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# Speciality Polyblend Systems of Crosslinkable Polyethylene and Poly(ethylene-vinyl acetate)

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Malt mixed blends of crosslinkable polyethylene (XLPE) with poly(ethylene-vinyl acetate) are studied over the entire composition range. The effect of increasing amount of EVA in the blend have been studied with respect to cure behaviour, physical properties and thermal behaviour together with failure mode. Both cure rate and scorch time increase as XLPE/EVA ratio decreases. Probable radical cross-linking mechanism is suggested. Thermal stability is governed by EVA content in the blend as is observed from isothermal ageing, DTA and TGA studies. SEM studies supports the change of failure mode from brittle to ductile as EVA content in the blend increases.

KEW WORDS Polyblend, crosslinkable polyethylene, EVA, thermostability, blend morphology.

## 1. INTRODUCTION

Investigations of multicomponent polymer blends are technologically important as illustrated by their commercial prominence. Though polymer pairs do tend to be incompatible but in contact exhibit varying degrees of segmental interdiffusion. The process is currently exciting both in terms of theoretical and experimental outlook.

Understanding the influence of covalent bonds on the multi-component polymer blend systems the technique of random intercrosslinking of polymer components can be one of many good approaches. When polyethylene is crosslinked its thermal characteristics are greatly enhanced.<sup>1</sup> Improvement of stress cracking, solvent resistance, weatherability as well as improvement of low temperature embrittlement have been reported.<sup>2,3</sup> The excellent electrical properties coupled with mechanical toughness makes crosslinked polyethylene (XLPE) an ideal insulant for use in electric cables.

Considerable published work exists concerning the investigations on crystalline/amorphous polymer blends.<sup>4-7</sup> Polyolefin blends have been utilized in many forms to achieve modifications yielding improved impact strength, flexibility

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and filler acceptance.<sup>8-10</sup> However phases separate at ambient temperature due to their low energy of interaction.<sup>11</sup> The effect of E:P ratio in XLPE/EPDM blends recently have been studied.<sup>12</sup> Many investigations on poly(ethylene-vinyl acetate) copolymer<sup>13,14</sup> have shown the possibility to get blends with several polymers. Considering the relatively bulky and polar nature of the acetoxy side chain an interaction with blend partner can be anticipated. Flow behaviour of XLPE/EVA polyblends have been reported.<sup>15</sup>

Here, we have studied the melt blends of XLPE and EVA. Our approach is to induce generation of free radicals on polymer chains and subsequent crosslinking between component polymers to produce network structure. We have reported state and rate of cure from the processability viewpoint. The technical properties were examined in terms of effect of blend structure on failure mechanism with the help of SEM and X-ray studies. The ageing behaviour was studied, supported by thermo-analytical techniques and a suggested mechanism is discussed.

## 2. EXPERIMENTAL

Crosslinkable polyethylene was XLPE-11 from IEL, India. This XLPE is inherently containing 1.8 phr of DCP. Ethylene vinyl acetate was EVA-508 from Union Carbide, USA. Melt mixing was carried out in a Brabender Plasticorder as before.<sup>15,16</sup> As XLPE is having DCP in it so no DCP is being added from outside and mixing thus involves blending of both the polymers. Formulation of blends is given in Table I.

Continuous measurements of cure characteristics at 160, 170 and 180°C were performed in a Monsanto Rheometer (R-100). Activation energy was determined from the change in optimum cure time ( $t_{90}$ ) with temperature of cure.<sup>17</sup> Ageing was done in an air oven at 150°C for 48 hrs. Isothermal ageing was performed at 200°C and percent loss in weight was measured at different time intervals until more or less constant weight is achieved. Ozone resistance was measured in ozone tester Model P3-C8 of Hampden Test Equipment Ltd., U.K. as per ASTM D-1149 method.

Thermal analysis of the samples was conducted at a Stanton Red-croft Thermal Analyser-STA 780 in nitrogen at a rate of 10°C/min within a temperature range of 30 to 600°C. The degree of crystallinity of blends was determined from the X-ray diffractogram following the method as earlier<sup>18</sup> using Philips PW 1729 generator with PW 1840 diffractometer (Holland), Ni filtered and  $\text{CuK}_\alpha$  radiation within the range of  $5^\circ < 2\theta < 50^\circ$ . Failure mechanism was studied before and after

TABLE I  
Blend formulations

Blend nos.	A	B	C	D	E	F	G
XLPE-11	85	70	60	50	40	30	15
EVA-50B	15	30	40	50	60	70	85

solvent extraction (at 50°C for 2 hrs in xylene) by SEM using Camscan-series 2 and E 5200 Auto sputter coater.

### 3. RESULTS AND DISCUSSION

#### 3.1. Rheometric study

The cure characteristics of the blends are shown as continuous curves of torque vs. time at 170°C in Figure 1. The torque increases with the increase in cure time after the induction period. As the XLPE is gradually replaced by EVA the torque value increases and after about 70% of EVA, the torque value decreases. The rate of cure increases as the XLPE/EVA ratio decreases upto 40:60 level beyond which the rate of cure decreases considerably. The scorch time of the blends increases as the XLPE is being replaced by EVA over the entire range of compositions studied (Figure 2). As observed the scorch time increases at a comparatively higher rate at higher level of EVA in the blend than at its lower level. The addition of EVA initially increases the minimum viscosity but at its higher level decreases the viscosity. The increase in temperature decreases the optimum cure time to a different extend depending on XLPE/EVA ratio. This is reflected while studying the activation energy as represented in Figure 3. As is revealed from the figure that the addition of EVA in XLPE decreases the activation energy of cure (plot-D) and remains more or less constant as the EVA content increases in the blend (plot-G).

The above results of rheometric studies can be explained by following

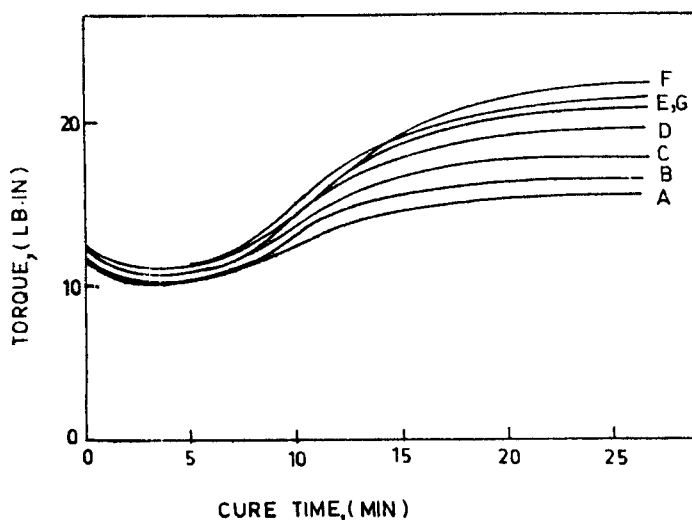


FIGURE 1 Rheograms of the blends at 170°C.

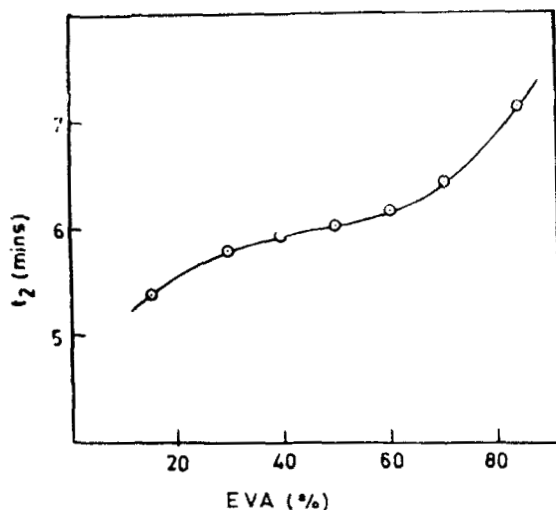


FIGURE 2 Variation of scorch time ( $t_2$ ) at 170°C with percentage of EVA in the blends.

crosslinking reaction mechanism in the blends given below

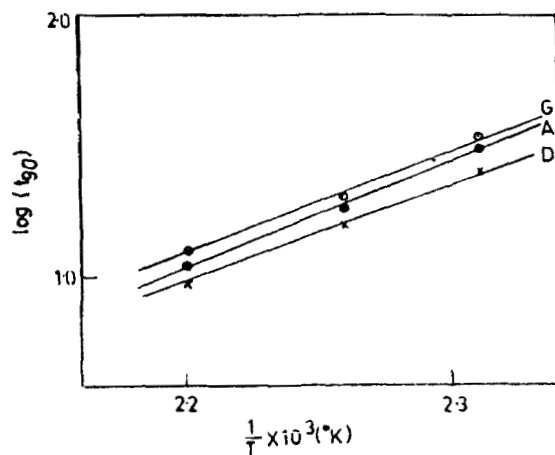
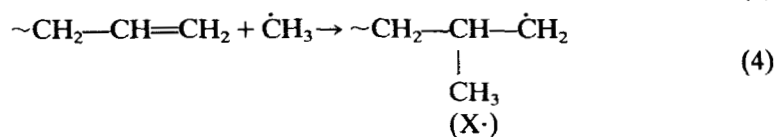
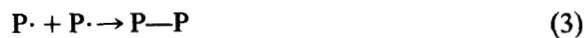
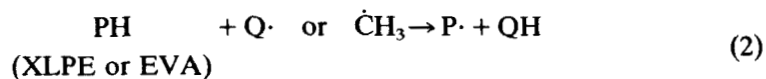
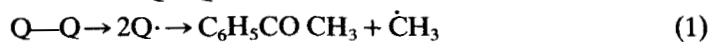
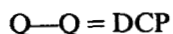


FIGURE 3 Activation energies of the blends.

For increased crosslinking, it is necessary that the stationary level of macro-radicals be more so that recombination of radicals prevail over the fragmentation of macroradicals.<sup>19</sup> As observed the increasing percentage of EVA in the blend increases the rate and state of cure upto a certain level. Crosslinking in XLPE may proceed via hydrogen ion abstraction from the methylene group through Eqs. (1), (2) and (3). The higher crosslinking due to EVA may proceed via hydrogen ion abstraction involving tertiary carbon atom and acetyl group of EVA.<sup>20</sup> The chain chain addition using the terminal vinyl groups in both XLPE and EVA (Eqs. 4 and 5) may also be a practical alternative for crosslinking. With the decreasing XLPE/EVA ratio the total concentration of DCP in the system decreases. Thus increasing rate of crosslinking and state of cure probably points towards the increasing cross-linking efficiency or increasing DCP decomposition in the system by some fragmentation products of EVA at the high temperature of cure. The possibility of chain extension reaction through the double bond in EVA which might have been formed during high temperature of DCP curing leading to high state of cure can not be ignored. The involvement of some by-products from EVA during the course of DCP reaction probably delays the onset of curing as observed from increasing scorch time. At still higher level of EVA the decrease in state and rate of cure may be attributed to the limiting concentration of DCP in the system as observed earlier.<sup>12</sup>

### 3.2. Stress-strain properties

The physical properties are shown in Table II which suggests the gradual decrease in modulus with the addition of EVA in XLPE. This observation is quite contradictory to the observed rheometric parameters where increasing EVA is accompanied by increase in state of cure upto a certain limit. At higher temperature of rheometric study, degree of crosslinking determines the state of cure and the plastic phase has no contribution. Whereas the stress-strain properties, as measured at ambient, is determined by the crystallinity of the

TABLE II  
Physical properties of blends (before and after ageing)

Blends nos.	A	B	C	D	E	F	G
Tensile strength in MPa	10.5	7.5	7.4	7.2	9.3	12.0	13.0
Modulus (300%) MPa	7.4	6.7	6.3	6.0	5.8	5.2	4.7
Elongation at Break in %	500	410	380	325	510	600	700
% Change in properties after ageing at 150°C for 48 hrs							
Tensile strength	-22	+46	+26	+2	-6	-25	-32
Modulus (300%)	-15	+12	+8	+6	+2	-7	-11
Elongation	-20	+34	+30	+23	+4	-17	-24
% change in properties after ozone ageing at 200 pphm at 40°C for 480 hrs							
Tensile strength	-2	-6	-11	-21	-27	-21	-26

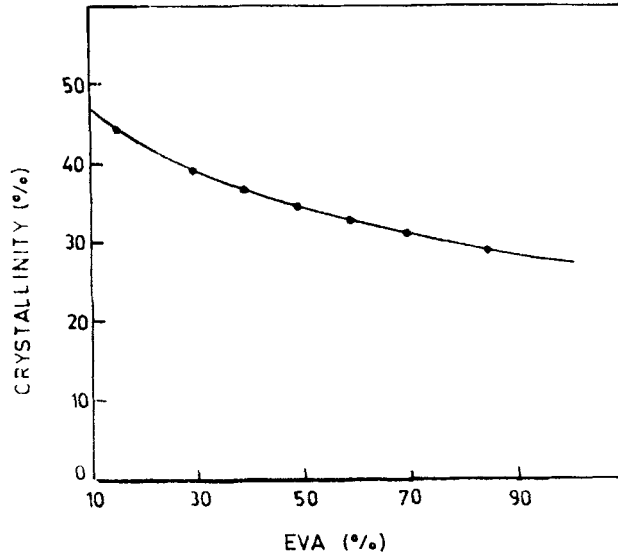


FIGURE 4 Variation of crystallinity with percentage of EVA.

XLPE. The degree of crystallinity has been plotted against the percentage EVA content in the blend (Figure 4) suggesting decrease in crystallinity as the XLPE/EVA ratio decreases. Hence the crystallinity of the blends seems to be a predominant factor in determining the modulus of the blend at ambient.

It is observed from stress-strain curve (Figure 5) that at the higher level of XLPE there is a yielding tendency and at higher strains there is rapid rise in stress. The necking behaviour is observed at higher level of XLPE. As the XLPE is being replaced by EVA, yielding tendency remains but to a lesser extent. The

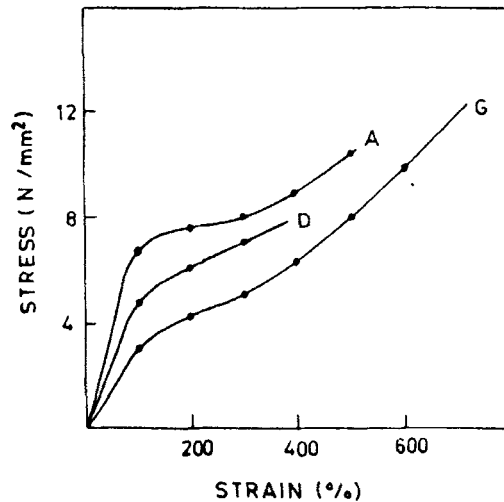


FIGURE 5 Stress-Strain plot of blends, A, D and G.

necking behaviour vanishes at the 50:50 level of XLPE/EVA blend accompanied by low tensile strength. At the higher level of EVA, however the elongation at break increases with no necking associated with high tensile strength which may be due to strain induced crystallization. It is observed from Table II that from 40:60 of XLPE/EVA ratio both tensile strength and elongation increase gradually which is in line with the stress strain curve.

### 3.3. Air and ozone ageing

Table II reveals that for the high XLPE/EVA blend and for high EVA/XLPE blends, there is decrease in physical properties on ageing.

However, within the blend ratio of 70:30 to 40:60 of XLPE/EVA the properties are enhanced on air ageing. It seems probable that on air ageing either new crosslinks are formed or there might be some formation of double bonds which acts as further crosslinking sites with increasing dosage of EVA in the blend. At higher level of EVA, the decrease in properties may be once again a contribution of unused double bonds because of low level of peroxide. On high temperature air ageing the blend G deforms and elongates suggesting a lower degree of cross-linking.

Ozone resistance were conducted at 200 pphm for 480 hrs at 40°C and 20 percent strain. Surprisingly no crazing was observed at the surface. In order to have a comparative assessments, these samples were tested for tensile strength and the deterioration is calculated considering initial tensile strength (Table II). As observed the percentage deterioration in tensile strength increases with the increase in EVA content in the blend which probably signifies the contribution of double bonds on increasing percentage of EVA.

### 3.4. Isothermal ageing

The percentage weight loss on isothermal ageing has been plotted against the time of ageing in Figure 6. There is an increase in weight loss with the ageing time for all the blends. The weight loss is greater for the blends as XLPE is being replaced by EVA. The rate of loss is also higher for increasing amount of EVA. There are two distinct stages of weight loss, initially very high and after 20 hrs a plateau is observed. The high amount of weight loss for the blends containing higher concentration of EVA probably suggests the decomposition of EVA portion isothermally. It is also observed that when the samples were solvent extracted and isothermally heated then the weight loss is more than with the unextracted sample. It seems to be probable, the unreacted DCP in the unextracted blends play a vital role in restricting the weight loss by fragmentation. It may be plausible that the DCP may go on crosslinking at the high temperature of study. Whereas, easy thermal degradation is encountered in the solvent extracted sample. This observation is further confirmed by isothermally heating the extracted and unextracted sample F. The unextracted sample shrinks and forms wrinkles on the surface, whereas the extracted sample melts and flows.



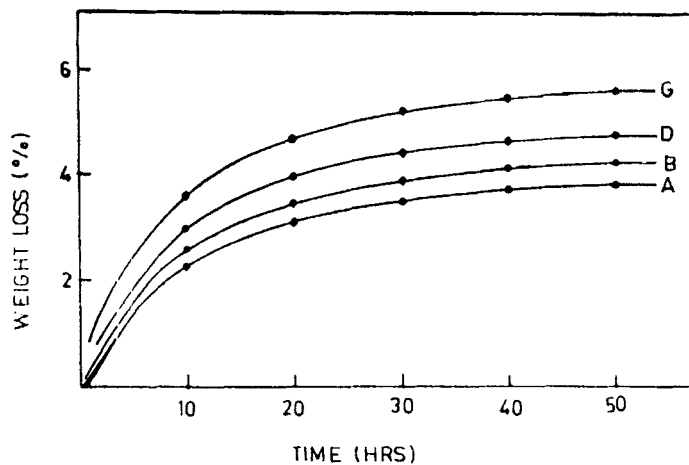


FIGURE 6 Variation of weight loss with the time of isothermal ageing.

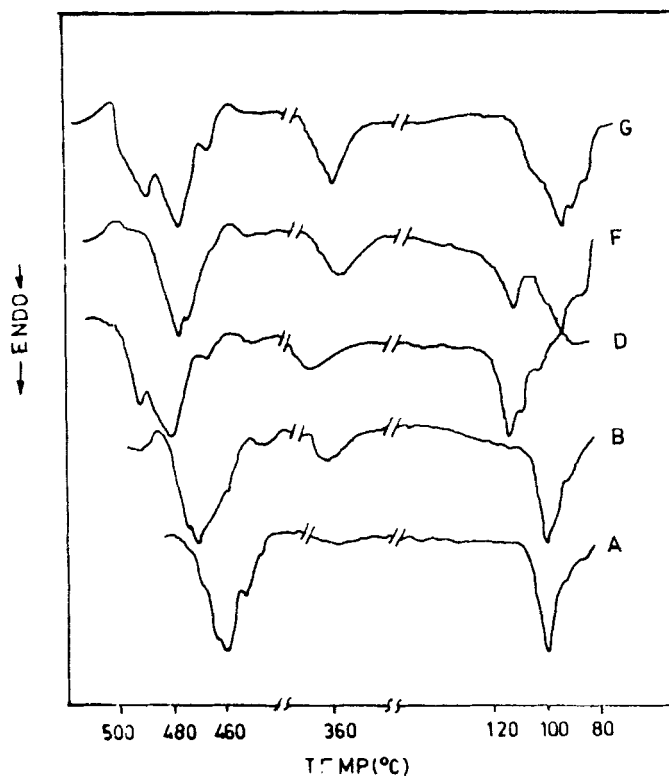


FIGURE 7 DTA plots of the blends in nitrogen atmosphere.

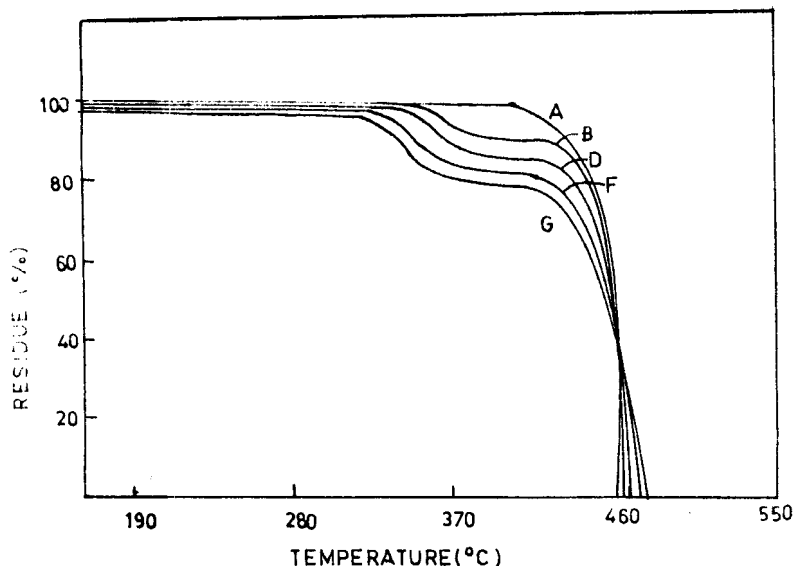


FIGURE 8 Thermograms of the blends in atmosphere.

### 3.5. Thermal analysis

The DTA plots are shown in Figure 7 for all the blend systems which suggest that endothermic reaction is occurring. The first sharp peak is observed around 90–110°C which corresponds to the melting point of XLPE. The second sharp peak is observed within 460°C to 480°C. A comparatively flat peak is observed at around 360°C which is very prominent for the blends containing higher percentage of EVA and this peak becomes sharper at higher level of EVA. As the XLPE/EVA ratio decreases the position of all the peaks shift slightly towards higher temperature side upto 50:50 level. Beyond this blend ratio peaks once again shift to the lower temperature side and remain more or less independent of composition. The first peak around 100°C is accompanied by no loss in weight as observed from TGA plot (Figure 8). The Figure 8 suggests that there exists a multistep degradation for the XLPE/EVA blends. The first weight loss occurs around 360°C and the second occurs around 460°C. The first weight loss step is also confirmed by DTG plot (not shown). At this stage, the weight loss increases with increase in EVA content in the blend suggesting thermal degradation resulting in escape of certain fragmentation product. However, the drastic loss at the higher temperature depicts the thermal stability of blends.

### 3.6. SEM studies of fractured surface

Fractured surface of the blends are studied under SEM in order to assess their fracture mode. At the high level of XLPE, the fractured surface appeared to be brittle although there is a plastic flow (Figure 9). As the EVA content in the blend increases, the mode of failure changes. At 50:50 level (Figure 10) where the low tensile strength at low elongation is observed accompanied by irregular

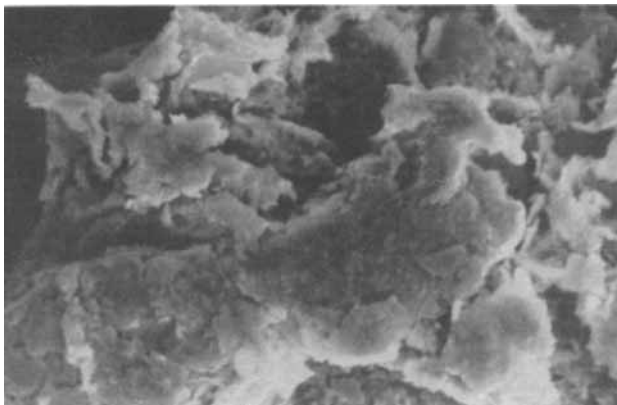


FIGURE 9 SEM fractogram (450 $\times$ ) of the blend A.

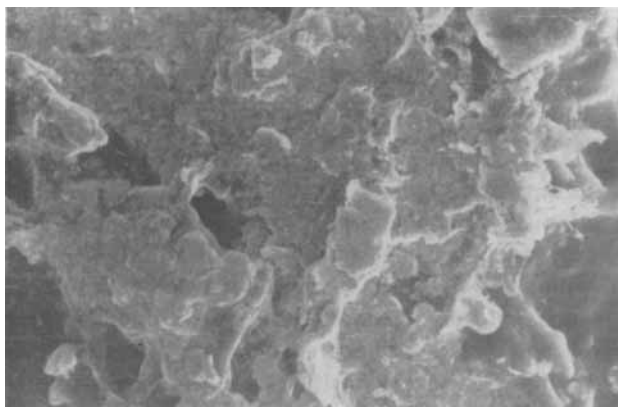


FIGURE 10 SEM fractogram (450 $\times$ ) of the blend D.

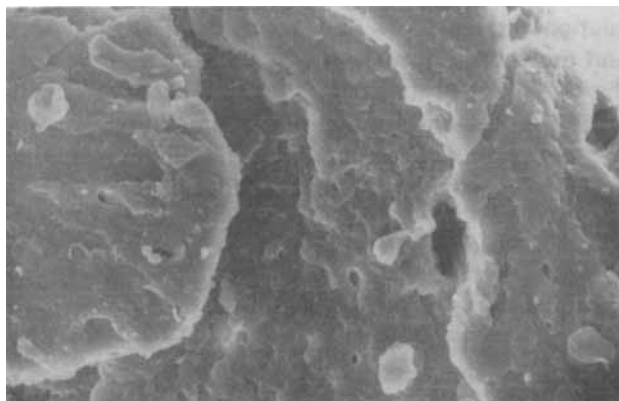


FIGURE 11 SEM fractogram (450 $\times$ ) of the blend G.

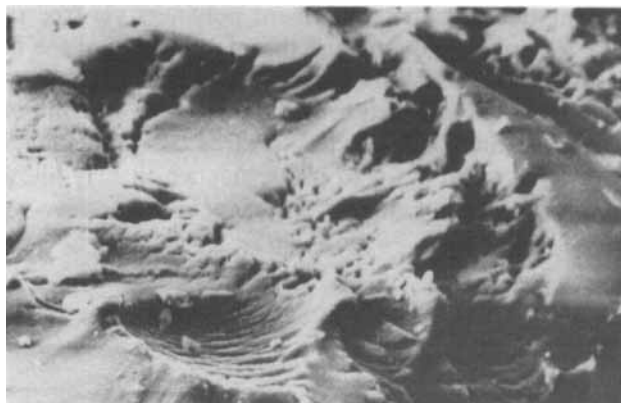


FIGURE 12 SEM fractogram (450 $\times$ ) of the blend B.

crack lines in different directions. These crack lines probably have originated at the interphase and the failure seems to be a combination of brittle and ductile. As the EVA content is increased further as in blend G the failure is of ductile type with no fibril formation associated with small holes (Figure 11).

In order to study the morphology of blends, extracted blends are studied under SEM. At the high level of XLPE, it forms the continuous phase (Figure 12, blend B) and EVA remains as dispersed phase. Whereas at higher level of EVA both the phases seems to remain as continuous as observed from Figure 13.

#### 4. CONCLUSIONS

XLPE and EVA gives rise to heterogeneous type of blends. However, this does not exclude blend compatibility in the melt. EVA enhances the state of cure of the blends. It also assists in enhancing peroxide cure rate which supports the



FIGURE 13 SEM fractogram (450 $\times$ ) of the blend F.

interchain crosslinking between the component polymers via free radical mechanism. Presence of EVA mainly governs the thermal stability of the blend systems. As EVA content increases, the failure mode of blends change.

A detailed investigation of interaction and degradation of component polymer chain and crystallization kinetics is needed towards the proper understanding of the compatibility criteria with regard to properties which may allow a successful blend application, superior to component polymers alone.

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