

Cure Characteristics of Ethylene Propylene Diene Rubber–Polypropylene Blends. I. Calculation of State of Cure in Blends Containing Conventional Sulfur Curing System Under Variable Time–Temperature Conditions

ABHIK SENGUPTA, BIDYUT BARAN KONAR

Department of Polymer Science and Technology, Calcutta University, Calcutta-700009, India

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ABSTRACT: Various blends of polypropylene and ethylene propylene diene terpolymer were prepared. In these blends, rubber phases were compounded with an optimum sulfur curing system. The equivalent cure time and state of cure of the mixes were studied in the temperature range from 120 to 190°C by a rheometer. The temperature-independent parameters (E_1 , E_2 , S_1 , and S_2) and specification of the temperature dependence curing rate constant (k) and induction period (t_0) were determined. The activation energies of the crosslinking reaction are almost similar for the virgin EPDM and EPDM/PP mixes. The value 9 Kcal/mol was considered sufficiently accurate for these mixes. A discussion of temperature-conversion factor of the mixes is also provided.

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INTRODUCTION

Many methods for predicting the state of the cure of rubber materials have been used. They have been applied to systems either like gum rubber or filler/resin/oil-loaded rubber. The problem of being able to calculate the cure in plastomer–elastomer blend specimens, wherein the temperature, time, and nature of plastomer is dependent, is one that has been recognized earlier. There is no rule similar to the rule of thumb in use for adjusting the cure time to different temperatures and for different plastomer–elastomer blend compositions and there have not been any monograph methods worked out for adjusting the cure times for blend compositions. The present work was a critical study on selected ethylene propylene diene and polypropylene (EPDM–PP) blends^{1–9} with special reference to the “activation energy of vul-

canization”¹⁰ and the “temperature coefficient of vulcanization”¹¹ for present-day plastomer–elastomer blend compositions. The equations used in the present article are based on the state of the cure in terms of temperatures, cure cycle time, and basic stock-curing parameters. It is a method of a rapid and systematic study of the main effects and interaction effects of these variables upon the state of the cure.

In the context of studies undertaken, it is important to mention the basic equations related to the vulcanization used for predicting the state of the cure in heterogeneous rubber blends. Claxton and Liska^{12,13} proposed

$$K = M/M_\alpha = 1 - e^{-k(t-t_0)} \quad \text{for } t \geq t_0 \quad (1)$$

where K is the fractional modulus state of the cure; M_α , the fully cured or maximum modulus value attained with increasing cure time; M , the equilibrium modulus value at time t ; k , a curing rate constant with dimensions of reciprocal time; and t_0 , the induction period or curing time before

Correspondence to: B. B. Konar.

the modulus starts to increase significantly. The dependence of the curing rate constant k and the induction period t_0 upon curing are correctly given by the Arrhenius-type equation as

$$k = Ae^{-E_1/R\theta} = e^{(S_1 - E_1/2\theta)} \quad (2)$$

$$t_0 = Be^{E_2/R\theta} = e^{(-S_2 + E_2/2\theta)} \quad (3)$$

where A and B are the dimensioned constants; E_1 and E_2 , the activation energies associated with the curing reaction and with the incipient cure reaction, respectively; R , the general gas constant (assumed equal to $2.0 \text{ cal mol}^{-1} \text{ g}^{-1}$); θ , the absolute temperature; and S_1 and S_2 , also temperature-independent parameters.

Again, eq. (1) can be rearranged to give the time, t_K , required to reach a fractional modulus cure K at temperature θ as

$$t_K = t_0 + \frac{1}{k} \ln(1 - K)^{-1} \quad (4)$$

where $0 \leq K \leq 1$.

At the reference temperature θ_r , the equivalent time t_{Kr} would be required to reach the same state of cure K . Therefore,

$$t_{Kr} = t_{0r} + \frac{1}{k_r} \ln(1 - K)^{-1} \quad (5)$$

So,

$$t_{Kr} = t_{0r} + (t_K - t_0) \frac{k}{k_r} \quad (6)$$

Using eq. (3) and substituting $\theta = \theta_r$, we obtain

$$t_{0r} = e^{(-S_2 + E_2/2\theta_r)} \quad (7)$$

From eqs. (7) and (3), we obtain

$$t_{0r}/t_0 = e^{[(E_2/2)(1/\theta_r - 1/\theta)]} \quad (8)$$

In a similar manner, we have

$$k_r = e^{(S_1 - E_1/2\theta_r)} \quad (9)$$

and

$$k/k_r = e^{[(E_1/2)(1/\theta_r - 1/\theta)]} \quad (10)$$

Thus, the equivalent time at reference temperature θ_r becomes

$$t_{Kr} = t_0 e^{[(E_2/2)(1/\theta_r - 1/\theta)]} + (t_K - t_0) e^{[(E_1/2)(1/\theta_r - 1/\theta)]} \quad (11)$$

So, the equivalent cure time at reference temperature θ_r can easily be calculated if the induction period t_0 as well as the time t_K are both known at temperature θ .

EXPERIMENTAL

Materials

The EPDM rubber (Royalene 301 T : DCPD polymer, nonstaining, from the Uniroyal Chemical Co.) used had a Mooney viscosity ML 1 + 4 (125°C) of 40 and a specific gravity of 0.87. The E/P ratio was 68/32. The polypropylene (PP) (EBI 0830 : IPCL, India) used has an MFI of 0.8. The other compounding ingredients were from standard sources.

Blends Preparation and Compounding

The EPDM-PP blend formulations (Table I) were used for the present work to determine the state of the cure. The recipes differed only in the dose of PP. The blends were prepared in three stages: The mastication of EPDM was done in a baby two-roll mill in its cold condition. PP was then mixed at a temperature about 60°C (first stage). The mix (EPDM/PP) was then passed through a laboratory-size extruder at 180°C (second stage). Finally, the blend was compounded with other ingredients (zinc oxide, stearic acid, sulfur, MBTS, and TMT) according to ISO 2393.

Rheometry

The cure characteristics for various blend compounds were evaluated using a Monsanto rheometer (R100) with a microdie and a 3° arc of oscillation at temperatures of 120, 130, 140, 150, 160, 170, 180, and 190°C , respectively, according to ASTM standard D 2084-88. The different parameters were determined from the rheographs of the respective blend compounds.

RESULTS AND DISCUSSION

The rheometer is still an important instrument for quality assurance in the rubber industry. Also, the instrument was proposed for calculation of the

Table I Formula for Experimental Compounds

Ingredients	Gum	A ₁	A ₂	A ₃	A ₄	A ₅
EPDM	100.00	100.00	100.00	100.00	100.00	100.00
PP	0	11.11	25.00	42.86	66.67	100.00
Zinc oxide	5.00	5.00	5.00	5.00	5.00	5.00
Stearic acid	1.20	1.20	1.20	1.20	1.20	1.20
Sulfur	2.00	2.00	2.00	2.00	2.00	2.00
MBTS	2.50	2.50	2.50	2.50	2.50	2.50
TMT	0.50	0.50	0.50	0.50	0.50	0.50
Total	111.20	122.31	136.20	154.06	177.87	211.20
EPDM:PP	100:0	90:10	80:20	70:30	60:40	50:50

state of the cure in rubber under variable time-temperature conditions.¹³ The elastomeric characteristics depend on the crosslink network developed during vulcanization. The present problem on measuring the state of the cure in PP-filled rubber has not been solved despite many studies.¹⁴ Since the value of the activation energy is critical in performing practical operations such as converting the cure time from one temperature

to another and for determining the curing effect produced during the heating (or cooling) part of the cure cycle, it is important to have some idea of how the activation energy varies from the gum to various blend systems.

Blends which contain an elastomer with a resinous thermoplastic are softened at higher temperatures due to the melting of the thermoplastic species. Also, there must be some form of interac-

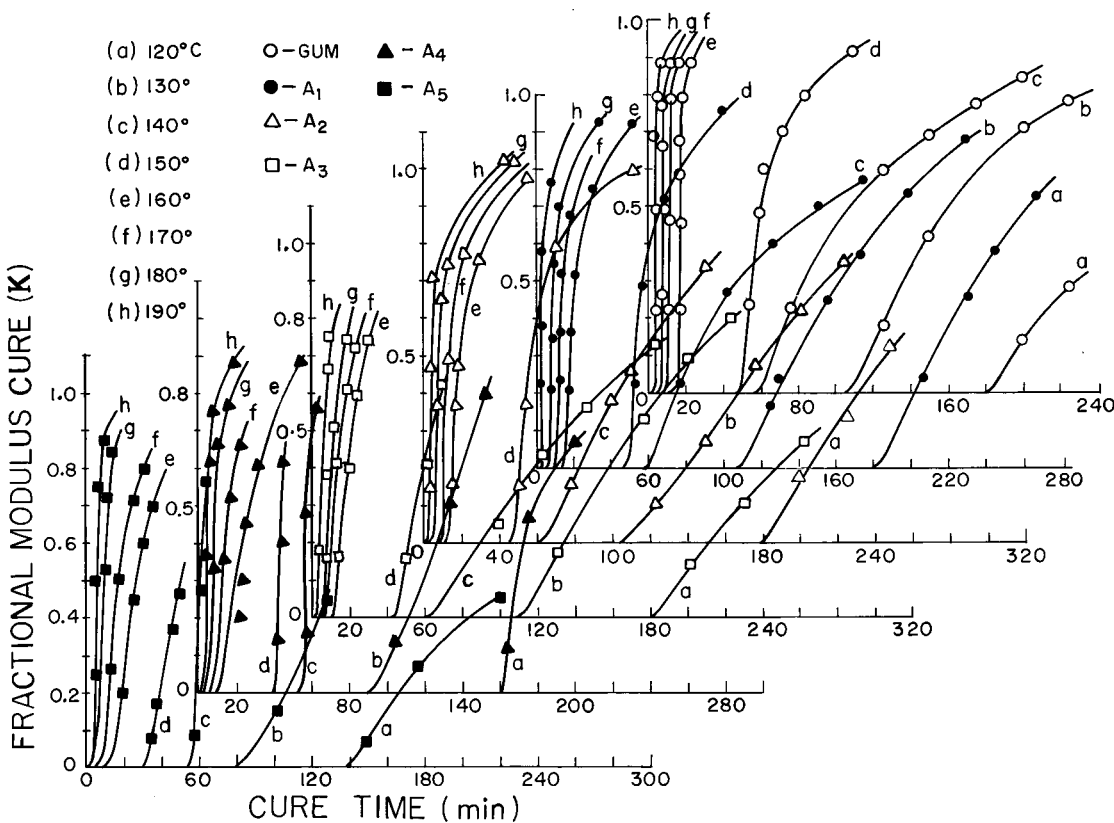


Figure 1 Fractional modulus cure curves of EPDM-PP blend compounds at different curing temperatures.

Table II Fractional Modulus Cure (Rheometric) Data for EPDM-PP Blend Compounds at Different Temperatures

		Temperature (°C)							
		120	130	140	150	160	170	180	190
Gum	t_0 (min)	185	110	60	50	15	10	8	4
	$k \times 10^4$	111	103	138	693	3465	3465	3465	6930
A ₁	t_0 (min)	185	110	60	50	15	10	8	4
	$k \times 10^4$	156	103	138	693	1386	1732	3465	6930
A ₂	t_0 (min)	184	112	63	48	15	10	8	4
	$k \times 10^4$	111	154	138	693	1386	1732	3465	6930
A ₃	t_0 (min)	183	113	63	45	14	8	7	4
	$k \times 10^4$	89	103	69	346	1109	1732	2079	6930
A ₄	t_0 (min)	160	95	60	40	12	8	6	4
	$k \times 10^4$	446	154	346	346	485	693	3465	6930
A ₅	t_0 (min)	142	80	54	32	10	6	4	4
	$k \times 10^4$	67	103	832	346	416	693	1732	6930

tion between the two phases.¹ The experimental parameters obtained from the rheometer trace are used to determine the effect of PP on the accelerated sulfur cure of EPDM.

According to eq. (1), it is seen that the fractional modulus K is dimensionless and takes on values ranging from 0 to 1 as t ranges from t_0 to ∞ . The fractional modulus cure curves of gum and PP-filled compounds (gum, A₁, A₂, A₃, A₄, A₅) at different curing temperatures are shown in Figure 1. The values of t_0 and K as obtained from Figure 1 are shown in Table II. As expected, the induction periods become reduced significantly on increasing the temperature in both the gum and blend compounds. The result shows that the difference of the induction period between gum and the 50% PP-filled compound gradually decreases with increasing temperature (120–180°C) and the difference is nil at temperature 190°C at which the PP species melt almost completely. Similarly, the curing rate constant k has a decreasing tendency with increasing PP loading except at 190°C, where the value (6930×10^4) is same as with the gum compound.

The activation energies E_1 and E_2 were evaluated from the straight-line slope in the plots $\log k$ vs. $1/\theta$ and $\log t_0$ vs. $1/\theta$ (Figs. 2 and 3). The values thus obtained are shown in Table III. The values of S_1 and S_2 calculated from the E_1 and E_2 values are also shown in Table III. The magnitudes of S_1 and S_2 have much significance because these are related to the frequency of encounters between two reactant molecules irrespective of whether or not they possess sufficient energy to

form a crosslink.¹⁵ The energy of activation, E_1 , values for gum EPDM and EPDM-PP blend compounds (7.11–11.17 Kcal/mol) are much lower than normally obtained for conventional elastomers^{16,17} (15–25 kcal/mol). A similar result ($E = 9.15$ kcal/mol) was obtained by a Shawbury curometer (Model Mark VI) for the gum EPDM vulcanizate.¹⁸ This indicates that both gum and blend compounds are very active in the presence of a sulfur-accelerator system. Among the blends, the result of the 30% PP blend (A₃) is slightly different (11.17 kcal/mol). This may be due to the nonuniform distribution of the curing system in the elastomer phases. The other results indicate that the activation energy has not been signifi-

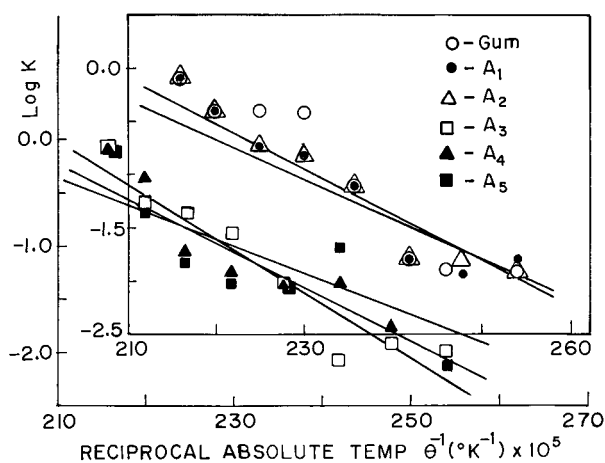


Figure 2 Temperature-independent cure parameters from the plot of $\log k$ vs. reciprocal absolute temperature.

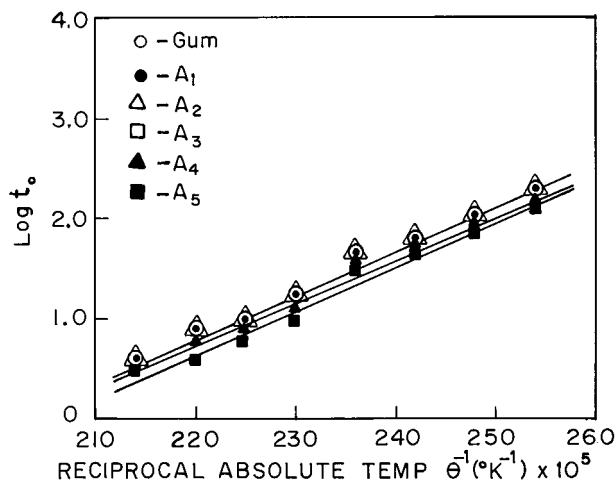


Figure 3 Temperature-independent cure parameters from the plot of $\log t_0$ vs. reciprocal absolute temperature.

cantly changed due to the blending of PP into the EPDM compounds.

For rubber compounds, a single activation energy will be accurate for practical purposes. Therefore, for all EPDM-PP blend compounds with the use of the sulfur-accelerator curing system, a value of 9 kcal/mol for the activation energy will be sufficiently accurate.

The plot of the conversion factor vs. temperature for the activation energy of 9 kcal/mol and an absolute reference temperature of 150°C depicted in Figure 4 shows that the line has a slight curvature. This behavior indicates that the ratio of the time-conversion factors of the EPDM-PP blend compounds corresponding to two temperatures separated by 10°C (temperature coefficient of vulcanization) will depend upon both the temperature and the activation energy of the blend curing systems. The present work shows almost a similar activation energy for different EPDM-PP blends. Thus, with the use of an average activation energy $E_0 = 9$ kcal/mol and a reference temperature corresponding to 150°C, a constant time conversion of about 1.3 per 10°C was shown (Fig. 4).

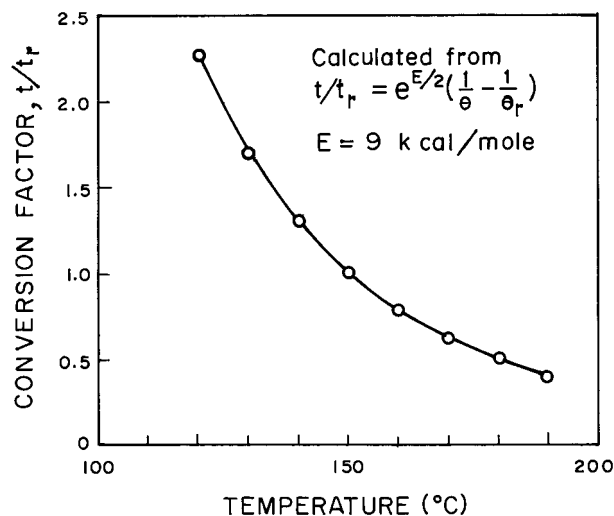


Figure 4 Temperature conversion factor vs. temperature.

CONCLUSIONS

The present article relates to studies on selected elastomer-plastomer poly blends like EPDM-PP with special reference to formation of a network of specific design, aimed at the establishment of the state of the cure for practical application at different temperatures.

The results indicate that due to the plastomer present in the blend at various proportions, the activation energies of the crosslinking reaction have no significant change from the virgin elastomer but that the induction period and curing rate constant changes. This is evident from the following:

1. Activation energies of blend compounds are within 7.11–11.17 kcal/mol, whereas for gum, it is 8.85 kcal/mol.
2. No appreciable change of the induction period up to 30% PP (A_3 compound) in the temperature range 120–180°C, but in 40 and 50% PP (A_4 and A_5 compounds), significant changes are noticeable. At 190°C,

Table III Basic Temperature-independent Cure Parameters

	Gum	A_1	A_2	A_3	A_4	A_5
E_1 (kcal/mol)	8.85	7.83	7.83	11.17	7.11	9.24
E_2 (kcal/mol)	9.67	9.06	9.31	9.31	9.31	9.17
S_1 (kcal/mol)	-2.75	-2.67	-2.67	-2.86	-2.29	-2.14
S_2 (kcal/mol)	-3.86	-3.90	-3.90	-3.90	-3.81	-3.62

it is same for all gum and PP-loaded compounds. Almost similar results are obtained for the curing rate constant.

3. A constant time conversion of 1.3 per 10°C is found for the sulfur vulcanization of EPDM-PP blends with a reference temperature corresponding to 150°C.

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