \lambda^{-2}) \tag{1}$$

where f is the stress based on the unstrained cross-sectional area, N is the number of moles of effective network chains per unit volume, k is the Boltzmann constant, T is the absolute temperature, and λ is the extension ratio.

An underlying assumption in the derivation of the classical elasticity equation is that the statistical distribution of chain end-to-end distances in the network is the same as for the assembly of free chains prior to crosslinking. Thus, if $\overline{r_i^2}$ is the mean square end-to-end distances of the chains in the undistorted isotropic network and $\overline{r_0^2}$ is the mean square end-to-end distance of unperturbed free chains, it is assumed that $\overline{r_i^2} = \overline{r_0^2}$. For an amorphous network prepared in the dry state, this is a reasonable assumption; chain segments in the bulk polymer cannot distinguish inter- from intramolecular contacts and the chains are unperturbed. Strictly, the above equality only applies at the vulcanization temperature. For chains having hindered internal rotation, $\overline{r_0^2}$ is temperature dependent, and at temperatures other than the vulcanization temperature,[3,4] $\overline{r_i^2} \neq \overline{r_0^2}$.

In the case of networks prepared in the presence of a diluent, an isotropic reference degree of swelling q_0 can be defined such that the mean square end-to-end distance of the network chains would be the same as in a solution of unperturbed chains in the same diluent, at the same concentration and temperature. The exact relationship between the degree of precure dilation q^* and the reference degree of swelling q_0 cannot be determined from a priori considerations. Taking a more strict account of the network chain statistics, as outlined above, leads to a modified stress–strain relationship, for simple elongation of unswollen networks, which may be written as[3]

$$f = NkT \left(\frac{\overline{r_i^2}}{\overline{r_0^2}}\right) (\lambda - \lambda^{-2}) \tag{2}$$

The stress–strain relationship thus obtained is not, however, sufficient to represent the experimentally observed behavior of rubber-like materials. In practice, the stress normally increases less rapidly than predicted at low strains and more rapidly than predicted at high strains. Because of the inadequacy of eq. (2), it is fairly common procedure to represent experimental data by the empirical equation of Mooney[5] and Rivlin[6]:

$$f = 2C_1(\lambda - \lambda^{-2}) + 2C_2(1 - \lambda^{-3}) \tag{3}$$

where C_1 and C_2 are empirical constants. In simple elongation, this equation represents experimental data reasonably well for values of λ in the range 1.2 to 3. At high extensions, the finite extensibility of the network chains causes the stress to increase more rapidly than predicted, while at low extension (in the region $\lambda = 1.0$), C_2 decreases and becomes zero in uniaxial compression.

Although it is not strictly justified, comparison of eq. (3) with eq. (2) has led to a general acceptance of the identity

$$2C_1 = \left(\frac{\overline{r_i^2}}{\overline{r_0^2}}\right) NkT \tag{4}$$

with the C_2 term of eq. (3) being taken to represent a deviation from the Gaussian expression. The origin of the C_2 term has been the source of considerable interest. A number of authors[7-9] have suggested that the C_2 term is associated with a slow stress relaxation process and arises from a failure to achieve equilibrium. Others have preferred to regard the C_2 term as representing a real equilibrium deviation arising from deficiencies in the Gaussian approximation, and several theoretical modifications have been developed.[10-13] None of these theories gives a satisfactory approach to the order of magnitude of experimentally observed values of C_2, and no molecular interpretation of C_2 is currently available. Thus, while C_1 can be related to the chain configuration parameters $\overline{r_i^2}$ (this parameter is specified by the initial test conditions) and $\overline{r_0^2}$ through eq. (4), no similar theoretical relationship is available for C_2, although it seems reasonable to assume that C_2 will also be dependent on these parameters.

In this study, the influence of precure dilation on the C_1 and C_2 terms of the Mooney-Rivlin equation has been investigated for an ethylene–propylene terpolymer, in an attempt to illuminate some aspects of the deviations from simple Gaussian theory.

EXPERIMENTAL

Oil-extended gum stocks of an ethylene–propylene terpolymer (Nordel 1070) were prepared by addition of oil to the raw polymer on a two-roll rubber mill. Curatives were added to each stock at a constant concentration, and samples were vulcanized in a mold.

Full details of compound formulations and cure are given in Table I. The cure time was selected on the basis of Monsanto ODR data: all curves reached the plateau region well before the cure time selected.

TABLE I
Compound Formulations and Cure[a]

	Sample No.					
	1	2	3	4	5	6
Nordel 1070, g	100	100	100	100	100	100
Edilex 27, g	0	22	44	66	88	110
Cure System, (moles/l.) $\times 10^2$						
TMT, 5.31						
MBT, 0.38						
S, 3.98						
ZnO, 5.23						

[a] All samples cured 15–60 min at 160°C.

Crosslinking in ethylene–propylene terpolymers is achieved through the pendant unsaturated sites present in the polymer at a low concentration (approx. 0.4 mole/kg 1,4-hexadiene in the polymer used). The extender oil, Edilex 27, was used as diluent because this low-viscosity paraffinic oil has been shown to be an inert medium for the vulcanization reaction.[14]

After vulcanization, the extender oil and any nonnetwork material was extracted under solvent reflux in a Soxhlet apparatus.

Stress–strain measurements were carried out on dumbell samples of approximately 7 mm^2 cross section in an Instron tensometer at six crosshead speeds between 0.2 and 50 in./min. Time-dependent effects contributing to the stress have been separated from the effects due to the inherent nonlinear response of the network by the method proposed by Smith.[15] According to this method, for each strain rate the stress at a series of selected elongations is plotted against the time t, given by $t = (\lambda - 1)/(d\lambda/dt)$, to achieve each particular elongation. Typical plots of log f versus log t for one of the networks are presented in Figure 1. None of the lines deviates from zero slope by more than a few per cent, and this behavior is typical of all the samples. From such plots, isochronal (1 min)
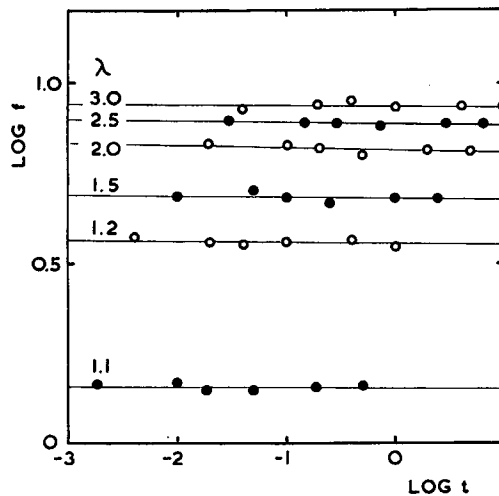
Fig. 1. Time dependence of stress–strain data in simple elongation over a range of strain rates from 0.2 to 50 in./min; t = time to reach selected strain.

stress data have been obtained and used to obtain the Mooney-Rivlin plots of $f/(\lambda - \lambda^{-2})$ versus λ^{-1}, shown in Figure 2.

The equilibrium degree of swelling of each vulcanizate was determined by immersing small samples in toluene and reweighing after rapid surface drying. The chain molecular weights M_c between continuous crosslinks were determined using the relationship developed by Hermans[16]:

$$M_c = \frac{- \bar{V}\rho[q^{-1/3}(q^*)^{-2/3} - q^{-1}]}{\ln(1 - q^{-1}) + q^{-1} + \chi q^{-2}} \tag{5}$$

where q is the equilibrium degree of swelling in solvent (toluene), q^* is the degree of dilation (by oil) at the time of vulcanization and is referred to in the subsequent text as the degree of preswelling, $\bar{V}$ is the molar volume of solvent, ρ is the rubber density, and χ is the Flory-Huggins interaction parameter.

RESULTS AND DISCUSSION

Values of $2C_1$ and $2C_2$ were obtained from the intercepts and slopes, respectively, of the linear regions of the Mooney-Rivlin curves (Fig. 2), and these are quoted in Table II. It is observed that both $2C_1$ and $2C_2$ decrease with increased degree of preswelling: the functional dependencies of $2C_1$ and $2C_2$ on the degree of preswelling q^* were determined from a plot of $\log C_1$ (and $\log C_2$) against $\log q^*$. As shown in Figure 3, linear plots are obtained having slopes of -0.46 for C_1 and -0.71 for C_2, calculated by the method of least squares. Thus, the Mooney constants of the preswollen networks are related to those of the network crosslinked in the dry state through
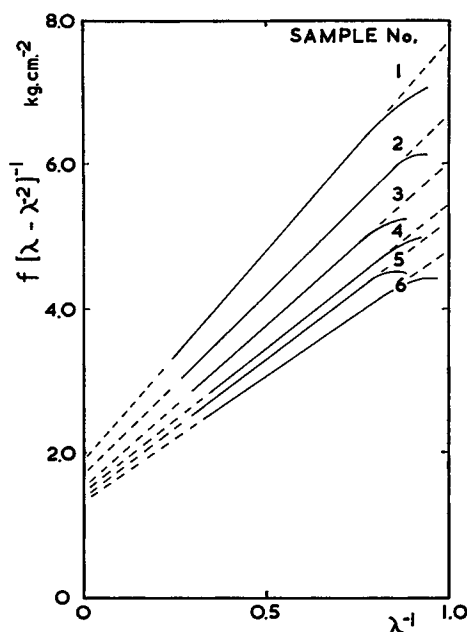
Fig. 2. Mooney-Rivlin plots for preswollen EPT vulcanizates extracted before testing.

TABLE II

	Sample No.					
	1	2	3	4	5	6
Diluent prior to cure, %	0	17.6	29.8	38.9	46.0	51.5
Volume degree of preswelling q^*	1.000	1.213	1.424	1.638	1.850	2.063
Equilibrium degree of swelling Q	3.513	3.827	3.796	4.420	4.576	4.627
Interchain molecular weight[a]						
$M_c \times 10^3$	3.2	3.2	2.6	3.3	3.1	2.8
Mooney constants,						
$2C_1$ kg/cm^2	1.90	1.70	1.52	1.48	1.40	1.36
$2C_2$	5.84	5.04	4.54	3.98	3.84	3.84
C_2/C_1	3.08	2.96	2.98	2.69	2.74	2.56

[a] Calculated from eq. (5), using $\chi = 0.429 + 0.218\,q^{-1}$, from Blanchard.[17]

$$(2C_1)_p = (2C_1)_d(q^*)^{-0.46}$$

$$(2C_2)_p = (2C_2)_d(q^*)^{-0.76} \tag{6}$$

where the subscripts p and d refer to networks prepared in the preswollen and dry states, respectively. As the values of M_c obtained from equilibrium swelling measurements, presented in Table II, indicate that all the networks have approximately identical crosslink densities, the observed systematic decrease of $2C_1$ is presumably associated with a change in the configurational parameter $\overline{r_0}^2$.
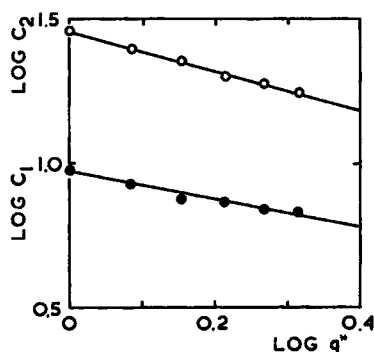
Fig. 3. Dependence of Mooney constants C_1 and C_2 on volume degree of swelling prior to cures (preswelling) q^*. For convenience, the ordinate axis (for C_1 and C_2) has been shifted by a factor of $+1$.

In a previous study of preswollen polyacrylate networks by Tobolsky et al.,[18] the stress–strain data were analyzed assuming the validity of eq. (3), and it is not clear whether deviations from ideal network behavior were observed. In the terms of these authors, the front factor Φ ($= \overline{r_i^2}/\overline{r_0^2}$) for a series of acrylates was found to decrease linearly with increase in the percentage of diluent present prior to crosslinking and to extrapolate to zero before the solvent reached 100%. Analysis of current data in this manner (see Fig. 4) shows that both C_1 and C_2 decrease linearly with increased amount of solvent, but much less rapidly than the data of Tobolsky.

If it is assumed that the diluent has no specific interaction with the polymer and that the network was formed instantaneously, then it is reasonable to assume that the reference degree of swelling q_0, defining the relaxed network state, can be identified with the dilation of the network prevailing at the time of crosslinking q^*. Then, by eq. (4), one would predict that the $2C_1$ value should decrease with preswelling as the $-\frac{2}{3}$ power of q^* (since under these conditions $\overline{r_0^2}$ would be proportional to $(q^*)^{\frac{2}{3}}$), i.e.,

$$(2C_1)_p = (2C_1)_d \, (q^*)^{-\frac{2}{3}} \tag{7}$$

The experimental data, as shown, indicate that $2C_1$ decreases more slowly than predicted by this relationship. Several possible factors may contribute to this effect, probably the most significant of which is concerned with the assumption of instantaneous network formation. Under the experimental conditions adopted, the network was formed by the introduction of successive crosslinks over an extended period of time. With each additional crosslink introduced, restraints are imposed on the thermal motion of the molecules which affect the configurations of the chains in the final network. It is anticipated from such considerations, that growth of the network will be accompanied by contraction of growing network fragments, and for this reason the reference degree of swelling may not be identified with that pertaining prior to cure, and eq. (7) will not apply. On the basis
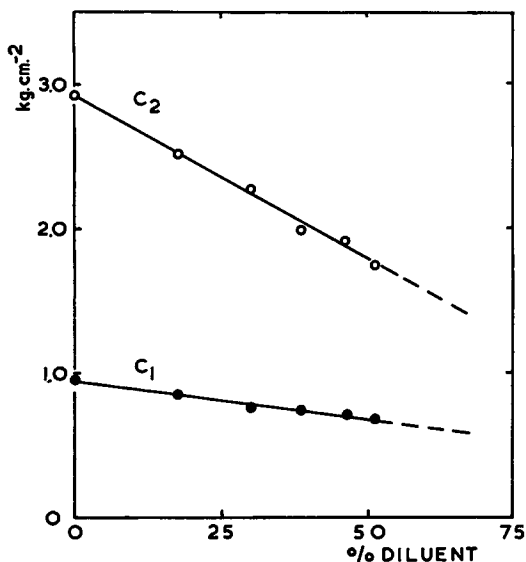
Fig. 4. Dependence of Mooney constants C_1 and C_2 on % diluent present prior to cure.

of a similar argument to the above, James and Guth[19] have proposed that a front factor should be present even for networks prepared in the dry state. Kinetic data obtained on the crosslinking of these networks show that the rate of crosslinking decreases with increased degree of preswelling.[14]   Problems related to restrictions against two chains cutting through one another, and associated excluded volume effects, will also contribute to changes in network topology on preswelling.   The presence of polysulfidic linkages that are thermally labile may reduce the likelihood of internal stress being built into the network during cure.

Time-dependent factors do not contribute significantly to the observed stress–strain behavior, since the approximately zero slopes of the lines in Figure 1 suggest that a close approach to equilibrium stresses has been achieved.   The occurrence of a slow relaxation process cannot, however, altogether be discounted.

Ethylene-rich samples of random ethylene–propylene terpolymers have been shown to crystallize upon stretching: the propensity of these polymers to stress-induced crystallizaton was reported to be a function of the ethylene–propylene ratio, decreasing with increased propylene content.[20] A degree of crystallization of 5–7% (at an elongation of 300%, at 24°C) was estimated from wide-angle x-ray diffraction data for a polymer of the following molar composition: 21.9% propylene, 77% ethylene, and 1.1% diene. The polymer used in the present study had a molar ethylene–propylene ratio of 64/36, as determined by infrared analysis.   It is anticipated that the tendency of this polymer to undergo stress-induced crystallization will be insignificant in the range of extension (0–300%) used in this investigation.

The variation of $2C_2$ with q^* is more difficult to interpret in view of the lack of any satisfactory molecular interpretation for this term. It is, however, significant that one important consequence of the dilation of the chain assembly prior to vulcanization will be to reduce the number of chain entanglements and to produce a concomitant reduction in the number of tanglements which become trapped on crosslinking. It may be speculated that the contribution of trapped entanglements to the total effective degree of crosslinking is included in the C_2 term and that the observed variation of this term with dilation characterizes the change in degree of chain entanglement. Since the experimental data refer to networks from which the diluent has been removed, possible contributions from floating chains, which may become entangled on extraction of the diluent will also be included.

The behavior of C_2 observed in the present study contrasts sharply with recently reported data for preswollen natural rubber networks,[21] where C_2 was observed to become approximately zero at moderate dilations. Extrapolation of the data in Figure 4 to infinite dilation does not give an intercept on the abscissa. Since the two sets of data cover different ranges of dilation (EPT $1.0 < q < 2.1$; NR $2.5 < q < 7.0$), the interesting possibility arises that at some intermediate concentration there may be a change in the characteristic behavior of C_2 with preswelling noted in the present study. Further experimental work in this area is required to investigate this possibility and to elucidate the molecular significance of such a phenomenon.

It should be remarked that the observed values of $2C_2$ and the ratio C_2/C_1 quoted in Table II are praticularly high when compared to typical values for natural rubber ($C_2 \sim 0.5\text{--}2.0$; $C_2/C_1 \sim 0.3\text{--}1.0$). These results, however, are not unique, and it is interesting to note in this respect that negative values of $2C_1$ have been obtained for ethylene–propylene vulcanizates with high values of $2C_2$.[22]

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