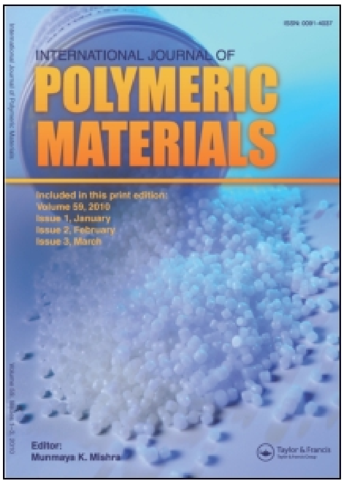

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Heat Shrinkable Polymer Blends Based on Grafted Polyethylene and Chlorosulphonated Polyethylene (Part I)

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Blend prepared by melt mixing of thermoplastic material-elastomer have gained considerable attention in recent years. Heat shrinkability of the polymer which depends on elastic memory can be introduced into the system in the form of an elastomeric phase. The present study deals with the measurement of heat shrinkability of the blend of grafted polyethylene with CSM. Interchain crosslinking between grafted polyethylene and elastomer improves the shrinkability. Crystallinity of the polymer blends also affected by interchain crosslinking, thus affecting the shrinkability. Probable interactions of the rubber and plastic phase are confirmed by IR spectroscopy. Extraction of the elastomeric phase is restricted due to interchain crosslinking as confirmed by SEM study.

Keywords: Polymer blends; grafted polyethylene; chlorosulphonated polyethylene

INTRODUCTION

The blends prepared by melt mixing of thermoplastic materials and elastomer have gained considerable attention, in recent years from shrinkability point of view [1-7]. When a drawn polymer sample is thermally annealed in an unstrained state, it shrinks. The shrinkage occurs as a consequence of an internal rearrangement of the structural

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*Corresponding author.

elements within the sample. This rearrangement has been brought about by the thermal release of stored internal strain. The internal strain had been stored in the polymer in the form of orientational entropy, and manifests itself as molecular orientation in the sample. The thermal release of this stored internal strain results in a change in the orientation state of the molecules in the sample which in turn manifests itself as shrinkage. There is very little published systematic information concerning the shrinkability of the blends.

Recently Das *et al.* [8] have studied the heat shrinkable behavior of polyolefin blends with elastomer like CSM. They suggested the importance of a crosslinked elastomeric phase to enhance the heat shrinkability of a blend system and at the same time to improve their flame retardency. Present study deals with the grafting of polyethylene and chlorosulphonated polyethylene and to access their heat shrinkable behavior relating to phase morphology.

EXPERIMENTAL

The blending formulations were shown in Table I. The used LDPE was 22 FA 002 with MFI 0.20 and density 0.912 gm/cc, from IPCL, India. The CSM was Hypalon-40 grade of Du-pont, USA. The blend ratio of LDPE/CSM was taken as 60 : 40 which were melt blended in a Brabender plasticorder for 10 minutes at 20 rpm. The temperature of mixing was 120°C. In presence of coupling agents and grafting materials the blends were cured in a compression mold for half an hour at 150°C. The vulcanizates were stretched both at ambient and elevated

TABLE I Mixing formulations

Sample	*LDPE (phr)*	*Hypalon (phr)*	*DCP (phr)*	*Maleic anhydride (phr)*	*Acrylic acid (phr)*	*Vinyl triacetoxy silane (phr)*	*Ethane diol (phr)*	*Diethanol amine (phr)*	*4,4′-diamino diphenyl methane (phr)*
1	60	40	.2	–	4	–	–	–	–
2	60	40	.2	4	–	–	–	–	–
3	60	40	.2	–	–	4	–	–	–
4	60	40	.2	4	–	–	2	–	–
5	60	40	.2	4	–	–	–	2	–
6	60	40	.2	4	–	–	–	–	2

temperatures like 120°C, 150°C, 180°C, 210°C. Then they were allowed to shrink at that temperature in which they were stretched. The lengthwise shrinkage was measured at various temperatures according to the formula

$$(Sh\%) = (L_{\mathrm{str}} - L_{\mathrm{shr}})/(L_{\mathrm{str}}) \times 100$$

L_{str} = length of the sample after stretching
L_{shr} = length of the sample after shrunk.

The cure characteristics were studied using a Monsanto Rheometer R-100 at 150°C. X-ray diffraction were studied using PW 1840 X-ray diffractometer with copper target (Cukα) at a speed of 0.05°C/sec, chart speed 10 mm/2θ, range 10,000 cps, and slit 0.2 mm, applying 40 kV, 20 mA current in order to have idea of crystallinity of the blends as effected by stretching. IR spectra were recorded on thin films of the samples using Perkin Elmer Spectrophotometer (Model 837) within range of 4000 to 400 cm^{-1}. Phase morphology was studied using specimens after differential solvent extraction (toluene) with the help of SEM (Camscan Series 2 and E 5200 Auto Sputter Coater).

RESULTS AND DISCUSSION

The percentage shrinkability at various temperatures were shown in Table II. It was observed that for all the samples the shrinkage was always less for room temperature stretched samples. Shrinkage increased as the temperature is increased. Shrinkage at 180°C was maximum in all the samples except for DCP/maleic anhydride systems. The sample melted and had flown probably due to lack of crosslinking in the system.

TABLE II Heat shrinkability of the blends at different temperatures

	1	2	3	4	5	6
RT	74	68	70	74	73	80
120°C	80.33	75	77	82	76	80
150°C	83	85	82	86	85	82
180°C	86	71	81	88	86	91
210°C	–	–	–	–	–	92

Effect of Crosslinking on Shrinkability

Continuous cure characteristic is observed through Monsanto Rheometer, R-100. Sample 6 shows the highest torque. Sample 1 shows slightly higher torque than sample-3 but lower torque than sample-6 (Fig. 1). Torque is not found to increase in other samples. So sample-6 is having highest interchain crosslinking than sample-1 and sample-3. Other samples have very little interchain crosslinking.

However, interchain crosslinking has a very profound effect on the shrinkability of the blend. It is found that sample-6, shows high shrinkability even at very high temperature. As no drastic flow occurred, we observed about 92% shrinkability at 210°C. Actually, high temperature stretching ability depends upon the interchain crosslinking. If there is little or no crosslinking, sample will flow at high temperature and consequently shows poor shrinkability at high temperature.

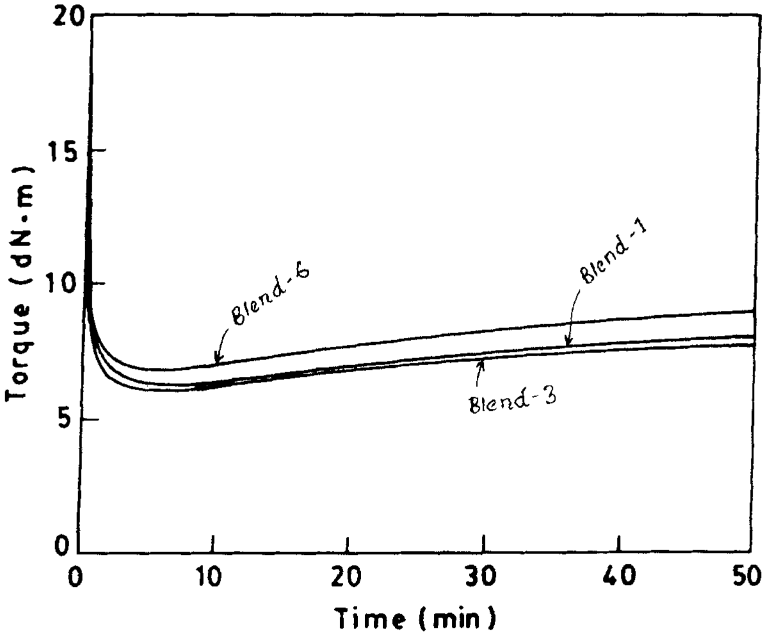


FIGURE 1 Rheometric plot of the blends at 150°C.

Effect of Crystallinity on Shrinkability of the Blends

X-ray diffractogram of the various blends have been shown in Figures 2, 3 and 4. It has been observed that the crystallinity of the original sample was higher than the shrunk sample, which was again higher than the H-T-stretched sample. Crystallinity of the samples was assumed to be coming from polyolefinic phase. During the stretching process the crystallites tend to break up into microlamellae and finally into still smaller units, possibly by unfolding or despiralizing of chains. Conformation of the polymer chain within the crystal is that of the lowest possible energy. Change in conformation of the lowest energy to higher energy is responsible for lower crystallinity of the sample under H-T-stretching condition [9].

It was seen that crystallinity of room temperature stretched sample is higher than high temperature stretched sample. As the stretching

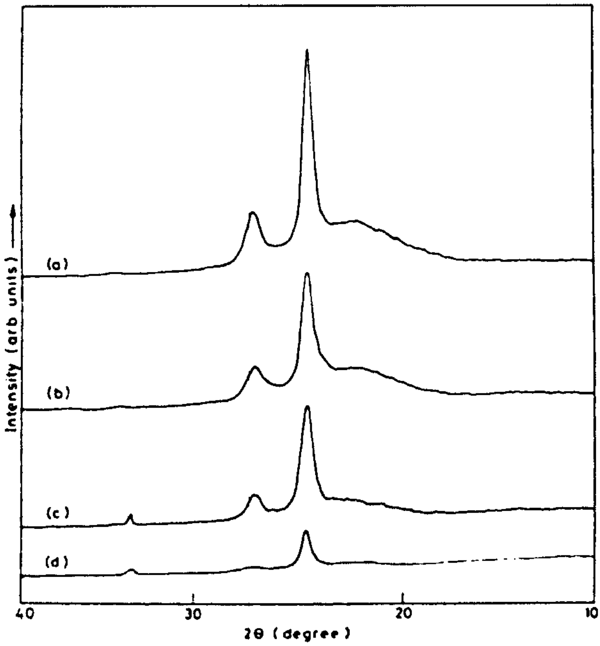


FIGURE 2 XRD data of the blend LDPE/Hypalon/Maleic anhydride/DCP/Ethanediol (a) usual sample; (b) shrunk sample; (c) stretched sample at 150°C; (d) stretched sample at 180°C.

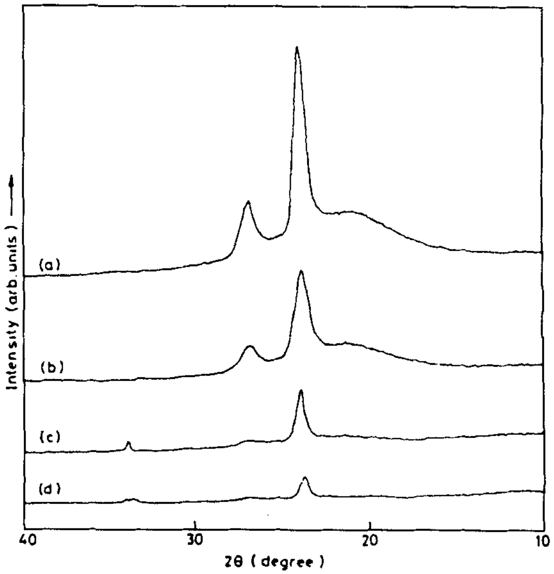


FIGURE 3 XRD data of the blend LDPE/Hypalon/Maleic anhydride/DCP/Diethanol amine (a) usual sample; (b) shrunk sample; (c) stretched sample at 150°C; (d) stretched sample at 180°C.

temperature increases, crystallinity decreases. Again, in majority of the cases shrinkability increases as the temperature increases. So, shrinkability increases as the volume fraction of amorphous material increases, because a portion of the molecule in the amorphous phase can coil easily to give more shrinkage. For sample-1, sample-2, sample-3 (contains no coupling agents), it is seen that sample-2 has lowest crystallinity of the stretched sample and gives highest shrinkability.

FT IR Spectrum of the Blends

Interchain crosslinking in the sample-1, 3 and 6 have also been confirmed from FT IR spectrum as shown in Figure 5.

Sample-1

The IR plot (Fig. 5a) reveals that here is a definite shift of the $>S=O$ stretching frequency of the $-SO_2Cl$ group which appears at

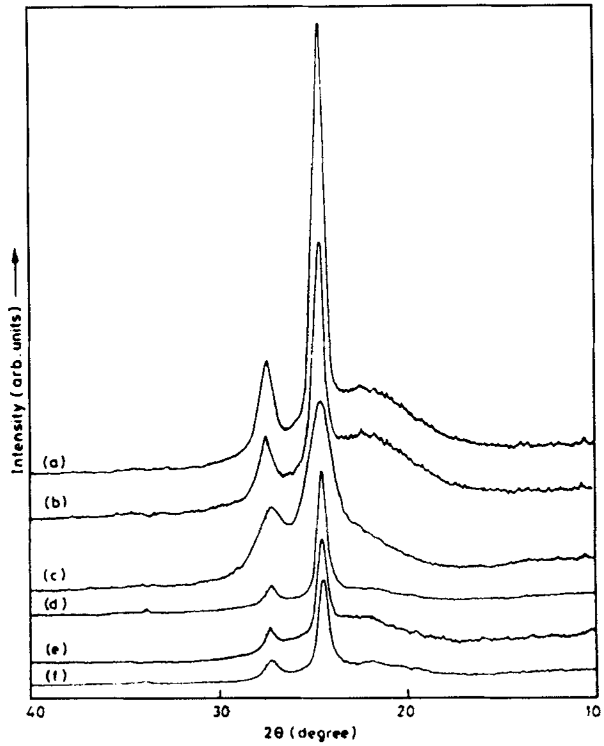


FIGURE 4 XRD data of the blend LDPE/Hypalon/Maleic anhydride/DCP/4,4′diaminodiphenyl methane (a) usual sample; (b) shrunk sample; (c) room temperature; (d) stretched sample at 150°C; (e) stretched sample at 180°C; (f) stretched sample at 210°C.

1377 cm^{-1} and 1156 cm^{-1} which are due to the change of environment of $>S{=}O$ group. There exist a strong absorption peak at 1735 cm^{-1} which is due to $C{=}O$ in ester group. The absence of O—H stretching frequency of the carboxylic acid between 2500–2700 cm^{-1} suggests the involvement of O—H group in the interchain crosslinking reaction. Another strong absorption band at 1261 cm^{-1} may be assigned to C—O peak in ester. The formation of double bond in the main chain, to certain extent, due to the elimination of —SO_2Cl group from chlorosulphonated polyethylene cannot be ignored as strong peaks appeared at 970 cm^{-1} and 1648 cm^{-1}. Based on the above a plausible

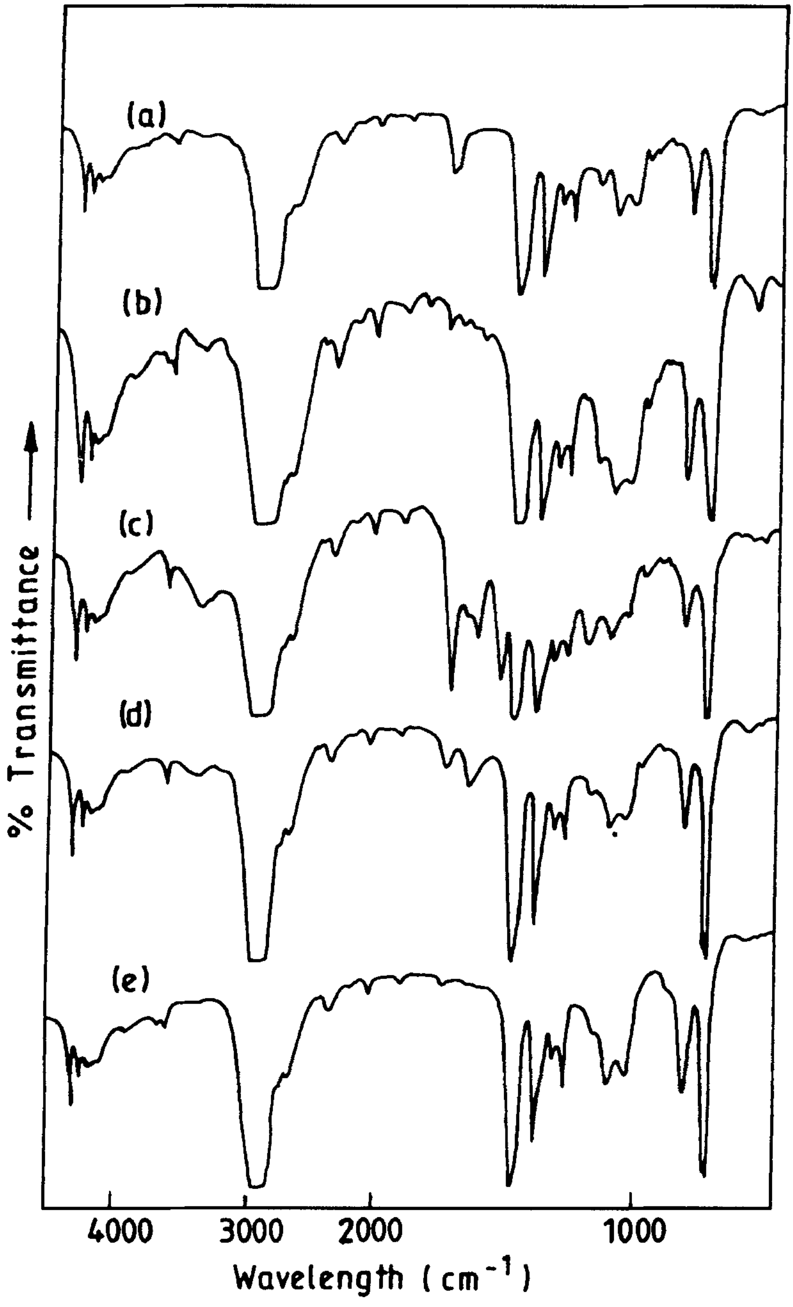
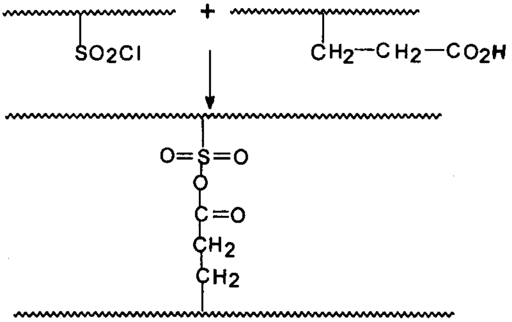


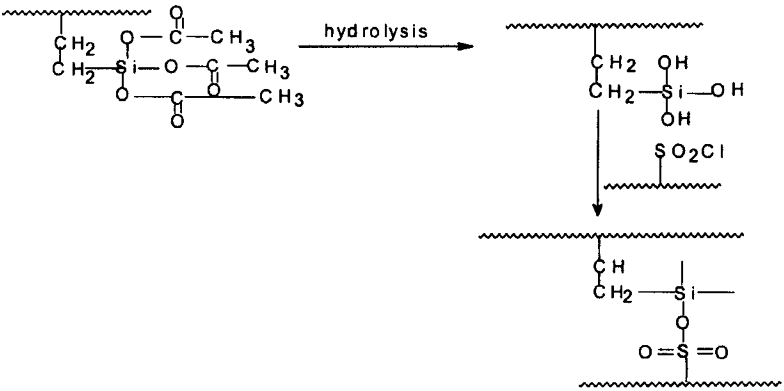
FIGURE 5 FTIR of the blends (a) LDPE/DCP/Hypalon/Acrylic acid; (b) LDPE/DCP/Hypalon/Vinylsilane; (c) LDPE/DCP/Hypalon/Maleic anhydride/4,4′ diaminodiphenylmethane; (d) LDPE/DCP/Hypalon/Maleic anhydride/Diethanolamine; (e) LDPE/DCP/Hypalon/Maleic anhydride/Ethane diol.



reaction mechanism for interchain crosslinking may be suggested as follows.

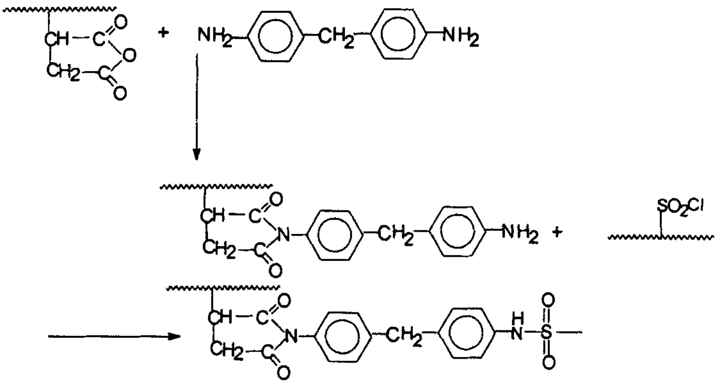
Sample-3

Figure 5b shows that there is a definite shift of the —SO_2Cl stretching frequencies which appears at 1377 cm^{-1} and 1156 cm^{-1} suggested the involvement of —SO_2Cl group in the interchain crosslinking. A strong absorption peak at 803 cm^{-1} which is due to the probable shift of Si—O bond stretching frequency (from Si—O—H) involving interchain crosslinking. A small but wider absorption peak at 3370 cm^{-1} suggests the reaction through Si—O—H but not to the total extent. The interchain crosslinking may be depicted as follows.



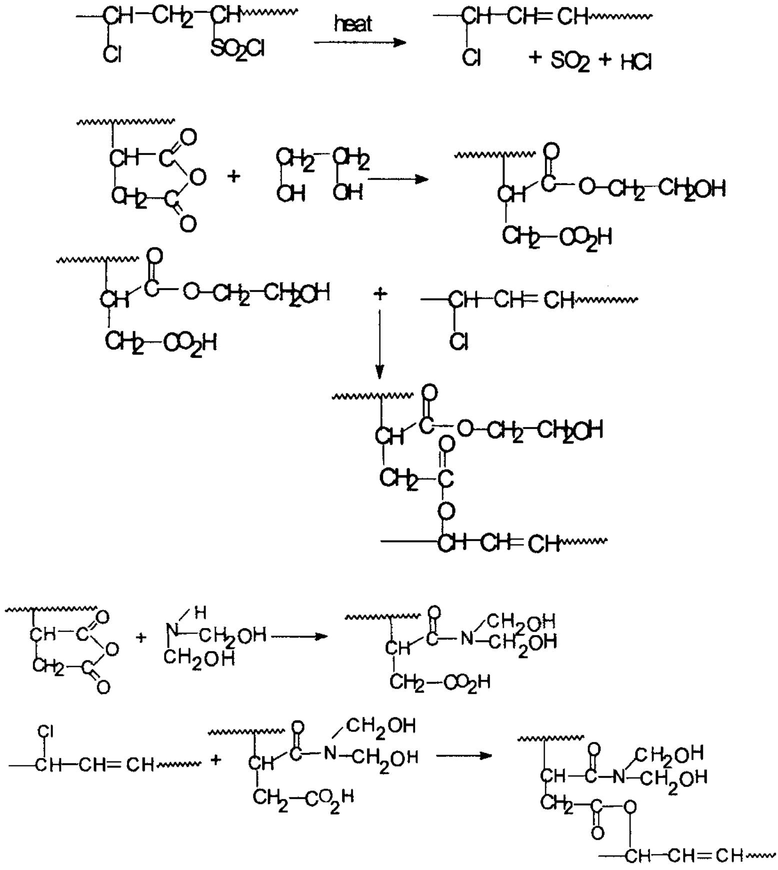
Sample-6

As observed from the IR plot (Fig. 5c) —SO_2Cl peak appears at 1377 cm^{-1} and 1181 cm^{-1} suggesting the involvement of —SO_2Cl in the interchain crosslinking [11]. This shift is due to the different environment of S=O in the blend system. A new peak appears at 1512 cm^{-1} which is due to N—H bond frequency of secondary amine suggesting the involvement of —NH_2 moiety of 4,4′diaminodiphenyl methane in the crosslinking reaction as suggested below. The peak appears at 1309 cm^{-1} due to the 'C—N' stretching of aromatic amine. The reaction mechanism may be suggested as below:



Sample-4 and Sample-5

The IR study revealed that the appearance of a small absorption peak at 1739 cm^{-1} may be assigned to >C=O group of ester. In the case of sample-5 (where coupling agent is diethanol amine) a new peak appears at 1637 cm^{-1} corresponding to the C=O stretch in amide group. The complete absence of -SO_2Cl peak in the system, however, could not prove completely the interchain crosslinking reaction [12]. It may be possible that somehow in the system the S=O environment is completely changed. It may also be possible that the —SO_2Cl is completely eliminated from the system by thermal degradation and thus could not be detected. However, the C=O peak as mentioned above, due to ester formation may arise from the crosslinking between C—Cl of hypalon and carboxylic moiety produced from anhydride as shown below:



Thermal Analysis

The DSC-TGA plots were shown in Figures (6a–d) and the degradation temperature and other thermal parameters like first degradation, second degradation temperature, heat of degradation, onset temperature of crosslinking and heat of crosslinking were shown in Table III and Table IV respectively.

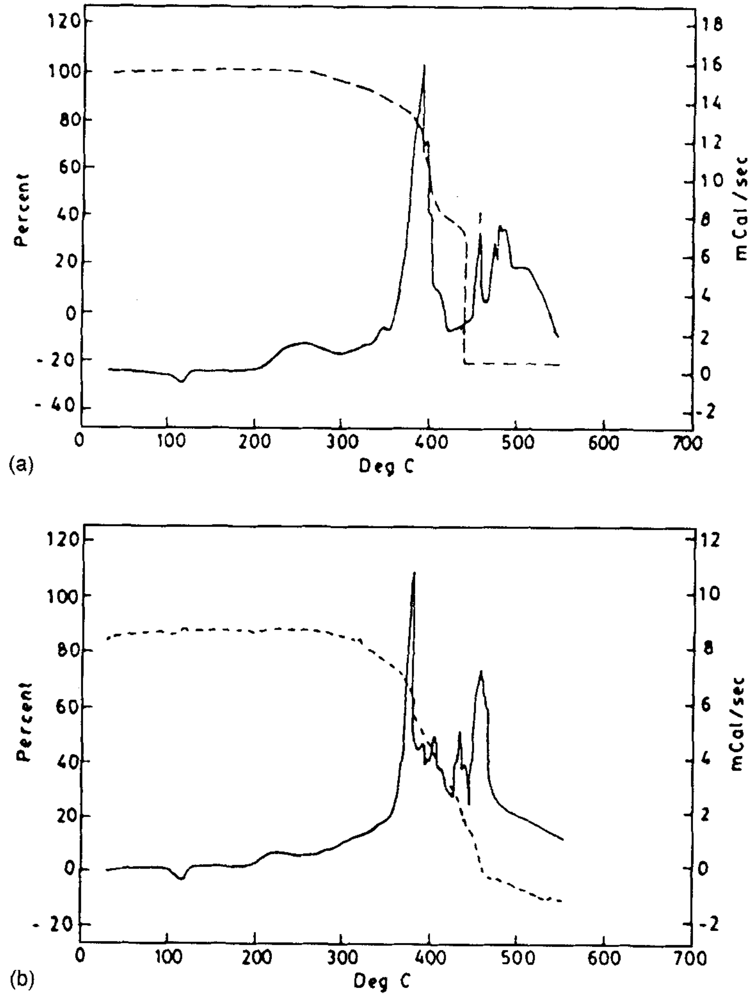


FIGURE 6 DSC plot of the blends (a) LDPE/DCP/Hypalon/Acrylic acid; (b) LDPE/DCP/Hypalon/Maleic anhydride/Ethane diol; (c) LDPE/DCP/Hypalon/Maleic anhydride; (d) LDPE/DCP/Hypalon/Vinyl silane.

All the figures revealed the two-stage degradation of the blend systems studied. The table showed higher heat of degradation for the acrylic and siloxane system may be due to interchain crosslinking through the coupling agent. The temperature of final degradation also shifted towards the higher side due to crosslinking. Higher heat of

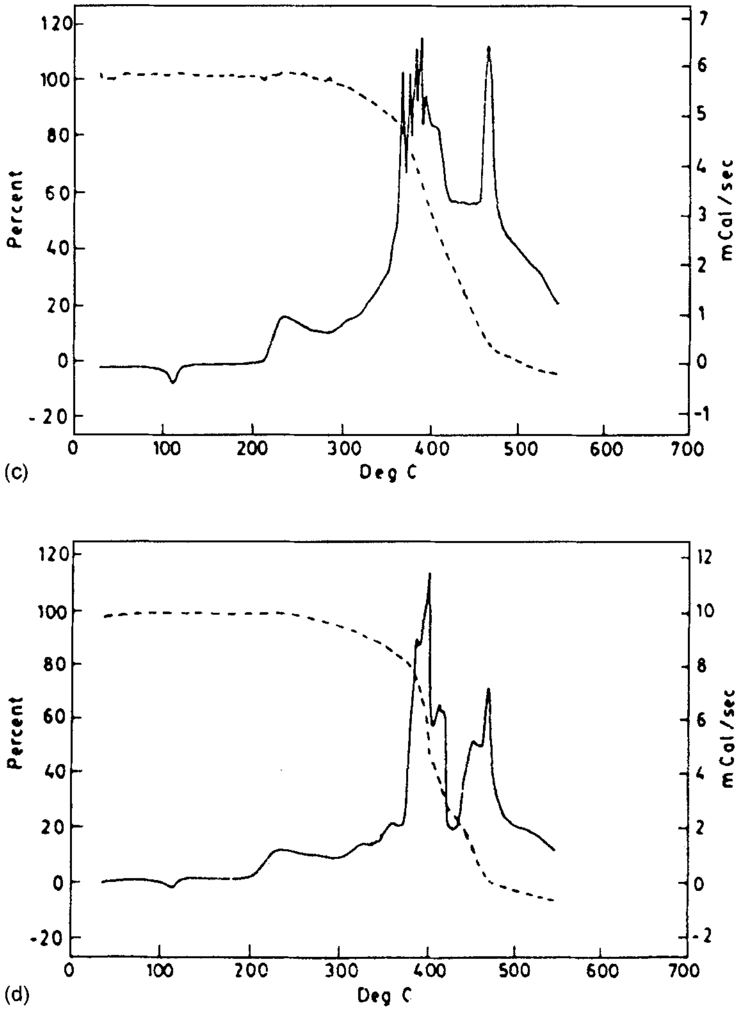


FIGURE 6 (Continued).

TABLE III DSC parameters of the blends

Sample	1*st.*	2*nd.*	*Heat* (*mcal/mg*)
1	308.75	388.06	400.92
2	316.59	371.87	328.53
3	297.85	401.9	438.6
4	299.23	382.33	321.84

TABLE IV Heat of crosslinking of blends

Sl. No.	*Onset temperature of crosslinking (°C)*	*Heat of crosslinking (mcal/mg)*
1	212.5	56.83
2	219.09	45.80
3	209.41	55.77
4	199.7	22.55
5	202	30.6
6	205	60.2

crosslinking for acrylic, siloxane and 4,4′diamino diphenyl methane suggested the probable interchain crosslinking. The higher onset temperature of crosslinking accompanied by lower heat of crosslinking of LDPE/DCP/MA/Hypalon system suggested the lack of interchain crosslinking. The interchain crosslinking for the ethanediol and diethanol amine system could not be explained in the usual way because of their low heat of crosslinking as observed which has already been explained in earlier section.

SEM Study of the Blend

The phase morphology of the blends (high temperature shrunk sample) have been studied by Scanning Electron Microscope after differential solvent extraction and represented in the Figures (7–9) for the blend Nos. 1, 3, 6 respectively. As observed from the Figures 7 and 8 rubbery phase remain somewhat globular in nature which were extracted easily by the solvent extraction as observed the extraction of

FIGURE 7 SEM Photograph of the blend Sample No. 1 (× 1000).

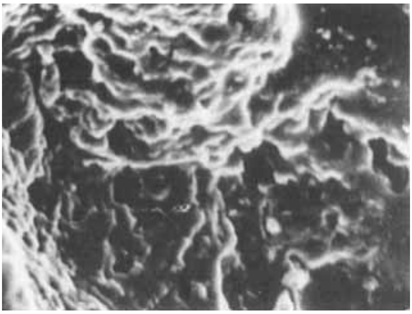


FIGURE 8 SEM Photograph of the blend Sample No. 3 (× 1000).

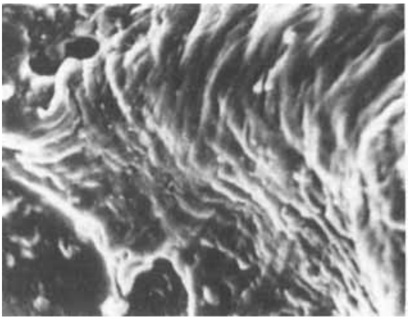


FIGURE 9 SEM Photograph of the blend Sample No. 6 (× 1000).

the rubbery phase is less when acrylic acid is used as grafting material then vinyl silane. The extraction of the rubber *y* phase is much restricted for the blend using 4,4′diamino diphenyl ethane (blend No. 6). Here the rubbery phase is elongated. The observation is in line with the Rheometric and FT IR studies confirming the interchain crosslinking between the rubber and plastic phase.

CONCLUSIONS

Shrinkability increased as the percent amorphity of the material is increased. The samples stretched at high temperature showed higher shrinkability than that observed at room temperature stretching. Sufficient interchain crosslinking gave rise to higher shrinkability at high temperature. Also interchain crosslinking resulted high expansibility at high temperature.

References

[1] Waler, B. M. (1979). Handbook of Thermoplastic Elastomers, Van Nostrand Reinhold, New York.

[2] Plochocki, A. P. (1978). *Polymer blends*, Academic, New York, **2**, ch. 21.

[3] Coran, A. Y. and Patel, R. P. (1980). *Rubber Chem. Technol.*, **53**, 141.

[4] Patra, P. K. and Das, C. K. (1997). *Journal of Polymer Engineering*, **17**, 231–244.

[5] Patra, P. K. and Das, C. K. (1997). *J. Reinforced Plastics and Composites*, **16**, 1111–1128.

[6] Patra, P. K. and Das, C. K. (1998). *Journal of Applied Polymer Science*, **68**, 597–603.

[7] Whelan, A. and Lee, K. S. (1982). Developments of Rubber Technology, Thermoplastic Rubbers, *Applied Polym. Sci.*, London.

[8] Patra, P. K. and Das, C. K. (1997). *Intern. J. Polym. Mat.*, **35**, 103–118.

[9] Rogovin, Z. A. (1974). *Advance in Polymer Science*, John Wiley and Sons, New York, pp. 150–184.

[10] Brydson, J. A. (1982). Plastics Materials, Butterwort Scientific, pp. 218–219.

[11] Gaylord, N. G. and Mehta (1982). *J. Polym. Sci. Polym. Lett.*, **20**, 481–482.

[12] Roychoudhury, A. and De, P. P. (1997). *J. Appl. Polym. Sci.*, **63**, 1761–1768.