

Properties and Microstructures of Ethylene-Propylene Terpolymers

M. C. KIRKHAM, *Dunlop Research Centre, Birmingham 24, England*

Synopsis

The properties of raw polymer and gum vulcanizates of several ethylene-propylene terpolymers with respect to thermal transitions, stress relaxation, and swelling behavior are discussed in relation to the influence of ethylene content and microstructure. It is shown that at high ethylene contents, the presence of associated regions, perhaps microcrystallites, in low concentration produces polymers having thermoplastic behavior. The degree of crystallinity is apparently very low, and polymers of nominally similar ethylene contents can exhibit disparate behavior reflecting differences in heterogeneity of molecular composition.

INTRODUCTION

Commercially available ethylene-propylene terpolymers are generally characterized by having ethylene contents in the range of 60 to 80 mole-% and contain a termonomer introduced in low concentration to provide pendant unsaturated sites for sulfur vulcanization.

The properties of the terpolymers depend markedly on composition.

The influence of composition on the thermal transitions of ethylene-propylene copolymers and terpolymers has been reported by several authors.¹⁻⁶ Some aspects of the effect of ethylene content on relaxation behavior have also been considered.⁷⁻⁹

It is the objective of the present paper to examine the effects of ethylene content and microstructure on the thermal and mechanical properties.

EXPERIMENTAL

Materials Used

The composition and molecular weight characteristics of the polymers studied are presented in Table I. The different polymers have been assigned a letter from A to F, and for convenience have been classified as being of high ethylene content (greater than 70 mole-% ethylene, assigned the numeral 1) or of medium ethylene content (60-70 mole-% ethylene, assigned the numeral 2).

Gum vulcanizates were prepared by adding 3.5 phr of Dicap R on a two-roll rubber mill and curing in a mold for 60 min at 150°C.

TABLE I
 Polymer Properties

Polymer	Termonomer		Propylene content, mole-%	Intrinsic viscosity, dl/g	$\bar{M}_v \times 10^{5b}$
	Type ^a	wt-%			
A-1	ENB	6.2	24	2.35	2.51
B-1	ENB	4.2	30	2.98	3.64
C-1	HEX	3.6	20	3.03	3.73
D-1	ENB	5.2	28	2.31	2.46
E-2	HEX	4.2	33	3.40	5.25
F-2	ENB	5.3	32	2.87	3.58

^a ENB = Ethyldenenorbornene; HEX = 1,4-hexadiene.

^b From $[\eta] = 7.24 \times 10^{-4} \bar{M}_v^{0.62}$ in cyclohexane at 31°C; based on a strictly alternating 1:1 EP structure obtained by hydrogenation of polyisoprene.

Experimental Methods

Differential scanning calorimetry and rolling-ball techniques have been used to investigate the thermal transitions which occur on heating the polymers over the temperature range -80°C to $+100^\circ\text{C}$.

Thermograms were obtained on a Perkin Elmer DSC-1B model differential scanning calorimeter at a programmed rate of heating of 8°C per minute. The rolling-ball spectrometer, which has been described elsewhere,¹⁰ measures changes in hysteresis loss by measuring the resistance to the rolling of small steel balls over the polymer surface. A spectrogram of hysteresis loss is recorded directly.

Small samples (ca. 0.5 g) of each of the uncured high-ethylene polymers were swollen in nine *n*-decane/benzene solvent mixtures. The mixtures contained 100, 80, 75, 60, 50, 40, 25, 20, 0% *n*-decane by volume, respectively. Since equilibrium swelling was not expected for the uncured samples, especially in good solvents, preliminary experiments were carried out to determine a suitable swelling time. After 48 hr, pseudoequilibrium in a poor solvent and only a slow rate of swelling increase in a good solvent mixture was noted. On the basis of these results, a 48-hr swelling time was selected, the solvent being changed twice during this period. Equilibrium swelling of vulcanizates was achieved in 48 hr.

After swelling, the samples were rapidly surface dried, weighed, deswollen under vacuum, and reweighed. The ratio of the swollen volume to the final dried volume of the polymer was calculated.

Stress-strain measurements were carried out on square-ended dumbbell samples ($25 \times 2.1 \times 2.5$ mm) on an Instron tensile tester at a cross-head rate of 20 in./min.

Stress relaxation behavior was studied in a simple spring-balance relaxometer fitted with an environmental chamber. Square-ended dumbbell samples were elongated to the desired extension at a constant rate and the subsequent relaxation followed by measuring the length of the calibrated retaining spring with a cathetometer.

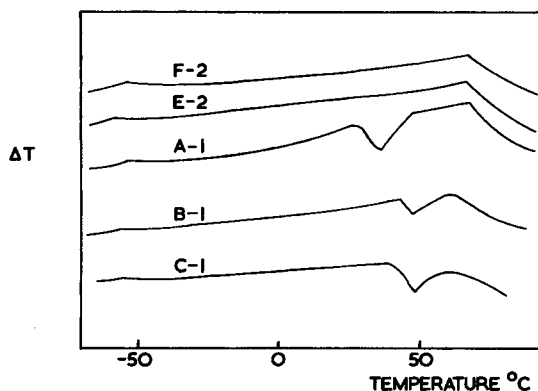


Fig. 1. Differential scanning calorimeter thermograms.

The thermoelastic response of the polymers was studied in the relaxometer. The samples were stretched to 50% extension; the temperature in the environmental chamber was raised in successive steps of approximately 3–5°C and the stress determined after a relaxation period of 10 min.

RESULTS AND DISCUSSIONS

Thermal Transitions

The DSC thermograms of the polymers studied are shown in Figure 1. Details of the transition temperatures are presented in Table II.

All the polymers have a second-order glass transition, T_g , in the region of –60°C; the absence of a composition dependence over the limited range of ethylene contents studied is in agreement with literature data.^{1,3,5}

The high-ethylene polymers have a broad endothermic transition, T_m , in the region of 30–50°C, probably resulting from the disaggregation or melting of disordered polyethylene crystallites. The low values observed suggest that only short ethylene sequences are involved in microcrystalline formation, and the breadth of the endotherms are indicative of a fairly wide distribution of aggregate sizes.

TABLE II
Transition Temperatures

Polymer	DSC			Loss spectrometer		
	T_g	T_m	T_a	T_g	T_1	T_2
A-1	–57	33	65	–27	—	—
B-1	–64	45	57	–26	65	107
C-1	–60	47	55	–29	60	110
E-2	–61	—	63	–34	—	—
F-2	–57	—	64	–29	25–80 (range)	—

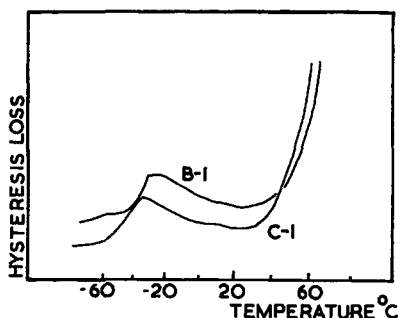


Fig. 2. Loss spectrograms of uncured high-ethylene polymers.

A third transition, T_a , characteristic of all the polymers occurs in the region of 55° to 65°C . In polymers B-1 and C-1, this transition immediately follows the melting endotherm and is not as well defined as in the other polymers. The nature of this transition is not clear: a similar transition reported to occur at 56°C in an ethylene-propylene block copolymer was assigned to amorphous polyethylene.²

Rolling-ball loss spectrograms of all the polymers have a glass transition loss peak in the region of -30°C . The approximate 30°C increase in T_g relative to the DSC values, arising from the frequency difference, corresponds to an approximate shift factor of 6°C per decade of time since the effective frequency of the loss spectrometer has been estimated to be of the order of 10^3 Hz and that of the DSC method to be of the order of 10^{-2} Hz.

High-ethylene polymers in general have two additional loss peaks. The first, T_1 , occurs in the region of 60°C and is presumed to be associated with the softening of the associated ethylene regions, as evidenced by the dramatic effect observed in the uncured samples shown in Figure 2. This peak is particularly sensitive to the thermal history of the sample. Samples slowly cooled from 150° to 60°C and annealed for 1 hr showed sharp peaks, whereas no peak was observed when samples were rapidly quenched in iced water (see Fig. 3). Assignment of this peak is not unambiguous since some medium-ethylene polymers, which have no DSC melting endotherm, also show thermal history-dependent transitions in this region (25 – 80°C), although generally of a more diffuse nature.

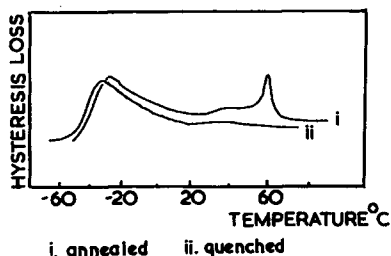


Fig. 3. Effect of annealing and quenching on loss spectrogram.

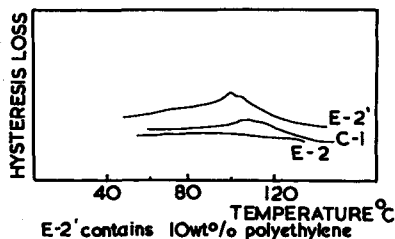


Fig. 4. High-temperature loss peak due to true ethylene crystallites.

The second weak loss peak, T_2 , occurs in the region of 110°C and is assigned to the melting of polyethylene crystallites of a degree of perfection more closely approaching that of the homopolymer, presumably present in small amounts. Addition of polyethylene (10%) in a medium-ethylene polymer simulates this loss (see Fig. 4).

Swelling Behavior

The volume degrees of swelling (q) of the uncured high-ethylene polymers A-1, B-1, and C-1 were plotted against the solvent solubility parameter (δ) in Figure 5. Solubility parameters of the solvent mixtures were estimated assuming the following volume fraction additivity relation:

$$\delta = \delta_1 v_1 + \delta_2 v_2 \quad (1)$$

where v_1 and v_2 are volume fractions and δ_1 and δ_2 are the solubility parameters of the pure solvents *n*-decane and benzene, respectively. All the polymers show the same trend in behavior with change in solvent composition, maximum swelling occurring at $\delta = 17.3$ to 17.5 (J/cm^3)^{1/2}. Using

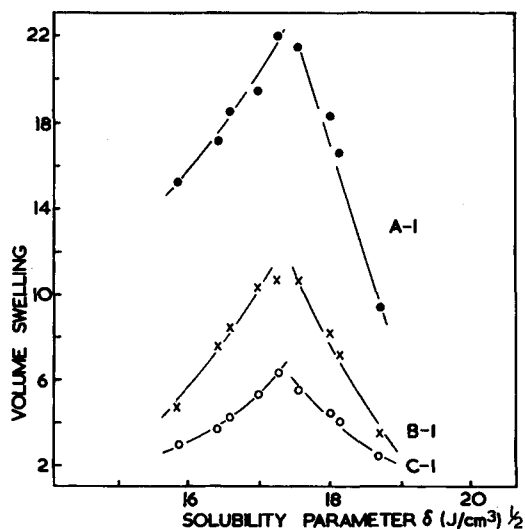


Fig. 5. Swelling of uncured high-ethylene polymers.

Smalls' method¹¹ of estimating δ , based on the principle of additivity of specific contributions from each characteristic molecular element in the polymer chain, a value of $17.2 \text{ (J/cm}^3\text{)}^{1/2}$ for ethylene contents of 70/80 mole-% (ignoring the small termonomer contribution) is obtained. The agreement with the experimental value is extremely good. Polymer D-1 and the medium-ethylene polymers all readily dissolved in the good solvents. Concomitant with the swelling of the high-ethylene polymers A-C was the extraction of a considerable soluble fraction; in the best solvent mixture, weight losses after 48 hr were 30%, 12%, and 5%, respectively.

These pseudoequilibrium phenomena arise from the effective network formed by the ethylene microcrystallites or associated regions. The absolute magnitude of the degrees of swelling indicate the extent of the network structures present.

The Flory-Rehner equation for equilibrium swelling of polymer networks¹² at high swelling ratios approximates to

$$M_c^{-1} = \left[\frac{0.5 - \chi}{V\rho} \right] q^{-5/3} \quad (2)$$

where M_c is the molecular weight between contiguous crosslinks, χ is the Flory-Huggins interaction parameter, V is the solvent molar volume, and ρ is the polymer density. Although true equilibrium swelling is not achieved in the present instance, application of the above equation to the swelling data for the high-ethylene polymers should give an approximate measure of the relative extents of their network structures. Values of $q^{-5/3}$ and their relative magnitudes are quoted in Table III and clearly indicate that differences in network structures of an order of magnitude exist.

TABLE III
Swelling Data

Polymer	A-1	B-1	C-1	E-2	F-2
Uncured Sample ^a					
$q^{-5/3} \times 10^2$	0.37	2.01	4.68	—	—
Ratio	1	5	12	—	—
Cured Sample ^b					
q	2.55	—	2.65	3.34	2.70
$M_c^{-1} \times 10^4$	6.50	—	5.70	2.80	5.38
Ratio	1.2 (A/F)	—	2.0 (C/E)	—	—

^a 48 Hours of swelling in a 50/50 (by volume) *n*-decane/benzene mixture.

^b Calculated assuming a constant polymer solvent (toluene/EPDM) interaction parameter $\chi = 0.48$.

A similar conclusion is arrived at by consideration of the equilibrium swelling of vulcanized samples. The apparent values of M_c^{-1} of corresponding high- and medium-ethylene polymers having the same termonomer have been compared. Values of M_c^{-1} , presented in Table III were calculated using the exact Flory-Rehner equation ignoring the nonswelling of the associated ethylene regions. The relative magnitudes of M_c^{-1} for high-

and medium-ethylene terpolymers based on hexadiene are 2.0 to 1, compared with 1.2 to 1 for the corresponding ethyldenenorbornene terpolymers. The differences in unsaturation levels (termonomer content) between the polymers is not expected to be a significant factor in peroxide vulcanizates. Any effect arising from this source would be likely to further exaggerate the disparity in behavior.

Stress-Strain Properties

The presence of associated or microcrystalline regions in the high-ethylene polymers contributes significantly to the stress-strain behavior of these materials. These regions act as both effective crosslinks and as reinforcing filler particles. The stress-strain curves for the raw polymers are shown in Figure 6. It is clear that the high-ethylene polymers exhibit network characteristics possibly enhanced by stress crystallization, while the medium-ethylene polymers exhibit the characteristic yield point and viscous flow of amorphous materials.

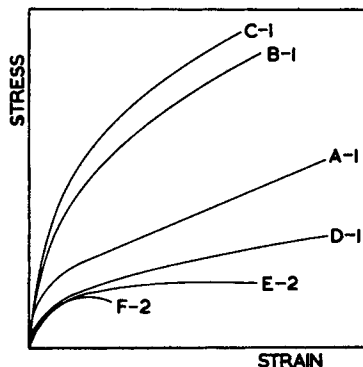


Fig. 6. Stress-strain curves of uncured gum polymers.

An apparent strain amplification factor was estimated for the reinforcement by comparing the modulus of corresponding high- and medium-ethylene polymer peroxide vulcanizates. The modulus G was calculated from the stress at 50% elongation ($\lambda = 1.5$) assuming the validity of the classical elasticity equation

$$\sigma = G(\lambda - \lambda^{-2}). \quad (3)$$

The comparative data presented in Table IV are in reasonable agreement with the estimates of relative extents of network structures based on equilibrium swelling.

Stress Relaxation Behavior

The stress relaxation behavior of the raw polymers is shown in Figure 7. The rate of stress decay of the medium-ethylene polymers is rapid and characteristic of unbranched polymers having narrow molecular weight distri-

TABLE IV
Stress-Strain and Stress-Relaxation Data

Property	Polymer					
	A-1	B-1	C-1	D-1	E-2	F-2
<i>Stress-Strain</i>						
Modulus ^a G_u	9.29	11.76	13.47	5.81	2.85	—
Modulus ^b G_e	9.73	12.58	15.32	—	6.25	9.29
Apparent strain amplification	1.0 (A/F)	1.3 (B/F)	2.4 (C/E) 1.6 (C/F)	—	—	—
<i>Stress-Relaxation</i>						
$c = (\log \sigma_1)$	1.100	1.161	1.199	0.798	—	—
m	0.059	0.066	0.048	0.083	—	—

^a Unvulcanized raw polymer (units MN/m²).

^b Peroxide vulcanizate.

butions. The time dependence of the relaxation modulus of the high-ethylene polymers is very gradual; the rate of relaxation over a period of six decades is typically of the order of 8% per decade based on the original stress (see inset Figure 7). The viscoelastic relaxation can be reasonably approximated by a linear relationship of the form

$$\log(\sigma_t) = c - m \log t \quad (4)$$

where c is a constant equal to the value of $\log(\sigma_t)$ at time $t = 1$ min, and m is the slope; values of c and m are given in Table IV.

Clearly in the high-ethylene polymers the normal entanglement network which accounts for the time-dependent stress decay of the amorphous polymers is supplemented by a second stress-supporting mechanism, the asso-

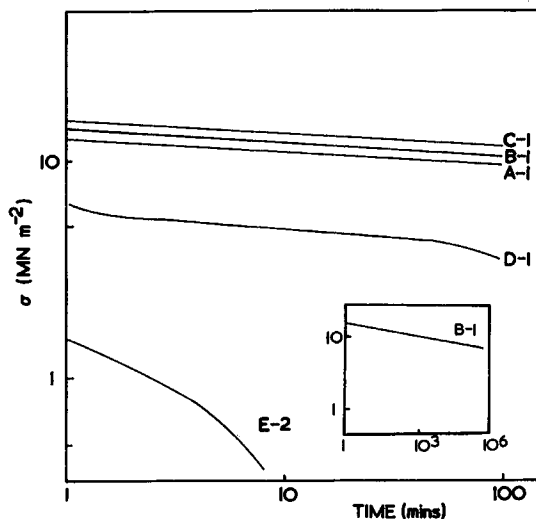


Fig. 7. Stress-relaxation curves of uncured polymers at room temperature.

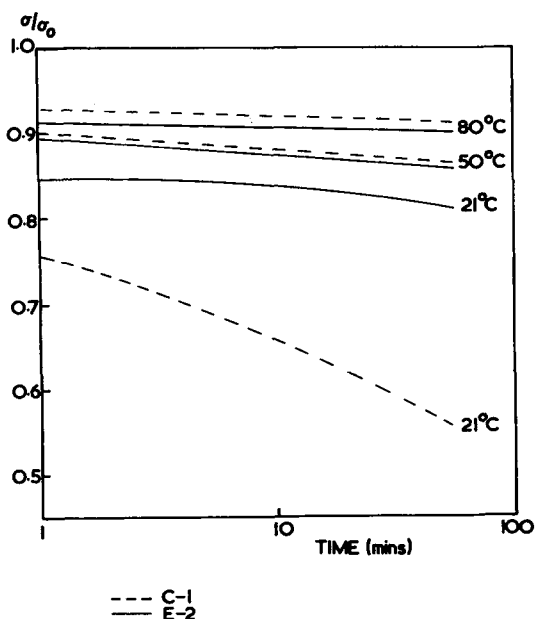


Fig. 8. Stress-relaxation curves of peroxide vulcanizates.

ciated or crystalline regions, characterized by long relaxation times. The type of behavior observed in these polymers is similar to that exhibited by lightly crosslinked networks.

The origin of the long-term stress decay has been further studied in peroxide vulcanizates. Data are presented in Figure 8, which shows the change in relaxation response with increase in temperature. At room temperature, the high-ethylene polymer C-1 exhibits a marked time-dependent relaxation modulus which does not reach equilibrium even after a relaxation period of 100 min. At 50°C, the time dependence of the relaxation modulus is dramatically reduced, consistent with melting of ethylene crystallites between 20° and 50°C, and at 80°C the response closely resembles that of the medium-ethylene polymer. Failure to achieve an equilibrium modulus in vulcanizates has been noted previously in natural rubber, though the origin of the persistent relaxation was not elucidated. In view of the closer approach to equilibrium obtained with increase in temperature, a viscoelastic mechanism would appear to be operative in the present case. Stress-induced crystallization with alignment of crystallites in the direction of strain causing a reduction in stress may be a contributory phenomenon.

The effect of the melting transition is particularly clear in the thermoelastic behavior of these materials; typical curves are shown in Figure 9. Although fairly rapid continuous relaxation of stress is occurring in the uncured samples, the initial stress-temperature coefficient is positive, which suggests the presence of a coherent network. As the temperature is raised, an inversion occurs in the region of 30°C, and the stress falls rapidly beyond

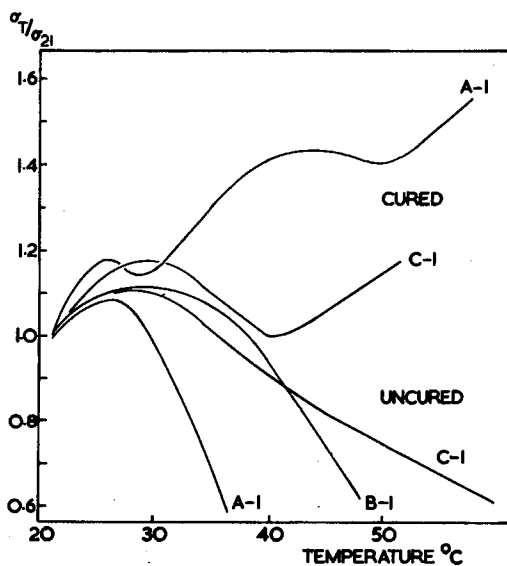


Fig. 9. Thermoelastic behavior of uncured and cured high-ethylene polymers.

this temperature (i.e., viscous flow occurs). Vulcanized samples in general show the same inversion temperature, although polymer A-1 has a second inversion at about 40°C. After the melting inversion, the stress-temperature coefficient again becomes positive as expected for an amorphous cross-linked network.

GENERAL DISCUSSION

It is evident from the preceding discussion that ethylene content and microstructure have major effects on the physical properties of the ethylene-propylene terpolymers.

The effect of microstructure is particularly marked in the series of three high-ethylene ENB polymers which have ethylene contents in the narrow range of 70-76%. Polymer D-1, containing 72 mole-% ethylene, while having a considerably longer terminal relaxation time than the amorphous lower-ethylene-content polymers, is readily soluble in good solvents, typical of an amorphous material. In contrast, polymer B-1, containing 70 mole-% ethylene but having a high intrinsic viscosity, exhibits truly thermoelastic behavior in having a very long terminal relaxation time, an effective equilibrium swelling in good solvents, and a positive stress-temperature coefficient in the unvulcanized state. Although having the highest ethylene content (76 mole-%), polymer A-1 shows intermediate behavior more closely approaching that of B-1. These variations in behavior are a consequence of differences in heterogeneity of molecular structure. Thus, the high soluble fraction noted in polymer A-1 strongly suggests a heterogeneous distribution of microstructures, with some chains having regular

ethylene sequences capable of crystallization and others not, the latter being soluble. The HEX polymer C-1 (80 mole-% ethylene), which has a very low soluble fraction, probably has a narrow distribution of microstructure.

The presence of structural features capable of strong association or crystallization is a function of the regularity of ethylene and propylene placements incurred during polymerization. While it is assumed that ethylene sequences are responsible for the observed behavior, since high ethylene contents are a necessary requirement, it must be recognized that other regular sequences could undergo alignment within the amorphous matrix to form strong associations capable of producing the observed effects. The low melting points observed are only consistent with relatively short ethylene sequences. No evidence of crystallinity was obtained by x-ray diffraction or infrared analysis.

The properties of the terpolymers are broadly similar to the corresponding ethylene-propylene copolymers, but the termonomer acts as a further randomizing group and can also affect chain branching through the second, less reactive double bond.

The author gratefully acknowledges the technical assistance of Miss C. Dodd.

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Received May 31, 1972

Revised August 22, 1972