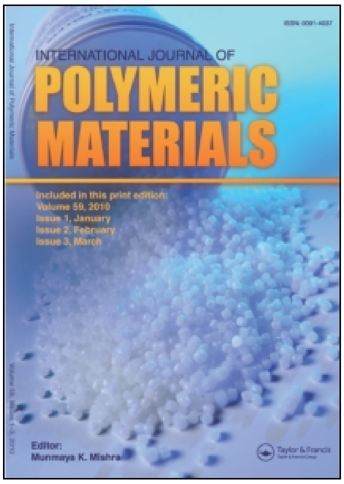

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Blends of Ethylene Vinyl Acetate (EVA) and Chlorosulphonated Polyethylene (CSM) with Reference to their Shrinkability

S. Raychowdhury[a]; C. K. Das[a]; K. N. Pandey[b]; G. N. Mathur[b]
[a] Materials Science Centre, I. I. T, Kharagpur, India [b] DMSRDE, Kanpur, India

To cite this Article Raychowdhury, S. , Das, C. K. , Pandey, K. N. and Mathur, G. N.(2000) 'Blends of Ethylene Vinyl Acetate (EVA) and Chlorosulphonated Polyethylene (CSM) with Reference to their Shrinkability', International Journal of Polymeric Materials, 45: 1, 135 — 147

To link to this Article: DOI: 10.1080/00914030008034874

URL: http://dx.doi.org/10.1080/00914030008034874

Intern. J. Polymeric Mater., 2000, Vol. 45, pp. 135–147
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Blends of Ethylene Vinyl Acetate (EVA) and Chlorosulphonated Polyethylene (CSM) with Reference to their Shrinkability

S. RAYCHOWDHURY[a], C. K. DAS[a,*], K. N. PANDEY[b]
and G. N. MATHUR[b]

[a] *Materials Science Centre, I. I. T, Kharagpur, India;*
[b] *DMSRDE, Kanpur, India*

(Received 3 June 1998)

The blends of ethylene vinyl acetate (EVA) and chlorosulphonated polyethylene (CSM) were investigated with respect to their shrinkability and micro-structure of the blends.

Keywords: Ethylenevinyl acetate; chlorosulphonated PE; shrinkage; cross-linking; blends; micro-structure

INTRODUCTION

Growing industrial needs of polymer blends prove that blending produce new materials with improved properties to meet the product specification with economic benefits. The blends prepared by melt mixing of thermoplastic materials and elastomer have gained considerable attention in recent years [1–6]. Heat-shrinkability of the polymer, which depends on the elastic memory, is being utilised in various applications mainly in the field of encapsulation. The elastic memory can be introduced into the system in the form of an elastomeric phase. Matsuki *et al.* [11] have studied the heat

---

*Corresponding author.

shrinkability of multilayered crosslinked stretched films having good tearstrength. Sunikawa *et al.* [12] investigated the heat-shrinkability of the tube made by blending PE with crosslinkable silicon grafted polypropylene. The use of EVA in blends is most important from the technological point of view. CSM shows excellent properties in terms of ozone and heat resistance.

The aim of the present investigation is to study the blends of ethylene vinyl acetate (EVA) and chlorosulphonated polyethylene (CSM) with reference to their shrinkability introducing preferential crosslinking in the elastomer phase. Shrinkability has been tried to correlate with the various processing parameters which change the micro-structure of the blends.

EXPERIMENT

Ethylene vinyl acetate (EVA) used was 1803 and CSM was of HYPALON 40 variety. The blends of EVA/CSM were made by gradual replacement of plastic with chlorosulphonated polyethylene (CSM), as shown in Table I in Brabender Plasticorder for 10 min at 30 rpm. The mixing temperature was 100°C. The curative system used was S/MBT/MBTS/ZDC. The blends were cured in a mould at 150°C for 10, 15, 20, 25, 30 min. By this operation the rubber phase is crosslinked and plastic phase remains as it is.

Lengthwise shrinkage was studied and was measured under two different conditions as given below:-

(a) Above vulcanizates were given stretching at ambient temperature. The shrinkage was measured then at 150°C temperature.

(b) Vulcanizates were stretched at 150°C, and shrinkage was measured at 150°C.

TABLE I Compounding formulation

Blend	1	2	3	4	5
EVA	80	60	50	40	20
CSM	20	40	50	60	80

S - 1.5 phr, MBT - 2 phr, MBTS - 1 phr, ZDC - 1 phr (phr based on elastomer).

Shrinkage (%) was measured as per formulation given below:

$$S_h(\%) = \frac{L_{\text{str}} - L_s}{L_{\text{str}}} \times 100$$

$S_h(\%)$ = % shrinkage,
L_{str} = Length of the sample after stretching,
L_s = Length of the sample after it is shrunk.

X-ray diffraction were studied using PW1840 X-ray diffractometer with cobalt target (CoK_α) in order to get the idea of the crystallinity of the blends. By SEM, phase morphology was studied using specimens after differential solvent (toluene) extraction. Differential Thermal Analysis (DTA) and ThermoGravimetric Analysis (TGA) were conducted using Shimadzu Thermal Analyzer (DT-40) in air at a rate of 10 c/min within the temperature range 25-600°C. To determine the glass transition temperature, Differential Scanning calorimetry (DSC) were carried out. Cure characteristics were studied on a Monsanto Rheometer R-100 at 150°C.

RESULTS AND DISCUSSION

In the composition range, as shown in Table I, blends of EVA and CSM were made. The curatives were then incorporated as per the compounding formulation shown in Table I. The corresponding properties were shown in the form of graphical plots.

A. Effect of Curetime and Elastomer Content on Shrinkability

The variation of shrinkability of the blends with curetime at constant elastomer content for both the high-temperature (H-T) stretched and room temperature (R-T) stretched samples were shown in Figure 1. It is clear from the figure that with increase in curetime the shrinkability of the blends increase in case of all the blends. H-T stretching is accompanied by high shrinkage followed by R-T stretched samples. With increase in cure time the shrinkability increases – this may be due to more crosslinking of the elastomeric phase. The variation of shrinkability with elastomer content at constant cure time is shown in Figure 2, It is obvious from the figure that at constant curetime the

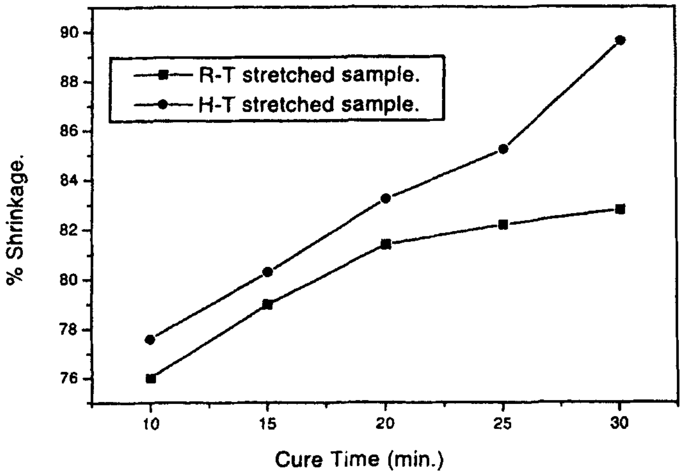

FIGURE 1 Variation of % shrinkage with Cure Time.

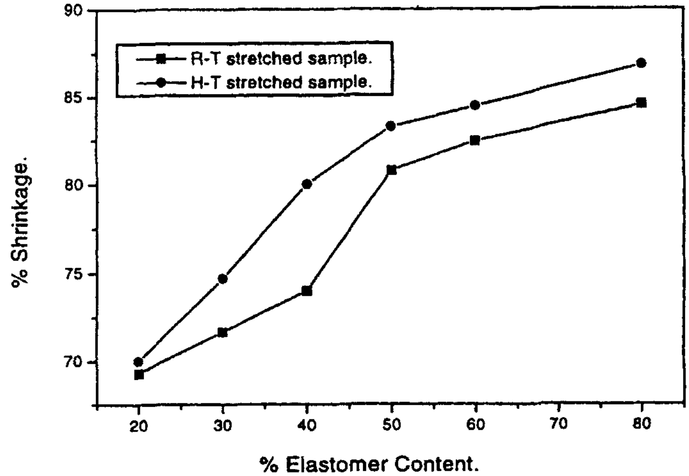

FIGURE 2 Variation of % shrinkage with % Elastomer Content.

increase in elastomer content increases the shrinkage of the blends for both R-T and H-T stretched samples. Here again the H-T stretched sample is getting an edge over R-T stretched samples. This increase in the shrinkage may be attributed to the increased elastomeric phase which are crosslinked. The extent of increase in shrinkability with elastomer content is higher for H-T stretched samples than that obtained in R-T stretched samples.

B. Effect of Crystallinity on the Shrinkage of the Blends

X-ray diffraction of the various blends is shown in Figures 3 and 4. For EVA/CSM = 80/20 the crystallinity of the R-T stretched sample is more than that of H-T stretched sample. Though the shrinkage of the latter is higher. Shrunk sample follow the same trend where R-T shrunk sample shows slightly higher crystallinity than the H-T shrunk sample. As the elastomer phase is increased in the blend (EVA/CSM = 60/40) the crystallinity decreases. Here again R-T

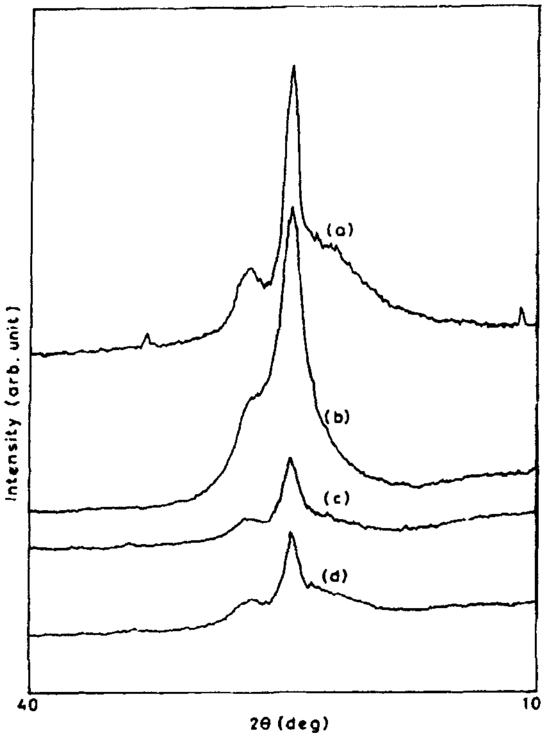

FIGURE 3 X-ray diffractograms. (a) EVA/CSM (80/20) original unstretched sample; (b) EVA/CSM (80/20) R-T stretched sample; (c) EVA/CSM (80/20) H-T stretched sample; (d) EVA/CSM (80/20) H-T shrunk sample.

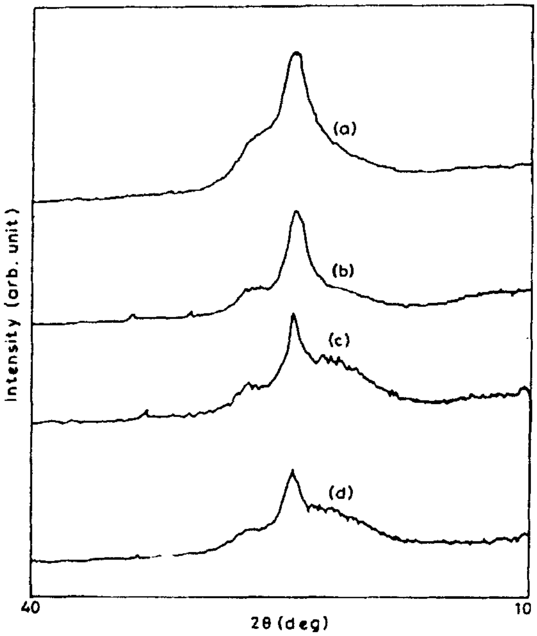

FIGURE 4 X-ray diffractograms. (a) EVA/CSM (40/60) R-T stretched sample; (b) EVA/CSM (40/60) H-T stretched sample; (c) EVA/CSM (40/60) R-T shrunk sample; (d) EVA/CSM (40/60) H-T shrunk sample.

stretched and R-T shrunk samples are having an edge over the H-T stretched and H-T shrunk samples respectively. As the CSM content is increased in the blends the differences in the crystallinity between R-T stretched and H-T stretched sample narrows down. Shrunk samples always accompanied by lower crystallinity, but the difference between the crystallinity of R-T stretched and R-T shrunk samples is wider than H-T stretched and H-T shrunk samples .This is irrespective of the blends ratio studied. Surprisingly original unstretched samples are having more crystallinity than that of both R-T and H-T shrunk sample. It is also noteworthy that the original unstretched is having more crystalline character than that of R-T stretched sample and this difference narrows down as the CSM content is decreased in the blends. The crystallinity is determined by the regularity of its molecular structure. In the case of blends the microstructural irregularity can occur depending on the blend ratio, side chain polar groups, the chain mobility, as affected by the mutual phase distribution and the cocontinuety. In the case of thermoplastic elastomer blends the mobility of the thermoplastic phase is hampered by the presence of partially crosslinked elastomeric phase and *vice versa*, depending on the temperature of stretching. At H-T stretching there may be some extra crosslinking formed which produces irregularities, thus reducing crystallinity. The higher crystallinity of the original sample may be due to the unrestricted chain mobility accompanied by flow during initial stretch of the molding when the elastomeric phase is being crosslinked. However, it needs more experimentation to arrive at a concrete conclusion.

C. Effect of Crosslinking

From the cure characteristics (Fig. 5) of EVA/CSM (80/20), (60/40), (40/60), (20/80), it is observed that the blend with 20% elastomer shows lower torque, *i.e.*, crosslinking of elastomeric phase is minimum which is responsible for minimum shrinkability and gradually it increases with elastomer content and for EVA/CSM (20/80) the torque is maximum as the crosslinking of elastomeric phase is maximum,

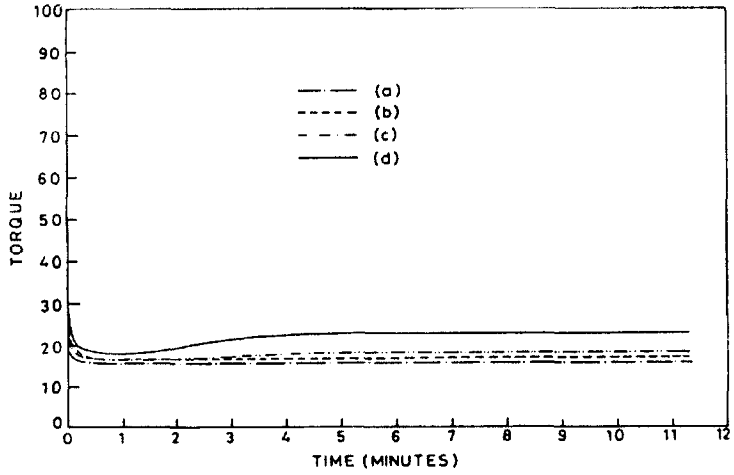

FIGURE 5 Variation of rheometric torque with cure time. (a) EVA/CSM (80/20) blend; (b) EVA/CSM (60/40) blend; (c) EVA/CSM (40/60) blend; (d) EVA/CSM (20/80) blend.

consequently shrinkability is higher. From the torque-rheometry it is clearly reflected that the extent of crosslinking of elastomer in EVA/CSM (20/80) is maximum which consequently gives the higher shrinkability of the blend.

D. DSC Analysis

DSC analysis (Fig. 6) suggest that with increase in elastomer content the glass transition temperature (T_g) goes down, may be due to lower crystallinity of the high elastomer containing blend, as confirmed by XRD as reported in previous chapter. Again for R-T stretched sample the T_g is lower than that of original one, but higher than that of H-T stretched sample (Fig. 7). This trend is same as in crystallinity, which is also clear from X-ray diffractograms. Here may be the cause that with increase in elastomer content the chain mobility of the plastic phase may increase and consequently T_g goes down. Chain mobility may increase due to increased disorderness, reduced molecular packing and reduction of interchain forces due to the presence of higher amount of elastomer in the plastic phase. However, the observed decrease in crystallinity, due to stretching, decreases T_g. This is may be due to the introduction of irregularities or disorderliness in the polymer chain, as

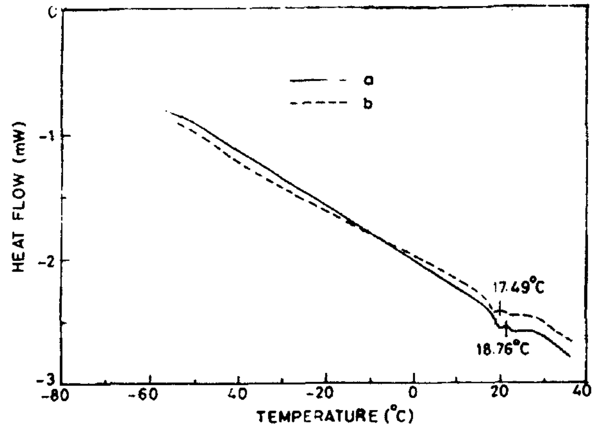

FIGURE 6 DSC plots (a) EVA/CSM (70/30) unstretched original sample; (b) EVA/CSM (30/70) unstretched original sample.

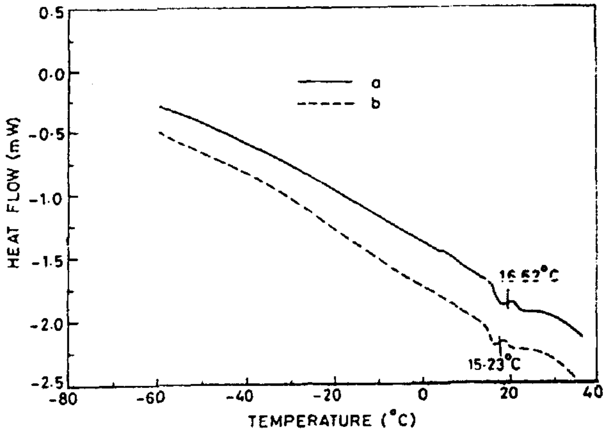

FIGURE 7 DSC plots (a) EVA/CSM (70/30) R-T stretched sample; (b) EVA/CSM (70/30) H-T stretched sample.

it is stretched as compared to the original unstretched sample. Here again the more disorderness, during high temperature stretching may be due to easy recoiling of the plastic chains at elevated temperature on melting the crystal domain.

High temp DSC study at higher temperature (Fig. 8) suggests that the melting peaks occur around 90°C and tend to vanish with increase in CSM content in the blend accompanied by sharp drop in percent weight retention. The initial degradation temperature shifts towards the lowerside as the CSM content is increased in the blends. However the two stage degradation is prominent at the higher level of CSM (60%). Heat of oxidative degradation is higher as the CSM content is increased in the blend (668 mcal/mg for 30% CSM and 811 mcal/mg for 60% CSM). However further processing of the blend at higher temperature decreases its thermal stability, *i.e.*, shifting the degradation temperature to lower temperature side accompanied by lower heat of degradation. As observed the EVA rich blend the multiple stage degradation occurred with number of exothermic degradation peaks, which again reduced on further heat treatment. With increased CSM dose the number of degradation peaks reduced to two (original unstretched) and further to one for H-T shrunk sample suggesting probably phase adhesion for CSM rich blends.

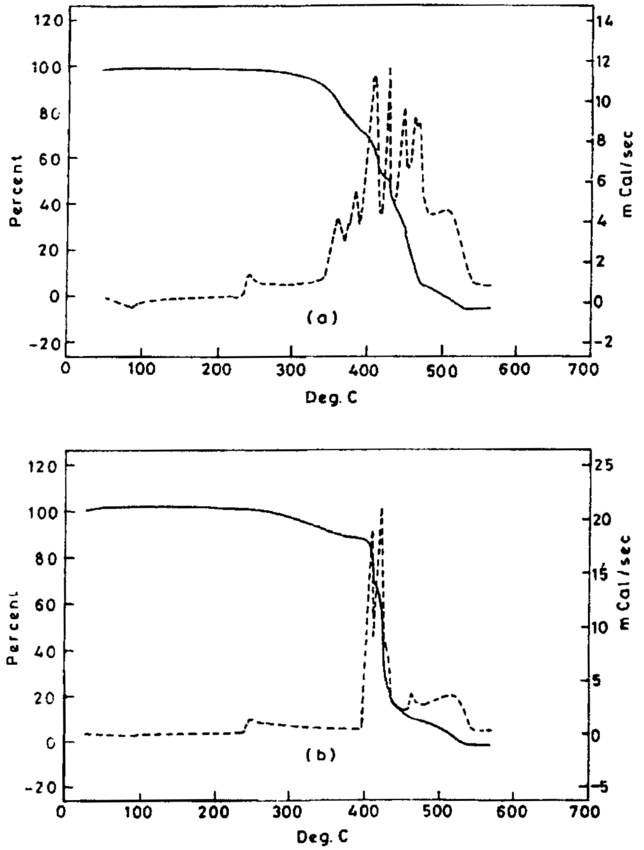

FIGURE 8 DSC plots (a) EVA/CSM (60/40) original unstretched sample; (b) EVA/CSM (20/80) original unstretched sample; (c) EVA/CSM (60/40) H-T shrunk sample; (d) EVA/CSM (20/80) H-T shrunk sample.

E. Study of Phase Morphology by SEM

The phase morphology of the blends have been studied by Scanning Electron Microscope after differential solvent extraction in Toluene in order to remove the elastomeric phase. The phase morphologies are shown in Figures 9–11. In the case of unstretched sample (Fig. 9) the elastomeric phase remains in the globular form. With the stretching of the specimen the elastomeric phase becomes elongated. Under an equivalent percentage of stretching the elastomer phase in R-T stretched

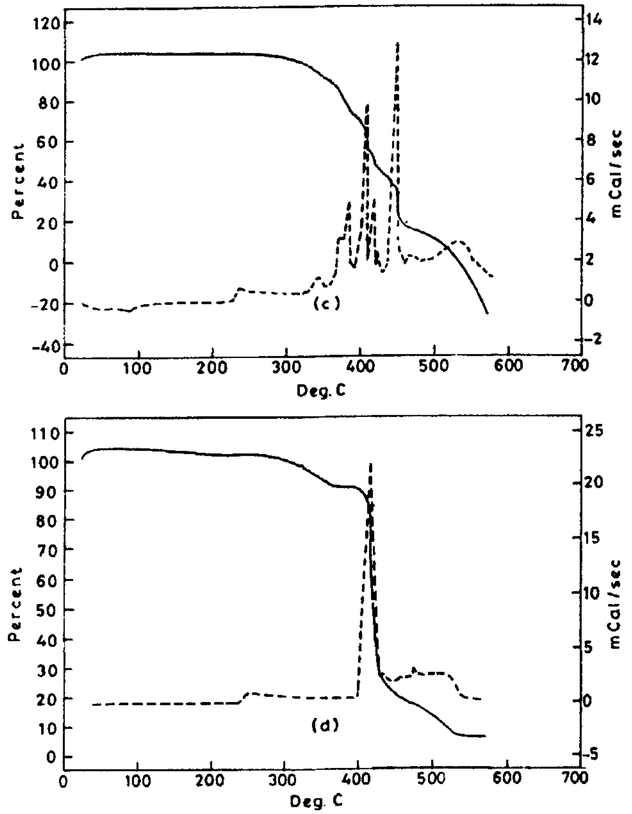

FIGURE 8 (Continued).

sample (Fig. 10) are elongated more than those observed in H-T stretched samples (Fig. 11). The more spherulite structure of the elastomer phase of the shrunk sample, results higher amount of shrinkage.

CONCLUSION

There is a mutual correlation between the processing parameters and the shrinkability of the blends. With increase in cure time and elastomer content shrinkability of blends increase both in case of H-T stretching and R-T stretching. H-T stretching sample generally shows

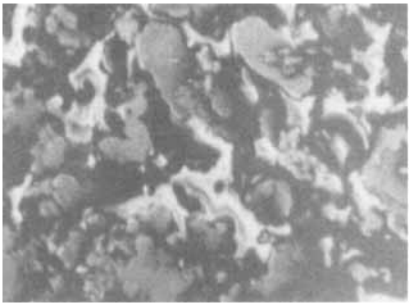

FIGURE 9 SEM photograph (800X) of EVA/CSM (60/40) unstretched sample.

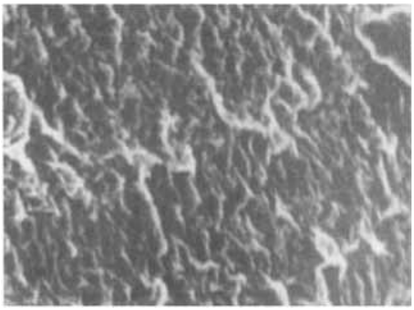

FIGURE 10 SEM photograph (800X) of EVA/CSM (60/40) R-T stretched sample.

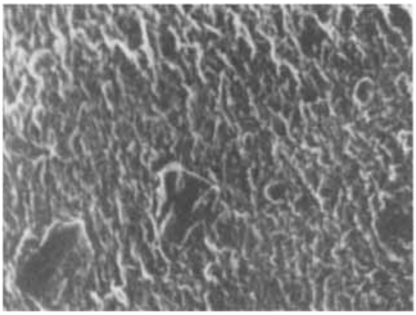

FIGURE 11 SEM photograph (800X) of EVA/CSM (60/40) H-T stretched sample.

higher shrinkability than R-T stretching sample. H-T extensibility depends on the crystallinity of the plastic phase. Processibility parameters which results in the extension of the elastomeric phases to rod like structures are always accompanied by high shrinkage at elevated temperature.

References

[1] Patra, P. K. and Das, C. K. (1997). *Int. J. Polymeric. Mater.*, **35**, 103–118.
[2] Patra, P. K. and Das, C. K. (1997). *J. Polymer Engineering*, **17**(3), 231.
[3] Plochocki, A. P. (1978). *Polymer Blends*, Academic, New York, Vol. 2, Chap. 21.
[4] Waler, B. M. (1979). *Handbook of Thermoplastic Elastomers*, Van Nostrand Reinhold. New York.
[5] Danesi, S. and Porter, R. S. (1978). *Polymer*, **19**, 448.
[6] Ramos De Valle, L. F. (1982). *Rubber Chem. Technol.*, **55**, 1341.
[7] Paul, D. R. and Newman, S. (1978). In: *Polymer Blends*, Academic Press, New York.
[8] Utracki, L. A. (1989). In: *Polymer Alloys and blends*, Hanser Publishers, Munich.
[9] Schwarz, H. F. (1980). *Elastomerics*, **112**(11), 17.
[10] Schwarz, H. F. (1982). *Rubber world*, **187**(2), 22.
[11] Matsuki, Yutaka, Mikami and Isamu. Agahi Chemicals Ltd., Jpn., Kokai Tokyo JP 06, 106, 668, 19th April 1994, Appl. 92/254, **624**, 24th September 1992.
[12] Sunikawa, T., Takeyuki, Shibata and Yoshizo. Mitsubishi Plastics Limited, Jpn. Kokai Tokyo Koho JP 0639921, 15 February 1994, Appl. 92/195, **280**, 22 July 1992.
[13] Brydson, J. A., *Plastic Materials*, 4th ed. Ch. 4.
[14] Edgar, O. B. and Hill, R., *J. Polymer Sci.*, **1952**, 81.
[15] Whelan, A. and Lee, K. S. (1982). Developments in Rubber Technology Thermoplastic Rubbers, *Applied Sc.*, London.
[16] Coran, A. V. and Patel, R. P. (1980). *Rubber Chem. Technol*, **53**, 141.
[17] Rizzo, G. and Sporado, G. (1984). *G. Polym. Eng. Sci.*, **24**, 264.
[18] Turi, A., *Thermal Characterisation of Polymeric Materials*, Ch. 3.