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KINETIC INVESTIGATION ON THE CURING OF ETHYLENE METHYL ACRYLATE – POLYDIMETHYL SILOXANE RUBBER BLENDS BY DIFFERENTIAL SCANNING CALORIMETRY

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Abstract

Curing reactions of ethylene methyl acrylate (EMA) polydimethyl siloxane (PDMS) rubber blends have been investigated by differential scanning calorimetry (DSC) and by Rheometry. The curing exoterms obtained from DSC curves have been analysed to derive the kinetic parameters associated with the curing process. Crosslinking of EMA–PDMS rubber blends follow first order kinetics. The effect of blend ratio and peroxide concentration on the crosslinking characteristics of the blends have also been investigated.

Keywords: DSC, kinetics, rubber

Introduction

The cure characteristics of elastomers by dicumyl peroxide with the help of Differential Scanning Calorimetry have been reported earlier by several authors [1–2]. Patel *et al.* [3] also have reported the cure kinetics of epoxy resin and phenol – furfural resin by DSC. But similar studies with the vulcanizable blends, both miscible and immiscible are scanty. Very recently Sen *et al.* [4] have reported the crosslinking of EPDM–PE blends by thermoanalytical technique. They found that crosslinking of EPDM–PE blends follow a first order kinetics. The curing exotherm increases but activation energy decreases with increase in EPDM concentration in the blends.

Polydimethyl Siloxane rubber (PDMS) has long been recognized as the rubber of choice for high and low temperature applications [5]. Both the number of

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uses of silicone elastomers and the volume used are increasing at a faster rate as a result of rapid advancement in all fields of technology. To meet this demand many new blends of silicone elastomer with other polymers have taken birth that necessitates higher performance under severe conditions.

On the other hand ethylene methylacrylate (EMA) has been chosen for its excellent solvent and oil resistance, excellent acid and alkali resistance, excellent environmental stress cracking resistance at elevated temperatures with superior mechanical properties. Besides, it has the advantage of a polar ester group and a reactive α-hydrogen atom, which can take part in chemical reaction with other functional polymers. In our earlier investigation [6], EMA and PDMS rubber blends are found to be miscible throughout the composition range as evidenced from a single composition dependent glass transition temperature.

In the present study we report the curing characteristics of EMA–PDMS rubber blends at various compositions and optimise the concentration of the peroxide with the help of a Rheometer and a differential scanning calorimeter. The kinetic parameters during vulcanization of the blends have also been investigated, by both the apparatus.

Experimental

Materials

Polydimethyl siloxane rubber containing small percentage of vinyl group (3.8% approximately, Silastic WC-50) was supplied by M/S. Dow Corning Inc., USA with the following specification: Specific gravity 1.15, brittle point –39°C.

Ethylene methyl acrylate copolymer (OPTEMA TC-120) was supplied by M/S. Exxon Chemicals Eastern Inc., Bombay with the following specifications: Methyl acrylate content 21%, melting point 81°C, melt flow index 6.0 deg/mm and density 0.94 g/cm^3. Dicumyl peroxide (DCP) 99% pure Dicup R from M/S. Hercules, Inc., USA was used, in the present investigation.

Preparation of the blend

Mixing of the individual components and the blends were carried out in a Brabender Plasticorder (PLE-330) at 180°C for 10 min at 100 rpm rotor speed. The molten mass was taken out and sheeted out in a two roll laboratory mill of size 150 mm×300 mm. The sheet was again charged in the plasticorder at 130°C, mixed thoroughly and dicumyl peroxide (Dicup R) was added. Mixing was continued for 2 min more to get a homogeneous mixture. The molten mass was then taken out and sheeted out in a two roll mill. The sheet was then vulcanised in a compression moulding press at 180°C under a pressure of 4.5 MPa for the respective optimum cure times as determined by a Monsanto Rheometer model R-100. Compositions of the binary blends are given in Table 1. Three different levels of DCP are used in each blend composition.

Table 1 Formulation of the blends

	Blend code				
	I	II	III	IV	V
EMA	100	70	50	30	0
PDMS	0	30	50	70	100
DCP	0.75, 1.5, 2.5	0.75, 1.5, 2.5	0.75, 1.5, 2.5	0.75, 1.5, 2.5	0.75, 1.5, 2.5

Differential scanning calorimetry

A Stanton Redcroft DSC (model STA 625) equipped with a computer Data Analyser (version C4.20) in nitrogen atmosphere was used throughout the study. Calibration of the instrument was done by the standard material (Indium). Crosslinking was studied under non-isothermal conditions at the heating rate of 10 deg·min^{-1}. The amount of the sample was approximately 7 mg in all cases.

Determination of cure characteristics

Monsanto Rheometer R-100 was used for this study. Cure characteristics was determined at a temperature 180°C. In Rheometer the rotor oscillation was of ±3° arc.

Determination of modulus

The tensile strength and the moduli at 100 and 300% strain were determined with the help of a ZWICK UTM (model 1445) as per ASTMD412-80.

Theory of kinetic analysis of the exothermic crosslinking

Reactions by DSC

The mathematical model generally used to describe the *n*th order kinetics of a chemical reaction given by Borchardt and Daniel [7] is as follow:

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

where $d\alpha/dt$ rate of reaction, s^{-1}
α fractional conversion (dimensionless)
$k(T)$ specific rate constant at temperature T, s^{-1}
n reaction order (dimensionless)

The temperature dependence of a reaction rate constant $k(T)$ is given by the Arrhenius equation,

$$k(T) = Ze^{-E/RT} \tag{2}$$

where, Z pre-exponential factor
E Energy of activation, (J/mole)
R gas constant (8.314 J/mol·K)
T absolute temperature (K)

Relation between DSC signal and reaction kinetics

The enthalpy of the system changes due to the decomposition of peroxide and subsequent crosslinking reactions. The DSC exotherm (Fig. 1) is used to measure the two basic parameters $d\alpha/dt$ and α. The method assumes that the heat evolved in a small time interval is directly proportional to the number of moles reacting during that time. The reaction rate is obtained by dividing the peak height (dH/dt) at temperature T by the total heat of reaction.

$$\frac{d\alpha}{dt} = (dH/dt)\ \Delta H_o \tag{3}$$

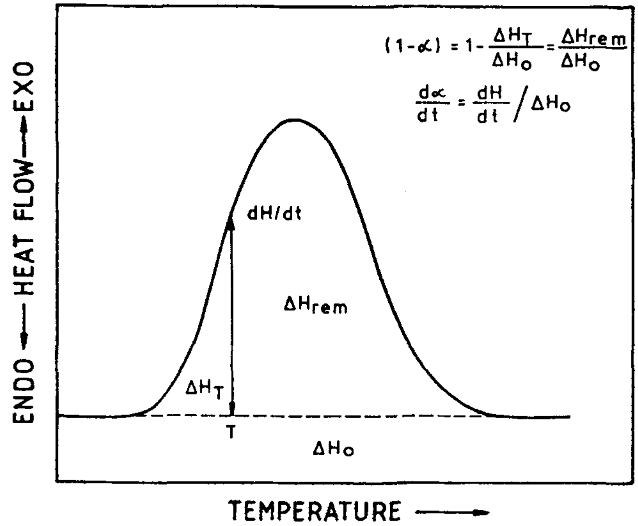


Fig. 1 Exotherm reaction of Borchard/Daniels kinetics

where H_o=the total peak area or the theoretical enthalpy. The fractional conversion 'α' is obtained by measuring the ratio of the partial area, H_T, at temperature T to the total peak area.

$$\alpha = \Delta H_T \,/\, \Delta H_o \tag{4}$$

$$\text{or, } 1 - \alpha = \Delta H_{rem} \,/\, \Delta H_o \tag{5}$$

Substituting Eq. (2) in Eq. (1) yields

$$\frac{d\alpha}{dt} = Ze^{-E/RT}\,(1 - \alpha)^n \tag{6}$$

Taking logarithm of Eq. (6) produces:

$$\ln(d\alpha/dt) = \ln Z - E/RT + n\ln(1 - \alpha) \tag{7}$$

Kinetic analysis of the crosslinking reaction was done by multiple linear regression analysis of Eq. (7) through a computer software programme.

Results and discussions

Non-isothermal curing behavior

A typical DSC trace of EMA–PDMS rubber blend at peroxide level of 1.5 phr is depicted in Fig. 2. It shows that the area under the curing exotherm gradually increases with the increase in PDMS content in the blends. The effect of blend ratio on the reaction exotherm, energy of activation and lnZ (preexponential factor) has been determined using three levels of DCP (namely 0.75, 1.5 and 2.5 phr respectively) which are presented in Table 2. The enthalpy change throughout the entire course of crosslinking reaction i.e., curing exotherm of the different blend system increases with an increase in the DCP content. This shows that heat of crosslinking reaction increases with increasing DCP content irrespective of blend ratio.

The rate of increase in reaction exotherm with DCP content is highest in PDMS, which gradually decreases with the increase in the wt% of EMA in the blends and becomes minimum for EMA. However, the effect of blend ratio on reaction exotherm becomes more pronounced for the DCP content beyond 1.5 parts. This may be due to the fact that the same amount of DCP induces higher degree of crosslinking in the PDMS rubber than in case of EMA. For all the blend systems the maximum rate of enthalpy change during crosslinking reaction occurs at the temperature of 190±3°C. This maxima for silicone rubber occurs at a lower temperature of 182±2°C.

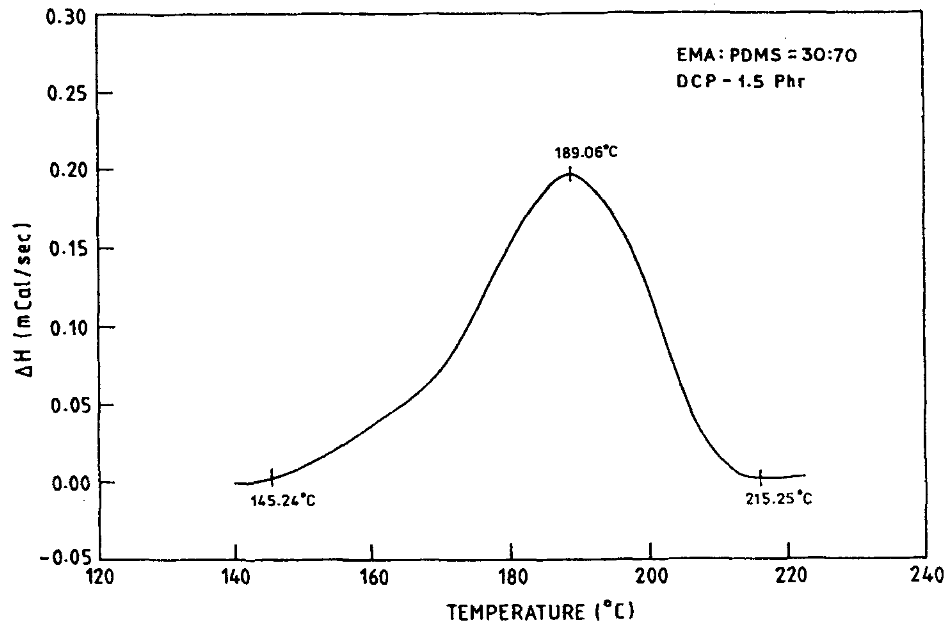


Fig. 2 Typical DSC trace showing curing exotherm of EMA–PDMS blend

In case of EMA, the crosslinking reaction starts at higher temperature of around 171°C but in case of PDMS the same starts at comparatively lower temperature of around 140°C. In case of the blends the crosslinking reaction starts at a temperature between these two temperatures depending upon the composition. As the proportion of EMA increases, the initiation of crosslinking reaction shifts towards a higher temperature. However, the curing reaction completes at a temperature of 210±5°C in all blends and individual components. It is well visualised from the above observations that in PDMS rubber the crosslinking reaction persists for a longer time and the same persists for a comparatively shorter time in EMA copolymer. Whereas, in the blend system the crosslinking reaction persists for longer time in 30:70 EMA:PDMS blend only. This may be due to the fact that the number of crosslinkable sites increases with the increase in proportion of PDMS in the blend and reduces gradually due to the exhaustion of most of the crosslinkable reactive sites of EMA.

Effect of blend ratio on activation energy of curing

The results of kinetic analysis shows that the activation energy of crosslinking reaction is almost independent of peroxide level for all the blend systems (Table 2). Similar observations have also been reported by Brazier and Schwartz [8] earlier for NR and EPDM systems. But it is visualised form our

Table 2 Results of the effect of DCP content on crosslinking reaction exotherm, activation energy and lnZ of the EMA-PDMS blends

Blend code	DCP (phr)	T_i^a °C	T_p^b °C	T_f^c °C	Crosslinking reaction exotherm (Hexo) $J \cdot g^{-1}$	Reaction order	Activation energy/ $kJ \cdot mole^{-1}$	lnZ
I	0.75	171.35	188.97	203.23	3.1	1	110	61
	1.5	171.13	188.92	209.16	4.0	1	117	59
	2.5	170.89	188.42	208.57	5.5	1	120	55
II	0.75	163.74	188.30	214.13	3.5	1	140	52
	1.5	163.49	192.72	216.09	4.6	1	145	55
	2.5	163.82	192.04	210.38	6.8	1	148	53
III	0.75	169.69	188.34	207.54	3.8	1	162	45
	1.5	171.02	187.21	204.25	4.7	1	175	50
	2.5	171.16	189.41	209.23	4.8	1	172	52
IV	0.75	153.39	187.45	209.99	4.5	1	185	47
	1.5	154.32	193.71	214.00	6.5	1	197	45
	2.5	145.24	189.06	215.25	8.2	1	190	46
V	0.75	134.62	188.94	210.10	6.0	1	138	38
	1.5	139.99	182.93	210.01	8.3	1	140	36
	2.5	129.79	184.85	215.00	12.4	1	135	28

[a] Onset temperature of crosslinking reaction, [b] Temperature of maximum rate of crosslinking, [c] Temperature of complete crosslinking reaction

present investigation that the activation energy of crosslinking reaction is strongly dependent upon the blend ratio. Activation energy increases appreciably with increasing proportion of PDMS in the blend system. The variation of activation energy for crosslinking reaction with the blend ratio is shown in Fig. 3. Activation energy is highest for 30:70 EMA:PDMS blend system at all concentrations of DCP. Again for the same DCP level (1.5 phr) in the blends activation energy is highest for 30:70 EMA:PDMS blend. Also it is interesting to observe that the experimental values of activation energy are higher than the theoretical values of activation energy obtained from additivity rule of the blend constituents. This indicates the presence of strong interaction between the polymer constituents in the blend. The presence of such interactions between the reactive functional groups of EMA and PDMS rubber has been already established by the authors [6] in a separate communication, which is found to be responsible for the miscibility of the blend constituents.

Reaction order and pre-exponential factor

It is observed from the kinetic analysis that the crosslinking reaction of EMA, PDMS and their blends in all proportions studied follow first order reaction kinetics when DCP is used as the lone curing agent (Table 2). The reac-

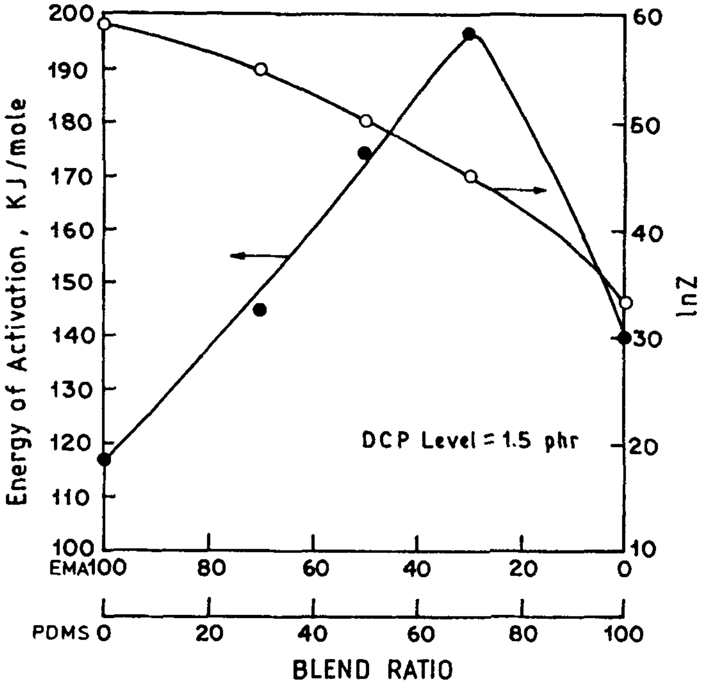


Fig. 3 Effect of blend ratio on activation energy and lnZ of crosslinking reaction

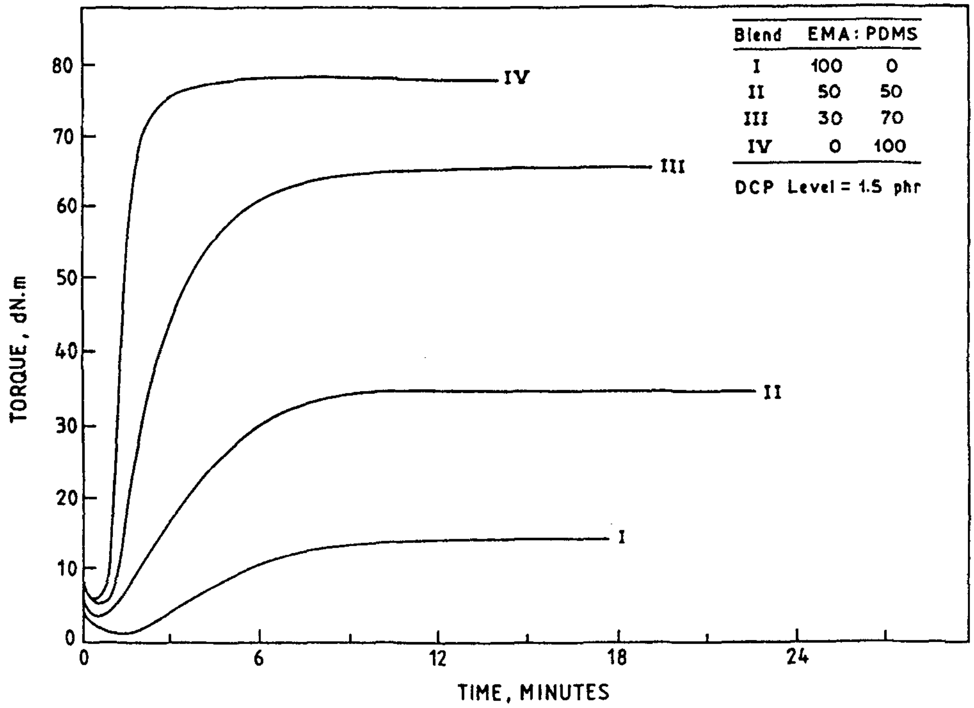


Fig. 4 Typical rheometric traces of different blend compositions showing torque development during the course of crosslinking reaction at DCP level of 1.5 phr

tion order is also independent of the level of DCP. But contrary to the activation energy the value of natural logarithm of pre-exponential factor (lnZ) for crosslinking reaction gradually decreases with the higher proportion of PDMS in the blend system. The same trend also has been found with the increase of DCP level in the pure components as well as blends. The variation of lnZ with blend ratio for the same DCP level (1.5 phr) is represented in Fig. 3. This shows that activation energy is strongly dependent on blend composition but lnZ is independent of the DCP level in the blend.

Rheometric studies of isothermal cure behavior

Rheometric data of EMA, PDMS and their blends at three different DCP doses at an isothermal temperature of 180°C are reported in Table 3. Rheometric traces of EMA, PDMS and for two blend systems 50:50 EMA:PDMS and 30:70 EMA:PDMS at a constant DCP level of 1.5 phr are shown in Fig. 4. On the other hand, Fig. 5 shows the rheometric traces of 30:70 EMA:PDMS blend at three different DCP levels. Rheometric trace of 70:30 EMA:PDMS blend is omitted from the Fig. 4 as it is not worthy to compare this system which is thermoplastic in nature. It is clearly observed from Figs 4 and 5 that the rate of rise in torque, a measure of rate of cure of the systems increased with DCP level as well as with increase in PDMS/EMA ratio in the blend systems. This has been very well reflected in the *Vr* values determined from equilibrium swelling studies of the systems which follow the same pattern (Table 3). This may be explained as due to rapid onset of curing on increasing the DCP level in the same blend composition and also due to the generation of more crosslinkable sites with increase in PDMS proportion in the blend system. As a result *Vr* which is a measure of crosslink density is maximum in case of PDMS rubber at higher proportion of DCP and is minimum with EMA copolymer which is less sensitive to peroxide crosslinking. In corollary, the scorch time and the optimum cure time decreases with increase in DCP level as well as increase in PDMS concentration in the blend; as shown in Table 3. These rheometric results support the observed curing behaviour obtained from non-isothermal DSC curves at higher crosslink density in 30:70 EMA:PDMS blends. In case of neat PDMS rubber, the cure rate is maximum at 1.5 phr level of the peroxide (DCP), indicating rapid attainment of the optimum cure, which shows a minimum time of 1.9 min where as at higher DCP concentration, the rate decreases, may be due to generation of more radicals than needed for crosslink formation. However, the crosslink density steadily increases. From the rheometric curves of 30:70

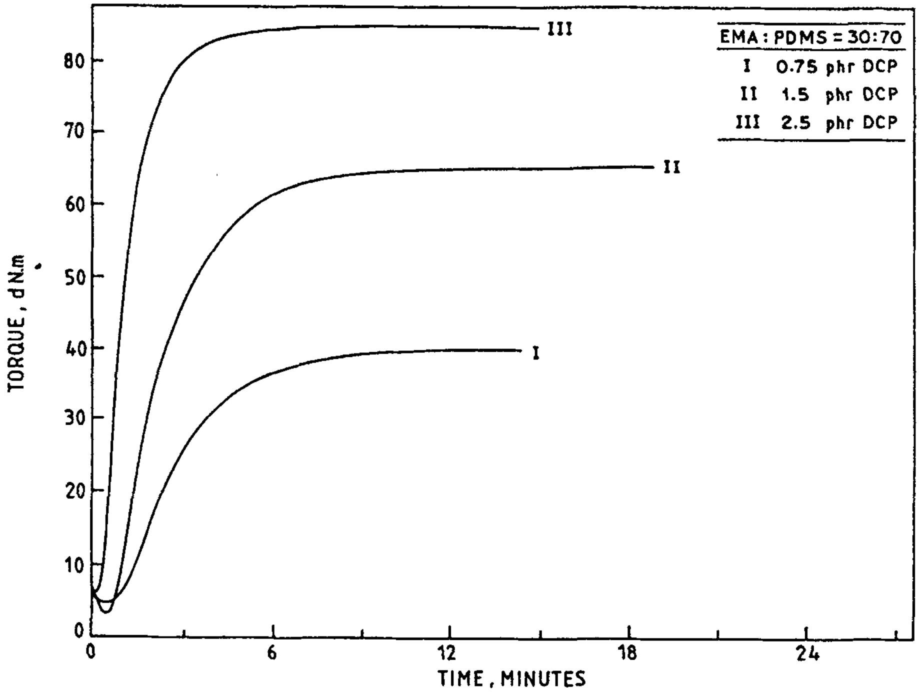


Fig. 5 Typical rheometric traces of 30:70 EMA:PDMS blend at different levels of DCP

Table 3 Cure characteristics and tensile properties of the blends at different DCP levels

Blend code	DCP level	Scorch time/ min	Optimum cure time/ min	Cure rate*	Tensile strength/ MPa	Elongation at break/ %	100% modulus/ MPa	300% modulus/ MPa	Work to rupture/ $J \cdot m^{-2}$	*Vr*
I	0.75	7.50	10.00	17	15.8	960	3.6	4.8	35304	0.09
	1.5	2.25	7.00	20	21.5	960	3.9	5.6	35304	0.12
	2.5	1.50	5.75	26	13.5	730	3.7	5.8	24232	0.17
II	0.75	2.25	6.25	23.5	12.5	530	3.2	6.4	14759	0.17
	1.5	1.50	6.50	20.0	17.2	765	3.8	7.0	26319	0.19
	2.5	1.37	5.60	23.5	11.3	450	4.2	8.3	7675	0.22
III	0.75	1.25	5.0	25.3	15.6	690	4.0	7.1	21559	0.20
	1.5	1.15	5.4	23.2	16.7	525	4.4	8.7	13283	0.24
	2.5	1.05	4.6	27.9	10.1	245	4.2	not measurable	5308	0.26
IV	0.75	1.25	5.12	25.6	12.6	598	3.2	6.8	19622	0.23
	1.5	0.90	4.6	27.2	13.2	420	4.2	9.7	7579	0.28
	2.5	0.90	4.3	29.4	10.2	312	3.9	8.2	4783	0.31
V	0.75	1.20	3.60	43.4	9.1	420	2.0	6.2	7583	0.31
	1.5	0.70	1.90	90.1	10.4	366	3.0	8.6	8161	0.33
	2.5	0.69	2.12	76.3	8.2	281	2.3	not measurable	5708	0.35

*Cure rate = $\frac{100}{t_{90} - t_2}$ where, t_{90} = optimum cure time in minutes, t_2 = scorch time in minutes

EMA:PDMS blend shown in Fig. 5 it is found that the torque development and rate of cure increases with an increase in the amount of DCP whereas scorch time and optimum cure time decreases due to rapid onset of curing. This imply that the crosslink density is higher with higher doses of DCP in the blends as is evident from calculation of *Vr* values for the blends and the pure components (Table 3). This has been further confirmed from the crosslinking reaction exotherms of the blends which increase with an increase of DCP level in the blend composition as well as with PDMS rubber proportion in the blend (Table 2).

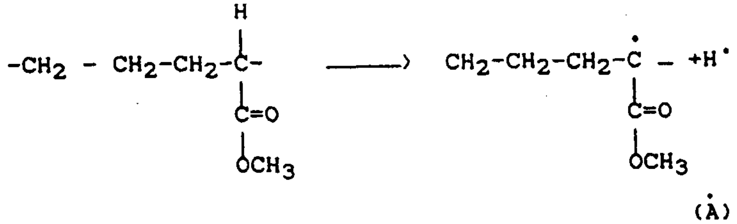
Mechanical properties of the blends

Tensile strength, modulus at 100% elongation and 300% elongation and work to rupture of EMA, PDMS and their blends at three different levels of DCP are compiled in Table 3. Tensile strength of EMA is the highest and that of PDMS is the lowest in the system. On the other hand, tensile strength of the blends decrease with an increase in the PDMS proportion in the blend. This is particularly so at higher concentrations of DCP in the blend system. This may be explained as due to lower tensile strength of PDMS elastomer at all DCP levels as compared to that of EMA copolymer. It is very interesting to observe that the 100 and 300% moduli of the blend increases gradually with an increase in the PDMS rubber proportion and tends towards a maximum in case of 30:70 EMA:PDMS blend at optimum proportion of DCP (1.5 phr) which may be attributed to both the grafting as well as crosslinking reactions to a maximum extent. The formation of such a three dimensional network structure or the graft copolymer has been discussed earlier [9]. However maximum interaction via chemical reaction between the EMA copolymer and PDMS rubber occurs at this proportion which enhances the moduli of the system. It is evident that the tensile moduli is more pronounced at 30:70 EMA:PDMS rubber. Similarly, tensile strength also exhibit a mild synergism in the blend with respect to the individual blend constituents. This is more prominent for both the tensile strength and moduli at the optimum concentration of DCP (1.5 phr). This has also been reflected in the work to rupture which although decreases with increase in PDMS rubber proportion in the system but shows a mild synergism. This has been amply supported by the DSC data of all the blends. The activation energy is found to be highest in the case of 30:70 EMA:PDMS rubber blend. In this system more number of new C–C bonds are formed due to grafting reaction between EMA and PDMS rubber as shown in the given scheme and also to additional C–C bond formation because of crosslinking by DCP.

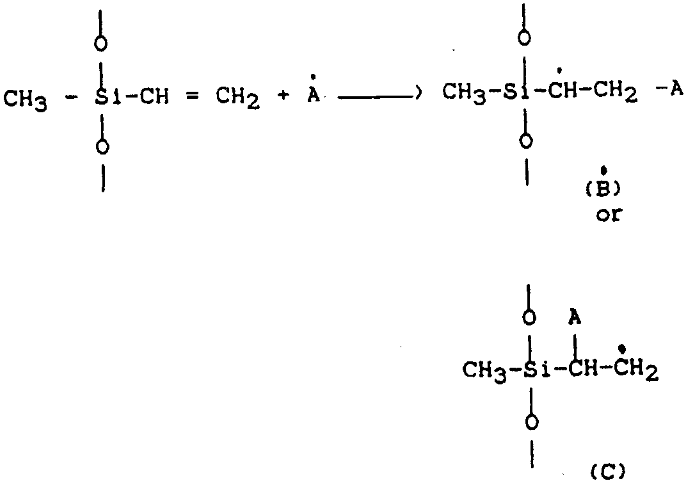
It is also observed that for each system the tensile strength increases, reaches a maximum then decreases with increasing DCP concentration, similar to that observed with increasing crosslink density in a rubber vulcanizate. This has been further supported by the *Vr* values. The DCP level of 1.5 phr, where maximum tensile strength obtained is the optimum DCP level.

General mechanism and discussion

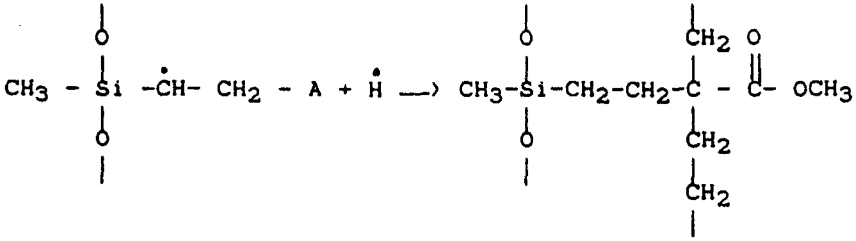
A plausible mechanism for the reaction between EMA and PDMS rubber forming EMA–g–PDMS rubber is given as follows:



1. The labile hydrogen atom at each α-carbon atom adjacent to the ester group of the ethylene methyl acrylate breaks homolytically to give a H radical and a macro radical A during melt processing under shear.



2. This macroradical 'A' thus generated is stable and attacks the vinyl site of the PDMS to give the intermediate radical B or C.



3. The intermediate macromadical B then takes up the H-radical thus liberated in earlier step to saturate the carbon radical forming a new $-CH_2-$ bridge. This process is instantaneous.

This results in the formation of a new carbon–carbon bond between EMA and PDMS rubber. In addition, presence of DCP initiates intermolecular crosslinking reactions between EMA grafted PDMS rubber resulting in the formation of a three dimensional interpenetrating network structure. Hence the strength is higher. Miscibility of the blends through chemical reaction [6] and mechanical as well as dynamic mechanical properties of the blends [9] have already been reported in separate communications.

Conclusions

1. The exothermic heat of crosslinking reaction of EMA:PDMS blends increase with the increase in PDMS:EMA ratio. For individual blend composition, the heat of reaction also increases with the increase in the dosage of DCP.
2. The energy of activation of the crosslinking reaction is almost independent of the level of DCP but it increases appreciably with increasing proportion of PDMS in the blend system.
3. Crosslinking reaction of EMA, PDMS and their blends follow a first order kinetics and reaction order is independent of DCP concentration. But pre-exponential factor for crosslinking reaction decreases gradually with the higher proportion of PDMS in the blend composition.
4. Tensile strength of the blends decrease with increasing ratio of PDMS:EMA in the blend systems but modulus gradually increases with the incorporation of PDMS in the blend.
5. The optimum concentration of DCP in all the blends and the pure components have been found to be 1.5 phr.

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Zusammenfassung — Mittels DSC und Rheometrie wurden die Härtungsreaktionen Gummigemischen aus Ethylenmethylacrylat (EMA) und Polydimethylsiloxan (PDMS) untersucht. Die Ableitung der kinetischen Parameter ist mit dem Härtungsprozeß verbunden. Die Vernetzung von EMA-PDMS Gummigemischen verläuft in einer Reaktion erster Ordnung. Der Einfluß von Gemischverhältnis und Peroxidkonzentration auf die Eigenschaften der Vernetzungsreaktion der Gemische wurde ebenfalls untersucht.