

# Effect of Cure Systems on Shrinkability of Polyolefin–EPDM Blends

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**ABSTRACT:** Effects of cure systems on shrinkability of polyolefin and EPDM blends have been studied as a function of cure time and amount of elastomers added. During measurement one of the parameters is kept constant while the other varies. The shrinkability of the blends increases with the increase in cure time when elastomer content is fixed. Similarly, at constant cure time higher loading of elastomer increases the shrinkability of the blends. Samples stretched under high temperature show higher shrinkability than those stretched under room temperature. Dicumylperoxide (DCP) is a more effective curing agent for making a particular set of blends more shrinkable than the sulfur. The changing morphological pattern with DCP-cured shrunk samples from those of sulfur cured samples is corroborated by the SEM studies where the elastomer phase appears to be globular in nature. The crystallinity of the blend depends on the dose and type of the elastomer used in polyolefin. The curing efficiency of the elastomer phase depends on the polyolefin used as blend partner. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 597–603, 1998

**Key words:** polyolefin; shrinkability; stretching; morphology; curing; vulcanizates

## INTRODUCTION

In recent years economic, technologic, and other regulatory pressures have gradually narrowed the further development of newer chemical varieties of polymers. The existing trend reveals a rapidly growing interest in research in the field of polymer blends as a major endeavor. A particular polymer may have a set of properties superior to another polymer, while this polymer may be rich in a different set of properties lacking in the former. By blending different polymers several properties can be improved while retaining some of the other properties.<sup>1–3</sup> The

blend prepared by melt mixing thermoplastics materials and elastomers have recently gained considerable attention. It is clear now that nearly all blends are comprised of one polymer domain dispersed in the matrices of the other polymers.<sup>4–6</sup> There is very little systematic information concerning the heat shrinkability of the polymer blend. The use of polyethylene in blends and composites is most useful from a technological point of view because of its nontoxicity. Very recently Patra and Das studied the flame retardancy and heat shrinkability of polyolefin/elastomer blends.<sup>7–9</sup> This article presents our study on the investigation of heat shrinkability of the blends of polyolefins and EPDM with sulfur and DCP as the curing agents through cure characteristics, crystallinity and morphology.

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## EXPERIMENTAL

The used HDPE was F46003, having MFI 0.30 and density 0.946 gm/cc. LLDPE was F19010, having MFI 0.90 and density 0.918 gm/cc. LDPE was 22 FA002 with MFI 0.20 density 0.912 gm/cc. The used EPDM was Nordel 1040. The blends of HDPE/EPDM, LDPE/EPDM, and LLDPE/EPDM were made by gradual replacement of polyethylene with EPDM in a Brabender plasticorder for 10 min at 20 rpm. The temperature of mixing was 150°C for HDPE/EPDM blends and 120°C for LLDPE/EPDM and LDPE/EPDM blends. The curative systems used are ZnO/S/TMTD and DCP to study the effect of two curing agents on the shrinkability of the blends. The blends thus prepared were allowed to cure in a hot press in a mold at 150°C for 5, 10, 15, and 20 min. This operation enabled the blends to be effected in two different ways because of the difference in the nature of crosslinking due to S and DCP. In the case of first curative system the rubber phase is crosslinked, leaving aside the plastic phase as such. When DCP is used, both the elastomeric phase and plastic phase are influenced but to a different extent. We have studied the lengthwise shrinkage which was measured under three different conditions (a) shrinkage was measured at 150°C for above vulcanizates; (b) vulcanizates were given stretching at ambient temperature and at 150°C and then the shrinkage of the stretched samples was measured at 150°C; (c) above vulcanizates were stretched at 150°C and cured under stretching conditions and then the shrinkage was measured at 150°C. Shrinkage (%) was measured as

$$\text{Sh } \% = [L_{str} - L_s]/L_{str} \times 100$$

where Sh % is percent shrinkage,  $L_{str}$  is length of the sample after stretching, and  $L_s$  is length of the sample after it is shrunk.

The cure characteristics were studied using a Monsanto Rheometer R-100 at 150°C. X-ray diffraction was studied using a PW 1840 X-ray diffractometer with copper target ( $\text{CuK}_\alpha$ ) at a speed of  $0.05^\circ 2\theta/\text{s}^{-1}$ , chart speed 10 mm/ $2\theta$ , range 10,000 cps,  $T_C$   $1 \text{ s}^{-1}$  and a slit of 0.2 mm applying 40 kV, 20 mA current in order to have the idea of crystallinity of the blends as affected by the extent of stretching. Phase morphology was studied using specimens after differential solvent extraction with the help of a scanning electron mi-

croscope, SEM (Camscan Series 2 and E5200 Auto Sputter Coater).

## RESULTS AND DISCUSSION

The blends of polyethylene and EPDM were prepared in the composition range as shown in Tables I and II and then the curatives were incorporated as per the compounding formulation shown in Tables I and II. Corresponding properties were shown in respective figures.

### Effect of Cure Time and Elastomer Content on Shrinkability of the Blends

The variation of shrinkability of the blends with cure time at constant elastomer content for both the high temperature (H-T) stretched and room temperature (R-T) stretched samples are shown in Figures 1 and 2, respectively. The figures show that with increase in cure time the shrinkability increases in case of all the blends. The extent of increase in shrinkability is more when DCP is used as the curing agent than that in case of the sulfur-cured system. LLDPE/EPDM blends show maximum shrinkability for both H-T and R-T stretched samples followed by LDPE and HDPE containing blends. Higher shrinkability of the blends when DCP is used as curing agent than the sulfur cured system may be due to the fact that sulfur acts as the bridging agent between two elastomer molecules, whereas DCP attack both the polymer chains to generate active sites leading to more efficient crosslinking, which results in higher shrinkability of the blends.<sup>10</sup> The increase in cure time increases the shrinkability of the blends. For a similar increase in cure time H-T stretched samples are found to show higher shrinkability than the R-T stretched samples. This difference in shrinkability of H-T stretched and R-T stretched samples is higher in the case

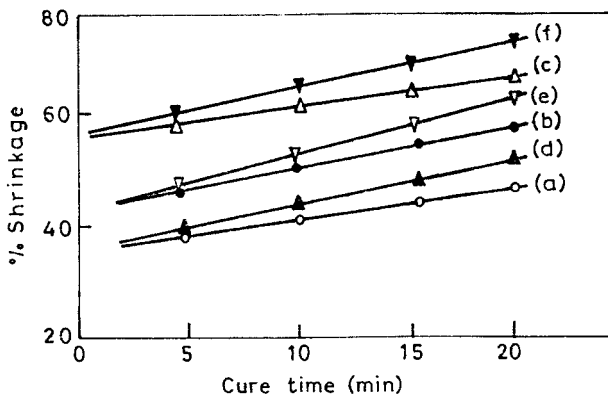
**Table I Compounding Formulations with ZnO/S/TMTD as Cure System**

Blend	I	II	III	IV
LLDPE/LDPE/HDPE	80	60	40	20
EPDM	20	40	60	80
ZnO	0.8	1.6	2.4	3.2
S	0.25	0.5	0.75	1.0
TMTD	0.25	0.5	0.75	1.0

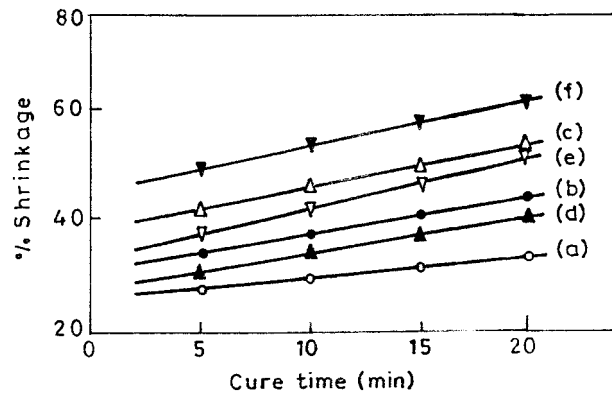
**Table II Compounding Formulations with DCP as Cure System**

Blend	I	II	III	IV
LLDPE/LDPE/HDPE	80	60	40	20
EPDM	20	40	60	80
DCP	1.0	1.0	1.0	1.0

of the DCP cured system than observed in case of the sulfur cured system. This may be due to more crosslinking of the elastomer phase at higher temperature owing to the decomposition of the curatives (DCP) to produce more active sites, thus initiating considerable crosslinking, which is not significantly feasible in case of an R-T stretched sample.<sup>11</sup> An increase in cure time means allowing the elastomer phase to crosslink for a longer period of time, resulting in efficient crosslinking, which is manifested in higher shrinkability.<sup>12</sup> The variation of shrinkability of the blends with elastomer content at constant cure time for both H-T stretched and R-T stretched samples is shown in Figures 3 and 4. It is evident from the figures that the increase in elastomer content increases the shrinkability of the blends for R-T and H-T stretched samples in case of both the sulfur and DCP cure systems. LLDPE/EPDM blends get an edge over the LDPE/EPDM and HDPE/EPDM blends so far as

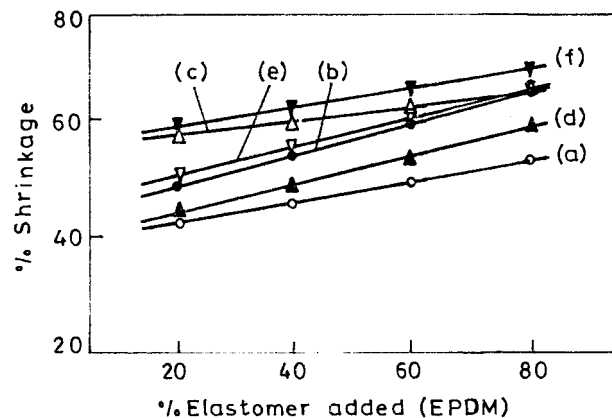


**Figure 1** Variation of shrinkage of the blends with cure time at constant elastomer content for H-T stretched samples: (a) HDPE/EPDM blend with sulfur as the curative; (b) LDPE/EPDM blend with sulfur as the curative; (c) LLDPE/EPDM blend with sulfur as the curative; (d) HDPE/EPDM blend with DCP as the curative; (e) LDPE/EPDM blend with DCP as the curative; (f) LLDPE/EPDM blend with DCP as the curative.

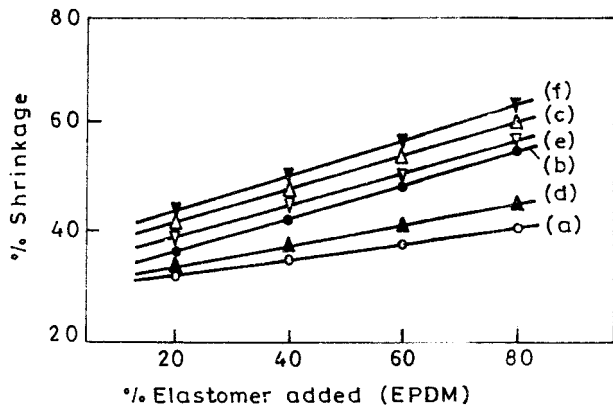


**Figure 2** Variation of shrinkage of the blends with cure time at constant elastomer content for R-T stretched samples: (a) HDPE/EPDM blend with sulfur as the curative; (b) LDPE/EPDM blend with sulfur as the curative; (c) LLDPE/EPDM blend with sulfur as the curative; (d) HDPE/EPDM blend with DCP as the curative; (e) LDPE/EPDM blend with DCP as the curative; (f) LLDPE/EPDM blend with DCP as the curative.

shrinkability is concerned. The extent of increase in shrinkability is higher for H-T stretched samples than R-T stretched samples in both the sulfur and DCP cure system. Here again the greater increase in shrinkability of the H-T stretched sample for DCP cure system is due to the decomposition of DCP resulting higher concentration of free radicals as discussed above.<sup>13</sup>



**Figure 3** Variation of shrinkage of the blends with elastomer content at constant cure time for H-T stretched samples: (a) HDPE/EPDM blend with sulfur as the curative; (b) LDPE/EPDM blend with sulfur as the curative; (c) LLDPE/EPDM blend with sulfur as the curative; (d) HDPE/EPDM blend with DCP as the curative; (e) LDPE/EPDM blend with DCP as the curative; (f) LLDPE/EPDM blend with DCP as the curative.



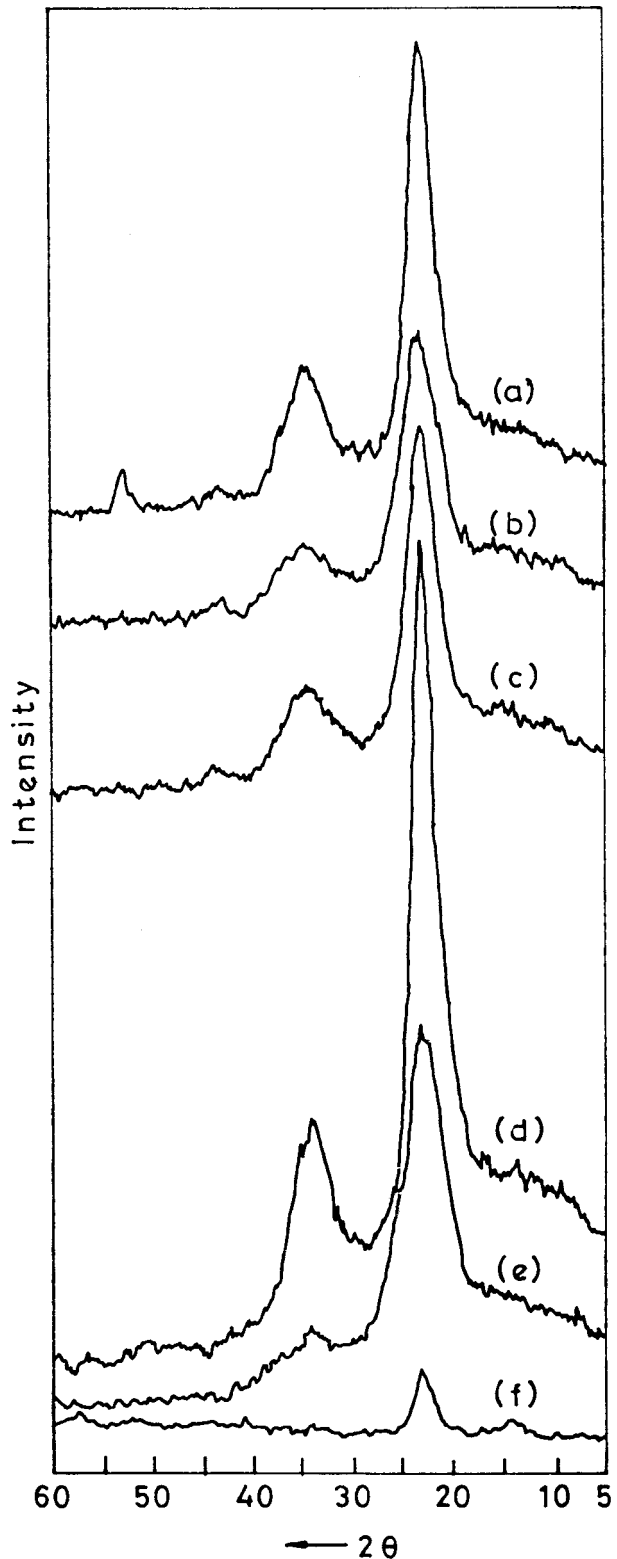
**Figure 4** Variation of shrinkage of the blends with elastomer content at constant cure time for R-T stretched samples: (a) HDPE/EPDM blend with sulfur as the curative; (b) LDPE/EPDM blend with sulfur as the curative; (c) LLDPE/EPDM blend with sulfur as the curative; (d) HDPE/EPDM blend with DCP as the curative; (e) LDPE/EPDM blend with DCP as the curative; (f) LLDPE/EPDM blend with DCP as the curative.

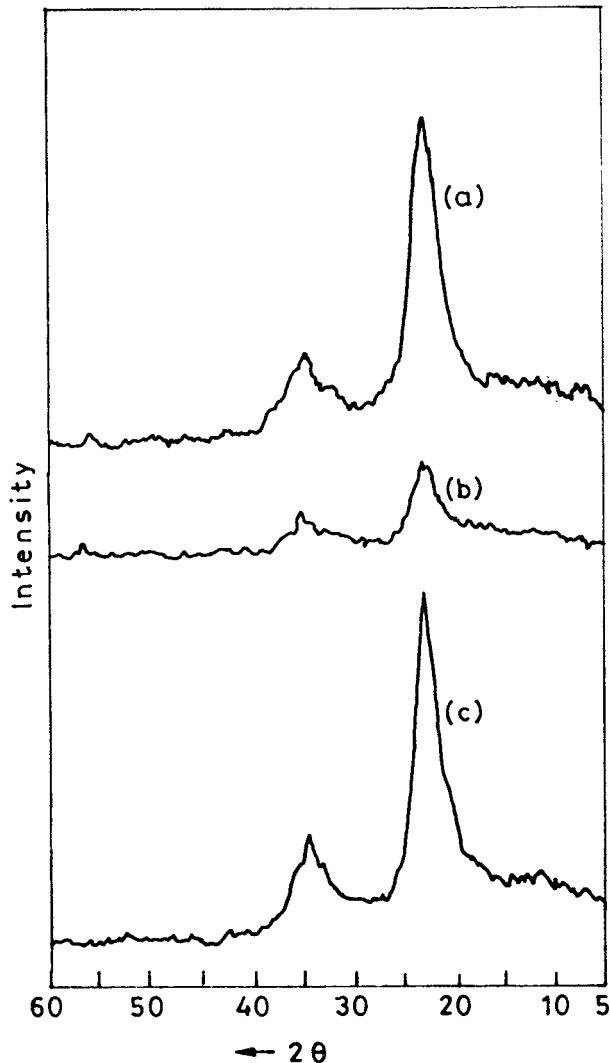
#### Effect of Crystallinity on the Shrinkability of the Blends

X-ray diffractograms of various blends have been shown in Figures 5 and 6. It has been observed that for a particular polyolefin/elastomer blend the unstretched sample is having higher crystallinity than the H-T stretched sample followed by an R-T stretched sample for both DCP cured system and sulfur cured system. LLDPE/EPDM blends (in the case of sulfur cure) get an edge over LDPE/EPDM blends and HDPE/EPDM containing blends for the equivalent blend ratio. For LLDPE containing blends in the sulfur cure system although H-T shrunk and H-T stretched samples have almost same crystallinity but R-T shrunk samples are more crystalline than R-T stretched samples. For LDPE/EPDM blends a slight difference occurs where H-T shrunk samples show higher crystallinity than H-T stretched

**Figure 5** X-ray diffractograms: (a) unstretched original sample of LDPE/EPDM (60/40) with sulfur as the curative; (b) H-T stretched sample of LDPE/EPDM (60/40) with sulfur as the curative; (c) H-T shrunk sample of LDPE/EPDM (60/40) with sulfur as the curative; (d) unstretched original sample of LDPE/EPDM with DCP as the curative; (e) H-T stretched sample of LDPE/EPDM (60/40) with DCP as the curative; (f) R-T shrunk sample of LLDPE/EPDM (60/40) with sulfur as the curative.

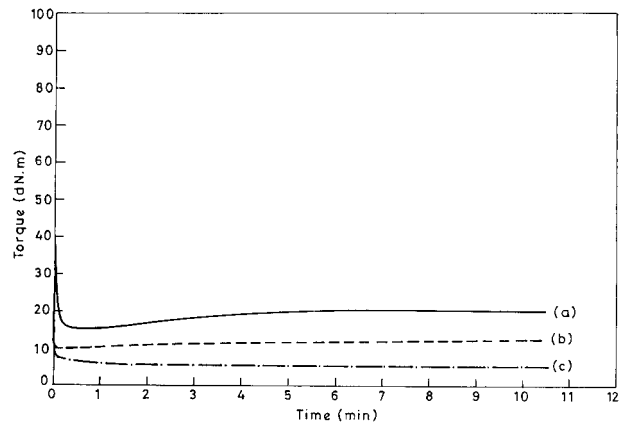
samples. For a particular blend system it is observed that the unstretched original sample in the DCP cure system has higher crystallinity than





**Figure 6** X-ray diffractograms: (a) H-T stretched sample of LLDPE/EPDM (60/40) with sulfur as the curative; (b) R-T stretched sample of LLDPE/EPDM (60/40) with sulfur as the curative; (c) H-T shrunk sample of LLDPE/EPDM (60/40) with sulfur as the curative.

the original unstretched sample in the sulfur cure system. The same trend is followed for H-T stretched and R-T stretched samples. For the blend systems studied, the crystallinity mainly depends on the polyolefin phase, while stretching the sample at high temperature the polyolefin phase flows more than that at room temperature stretching, making the blend more crystalline in the former case. The low crystallinity of H-T and R-T stretched samples than the unstretched original samples may be due to the breakage of the elastomer phase at such high elongation of stretching producing voids in the structure thus

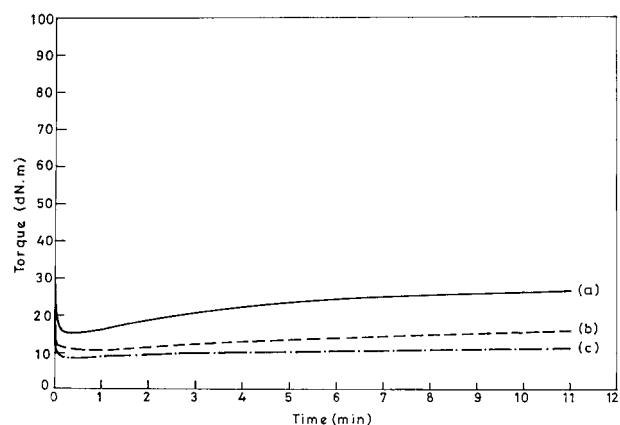


**Figure 7** Torque rheometry: (a) LLDPE/EPDM (60/40) with sulfur as the curative; (b) LDPE/EPDM (60/40) with sulfur as the curative; (c) HDPE/EPDM (60/40) with sulfur as the curative.

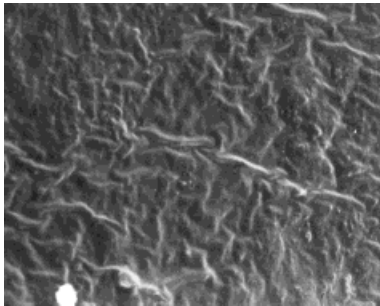
loss of regularity. However, it needs more experimentation to conclude. One noteworthy observation is that for unstretched blend samples HDPE containing blends have higher crystallinity, followed by LLDPE and LDPE containing blends.

#### Effect of Crosslinking

It is observed from the continuous cure characteristics through the Monsanto Rheometer, R-100, that the increase in elastomer content increases the degree of crosslinking for a particular cure system. The extent of increase in crosslinking is more in the case of DCP cure systems. For a particular blend ratio DCP cure systems have a higher extent of crosslinking than the sulfur cure system (Figs. 7 and 8). This is due to the involve-



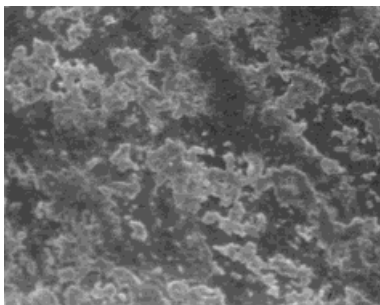
**Figure 8** Torque rheometry: (a) LLDPE/EPDM (60/40) with DCP as the curative; (b) LDPE/EPDM (60/40) with DCP as the curative; (c) HDPE/EPDM (60/40) with DCP as the curative.



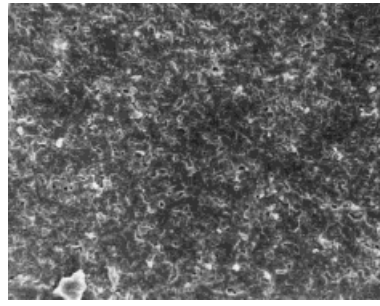
**Figure 9** SEM photograph (800 $\times$ ) of H-T stretched sample of LLDPE/EPDM (60/40) with DCP as the curative.

ment of both the phases in crosslinking when DCP is used as the crosslinking agent, whereas in the case of the sulfur cure system only the elastomer phase is responsible for crosslinking, not the thermoplastic phase. Again, for a particular polyolefin elastomer blend ratio the LLDPE containing blends have a higher state of cure followed by LDPE and HDPE (Fig. 8). This trend holds good for both the DCP and sulfur cure systems.

The more crosslinking in the structures the more is the entanglement in the chain segments, which results in the retraction of the sample, i.e., higher shrinkability. For the LLDPE/EPDM blend system the DCP attacks both the polymer chains to produce a considerable higher number of active sites than the sulfur cure system, which acts as the bridge between elastomer chains, only thus the higher efficiency of the DCP to crosslink the polymers makes the blend more shrinkable than the sulfur cure blends of the same samples.<sup>14</sup> However, authors fail to understand the increased crosslinking efficiency for LLDPE/EPDM followed by LDPE/EPDM and HDPE/EPDM blends for sulfur crosslinking. Probably it needs more experimentation to explain this above phenomenon.



**Figure 10** SEM photograph (800 $\times$ ) of H-T stretched sample of LLDPE/EPDM (60/40) with sulfur as the curative.

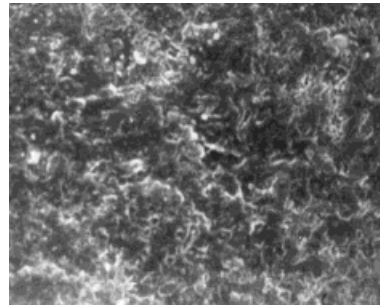


**Figure 11** SEM photograph (800 $\times$ ) of H-T shrunk sample of LLDPE/EPDM (60/40) with DCP as the curative.

### SEM Study

Phase morphology was studied by SEM after differential solvent extraction of EPDM. They are represented in Figures 9–12.

Comparing the H-T stretched samples of the DCP cure system and sulfur cure system of LLDPE/EPDM blends (Figs. 9 and 10) it can be seen that the elastomer phase is elongated more in the DCP cure system. This may be due to difference in the efficiency of DCP and S as crosslinker.<sup>15</sup> In case of DCP as a curing agent both the plastic and elastomer phases are crosslinked, which may result increase in viscosity. The higher values of shrinkability of the DCP cure systems may be due to the more extensibility of the plastic phase than the sulfur cured samples and LLDPE gives a higher value, which may be because of its structural influence on the curing agent. The SEM of the shrunk samples after H-T stretching of LLDPE/EPDM of the DCP cure system and sulfur cure system are shown in Figures 11 and 12. It is clearly observed from the figures that the elastomer phase is more globular in nature in the DCP cure system, which is represented as tiny black



**Figure 12** SEM photograph (800 $\times$ ) of H-T shrunk sample of LLDPE/EPDM (60/40) with sulfur as the curative.

droplets, thus offering more shrinkability than the latter, where the spherulitic structure, with a larger domain of elastomer phase, is not that prominent.

## CONCLUSIONS

With increase in cure time the shrinkability of the blends increases. Increased elastomer content in the blend enhances the shrinkability. The samples stretched under high temperature (H-T) show higher shrinkability than that observed in room temperature (R-T) stretched samples. The blends with DCP as the curing agent get an edge over the blends with sulfur as a curing agent so far as shrinkability is concerned. The crystallinity of the blends varies depending on the dose and type of elastomer used in polyolefins. The curing efficiency of the elastomer phase depends on the types of polyolefins as blend partners. LLDPE/EPDM blends are found to show greater shrinkability than the other blend systems studied.

## REFERENCES

1. W. M. Hess, et al., *Rub. Chem. Tech.*, **66**, 329 (1993).
2. A. Y. Coran and S. Lee, *Rub. Chem. Tech.*, **65**, 231 (1992).
3. E. T. McDonel, et al., in *Polymer Blends*, Vol. 11, D. R. Paul, et al., Ed., Academic Press, New York, Chap. 19.
4. P. Mukhopadhyay and C. K. Das, *J. Appl. Polym. Sci.*, **39**, 49 (1990).
5. L. F. Ramos-De Valle, *Rub. Chem. Tech.*, **55**, 1341 (1982).
6. S. Danesi and R. S. Porter, *Polymer*, **19**, 448 (1978).
7. P. K. Patra and C. K. Das, *Intern. J. Polym. Mat.*, **35**, 103 (1997).
8. P. K. Patra and C. K. Das, *J. Polym. Eng.*, **17**, 231 (1997).
9. P. K. Patra and C. K. Das, *J. Reinf. Plast. and Compos.*, **16**, 1111 (1997).
10. G. Geuskens, Ed., *Degradation and Stabilisation of Polymers*, Applied Science, London, 1975.
11. E. L. Hawkins, Ed., *Polymer Stabilisation*, Wiley-Interscience, New York, 1972.
12. M. Petric, O. Gal, and D. Babic, Changes of Supermolecular Structure of Polymer Materials at Various Processing, *Radiat. Physics. Chem.* (in press).
13. C. J. Pedersen, *Int. Eng. Chem.*, **41**, 924 (1949).
14. B. N. Leyland and J. T. Watts, *Chapter in Developments with Natural Rubber*, J. A. Brydson, Ed., Maclaren, London, 1967.
15. J. C. Ambelang, R. H. Kline, O. M. Lorenz, C. R. Parks, C. Wadelin, and J. R. Shelton, *Rub. Chem. Technol.*, **36**, 1497 (1963).