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An investigation into the mechanical properties and curing kinetics of blends of low-density polyethylene and polydimethyl siloxane rubber

R.N. Jana, H.P. Bhunia, G.B. Nando*

Rubber Technology Centre, Indian Institute of Technology, Kharagpur–721302, India

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Abstract

Curing reactions of low-density polyethylene (LDPE) and polydimethylsiloxane (PDMS) rubber blends have been investigated by Differential Scanning Calorimetry (DSC) and by Rheometry. From the DSC thermograms the kinetic parameters have been calculated. The order of the reaction has been found to be first order. The optimum level of peroxide was found to be 1.5 pbw. The activation energy of the blends was found to be higher than that calculated as per additivity rule which is indicative of an interaction of the blends constituents. Improved mechanical properties of the blends on curing is indicative of cure compatibility of the blends. © 1997 Elsevier Science B.V.

Keywords: DSC; Kinetic parameters; Mechanical properties; Rheometry

1. Introduction

Curing kinetics of different elastomers by dicumyl peroxide with the help of DSC have been reported by several authors [1–3]. The curing kinetics were also studied for epoxy resins [4,5], rubber modified epoxides [6–8], glass-reinforced composites[9] of diglycidyl ether of bis phenol-P epoxy resin, polyester [8], PE-poly butadiene blends [10], EPDM–PE blends [11] and PDMS–EMA blends [12] and so on.

Low density polyethylene (LDPE) is the base polymer used most extensively in compounding for wire and cable insulations. It has replaced other insulating materials such as styrene butadiene rubber (SBR), ethylene propylene diene rubber (EPDM), chloroprene rubber (CR) and others in a wide range of applications, because of its superior mechanical and insulating properties. Moreover, insulation thickness has been reduced resulting in lower weight and compactness of the cables. Polyethylene can be cross-linked with PDMS in presence of peroxides (e.g. dicumyl peroxide) at a temperature of 170–180°C.

Poly dimethylsiloxane (PDMS) rubber has long been recognised as the rubber of choice for high and low temperature applications. Both the number of 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 adverse conditions.

In the present investigations the blends of LDPE and PDMS rubber have been studied because of the fact that they find an attractive application in the cable industry as an insulating compound. Attempts have been made to co-cure LDPE–PDMs rubber blends so

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*Corresponding author.

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that the product will give rise to an improved insulation with higher thermal stability and higher service temperature than that experienced with LDPE only. The main objectives of the present investigations are,

1. to optimise the level of DCP in the blends,
2. to determine the order of the reaction,
3. to find the activation energy of the exothermic curing reaction and
4. to find the exothermic heat of the crosslinking reaction of the blends.

2. Experimental

2.1. Materials

Low density polyethylene (LDPE) (Indothane 20XL020) having a density of 919 kgm^{-3}, MFI of 2.0 g min^{-1}, and melting point of 112°C was supplied by the Indian Petrochemicals Corporation (Baroda, India). Polydimethyl siloxane rubber (Silastic WC-50) containing approximately 3.8% of vinyl groups, having a density of 115 kgm^{-3}and brittle temperature of −39°C was supplied by M/S. Dow Corning, U.S.A. Dicumyl peroxide (Dicup-40, 40% with calcium carbonate) used was supplied by NICCO Corpn (Athpur, India).

2.2. Preparation of the blends

Melt processing of individual components and the blends were carried out in a Brabender Plasticorder (PLE-330) at 180°C for 10 mins at 100 rpm rottor speed. The molten mass was taken out and sheeted in a two roll laboratory mill of size 150 mm × 300 mm. The sheet was again charged into the plasticorder at 130°C, mixed thoroughly with dicumyl peroxide (Dicup 40). Mixing was continued for 2 more minutes to get a homogeneous mixture. The molten mass was subsequently vulcanised in a compression moulding press at 180°C under a pressure of 4.5 MPa for the respective optimum curve times as determined by a Monsanto Rheometer model R-100. The blends have been coded as P_{100}, P_{75}, P_{25} and P_0, the subscripts denoting the proportion of LDPE in the blend. To each blend and the pure components DCP was added in proportions varying from 0.75, 1.5,3.0, 4 & 5 pbw separately.

2.3. Differential scanning calorimetry

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

2.4. Determination of cure characteristics

Monsanto Rheometer R-100 was used for studying the cure characteristics of the blends at a temperature of 180°C. The rotor oscillation of the Rheometer was of ±3° arc.

2.5. Determination of modulus

The tensile strength and the moduli of the blends at 100 and 300% strain were determined with the help of a ZWICK UTM (model 1445) as per ASTMD412-80 at room temperature (25°C).

2.6. Mathematical model for curing reaction

The mathematical model generally used to describe the n-th order kinetics of a chemical reaction given by Borchardt and Daniel is as follows:

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

where,

$d\alpha/dt$ = rate of reaction , s^{-1}
α =fractional conversion
$k(T)$ =specific rate constant at temperature T,s^{-1}
n =order of the reaction (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/mole.K)
T =absolute temperature (K)

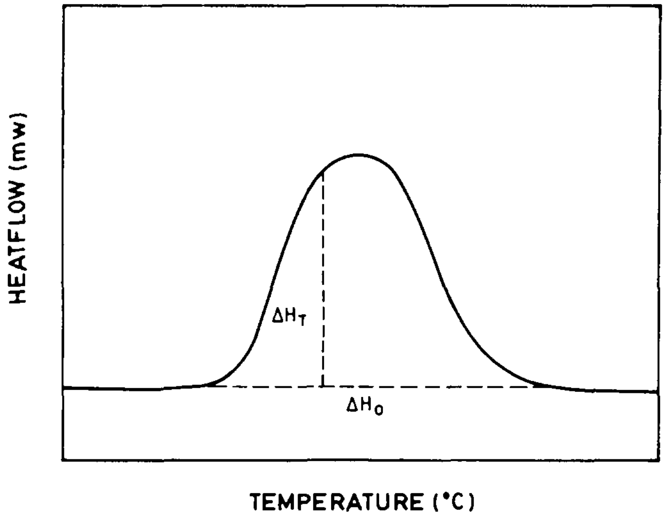


Fig. 1. Exothermic reaction of Borchardt-Daniel's kinetics.

The enthalpy of the system changes due to the decomposition of peroxide and subsequent crosslinking reactions. The DSC exotherm is used to measure the two basic parameters $d\alpha/dt$ and α (Fig. 1)

The method assumes that the heat evolved in a small time interval is directly proportional to the number of the 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 the reaction (ΔH_0). i.e.

$$d\alpha/dt = (dH/dt)/\Delta H_0 \tag{3}$$

where, ΔH_0= total peak area or the theoretical enthalpy. The fractional conversion α is obtained by measuring the ratio of the partial area,

$$\Delta H_T/\Delta H_0 \tag{4}$$

Substituting Eq. (2) in Eq. (1) we get,

$$d\alpha/dt = Ze^{-E/RT}(1-\alpha)^n \tag{5}$$

Taking the logarithm of Eq. (5) we get

$$\ln(d\alpha/dt) = \ln Z - E/RT + n\ln(1-\alpha) \tag{6}$$

Kinetic analysis of the crosslinking reaction was done by multiple linear regression of Eq. (6) through a computer software programme.

3. Result and discussions

3.1. Reaction exotherm

A typical DSC trace of LDPE–PDMS rubber blend at peroxide level of 1.5 phr is depicted in Fig. 2. It is found that the area under the curing exotherm gradually increases with increase in PDMS rubber content in the blends. The effect of blend ratio on the reaction exotherm, order of reaction, energy of activation and lnZ has been determined using four levels of DCP (namely 0.75, 1.5, 3.0, 4.5 pbw respectively) as explained earlier and are presented in Table 1. 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. The shows that heat of crosslinking reaction increases with increasing DCP content irrespective of the blend ratio.

The rate of increase in reaction exotherm with DCP content is highest in PDMS, which gradually decreases with an increase in the wt% of LDPE in the blends and becomes minimum for LDPE. However, the effect of blend ratio on reaction exotherm becomes more pronounced beyond 1.5 parts of DCP content. 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 LDPE. For all the

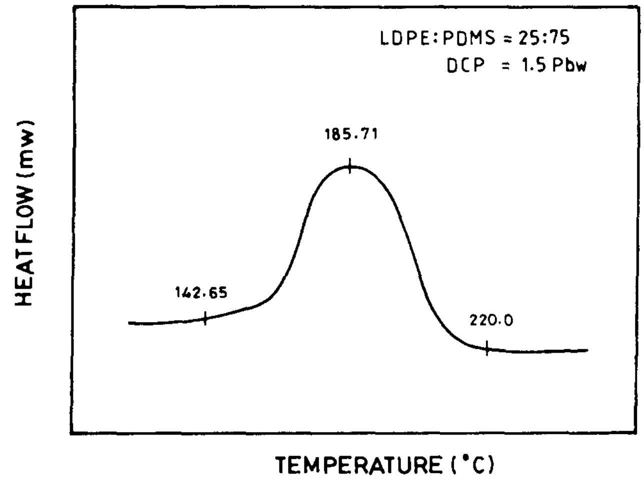


Fig. 2. Typical DSC trace showing curing exotherm of LDPE: PDMS rubber blend.

Table 1
Effect of DCP content on the crosslinking reaction exotherm activation energy and lnZ of the LDPE–PDMS rubber blends

Blend code	DCP (pbw)	Ti (°C)	Tp (°C)	Tf (°C)	ΔHexo J g^{-1}	Reaction order	Activation energy kJ mol^{-1}	lnZ
P_{100}	0.75	148.57	196.19	228.57	11.3	1.0	207.44	55.18
	1.50	157.14	192.85	214.28	12.16	1.0	219.00	58.37
	3.00	137.14	196.19	219.04	30.88	1.0	257.38	62.28
	4.50	150.00	191.42	221.42	32.97	1.0	286.27	77.29
P_{75}	0.75	152.38	182.86	213.34	10.72	1.0	170.31	45.34
	1.50	140.95	190.47	219.04	20.32	1.0	173.15	45.73
	3.00	133.33	190.47	226.67	33.87	1.0	170.83	46.63
	4.50	137.14	194.28	219.04	43.28	1.0	182.84	48.25
P_{50}	0.75	143.16	188.96	229.40	17.80	1.0	138.29	36.25
	1.50	140.95	188.57	219.04	19.16	1.0	142.66	38.37
	3.00	142.86	186.67	228.57	33.68	1.0	160.09	42.58
	4.50	140.95	190.47	217.14	46.45	1.0	168.42	45.95
P_{25}	0.75	129.52	184.76	217.14	20.14	1.0	98.79	26.13
	1.50	142.65	185.71	220.00	26.73	1.0	97.89	25.06
	3.00	129.52	186.67	224.76	43.35	1.0	108.35	27.86
	4.50	142.85	190.47	220.95	43.78	1.0	110.39	29.52
P_0	0.75	150.00	185.71	217.14	17.64	1.0	47.86	12.98
	1.50	140.00	185.71	221.42	33.12	1.0	46.19	12.35
	3.00	118.09	190.47	219.04	60.03	1.0	45.06	10.80
	4.50	128.57	185.90	220.00	72.34	1.0	57.55	13.86

blend systems the maximum rate of enthalpy change during crosslinking reaction occurs at a temperature of 188±6°C. This maxima for silicone rubber occurs at a lower temperature of 182± 2°C.

In case of LDPE, the crosslinking reaction starts at higher temperature of around 150°C but in case of PDMS the same starts at comparatively lower temperature of around 135°C. This may be due to vinyl groups present in the silicone rubber in the side chains which are more labile than methyl hydrogen. In case of the blends the crosslinking reaction starts at a temperature in between these two temperatures. As the proportion of PDMS rubber increases in the blends the initiation of crosslinking reaction shifts towards a lower temperature. However, the curing reaction completes at a temperature of 220±3°C in all blends and individual components. It is well visualised from the above observation that in PDMS rubber the crosslinking reaction persists for a longer time and that for LDPE for a shorter time.

3.2. *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 [13] for NR and EPDM systems. But from our investigation it is found that the activation energy of crosslinking reaction is strongly dependent upon the blend ratio. Activation energy decreases appreciably with increasing proportion of PDMS in the blend system. The variation of activation energy and lnZ for crosslinking reaction with the blend ratio is shown in Fig. 3. An interesting observation from the above result is that the experimental activation energy of the blend vulcanizates are not very much different from the theoretical value of activation energy calculated as per additivity rule of the blend constituents. This is indicative of the absence of any intermolecular interaction between the blend constituents during reactive processing. Whereas intramolecular as well as intermolecular crosslinking between the individual polymeric chains is likely to occur in the presence of the peroxide crosslinking agent during curing. Consequently a three dimensional network structure of the cocured blend is formed. Moreover, DCP is more reactive towards the vinyl groups of PDMS than the reactive sites of LDPE. Thus LDPE is lightly crosslinked and is more likely to be penetrated into the network formed by PDMS resulting in almost a semi-interpenetrating polymer network structures (semi-IPN). Since at higher temperature, viscosity of LDPE is lower than that of PDMS rubber, LDPE remains in the continuous phase. Depending upon the proportion of PDMS rubber, it will remain either in dispersed phase or in

Table 2
Cure characteristics and tensile properties of the blends at different DCP levels

Blend code	DCP (pbw)	Scorch time (min)	Optimum cure time (min)	Cure rate	T.S. (MPa)	Eb (%)	100% mod. (MPa)	300% mod. (MPa)	Hard ness (Shore A)	Vr
P_{100}	0.75	3.00	6.50	28.60	12.50	855	6.8	7.2	92	0.10
	1.50	2.50	6.50	25.00	12.80	810	7.7	8.4	92	0.12
	3.00	2.00	6.50	22.20	12.40	805	6.5	7.6	95	0.12
	4.50	1.50	6.00	22.20	12.40	785	4.6	6.7	94	0.13
P_{75}	0.75	2.75	7.50	21.05	9.90	810	6.0	6.8	86	0.13
	1.50	2.50	7.00	22.22	10.00	795	6.3	7.1	87	0.15
	3.00	2.00	6.75	21.05	9.80	760	5.9	6.7	86	0.16
	4.50	2.00	6.50	12.50	9.80	740	5.7	6.2	88	0.19
P_{50}	0.75	1.50	6.00	22.20	7.10	780	5.1	6.2	84	0.18
	1.50	1.50	6.00	22.20	7.20	770	5.6	6.5	85	0.20
	3.00	1.25	5.25	25.00	7.10	766	5.0	6.3	85	0.23
	4.50	1.25	5.00	26.67	7.00	750	4.8	6.0	86	0.24
P_{25}	0.75	1.00	5.00	25.00	6.30	760	5.0	6.0	74	0.22
	1.50	1.00	4.50	28.57	6.35	712	5.3	6.1	76	0.23
	3.00	0.75	4.00	30.76	6.25	705	5.1	6.0	78	0.25
	4.50	0.75	4.00	30.76	6.21	680	4.9	5.6	78	0.26
P_0	0.75	1.00	2.75	57.20	8.60	510	2.5	6.5	62	0.30
	1.50	0.75	2.10	74.07	10.80	360	2.8	6.9	64	0.31
	3.00	0.75	2.00	80.00	8.70	300	2.5	5.8	65	0.32
	4.50	0.60	1.80	83.30	9.70	290	2.3	not measurable	67	0.35

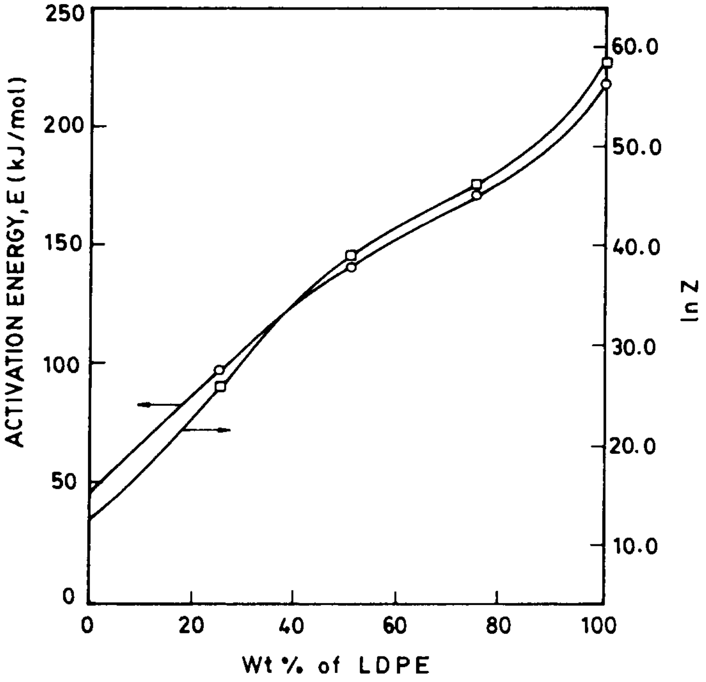


Fig. 3. Effect of blend ratio on activation energy and lnZ of crosslinking reaction (DCP=1.5 pbw)

co-continuous phase. This may facilitate the formation of semi-interpenetrating polymer network.

3.3. Reaction order and pre-exponential factor

It is observed from the kinetic analysis that the crosslinking reaction of LDPE , PDMS and their blends in all proportions follow first order reaction kinetics when DCP is used as the curing agent (Table 1). The reaction order is also independent of the level of DCP. Both the activation energy and the value of natural logarithm of pre-exponential factor (lnZ) for crosslinking reaction gradually decreases with an increase in the proportion of PDMS rubber in the blend. Where as the reverse is observed with the increase of DCP level in the pure components as well as in the blends. The variation of lnZ with blend ratio for the same DCP level (1.5 pbw) is represented in Fig. 3.

3.4. Rheometric studies of isothermal cure behavior

Rheometric data of LDPE, PDMS and their blends at four different DCP doses at an isothermal temperature of 180°C are reported in Table 2. Rheometric traces of LDPE, PDMS and three blend systems at a constant DCP level of 1.5 pbw are shown in Fig. 4. On the other hand, Fig. 5 shows the rheometric traces of 25 : 75 LDPE : PDMS (as a typical example) at four different DCP levels. It is clearly observed from Fig. 4 and Fig. 5that the rate of rise in torque, a measure of rate of curve of the systems increased with DCP level as well as with increase in PDMS/LDPE ratio in the blend systems. This has been very well reflected in the Vr values determined from equilibrium swelling studies of the systems which follows the same pattern (Table 2). This may be explained as due to the rapid onset of curing on increasing the DCP level in a constant blend composition and also due to the generation of more cure 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 LDPE which is less sensitive to peroxide crosslinking. The scorch time and the optimum cure time decreases with increases in DCP level as well as PDMS concentrations in the blend, as shown in Table 2. These rheometric results support the observed curing behaviour obtained

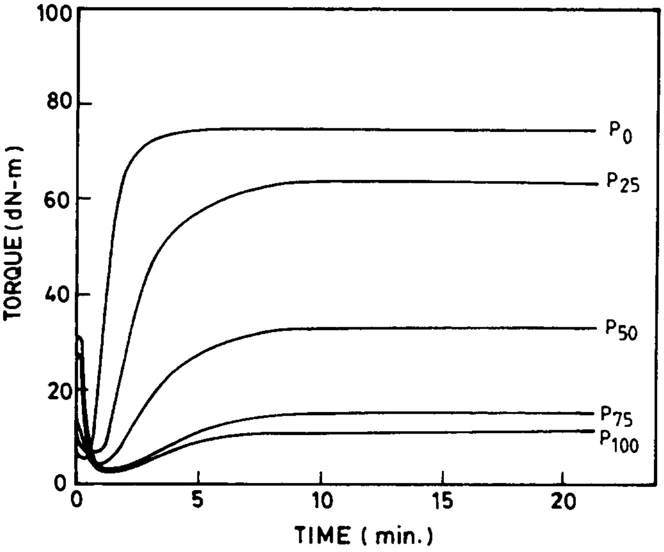


Fig. 4. Rheographs of different blends (DCP=1.5 pbw).

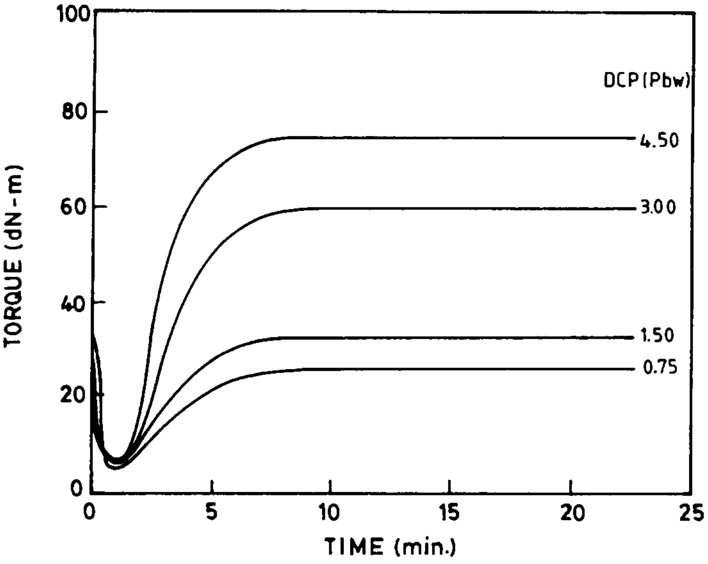


Fig. 5. Rheographs of P_{50} blend at different level of DCP.

from non-isothermal DSC curves. For all cases the cure rate increases with increasing DCP level.

3.5. Mechanical properties of the blends

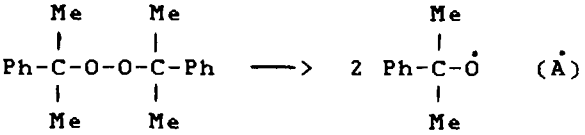
Tensile strength, modulus at 100% and 300% elongation and hardness of LDPE, PDMS and their blends at four levels of DCP are compiled in Table 2. Tensile strength of LDPE is highest and that of PDMS is the lowest in the system. On the other hand, tensile strength of the blends decrease with an increase in the PDMS proportion in the blend. This may be explained as to the lower tensile strength of PDMS elastomer at all DCP levels as compared to that of

LDPE. From the tensile strength data, it is seen that 1.5 pbw of DCP imparts highest strength properties in all the blends and pure components, hence is taken as the optimum level. Elongation at break gradually decreases with increase in PDMS rubber content and DCP level in the blends. Hardness marginally increase with peroxide level, where as it decrease with increased proportion of PDMS rubber in the blends because of an increased amorphous character of the matrix. As the extent of crosslinking increases, the Vr value also increases. This is reflected in Table 2, which shows an increase in Vr values with an increase in DCP level as well as PDMS.

4. General mechanism and discussion

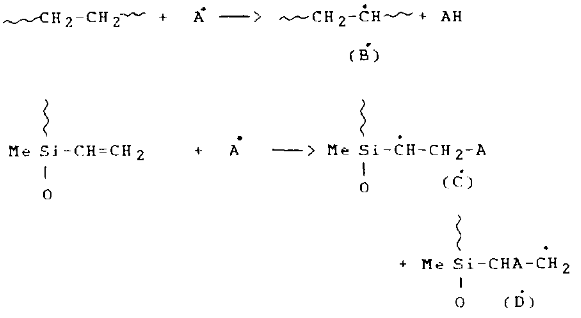
A plausible mechanism for the curing reaction between LDPE and PDMS rubber in presence of peroxide is given below.

1. A first order chemical reaction for thermal decomposition of peroxide is to produce oxyradicals.



$$\text{Ph-}\underset{\text{Me}}{\overset{\text{Me}}{\text{C}}}\text{-O-O-}\underset{\text{Me}}{\overset{\text{Me}}{\text{C}}}\text{-Ph} \longrightarrow 2\ \text{Ph-}\underset{\text{Me}}{\overset{\text{Me}}{\text{C}}}\text{-}\dot{\text{O}} \qquad (\dot{\text{A}})$$

2. Peroxy radical interaction and abstraction of hydrogen atoms from the polymeric chains, resulting in the formation of free radical site on the polymeric chains of LDPE and PDMS.



$$\sim\text{CH}_2\text{-CH}_2\sim + \dot{\text{A}} \longrightarrow \sim\text{CH}_2\text{-}\dot{\text{C}}\text{H}\sim + \text{AH} \quad (\dot{\text{B}})$$

$$\text{Me}\underset{\text{O}}{\text{Si}}\text{-CH=CH}_2 + \dot{\text{A}} \longrightarrow \text{Me}\underset{\text{O}}{\text{Si}}\text{-}\dot{\text{C}}\text{H-CH}_2\text{-A} \ (\dot{\text{C}}) + \text{Me}\underset{\text{O}}{\text{Si}}\text{-CHA-}\dot{\text{C}}\text{H}_2 \ (\dot{\text{D}})$$

3. Polymeric radical chains then become dead by homo or cross termination, evidently the latter one produces the C–C bond between PDMS and LDPE. The intermediate macroradicals ($\dot{B}, \dot{C}, \dot{D}$) may also take up H radical from the virgin polymers, thus generating more active macroradicals. PDMS is more reactive towards peroxide than LDPE. So the macroradicals ($\dot{C}$ or $\dot{D}$) will be preferably formed by reacting with peroxide oxyradical rather than that from polyethylene macroradical ($\dot{B}$).

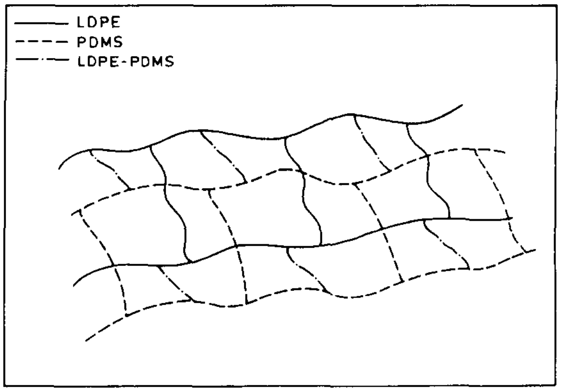
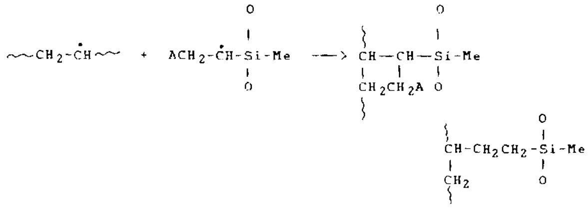


Fig. 6. IPN of crosslinked LDPE–PDMS rubber blends.



$$\sim\text{CH}_2\text{-}\dot{\text{C}}\text{H}\sim + \text{ACH}_2\text{-}\dot{\text{C}}\text{H-}\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}\text{-Me} \longrightarrow$$

The possible structure of the interpenetrating polymer network resulted may be presented as Fig. 6

5. Conclusion

1. Activation energy of curing reaction is dependant on peroxide level and also on the blend composition. With increasing PDMS content it decreases and become minimum for neat PDMS
2. The order of the curing reaction is found to be first order.
3. Crosslinking reaction exotherm for LDPE is minimum and that for PDMS is maximum. The blends have an intermediate value. For a constant blend ratio with increase in DCP level the reaction exotherm increases.

4. Optimum level of DCP based on maximum strength properties experienced by the vulcanizates has been found to be 1.5 pbw

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