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EFFECT OF CROSS-LINKING ON THE CRYSTALLIZATION AND FUSION BEHAVIOUR OF POLYETHYLENE–ETHYLENE PROPYLENE DIENE TERPOLYMER BLENDS

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ABSTRACT

The effect of blend ratio and cross-linking in ethylene propylene diene terpolymer (EPDM) and polyethylene (PE) blends on the crystallization and fusion processes of PE were studied. The cross-linking was varied by varying the level of dicumyl peroxide (DCP) from 0.5 to 5 parts. The melting point, percentage crystallinity, heat of fusion and entropy of fusion all decrease with increasing EPDM content in the blend composition. All these properties are further reduced on cross-linking and the extent of reduction depends on the amount of DCP used and the blend composition. A relation between the melting point reduction and the high-temperature modulus was developed in order to predict the properties and the effect of cross-linking on the crystallization behaviour of the blend systems.

INTRODUCTION

Rubber–plastics blends have gained considerable importance in recent years because of their ease of processing, low cost and favourable physical properties. Of the large number of blends reported [1–3], ethylene propylene diene rubber (EPDM) and polyolefin blends find the largest number of applications. Recently, the authors have been attempting to exploit these blends with suitable modifications for the insulation of low-voltage cables to extra-high-voltage cables, hot-water pipes, etc. These applications require cross-linking of the EPDM phase in EPDM–PE blends. Cross-linking of polyethylene (PE) also improves its hot deformation properties and continuous operating temperature and short circuit temperature when applied in cable applications. Dynamically vulcanized thermoplastic rubber resulted in an improved high-temperature modulus [1].

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Several workers have reported on the properties of EPDM–PE and EPDM–PP blends [4,5]. Blends of low-density polyethylene and high ethylene content EPDM rubber show tensile synergism. Modification of polyolefins for better impact properties by using EPDM rubber has also been reported [3]. The effect of cross-linking on the properties of EPDM–PE blends has not received much attention, although it is well known in the area of rubber technology that all the technical properties of these blends are guided by cross-link density [1].

In general, the effect of blending EPDM with PE as well as the effect of its cross-linking on crystallization and the fusion process of PE are of relevance to the understanding and characterization of the cross-linked PE–EPDM blends. Of particular interest is the effect of cross-linking and blend composition on the crystallization process through its diffusional mobility, nucleation and growth. Most of the efforts expended in the past have been aimed at studying the influence on the mechanical properties of the cross-linking PE by various peroxides [6–8]. Studies on the influence of cross-linking, crystallization, structural and fusion studies of PE have been done by Kao and Philips [9] and de Boer and Pennings [10].

In the present paper the effects of blend ratio and degree of cross-linking on the crystallization, fusion and melting of PE–EPDM blends are reported.

EXPERIMENTAL

Materials

Low density polyethylene (LDPE) (Hanyang polyethylene, Hanyang Chemical Corporation) of density 0.915 g cm^{-3} and melt index 2.0 g (10 $\mathrm{min})^{-1}$ (ASTM D1238), ethylene propylene cyclopentadiene terpolymer (Keltan 520 of DSM) and Dicup R (99% dicumyl peroxide (DCP), of Hercules, Inc.) were used.

Blend preparation and DCP mixing

Blends of PE and EPDM were prepared in a Brabender plastic order (PLE-330) using a cam-type mixing head (N5OH) at a temperature of 115 °C, DCP was mixed in the Brabender chamber. Finally, each mix was refined through tight nip of 6 × 12 in two roll mill set at a temperature of 115 °C and sheeted out to 0.5-mm thickness. The compositions of the binary blends are listed in Table 1. Six different levels of peroxide were used for each blend composition.

TABLE 1

Formulation of the blends

	Blend					
	I	II	III	IV	V	VI
PE	100	80	60	40	20	–
EPDM	–	20	40	60	80	100
DCP	0.5, 1, 2, 3, 4, 5	0.5, 1, 2, 3, 4, 5	0.5, 1, 2, 3, 4, 5	0.5, 1, 2, 3, 4, 5	0.5, 1, 2, 3, 4, 5	0.5, 1, 2, 3, 4, 5

Differential scanning calorimetry

A Mettler DSC-20 of a TA-3000 system with a TC-10 A microprocessor was used throughout the study. A normal calibration procedure with standard material (indium) was used. The heating rate was 10 °C min^{-1} for the fusion studies.

Determination of high-temperature modulus

The modulus was determined at 130 °C at a rate of 10 cm min^{-1} jaw separation using a dumbbell specimen (ASTM-D 412-80) in a Zwick UTM (model 1445).

Determination of degree of swelling (swelling ratio)

Previously weighed samples were allowed to swell in xylene at 120 °C for 24 h to reach swelling equilibrium, after which the test pieces were dried on the surface and rapidly weighed into stoppered bottles. The samples were then dried to constant weight in a vacuum oven at 60 °C. The weight difference between the swollen and dry test piece gave the weight of the solvent, the value of which divided by the density of solvent gave v_1. In the same way, v_2 was obtained from the weight and density of the dry test piece. The degree of swelling or swelling ratio q was calculated as

$$q = \frac{v_2}{v_1 + v_2}$$

RESULTS AND DISCUSSION

Non-isothermal melting behaviour

Typical DSC traces of a few PE–EPDM compositions with the same peroxide level are shown in Fig. 1. The traces show that the melting (peak)

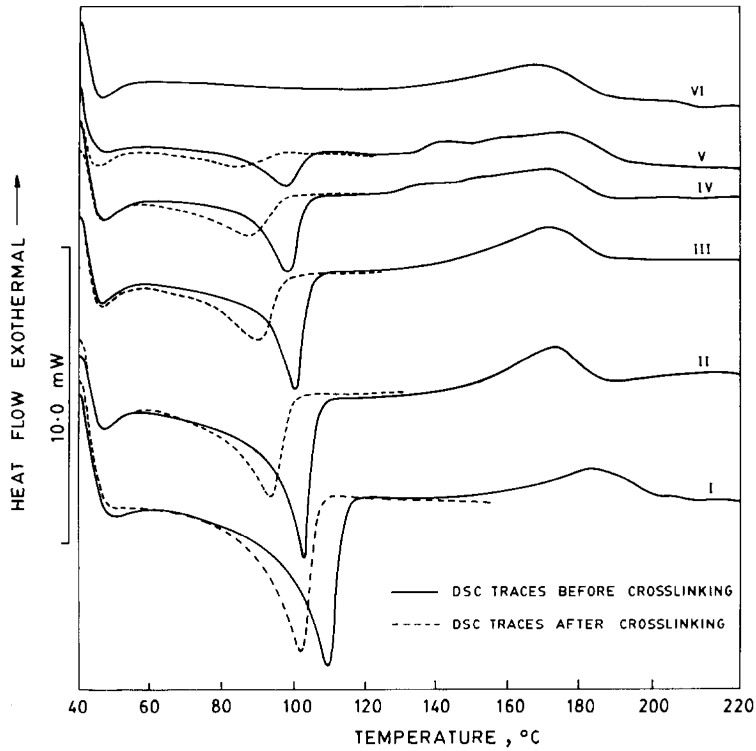

Fig. 1. Typical DSC traces showing the effect of cross-linking and blend composition on the melting characteristics of PE in PE–EPDM blends. **I**, PE 100; **II**, PE 80 + EPDM 20; **III**, PE 60 + EPDM 40; **IV**, PE 40 + EPDM 60; **V**, PE 20 + EPDM 80; **VI**, EPDM 100.

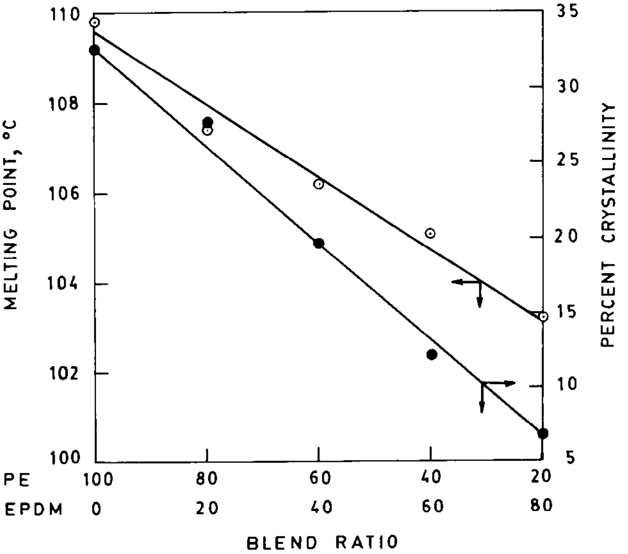

Fig. 2. Effect of blend ratio on the melting point and percentage crystallinity of PE in the PE–EPDM blends.

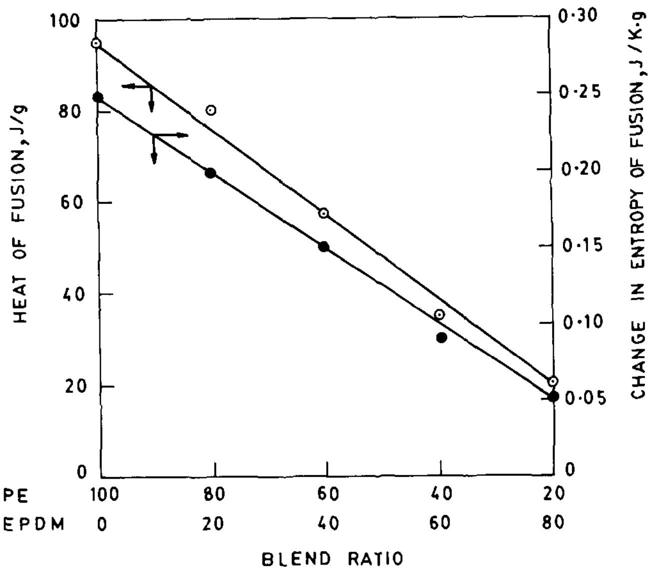

Fig. 3. Effect of blend ratio on the heat of fusion and entropy change on fusion of PE in PE–EPDM blends.

temperatures and the area under the melting endotherms decrease gradually with increasing EPDM content of the blends. Plots of the melting point and the percentage crystallinity of the different PE–EPDM blends versus blend compositions are shown in Fig. 2. Both the melting point and the percentage crystallinity decrease linearly with increasing EPDM content of the blends. Lindsay et al. [4] have reported the partial miscibility between melts of LDPE and EPDM. The depression in the melting point (Figs. 1 and 2) may arise from morphological changes such as imperfections in the crystals and a reduction in lamellar thickness as observed for other blends [11,12]. The partial structural similarity between PE and EPDM may cause partial miscibility and a decrease in the melting point and percentage crystallinity [13].

From the linear plot of melting point versus blend ratio it is possible to determine with reasonable accuracy the composition of the blend by observing its melting point. Similarly, plots of the heat of fusion and the entropy change on fusion versus blend ratio (Fig. 3) show linear dependence. The heat of fusion decreases with decreasing PE content of the blends. The results are similar to those reported for *i*PP/HDPE/EPDM blends [14].

Effect of cross-linking on crystallinity and heat of fusion

The effect of cross-linking on the melting point, percentage crystallinity, enthalpy of fusion and entropy of fusion using various levels of DCP were

TABLE 2

Results of the effect of cross-linking by various levels of DCP content on melting point, heat of fusion, crystallinity and entropy of fusion of the PE-EPDM blend **II**

Sample no.	Composition		Melting point (° C)			Heat of fusion (J g^{-1})			Crystallinity (%)			Entropy (J K^{-1} g^{-1})		
	PE-80+ EPDM	DCP	Initial	After curing	Differrence	Initial	After curing	Difference	Initial	After curing	Difference	Initial	After curing	Difference
IIA	20	0.5	107.4	102.9	4.5	80.2	69.7	10.5	27.9	24.0	3.9	0.200	0.185	0.015
IIB	20	1.0	108.2	102.6	5.6	79.9	66.6	13.3	27.6	23.0	4.6	0.210	0.177	0.033
IID	20	2.0	108.2	100.6	7.6	75.6	61.0	14.6	26.1	21.0	5.1	0.198	0.163	0.035
IIF	20	3.0	107.8	98.0	9.8	73.7	53.1	20.6	25.4	18.3	7.1	0.194	0.143	0.051
IIH	20	4.0	107.6	95.4	12.2	76.3	49.1	27.2	26.3	16.9	9.4	0.200	0.133	0.067
IIJ	20	5.0	106.6	92.0	14.6	74.7	43.7	31.0	25.7	15.1	10.6	0.197	0.120	0.077

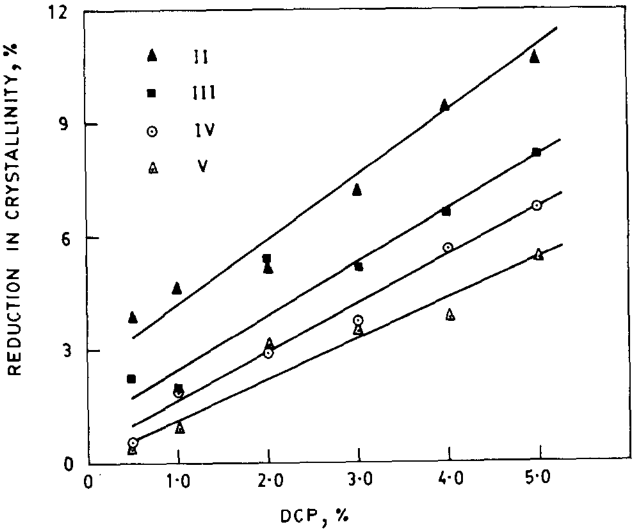

Fig. 4. Effect of DCP content on the reduction in crystallinity of PE in PE–EPDM blends **II–V**. For blend compositions see legend to Fig. 1.

determined and the results for system **II** (PE : EPDM = 80 : 20) are presented in Table 2.

Plots of the reduction (depression) in the percentage crystallinity versus DCP content and the reduction in the heat of fusion versus DCP content are presented in Figs. 4 and 5, respectively. It can be seen from Fig. 4 that the reduction in percentage crystallinity increases linearly with DCP content or

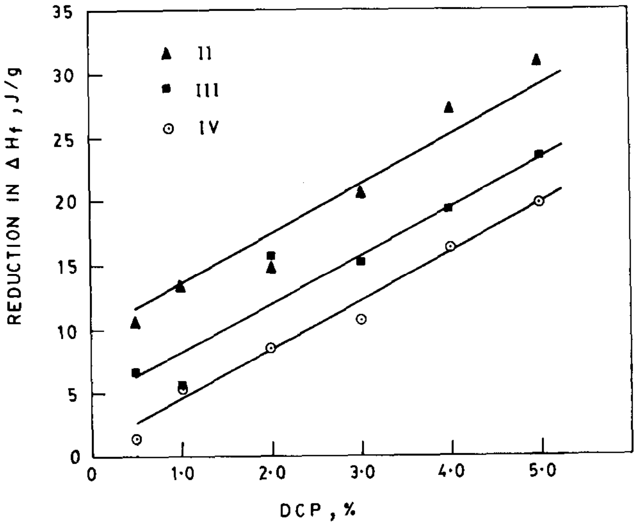

Fig. 5. Effect of DCP content on the reduction in ΔH_f of PE in PE–EPDM blends **II–IV**. For blend compositions see legend to Fig. 1.

degree of cross-linking. However, the slopes of the straight lines decrease with increasing EPDM content, revealing that the effect of cross-linking on reducing the crystallinity becomes less pronounced with increasing EPDM content in the blends. This effect is due to the lower initial crystallinity of the blends. Figure 5 shows that the reduction in the heat of fusion on cross-linking also increases with increasing DCP content. However, unlike the effect on crystallinity, here the effect of cross-linking on the reduction in the heat of fusion is independent of blend ratio as revealed by the parallel lines for the three blends. The other two systems also behave in the same way. Similar observations have been reported for the cross-linking of polyethylene [9,10].

Effect of cross-linking on melting point

The results of the effect of cross-linking on the melting point are presented in Fig. 6 as a plot of the melting point reduction on the cross-linking of different blends versus percentage DCP. The plot shows that the reduction in the melting point increases directly with DCP content or degree of cross-linking up to at least 4 parts of DCP. When the DCP content is increased above 4 parts the effect on melting point reduction is not so significant. This is due to the fact that the cross-linking reaction is completed with 4 parts of DCP.

It is, however, interesting to note that the reduction in the melting point with reduced DCP content is strongly dependent on the blend ratio. All the

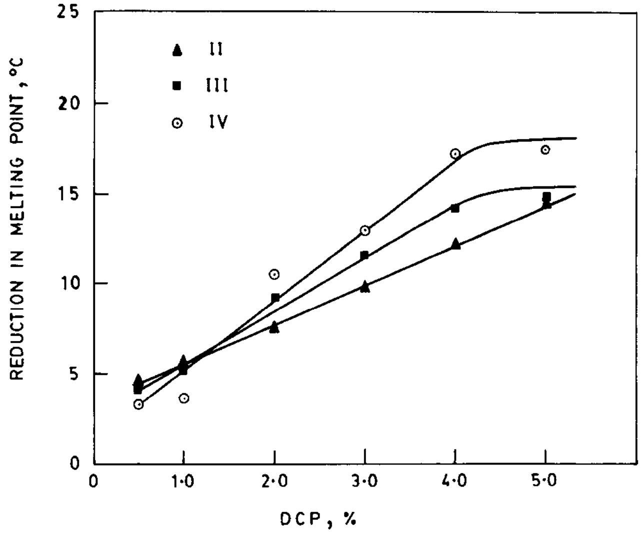

Fig. 6. Effect of DCP content on the reduction in the melting point of PE in PE–EPDM blends **II–IV**. For blend compositions see legend to Fig. 1.

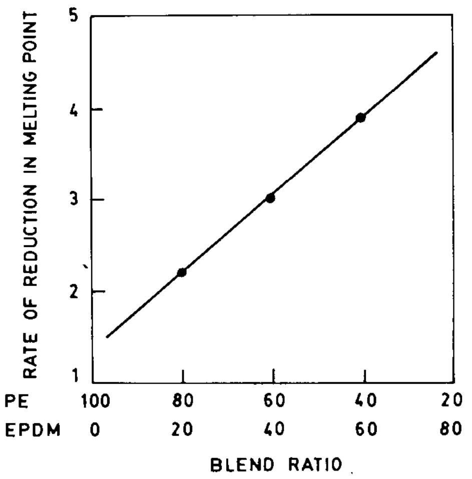

Fig. 7. Effect of blend ratio on the rate of reduction in the melting point.

blends studied show the same trend. This rate of reduction in melting point is also a function of the blend ratio (Fig. 7): with higher EPDM content there is a large reduction in the rate.

The peak (melting) temperature designates the temperature at which the bulk of the crystal melts [15]. Due to a high degree of branching, LDPE forms thin crystals even before cross-linking occurs, which is further reduced by blending with EPDM. Moreover, it is possible that by introducing cross-links, although in amounts smaller than the branches, the C–C bonds which are formed between the molecular chains during cross-linking could reduce further (limit) the maximum thickness attainable such that no thickening is possible following the initial attachment of the polymer chain to the growing crystal by decreasing the molecular order of the system and molecular mobility in the melt. Another possibility is that the incorporation of cross-links into the system results in stress along the crystallizing chain which opposes the incorporation of additional members of the same chain and thereby limits the initial length of the chain that can be incorporated into the crystal and/or the extent of the thickening process [9]. Either way, the question remains as to how the melting-point reduction is related and varies with the blend ratio and degree of cross-linking. It has already been shown that the rate of decrease in the heat of fusion with DCP content is invariant for all the blend ratios studied. This suggests that the variation in the rate of reduction on the melting point must be caused by a change in the entropy of fusion. That such a variation can occur must be beyond question, but the problem lies in determining the exact relationship. Therefore, any change in the entropy of fusion with the level of cross-linking may be related to the variation in lamellar thickness.

Effect of cross-linking on the change of entropy of fusion

It is possible to calculate the change in the entropy ΔS of fusion at the observed melting point T_m with the consideration that the free-energy change at this point is zero. Thus

$$\Delta H_f = T_m \Delta S$$

$$\Delta S = \Delta H_f / T_m \qquad (1)$$

The results for the systems **II**–**IV** are plotted in Fig. 8 as a function of DCP content. It is clear that as the DCP content increases or the extent of cross-linking increases, the entropy of fusion of the cross-linked materials decreases and hence the differences between the entropy of fusion of the non-cross-linked and the cross-linked states increase. The observed trends might be caused by decreasing lamellar thickness, as incorporation of cross-links into the system would be expected to reduce the probability of entering $-CH_2$ groups into the lamellar during crystallization. Again the effect of cross-linking on the difference of entropy of fusion between non-cross-linked and cross-linked state shows a slight decrease (as seen from the decrease in slope) from systems **II** to **IV** (Fig. 8). Systems **I** and **V** also show a similar trend. Reduction in the entropy of fusion causes an increase in the melting point. Although the observation of a reduction in both melting point and entropy of fusion with cross-linking seems to contradict the above statement, the decrease in the change of entropy of fusion on cross-linking is well corroborated by the increase in the melting-point

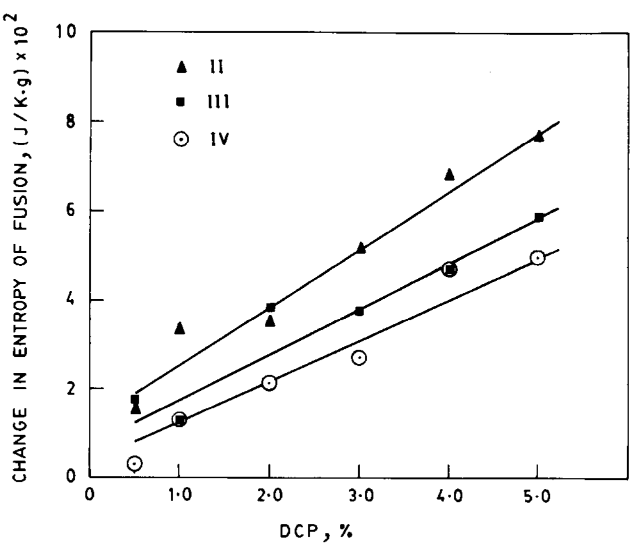

Fig. 8. Effect of DCP content on the change in entropy of fusion of PE in PE–EPDM blends **II**–**IV**. For blend compositions see legend to Fig. 1.

reduction for different blends when the change of enthalpy of fusion remains invariant with blend composition.

Relationship between degree of cross-linking and melting-point reduction

The melting-point reduction on cross-linking can be explained according to Flory [16,17] as the result of a reduction in the concentration of segments of a length suitable for crystallization, just as for the crystallization of co-polymers. Akana and Stein [18] derived an expression for the melting-point depression of the *trans*-1,4-poly(butadiene) network as

$$\frac{T_m^0 - T_m}{T_m T_m^0} = \left(\frac{R}{\Delta H_f}\right) K M_0 \frac{1}{M_c} \tag{2}$$

where T_m^0 and T_m are the melting point of the non-cross-linked and cross-linked networks, R is the molar gas constant, ΔH_f is the heat of fusion per monomer unit, M_0 is the molecular weight of the monomer unit, K is the number of monomer units excluded from the crystal per network chain and M_c is the molecular weight between cross-links.

De Boer and Pennings [10] used the following expression for ultra-high-molecular-weight polyethylene as

$$\frac{T_m^0 - T_m}{T_m T_m^0} = \frac{R}{\Delta H_f}(K\nu_c + 2\delta\epsilon) \tag{3}$$

where ν_c is the concentration of the intermolecular cross-link units, ϵ is the entanglement concentration (in mol dm^{-3}), and K and δ are the weight factors for the different types of chain units. However, for blend systems where the cross-linking efficiencies are different for the two polymers and the interfaces play a role in determining the properties of composites, it may not be relevant to calculate $1/M_c$ or ν_c due to lack of precise determination of the parameters. Therefore, by considering that above the melting temperature of poly(ethylene) the blend systems behave like a rubber network and follow the statistical theory of rubber-like elasticity, the elastic modulus (E) can be equated using ν_c. With this prediction, the stress–strain behaviour of the cross-linked blend system for simple extension is given by

$$f = 2A(\lambda - \lambda^{-2})(C_1 + C_2\lambda^{-1}) \tag{4}$$

where f is the force required to extend the sample to an extension ratio λ [19] and

$$C_1 = \tfrac{1}{2}\nu kT \tag{5}$$

or alternatively

$$C_1 = \tfrac{1}{2}\rho RT M_c^{-1} \tag{6}$$

where ν is the density of network chains per unit volume, M_c is the number

average molecular weight of the chain segments between adjacent cross-links, ρ is the density, k is Boltzmann's constant, R is the gas constant, and T is the absolute temperature.
Again

$$\frac{1}{M_c} = \frac{E}{3\rho RT} \tag{7}$$

where E is the elastic modulus.
Now, equating eqns. (5) and (6) and putting that value into eqn. (7) gives

$$\nu = E/3kT \tag{8}$$

However, if E is expressed in MPa and the cross-link density is expressed in terms of the molar cross-link density, i.e. moles of cross-link per unit volume (in mol dm^{-3}), then by dimensional analysis eqn. (8) becomes

$$\nu_c = \frac{E}{3kTN} \times 10^3 \tag{9}$$

where ν_c is the concentration of the intermolecular cross-linked units (in mol dm^{-3}) and N is Avogadro's number.

Therefore, the eqn. (3) can be written in the form

$$\frac{T_m^0 - T_m}{T_m T_m^0} = \frac{R}{\Delta H_f} C\left(\frac{E}{3kTN}\right) \times 10^3 \tag{10}$$

or

$$\frac{T_m^0 - T_m}{T_m T_m^0} = \frac{C}{3\,\Delta H_f T} E \times 10^3 \tag{11}$$

where C is a constant measuring the number of $-CH_2$ units excluded from crystallization per cross-linked unit, and ΔH_f, the heat of fusion per unit volume, is 2.5×10^5 J dm^{-3} [10].

A plot of $(T_m^0 - T_m)/(T_m^0 T_m)$ versus E, as presented in Fig. 9, gives a straight line passing through the origin with a positive slope and satisfying almost all the points of the different blend compositions. From this slope the value of C was obtained as 17 which implies that 17 $-CH_2$ units are excluded from participating in the crystallization per unit effective network. This number is very close to the reported value of 20 for ultra-high-molecular-weight polyethylene when cross-linked in melt, and 60 when cross-linked in solution [10]. For *trans*-1,4-polybutadiene the reported value is 10 [18].

Because of the zero intercept, the plot further proves that there is no such entanglement which may act as an effective cross-link. Moreover, it proves that although the rate of melting-point reduction increases with increasing EPDM/PE blend ratio, the number of $-CH_2$ units prevented from crystallizing per cross-link formation is constant, irrespective of blend composition

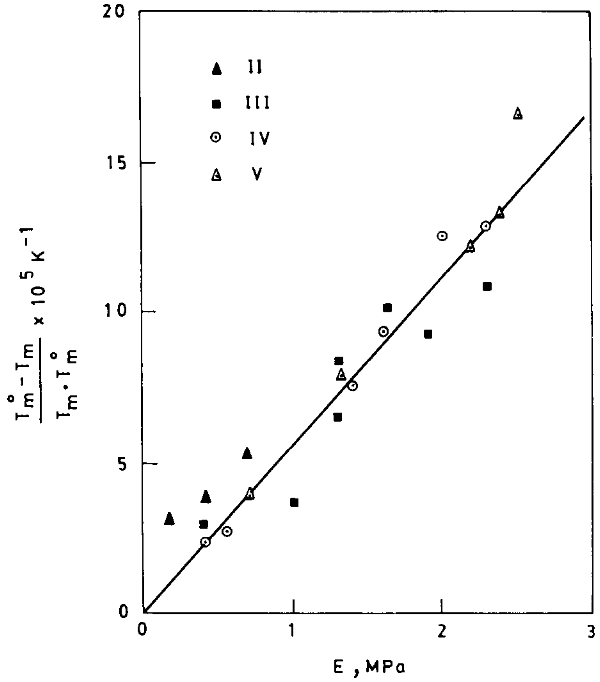

Fig. 9. Plot of $(T_m^0 - T_m)/T_m^0 T_m$ versus E for blends **II**–**V**. For blend compositions see legend to Fig. 1.

and degree of cross-linking. This also suggests that the increase in the rate of melting-point reduction with increasing EPDM content of the blends is due to the increasing degree of cross-linking as revealed by the increasing value

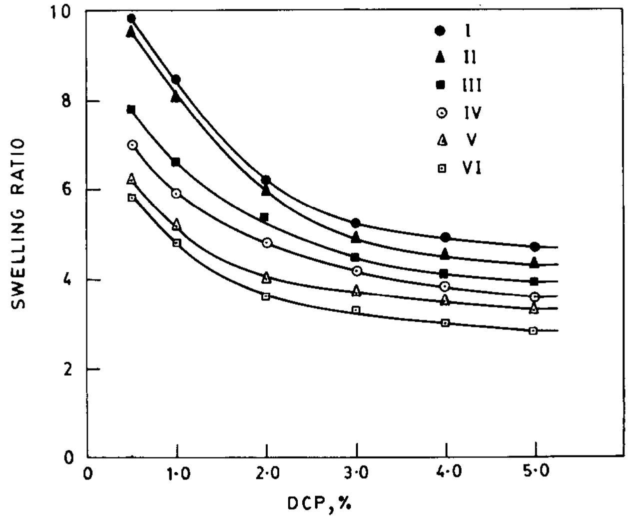

Fig. 10. The influence of DCP content on the swelling ratio for blends **I**–**VI**. For blend composition see legend to Fig. 1.

of modulus and decreasing value of swelling ratio (see below). This fact is also in agreement with the results observed from the effect of cross-linking on the change in the enthalpy and entropy of fusion.

Degree of cross-linking in PE–EPDM blends

The degree of cross-linking increases as the EPDM content of the blend increases, as revealed by the swelling measurement. Plots of the swelling ratio versus the DCP content of blends **I–VI** are presented in Fig. 10. It can be seen from these plots that as the EPDM/PE ratio increases the swelling ratio decreases, i.e. the degree of cross-linking increases. This increase in cross-linking is due to the presence of unsaturation in the EPDM which makes it more efficient for cross-linking.

CONCLUSIONS

The presence of EPDM reduces the heat of fusion, percentage crystallinity, melting point and entropy change on fusion of PE in PE–EPDM blends. Cross-linking of the blends further reduces the above properties significantly and the extent of the reduction depends on both the blend ratio and the degree of cross-linking. A relationship has been developed between the melting-point reduction and the high-temperature modulus, which could predict the degree of influence on the above properties by the insertion of a cross-link unit. The number of $-CH_2$ units excluded from crystallization per unit cross-link formation is 17 and the number is independent of blend composition and degree of cross-linking.

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