STUDIES ON CROSSLINKING OF EPDM-PE BLENDS BY THERMOANALYTICAL TECHNIQUES

Achintya K. Sen*, A. S. Bhattacharyya*, P. P. De** and Anil K. Bhowmick**+

*R & D CENTRE, FORT GLOSTER INDUSTRIES LTD (CABLE DIVISION), HOWRAH - 711310, INDIA
**RUBBER TECHNOLOGY CENTRE, INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR - 721302, INDIA

The effect of blend ratio and peroxide concentration on crosslinking characteristics of EPDM-PE blends were studied by Differential Scanning Calorimetry, Brabender plasticorder and Rheometer. Crosslinking of EPDM-PE blends follows first order reaction kinetics. The curing exotherm increases but activation energy decreases with increase in EPDM content in the blends. The same however increases with the increase in concentration of DCP upto a certain level, while the activation energy is almost independent of peroxide concentration. The cure rate increases whereas optimum cure time and energy consumption for curing decrease with increase in the EPDM-PE ratio. A method for determination of crosslinking efficiency in the case of blend systems was developed from high temperature modulus to predict the properties and the curing behaviour of the blends.

Recently, a large number of EPDM-PE blends is found to have potential to replace conventional material in cable insulation compound. For stability of the compounds cross-linking of the rubber phase in the blend is essential. Mainly organic peroxides have been used to induce crosslinks into PE via free radical formation [1-5]. Vulcanization of EPDM either by peroxide or sulfur is almost always being used. It is needless to say that the properties which are also dependent on the morphology and interaction between components will change with the introduction of crosslinks. For crosslinking of both EPDM and PE, peroxides are the most useful agent.

+ Author for correspondence.

Peroxides are also used for graft modification (funktionalization) of the PE-EPDM blends for a few applications. It is important to know fect the grafting process as well as crosslinking process. For example, the functionalizationof PE and EPDM through the peroxide initiated grafting of unsaturated monomers is often accompanied by crosslinking [6]. The effect of the concentration of the peroxide and blend ratio on crosslinking of PE-EPDM blends has not received much attention, although it is known in this field that all the technical properties of the blends are strongly dependent on the cure rate and degree of crosslinking [7, 8].

Most of the works done in the past have been aimed at studying the influence of crosslinking of PE by various peroxides on the mechanical properties [1-3] and crystallization and fusion properties [4, 5]. Recently, the authors have reported the effect of crosslinking on crystallization and fusion behaviour of PE-EPDM blends [9]. Braizer and Schwartz studied the Dicumylperoxide (DCP) induced crosslinking of EPDM and a few other elastomers by Differential scanning calorimetry [10]. Thermoplastic elastomeric composition based on poly-olefins - EPDM blends were made by dynamic vulcanization using either peroxide or sulfur-accelerator system, the properties of which were dependent on the degree of crosslinking of EPDM in the blends and its ratio [11-13]. Keller studied the influence of molecular structure i.e., both type and concentration of diene as well as the type of peroxide and coagent in EPDM vulcanization [14]. Both peroxide and sulfur vulcanization of EPDM have been described in details in the review articles by Loan [15] and Baldwin and Verstrate [16]. Varma *et al.* worked on HDPE/EPDM blends [17].

In the present work, we report an observation on the crosslinking of EPDM-PE blends using Differential scanning calorimetry, Brabender plasticorder and Rheometer. The effect of peroxide concentration and blend ratio has been included.

Experimental

Materials

Low density polyethylene (LDPE) - Hanyang polyethylene, Hanyang Chemical Corporation of density 0.915 $g \cdot cm^{-3}$ and melt index 2.0g$\cdot$(10 min)$^{-1}$ (ASTM D 1238), ethylene propylene dicyclopentadiene terpolymer (Keltan 520 of DSM) and Dicup R (99% dicumyl peroxide (DCP), of Hercules, Inc) were used.

Blend preparation and DCP mixing

The techniques of blend preparation and DCP mixing have already been described in the earlier communication [9]. Compositions of the binary blends are given in Table 1. Six different levels of DCP were used for each blend composition.

Table 1 Formulation of the blends

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

Differential scanning calorimetry

A Mettler DSC-20 of a TA-3000 system with a TC-10A microprocessor was used throughout the study. Calibration of the instrument was done by the standard material (Indium). Crosslinking was studied at the heating rate of 10 deg/min.

Determination of cure characteristics

Monsanto Rheometer R-100 and Brabender plasticorder PLE-330 with N-50 H mixing head were used for this study. Cure characteristics were determined at a temperature of 170° in both the cases. In the case of Rheometer the rotor oscillation was of $\pm3^\circ$ arc and in the case of Brabender plasticorder the rotor rpm was kept at 30 in each experiment.

Determination of gel fraction

Previously weighed samples (cut into a number of small pieces) were allowed to swell for extraction of the soluble portions in xylene at 120° for 24 h. The samples were then dried to constant weight in a vacuum oven at 60°. The percentage of the weight remained with respect to the initial weight gave the gel fraction.

Determination of high temperature modulus

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

Theory of kinetic analysis of the exothermic crosslinking reactions by DSC

The mathematical model generally used to describe the kinetics of a chemical reaction is [18]:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1}$$

where, $\frac{d\alpha}{dt}$ = rate of reaction, (sec^{-1})

    k = reaction rate constant, (sec^{-1})

    α = fraction reacted (growing from 0 to 1)

    n = order of the reaction

The temperature dependence of a reaction rate constant is given by the Arrhenius equation,

$$k = k_0 \cdot e^{-(E_A/RT)} \tag{2}$$

where,

    k_0 = pre-exponential factor

    E_A = energy of activation in J mole^{-1}

    R = gas constant.

Relation between DSC Signal and Reaction kinetics

The enthalpy of the system changes due to the decomposition of peroxide and subsequent crosslinking reactions. Every fraction of polymer matrix being crosslinked produces a certain change in enthalpy, which can be mathematically expressed as

$$d\alpha = \frac{dH}{\Delta H_{tot}} \tag{3}$$

where,

ΔH_{tot} = measured enthalpy of reaction in mJ

dH = total peak area

differentiating equation (3) with respect to time yields

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_{tot}}$$

or,

$$\dot{\alpha} = \frac{\dot{H}}{\Delta H_{tot}} \tag{4}$$

Thus the rate of reaction is directly proportional to DSC signal. From the proportionality of the degree of conversion and the respective enthalpy change it becomes

$$\alpha = \frac{\Delta H_{part}}{\Delta H_{tot}} \tag{5}$$

and

$$(1 - \alpha) = \frac{\Delta H_r}{\Delta H_{tot}} \tag{6}$$

Where ΔH_r is the remaining area of the DSC peak. The pictorial demonstration is given schematically in Fig. 1.
Combination of Eqs (1) and (2) results
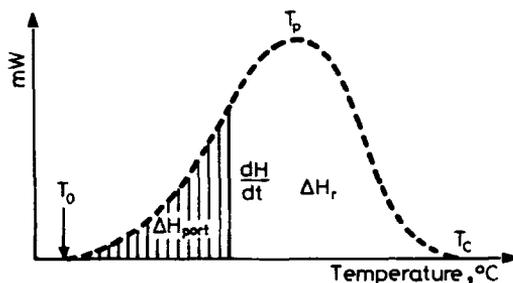
Fig. 1 DSC trace of exothermic crosslinking reaction at a linearly increasing temperature

$$\alpha = k_0 \cdot e^{-E_A/RT} (1-\alpha)^n \tag{7}$$

Substituting the value of α and $(1-\alpha)$ from Eqs (4) and (6) and converting into logarithmic form gives

$$\ln \frac{\dot{H}}{\Delta H_{tot}} = \ln k_0 + E_A \left(-\frac{1}{RT} \right) + n \ln \frac{\Delta H_r}{\Delta H_{tot}} \tag{8}$$

Kinetic analysis of the crosslinking reaction was done by multiple linear regression analysis of Eq. (8) through the inbuilt software.

Results and discussions

Non-isothermal curing behaviour

Typical DSC traces of a few PE-EPDM blend compositions with the same peroxide level have been plotted in Fig. 2, which show that the area under curing exotherm gradually increases with the increase in EPDM content of the blends. The effect of blend ratio on reaction exotherm, energy of activation and $\ln k_0$ (preexponential factor) was determined using various levels of DCP and the results for System III (PE:EPDM = 60:40) are presented in Table 2. The enthalpy change throughout the entire course of crosslinking reaction i.e., curing exotherm of the different blend systems have been plotted against the DCP content increases the exothermic heat of crosslinking reaction increases. All other systems follow the same trend.
The rate of increase in reaction exotherm with DCP content is highest for EPDM, which decreases gradually with the increase in the amount (proportion) of PE in the blends and becomes minimum for PE. However, the effect of blend ratio on reaction exotherm becomes more pronounced for the DCP content beyond 3 parts. This may be due to the fact that the same amount of DCP induces higher degree of crosslinking into the EPDM than PE. The rate of increase of reaction exotherm for system II reduces significantly with more than 3 parts of DCP probably due to the exhaustion of most of the crosslinkable reactive sites of PE. All the systems have exhibited the maximum rate of enthalpy change during crosslinking reactions at the temperature of $181 \pm 3°$.
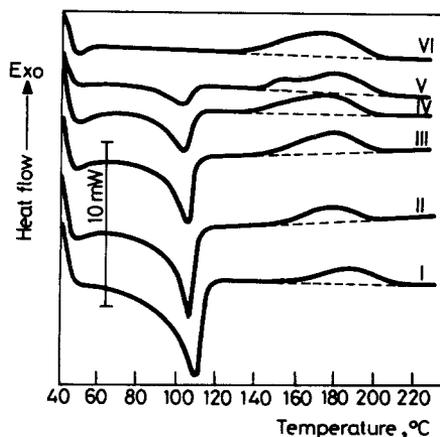
Fig. 2 Typical DSC traces showing the curing exotherm of different blend compositions.
I, PE 100; II, PE 80 + EPDM 20; III, PE 60 + EPDM 40; IV, PE 40 + EPDM 60;
V, PE 20 + EPDM 80; VI, EPDM 100

Effect of blend ratio on activation energy of curring

As obtained from the kinetic analysis, the activation energy of crosslink-ing reaction is almost independent of peroxide level for all the blend systems (Table 2). Similar observations were also reported by Braizer and Schwartz for NR and EPDM [10].

Table 2 Results of the effect of variation of DCP content on crosslinking reaction exotherm, energy of activation and $\ln k_o$ of the PE-EPDM blends III

Sample No.	Composition		Crosslinking reaction exotherm (H_{exo}),	Reaction order	Energy of activation,	$\ln k_o$
	PE-60 EPDM	DCP	J/g		kJ/mole	
IIIA	40	0.5	13.1	1	116	25
IIIB	40	1.0	16.6	1	114	26
IIID	40	2.0	20.7	1	117	25
IIIF	40	3.0	35.6	1	123	29
IIIH	40	4.0	42.1	1	120	27
IIIJ	40	5.0	49.5	1	-	-

They have obtained the activation energy of EPDM as 140 kJ·mol^{-1} whereas the value in the present experiment is 105 kJ·mol^{-1}. This difference

in activation energy may be due to the difference in diene content as well as the structure of the diene in EPDM.

But the activation energy of crosslinking reaction is strongly dependent on the blend ratio. The variation of activation energy for crosslinking reaction with blend ratio is shown in Fig. 4. It is observed form Fig. 4 that the energy of activation decreases with increase in proportion of EPDM in the blend. However, energy of activation decreases marginally beyond PE/EPDM blend ratio of 40/60 probably due to the higher degree of crosslinking mainly in the EPDM phase.

Reaction order and pre-exponential factor

It is observed from the kinetic analysis that the crosslinking reaction of PE, EPDM and their blends in any proportion follow first order reaction kinetics when DCP is used as a lone curing agent. The reaction order is also independent of the level of DCP. Similar to the energy of activation the value of natural logarithm of pre-exponential factor ($\ln k_0$) for crosslinking reaction is independent of DCP level, but varies with the blend ratio. The variation of $\ln k_0$ with blend ratio is represented in Fig. 4. It is observed from the Fig. 4 that the value of $\ln k_0$ decreases with increase in the EPDM/PE ratio in the similar way as energy of activation.
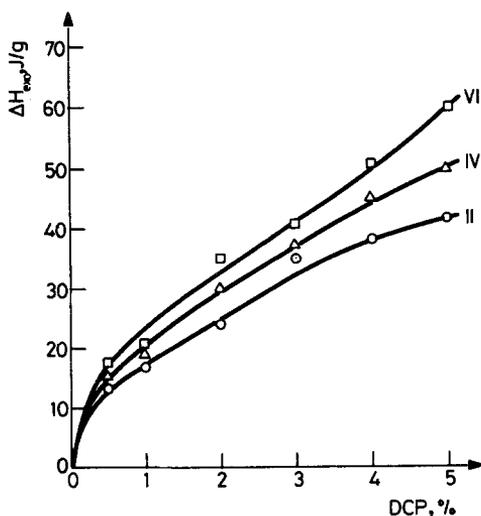

Fig. 3 Effect of DCP content on the curing exotherm of different EPDM - PE blend. For composition see legend to Fig. 1

Isothermal curing behaviour

The course of crosslinking reactions i.e., the degree of conversions from uncrosslinked (thermoplastic) state to the crosslinked network at different isothermal temperatures were calculated through the inbuilt software. The software used the data obtained from non-isothermal (dynamic) DSC of each individual experiment. The results as a plot of degree of conversion (α) with time at three different isothermal temperatures (160°, 170° and 180°)
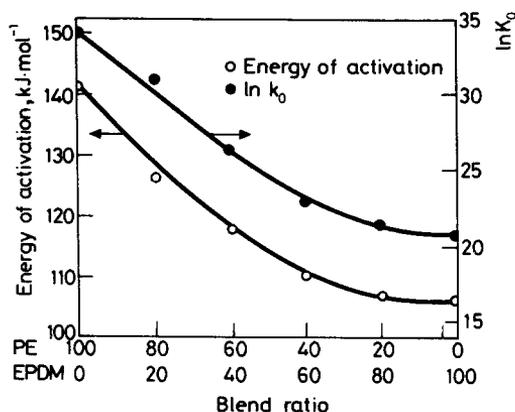

Fig. 4 Effect of blend ratio on activation energy and $\ln k_0$ of crosslinking reaction

are presented in Fig. 5 for the systems I, III and IV. All the systems contain the same level of DCP (3 parts). The figure shows that the degree of conversion at a particular time is always higher for that system which contains higher amount of EPDM. This means that the rate of conversion at any isothermal temperature increses with the increase in EPDM/PE ratio. All other systems also follow the similar trend. This variation in rate of conversion is in line with the results observed in Fig. 3 that there are higher change in enthalpy for the systems which have higher EPDM/PE ratio. This higher rate of conversion is also in agreement with that of lower energy of activation for these systems (Fig. 4). It is also observed from Fig. 5 that the rate of conversion for all the systems increases with the isothermal curing temperature.
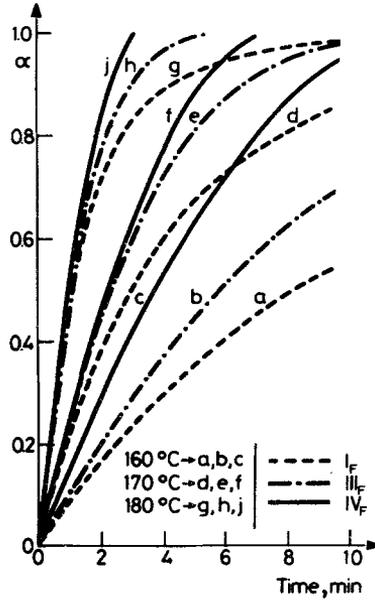
Fig. 5 Plot of DSC traces showing extent of crosslinking reaction *vs.* time at different isothermal temperatures. For blend compositions see legend to Fig. 1. Suffix F denotes that compositions contain 3 parts of DCP

Rthometric studies of isothermal cure behaviour

Rthometric traces as a torque versus time of a few systems at an isothermal temperature of 170° are shown in Fig. 6. All the systems contain the same level of DCP (2 parts). Here it is clearly observed from Fig. 6 that the torque development (which is a measure of crosslink density) and cure rate increase whereas scorch time and cure time decrease with increase in EPDM/PE ratio. This is true for all the systems. Traces of systems I and II are ommitted from this Figure as it is not worthy to compare these systems which are thermoplastic in nature and measured at ±5° arc. These rheometric results are almost similar in behaviour with that observed in the plot of α versus t (Fig. 5) obtained from DSC. The effect of variation of DCP level on curing of the different blend systems were also studied. Rheometric curves of system IV (PE:EPDM = 40:60) with various levels of DCP are shown in Fig. 7. Figure 7 shows that the torque development and rate of cure increase with the increase in the amount of DCP whereas the scorch

time and optimum cure time decrease. Similar trend is also observed for other systems. Rheometric studies of a few compositions of the system IV and VI were also carried out at different isothermal temperatures. It was found that scorch time and optimum cure time decrease whereas cure rate increases with the increase in curing temperature, similar in line with the observation of Fig. 5.
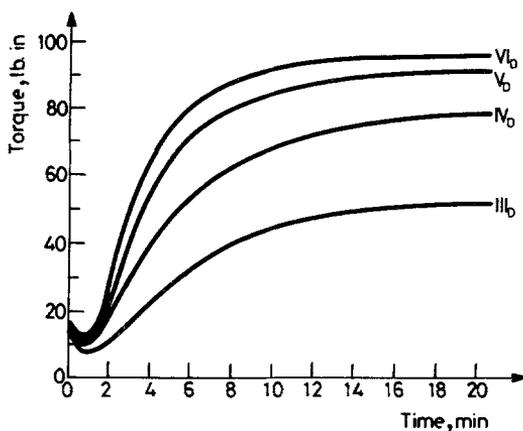

Fig. 6 Typical Rheometric traces of different blend composition showing torque development during the course of crosslinking reaction. For compositions see legend to Fig. 1. Suffix D denotes that compositions contain 2 parts of DCP

Dynamic curing behaviour and mechanical energy for crosslinking

For studying the cure characteristics of PE, EPDM and its blends under dynamic conditions, crosslinking of a few compositions (of all the systems) was carried out in the Brabender mixing chamber. The cure behaviour is shown inf Fig. 8 by a plot of torque development during the course of crosslinking reactions versus time. It is observed form Fig. 8 that with the increase in EPDM/PE ratio in the blends crosslinking rate has been increased considerably. This result is in line with that found in DSC experiment (Fig. 5) and rheometric studies (Fig. 6). As expected the scorch time and optimum cure decrease with the increase in proportion of EPDM in the blends. Scorch time and optimum cure time are calculated as time corresponding to 2 unit torque rise and 90% of maximum torque rise respectively. Figure 8 also shows that on increasing the DCP level from 1 part to

3 parts the cure rate increases significantly with the decrease in cure time and scorch time. All other compositions studied show similar type of behaviour when crosslinked under dynamic conditions.
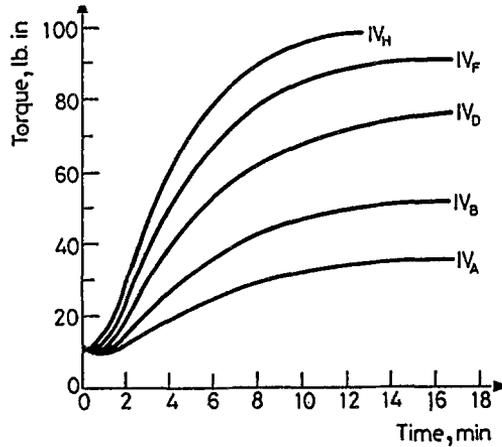

Fig. 7 Typical Rheometric traces of composition IV (PE-40 + EPDM 60) showing the variation of core characteristics with DCP contain

The consumption of mechanical energy for crosslinking has been calculated by integrating the area under torque and multiplying it by the angular velocity of the rotor. Mathematically this may be expressed [19].

$$E = M \cdot t \cdot w \qquad (9)$$

where, E = Mechanical energy
M = torque (N, m)
t = time, (min)
w = angular velocity (min^{-1})
= 2π rpm of the rotor (min^{-1})

The mechanical energy required for crosslinking of different blend systems with different levels of DCP is plotted in Fig. 9. Figure 9 shows that energy consumption drops significantly on addition of EPDM to PE upto the blend ratio of PE:EPDM = 60:40. This may be due to the increaed rate of crosslinking reaction imparted by the presence of EPDM. However, on further decrease in PE/EPDM ratio the energy consumption increases mar-
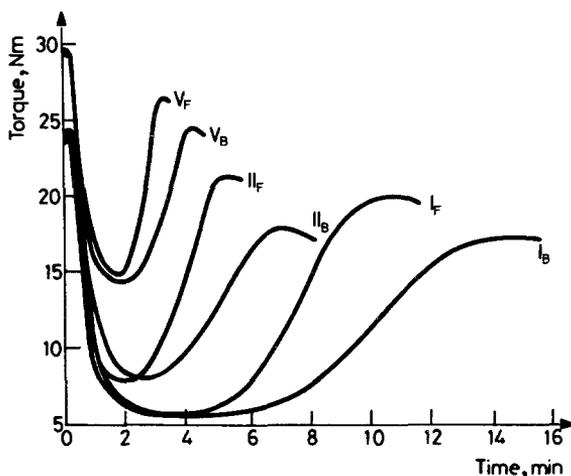
Fig. 8 Typical Brabender traces of dynamic crosslinking of different blend composition. For compositions see legend to Fig. 1. Suffix B and F denote that composition contains 1 and 3 parts of DCP respectively

ginally. This is because of higher crosslinking rate is off-set by the high initial viscosity and hence, higher minimum torque of these systems. It is also observed from Fig. 9 that energy consumption for crosslinking with 3 parts of DCP is considerably less than with 1 part of DCP for all the systems. Similar trend is observed also with other parts of DCP. This decrease in energy consumption with increase in DCP level may be due to the increase in cure rate with DCP levels.

Comparison of cure rate and optimum cure time

Cure rate and optimum cure time determined through three different techniques - Rheometer, Brabender Plasticorder and DSC of the Composition III_D are compared in Fig. 10. Cure rate has been calculated by the general formula $\dfrac{100}{t_{90} - t_2}$. For Rheometer and Brabender Plasticorder t_{90} and t_2 are the optimum cure time and scroch time while in the case of DSC t_{90} and t_2 are considered as the time corresponding to 90% and 20% conversion respectively. It is observed from the Fig. 10 that both cure rate and optimum cure time vary with the techniques of measurement. It is quite natural as the curing conditions are different for the three techniques. In Brabender Plasticorder shear force imparted on the material during cure is much higher
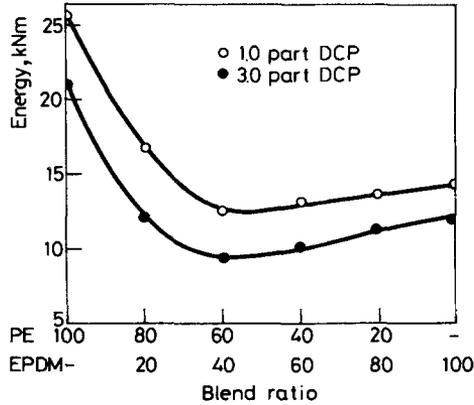
Fig. 9 Plot of energy consumption during the course of crosslinking reaction *vs.* blend ratio

compared to that of Rheometer. hence, in the case of Brabender plasticorder optimum cure time is lower and crosslinking rate is much higher than that obtained by Rheometer. In DSC sample size is very small and curing occurs in absence of mechanical shear and hence, cure time and cure rate are more similar to that of Rheometer.

Degree of crosslinking and cure efficiency

It is observed from the DSC, Rheometric and Brabender studies that crosslinking efficiencies are different for PE and EPDM as well as it also differs with blend compositions. Moreover, interfaces play a role in the case of blends and as such, it may not be relevant to calculate the degree of crosslinking from swelling measurement due to lack of precise determination of the parameters. In the earlier communication the authors deduced an equation relating melting point reduction and high temperature modulus of the said blends and also derived an expression relating modulus to crosslinking density [9] as

$$\nu_c = \frac{E}{3kTN} \cdot 10^3 \qquad (10)$$

where,
   ν_c = moles of crosslink per unit volume (mol·dm^{-3})

E = Elastic modulus (MPa)
k = Boltzmann's constant
T = Experimental temperature ($^\circ$A)
N = Avogadro's number

Crosslinking efficiency is calculated from the slope of the straight line obtained through the plot of ν_c vs. peroxide concentration [20]. For comparing crosslinking efficiencies of the blends $\dfrac{10^3 E}{3kTN}$ is plotted as a function of peroxide concentration in Fig. 11. It is observed from Fig. 11 that at a given concentration (except for high concentration) of DCP a straight line is obtained for each individual blend passing through the origin. The zero intercept of the straight line for zero concentration of peroxide proves that there is no trapped entanglements which can contribute as effective chain density, as observed in our earlier studies for the same blends [9]. The plot also shows that the slope of the straight lines is strongly dependent on the blend ratio and the value of the slope i.e., crosslinking efficiency increases with increase in the EPDM/PE ratio. All other systems studied show the similar trend. Crosslinking efficiency drops at higher concentration of DCP due to depletion of available reactive sites.
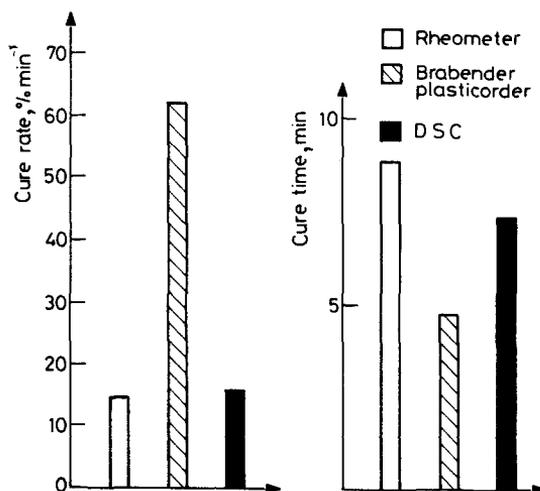

Fig. 10 Comparison of cure rate and cure time determined by different techniques
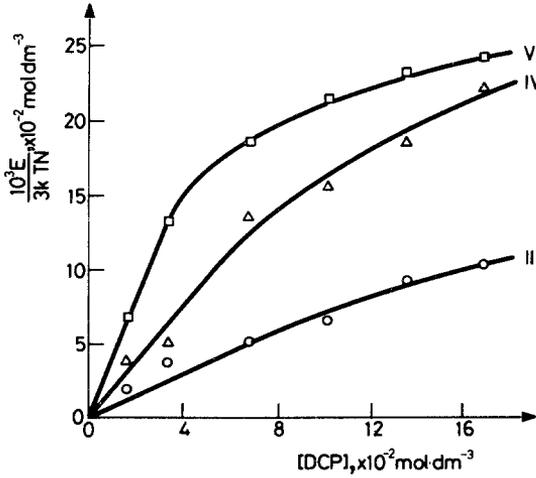
Fig. 11 Plot of $\dfrac{10^3 E}{3kTN}$ vs. DCP concentration of different blends
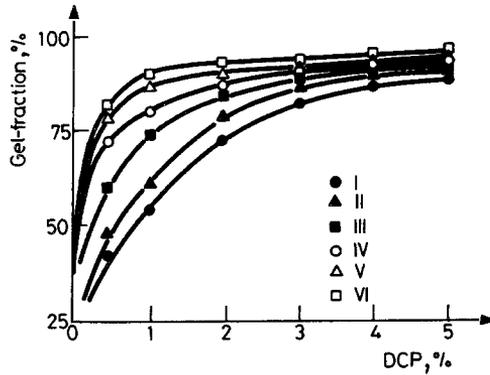

Fig. 12 The effect of DCP content on the gel fraction for different blends. For blend compositions see legends to Fig. 1

The crosslinking efficiency calculated from the slope is 0.7 for system II (PE/EPDM = 80/20), 1.9 for system IV (PE/EPDM = 40/60) and 4 for system V (PE/EPDM = 20/80). These results are in agreement with efficiencies of peroxide cure as unity for NR, 10 for Br, 12.5 for SBR [10] and 3.46 for EPDM containing termonomer 5-methylene 2-norborene [16].

The degree of crosslinking increases as the EPDM content of the blend increases which is also revealed by the gel fraction measurement. Plots of gel fraction versus DCP content of the blends I-VI are presented Fig. 12. It can be observed from these plots that as the EPDM/PE ratio increases, the gel fraction increases i.e., the degree of crosslinking increases. Similar results were obtained during earlier studies of swelling ratio of the same blends [9]. This increase in degree of crosslinking is due to the presense of allylic hydrogens in the EPDM which makes it more efficient for crosslinking.
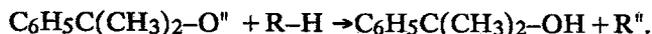
General mechanism and discussion

The general scheme of the crosslinking reaction initiated by thermal decomposition of DCP can be given in the following form:
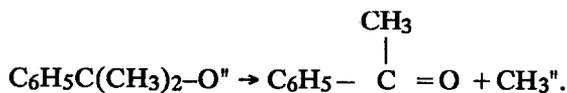I. Thermal decomposition of DCP

$$C_6H_5C(CH_3)_2 -O-O-C(CH_3)_2C_6H_5 \rightarrow 2\ C_6H_5C(CH_3)_2-O".$$
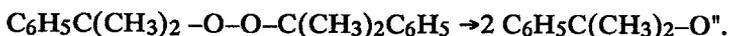
II. Hydrogen abstraction by cumyloxy radicals from polymer chains.

$$C_6H_5C(CH_3)_2-O" + R-H \rightarrow C_6H_5C(CH_3)_2-OH + R".$$

III. Disproportionation of cumyloxy radical to acetophenone and methyl radical

$$C_6H_5C(CH_3)_2-O" \rightarrow C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{C} =O\ + CH_3".$$

IV. Disproportionation of cumyl alcohol to α/methyl styrene and water

$$C_6H_5C(CH_3)_2-OH \rightarrow C_6H_5-C-\overset{\overset{\displaystyle CH_3}{|}}{C} =CH_2\ + H_2O.$$
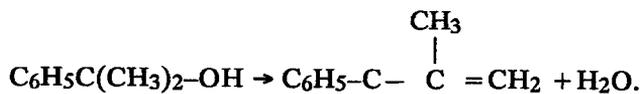
V. Hydrogen abstraction by methyl radical from polymer chain

$$CH_3 " + R-H \rightarrow CH_4 + R ".$$

VI. Combination of polymer chain radicals with formation of crosslink.

$$R'' + R'' \rightarrow R - R$$
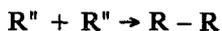
Here R– H represent either PE or EPDM chains.

Though it has been reported that increasing reaction temperature favours the disproportionation of cumyloxy radicals to methyl radicals, it does not alter the final chain radical (R'') concentration as CH3'' produced by disproportionation is also capable of H'' abstraction from polymer chain [10].

The total ethalpy change as obtained in DSC corresponds to the summation of the enthalpy changes of each reaction from I to VI. Reaction I i.e., homolytic scission of DCP to cumyloxy radicals may be considered as constant. The activation energy of DCP decomposition over the same scan rate is 133 kJ·mol^{-1} and in agreement with that obtained by others [10]. So, the remaining reactions may be considered as responsible for the variation in net enthalpy change with blend ratio.

As polyethylene is a saturated polymer, crosslinking demands the abstraction of hydrogen atoms from the polymer backbone and subsequent coupling of the polymer radicals. Ease of hydrogen abstraction from alkanes declines in the order tertiary > secondary> primary and the reactivities of the radicals produced are int he reverse order. But the observed selectivity will depend on relative population of the C–H bonds and their disposition in the molecule. In the case of EPDM the reactivity increases due to the presence of two active allylic hydrogen in the pendant diene components as shown in Fig. 13. These internal olefins tend more to react via the allylic hydrogen abstraction route to yield the relatively stable allylic radical [16]. So, EPDM shows lower energy of activation and higher crosslinking rate as revealed by DSC, Rheometric and Brabender studies. The crosslinking efficiency is regulated by the instantaneous concentration of active radicals
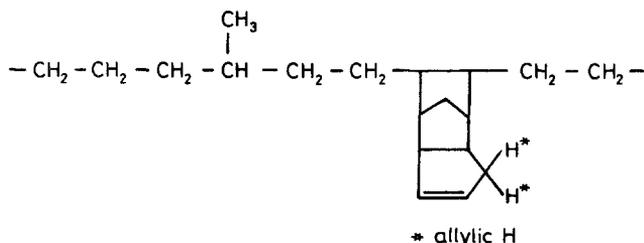

Fig. 13 Structure of ethylene propylene dicyclopentadiene terpolymer having allylic H atoms

and the nature of groupings attached to $-\overset{|}{\underset{|}{C}}$. As both of these factors affect the enthalpic and entropic driving forces to a given reaction.

In the case of EPDM, lower activation energy for allylic H" abstraction and higher stability of allylic radical always favour for a higher degree of crosslinking over PE at a particular concentration of DCP. Hence, as EPDM/PE ratio increases, the crosslinking efficiency also increases.

Conclusion

1. The exothermic heat of crosslinking reaction of PE-EPDM blends increases with the increase in EPDM/PE ratio. For individual blend composition, the heat of reaction also increases with the increase in the dosage of DCP to a certain level.
2. The energy of activation of the crosslinking reaction is almost independent of the level of DCP but it decreases with the increase in EPDM/PE ratio. Pre-exponential factor for crosslinking reaction follow the similar trend as energy of activation.
3. Rheometric studies show that the rate of crosslinking reaction increases with the increase in EPDM/PE ratio and DCP level.
4. Brabender results also reveal that the crosslinking rate increases whereas the energy consumption during crosslinking reaction decreases with increase in EPDM/PE ratio and dosage of DCP.
5. Gel fraction i.e., degree of crosslinking reaction increases with the increase EPDM/PE ratio and DCP level.
6. Crosslinking efficiency also increases with the increase in EPDM/PE ratio.

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Zusammenfassung — Mittels DSC, Brabender Plasticorder und Rheometer wurde der Einfluß von Mischungsverhältnis und Peroxidkonzentration auf den Vernetzungsverlauf von EPDM-PE-Gemischen untersucht. Die Vernetzung von EPDM-PE-Gemischen verläuft nach einer Reaktion erster Ordnung. Je höher der Anteil von EPDM im Gemisch, um so exothermer ist die Vernetzung und um so kleiner ist die dazugehörige Aktivierungsenergie. Mit dem Anwachsen der DCP-Konzentration bis zu einem gewissen Niveau wächst der exotherme Charakter, während die Aktivierungsenergie fast unabhängig von der Peroxidkonzentration ist. Mit dem Anstieg des EPDM/PE-Verhältnisses wächst die vernetzungsgeschwindigkeit, während die optimale Vernetzungszeit und der Energieverbrauch für die Vernetzung sinken. Es wurde ein Verfahren zur Bestimmung der Vernetzungseffizienz bei Mischsystemen entwickelt, um Eigenschaften und Vernetzungsver- halten von Gemischen voraussagen zu können.