

This article was downloaded by:

On: 19 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

Blends of Polyolefins and Chlorosulphonated Polyethylene (CSM) with Special Reference to their Shrinkability and Flame Retardancy

P. K. Patra^a; C. K. Das^a

^a Materials Science Centre, India

To cite this Article Patra, P. K. and Das, C. K.(1997) 'Blends of Polyolefins and Chlorosulphonated Polyethylene (CSM) with Special Reference to their Shrinkability and Flame Retardancy', *International Journal of Polymeric Materials*, 35: 1, 103 – 118

To link to this Article: DOI: 10.1080/00914039708039757

URL: <http://dx.doi.org/10.1080/00914039708039757>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Blends of Polyolefins and Chlorosulphonated Polyethylene (CSM) with Special Reference to their Shrinkability and Flame Retardancy

P. K. PATRA and C. K. DAS

Materials Science Centre, I.I.T. Kharagpur, India

(Received 26 July 1996)

Shrinkability and flame retardancy of polyolefine blends with chlorosulphonated polyethylene is investigated. Correlations between shrinkability and blend microstructure are suggested.

Keywords: Polyolefines; chlorosulphonated polyethylene; blends; shrinkability; flame retardancy; microstructure

INTRODUCTION

Polymer blends have become an important area of research because of their growing industrial importance. Polymer blending, starting from conventional polymers offers an economic realisation of high performance target properties. The blends prepared by melt mixing of thermoplastic materials and elastomer have gained considerable attention in recent years [1–5]. The incorporation of crosslinking agents improves the mechanical properties of the blends [6–8]. A number of papers, concerned with establishing the compatibility or incompatibility of blends of various elastomers, have appeared [1–11]. It is now a common knowledge that nearly all blends are comprised of one polymer domain dispersed in matrices of the other polymers. But there is

very little published systematic information concerning the shrinkability and flame retardancy of elastomer blends. The use of polyolefin in blends and composites is most important from the technological point of view. Chlorosulphonated polyethylene (CSM) shows excellent properties in terms of ozone resistance, high temperature (H-T) resistance and flame resistance.

Matsuki *et al.* [12] have studied the heat shrinkability of multi-layered cross linked stretched films having good tear strength. T. Sunikawa *et al.* [13] investigated the heat shrinkability of the tube made by blending PE with cross linkable silicone grafted polypropylene. This paper presents out study on the investigation of heat shrinkability and flame resistance of polyolefins viz. LDPE, LLDPE and HDPE blended with CSM. Efforts have been given to correlate shrinkability with various processing parameters which on the other hand change the microstructure of the blends.

EXPERIMENT

HDPE used is F46003 having MFI 0.30 and density 0.946 gm/cc. LLDPE is F 19010 having MFI 0.90 and density 0.918 gm/cc. LDPE is 22FA002 with MFI 0.2 density 0.912 gm/cc CSM is hypalon 40. The blends of HDPE/CSM, LDPE/CSM, and LLDPE/CSM were made by gradual replacement of polyolefins with chlorosulphonated polyethylene (CSM) [shown in Tab. I] in Brabender plasticorder (PLE 330) for 10 minutes at 30 rpm. The temperatures of mixing was 150°C for HDPE/CSM, and 115 C for LLDPE/CSM and LDPE/CSM respectively. The curatives system used is Pb_3O_4 /MBTS/TMTD (Tab. II). The blends thus prepared were allowed to cure in a hot press in a mould at 150°C for 5, 10, 15 and 20 minutes. This operation enabled

TABLE I Compounding formulation

<i>Blend</i>	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>
LLDPE, LDPE, HDPE	80	60	40	20
CSM	20	40	60	80

Pb_3O_4 - 5 Phr; MBTS - 0.5 Phr; TMTD - .3 Phr (Phr based on elastomer).

TABLE II Flame retardancy of the sample with and without flame retardants

Sample	Ratio (W/W)	LOI
LDPE/CSM	80:20	23
LDPE/CSM	40:60	26
LDPE/CSM/Sb ₂ O ₃	40:60	28
LDPE/CSM/TPT	40:60	30
LLDPE/CSM	80:20	24
LLDPE/CSM	40:60	26
LLDPE/CSM/TPP	40:60	31
LLDPE/CSM/Sb ₂ O ₃	40:60	29
HDPE/CSM	80:20	22
HDPE/CSM	40:60	23
HDPE/CSM/Sb ₂ O ₃	40:60	25
HDPE/CSM/TPP	40:60	27
LDPE/CSM/Sb ₂ O ₃ /chlorohor	80:20	32
LDPE/CSM/TPP/Zn-metaborate	40:60	32
LLDPE/CSM/Sb ₂ O ₃ /chlorohor	80:20	33
LLDPE/CSM/TPP/Zn-metaborate	40:60	31
HDPE/CSM/Sb ₂ O ₃ /chlorohor	80:20	30

the rubber phase to crosslink with plastic phase remaining as it is. We have studied the lengthwise shrinkage and shrinkage was measured under three different conditions as given below:

- Shrinkage was measured at 150°C for above vulcanizates.
- Above vulcanizates were given stretching at ambient and at 150°C and then the shrinkage of the stretched samples was measured at the same temperature.
- Above vulcanizates were stretched at 150°C and cured under stretching conditions and then shrinkage was measured also at 150°C.

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

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

$$S_h(\%) = \% \text{ shrinkage}$$

L_{str} = length of the sample after stretching

L_s = length of the sample after it is shrunk.

Flame retardancy of the blends was measured in terms of LOI without and with the flame retardants. Specification for LOI tester is ASTM D 2863-77. Infrared spectra of the blended polymers were taken on the thin film of the samples of uniform thickness. Phase morphology was studied using specimens after differential solvent (toluene) extraction with the help of scanning electron microscope, SEM (Camscan series 2 and E5200 Auto Sputter Coater). 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. Differential Scanning Calorimetry (DSC) studies were carried out using Stanton Redcroft Thermal Analyzer STA-625, in a nitrogen atmosphere to determine the glass transition temperature. X-ray diffraction were studied using PW1840 X-ray diffractometer with copper target (CuK_α) at a speed of 0.05°/2 θ /sec, chart 10 mm 2 θ , range 10,000 c/s, T.C. 1 sec, and a slit of 0.2 mm, applying 40 KV, 20 mA current in order to get the idea of the crystallinity of the blends as affected by the extent of stretching.

RESULTS AND DISCUSSION

Blends of polyolefins and CSM were made in the composition range as shown in the Table-I, and then the curatives and fillers were incorporated as per the compounding formulation shown in Table-I. The corresponding properties were shown in figures.

A. Effect of Cure Time and Elastomer Content on Shrinkability

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 Figure (1). The figure shows that with increase in cure time the shrinkability of the blends increases in case of all the blends. The LLDPE/CSM blends show the highest shrinkability both for R-T and H-T stretched sample. H-T stretching is accompanied by high shrinkage followed by R-T stretched samples. It is found that LLDPE/CSM blends show highest values of shrinkability followed by LDPE/CSM and HDPE/CSM blends. Increase in cure time increases the shrinkability.

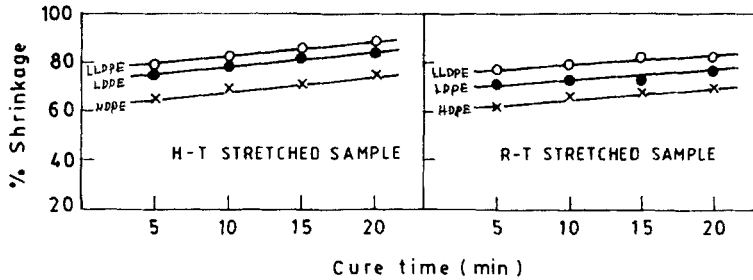


FIGURE 1 Variation of % Shrinkage with cure time.

This may be due to more crosslinking of the elastometric phase. The rate of enhancement of shrinkability with cure time of LLDPE/CSM blends is higher than other blend systems studied both in case of H-T stretched and R-T stretched samples. This rate of enhancement of shrinkability is always higher in case of the H-T stretched samples.

The variation of shrinkability with the polyolefines/CSM ratio at constant cure time is shown in Figure (2). It is evident from the figure that at constant cure time the increase in the elastomer content increases the shrinkage of the blends for both R-T and H-T stretched samples. Here again LLDPE/CSM blends are having edge over LDPE/CSM and HDPE/CSM so far as shrinkage is concerned for both R-T and H-T stretched samples. The rate of increase in shrinkability with elastomer content is maximum in case of LLDPE/CSM in

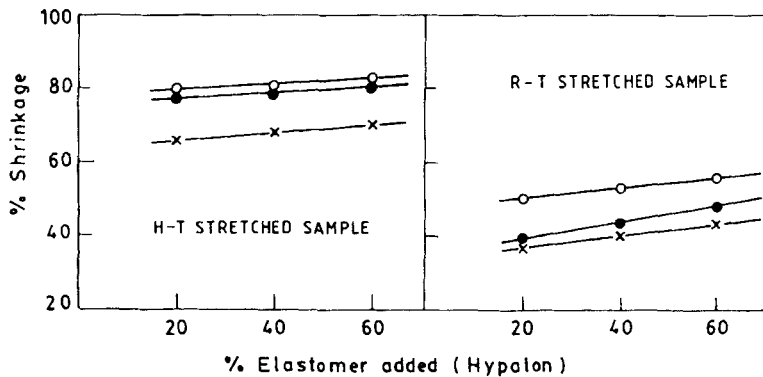


FIGURE 2 Variation of % Shrinkage with elastomer content.

both the cases. Again the extent of enhancement in shrinkability with elastomer content for H-T stretched samples is always higher than that for R-T stretched samples. This increase in the shrinkability 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 observed in R-T stretched samples.

B. Effect of Crystallinity on Shrinkability of the Blends

X-ray diffractogram of the various blends are shown in Figure (3) and Figure (4). For LDPE CSM (80:20) the crystallinity of the room temperature stretched samples is more than that of H-T stretched samples still the shrinkage of latter is higher. This may be due to the fact that elastomer phase can not get crosslinked as much as it does in case of H-T stretched samples. But when one increases the elastomer content it is found that H-T stretched samples always show higher crystallinity this is the case with LDPE CSM (40:60) blends. For LLDPE/CSM containing blends in both the cases it is found that for H-T stretched samples the crystallinity is higher than the R-T stretched samples causing higher shrinkability, but for (40:60) LLDPE/CSM blends shrinkability is much higher than that of (80:20) blends. The ability of a material to crystallize is determined by the regularity of its molecular structure. A regular structure is potentially capable of crystallizing whilst an irregular structure will tend to give amorphous polymer. In the case of polymer blends the structural irregularities can occur depending on the blend ratio and chain mobility of one phase by the presence of the other. The latter factor is the predominant one in the case of thermoplastic elastomer blends where the elastomeric phase is partially crosslinked. As observed from the Figure 3 and Figure 4 the crystallinity of LDPE CSM (80:20) is more for R-T stretched samples but this trend reverses as the elastomeric content is more (40:60), whereas for LLDPE/CSM (80:20 and 40:60) and HDPE/CSM (80:20 and 40:60) blends the H-T stretching gives rise to higher crystallinity than the R-T stretching. LLDPE and HDPE are more crystalline in nature so their chain mobility is restricted, and hence the effect of CSM phase is the predominant factor in determining the crystallinity both at high (150 °C) and R-T stretching. LDPE being branched and low crystallizing it's effect on stretching at room temperature is the predominant factor.

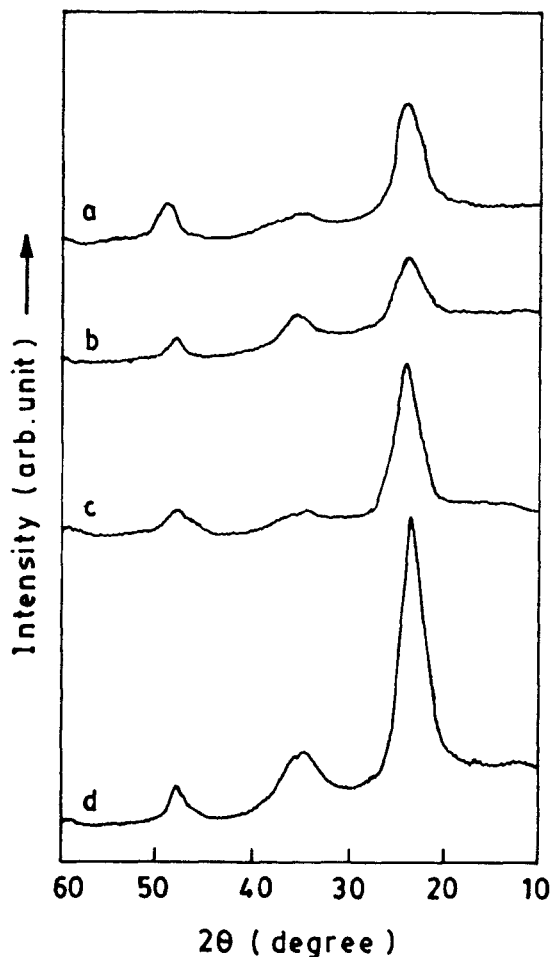


FIGURE 3 X-Ray Diffractograms. (a) LDPE/CSM (40/60) H-T stretched sample; (b) LDPE/CSM (40/60) R-T stretched sample; (c) LDPE/CSM (80/20) H-T stretched sample; (d) LDPE/CSM (80/20) R-T stretched sample.

C. IR Spectral Analysis

IR spectral analysis (Fig. 5) shows that hypalon (CSM) peaks occur at 1363 cm^{-1} for all the blends. For HDPE/CSM (40/60) blend the absorbance is maximum about 80% which means that SO_2Cl remains as such i.e. very less crosslinking has been introduced into CSM phase which results in much smaller shrinkage. In case of LDPE/CSM

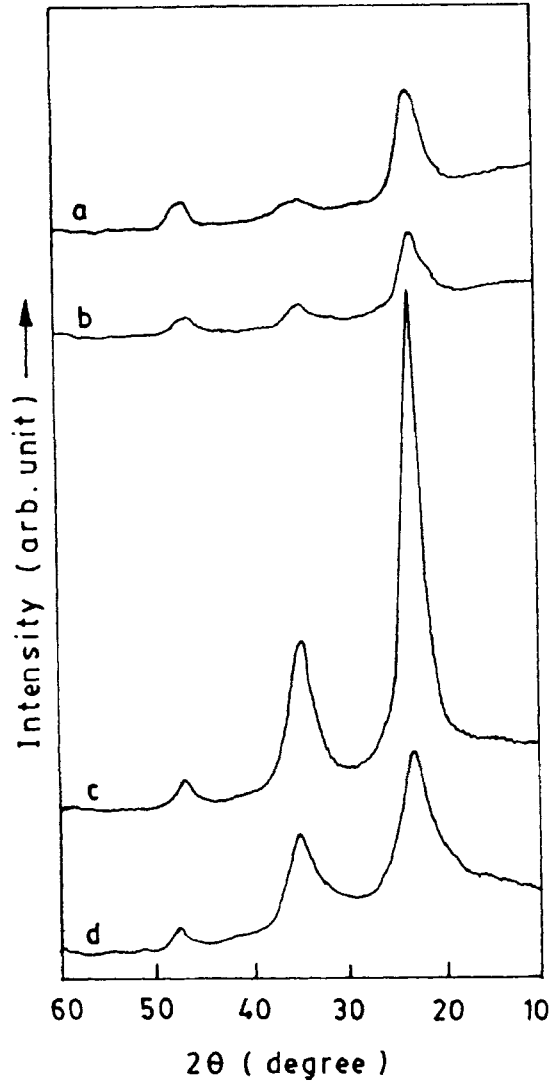


FIGURE 4 X-Ray Diffractograms. (a) LLDPE CSM (40/60) H-T stretched sample; (b) LLDPE CSM (40/60) R-T stretched sample; (c) LLDPE CSM (80/20) H-T stretched sample; (d) LLDPE CSM (80/20) R-T stretched sample.

(40/60) the absorbance is about 68% i.e. medium absorbance has occurred causing better amount of cross linking in elastomer phase which results in much better shrinkage than the HDPE/CSM blends.

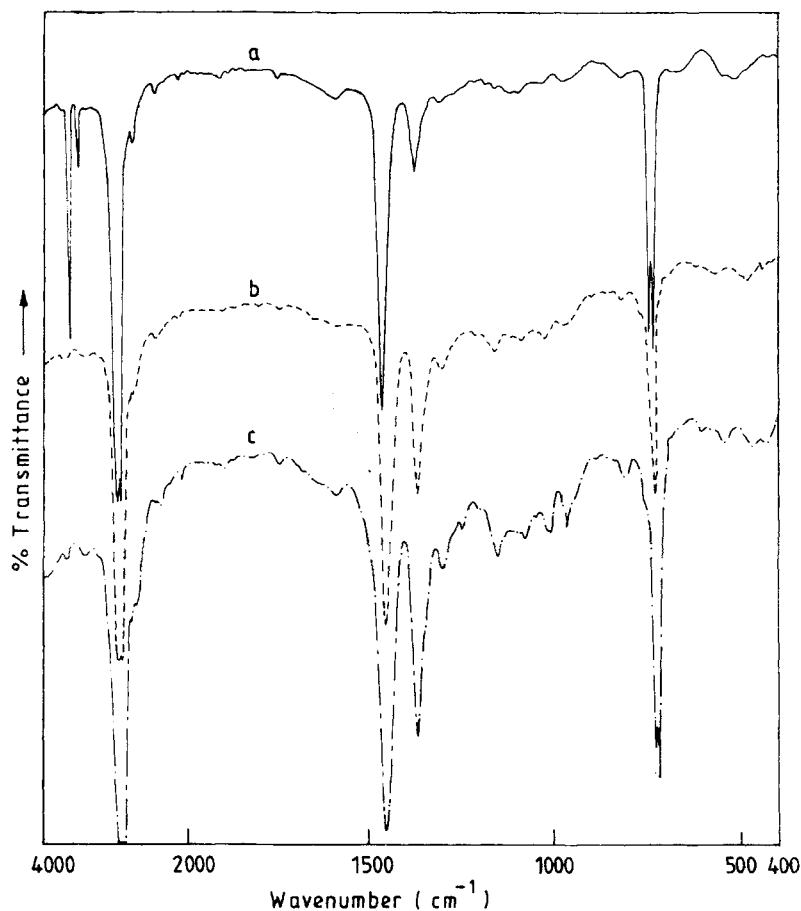


FIGURE 5 IR Spectrum. (a) LLDPE/CSM (40/60); (b) LDPE/CSM (40/60); (c) HDPE/CSM (40/60).

In case of LLDPE/CSM (40/60) blends the absorbance is only 32% resulting considerable amount of crosslinking into the elastomer phase which results in maximum shrinkability of the blends.

D. Effect of Crosslinking

It is found from the continuous cure characteristics through Monsanto Rheometer R-100 that Torque found in case of HDPE/CSM (40/60) is

lowest i.e. the crosslinking is minimum which is responsible for minimum shrinkability. The torque found in case of LDPE/CSM (40/60) is higher than that found in case of HDPE/CSM (40/60) so we can say that because of higher crosslinking in elastomer phase in case of LDPE/CSM blend the shrinkability is higher. From torque rheometry it is clearly reflected that the extent of crosslinking of elastomer in (LLDPE/CSM) blend is maximum which results in maximum shrinkability of the blends.

E. DSC Analysis

DSC analysis (Fig. 6) suggests that for high elastomer containing (60%) blends with LDPE, LLDPE, HDPE the stretched samples are having the lower glass transition temperature although they are having high crystallinity. This phenomena may be due to the effect of increased disorder, reduced molecular packing and reduction of inter-chain forces due to the presence of higher amount of elastomeric phase in the polyolefins. However at lower level of CSM the earlier trend reversed where increased crystallinity due to stretching increases the T_g . From the DTA curves (Fig. 7) it is observed that for a constant

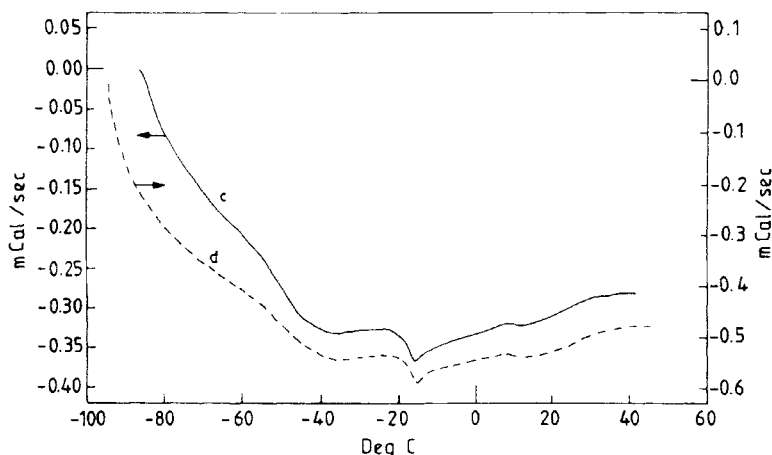


FIGURE 6 DSC Plots. (a) LLDPE CSM (40/60) H-T stretched sample; (b) LLDPE/CSM (40/60) unstretched original sample; (c) HDPE/CSM (40/60) H-T stretched sample; (d) HDPE CSM (40/60) unstretched sample.

polyolefin/elastomer ratio (40/60) the melting peak for high temperature stretched sample of LLDPE/CSM is 253°C, that of same stretched samples of LDPE/CSM and HDPE/CSM are 255°C and 267°C. This tendency of lowering melting temperature is more in case

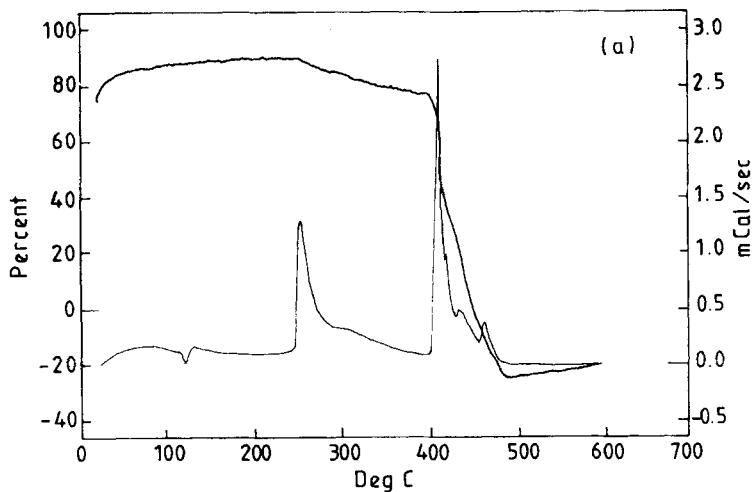


FIGURE 7 DTA and TGA Plots. (a) LLDPE/CSM (40/60) H-T stretched sample; (b) LDPE/CSM (40/60) H-T stretched sample; (c) HDPE/CSM (40/60) H-T stretched sample.

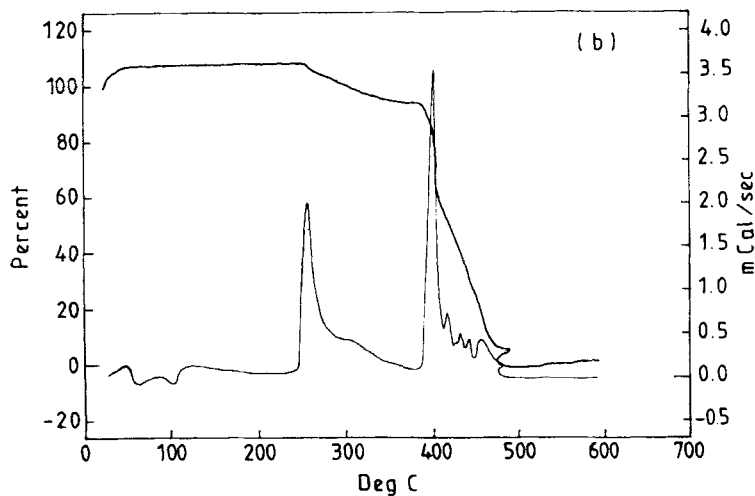


FIGURE 7b (Continued).

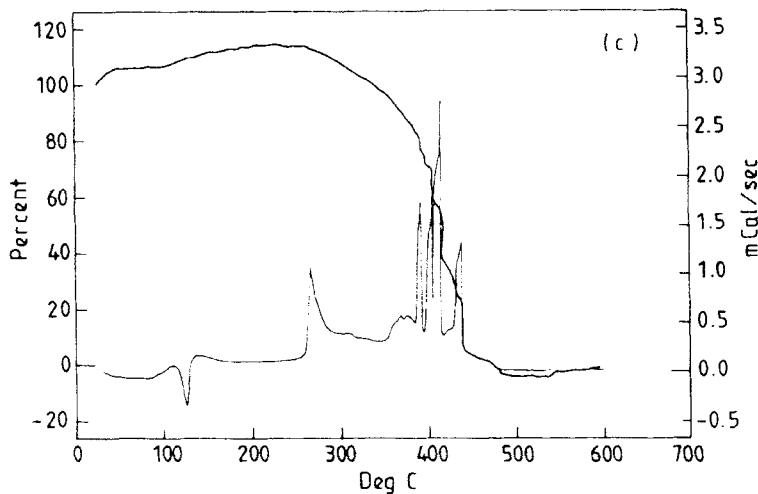


FIGURE 7c (Continued).

of LLDPE/CSM blend followed by LDPE/CSM and HDPE/CSM. Effect of crystallinity is reflected in the endothermic melting peaks, so one can say that LLDPE/CSM is more crystalline than the other two and where HDPE/CSM is the least. The melting peak of LDPE/CSM (40/60) unstretched original sample is 260°C which in case of high temperature stretched sample is 255°C i.e. unstretched sample is less crystalline than that of the H-T stretched sample. This is the trend observed in all the blend system studied.

F. 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 the Figures 8, 9, 10 and 11. In the case of unstretched samples (Fig. 8) the elastomeric phase remains in the globular form. When the samples are stretched the elastomeric phase are elongated. Under equivalent percentage of stretching the elastomeric phase in R-T stretched samples (Fig. 9) are elongated more than that of H-T stretched samples (Fig. 10). Amongst the polyolefins studied here the CSM phase in LLDPE and HDPE are stretched more or less to an



FIGURE 8 SEM Photograph (800X) of unstretched LLDPE/CSM (60/40) sample.



FIGURE 9 SEM Photograph (800X) of LLDPE/CSM (60/40) R-T stretched sample.



FIGURE 10 SEM Photograph (800X) of LLDPE/CSM (60/40) H-T stretched sample.

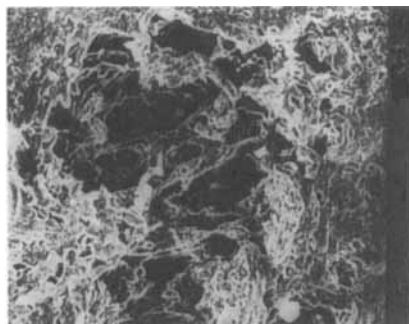


FIGURE 11 SEM Photograph (800X) of HDPE/CSM (60:40) blend.

equivalent extent. However the higher shrinkage in LLDPE may be due to the higher extent of stretching of the blends. The SEM photographs of the shrunk samples suggests the more spherulite structure of the elastomeric phase resulting higher amount of shrinkage, comparing the LLDPE and HDPE blend, in the HDPE/CSM blend (Fig. 11) the elastomeric domains are somewhat larger in size which may be because of lower extent of crosslinking of CSM phase, the reasons of which still remain to be explored.

FLAME RETARDANCY STUDY

For the flame retardancy study we have used the following flame retardants.

$\text{Sb}_2\text{O}_3 - 2.0 \text{ Phr}; \text{TBB} - 2.0 \text{ Phr}; \text{Sb}_2\text{O}_3/\text{TBB} - (2/2 \text{ Phr})$

$\text{Zn-metaborate}/\text{TBB} - (2/2 \text{ Phr}); \text{Chlorohor} - 2 \text{ Phr}.$

$\text{Chlorohor}/\text{Sb}_2\text{O}_3 - (2/2 \text{ Phr}).$

It has been observed that with the addition of flame retardants the shrinkability of the blends are hampered to some extent. For high elastomer containing (60%) blends the reduction in shrinkage occurs to a very small extent in case of H-T stretched samples but for the low elastomer containing blends the shrinkability value is sacrificed to larger

extent. Another observation is that stretchability of the H-T stretched blends decreases to some extent with the addition of flame retardants. This observation may be the result of lower compatibility of flame retardants in the polyolefin phase at its higher level, suggesting the efficiency of flame retardants in the higher level of elastomeric phase. The observed flame retardancy may be due to formation of SbCl_3 which generates Cl^\bullet to entrap the flame propagating radicals like H^\bullet , OH^\bullet , O^\bullet etc. and does not allow the flame to propagate [14]. Another reason may be because of higher size of antimony, chlorine liberation is feasible which liberates as Cl^- and reacts with the flame propagating species as mentioned earlier [15]. Another cause may be due to the fact that polymer structure after addition of flame retardants, are modified in such a way that char formation is facilitated thereby resisting the flame [16].

CONCLUSION

There is mutual correlation between the processing parameters and the shrinkability of the blends. H-T stretching is accompanied by higher heat shrinkage. H-T extensibility depends on the crystallinity of the polyolefine phase. Incompatible blends have an edge over compatible one so far as shrinkage is concerned. Addition of flame retardants reduces the extensibility and shrinkability of the polymer blends. Processability parameters which results extension of elastomeric phase to rod like structure is always accompanied by high shrinkage at the elevated 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, Chap. 21.
- [3] Whelan, A. and Lee, K. S. (1982). Developments in Rubber Technology Thermoplastic Rubbers, Applied Science, London.
- [4] Danesi, S. and Porter, R. S. (1978). *Polymer*, 19, 448.
- [5] Ramos De Valle, L. F. (1982). *Rubber Chem. Technol.*, 55, 1341.
- [6] Campbell, D. S., Elliot, D. J. and Wheelans, M. A. (1978). *NR Technol.*, 9, 21.
- [7] Coran, A. Y. and Patel, R. P. (1980). *Rubber Chem. Technol.*, 53, 141.
- [8] Coran, A. Y. and Patel, R. P. (1980). *Rubber Chem. Technol.*, 53, 781.

- [9] Min, K. and White, J. I. (1984). *Polym. Eng. Sci.*, **24**, 264.
- [10] Rizzo, G. and Sporado, G. (1984). *Polym. Eng. Sci.*, **24**, 264.
- [11] Utracki, L. A. (1984). *Proc. IX Int. Congress on Rheology Micro.*, p. 567.
- [12] 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.
- [13] 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.
- [14] Flame-Retardant Polymeric Materials, edited by Menachem Lewin, S. M. Atlas and Eli M. Pearce. Ch. 2. Y. P. Khanna and Eli M. Pearce.
- [15] Lindeman, R. F. (1969). *Ind. Eng. Chem.*, **61**, 70.
- [16] Pitts, J. J. Fire Flammability, J. (1972). **3**, 51.