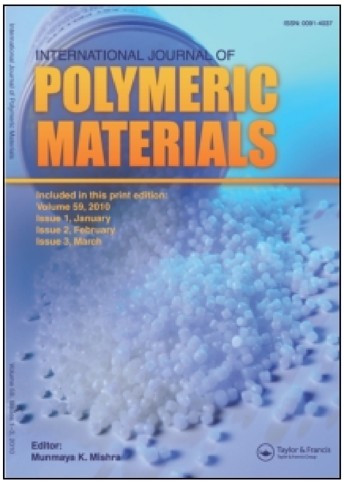

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Prithu Mukhopadhyay[a]; C. K. Das[a]
[a] Materials Science Centre, IIT Kharagpur, India

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Effect of Crosslinking on the Structure, Properties and Failure Mechanisms of XLPE and Crosslinked Butyl Elastomer Blends

PRITHU MUKHOPADHYAY† and C. K. DAS
Materials Science Centre, IIT Kharagpur, India 721302

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The polyblend systems consisting of crosslinkable polyethylene (XLPE) and the crosslinked butyl rubbers were studied. Two types of crosslinked butyl rubbers viz XL-20 (80% crosslinked) and XL-50 (50% crosslinked) were considered in order to find out the effect of crosslinking of the elastomer on the structure, properties and mode of failure of the blends. Properties are correlated with the crystallinity of the blends as determined by X-ray analysis. Both the rate of cure and state of cure are improved by the incorporation crosslinked butyl rubber in XLPE with more advantage in the case of lower crosslinked butyl (XL-50). At the lower level of crosslinked butyl the physical properties and the swelling is governed by the crystallinity of the blend and XL-20 containing blends exhibit lower swelling than XL-50 containing blends. Lower degree of crosslinking in butyl rubber (XL-50) gives rise to more thermally stable blends. Smooth failure is obtained in the case of low degree of crosslinking in the elastomeric phase, viz. XL-50 containing blends. However the fracture in XL-20 containing is accompanied by fibre and cavity formation. Results are discussed considering the structure of butyl rubbers having different degree of crosslinking and a probable mechanism has been put forward.

KEY WORDS Polyblends, polyethylene, butyl rubber, crosslinking, properties.

1. INTRODUCTION

The study of multicomponent polymer blends is of growing importance. Though most of them are incompatible due to the thermodynamic restriction imposed by their large chain length yet are exciting from scientific and technological point of view.

Polyolefin blends have been utilized in many forms to achieve modifications yielding improved impact strength, flexibility and filler acceptance.[1–3] Blends of various elastomers with polyolefins have interesting properties which are not the averages of the components.[4,5] Several advantages of cross-linked polyethylene (XLPE) have been reported.[6,7] Considering the potential of XLPE in cable industries we have taken up a series of investigation on polyblends of XLPE and other elastomers. Flow behaviour, thermal stability, physical properties and failure of XLPE in blends with EPDM, Silicons and EVA have been reported.[8–10]

Here, we have studied the melts blends of XLPE, which inherently contains dicumyl peroxide with crosslinked butyl elastomers of different degree. XL-butyls have been found to be an effective partner in polyblend systems.[11,12] Keeping in view the influence of covalent bonds on the multicomponent polymer blends, our approach is to induce generation of free radicals by heat and mechanical shear on polymer chains and subsequent crosslinking between component polymers to produce network structure. We have reported the state and rate of cure from the processability view point. The physical properties were examined in terms of effect on blend structure and on failure mechanism with the help of SEM and X-ray studies. The ageing behaviour was studied and supported by thermo-analytical techniques and a suggested mechanism is discussed.

2. EXPERIMENTALS

Formulation of blends are given in Table I. XL-20 (80% cross-linked) and XL-50 (50% crosslinked) were from Polysar Ltd., Canada and XLPE-11 were from IEL Ltd., India. Blends of XLPE and crosslinked butyls (XL-20 and XL-50) were prepared in a Brabender Plasticorder at 80 rpm and 120°C following the procedure earlier.[13] Continuous measurements of cure characteristics at 160°C, 170°C and 180°C were evaluated with the help of a Monsanto Rheometer (R-100) in order to estimate the extent of curing ($T_{max}-T_{min}$), scorch safety and cure time. Curing was done at 170°C upto the optimum extent (t_{90} mins) in a specially designed mould which could easily be opened after cooling. Activation energy was determined from the knowledge of change in optimum cure time (t_{90}) with temperature of cure as earlier[5,9] i.e., from the slope of straight line plot of log (t_{90}) versus $1/T$. Swelling coefficient was determined by swelling the blends in toluene at ambient up to equilibrium.[14] It is determined from the formula as

TABLE I

Blend formulations

Blend nos.	A	B	C	D	E	F	G	A′	B′	C′	D′	E′	F′	G′
XLPE-11 (Crosslinkable polyethylene)	85	70	60	50	40	30	15	85	70	60	50	40	30	15
XL-20 (Crosslinked butyl)	15	30	40	50	60	70	85	—	—	—	—	—	—	—
XL-50 (Crosslinked butyl)	—	—	—	—	—	—	—	15	30	40	50	60	70	85

given

$$\text{Swelling coefficient } Q = \frac{m - m_0}{m_0} \times \frac{1}{\rho}$$

m = mass of swollen sample, m_0 = original mass of the sample, ρ = density of swelling agent.

Tensile properties were measured on a universal testing machine. Ageing was done in an air oven at 150°C for 48 hrs and changes in properties were measured. Isothermal ageing was conducted at 250°C and percent loss in weight was measured at times until more or less constant weight was achieved. The samples after isothermal ageing were swelled in toluene to equilibrium and percent volume swell were determined.

Thermal analysis (Thermogravimetric analysis and Differential thermal analysis) of the samples was conducted at Stanton Redcroft Thermal Analyser—STA 780 in nitrogen at a rate of 10°C/min within the temperature range of 30–600°C. The degree of crystallinity of the blends was determined from the X-ray diffractogram following the method as earlier[5] using Philips PW1729 generator with PW1840 diffractometer (Holland), Ni-filtered and CuK$_\alpha$ radiation within the range of $5° < 2\theta < 50°$. Fractured surface was studied with SEM using Camscan—Series 2 and E 5200 Auto sputter coater. SEM was taken using gold coated sample at 20 kV, 10^{-5} Torr and 15° tilt.

3. RESULTS AND DISCUSSION

3.1. Cure characteristics

The cure characteristics of XLPE/XL-20 and XLPE/XL-50 blends are shown as representative examples at 170°C in Figures 1 and 2 respectively. The rate and state of cure increase as the XLPE/XL-butyl ratio decreases, attain a maximum at about 40:60 level and then decrease with further addition of XL-butyl elastomer in the blends. Higher rate and state of cure have been observed for XL-50 containing blends. In both XL-20 and XL-50 blends optimum cure time and induction time decrease as the XL-butyl content is increased in the blends, attains a minimum and then rises again on further addition of elastomer in the blends. As observed in Figure 3 the optimum cure time is comparatively less for XL-50 blends than that for XL-20 blends. However, initial replacement of XLPE with XL-butyl has marginal effect on cure time depending on the degree of crosslinking. Degree of crosslinking has marked effect only at higher level of XL-butyls. This is true for all the temperatures of study. Increase in temperature decreases optimum cure time and scorch time with marginal variation in rheometric state of cure. However at higher temperature the appreciable reversion is observed for high XL-butyl containing blends and this rate of reversion is comparatively high in case of XL-20 containing blends.

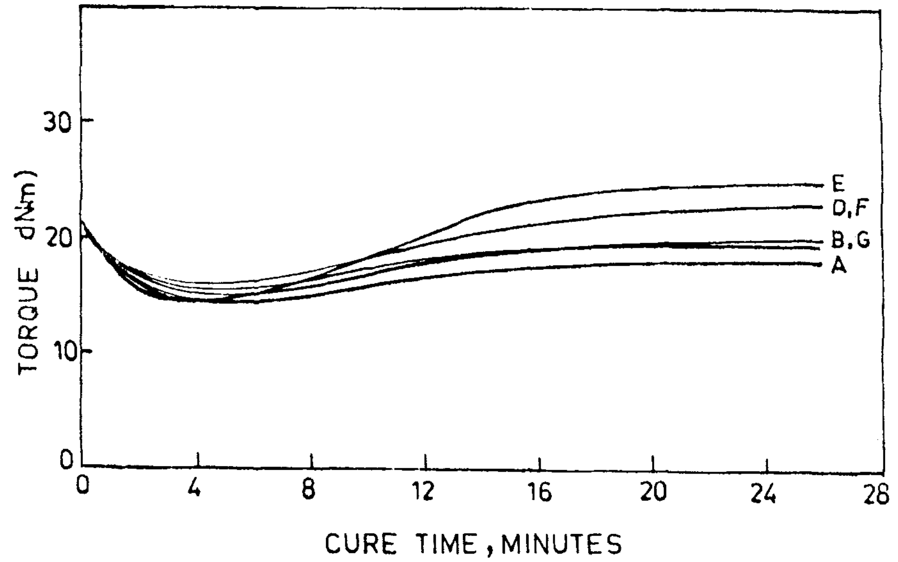


FIGURE 1 Rheometric study of XLPE/XL-20 blends at 170°C.

The variation of optimum cure time with inverse of absolute temperature as shown in Figure 4 has been found to follow a straight line path, the slope of which gives the activation energy which is independent of degree of crosslinking in butyl elastomers up to around 50:50 level in blends with XLPE. Beyond this level the XL-50 containing blends show slightly higher activation energy than the XL-20

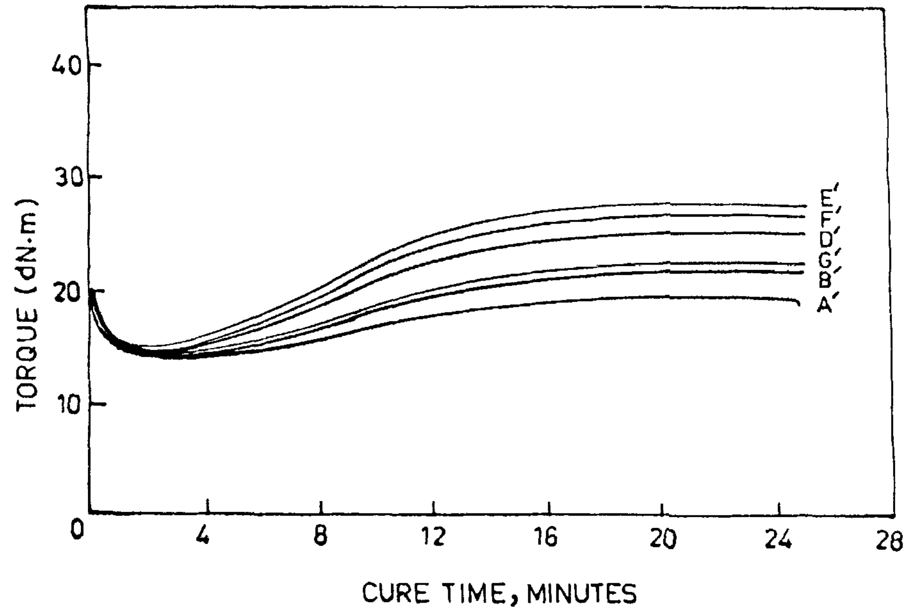


FIGURE 2 Rheometric study of XLPE/XL-50 blends at 170°C.

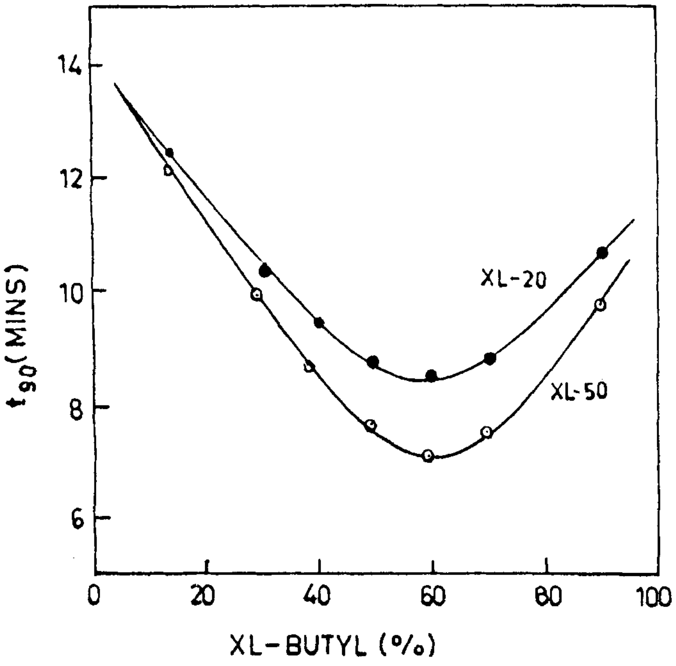


FIGURE 3 Variation of optimum cure time (t_{90}) with XL-butyl content.

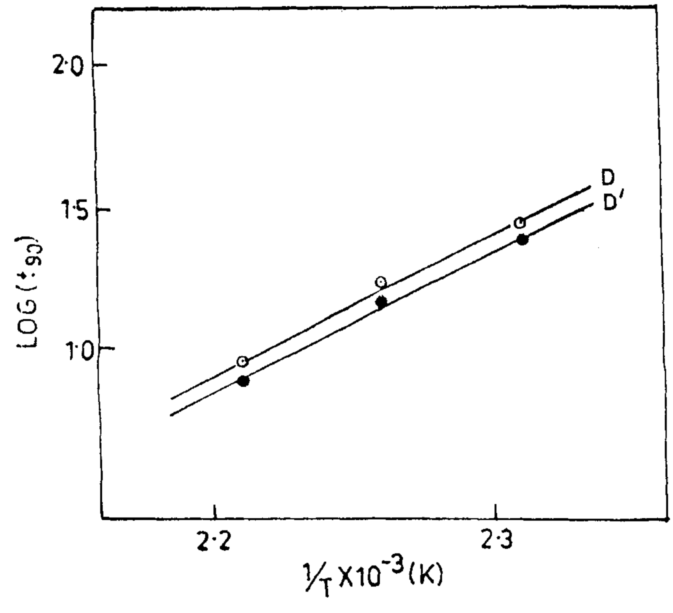


FIGURE 4 The variation of log(t_{90}) with $1/T$ for the blends D and D′.

containing blends with XLPE. However, the addition of XL-butyl decreases the activation energy of the blends. It may be that increasing unsaturation with increase in XL-butyl elastomer play a vital role in reducing the activation energy of cure. The higher activation energy of XL-50 containing blends at its higher level than that of XL-20 containing blends is probably due to the oxidation of unreacted vinyl groups (via epoxy to acids) under catalytic effect of DCP present in the system.

3.2. Stress–strain properties

The stress–strain curves have been shown in Figure 5 for the blends cured at 170°C. The physical properties are given in Table II for all the blends. As is seen the replacement of XLPE with XL-butyl decreases the modulus and tensile strength but increases the elongation at break. At high level of XLPE yielding tendency is observed accompanied by necking but strain induced crystallization seems to be absent. With increasing XL-butyl content this necking tendency diminishes and at its higher level no yielding tendency is observed. The degree of crosslinking in the elastomer has very marked effect on the physical properties which are also composition dependent of the blends. At lower level of XL-butyl, the XL-20 exhibit higher modulus, tensile strength and elongation but no sooner XL-butyl content becomes higher (at about fifty percent), the modulus and tensile

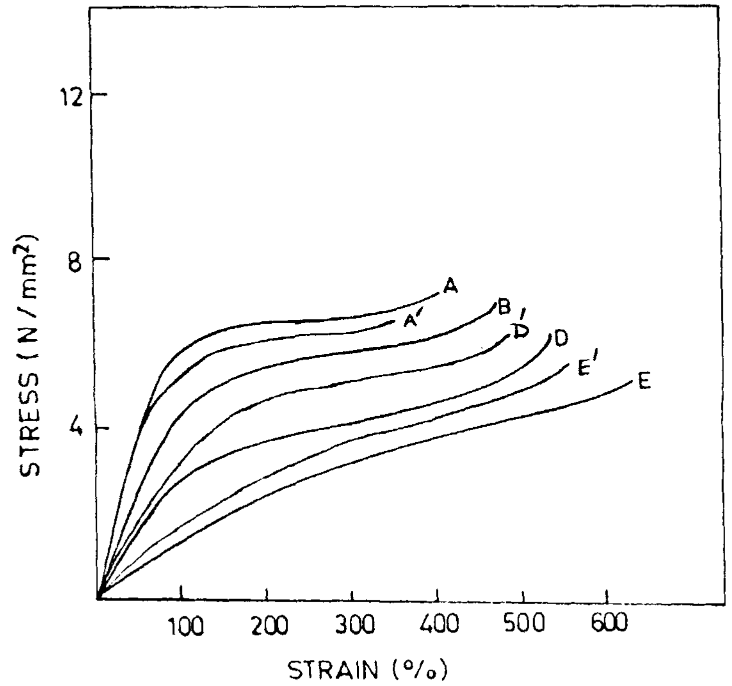


FIGURE 5 Variation of stress with strain for the blends XLPE/XL-20 and XLPE/XL-50.

TABLE II

Physical properties before and after ageing

	A	B	C	D	E	F	G	A′	B′	C′	D′	E′	F′	G′
Modulus (200%) (Kg/cm^2)	64.0	54.0	48.0	42.0	32.0	26.0	22.0	60.0	52.0	46.0	44.0	35.0	29.0	24.0
Tensile strength (Kg/cm^2)	76.0	72.0	69.0	65.0	60.0	57.0	55.0	73.0	69.0	67.0	65.0	62.0	60.0	55.0
Tear (Kg/cm)	49.0	45.0	40.0	37.0	34.0	32.0	30.0	47.0	42.0	38.0	36.0	35.0	34.0	31.0
Set (%) (at 200% elongation)	18.0	15.0	12.0	9.0	6.0	6.5	8.0	14.0	11.0	9.0	7.0	4.5	6.0	8.0
Elongation at Break (%)	420	460	490	530	610	640	620	370	390	420	470	550	570	550
Percentage change in properties after ageing at 150° for 48 hrs														
Modulus (200%)	+2.3	+1.4	−2.1	−5.3	−6.2	−4.8	−4.9	+3.9	+5.1	+4.2	−1.8	−4.0	−3.5	−3.8
Tensile strength	−10.2	−13.8	−15.4	−18.8	−18.2	−16.6	−16.2	−9.4	−12.6	−14.8	−16.9	−17.0	−15.8	−14.9
Elongation at break	−15.6	−17.0	−19.2	−19.0	−18.4	−17.8	−18.0	−12.8	−14.0	−15.6	−16.8	−17.5	−16.8	−16.5

strength become higher for XL-50 containing blends with lower elongation at break compared to XL-20 containing blends.

The above observations of blend ratio dependence of physical properties contradict the cure characteristics studies. Though increased state of cure is observed, the modulus goes on decreasing with increasing XL-butyl content. It seems probable that the crystallinity of the blends plays a dominant role in determining the modulus. As observed from Figure 6 the crystallinity decreases gradually with the increase in XL-butyl content and with a faster rate beyond 50:50 level. Throughout the entire range of blend ratio, XL-20 exhibit higher crystallinity than the XL-50 containing blends. At lower level of crystallinity, the increased state of cure for XL-50 containing blends has predominant effects on enhanced physical properties than that with XL-20 in the blends.

Percentage set is always higher for the XL-20 containing blends than that of XL-50 containing blends. As the XLPE/XL-butyl ratio decreases the set value also decreases but at a still higher level of XL-butyls, the set value once again increases which may be due to phase separation. Tear strength (Table II) is little higher for XLPE/XL-20 blends at the lower level of XL-butyl but at the higher level the XLPE/XL-50 blends has an edge over the former.

The swelling coefficient has been determined and shown in Figure 7. The swelling in solvent at ambient temperature and pressure is increased as the XLPE/XL-butyl ratio decreases. Here again both the crystallinity and the state of cure play a vital role in swelling. As the crystallinity decreases with increasing

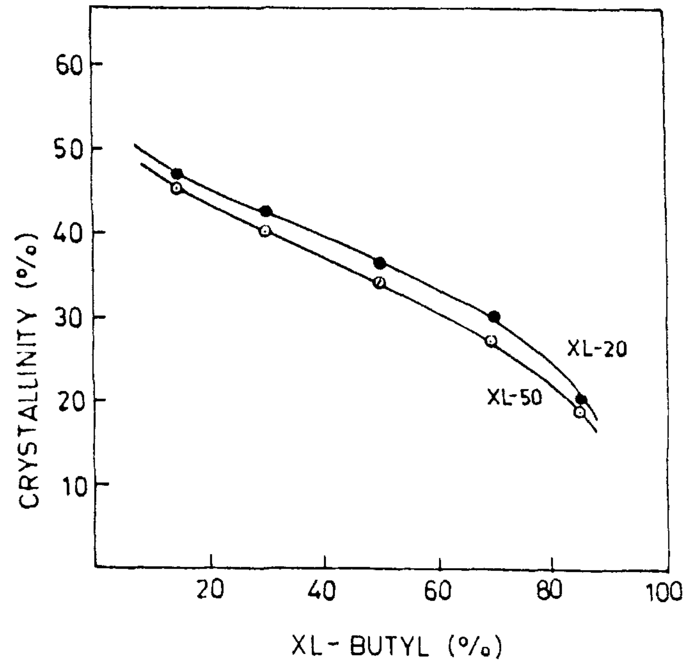


FIGURE 6 Variation of crystallinity with XL-butyl content.

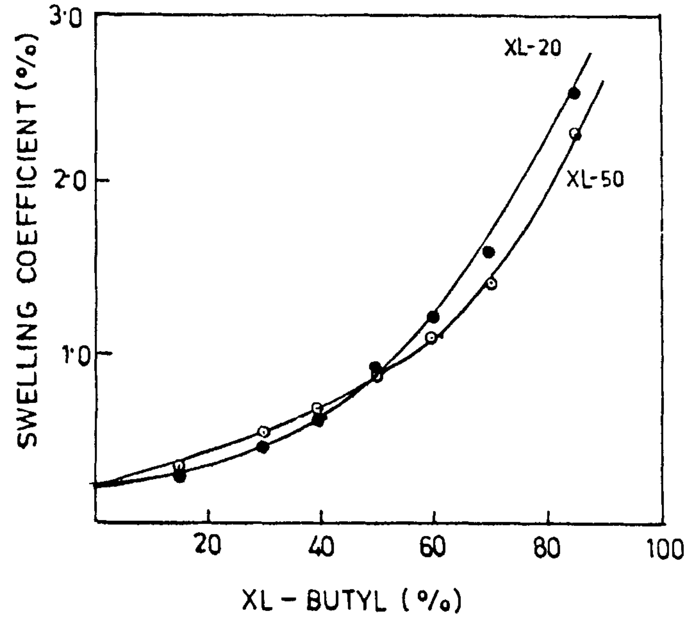


FIGURE 7 Variation of swelling coefficient with XL-butyl content.

XL-butyl, the swelling increases and the rate is enhanced beyond fifty percent of XL-butyl where a drastic decrease in crystallinity is observed. Swelling is found to be more in the region where the state of cure has increased. The degree of crosslinking in butyl has prominent effect on swelling. At lower level of XL-butyl, the XL-20 blends exhibit low swelling and at its higher level blends containing XL-50 exhibit low swelling.

3.3. Ageing behaviour

The ageing characteristics are shown in Table II for the blends. A decrease in tensile strength and elongation at break on ageing is observed. The modulus however, increases marginally at high XLPE/XL-butyl blends and decreases at lower XLPE/XL-butyl ratio on ageing. The modulus decreases as the XL-butyl content increases in the blend. This decreases in properties are more in case of XLPE/XL-20 blends than that of XLPE/XL-50 blends. Again this decrease in properties are somewhat restricted at very high level of XL-butyl blends where the amount of peroxide becomes very low in the systems.

Isothermal ageing was conducted at 250°C and is represented graphically in Figure 8. Three distinct stages of weight loss are observed. Initially, the rapid rise in loss up to 10 hrs is followed by slow increase up to 40 hrs and beyond which the loss again tends to rise fast. This type of behaviour is true for both XL-butyl and XL-50 blends with XLPE. Throughout the period of study, the weight loss increases as the XLPE/XL-butyl ratio decreases. However, at very high level of XL-butyl (85%) the weight loss decreases. It can be assumed that the presence of

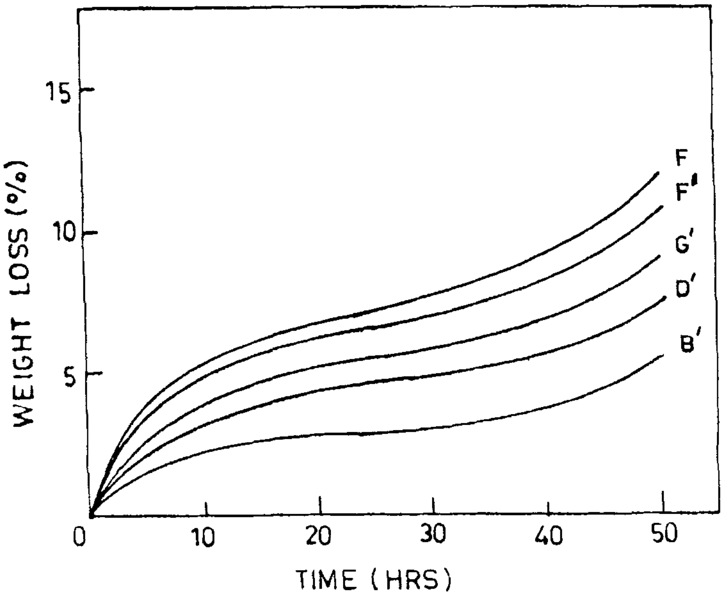


FIGURE 8 Variation of weight loss with time for the blends in isothermal ageing.

adequate peroxide play a major role in loss in weight during isothermal heating. It is also observed that XL-20 containing blends are more prone towards weight loss (plot-F) than the XL-50 containing blends (plot-F′) which suggests more fragmentation in case of XL-20 containing blends. Above views are confirmed by the swelling of isothermally aged samples in the solvent. Table III suggests more volume swell for the samples containing more XL-butyl blends and more percentage extraction up to a certain level. At high XL-butyl blend (F′) the volume swell again decreases with lower level of extracted materials. However, the percentage volume swell is more with XL-20 together with high percentage of extraction than that with XL-50 containing blends (F′ and F). Thus it may be logical to assume that the presence of peroxide helps in fragmentation process in XL-butyls, under high temperature condition to a varying extent depending on the degree of cross-linking present in butyls.

TABLE III

Swelling behaviour of the blends after isothermal ageing

Blend nos.	% Volume swell	% Soluble portion
A′	52.0	10.3
B′	68.0	23.7
F′	47.0	9.2
F	128.0	35.6

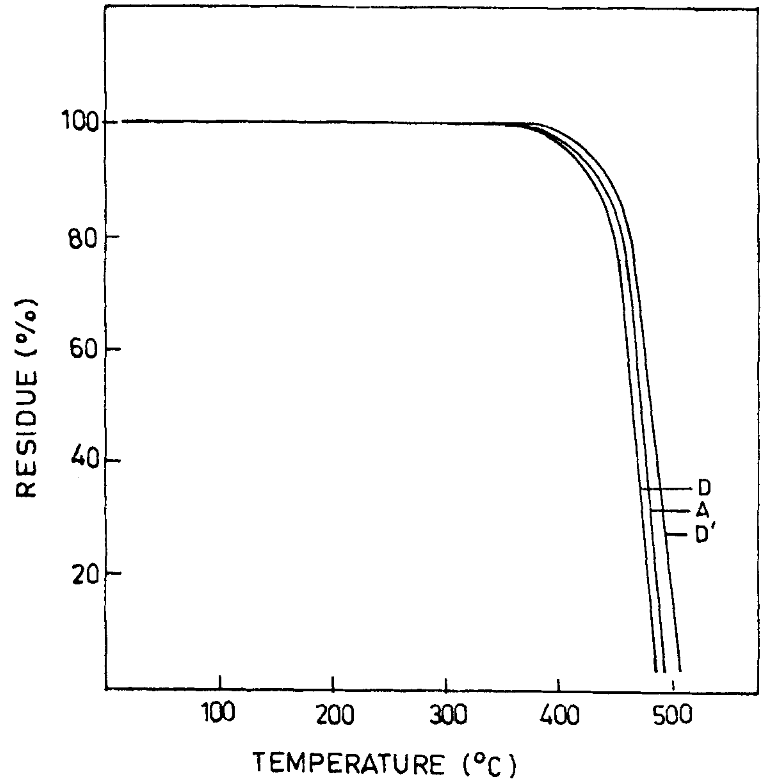


FIGURE 9 TGA plot for the blends A, D and D'.

3.4. Thermal analysis

Thermal stability of the blends were studied and represented as TGA and DTA plots in Figures 9 and 10 respectively. As observed under the conditions studied, the degradation starts at about 400°C for all the blends. But the rate of thermal degradation varies with the blend ratio and degree of crosslinking present in XL-butyls. The rate of weight loss is more as the XLPE is being replaced by XL-butyls. Again the rate of weight loss is found to be less for XL-50 containing blends. Unlike other previous blend systems a single step degradation is observed in these blends irrespective of the type of butyl elastomers.

DTA plots are characterized by two endothermic peaks, one around 100°C which may be due to melting of XLPE and the other around 450°C which may be due to thermal degradation of the blend systems. As the XLPE is being replaced by the XL-butyl both the peaks become wider, i.e., for blends no sharp melting is observed both at high and low temperature. This may be attributed to the lowering crystallinity as observed in Figure 6. At high XL-butyl level (D) the melting is also not sharp and in case of both the processes the energy requirement seems to be higher. At both low and high temperatures the XL-50 containing blends (D') are characterized by wider peaks and more peak area, as observed, than XL-20 containing blends (D) suggesting more energy requirement for the

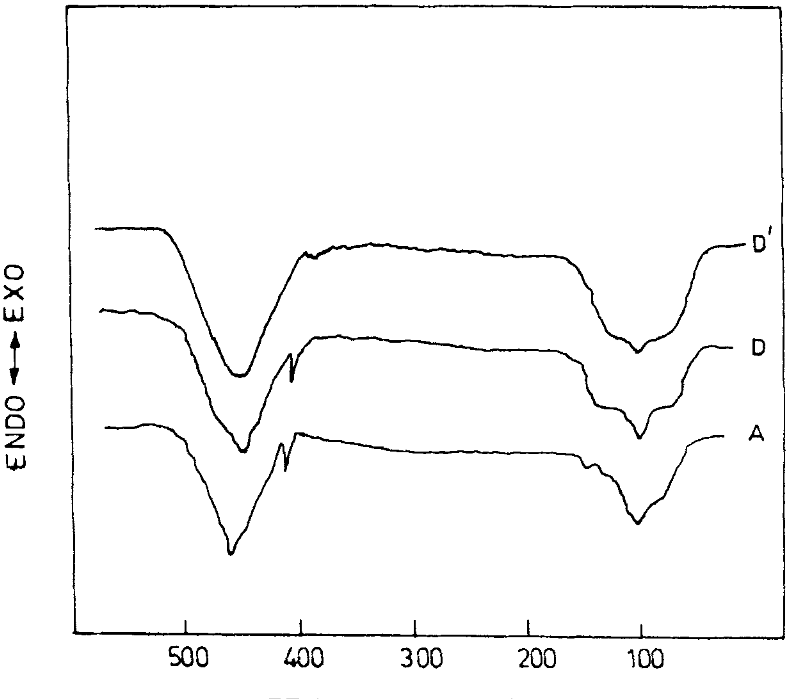


FIGURE 10 DTA plot for the blends A, D and D'.

former. A small peak is observed in case of XL-20 blends around 400°C which is absent in XL-50 containing blends may be due to early fragmentation of XL-20 containing blends.

3.5. SEM STUDIES OF FRACTURE SURFACE

The fracture mechanism of the blends are studied from the SEM of fracture surface and are shown in Figures 11 to 15. As observed the fracture mode changes with the change in XLPE/XL-butyl blend ratio and with the degree of crosslinking in XL-butyls. For the XLPE/XL-20 blends at lower level of XL-20 the fracture mode is characterized by fibre and cavity formation (Figure 11) and stress paths are unidirectional. As the XL-20 content increases the smooth failure with sinosoidal foldings are observed with deeper cavitation within the foldings. The height of the foldings are more but frequency is less (Figure 12) compared to the fracture surface at high XL-20 content (Figure 13). Here, foldings are separated by a number of layers with less deep cavitation and height of the foldings. In case of XLPE/XL-50 blends at its higher level of XLPE (Figure 14) smooth layer type of failure is observed without any fibre formation. Here also fracture surface is associated by cavity formation but shallow compared to XL-20 blends. At the high level of XL-50 (Figure 15), smooth failure with stress path in

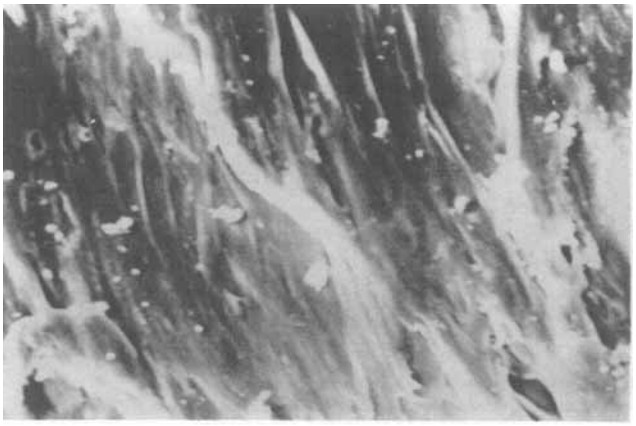


FIGURE 11 SEM of fracture surface for the blend A at (400X)

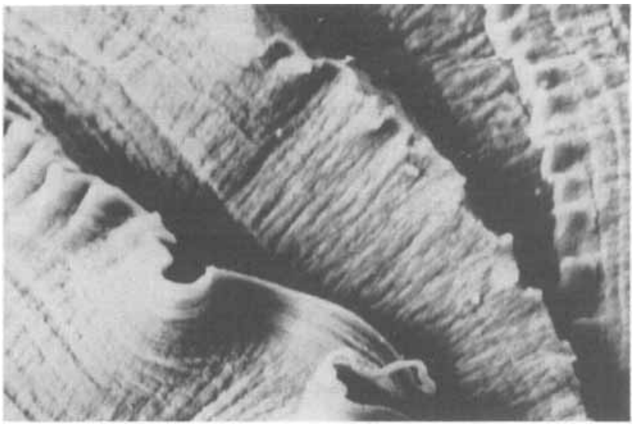


FIGURE 12 SEM of fracture surface for the blend D at (400X)

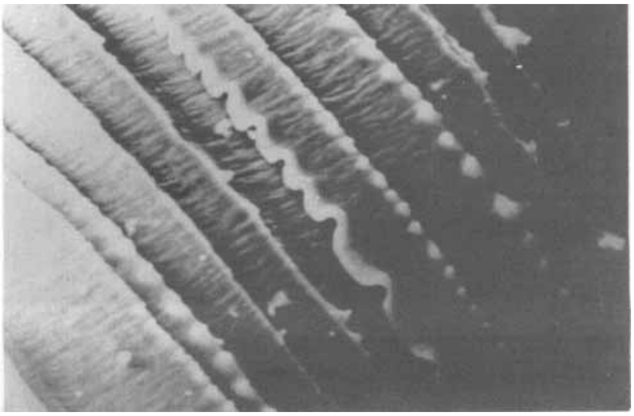


FIGURE 13 SEM of fracture surface for the blend G at (400X)

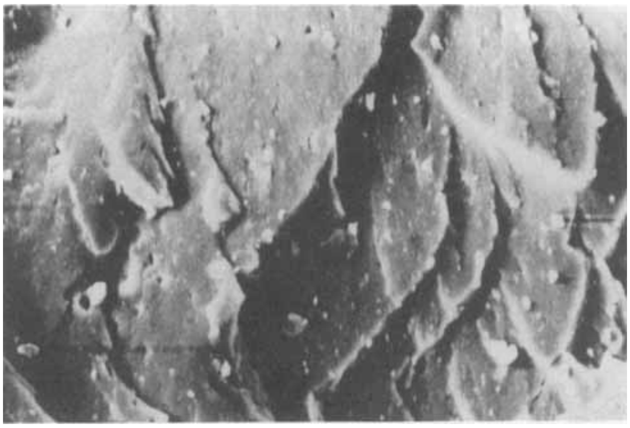
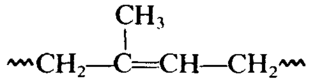


FIGURE 14 SEM of fracture surface for the blend A′ at (400X)

different directions are observed. Neither cavitation nor foldings are observed almost like a failure that is found in elastomers only.

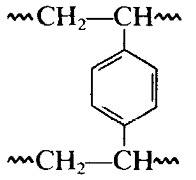
As is already known that XL-butyl is a terpolymer of isobutylene, isoprene and divinyl benzene. The DVB causes crosslinking during polymerization,[15] the extent of which is measurable by dissolving in di-isobutylene. XL-20 and XL-50 have 20% and 50% solubility in solvent i.e., are 80% and 50% crosslinked respectively. There may be three peroxide crosslinking sites in XL-butyls. The first is isoprene, second is benzylic hydrogen attached to DVB and the third at unreacted DVB groups as shown

[X]



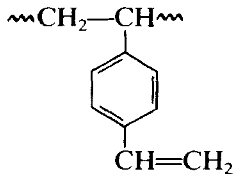
$$\sim CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2\sim$$

[Y]



and

[Z]



As observed from the rheometric studies the rate and state of crosslinking increase as the XL-butyl proportion is increased in the blends. This strongly supports the view that either the crosslinking efficiency of peroxide is increased or the decomposition rate of peroxide is enhanced coupled with chain extension

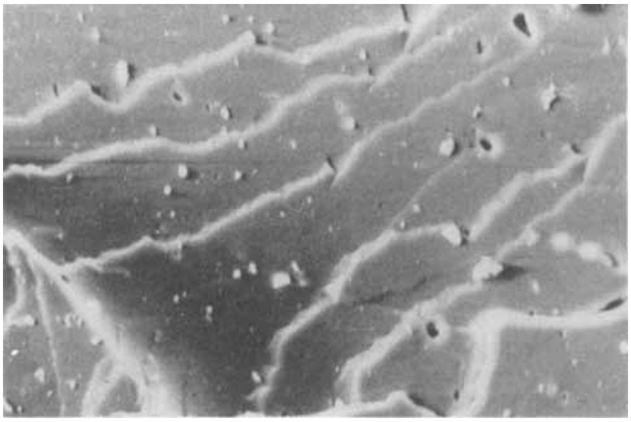


FIGURE 15 SEM of fracture surface for the blend D′ at (400X)

through double bonds. The probable mechanism may explain the results well as

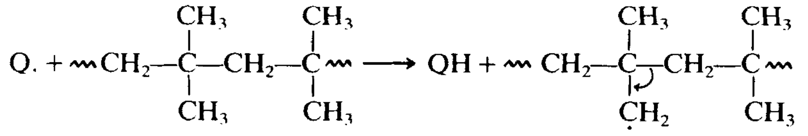
$$\underset{(DCP)}{Q{-}Q} \rightarrow 2Q^{\cdot} \tag{1}$$

$$Q^{\cdot} + X, Y, Z \rightarrow \dot{X}, \dot{Y} \text{ and } \dot{Z} \tag{2}$$

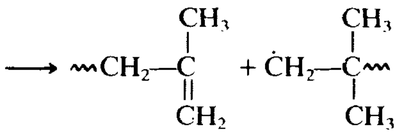
$$\text{Radicals } (\dot{X}, \dot{Y}, \dot{Z}) \rightarrow \text{Crosslink} \tag{3}$$

Higher crosslinking efficiency may be due to the polymerization of pendant double bonds in unreacted DVB (through $\dot{Z}$) which is highly reactive. However, the enhanced reactivity of isoprene by DVB or the contribution of benzylic hydrogen in peroxide cure cannot be ignored although to a minor extent.[16] This can be probably explained by the higher rate and state of cure observed for XL-50 blends assuming the unreacted DVB groups to be more in XL-50. As seen up to sixty percent replacement of XLPE by XL-butyl increases the state of cure with higher curing rate although the level of peroxide is being reduced. The amount of peroxide in forty percent XLPE may be sufficient for the full utilization of pendant vinyl groups in XL-butyls. Beyond this limit both the rate and state of cure decreases which may be due to insufficient peroxide level in the systems.

Thermal stability of the blends are due to the state of cure and the residual peroxide present in the systems. It is probable that the amount of unreacted peroxide is more in XL-20 containing blends rendering it less thermally stable through enhanced degradation. The degradation may be represented as



$$Q. + \sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}\sim \longrightarrow QH + \sim CH_2-\overset{CH_3}{\underset{\dot{C}H_2}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}\sim \qquad (4)$$



$$\longrightarrow \sim CH_2-\overset{CH_3}{\underset{CH_2}{C}} + \dot{C}H_2-\overset{CH_3}{\underset{CH_3}{C}}\sim \qquad (5)$$

The chain scission results in low molecular weight fragmented products. This type of chain scission is less in case of XL-50 containing blends. The degradation on ageing is somewhat restricted at the high level of XL-butyl may be due to less peroxy residues to cause scission.

4. CONCLUSION

Improved cure rate and state of cure can be achieved by blending XLPE with XL-butyl rubber up to a level of 60% of XL-butyl. Low degree of crosslinking has been found to be advantageous. At lower level of XL-butyl the physical properties are determined by crystallinity similar to swelling behaviour, but at its higher level the state of cure determines the properties. XL-50 gives higher thermally stable blends than XL-20. More plastic deformation is observed in XL-20 blends whereas rubbery deformation is experienced with XL-50 blends. Fracture is associated with cavitation in high crosslinked butyl blends whereas smooth rubbery failure is observed in low crosslinked butyl blends.

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