Structure–Shrinkability Correlation in Polymer Blends of Ethylene Vinyl Acetate and Chlorosulfonated Polyethylene

S. RAY CHOWDHURY, C. K. DAS

Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India

Received 20 August 1999; accepted 3 January 2000

ABSTRACT: Heat shrinkability, which is a collective property of polymers, is being utilized in various applications, mainly in the field of encapsulation. Elastic memory is introduced into the system in the form of an elastomeric phase. Here the blends of ethylene vinyl acetate and chlorosulfonated rubber were studied with reference to their shrinkability. It was found that an increase in the elastomer content increased the shrinkage and an increase in cure time also increased the shrinkage. It was seen that high temperature (H-T) stretched samples showed higher shrinkage than the low (room) temperature (R-T) stretched one. Generally, the crystallinity of the H-T stretched sample was higher than that of the low temperature stretched sample, which was again higher than that of the original unstretched sample; but for the low elastomer content blend the crystallinity of the R-T stretched sample was found to be greater than the corresponding H-T stretched one. The H-T differential scanning calorimetry showed that an increase in the CSM content caused the stability toward oxygen to increase. The first decomposition temperatures were found to be higher and the second decomposition temperatures appeared to be lower for the H-T shrunk sample than the corresponding unstretched sample. The rate of degradation appeared to be enhanced initially, then after 50% decomposition the rate started going down compared to the usual unstretched sample. From SEM it was seen that the H-T stretched sample was more elongated than the R-T stretched one. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 707–715, 2000

Key words: ethylene vinyl acetate; chlorosulfonated polyethylene; shrinkability; curing; stretching; X-ray diffraction; morphology

INTRODUCTION

In attaining materials whose properties can be tailored to a specific application, a multicomponent polymer is of increasing importance. To achieve a desired set of characteristic properties, blending is the easiest and most popular means. Polymer blends have come to the fore as such a major endeavor. The blends by melt mixing of thermoplastic materials and elastomer have gained considerable attention in recent years. It is well known that nearly all blends are comprised of one polymer domain dispersed in the matrices of the other polymer.[1–5]

Molecular orientation results in increased stiffness, strength, and toughness, as well as resistance to liquid and gas permeation, crazing, and microcracks, in the direction or plane of the orientation. Orientation in effect provides a means of tailoring and improves the properties of plastics.[6] The heating and subsequent shrinking of these oriented materials can result in useful properties. It is used, for example, in heat shrinkable flame retardant polypropylene tube, cable, wrap, heat shrinkable furniture webbing, pipe filling, medical devices, and encapsulation.[6]

Correspondence to: Prof. C. K. Das.

Journal of Applied Polymer Science, Vol. 78, 707–715 (2000)
© 2000 John Wiley & Sons, Inc.

Stretching at high temperature (H-T) decreases dimensional stability, because the molecules are stretched into the statistically improbable conformation of a thermodynamically high energy level.[7] The decreased conformational entropy results in a positive free energy (i.e., far from thermodynamic equilibrium). The stretched state thus provides a driving force that causes the materials to snap back,[8] resulting in a macroscopic recovery in dimension to the original state.

In partially crystalline polymers, orientation can be obtained by two different methods: by hot drawing above the melting point (T_m) followed by quenching and by cold stretching [$T_g < T_{\text{def}}$ (deformation temperature) $< T_m$] between the glass-transition temperature (T_g) and the melting point. In the latter case we are dealing with deformation in the solid state, wherein changes in the shape and alignment of the crystallites lead to orientation.[9] The oriented stretched structure represents a frozen-in morphology that starts to change immediately and move to a more stable (lower energy and higher entropy) original randomly coiled conformation as soon as the mobility of its constituents parts, amorphous layer, and crystallite block is sufficiently increased by the increase in temperature.

The total linear deformation of the oriented sample may be described by three rheological components[10]:

1. an instantaneous elastic component, E_1, caused by bond deformation or bond stretching, which is completely recoverable when the stress is released (Hookian behavior);
2. a viscoelastic component, E_2, caused by uncoiling, which is frozen into the structure when cooled; and
3. a plastic (viscous) component, E_3, caused by molecules slipping over each other, which is nonrecoverable.

The viscoelastic component can serve as a measure of the degree of recoverable orientation, which is the thermoelastic shrinkage.[8]

In this present study elastic memory was introduced into the system in the form of an elastomeric phase. If the plastic phase is incorporated, stretching will be easier and at H-T; the plastic phase is in the molten state, so it can flow easily and enhance the extensibility of the elastomer and plastic blend. Very recently Patra and Das studied heat shrinkable polyolefin/elastomer blends.[3–5] The aim of the present investigation was to study the blends of ethylene vinyl acetate (EVA) and chlorosulfonated polyethylene rubber (CSM) with reference to their shrinkability, which we tried to correlate with various processing parameters that may change the microstructure of the blends.

Table I Compounding Formulation

	Blend Code				
	R_{20}	R_{30}	R_{50}	R_{70}	R_{80}
Ethylene vinyl acetate	80	70	50	30	20
Chlorosulfonated polyethylene	20	30	50	70	80

EXPERIMENTAL

Materials

The thermoplastic used was PILENE EVA-1802 supplied by Polyolefins Industries Limited (PIL), India. The vinyl acetate content was 18 wt %, the specific gravity was 0.937, and the melt flow index was 2.0 g/10 min.

The CSM was of the Hypalon- 40 variety and was supplied by Du Pont. The chlorine content was 35%, and the sulfur content was 1–1.5% by weight as —SO_2Cl. The compounding formulation is given in Table I.

Preparation of Blend

The blends of EVA/CSM were prepared by gradual replacement (shown in Table I) of the plastic (EVA) with the elastomer (CSM) in a Brabender Plasticorder for 10 min at 30 rpm. The mixing temperature was 100°C. The blends were cured in a mold at 150°C for 10, 20, 30, 40, 50, and 60 min at a 2800 psi pressure in an electrically heated press without adding curatives. Slabs of uniform thickness were prepared by compression molding. The specimens cut from the molded slab were used for shrinkage measurement and these were used for conducting the technical studies.

Lengthwise shrinkage was studied and measured under four different conditions: the above vulcanizates were stretched at ambient temperature, and the shrinkage was then measured at 150°C; the vulcanizates were stretched at 100,

150, and 180°C and shrinkages were measured at corresponding temperatures.

The shrinkage (%) was measured according to the following equation:

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

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

X-Ray Diffraction Analysis

The X-ray diffraction was studied using a PW 1840 X-ray diffractometer with a cobalt target (CoKα) at a scanning rate of 0.05° 2θ/s. The chart speed was 10 mm/2θ, the range was 5000 c/s, and the T.C. was 1 s. We used a slit of 0.2 mm while applying a 40-kV, 20-mA current. We noted the change of the crystallinity of the blends that was affected by processing (stretching followed by shrinking).

The area under the crystallinity and amorphicity were determined in arbitrary units. The degree of crystallinity X_c and the amorphous content X_a were measured using the relationships

$$X_c = I_c/[I_a + I_c]; \quad X_a = I_a/[I_a + I_c]$$

where I_c and I_a are the integrated intensities corresponding to the crystalline and amorphous halo, respectively. The peak half-width (β), crystallite size (P), interplaner distance (d), and interchain distance (r) were calculated as follows[11]:

$$\beta = \text{area of peak/height of peak} \times 1/5$$

$$P = 92.45/\beta \cos \theta$$

$$d = 1.792/2 \sin \theta$$

$$r = (5/8) \times (\lambda/\sin \theta).$$

Thermal Analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies were carried out using a Stanton Redcroft STA-625 thermal analyzer in a temperature range of 25–600°C at a heating rate 10°C/min in air.

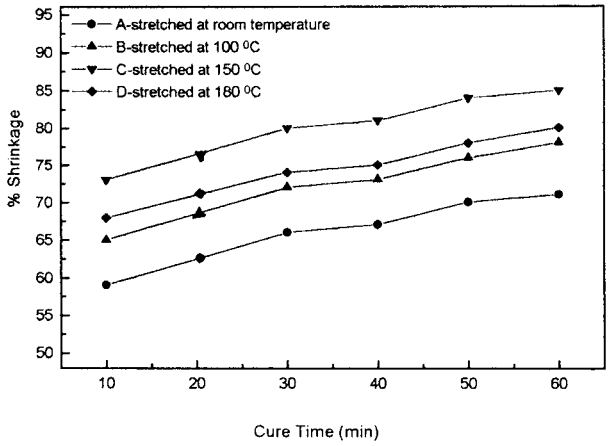

Figure 1 The variation of shrinkage (%) with cure time at a constant elastomer content.

Scanning Electron Microscopy (SEM) Study

Pellets of the blends were etched in toluene for 48 h at room temperature for extracting out the elastomer (CSM) phase. The phase morphology of the etched surface of the blends was studied in a scanning electron microscope (cam scan series II model) using an auto sputter coater with gold at a 0° tilt angle.

RESULTS AND DISCUSSION

Effect of Cure Time and Elastomer Content on Shrinkage of Blends

The variation of shrinkage with cure time at a constant elastomer content at four different temperatures (ambient, 100, 150 and 180°C) is shown in Figure 1. The figure shows that an increase in cure time increases the shrinkability, which is reported in many cases.[12,13] An increase in cure time increases the amount of self-crosslinking (no curative is added here). With an increase in CSM-40 the active functional group —SO_2Cl is increased in number, so the chance of interchain crosslinking is increased by means of a chemical reaction of the —SO_2Cl group of CSM-40 with the acetate group of EVA (18% VA). Actually the polymer chains in the stretched condition exit in four states and they could be classified into crystalline and amorphous states of coiled and extended chains.[14,15] Only the extended state could provide a driving force for contraction of the stretched sample.[16] A driving retraction force is provided by comparatively highly oriented amorphous mate-

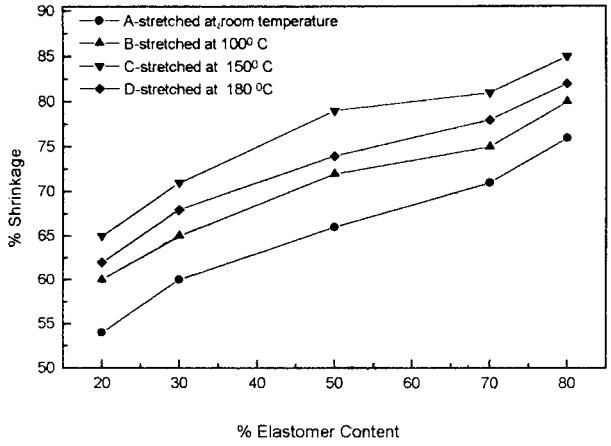

Figure 2 The variation of shrinkage (%) with elastomer content at a constant cure time.

rials. The amount of shrinkage depends on the concentration and orientation of the oriented amorphous materials[15] and the memory points that depend upon crosslinks. Because a longer cure time produces more crosslinks, there are more memory points; hence, an increase in cure time increases the recovery (i.e., higher shrinkage will be obtained). Again Figure 2 shows that an increase in elastomer content increases the shrinkage. Recoiling is a collective process of retraction provided by comparatively highly oriented amorphous materials, as well as memory points. The higher the elastomer content, the higher the amorphous phase; so, during stretching the concentration and orientation of the oriented amorphous materials are heightened; hence, there will be more of a tendency of the extended state to revert to a randomly coiled conformation, thus increasing shrinkage.

Effect of Temperature on Shrinkage

Figures 1 and 2 show that H-T stretched samples show higher shrinkage than room temperature (R-T) stretched samples.

According to Capaccio and Ward,[17] two factors are involved in the shrinkage of the R-T stretched (below T_m) sample: one is the contraction of the amorphous chain and the other is the reorganization of the crystalline phase in which deformation occurred in crystals and the lamellae of crystals could slip and orient. If the crystal deformation is less than the contribution of the second factor will contribute less to the recovery and the first factor will only control the shrinkage. Moreover, in the R-T stretched sample the tendency of the amorphous chain to contract was found to be less compared to the H-T stretched sample; as for the latter, the concentration and orientation of the oriented materials is enhanced by the presence of the molten plastic phase with more freedom to flow. Shrinkage of the blend stretched at 150°C has an edge over stretching at 100°C. At 150°C the amount of viscoelastic deformation is higher than that at 100°C (the T_m of EVA is 90°C). So the recovery due to frozen-in internal stress is found to be greater[9] at 150°C. On the other hand, the shrinkage at 180°C is appreciably lower than that at 150°C. At a higher temperature (180°C) a substantial fraction of the initial elastic deformation is transformed into plastic deformation.[14] At 180°C the desired alignment component of the deformation, E_2, will be a smaller property of the total deformation; this is mainly because of the viscous flow, E_3, which increases as the temperature is increased, resulting in low recovery at 180°C. Tie molecules may also play a role here. During stretching, tie molecules that contact crystal blocks on different fibrils (from a microfibrillar model[15]) are enormously extended. Those tie molecules are partly responsible for shrinkage. It should be remembered that the effect of pulling some chain sections partially out of the crystal block in which the tie molecules are anchored during annealing increases the contour length. So, as a result, the ratio between the contour length and the end to end distance of the tie molecule is increased, allowing relaxation of the initially stretched tie molecules.[15,18] That may be the cause here for dropping of the retractive force; thus, less shrinkage is obtained at 180°C.

Crystallinity and Shrinkage of Blends

X-ray diffractograms of various blends are shown in Figure 3 and the crystallinity (%) is shown in Table II. With the gradual incorporation of rubber (30 and 70 parts) the crystallinity is 43 and 30%, respectively, for unstretched samples. Crystallinity is affected by blend composition and crystallization conditions such as temperature, pressure, orientation, molecular weight, and diluent.[19] The degree of crystallinity is almost independent of the chemical composition of the amorphous phase. The crystallization of the plastic (EVA) segments is controlled by the segmental diffusion rate of the other polymer chains.[19] During annealing of the blends, recrystallization of the blends occurs after molding, depending on the

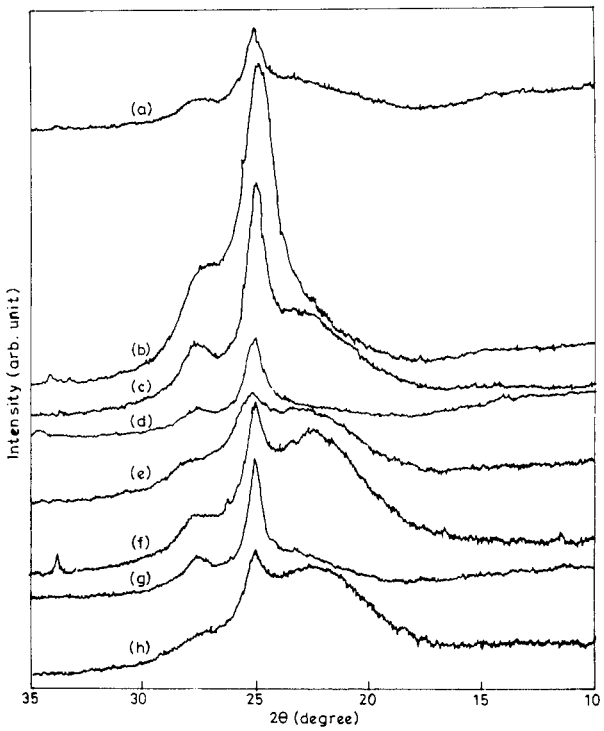

Figure 3 X-ray diffractograms of the R_{30} original unstretched sample (curve a), R_{30} R-T stretched sample (curve b), R_{30} H-T (150°C) stretched sample (curve c), R_{30} H-T (150°C) shrunk sample (curve d), R_{70} original unstretched sample (curve e), R_{70} R-T stretched sample (curve e), R_{70} R-T stretched sample (curve f), R_{70} H-T (150°C) stretched sample (curve g), and R_{70} H-T (150°C) shrunk sample (curve h).

above-mentioned factors. For the R_{30} and R_{70} blends the crystallinity of the R-T stretched sample was greater than that of the unstretched original sample. Again the crystallinity of the H-T stretched (150°C) sample was greater than the R-T stretched one in the R_{70}; but for R_{30} the observation was the reverse: the R-T stretched sample showed the highest crystallinity, even more than the H-T stretched one. The crystallinity of the H-T shrunk sample was greater than the original sample but less than the R-T and H-T stretched samples. For R-T stretching the crystallinity increases due to the orientation of the crystallites along the stretching direction. In addition, some new crystal domains were formed (strain-induced crystallization). But for the H-T stretched sample recrystallization occurred during annealing. Stretching of an unoriented polymer blend leads to orientation of macromolecules along the stretching direction and simultaneously leads to an increase in the effectiveness of intermolecular interactions that are due to increased alignment correlation of the neighboring molecular subunits.[16] However, at H-T most of the original constraints, which may prevent crystallization during drawing, are removed during heating by the increase of the contour length. This permits some chains in the heated sample to move and to align some sections as needed for the crystallization to a much larger extent than at the end of the drawing when the contour length is not substantially larger than the end to end distance.[18] Hence, these section can crystallize. Thus, because of less freedom, there will be less chain folding of the polymer chain segments in the R-T stretched sample. Again, in the H-T stretched sample the sample is in the molten state; so, because of thermal fluctuation, some new nuclei of ordered materials may form.[20] According to the molecular model of Jordon et al.,[21] the region of the semicrystalline materials becomes unstable and melts under a high local value of stored elastic energy at the drawing temperature, so rapid extension and subsequent recrystallization occurs. In the R_{30} the amount of plastic is high, so the probability of strain-induced crystallization is higher. For the H-T shrunk sample the subsequent crystallization occurs because of regular chain folding, which need not involve any chain length change. This occurs only if time is available, the temperature condition is right,[22] and the blend ratio is suitable. Here during shrinking at 150°C some crystal networks may have melted; but after shrinking again recrystallization occurred, but not up to the extent as in the R-T and H-T stretched samples.

Crystallite size while stretching was reduced and the percent crystallinity increased, suggesting formation of new crystal domains. The mechanical orientation of the molecules assists the production of nuclei by bringing molecular segments into favorable juxtaposition, leading to a reduction in the configurational entropy change needed for nucleus formation.[23] Nucleation was favored for the R-T stretched sample which was observed from the values of the percent crystallinity and crystallite size. But in the H-T stretched sample, crystal growth was favored compared to the R-T stretched one. This was probably due to the attainment of favorable conditions (composition and temperature), which helped self-diffusion of the folded molecules along its own backbone during annealing at high temperature.[24] Note that for both the above cases the crystallite size for the H-T shrunk sample was

Table II Parameters Evaluated from X-Ray Diffraction Studies

Sample Code	Peak Angle (θ°) Low	Peak Angle (θ°) High	Crystallinity (%)	Crystallite Size (Å) Low	Crystallite Size (Å) High	Interplaner Distance (Å) Low	Interplaner Distance (Å) High	Interchain Distance (Å)
R_{30}								
Unusual unstretched	12.60	13.80	43	78.94	58.88	4.10	3.75	5.55
R-T stretched	12.25	13.50	76	47.30	29.71	4.22	3.83	5.10
H-T stretched (150°C)	12.50	13.75	52	72.80	49.98	4.16	3.80	5.05
H-T shrunk (150°C)	12.50	13.85	48	72.84	47.59	4.15	3.75	5.64
R_{70}								
Usual unstretched	12.55	13.75	30	78.95	53.59	4.14	3.79	5.77
R-T stretched	12.50	13.70	39	39.46	37.58	4.14	3.80	5.64
H-T stretched (150°C)	12.55	13.50	45	67.65	49.42	4.15	3.83	5.59
H-T shrunk (150°C)	12.50	13.50	37	43.04	39.66	4.13	3.78	5.67

less than that of the unstretched samples. Depending on the time and temperature, chain folding starts after the recovery.[22] So crystal growth is not favored to such extent and the crystallites become smaller in size compared to the unstretched samples. Here it should be highlighted that the unstretched original samples had the biggest crystallites. This indicated that the molding process followed by annealing favors the crystal growth process as compared to R-T stretching, H-T stretching, and H-T shrinking.

If the interplaner distance (d) is focused, when the quantity of CSM added is increased the d value is increased, which may quite reasonably be attributed to some interaction between the chains of the two components, which results in the increase of the interplanar spacing of the planes over which the molecules of each are arranged.[25] Again, we saw that with stretching (R-T and H-T) the d values were increased, which again corresponded to the percent crystallinity in the EVA-rich blend (R_{30}). Thus, it can be safely said that during stretching, although crystallinity is increased, some interaction due to orientation occurs. However, this observation was not so prominent in the case of elastomer-rich blends. From Table II we can see that the interchain distance (r) of the EVA phase is appreciably increased on the addition of CSM. This increase may possibly be due to the migration of some CSM molecule into the interchain space of the EVA polymer.[25] Again the decrease in r values with stretching may quite reasonably be attributed to the orientation (i.e., close packing of the polymer chains).

Recovery properties of stretched samples strongly depend on the crystalline structure.[15] In semicrystalline polymers shrinkage is mainly related to the changes in the amorphous phase.[9,26,27] The oriented chain in the amorphous phase of the stretched sample (cooled to R-T) was internally stressed and restricted to relaxation by crystallization.[16] Upon heating to the T_m or above, the stretched sample without external constraints relaxed to an isotropic state, resulting in a macroscopic recovery in the dimension of the original state.[17,28] As with the increase in crystallization, the internal stress is increased and the occurrence of disorientation is high. So the H-T stretched sample with higher crystallinity usually shows higher shrinkage than the R-T stretched one, but in the R_{30} the shrinkage obtained for the H-T and R-T stretched samples

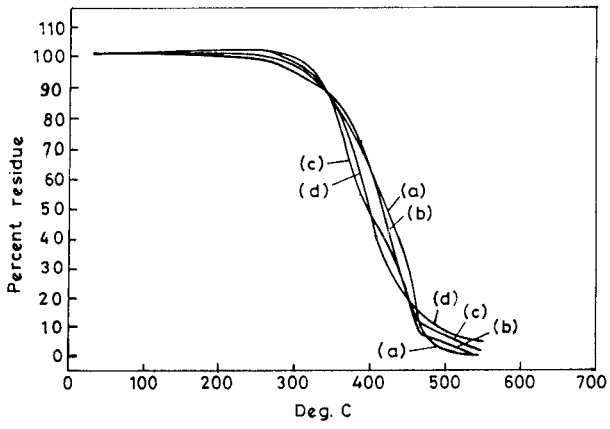

Figure 4 TGA plots of the R_{30} original unstretched sample (curve a), R_{70} original unstretched sample (curve b), R_{30} H-T shrunk sample (curve c), and R_{70} H-T shrunk sample (curve d).

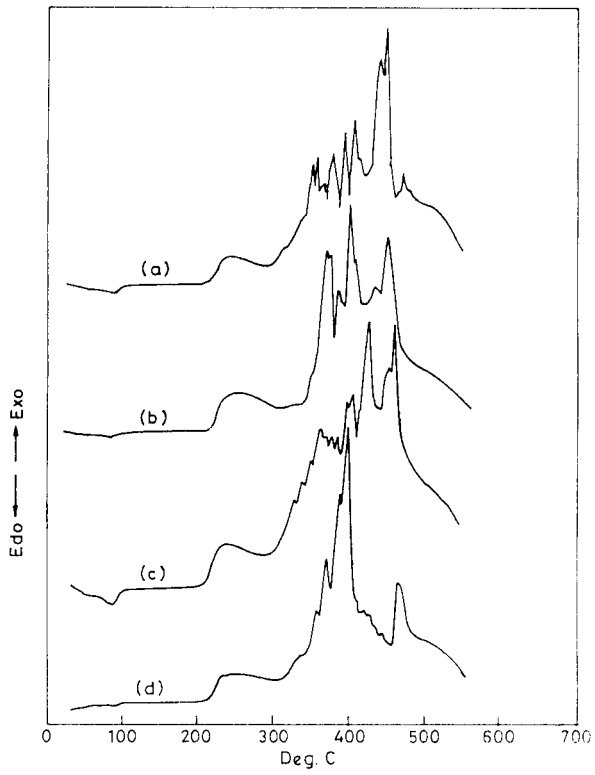

Figure 5 DSC plots of the R_{30} original unstretched sample (curve a), R_{70} original unstretched sample (curve b), R_{30} H-T shrunk sample (curve c), and R_{70} H-T shrunk sample (curve d).

may be confusing apparently. Here, because of the advantage of the easy flow of the plastic phase, the orientation may be associated with a higher concentration and a higher degree of extension, thus producing higher shrinkage in the H-T stretched sample, although with less crystallinity compared to the corresponding R-T stretched one. The R_{30} with higher crystallinity should have showed higher shrinkage than R_{70} at both temperatures, but a higher amorphous elastomeric phase, which was probably due to a higher concentration and more extension of orientation, provided higher shrinkage.

Thermal Analysis

TGA and DSC (30–600°C) plots are displayed in Figures 4 and 5, respectively, and the results of TGA and DSC are summarized in Table III. It is obvious that the melting peak for the R_{30} blend occurs at 90°C, which is shifts slightly to the lower side in the R_{70} (86°C). With further H-T processing (H-T shrinking) the T_m remained unchanged. It is clear from the TGA that the blends underwent two steps of degradation. In the first the onset decomposition temperature (T_1) shifted to the higher side with the increase in elastomer content. The trend of change of the second onset decomposition temperature (T_2) was also the same with the increase in elastomer content. So it is evident that the elastomer-rich blend was more stable thermally compared to the plastic-rich blend. Because the interchain crosslinking through the chemical reaction was increased with the increase in the CSM with the active SO_2Cl, in the elastomer-rich blend the stability was expected to be higher. For the H-T shrunk samples the T_1 was higher and T_2 was lower than that of the corresponding original unstretched samples. During shrinking the orientation is lost, so intermolecular interaction is also lost to some extent, so there is more of a chance of oxygen attack. Thus, the onset temperature of oxidative degradation is lower.

The 50% decomposition temperature (T_{50}) is decreased appreciably as the elastomer content is increased. On the other hand, the T_{50} values of the H-T shrunk samples revealed that those degrade rapidly compared to the unstretched original sample. When the T_{90} values were considered, we found that an increase in the elastomer content increased the T_{90} appreciably, confirming

Table III TGA and DSC Results

Samples	T_m (°C)	T_1 (°C)	T_2 (°C)	T_{50} (°C)	T_{90} (°C)	H_1 (mcal/mg)	H_2 (mcal/mg)
R_{30}	90	240	313	417	453	50	981
R_{70}	86	250	350	410	469	99	671
R'_{30}	90	249	302	400	482	42	763
R'_{70}	86	257	342	400	533	75	521

R, the original unstretched sample; R′, the shrunk sample.

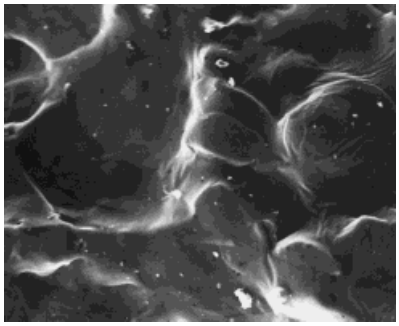

Figure 6 An SEM photograph (original magnification $\times$1000) of the R_{70} original unstretched sample.

that the rate of decomposition is slower in the presence of oxygen (second step degradation is oxidative degradation). The heat of first degradation (H_1) was higher for the elastomer-rich blend, but the heat of oxidative degradation (H_2) appeared to be lower. Oxidation of the polymer occurs in the amorphous region, because the crystallites are impermeable to oxygen.[29] Again it is evident that the rate of the chemical initiating step is dominated by the physical accessibility of the polymer structure.[30] In this case the elastomer-rich blend comprised a larger amorphous phase and more interchain crosslinks. If we concentrate on the H-T shrunk sample, the H_2 is found to be lower than the unstretched original sample. Shrinking occurs because of the recoiling of polymer chains, so the free zone in the shrunk sample is increased. Thus, the probable area to be attacked by oxygen becomes naturally lower, and, consequently, H_2 goes down in the H-T shrunk sample.

Study of Phase Morphology

The phase morphology was studied by SEM after differential solvent extraction of the CSM by toluene (Figures 6–9). Observe that the elastomeric phase remains in a globular form in the original unstretched sample (Fig. 6). When the specimen is stretched, the elastomer phase becomes elongated. Under an equivalent percentage of stretching the elastomer phase in the H-T stretched sample (Fig. 8) is elongated more than those observed in the R-T stretched samples (Fig. 7). So the H-T stretched sample has more of a tendency to snap back to its original state compared to the R-T stretched one. Thus, the shrinkage in the H-T stretched sample is greater. Again, the SEM photograph of the shrunk sample (Fig. 9) suggests a more spherulitic structure of the elastomer phase, resulting in a retraction.

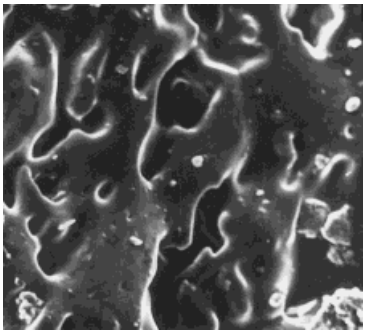

Figure 8 An SEM photograph (original magnification $\times$1000) of the R_{70} H-T stretched sample.

CONCLUSIONS

A mutual correlation between the processing parameters and shrinkage of the blend was found. The shrinkage property of a blend depends on the ratio of the constituents, and elastomer-rich blends show higher shrinkage. Cure time plays an important role: the greater the cure time, the

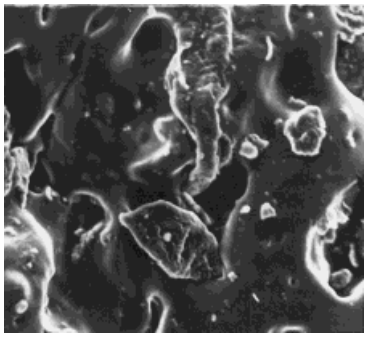

Figure 7 An SEM photograph (original magnification $\times$1000) of the R_{70} R-T stretched sample.

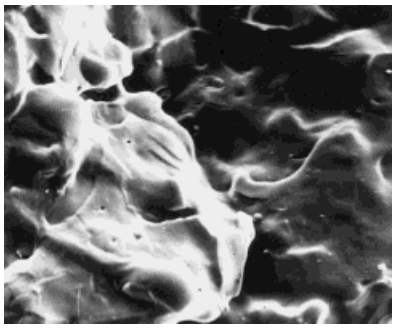

Figure 9 An SEM photograph (original magnification $\times$1000) of the R_{70} H-T shrunk sample.

higher shrinkage. With an increase in temperature the shrinkage goes on increasing but a transition occurs at around 150°C, beyond which the shrinkage decreases. Generally, the H-T stretched sample is oriented more than the R-T stretched one. The shrinkage is associated with crystallinity, which is changed on processing. The processing affects the stability of the sample. The first and second degradation temperatures in the elastomer-rich blend are higher compared to the plastic-rich blend. The first degradation temperature for the H-T shrunk sample is higher than the original unstretched one, but the second degradation temperature is slightly lower. An increase in the causes the elastomer T_{50} to go down and the T_{90} to go up. The heat of oxidative degradation (H_2) is less for the elastomer-rich blend compared to the plastic-rich blend. But the H-T shrunk sample degree of oxidative degradation is less compared to the corresponding original unstretched sample.

REFERENCES

1. Ramos-De Valle, L. F. Rubber Chem Technol 1982, 55, 1341.
2. Danesi, S.; Porter, R. S. Polymer 1978, 19, 448.
3. Patra, P. K.; Das, C. K. Int J Polym Mater 1997, 35, 103.
4. Patra, P. K.; Das, C. K. J Polym Eng 1997, 17, 231.
5. Patra, P. K.; Das, C. K. J Appl Polym Sci 1998, 68, 597.
6. Rosato, D. V. Rosato's Plastic Encyclopedia and Dictionary; Hanser: Barcelona, 1993; p 508.
7. Rosato, D. V. Rosato's Plastic Encyclopedia and Dictionary; Hanser: Barcelona, 1993; p 511.
8. Ohma, J.; Monson, L.; Sperling, H. Polym Blends Compos 1981, 5, 69.
9. Ram, A.; Tadmor, Z.; Schwartz, M. Int J Polym Mater 1977, 6, 57.
10. Karam, J.; Williams, J. L. Mod Plast 1953, 30, 119.
11. Alexander, L. E. X-Ray Diffraction Methods in Polymer Science; Wiley–Interscience: New York, 1969.
12. Patra, P. K.; Das, C. K. J Reinforced Plast Compos 1997, 16, 1111.
13. Patra, P. K.; Das, C. K. J Appl Polym Sci 1997, 39, 239.
14. Dechndia, F.; Russo, R.; Vittoria, V. J Polym Sci Polym Phys 1982, 20, 1175.
15. Wang, M.; Zhang, L. J Polym Sci Polym Phys 1999, 37, 101.
16. Pakula, T.; Trznadel, M. Polymer 1985, 26, 1011.
17. Capaccio, G.; Ward, I. M. Colloid Polym Sci 1982, 46, 260.
18. Pietralla, M.; Grossmann, H. P. Polym Sci Polym Phys 1982, 20, 1193.
19. Martuscelli, E.; Riva, F.; Sellitti, C.; Silvestre, C. Polymer 1985, 26, 270.
20. Turnbull, D.; Fisher, J. C. J Chem Phys 1949, 17, 71.
21. Jordon, M. E.; Juska, T. D.; Harrison, I. R. Polym Eng Sci 1986, 26, 690.
22. Wilson, M. P. W. Polymer 1974, 15, 277.
23. Andrews, E. H. Proc R Soc 1964, A277, 562.
24. Reneker, D. H. J Polym Sci Polym Phys 1967, 59, 539.
25. Datta, A. K.; Bhattacharya, S.; Das, C. K. J Polym Sci Polym Chem 1987, 25, 1177.
26. Nobbs, J. H.; Bower, D. I.; Ward, I. M. Polymer 1976, 17, 25.
27. Bower, D. I.; Korybut-Daszkiewict, K. K. P.; Ward, I. M. J Appl Polym Sci 1983, 28, 1195.
28. Sarvaranta, L. J Appl Polym Sci 1995, 56, 1085.
29. Billingham, N. C. Atmospheric Oxidation and Antioxidants, 2nd ed.; Elsevier: New York, 1993; Vol. II, Chap. 4.
30. Scott, G.; Gilead, D. Degradable Polymers: Chapman & Hall: New York, 1995.