

Aspects of the Thermal and Dynamic Mechanical Behavior of EPDM Rubbers

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Synopsis

The influence of both ethylene content and the degree of crystallinity on the thermal and dynamic mechanical properties of certain commercial EPDM rubbers were investigated using the TMA, DSC, and Rheovibron techniques. The six materials chosen for this study were Nordel 1560, Intolan 260, Royalene 1812, Vistolan 3708, Intolan 255, and Keltan 778.

INTRODUCTION

Much has now been written about the synthesis,¹ characterization,²⁻⁶ and properties⁷⁻¹¹ of the two commercial types of ethylene-propylene rubber. The first of these is simply a chemically saturated ethylene-propylene copolymer (EPM), which, if required, may be peroxide vulcanized. The second is a terpolymer (EPDM) with a low diene content, which permits sulphur vulcanization.

The desirable rubbery properties of these terpolymers are influenced by a number of parameters,⁷ which include the propylene content, the monomer sequence distribution, the molecular weight, and the molecular weight distribution.

This paper presents the results of some thermal and dynamic mechanical studies carried out on six commercial EPDM rubbers.

TABLE I
Materials used in the Investigation

Material ^a	Manufacturer
Nordel 1560	Du Pont
Intolan 260	International Synthetic Rubber
Royalene 1812	Uniroyal
Vistolan 3708	Esso
Intolan 255	International Synthetic Rubber
Keltan 778	Dutch State Mines

^a The diene comonomer is ethylidene norbornene, except for Nordel 1560 in which 1,4-hexadiene has been used.

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EXPERIMENTAL

Materials

The terpolymers chosen for this investigation are listed in Table I. The characterization data are presented in Table II.

Fabrication of Sheet

(a) **Virgin Rubber.** Prior to final sheeting on a hot press, the rubbers were, if necessary, granulated and then sheeted at a temperature of around 160°C for 4–5 min on a two-roll mill. The milled sheet was then hot pressed at 160°C at a pressure of about 7.7 MN m⁻² for 6 min and then allowed to cool in the press.

(b) **Crosslinked Rubber.** The six rubbers were milled as before for 3 min, then 2.5% by weight of dicumyl peroxide was added and the mixture was compounded by allowing eight mill passes (about 2 min) at a temperature of 150°C. After determining the cure time with a Monsanto Rheograph, the sheets were prepared by hot pressing at 160°C for 25 min.

TABLE II
Characterization Data

Material	$\bar{M}_n \times 10^{-3}$ ^a	\bar{M}_w/\bar{M}_n ^b	E/P ^c	Blockiness factor ^d	Crystallinity ranking ^e
Nordel 1560	98	6.4	82:18	1.54	1
Intolan 260	100	3.8	82:18	1.75	2
Royalene 1812	71	4.6	81:19	1.41	3
Vistolan 3708	64	8.5	75:25	1.11	4
Intolan 255	61	8.3	77:23	1.19	5
Keltan 778	60	1.2	76:24	1.04	6

^a Determined using a Mechrolab High Speed Membrane Osmometer (model 501) with toluene at 37°C as solvent.

^b Determined by gel permeation chromatography using a Waters Associates instrument (model 502).

^c Determined by the technique described in Ref. 6. Ratio by weight.

^d Determined from the ¹³C NMR spectra.

^e Determined by a wide angle x-ray diffraction technique.

TABLE III
100% Modulus and Longitudinal Sonic Velocity (V_L) of Sheeted Samples

Material	100% modulus $\times 10^{-5}$ (N m ⁻²)	V_L ^a (km sec ⁻¹)
Nordel 1560	17.9	1.673
Intolan 260	18.5	1.669
Royalene 1812	10.4	1.612
Vistolan 3708	9.6	1.605
Intolan 255	6.7	1.582
Keltan 778	6.8	1.569

^a Frequency was 1 MHz.

Techniques

Thermal Measurements. For the differential scanning calorimetry measurements, a Perkin-Elmer DSC-1B instrument was used at a heating rate of 16°C/min. The thermomechanical analysis curves were obtained with a Du Pont Thermomechanical Analyser fitted with a penetration probe. The applied load was 5 g and the heating rate was 10°C/min.

Dynamic Mechanical Measurements. These measurements were made using a Rheovibron Dynamic Viscoelastometer (model DDV-II-B) at a frequency of 110 Hz. The temperature range was scanned at a rate of about 1°C/min.

RESULTS AND DISCUSSION

As can be seen from Table II, the samples fall into two groups as far as composition is concerned. The first three materials contain around 82% ethylene, while the remaining three have an approximately 76% ethylene content.

A number of papers²⁻⁵ have been published in which ¹³C NMR has been used to determine the ethylene/propylene ratio and the blockiness of these polymers. It is possible to identify peaks in the ¹³C spectra that may be ascribed to methylene units which are, respectively α , β , and γ to the propylene methine group. The methylene units more remote all contribute to the same δ signal. A measure of the degree of blockiness of the samples may then be obtained from the ratio

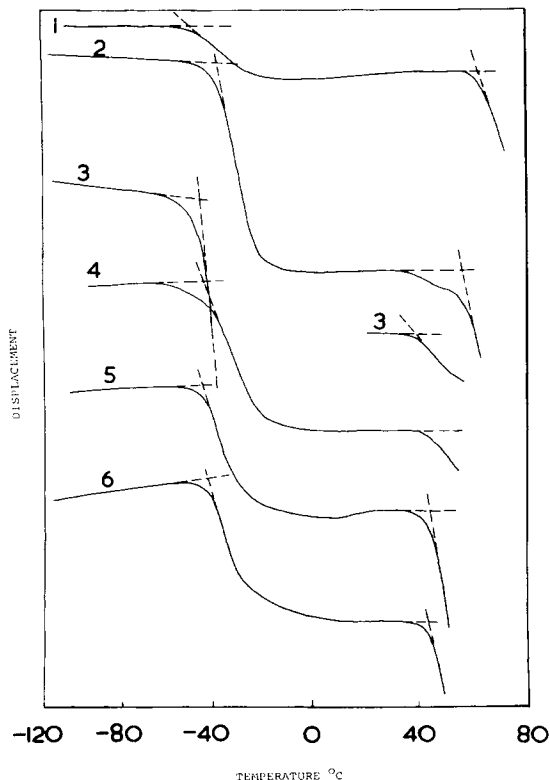


Fig. 1. TMA thermograms of Nordel 1560 (1), Intolan 260 (2), Royalene 1812 (3), Vistolan 3708 (4), Intolan 255 (5), and Keltan 778 (6).

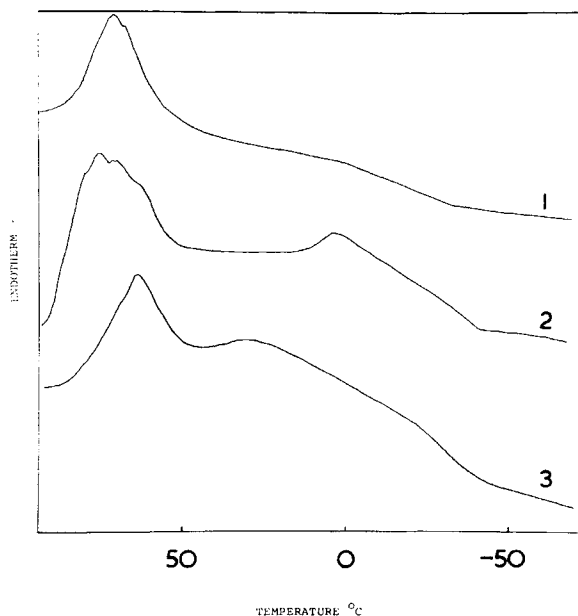


Fig. 2. DSC thermograms of Nordel 1560 (1), Intolan 260 (2), and Royalene 1812 (3).

of the height of the δ signal to the sum of the α , β , and γ peak heights. Thus, it is at least possible to arrange the six samples in order of increasing blockiness even if it is not possible to obtain highly reliable quantitative information about the blockiness of individual samples.

As can be seen from Table II, there is at least a general accord between the blockiness factor and the measured degree of crystallinity. In this work it was

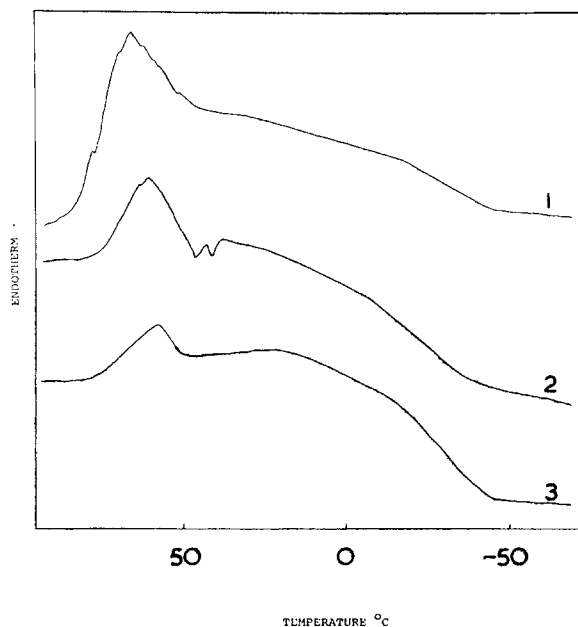


Fig. 3. DSC thermograms of Vistolan 3708 (1), Intolan 255 (2), and Keltan 778 (3).

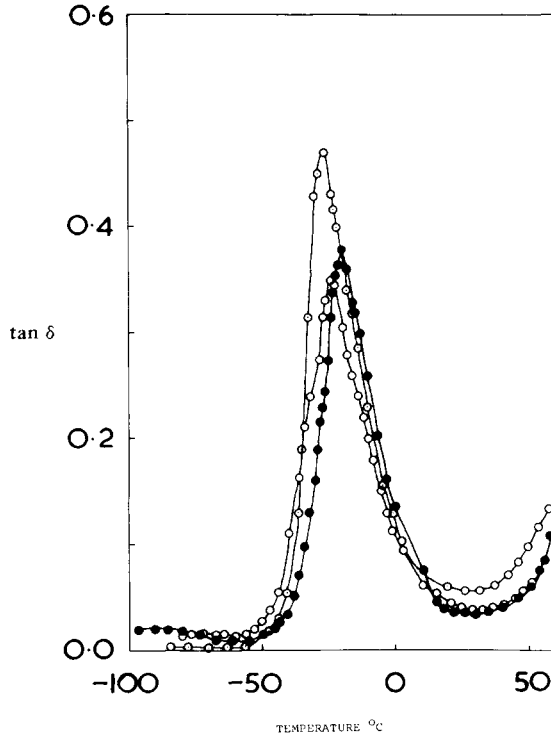


Fig. 4. $\tan \delta$ vs temperature curves for Nordel 1560 (○), Intolan 260 (●), and Royalene 1812 (○).

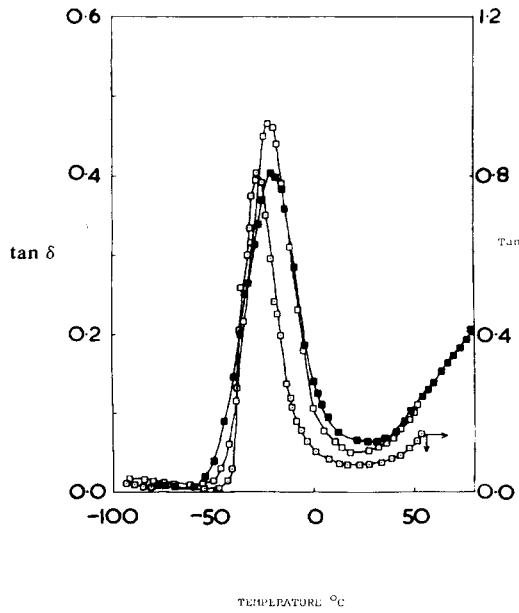


Fig. 5. $\tan \delta$ vs temperature curves for Vistolan 3708 (■), Intolan 255 (□), and Keltan 778 (□).

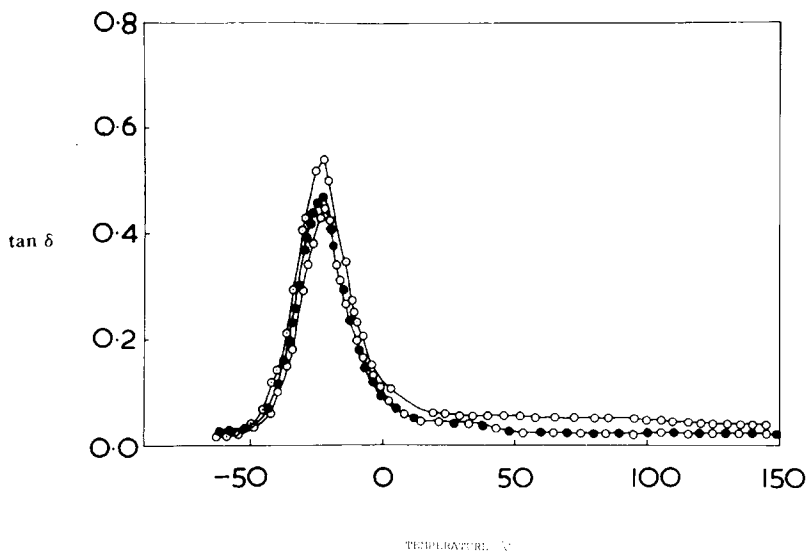


Fig. 6. $\tan \delta$ vs temperature curves for Nordel 1560 (○), Intolan 260 (●), and Royalene 1812 (⊙). Crosslinked samples.

found that the degree of crystallinity was somewhat variable between supposedly identical samples being apparently very sensitive to the processing conditions. However, it is also true to say that it is difficult to measure with precision low levels of crystallinity in polymers. The Nordel 1560 sample was the most crystalline at around 17%, while the Keltan 778 sample was at most only 2% crystalline. To ensure sampling uniformity, all test pieces for TMA, DSC, and dynamic mechanical testing were taken from the same area of a particular sheet, and the sheets of all six materials were prepared with great care under, as nearly as possible, the same conditions. Even when differences in the crystallinity level for individual sheets of a particular rubber were observed, the rank order of the six samples in Table II did not change. The lack of complete correlation between crystallinity ranking and the blockiness factor is thought likely to arise because certain samples have a significant number of relatively short blocks, which are not readily incorporated in crystallites.¹²⁻¹⁴

It is clear from Table III that within experimental error both the 100% modulus and V_L decrease, as would be expected, as the level of crystallinity decreases.

Figures 1-3 and Table IV present the results of both TMA and DSC investigations on the virgin polymers. It is immediately clear that in both types of

TABLE IV
TMA and DSC Transition Data

Material	TMA		DSC	
	T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)
Nordel 1560	-49	62	-40	51
Intolan 260	-38	56	-44	49
Royalene 1812	-46	40	-46	46
Vistolan 3708	-44	44	-49	42
Intolan 255	-43	44	-43	—
Keltan 778	-42	44	-50	41

TABLE V
Rheovibron T_g and $\tan \delta_{\max}$ Data for Both the Virgin and the Crosslinked Samples

Material	Virgin		Crosslinked	
	T_g ($^{\circ}\text{C}$)	$\tan \delta_{\max}$	T_g ($^{\circ}\text{C}$)	$\tan \delta_{\max}$
Nordel 1560	-24	0.35	-22	0.45
Intolan 260	-20	0.38	-23	0.47
Royalene 1812	-25	0.47	-22	0.54
Vistolán 3708	-21	0.41	-24	0.64
Intolan 255	-22	0.47	-21	0.60
Keltan 778	-28	0.81	-26	0.80

investigation a glass transition (T_g) and a crystalline melting transition (T_m) are observed. In the TMA experiments the position of the T_g does not change very markedly or in any systematic fashion from sample to sample. This is also the situation for the T_g values determined by DSC. However, both techniques show that crystalline melting occurs at a higher temperature for the more crystalline samples, as the values for both Nordel 1560 and Intolan 260 are significantly different from those of the other materials.

The TMA thermograms show little indication, except that for Intolan 260, of any premelting of small, imperfect crystallites, but the DSC experiments do exhibit such evidence. Nordel 1560 shows only a melting endotherm, but Intolan 260 (2°C) and to a lesser extent Royalene 1812 (30°C) have premelting regions. The DSC thermogram for Intolan 255 is complex in the melting region, which precludes the determination of a reliable T_m value.

TMA and DSC thermograms were not obtained for the peroxide crosslinked samples, but x-ray evidence indicated a significant reduction in the levels of crystallinity.

In Figures 4 and 5, which show $\tan \delta$ vs temperature data for all six polymers, it is clear that the glass transition occurs at a temperature that lies between those

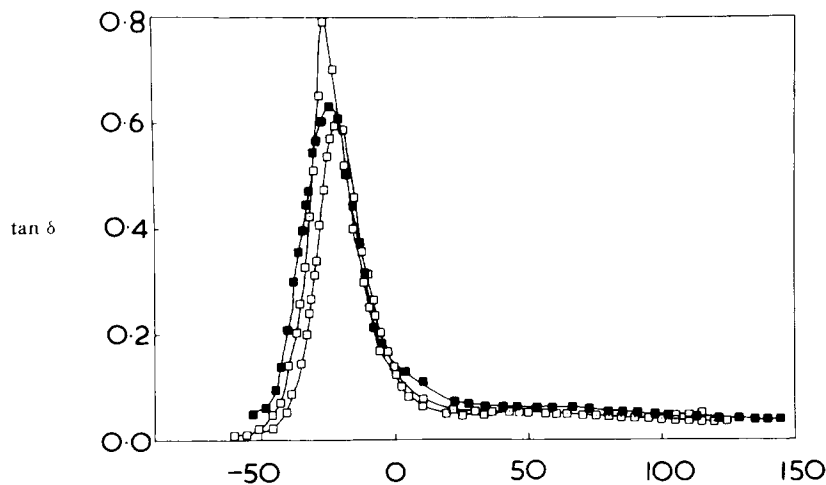


Fig. 7. $\tan \delta$ vs temperature curves for Vistolán 3708 (■), Intolan 255 (□), and Keltan 778 (○). Crosslinked samples.

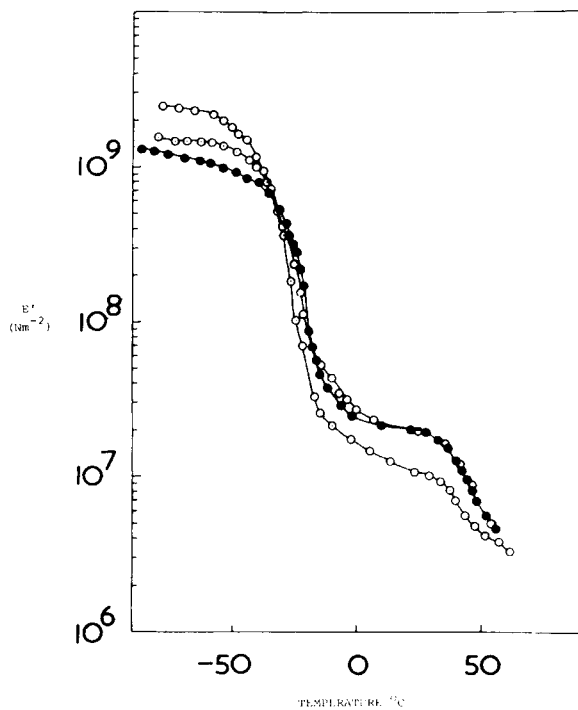


Fig. 8. Storage modulus (E') vs temperature curves for Nordel 1560 (○), Intolan 260 (●), and Royalene 1812 (○).

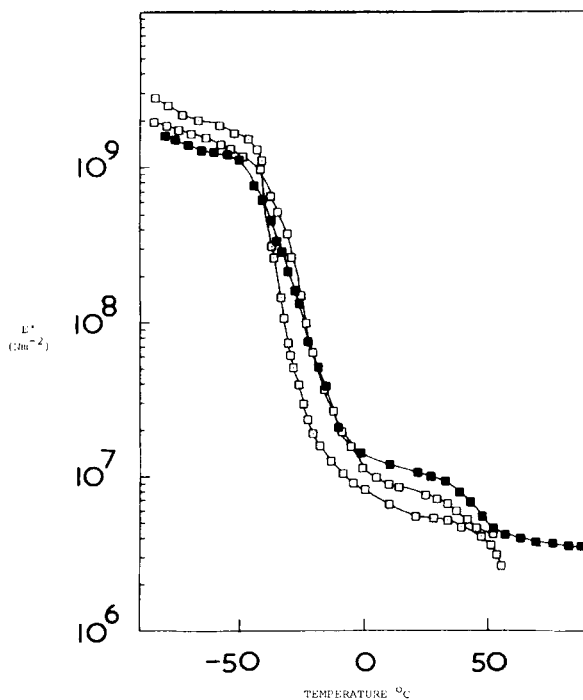


Fig. 9. Storage modulus (E') vs temperature curves for Vistolan 3708 (■), Intolan 255 (□), and Keltan 778 (□).

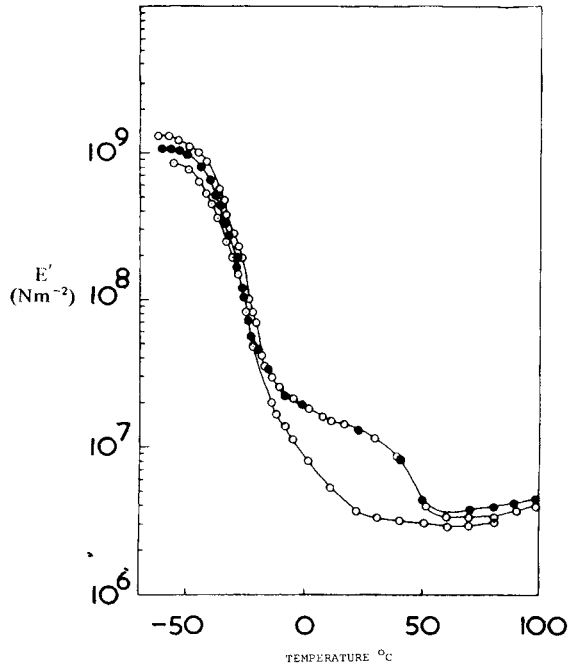


Fig. 10. Storage modulus (E') vs temperature curves for Nordel 1560 (\circ), Intolan 260 (\bullet), and Royalene 1812 (\circ). Crosslinked samples.

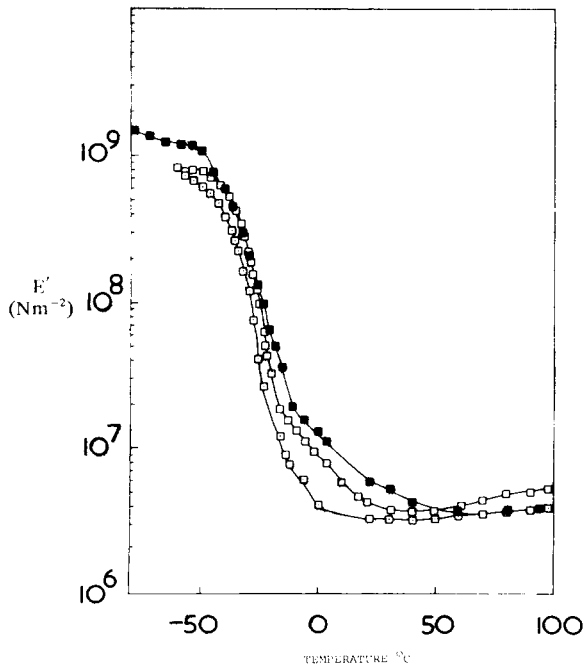


Fig. 11. Storage modulus (E') vs temperature curves for Vistolan 3708 (\blacksquare), Intolan 255 (\square), and Keltan 778 (\square). Crosslinked samples.

of the homopolymers, but is much closer to the T_g of polypropylene than would be predicted by the simple equations¹⁵ which are often applicable to copolymers.^{14,16-18} The T_g did not vary (Table V) in any regular way as the ethylene/propylene ratio changed. However, there is, as would be expected, a more or less systematic increase (Table V) in the maximum value of $\tan\delta$ ($\tan\delta_{\max}$) as the level of crystallinity changes. It is also noted that for all six samples, the $\tan\delta$ -temperature dispersions are narrow, indicating at least a significant degree of compatibility between the two major comonomers.

In this work the temperature was not taken low enough to detect the Schatzki type of motion,¹⁹ which would be expected in such substantially amorphous hydrocarbon polymers. The virgin EPDM rubbers became too soft to handle in the dynamic mechanical apparatus at around 60°C.

Figures 6 and 7 show the equivalent data for the peroxide vulcanized samples. Here again the $\tan\delta$ dispersions are narrow with the T_g 's not being significantly different (Table V) from those of the corresponding uncrosslinked samples. It is thought that the increase in crosslinking by the peroxide is balanced by the already-mentioned decrease in crystallite crosslinking, consequently leaving the T_g 's relatively unaffected. Table V also shows that $\tan\delta_{\max}$ is increased on crosslinking in all cases except for the initially virtually noncrystalline Keltan 778. This is again ascribed to the observed decrease in the overall degree of crystallinity on crosslinking. Only in the Keltan 778 sample is the crystallinity level initially so low as not to influence $\tan\delta_{\max}$. The $\tan\delta$ vs temperature curves for the crosslinked Nordel 1560 and Intolan 260 samples (Fig. 6) show a slight drop at the crystalline melting point of around 45°C. For the other samples where the levels of crystallinity are distinctly lower melting was not detected by such a change in $\tan\delta$, which requires that the dynamic loss modulus (E'') decreases more rapidly than the dynamic storage modulus (E'). All the vulcanized samples show the expected extended rubbery plateau (Figs. 6 and 7) with $\tan\delta$ virtually unchanged up to around 150°C, at which temperature the experiments were concluded.

The dynamic storage moduli curves are shown for the virgin and the crosslinked samples in Figures 8-11. The glassy moduli of the virgin samples lie between 1 and 3×10^9 N m⁻² with no observable trends as far as ethylene/propylene ratio and crystallinity are concerned. However, the rubbery moduli of the lower ethylene/propylene ratio materials are somewhat lower than those of Nordel 1560, Intolan 260, and Royalene 1812, which have a higher ethylene content and are more crystalline. The softening of the virgin samples at around 50°C coincides with the crystalline melting transitions.

The reduction in the degree of crystallinity on peroxide vulcanizing causes the glassy moduli (Figs. 10 and 11) of the crosslinked materials to be somewhat lower than those of the virgin samples. Only the E' vs temperature curves of Nordel 1560 and Intolan 260 exhibit crystalline melting. This occurs in both cases at around 40°C.

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