

Studies on Dynamic and Static Crosslinking of Ethylene Vinyl Acetate and Ethylene Propylene Diene Tercopolymer Blends

S. MISHRA,¹ B. BAWEJA,² R. CHANDRA²

¹ Department of Chemical Technology, North Maharashtra University, Jalgaon 425 001, M.S., India

² Centre for Advanced Studies and Research in Polymer Science and Technology, Department of Applied Chemistry, Delhi College of Engineering, Kashmere Gate-Delhi 110 006, India

Received 2 September 1998; accepted 28 February 1999

ABSTRACT: The effect of blend ratio on the crosslinking characteristics of ethylene vinyl acetate and ethylene propylene diene tercopolymer (EVA-EPDM) blends was studied by differential scanning calorimetry and a torque rheometer (Rheocord-90). The activation energy decreases with an increase in EVA content in the blend. The cure rate increases whereas the optimum cure time and energy consumption for curing decrease with an increase in the EVA/EPDM ratio. The dynamic curing obtained by the torque rheometer is very fast compared to the static curing obtained by differential scanning calorimetry. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2756–2763, 1999

Key words: EVA-EPDM blends; dynamic curing; static curing; curing rate

INTRODUCTION

Ethylene propylene diene tercopolymer (EPDM) and ethylene propylene copolymer (EPM) have been used as toughening agents for polyolefins such as isotactic polypropylene, HD polyethylene (PE), and low density PE. The blend of ethylene vinyl acetate (EVA) with EPDM, however, has received little attention. Some studies on the effect of rubber composition on EVA have been reported¹ to improve flex cracking resistance, low temperature properties, and resilience. Crosslinking of the rubber phase in the blend is essential for the stability of the compounds. Mainly organic peroxides have been used to induce crosslinking into PE and EVA via free radical formation.^{2–6} Vulcanization of EPDM by either peroxide or sulfur is almost always used. Obviously, the properties that are also dependent on the morphology and interaction between compo-

nents will change with the introduction of crosslinks. Peroxides are the most useful agents for crosslinking of EPDM and EVA.

Brazier and Schwartz⁷ studied the dicumyl peroxide (DCP) induced crosslinking of EPDM and a few other elastomers by differential scanning calorimetry (DSC). They found that the degradation of DCP alone results in an exothermic enthalpy change of 250 kJ/mol. They used the method of Borchardt and Daniels for data reduction and calculation of apparent activation energy.

Dynamic curing has certain merits over static curing because the material remains in active form and it can be stored and processed later.

Thermoplastic elastomeric compositions based on polyolefin EPDM blends were made by dynamic vulcanization using either a peroxide or sulfur accelerator system, the properties of which were dependent on the degree of crosslinking of EPDM in the blends and its ratio.^{8–10} Kelkar studied the influence of molecular structure (i.e., the type and concentration of diene as the type of peroxide and coagent in EPDM vulcanization).¹¹

Correspondence to: S. Mishra.

Journal of Applied Polymer Science, Vol. 74, 2756–2763 (1999)
© 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/112756-08

Table I Effect of Blend Ratio on Activation Energy of Curing

Sr. No.	EVA-EPDM Blend Ratio	Energy of Activation (kJ/mol)	Preexponential Factor
1	80 : 20	86.6	9.3
2	60 : 40	98.9	10.9
3	40 : 60	101.0	11.0
4	20 : 80	110.0	12.2
5	00 : 100	126.0	14.2

Sen et al.¹² studied the effect of blend ratio and peroxide concentration on crosslinking characteristics of blends. Vulcanization of EPDM by peroxide and sulfur have been described in two detailed review articles.^{13,14}

In the present work the effect of the blend ratio on static and dynamic crosslinking of an EVA-EPDM blend was studied in detail by DSC and a torque rheometer, respectively. The mechanical energy required for dynamic crosslinking of the EVA-EPDM blend and the rate of crosslinking

were also calculated for static and dynamic curing.

EXPERIMENTAL

Materials

The materials used were EVA-PILENE 2806 [0.950 g/mL density, 6 g/10 min melt flow index (MFI)] obtained from Polyolefin Industries Limited, EPDM rubber JSR 21 {ethylene 64%, Moony viscosity [ML (1 + 8), 127°C] 20} from Japan Synthetic Rubber, and 99% pure DCP from Hercules Inc.

Blend Preparation and DCP Mixing

Four blends containing 20 : 80, 40 : 60, 60 : 40, and 80 : 20% (w/w) EPDM rubber were prepared. The EVA and pieces of EPDM were mixed by hand in an appropriate ratio and then fed into the Rheocord-90 internal mixer Rheomix-600, which was maintained at a set temperature of 100°C. The mixing was continued till a constant value of

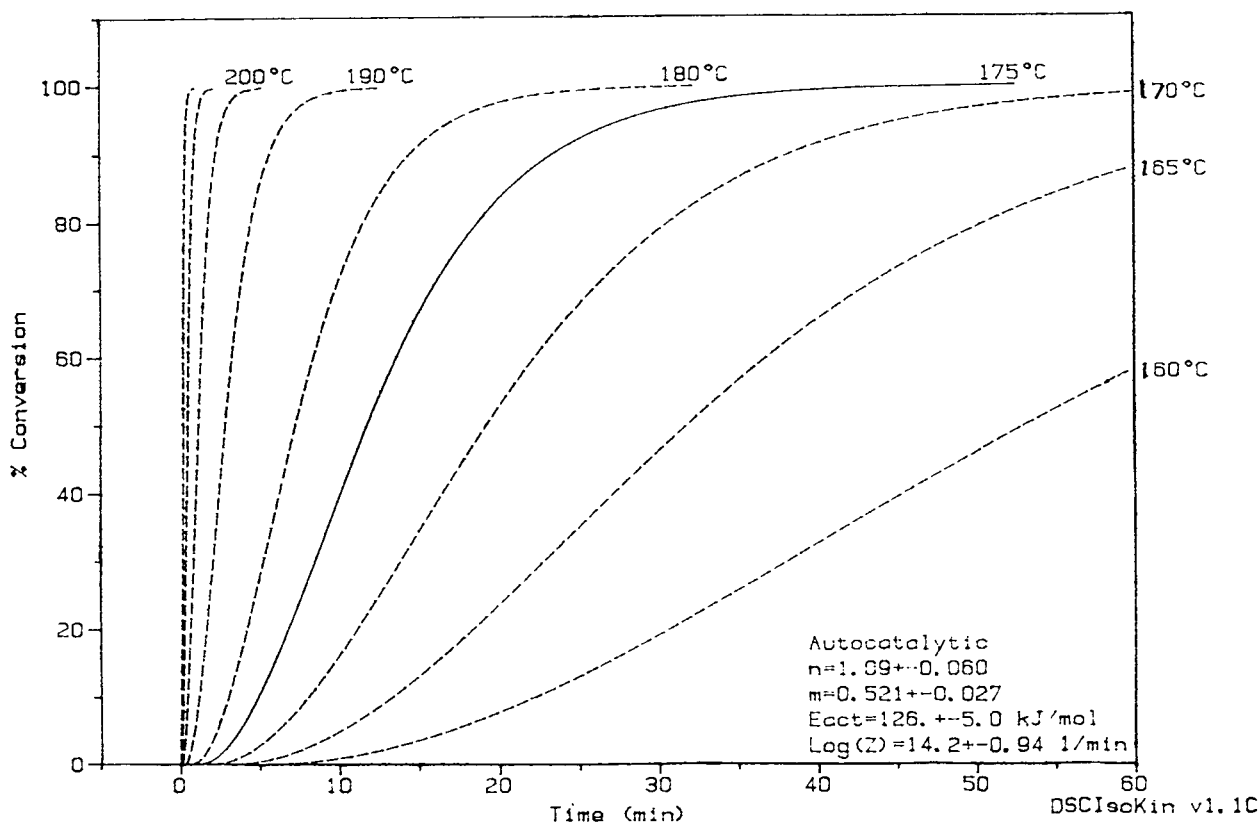


Figure 1 Static curing (% conversion) of EPDM : EVA (100 : 0) blend at different times and temperatures.

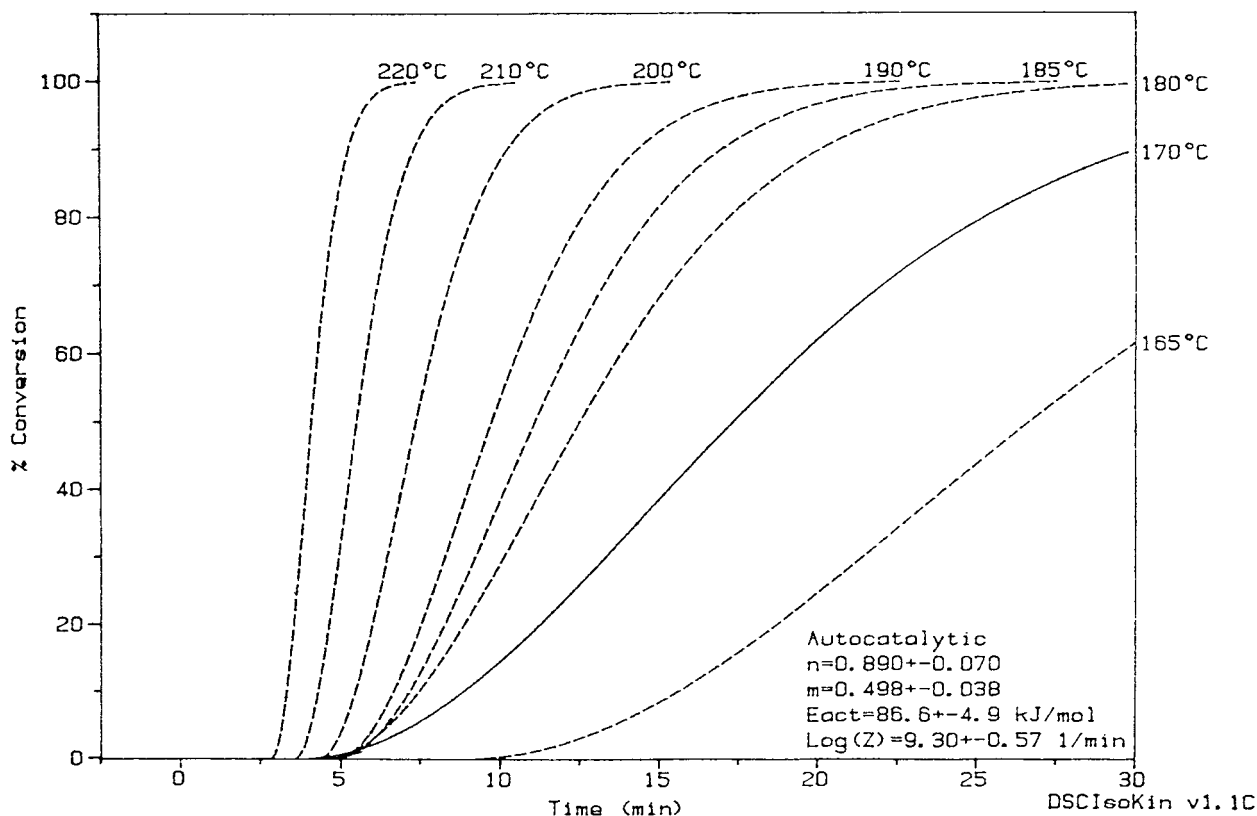


Figure 2 Static curing (% conversion) of EPDM : EVA (80 : 20) blend at different times and temperatures.

torque, and the mixer was allowed to cool. A calculated quantity of DCP (1% by wt) was added to the blend at a temperature of 100°C to avoid any crosslinking at this stage, and it was mixed for 2 min. The rotor was kept at 50 rpm in each experiment.

DSC

A Dupont thermal analyzer with a DSC model 990 was employed for this purpose. Calibration of the instrument was done by the standard material (indium). For a DSC run, 10 ± 2 mg of sample was placed in the aluminum pan and the DSC scans were obtained at isothermal temperatures of 165, 170, and 175°C in static air for each blend.

Theory of Kinetic Analysis of Exothermic Crosslinking Reaction by DSC

There are several methods that have been suggested for determining the kinetic parameters from the exotherm. These include an isothermal curing reaction, a multiple heating rate method, or a single DSC trace using n th-order kinetics,

which is also known as the Borchardt and Daniels method.

Autocatalyzed Versus n th-Order Reaction

Autocatalyzed reactions are characterized by a maximum heat evolution at 30–40% of the reaction in the isothermal DSC signals. Also, these systems often appear to show an induction period during which no apparent reactions occur.¹⁵ The induction time depends on the initial concentration of catalyst or the reaction rate constant of the parallel reaction that produces the intermediate species. On the contrary, the n th-order rate expression predicts that the maximum heat evolution will occur near $t = 0$.

The multiple heating rate method and the Borchardt and Daniel method are not quantitatively applicable to autocatalyzed systems. The isothermal analysis can be performed using either of two basic models, n th order^{14,15} or autocatalyzed.^{16–18} Because our system shows autocatalytic behavior, isothermal kinetic software was therefore used for the kinetic study in the present work.

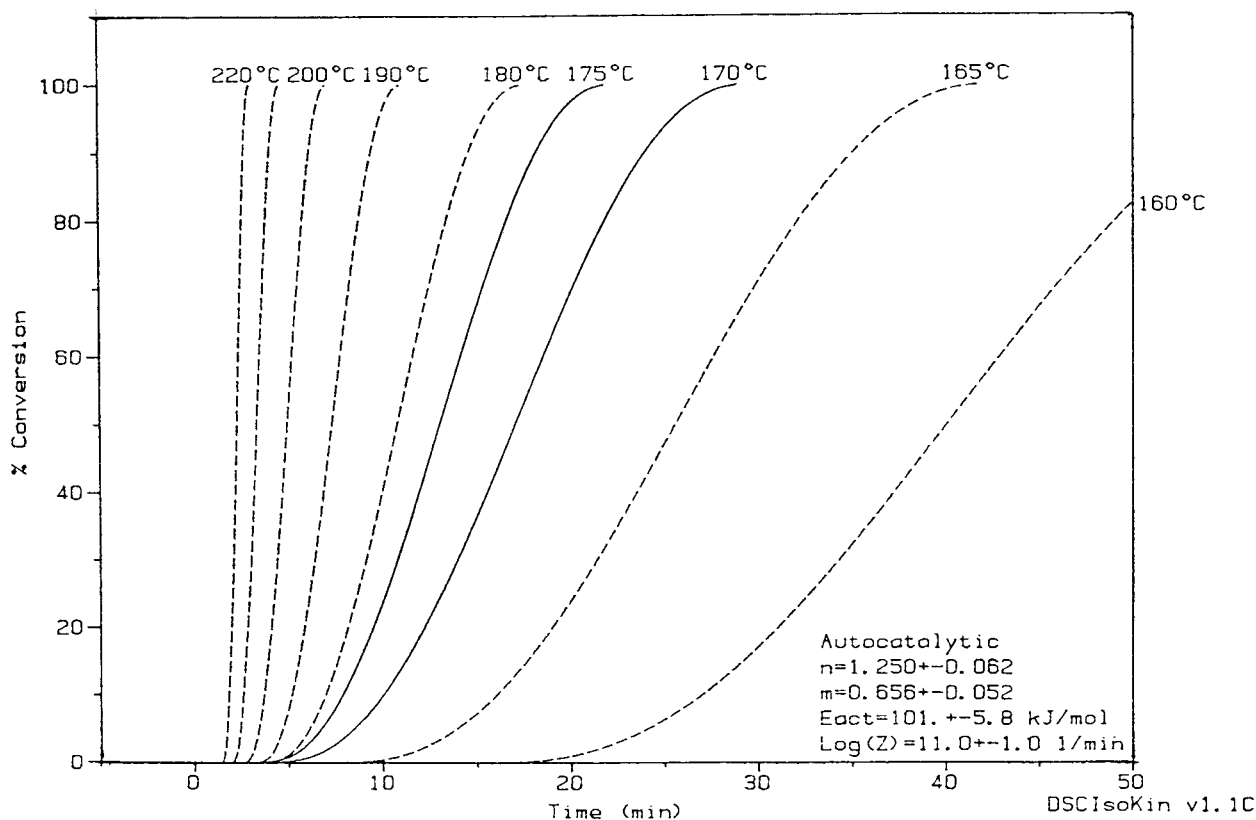


Figure 3 Static curing (% conversion) of EPDM : EVA (60 : 40) blend at different times and temperatures.

Determination of Curing Rate

Cure rate and optimum cure time were determined through two different techniques (DSC and Rheocord-90) of the composition EB₄₀. The cure rate was calculated from the general formula $100/t_{90} - t_2$. For DSC t_{90} and t_2 are considered as corresponding to 90 and 20% conversion. With the Rheocord the t_{90} and t_2 are the optimum cure time and scorch time, respectively.

RESULTS AND DISCUSSION

Isothermal Static Curing Behavior

As obtained from the kinetic analysis, the activation energy of the crosslinking reaction of EVA-EPDM blends is strongly dependent on the blend ratio. The variation of activation energy for the crosslinking reaction with the blend ratio is shown in Table I. The energy of activation of EPDM was found to be 126 kJ/mol. Braizer and Schwartz⁷ also studied the activation energy for EPDM and other elastomers. They obtained the activation energy of EPDM as 140 kJ/mol. This

difference in activation energy may be due to the difference in the diene contents, as well as the structure of diene in EPDM. Observe from Table I that the energy of activation increases with a decrease in the proportion of EVA in the blend.

Reaction Order and Preexponential Factor

We observed from the kinetic analysis that when DCP is used as the lone curing agent the crosslinking reaction of EVA-EPDM blends in any proportion follows first-order reaction kinetics. Similar to the energy of activation, the value of the natural logarithm of the preexponential factor ($\ln k_0$) for the crosslinking reaction varies with the blend ration (Table I) and was found to increase with a decrease in the EVA/EPDM ratio as in the energy of activation.

Time-Temperature Curing Behavior

The course of crosslinking [i.e., the degree of conversion from the uncrosslinked (thermoplastic) state to the crosslinked network at different isothermal temperatures] was calculated through

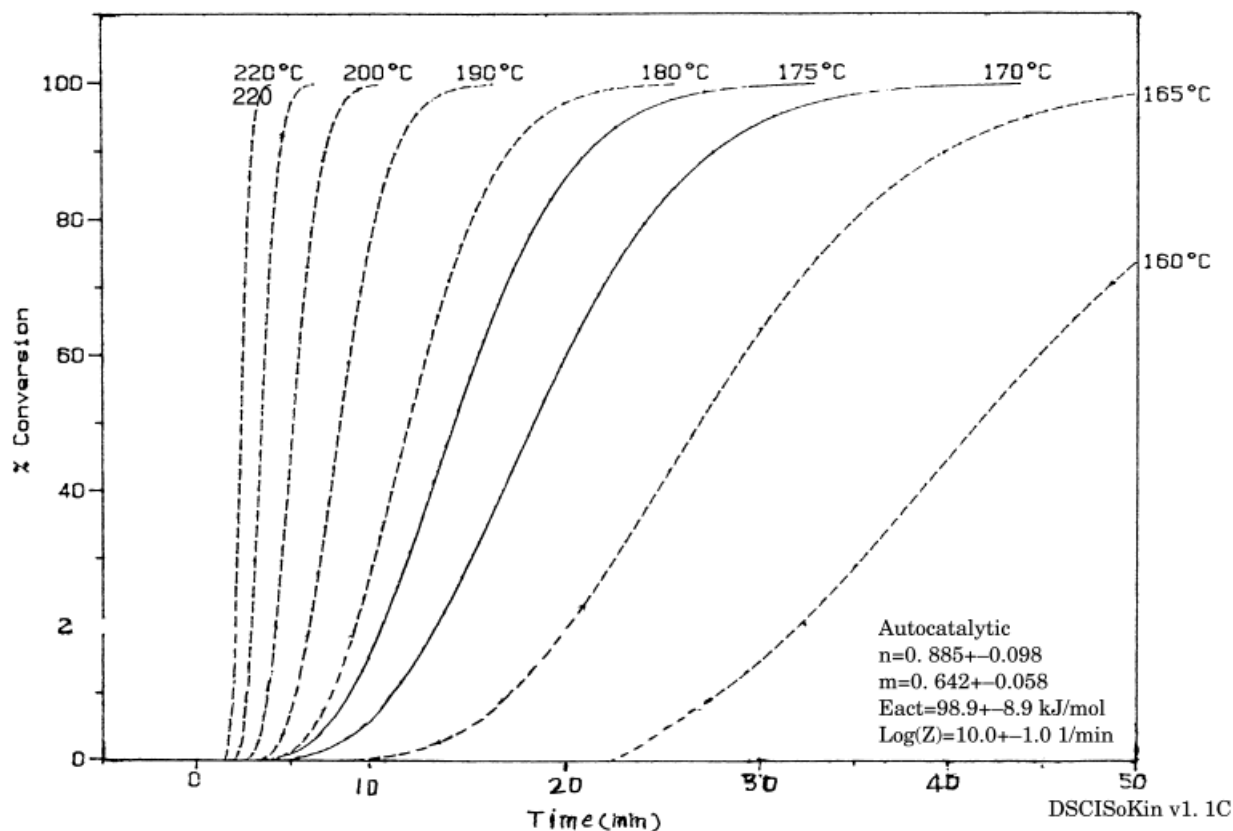


Figure 4 Static curing (% conversion) of EPDM : EVA (40 : 60) blend at different times and temperatures.

in-house software. The results of conversion α with rate at different isothermal temperatures are shown in Figures 1–5 for all the systems. The figures show that the degree of conversion at a particular time is always higher for the system that contains a smaller amount of EPDM. This means that the rate of conversion at any isothermal temperature increases with a decrease in the EVA/EPDM ratio. The variation in the rate of conversion corresponds to the results observed in Table I: there are lower energies of activation for the systems that have lower EVA/EPDM ratios. Figures 1–5 also show that the rate of conversion for all the systems increases with an increase in isothermal curing temperature.

Dynamic Curing Behavior

For studying the cure characteristics of EVA-EPDM blends under dynamic conditions, crosslinking of various systems was carried out in a Haake Rheocord-90 mixer chamber. The cure behaviors are shown in Figure 6(a) by the course of the crosslinking reaction versus time at 170°C. Figure 6(b) and Table II show that with an in-

crease in the EVA/EPDM ratio in the blends the crosslinking rate increases considerably. These results support the findings of DSC experiments.

Table II shows that the energy consumption drops significantly on the addition of EVA to EPDM. This may be due to the increase in the rate of the crosslinking reaction and the lower initial viscosity and hence the lower minimum torque imparted by the presence of EVA. Our earlier work¹⁹ established that when the low viscosity polymers like high density PE (HDPE) get crosslinked with EPDM *in situ*, an interpenetrating network is formed where crosslinked HDPE and crosslinked EPDM become toughened, leading to higher crosslink density.

The cure rate and optimum cure time of the 60/40 (EVA-EPDM) composition were determined through two different techniques (DSC and Rheocord-90), and the results are compared in Figure 6(a,b); the cure rate and optimum cure time vary with the measurement techniques. This is quite natural because the curing conditions are quite different for the two techniques. In the Rheocord the shear force applied to the material during

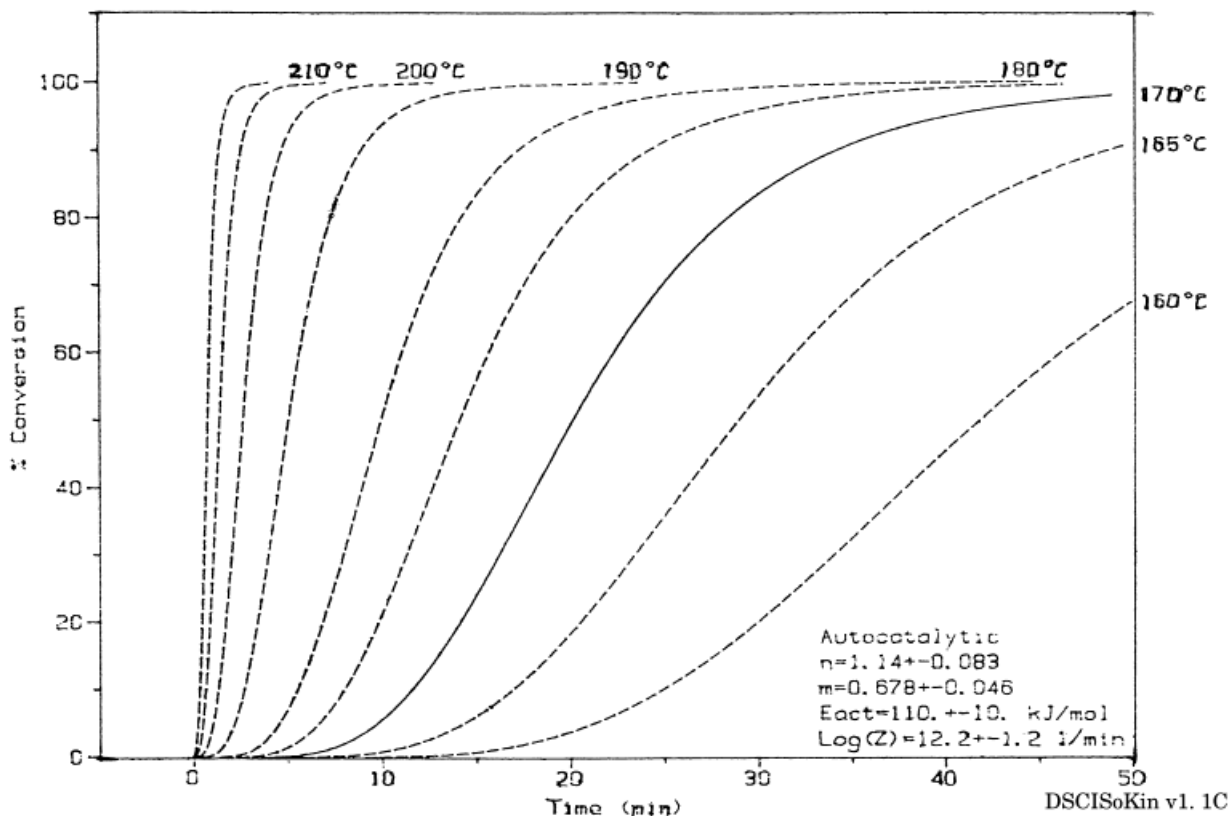
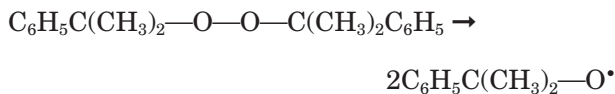


Figure 5 Static curing (% conversion) of EPDM : EVA (20 : 80) blend at different times and temperatures.

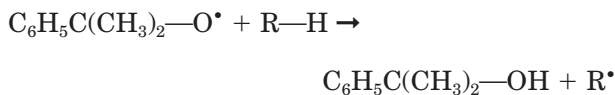
cure is much higher than with DSC (no mechanical shear force is applied). Hence, in the Rheo-record the optimum cure time is lower and the crosslinking rate is much higher than that obtained by DSC.

General Curing Mechanism

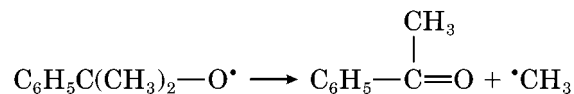
The general scheme of the crosslinking reaction initiated by the thermal decomposition of DCP can be given in the following form: the thermal decomposition of DCP,



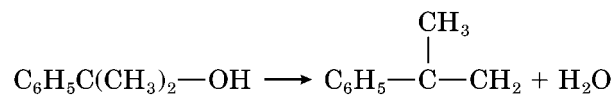
hydrogen abstraction by the cumyloxy radical from polymer chains,



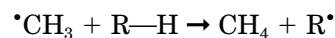
disproportionation of the cumyloxy radical to acetophenone and methyl radical,



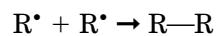
disproportionation of cumyl alcohol to methyl styrene and water,



hydrogen abstraction by the methyl radical from the polymer chain,



combination of polymer chain radicals with the formation of a crosslink,



Here R—H represents either EVA or EPDM.

Although Brazier and Schwartz reported that an increase in reaction temperature favors the disproportionation of cumyloxy radicals to a methyl radical (R) concentration as CH_3 produced by disproportionation, it is also capable of H abstraction from polymer chains.⁷

Because EVA is a saturated polymer, crosslinking demands the abstraction of hydrogen atoms from the polymer backbone and subsequent coupling of the polymer radicals. The ease of hydrogen abstraction from alkanes declines in the

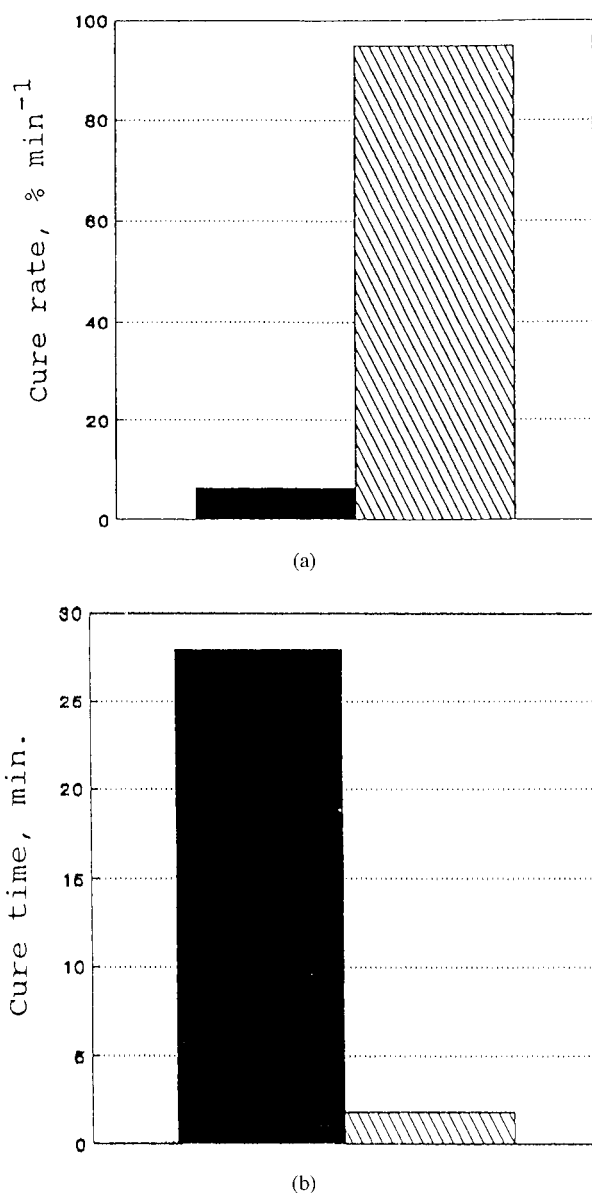


Figure 6 Comparison of (a) cure rate and (b) cure time of DSC (black bars) and Rheocord (hatched bars) curing of EPDM-EVA blend.

Table II Effect of EVA on Cure Rate, Total Torque, and Work Energy at 50 rpm Rotor Speed in EVA-EPDM Blends

Sr. No.	EVA-EPDM Blend Ratio	Cure Rate (MG/min)	Total Torque (MKM)	Mechanical Energy (kJ/g)
1	80 : 20	1026.7	2.42	196.13
2	60 : 40	696.3	3.0	243.2
3	0 : 100	499.1	4.37	354.15

order tertiary > secondary > primary, and the reactivities of the radicals produced are in the reverse order. But the observed selectivity will depend on the relative population of the C—H bonds and their disposition in the molecule. In the EVA the reactivity increases because of the presence of three acetoxy hydrogens in the pendant acetate component (28%) compared to three allylic hydrogens in the pendant diene components (6.7%) of EPDM. The EVA tends more to react via the acetyl hydrogen abstraction route and yields the relatively stock acetyl radical. So, as the EVA content in the blend increases, the energy of activation decreases and the crosslinking rate increases as revealed by the DSC and Rheocord studies.

CONCLUSION

The energy of activation of the crosslinking reaction decreases with an increase in the EVA/EPDM ratio. The preexponential factor for the crosslinking reaction follows a trend similar to the energy of activation. The Rheocord results also revealed that the crosslinking rate increases whereas the energy consumption during the crosslinking reaction decreases with an increase in the EVA/EPDM ratio.

REFERENCES

1. Product catalogues ROYALENE-EPDM, Properties and Applications; Uniroyal Chemical Company, Inc.: Naugatuk, CT., 1982
2. Manley, T. R.; Qayyum, M. M. *Polymer* 1971, 12(171), 176.
3. Anderpoulas, A. G.; Kampouris, E. M. *J Appl Polym Sci* 1986, 31, 1061.
4. Kampouris, E. M.; Anderpoulas, A. G. *J Appl Polym Sci* 1986, 34, 1209.
5. Kao, Y. A.; Philips, P. J. *Polymer* 1986, 27, 1669.
6. Boer, J. D.; Pennings, A. J. *Polymer* 1982, 22, 1944.

7. Brazier, D. W.; Schwartz, N. V. *Thermochim Acta* 1980, 39, 7.
8. Coran, A. Y.; Patel, R. *Rubber Chem Technol* 1980, 53, 141.
9. Coran, A. Y.; Das, B.; Patel, R. P. U.S. Patent 4,130,535, 1978.
10. Krasge, E. N.; Paul, D. R.; Newman, S., Eds. *Polymer Blends*; Academic Press: New York, 1978; Vol. 2, Chapter 20.
11. Kelkar, R. C. *Rubber Chem Technol* 1988, 61, 238.
12. Sen, A. K.; Bhattacharya, A. S.; De, P. P.; Bhowmick, A. K. *Thermal Anal* 1991, 37, 19.
13. Waters, D. N.; Paddy, J. L. *Anal Chem* 1988, 60, 53.
14. Widmann, G. In *Thermal Analysis*; Buzas, I., Ed.; Heyden: London, 1975; p 359.
15. Widmann, G. *Thermochim Acta* 1975, 12, 331.
16. Keenan, M. R. *J Appl Polym Sci* 1987, 33, 1725.
17. Sourour, S.; Kamal, M. R. *Thermochim Acta* 1976, 14, 41.
18. Sichiona, W. J. Du Pont Application Brief TA-93; DuPont: Wilmington, DE .
19. Chandra, R.; Mishra, S.; Parida, T. R. *Polym Int* 1995, 37, 141.