Studies on Blends of Ethylene Vinyl Acetate and Polyacrylic Rubber with Reference to Their Shrinkability

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ABSTRACT: Preferential crosslinking was introduced in the rubber phase of a blend of ethylene vinyl acetate (EVA) and polyacrylic rubber (AR-801). The heat shrinkability of the polymer blends was measured at room temperature (RT) and at a high temperature (HT) of 150°C. Various parameters were tried for a correlation with shrinkability. Shrinkability goes up with the increase in rubber content and is increased with increasing cure time in blends of a fixed ratio. The crystallinity of an HT (at 150°C) stretched sample was higher than that of a RT stretched sample, which was higher than that of the shrunk and original sample. The continuous cure characteristics, showed that the torque was increased with the rubber content. High temperature DSC demonstrated that the increase in AR-801 content decreased the stability and further HT processing increased the stability. SEM showed that the rubber phase was more elongated in the HT stretched sample compared to the RT stretched sample. In the shrunk sample the rubber phase was more globular. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2088–2095, 2000

Key words: ethylene vinyl acetate; polyacrylic rubber; shrinkability; curing; stretching; morphology; vulcanizates

INTRODUCTION

The blends prepared by melt mixing of thermoplastic materials and rubber have met industrial needs in recent years.[1–5] The heat shrinkability of the polymer, which depends on the elastic memory, has been applied in mainly encapsulation and cable insulation. Elastic memory can be introduced into the system in the form of a rubbery phase in a thermoplastic material. Matsuki et al.[6] studied the heat shrinkability of multilayered crosslinked stretched films with good tear strength. Sunikawa et al.[7] investigated the heat shrinkability of a tube made by blending polyethylene with crosslinkable silicon grafted polypropylene. Recently, Patra and Das[1,2] studied the shrinkability of blends of polyolefins with different rubbers. The use of ethylene vinyl acetate (EVA) in blends is most important from the technological point of view, mainly because of its good environmental stress crack resistance. On the other hand, polyacrylic rubber (AR-801, TOA AC-RON) is inherently resistant to temperature (−15 to +180°C) and oil at elevated temperature and oxidation, ozone, and sunlight (UV) discoloration.

The aim of the present investigation was to study the blends of EVA and AR-801 with reference to their shrinkability by allowing only the rubber phase to be cured. We tried to correlate shrinkability with various processing parameters, which may change the microstructure of the blends.

EXPERIMENTAL

Materials

The thermoplastic used was Pilene EVA-1802 supplied by Polyolefins Industries Limited (PIL),

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Table I Compounding Formulation

Blends	R_{20}	R_{40}	R_{50}	R_{60}	R_{80}
EVA	80	60	50	40	20
AR-801	20	40	50	60	80

India. The VA content was 18 wt %, the specific gravity was 0.937, and the melt flow index was 2.0 g/10 min. The AR-801 TOA ACRON poly-(acrylic esters), which have active halogen cure sites for fast cure, was supplied by TOHPE Corporation Limited, Japan. The Mooney viscosity was 56 at 100°C. The curative systems are given in Table I.

Preparation of Blends

Five sets of blends were prepared by melt mixing at 90–100°C in a Brabender Plasticorder for 10 min at 30 rpm. The EVA was first allowed to melt for 2 min, then rubber was added followed by curatives. The mixes so obtained were sheeted out under hot conditions through an open mill set at a 2-mm nip gap. The ratios of plastic and rubber in the blends are given in Table I.

The curative system used was Pb_3O_4, 2 phr (parts/100 g); cyclohexyl benzthiazyl sulfenamide, 2 phr; and sulfur, 1 phr (phr based on rubber).

The sheets were compression molded at 150°C for 10, 15, 25, and 30 min at a pressure of 19.5 MPa in an electrically heated press. The mold was cooled slowly under compression. This operation crosslinked the rubber phase and kept the plastic phase intact as because the EVA was cured only by organic peroxides. The measured shrinkage was in the lengthwise direction and under two different conditions. The vulcanizates were stretched at ambient temperature, the vulcanizates were stretched at 150°C, and the shrinkage was measured at 150°C.

The formula given below was used to measure the shrinkability:

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

where S_h is the percentage shrinkage, L_{str} is the length of the sample after stretching, and L_s is the length of the sample after it is shrunk. The vulcanizates were kept at 150°C for 15 min before stretching and before measuring the shrinkabil-ity. The measurement of length was done at ambient temperature for all cases.

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, a chart of 10 mm/2θ, a range of 5000 count/s, a Time Const. of 1 s, and a slit of 0.2 mm while applying a 40-kV, 20-mA current to find the crystallinity of the blends as affected by the extent of stretching.

The areas under the crystallinity and amorphous conent in Xrd plots were determined in arbitrary units; the degree of crystallinity X_c and the amorphous conent 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 crystalline and amorphous halos, respectively.[8]

Cure Characteristics

The cure characteristics of the blends were studied on a Monsanto R-100 rheometer at 150°C for 60 min.

DSC

The DSC studies were carried out using a Stanton Redcroft STA-625 thermal analyzer in a temperature range from −60 to 45°C at a heating rate of 10°C/min in the presence of a nitrogen atmosphere to determine the glass-transition temperature (T_g) values. The TGA/DSC studies were carried out using the same instrument in the temperature range of 25–600°C at a heating rate of 10°C/min in air to procure the degradation pattern.

SEM Study

Pellets of the blends were etched in toluene for 48 h at room temperature for extracting the AR-801 phase. The phase morphology of the etched surface of the blends was studied in a scanning electron microscope (Cam Scan Series II) after sputter coating the surface with gold at a 0° tilt angle.

RESULTS AND DISCUSSION

Effect of Cure Time and Rubber Content on Shrinkability

The variations of the shrinkability of the blends with cure time at a constant rubber content for
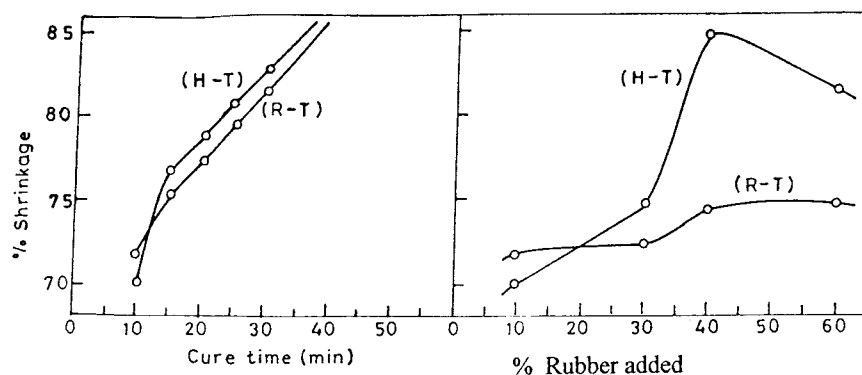
Figure 1   The variation of the percent shrinkage with cure time (left) and the variation of the percent shrinkage with the percent rubber content (right).

the high temperature (HT) and room temperature (RT) stretched samples are shown in Figure 1 (left). It is clear from the figure that the shrinkability of the blends is increased with cure time for all blends. The HT stretching shows higher shrinkability followed by the RT stretched samples. In this case only the rubbery phase is crosslinked. The greater the cure time the greater the amount of crosslinking so the greater the elastic memory, which helps the recovery of the stretched sample. Thus, an increase in the cure time increases the elastic memory and the subsequent recovery, so the shrinkability is greater. The variation of shrinkability with rubber content at constant cure time is shown in Figure 1 (right). Observed from the figure that at a constant cure time the increase in rubber content increases the shrinkage of the blends for both RT and HT stretched samples. Shrinkage of the blend is contributed by the ability to recover the amorphous oriented materials. When there is more rubber phase the elastic memory is enhanced (because the rubber phase is only crosslinked), thus increasing the shrinkability. With a change of the cure time and elastomer content, HT stretched samples showed higher shrinkage than RT stretched samples. In an HT stretched sample the plastic phase is in the molten state, so it can flow easily and naturally the stretchability will be higher so the shrinkability will be greater. However, a 10-min cure time at constant rubber content and 10% rubber loading at a fixed cure time caused the exception as is seen in Figure 1. In these cases the RT stretched samples showed higher shrinkability than the HT stretched samples. Here the amount of crosslinking was lower for both cases because the cure time was lower and there was less rubber, so in this

case the role of elastic memory for recovery of the sample was not important. The amount of plastic was higher, so during the RT stretching (T_m) more deformation occurred in crystals of plastic and the lamellae of the crystals could slip and orient unlike HT stretching because the plastic phase was in the molten stage. According to Capaccio and Ward,[9] rapid reorganization of the crystallized phase may have caused a higher amount of shrinkage in the RT stretched one.

Effect of Crystallinity on Shrinkability of Blends

The X-ray diffractograms of various blends are shown in Figures 2 and 3 and the crystallinity is shown in Table II. We found that for EVA/AR-801 (80/20) there was more crystallinity of the HT stretched sample than the RT stretched sample, which is followed by the HT shrunk sample. The HT shrunk sample had even greater crystallinity than the original unstretched sample. The higher amount of shrinkability for the HT stretched sample with higher crystallinity may be due to the contribution of the crosslinked rubber phase. For the blend systems studied the crystallinity mainly depends on the EVA phase, while stretching the sample at HT caused the plastic phase to flow more than that at RT stretching, making the blend more crystalline in the former case. The ability of a material to crystallize is determined by the regularity of its molecular structure.[10] A regular structure is potentially capable of crystallizing while an irregular structure will tend to give an amorphous polymer. It is believed that during stretching the regularity increases. With an increase in the rubber content the
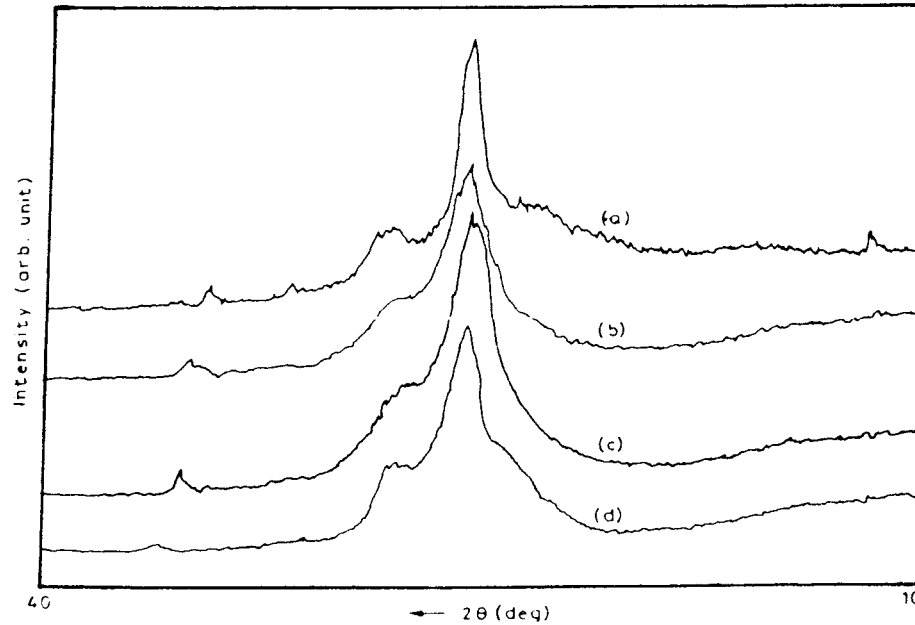
Figure 2 The X-ray diffractograms of the EVA/AR-801 (80/20) blend: (a) the usual unstretched sample, (b) the RT stretched sample, (c) the HT stretched sample, and (d) the HT shrunk sample.

trend was found to not be exactly the same as in the lower rubber content where the crystallinity was decreased and shrinkability was increased. This may be due to the higher crystallinity that may oppose the shrinkage of the blend.[11] The crystallinity of the HT stretched sample (EVA/ AR-801 = 40/60) became even less than the HT shrunk one, although the difference is not so large, which is depicted in Figure 3.

In blends a microstructural irregularity can occur, depending on the blend ratio, side chain polar groups, and chain mobility, which are af-
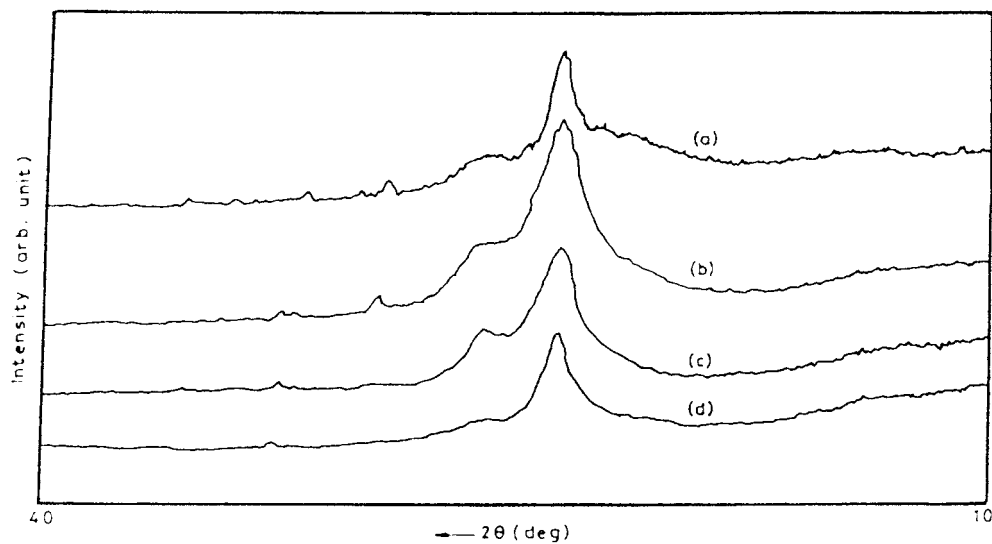

Figure 3 The X-ray diffractograms of the EVA/AR-801 (40/60) blend: (a) the usual unstretched sample, (b) the RT stretched sample, (c) the HT stretched sample, and (d) the HT shrunk sample.

Table II Parameters Evaluated from X-Ray Diffraction Studies

Sample	Percentage of Crystallinity	
	Low Angle (12.5°)	High Angle (13.8°)
EVA/AR-801 (80/20)		
Unstretched	25.5	7.5
RT stretched	55.0	12.5
HT stretched	57.0	16.0
HT shrunk	37.5	10.5
EVA/AR-801 (40/60)		
Unstretched	25.5	7.0
RT stretched	50.25	16.75
HT stretched	42.80	21.4
HT shrunk	52.80	14.4

fected by the mutual phase distribution and co-continuity.[10] In thermoplastic rubber blends the mobility of the thermoplastic phase is hampered by the presence of a partially crosslinked rubbery phase and vice versa, depending on the temperature of stretching.[12] At HT stretching there may be extra crosslinking formed. This rubber with a higher amount of crosslinking may produce irregularities that disturb the crystal domain, thus reducing the crystallinity in the elastomer-rich blend.

Effect of Crosslinking

The continuous cure characteristics as found through the Monsanto R-100 rheometer showed (as in Fig. 4) that the torque of the blends with lower rubber content is lower (i.e., the extent of crosslinking in the rubber phase is lower). The reason is that only the rubber phase is cured by the curative system used, leaving the plastic phase as such. The increase in rubber content increases the degree of crosslinking in a blend. The more crosslinking there is the more will be the entanglement in the chain segments, which results in the retraction of the sample (i.e., higher shrinkability).[13] The depicted torque rheometry clearly reflects that the extent of crosslinking of the rubber in the EVA/AR-801 (20/80) is maximum, which consequently gives the maximum shrinkability of the blend, and in EVA/AR-801 (80/20) the degree of crosslinking is minimum, which causes minimum shrinkability.

DSC Analysis

The low temperature DSC showed an endothermic peak corresponding to a second-order transition occurs at −35°C for the unstretched original sample (EVA/AR-801 = 80/20), which is attributed to the T_g of the above blend. The same blend
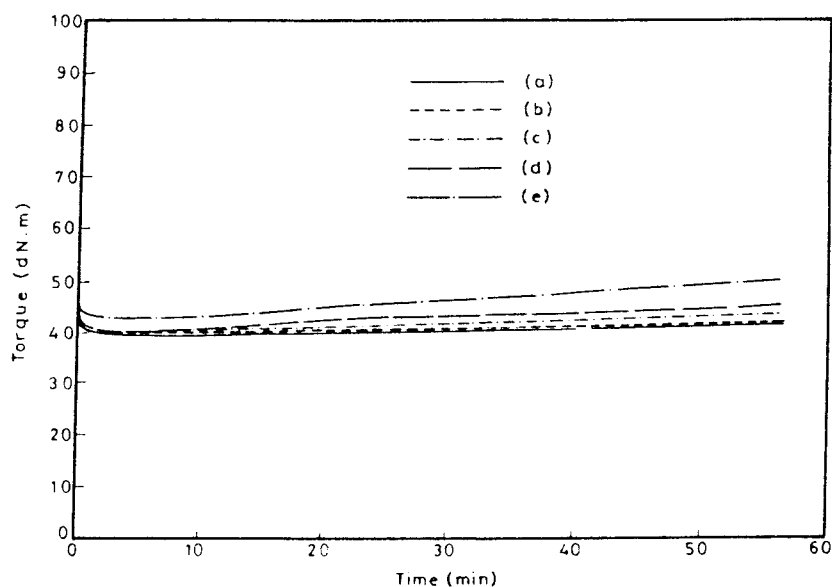

Figure 4 The variation of rheometric torque with cure time: (a) the EVA/AR-801 (80/20) blend, (b) the EVA/AR-801 (60/40) blend, (c) the EVA/AR-801 (40/60) blend, (d) the EVA/AR-801 (20/80) blend, and (e) the EVA/AR-801 (0/100) blend.
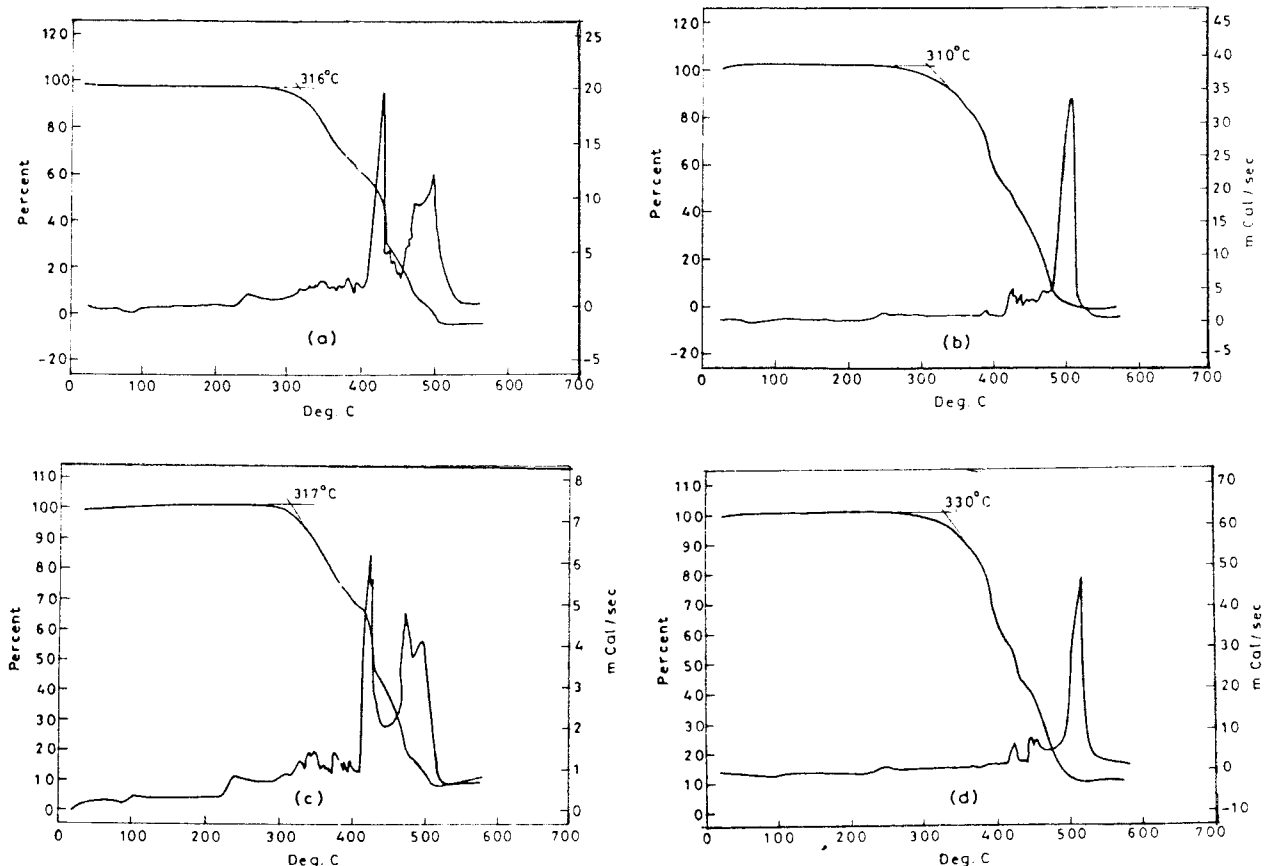
Figure 5 TGA/DSC plots of the (a) the EVA/AR-801 (60/40) usual unstretched sample, (b) the EVA/AR-801 (20/80) usual unstretched sample, (c) the EVA/AR-801 (60/40) HT shrunk sample, and (d) the EVA/AR-801 (20/80) HT shrunk sample.

when RT stretched shows a T_g at $-39°C$. But the HT stretched sample shows two T_gs: one at $-37°C$ and the other at $-12°C$, which is not prominent. In the HT shrunk sample again two T_gs appear at -35 and $-17°C$; the latter is more prominent than that of the HT stretched one. As observed, the heat treatment (on both HT stretched and shrunk) produces two T_gs. This may be due to two polymer phases,[14–17] suggesting phase separation during stretching and shrinking.

The blends of EVA were characterized by two-step degradation. The HT study (Fig. 5) suggests that the peaks occurring at around 90°C are attributed to the melting of EVA in the blend without weight loss, which tends to vanish with an increase in AR-801 content in the blend. This is followed by a sharp drop in the permanent weight retention. The first oxidative peaks appear at between 310 and 330°C for the blends with the start of weight loss. Between

420 and 490°C there were another couple of peaks associated with drastic weight loss, corresponding to oxidative degradation. The heat of oxidative degradation (H_d) was higher as the AR-801 content was increased in the blend (3210 mJ/mg for 40% AR-801 and 3427 mJ/mg for 80% AR-801). This means the stability toward oxygen decreased with an increase in rubber content.[18] Again, on further HT processing the stability toward oxygen decreased for the lower rubber content blend, but for the higher rubber content blend the oxidation stability increased.

Table III shows that for the original unstretched sample the initial degradation temperature (T_i) was decreased with an increase in rubber content (i.e., thermal stability in this vicinity was reduced). However, further processing of the blend at a higher temperature increased the thermal stability of the blends, the extent of which was higher in the AR-801-

Table III   TGA/DSC Results

Samples	T_i (°C)	T_{50} (°C)	T_{90} (°C)	H_d (mJ/mg)
R_{40}	316	426	502	3210
R_{80}	310	418	497	3427
R'_{40}	317	428	498	3774
R'_{80}	330	432	507	2061

T_i, onset temperature; H_d, heat of oxidative degradation; R, the usual unstretched sample with the suffix representing the weight percent of the rubber; R', the high temperature shrunk sample.

rich blend. This is consistent with the T_{50} (temperature at which 50% degradation occurs) and T_{90} (temperature at which 90% degradation occurs). The trends of the T_{90} values were consistent with the heat of oxidative degradation. The trend was different from the T_i and T_{50} values in only the R_{40} and R'_{40}. This was mainly due to the involvement of oxygen in the degradation process, which was predominant in the higher rubber content blend. This phenomenon was somewhat restricted because of further processing (HT shrinking of the blends), particularly for rubber-rich blends.

Study of Phase Morphology by SEM

The phase morphologies were studied by SEM after differential solvent extraction of AR-801. They are depicted in Figures 6–8. In comparing the HT stretched samples with the RT stretched sample it can be seen that the rubber phase is elongated more in the HT stretched sample (Figs. 6, 7). This may be due to extensibility of the molten plastic phase, which results in easy stretching. The SEM of the shrunk samples after HT stretching is shown in Figure 8. It is clearly
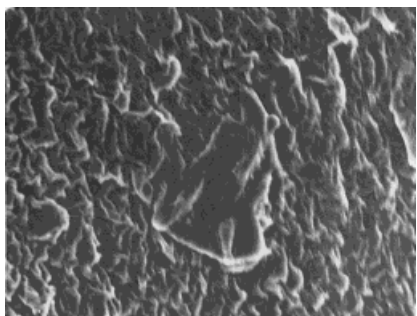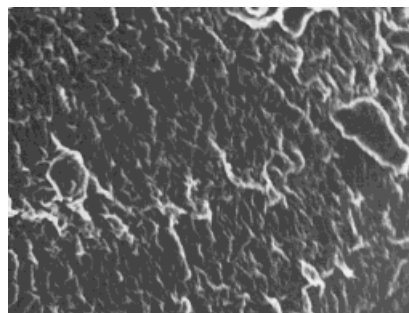

Figure 7   An SEM photograph (1000×) of the EVA/AR-801 (40/60) HT stretched sample.

observed from the figures that the rubber phase is more globular (less elongated) in nature in the shrunk sample (stretched at high temperature), thus offering more shrinkability than the latter.

CONCLUSION

A mutual correlation between the processing parameters and shrinkability of the blend was found. An increase in the cure time and rubber content increased the shrinkability in the HT stretching and RT stretching. Generally, the HT stretched sample showed higher shrinkability than the RT stretched sample. The HT extensibility depended on the crystallinity of the plastic phase. Shrinkability generally increased with a decrease in the crystallinity in the blends. For the higher rubber content blend the heat of oxidative degradation was higher. On further higher temperature processing, the stability toward oxygen decreased for the lower rubber content blend and for the rubber-rich blend the reverse was true. Processability parameters that resulted in the extension in the rubber phase to a rodlike structure
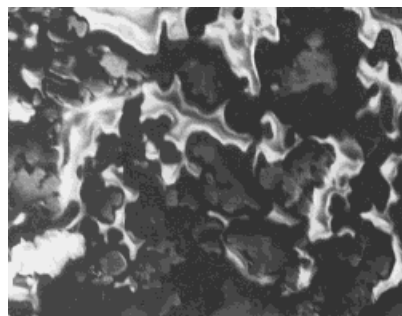

Figure 6   An SEM photograph (1000×) of the EVA/AR-801 (40/60) RT stretched sample.

Figure 8   An SEM photograph (1000×) of the EVA/AR-801 (40/60) HT shrunk sample.

were always accompanied by high shrinkage at elevated temperature.

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