Effect of Rubber Content on Mechanical Properties and Heat Shrinkage of Ethylene Vinyl Acetate Copolymer Blended with Epoxidized Natural Rubber

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ABSTRACT: Ethylene vinyl acetate (EVA, 18 mol % vinyl acetate) and epoxidized natural rubber (ENR, 50 mol % epoxidation) were blended in an internal mixer and compared to EVA. Dicumyl peroxide (DCP) was used as a curing agent. The blends consisted of 10–50 wt % of ENR and were compared with crosslinked EVA in terms of heat shrinkage, mechanical properties, and degree of crystallinity. It is found that the blends showed a decrease in mechanical properties with increasing ENR content because DCP was not a good vulcanizing agent of ENR. The addition of ENR did not affect heat shrinkability of EVA. The maximum heat shrinkage obtained was 80% for EVA and the blends. ENR did not affect thermal properties of EVA investigated by the differential scanning calorimetry. The X-ray diffractometry showed discrepancy in degree of crystallinity before and after specimen stretching and after heat shrinking. It is believed that ENR particles decreased molecular orientation of EVA resulting in a decrease in degree of crystallinity but the remained orientation was sufficient for heat shrinking. The blend showed better extrudability than EVA after increasing take-up speed. Therefore, the extruded tube prepared from the blend provided higher heat shrinkage than EVA tube. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1817–1825, 2009

Key words: blends; rubber; crosslinking; heat shrinkage; ethylene vinyl acetate

INTRODUCTION

Heat shrinkable polymers may be referred to shape-memory polymers.[1] These polymers could remember the previous shape. Once they are activated with enough heat energy, they return to the previous shape or its original dimensions. This phenomenon is also referred as "shape memory", "memory effect", and "elastic memory". Factors involving shape memory include chain entanglement, crosslinking, crystallization, highly oriented amorphous chains, and formation of domain structure. Shape of the products after returning to the previous shape is controlled by many methods, i.e. heating up to glass transition temperature and quenching, melting and recrystallization, or melting and phase separation. A process of returning to the previous shape is a change in only physical structure, but not chemical structure of polymer molecules. Heat shrinkable polymers have been applied to many applications, i.e. toys, containers, sporting goods, packaging materials, pipe-fitting, electric equipment, encapsulation, tight insulating covers, and joining of pipe.

Heat shrinkability of ethylene vinyl acetate (EVA) copolymer has been reported in the case of pure EVA[2–4] and polymer blends.[5,6] EVA was crosslinked by irradiation[2,3,7,8] or dicumyl peroxide (DCP).[4,5,9–12] Polyethylene has been used for blending with EVA.[7–9] There were many blends between EVA and synthetic rubbers for heat shrinkability purpose, including polyacrylic rubber,[10] polyurethane,[11,12] epichlorohydrin,[13] chlorosulfonated polyethylene,[14–16] and carboxylated nitrile rubber.[5,6] Although there are a few articles reporting on EVA/epoxidized natural rubber (ENR) blend[17–20]; however, based on our knowledge, there is no publication of heat shrinkability of EVA/ENR blend.

The objective of this study was to study the effect of ENR content on the heat shrinkability of EVA. Correlation of shrinkability with heat shrink conditions and microstructure of the blends was investigated and some mechanical properties of the blends were determined as well.

EXPERIMENTAL

Materials

EVA copolymer (Polene® EVA N8038, 18% vinyl acetate content) was produced by TPI Polene (Thailand)
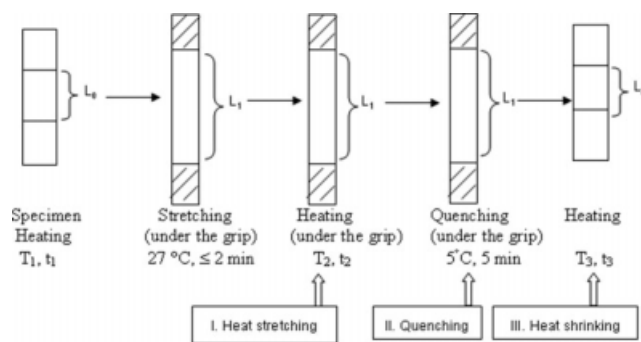
Figure 1 Schematic diagram showing a process of heat shrinking test.

PCL (Bangkok, Thailand; melt index 2.0 g/10 min). ENR (Epoxyprene® 50, 50 mol % epoxidation) was produced by Muang Mai Guthrie PCL (Suratthanee, Thailand). DCP was used as a curing agent and supplied by K.S. Mashukit Co. (Bangkok, Thailand).

Blend preparation

The polymer blends were prepared initially by melting the EVA and then the ENR was added until a constant torque was obtained. After that DCP was added. Blending was operated in an internal mixer (Brabender® Mixer 350E Duisburg, Germany) at 100°C with a rotor speed of 70 rpm. Total time of blending was about 6.50 min. DCP concentration was based on 100 wt % of polymers (EVA and ENR), referred to per hundred (phr). Polymer blends contained 10–50 wt % of ENR. Compression molded specimens were prepared at 160°C for 10 min to obtain a 2-mm thick sheet.

Testing

Tensile properties, thermal ageing, and tear resistance were carried out according to ASTM D412 Die C, ASTM D573, and ASTM D624, respectively. Eight specimens were used for every sample. Testing speed was 500 mm/min by using LLOYD® LR10K (Fareham, England). Thermal ageing was conducted at 70°C for 7 days in a gear oven (Tabai Espec. Corp., GPHH-100, Taipei, Taiwan). Changes in the tensile properties after thermal ageing were calculated based on eq. (1):

$$P = \left[\frac{A - O}{O}\right] \times 100 \qquad (1)$$

where P is the percentage change in the property, O is the original value, and A is the value after ageing. Heat shrinkability was tested at various testing conditions. Process of testing method is described in Figure 1 and consisted of three steps: heat stretching, quenching, and heat shrinking. A 5×60 mm² rec-

tangular specimen was used. The specimens may be heated at temperature T_1 for time t_1 before stretching. Specimens were stretched slowly at room temperature until reaching the required extension (L_1). The stretched specimens were held in the grips and heated at temperature T_2 for time t_2 (heat stretching step) and immersed in ice water at 5°C for 5 min (quenching step). The specimens were released from the grips and heated again at temperature T_3 for time t_3 (heat shrinking step). Condition of heat shrink test was indicated as $T_1,t_1/T_2,t_2/T_3,t_3$. Heat shrinkability was explained in terms of heat shrinkage and calculated by using eq. (2):

$$\text{Heat shrinkage}(\%) = \frac{L_1 - L_2}{L_2} \times 100 \qquad (2)$$

where L_1 is the length after stretching and L_2 is the length after shrinking. The measurement of L_2 is done at ambient temperature. Three specimens were tested for every sample and the average value was reported.

Characterization

Degree of swelling in p-xylene was performed at 110°C for 9 h and calculated based on eq. (3):

$$\text{Degree of swelling (\%)} = \frac{w_s - w_o}{w_o} \times 100 \qquad (3)$$

where w_o and w_s are specimen weights before and after swelling test. Three specimens were used for every sample. Degree of crystallinity was determined by an X-ray diffractometer (XRD; Phillips® TW1830, Almelo, Netherlands) and a differential scanning calorimeter (DSC; Perkin-Elmer® DSC7, Norwalk, CT). Degree of crystallinity from XRD measurement was calculated from ratio of area of crystalline phase to total area (crystalline and amorphous phases). The area under the crystalline and amorphous fractions were determined in arbitrary units. The ΔH_f of 100%
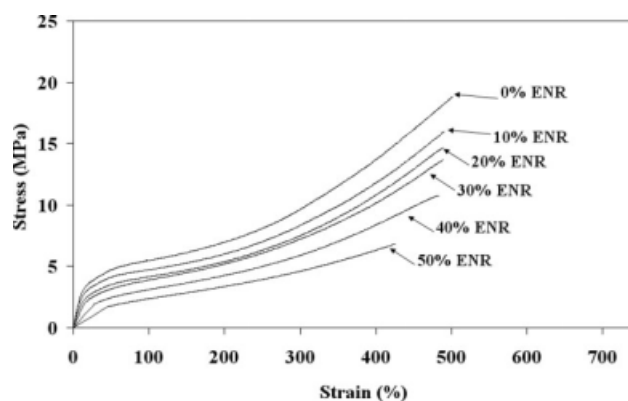

Figure 2 Stress–strain curves of EVA and EVA/ENR blends.

TABLE I
Tensile Properties of EVA and EVA/ENR Blends Containing 0.5 phr of DCP

ENR (wt %)	E^a (MPa)	σ_y^b (MPa)	ε_y^c (%)	σ_b^d (MPa)	ε_b^e (%)
0[f]	38.84 ± 1.59	3.62 ± 0.32	9.42 ± 0.81	15.85 ± 1.12	733 ± 38
0	33.31 ± 1.19	3.12 ± 0.07	9.38 ± 0.42	23.14 ± 2.91	634 ± 71
10	25.72 ± 1.03	2.92 ± 0.10	11.38 ± 0.49	16.69 ± 2.30	508 ± 58
20	21.97 ± 1.28	2.41 ± 0.08	10.98 ± 0.68	13.70 ± 1.73	495 ± 84
30	13.33 ± 1.06	2.16 ± 0.09	16.27 ± 1.24	13.64 ± 0.74	492 ± 41
40	8.82 ± 0.97	1.88 ± 0.07	21.58 ± 2.42	10.28 ± 0.95	466 ± 57
50	3.77 ± 0.46	1.82 ± 0.11	48.88 ± 6.05	7.08 ± 0.69	445 ± 68

[a] Young's modulus.
[b] Yield stress.
[c] Yield strain.
[d] Stress at break.
[e] Elongation at break.
[f] Without DCP.

crystallinity of EVA18 was 287.969 J/g.[5] Dynamic mechanical thermal properties were investigated by Rheomtric Scientific® DMTA V (Piscataway, NJ) under the tension mode with strain control of 0.01% at 1 Hz and the heating rate was 2°C/min. Freeze fractured surfaces were etched by methyl ethyl ketone at 60°C for 1 h before observation with a scanning electron microscope (JEOL® JSM5800LV, Tokyo, Japan).

Extruded tube preparation and heat shrinkage testing

EVA and the 10% ENR-blend containing 0.5 phr of DCP were extruded with the single screw extruder (Brabender® Extruder 19/25D, Duisburg, Germany). Take-up speed was varied to obtain different stretching ratios. This extruder is a conventional one and there is no accessory for expanding tube diameter; therefore, heat shrinkage of the tube was determined only on the tube length.

RESULTS AND DISCUSSION

Mechanical properties and blend morphology

Stress–strain curves and tensile properties of EVA and the blends are displayed in Figure 2 and Table I, respectively. The addition of ENR decreased tensile properties of EVA. This relates to blend morphology and also depends on vulcanized ENR. Although ENR is able to be vulcanized with DCP, but tensile properties of this vulcanizate are much lower than that of vulcanized with sulfur. DCP is not a good vulcanizing agent for natural rubber and its derivatives. The main function of DCP in the prepared blends was as a crosslinking agent of EVA, which was the continuous phase. It is well understood that crystallinity and crosslinking are key factors of heat shrinkability. Crystallinity of EVA18 is not as high as conventional polyethylene and the EVA used in this study yielded 12% of crystallinity. Consequently, crosslinking of EVA was required to obtain higher heat shrinkage. DCP decreased modulus and elongation at break but

TABLE II
Changes in Tensile Properties after Thermal Ageing of EVA and EVA/ENR Blends Containing 0.5 phr of DCP

ENR (wt %)	ΔE^a (%)	$\Delta\sigma_y^b$ (%)	$\Delta\varepsilon_y^c$ (%)	$\Delta\sigma_b^d$ (%)	$\Delta\varepsilon_b^e$ (%)
0[f]	19.32	5.39	−12.17	12.71	10.62
0	33.05	16.67	−12.26	−22.30	−3.79
10	22.24	0.00	−18.01	49.43	52.56
20	23.26	6.64	−13.21	34.53	34.34
30	48.01	3.70	−29.69	13.27	20.12
40	70.86	−7.98	−46.66	10.49	10.72
50	78.78	−6.59	−46.71	23.73	28.76

[a] Young's modulus.
[b] Yield stress.
[c] Yield strain.
[d] Stress at break.
[e] Elongation at break.
[f] Without DCP.

TABLE III
Tear Strength and Degree of Swelling of EVA and EVA/ENR Blends Containing 0.5 phr of DCP

ENR (wt %)	Tear strength (kN m^{-1})	Degree of swelling[a] (%)
0[b]	72.41 ±1.62	Dissolved
0	65.07 ± 3.98	1145
10	58.83 ± 1.63	1426
20	54.57 ± 3.17	1403
30	48.56 ± 2.37	1385
40	40.35 ± 3.56	1498
50	33.45 ± 2.81	1379

[a] 9 h.
[b] Without DCP.

increased tensile strength of EVA (Table I). Changes in tensile properties after thermal ageing of the blends showed different results as tabulated in Table II. Higher ENR content showed more increase in modulus. Tensile strength and elongation at break of the blends also increased. These phenomena indicate the occurrence of vulcanization during thermal ageing. However, the changes in the two latter properties did not relate to ENR content. The addition of ENR made EVA softer so that tear strength of the blends decreased with increasing ENR content (Table III). Degree of swelling was used to verify the occurrence of crosslinked molecules. It is found that DCP was able to crosslink EVA. EVA without DCP was completely dissolved in hot xylene whereas the crosslinked EVA showed high degree of swelling (Table III). The degree of swelling increased from 1145% (0% ENR) to a maximum of 1498% (40% ENR). The increase in degree of swelling of the blends was due to the addition of ENR. The blend samples became irregular shape after swelling whereas the EVA sample still remained round shape. This may be due to that ENR may not have properly crosslinked by DCP, causing the decrease in tensile properties and high degree of swelling of the blends. To investigate the appropriate swelling time, swelling test of crosslinked
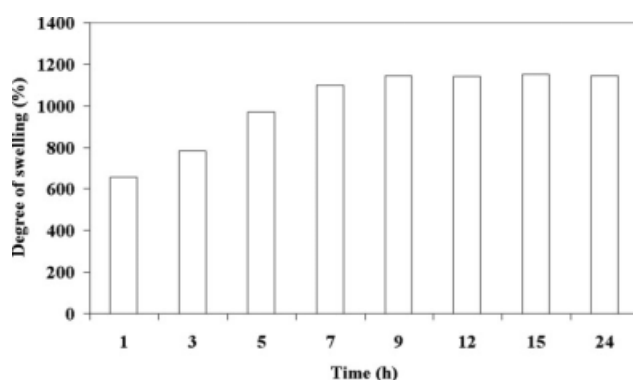

Figure 3 Effect of swelling time on degree of swelling of EVA.

EVA was operated at different swelling times. The result shown in Figure 3 confirms that swelling time at 9 h reached equilibrium of swelling.

Figure 4 represents DMTA spectra of EVA and the 10% ENR-blend, showing storage modulus (E'), loss modulus (E''), and tan δ. EVA showed lower storage modulus and loss modulus than the blend after sub-zero temperature, particularly below −20°C. The much higher storage modulus of the blend may be due to the rigidity of the glassy state of ENR in the blend. Unfortunately, tan δ of EVA was very broad and overlapped with that of ENR. The tan δ of the blend in Figure 4(b) shows a peak at −18°C and a shoulder at 5°C similar to that of ENR containing 0.5 phr of DCP as shown in Figure 5. The temperature at maximum tan δ of the blends containing 30 and 50% ENR in Figure 5 shifted to the lower temperature than that of pure ENR. These broad peaks remained in the range of transition temperature of ENR. This behavior has been found in EVA15/ENR50 blends reported by Mohamad et al.[18] In this study, the mixing time of ENR sample was only 4 min whereas that of the blends was 6.50 min. It is known that DCP can oxidize natural rubber;
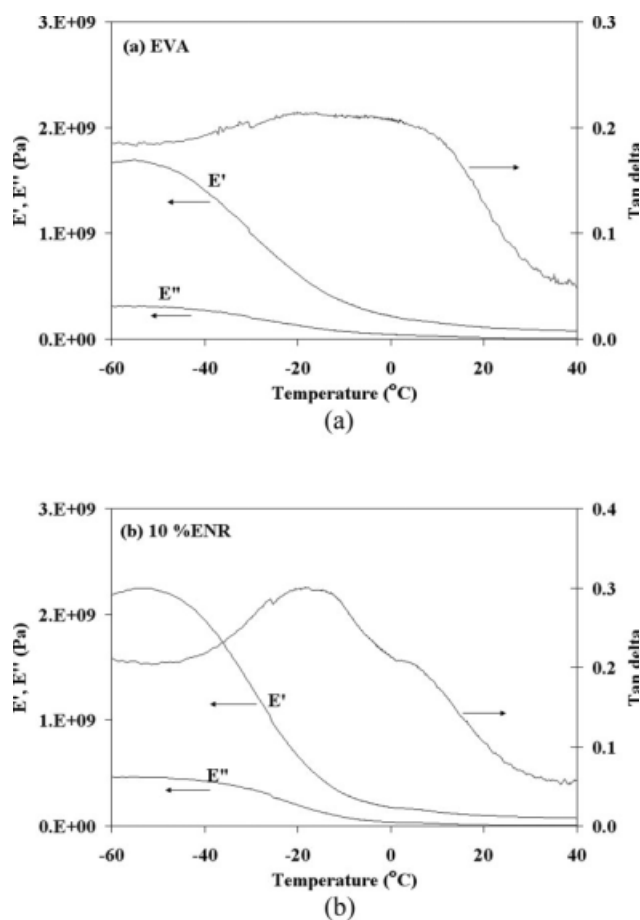

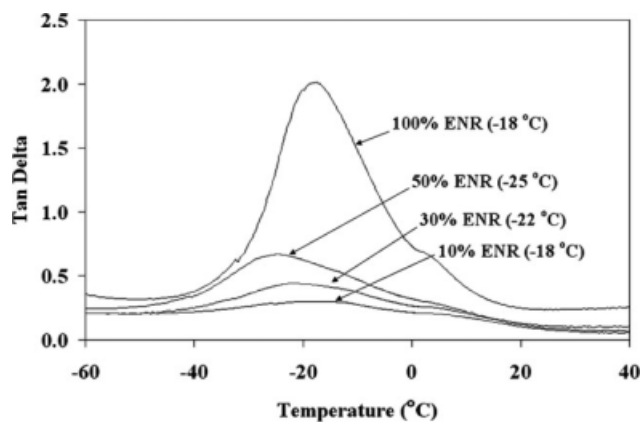**Figure 4** Storage modulus (E'), loss modulus (E''), and tan δ of EVA (a) and the 10% ENR-blend (b).

Figure 5 The tan δ of ENR and the blends.

therefore, there was a possibility that ENR was oxidized, leading to decrease T_g. Furthermore, efficiency of crosslinking in each phase in the polymer blends is different in that of the virgin parent polymers. In this study, it seemed that DCP preferred to crosslink EVA more than ENR due to swelling test results. As a result, crosslinking of ENR in the blends may be different from the virgin ENR. Based

on both possibilities, the blends showed lower T_g. However, the 10% ENR-blend showed no change in T_g due to small concentration of ENR.

It was reported the weak dipole–dipole interaction of the epoxy groups with acetate groups of EVA/ENR blends based on FTIR analysis.[17] Moreover, regarding to polarity of EVA and ENR, this blend should be compatible. This assumption was supported by SEM micrographs. Without surface etching, ENR particles were difficult to observe [Fig. 6(a)] and voids of the ENR particles were clearly noticed after surface etching with methyl ethyl ketone [Fig. 6(b–d)]. The particle sizes increased with increasing ENR content. The average particle size of ENR was <1 μm in the blends containing ENR ≤ 30%. The 50% ENR-blend showed very large particles resulting to the very low tensile properties of the blend. Similar blend morphology was observed in the uncrosslinked EVA15/ENR50 blends.[18]

Heat shrinkability

Heat shrinkage of EVA and the blends at various extensions are revealed in Table IV. Samples were
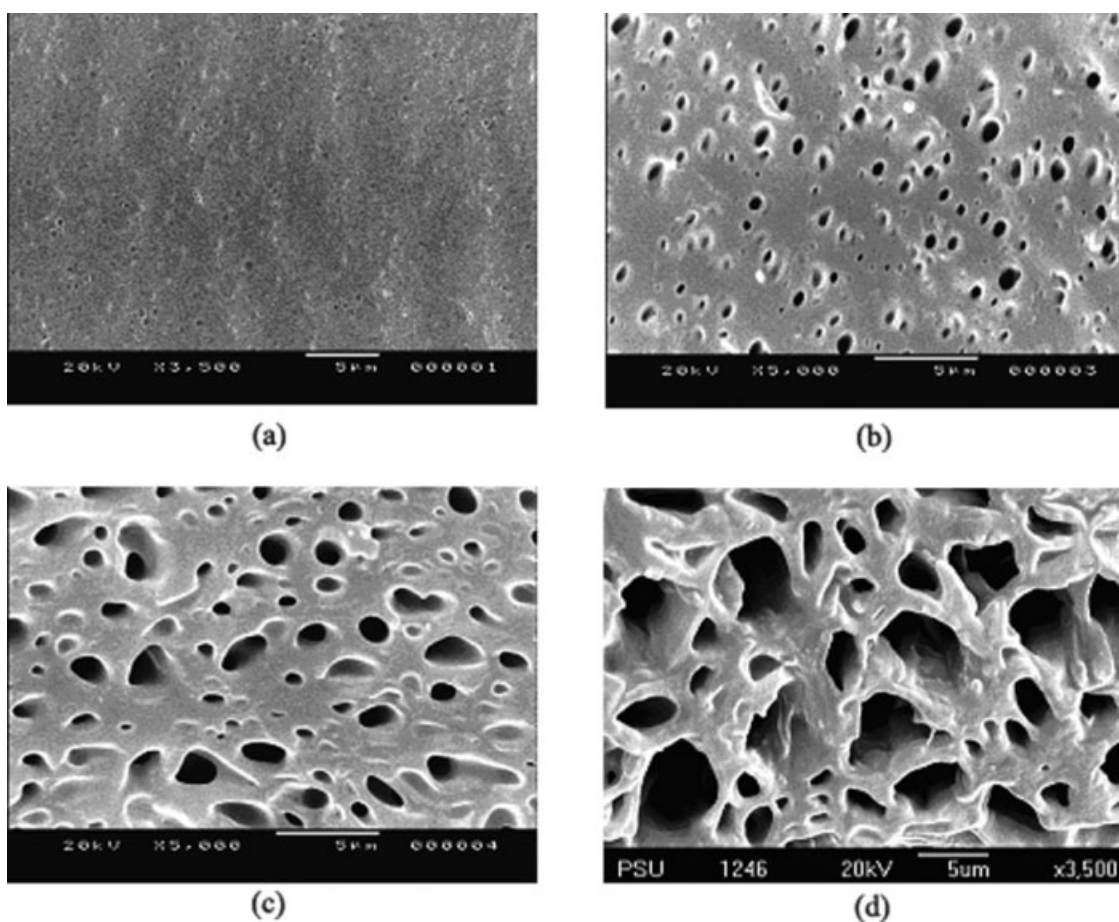

Figure 6 SEM micrographs of freeze-fractured surfaces of the 10% ENR-blend before etching (a) and after etching with methyl ethyl ketone: the 10% ENR-blend (b), the 30% ENR-blend (c), and the 50% ENR-blend (d).

TABLE IV
Effect of Extension on Heat Shrinkability of EVA
and EVA/ENR Blends Containing 0.5 phr
of DCP Tested at 90,5/90,5/120

ENR (wt %)	Heat shrinkage (%) at extension			
	100%	200%	300%	400%
0[a]	44	46	—[b]	—[b]
0	48	57	68	77
10	49	56	69	74
30	51	58	62	71
50	33	60	68	76

[a] Without DCP.
[b] Specimens broke during heat stretching.

TABLE VI
Effect of Specimen Heating Temperature (T_1,t_1)
on Heat shrinkability of EVA and the 10%
ENR-Blend Containing 0.5 phr of DCP

$T_1,t_1/T_2,t_2/T_3,t_3$	Extension (%)	Heat shrinkage (%)	
		0% ENR	10% ENR
$T_{room}/90,5/120,1$	200	70	70
	300	76	77
	400	80	80
$90,5/90,5/120,1$	200	57	56
	300	68	69
	400	77	74
$100,5 /90,5/120,1$	200	67	65
	300	75	74
	400	79	78

heated at 90°C for 5 min before stretching at room temperature. Uncrosslinked EVA showed lowest heat shrinkage and was unable to be stretched to 300–400%. The addition of ENR did not increase heat shrinkability of EVA. All samples exhibited higher heat shrinkage at higher extension due to higher molecular orientation of EVA, resulting in more driving force for returning to original shape after thermal activation. Heat shrinkage of EVA and the blends slightly increased when T_1 was room temperature (Table V). Nonetheless, all samples showed same high heat shrinkability, 80%. It should be remarked that the big particles of ENR, i.e., 5 μm in the 50% ENR-blend, did not hinder shrinkability of EVA when extension was 200% or more. There was an attempt to observe freeze-fractured surface of the stretched samples of the blends but it was unable to prepare such specimens due to high toughness of oriented molecules along the chain direction. The effect of ENR on heat shrinkage of EVA in this study was different from other blends. Polyacrylic rubber,[10] polyurethane,[11] chlorosulfonated polyethylene,[14] and carboxylated nitrile rubber[5] increased heat shrinkage of EVA. The discrepancy should be resulted from better crosslinked in those rubbers than ENR. Furthermore, there was an optimum crosslinking in rubber phase to provide high heat shrinkage of the blend.[10,11]

Obviously, ENR content did not significantly effect on heat shrinkability of EVA. Regarding to mechanical properties, the lower ENR provided the higher

mechanical properties. As a result, the 10% ENR-blend was selected for further studying in comparison with the blends with higher ENR contents. Based on the preliminary study, the condition of $T_2,t_2/T_1,t_1$ at 90,5/120,1 was the best one. Specimen stretching is the critical process in this study and it was necessary to ensure that there was no internal stress in the specimen. Because the stretching process was carried out at room temperature; therefore, the specimen should have enough flexibility for stretching. The effect of specimen heating before stretching was reinvestigated by increasing temperature to 100°C. It is found that heat shrinkage of EVA and the 10% ENR-blend did not significantly change compared with nonheated specimens and slightly higher compared with T_1 at 90°C (Table VI). Generally speaking, it is not essential to heat specimen before stretching in this study. This is because the melting temperature of EVA and the blends are below 90°C.

It is known that crosslinking is one of the key factors for heat shrinkability. Data described earlier were derived from specimens containing 0.5 phr of DCP and cured at 10 min. So as to guarantee that this curing time was appropriate, two more cure times were tested. No significant differences in heat shrinkage and degree of swelling of EVA containing 0.5 phr of DCP cured at 10, 30, and 60 min (Table VII). Therefore, we selected 10 min as a cure time. Another

TABLE V
Heat Shrinkability of EVA and EVA/ENR Blends
Containing 0.5 phr of DCP Tested at
$T_{room}/90,5/120,1$ and Extension of 400%

ENR (wt %)	Heat Shrinkage (%)
0	80
10	80
20	80
30	80
40	80
50	79

TABLE VII
Effect of Cure Time on Heat Shrinkage and
Degree of Swelling of EVA

Cure time (min)	Heat shrinkage (%)[a]	Degree of swelling (%)[b]
10	74	1145
30	73	1095
60	73	1179

[a] Testing condition = $T_{room}/90,5/120,1$ and 240% extension.
[b] 9 h.

TABLE VIII
Effect of DCP Content on Heat Shrinkage and
Degree of Swelling of EVA

DCP (phr)	Heat shrinkage (%)[a]	Degree of swelling (%)[b]
0.5	74	1145
1	73	913
2	Broken	680

[a] Testing condition = T_{room}/90,5/120,1 and 240% extension.
[b] 9 h.

concerned parameter was DCP concentration. Table VIII shows effect of DCP content on heat shrinkage and degree of swelling of EVA. EVA containing 2 phr of DCP was unable to be stretched at 240% extension due to too much crosslinking. Degree of swelling decreased with increasing DCP content but heat shrinkage was similar. This phenomenon was found in the 10% ENR-blend (Table IX). These results imply that numbers of crosslink in the specimens containing low DCP content, 0.3–0.5 phr, were enough for heat shrink performance. Too much crosslinking became a disadvantage of heat shrinkability. Remarkably, degree of swelling of EVA containing 2 phr of DCP and that of the blend containing 1 phr of DCP were similar, but the blend was able to be stretched at 240% extension whereas EVA was unable to do so. This should be attributed from the presence of ENR which increased flexibility of the blend.

Degree of crystallinity

It is well established that heat shrinkability of polymer relates to molecular orientation. This orientation can be characterized in view of degree of crystallinity because orientation-induced crystallization can take place during the process of heat stretching and subsequently quenching. Higher degree of crystallinity indicates higher molecular orientation. By stretching, the linear polymer molecules are oriented in the direction of applied stress and the crystallinity increases due to increase in the extent of molecular packing. Degree of crystallinity can be determined by DSC and

TABLE IX
Effect of DCP Content on Heat Shrinkage and
Degree of Swelling of the 10% ENR-Blend

DCP (phr)	Heat shrinkage (%)[a]	Degree of swelling (%)[b]
0.3	80	2237
0.5	80	1426
0.7	80	1079
1	79	673

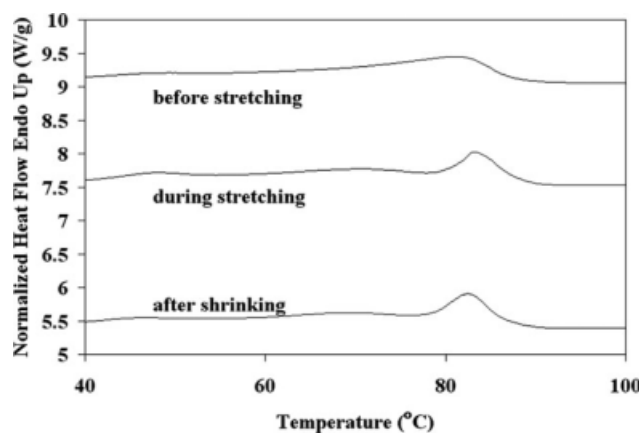[a] Testing condition = T_{room}/90,5/120,1 and 240% extension.
[b] 9 h.

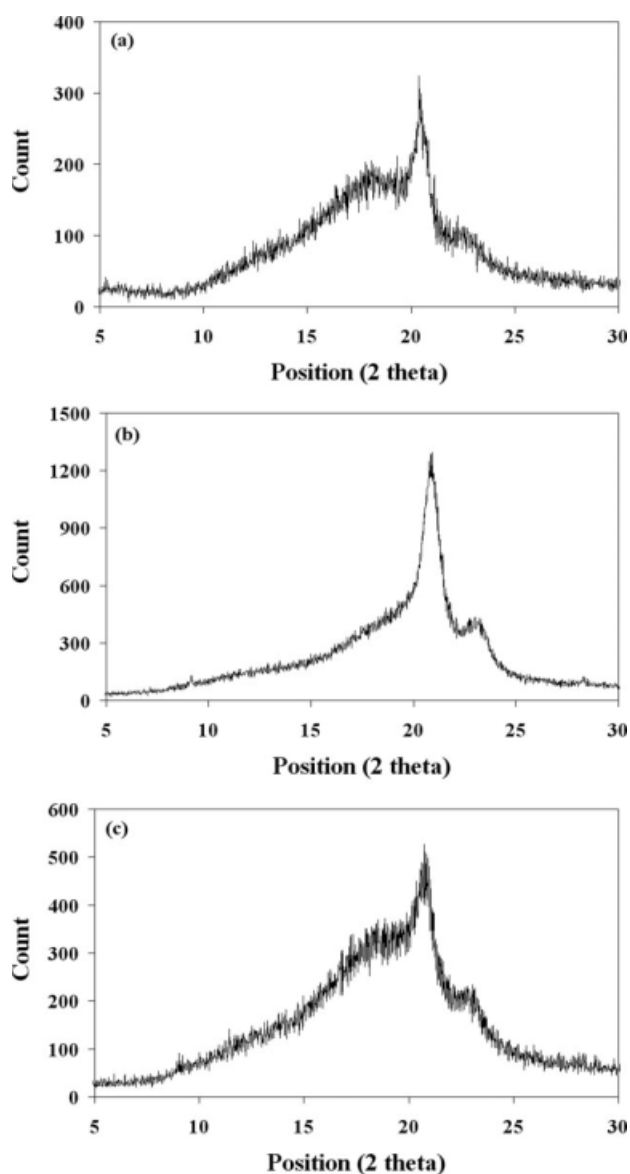**Figure 7** The first heating DSC thermograms of the 10% ENR-blend containing 0.5 phr DCP.

Figure 8 XRD diffraction pattern of the 50% ENR-blend containing 0.5 phr DCP: (a) before stretching, (b) during stretching, and (c) after shrinking.

XRD techniques. For this purpose, the large specimens were prepared because of the limitation in specimen size of XRD measurement. The specimen width of 30 mm was used and the width became 15 mm after stretching. The specimen was heated at 100°C for 5 min before stretching. The set of specimens was characterized in terms of before stretching, during stretching, and after heat shrinking. Extension was performed at 100–400%. DSC thermogram of the first heating scan was recorded. Unfortunately, no difference in degree of crystallinity of the 10% ENR-blend among those three steps (Fig. 7). The degree of crystallinity of all steps was in the range of 11–12% for all extensions. ENR showed no influence in thermal property of EVA. T_m and degree of crystallinity of this blend were similar to that of EVA pellet. Keep in mind that DSC is a technique only for investigation of crystallinity and unable to detect the molecular orientation. DSC results imply that the addition of ENR and the stretching process did not increase crystalliniy of EVA.

XRD is one of the powerful techniques to characterize molecular orientation. Based on XRD technique, molecular orientation could be accounted into a part of crystallinity and only the amorphous phase will be in the halo region. It was successful in this study to differentiate degree of crystallinity of specimens in those three steps by using XRD technique. Figure 8 represents XRD diffraction pattern of the 50% ENR-blend. The increase in signal intensity and sharper peak were observed in the stretched specimen [Fig. 8(b)]. Furthermore, the amorphous halo significantly decreased as well. Degree of crystallinity obtained from XRD technique of EVA and the blends are exhibited in Figure 9. All samples showed highest degree of crystallinity in the stretching step and degree of crystallinity increased with increasing extension. This agrees with theory that higher extension yields higher molecular orientation. It is not unusual that degree of crystallinity after heat shrinking was higher than that of before stretching because this phenomenon was reported earlier.[3,10,11] Those articles also reported the changes in crystallite size before and after heat shrinking. The smaller crystallite size was found in the stretched samples and the larger size was detected after shrinking. They proposed that the small crystallite size was melted during heat shrinking step. The increase in degree of crystallinity in the stretched samples should arrive from the small crystallite size taking place due to orientation-induced crystallization and the higher degree of crystallinity in the shrunk sample than that of the virgin sample should be due
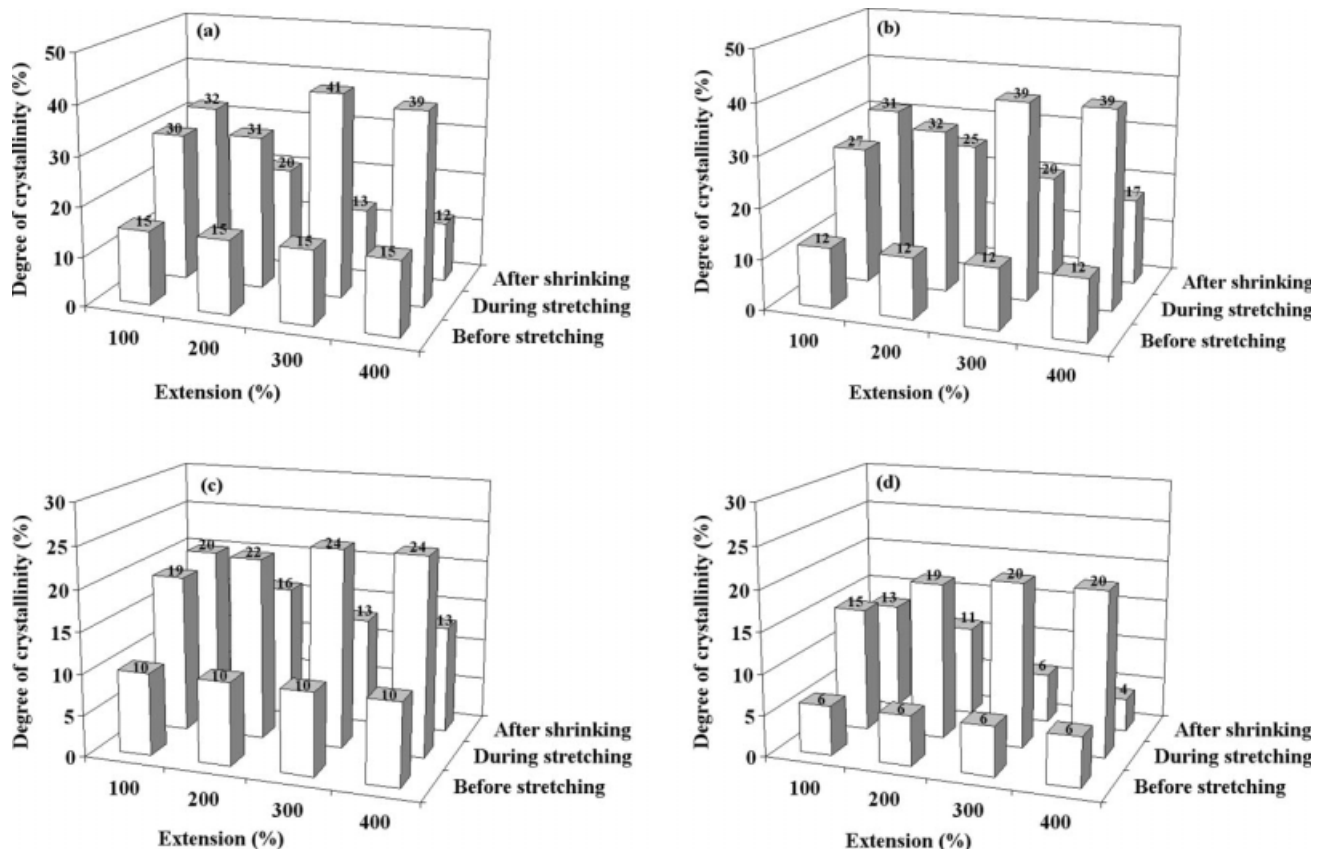

Figure 9 Degree of crystallinity obtained from XRD: (a) EVA, (b) the 10% ENR-blend, (c) the 20% ENR-blend, and (d) the 30% ENR-blend.

TABLE X
Effect of ENR on Extrudablity and Heat Shrinkage of EVA Tube

ENR (wt %)	Take-up speed (rpm)	Outer diameter (mm)	Thickness (mm)	Heat shrinkage (%)
0	10	8.18 ± 0.07	0.29 ± 0.02	66 ± 0.7
	12	Extrudate broke during rolling		
10	10	4.60 ± 4.08	0.48 ± 0.03	61 ± 0.1
	12	4.23 ± 0.12	0.45 ± 0.02	65 ± 0.1
	14	3.40 ± 0.12	0.37 ± 0.06	73 ± 0.6
	16	Extrudate broke during rolling		

to the new crystal from stretching process. Unfortunately, it was unable to identify the crystallite size in this study at the present time. As shown in Figure 9, it seems that ENR decreased degree of crystallinity of EVA. Considering the amount of crystallizable phase in the blend, there was only one phase, EVA, responding to crystallization. For that reason, the normalized degree of crystallinity could be applied to the blends. This approach will provide higher values. However, the normalized degree of crystallinity was still lowered than the apparent degree of crystallinity in the blends containing 20 and 30% ENR. The present results reveal that although degree of crystallinity and molecular orientation of the blends decreased with ENR but heat shrinkability did not change. This means that although ENR particles decreased molecular orientation of EVA but the remained molecular orientation was sufficient for heat shrinking. Another aspect of this contradiction may be due to different scaling measurement. XRD determines the microscopic level whereas heat shrinkability determines the macroscopic level.

Heat shrinkage of extruded tube

Even though the above results reflect that ENR did not affect heat shrinkabilty of EVA and it lowered the mechanical properties of EVA. However, the advantage of ENR appeared in the preparation process of extruded tube. Without ENR, the extruded tube broke when the take-up speed was faster than 10 rpm (Table X). The 10% ENR-blend displayed higher extension resulting in higher heat shrinkability. The presence of ENR also changed extrudate characteristics. The blend showed smaller outer diameter but larger thickness of the EVA tube. These characteristics involved die swell and melt viscosity. Nevertheless, extrudate characterization is beyond the scope of this study.

CONCLUSION

Mechanical properties of the blends decreased with increasing ENR content due to inefficiency crosslinking in ENR phase in the blends. The maximum heat shrinkage obtained was 80%. Although ENR content showed significant changes in rubber particle size and degree of crystallinity determined from XRD technique, ENR did not affect heat shrinkability of the blends. It is believed that ENR particles decreased molecular orientation of EVA but the remained molecular orientation was sufficient for heat shrink. The blend showed better extrudability than EVA after increasing take-up speed. Therefore, the extruded tube prepared from the blend provided higher heat shrinkage than EVA tube.

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