Effect of E/P Ratio and VA Content on Flow Behavior of EPDM and EVA Blends

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SYNOPSIS

The effect of E/P ratio of EPDM rubber and VA content of EVA copolymer on the flow behavior along with the extrudate morphology of EVA and EPDM blends have been studied as a function of shear rate and processing temperature. High E/P ratio EPDM rubber and low VA content EVA render high viscosities to the blend within the temperature range studied. The same trends hold true for extrudate swell. Stored elastic energy and relaxation time are higher for high E/P ratio EPDM and low VA content EVA. However, compositions with low E/P ratio EPDM exhibit higher shear modulus. At a particular blend composition these rheological parameters show a change in their pattern. Melt fracture occurs to a larger extent for the high E/P ratio EPDM in its blend with low VA content EVA. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The technique of blending of two or more polymers to produce a balanced combination of properties for the specific end-use requirements is a very active area in the field of polymer processing. Flow behavior of polymeric fluids within a duct is at the heart of all extrusion processes. The blends prepared from thermoplastic materials and elastomers by melt mixing have gained considerable attention in recent years.[1-5] Utracki et al.[6] studied the flow behavior of various polyethylene blends. He also studied the filler effects on the flow of polyethylene.[7] Plochocki[8] investigated the melt elasticity of the LDPE/PP blends using extrudate swell and relaxation spectra. Feng et al.[9] studied the morphology of PP and EPR blends and used EPR as a compatibilizer for PE/PP blends. Recently Das et al.[10-14] studied the rheological behavior of XLPE/EPDM, XLPE/EVA, and EVA/EPDM with the help of torque rheometry and capillary rheometry.

Here, we have studied the flow behavior of polyblends of EPDM rubber and EVA copolymer by capillary rheometry. The technique is chosen because it is relatively simple and closely resembles most commercial extrusion processes. The effects of shearing on the melt viscosity, extrudate swell, and other rheological parameters related to extrudate morphology have been reported. Efforts have been particularly made to detect the effect of E/P ratios and VA content of EPDM and EVA, respectively, on the blend rheology.

EXPERIMENTAL

Blend formulations are given in Table I. Blending was carried out in a Brabender Plasticorder at 60 rpm and 120°C for 10 min for thermoplastic EVA and at 40°C for elastomeric EVA. A Gottfart rheograph 2001 was used for rheological measurements. The rheograph 2001 was a high-pressure constant-speed capillary rheometer with microprocessor. The barrel temperature of the rheometer was controlled by three electronic temperature controllers. One minute heating time in the barrel was allowed for each blend. The L/D ratio of the capillary was 40. Each of the two types of EPDM rubbers with different E/P ratios were blended with two types of EVA copolymers having different VA contents giving 4 sets of blends. EPDMs were Intolan-255 (E/P = 80/20) from International Rubber Co., U.K.

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Table I Blend Formulations, Blend Compositions, and Corresponding Compound Numbers

EPDM Rubber									
(Royalen-501/Intolan-255)	100	80	70	60	50	40	30	20	—
Poly(ethylene-*co*-vinyl acetate)									
(Elvax-460/Levaprene-450)	—	20	30	40	50	60	70	80	100
A-series	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9
Royalene-501									
Elvax-460									
B-series	B_1	B_2	B_3	B_4	B_5	B_6	B_7	B_8	B_9
Royalene-501									
Levaprene-450									
C-series	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
Intolan-255									
Elvax-460									
D-series	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9
Intolan-255									
Levaprene-450									

Royalene-501, ML_{1+4} (120°C) = 40; E/P = 57/43
Intolan-255, ML_{1+4} (120°C) = 70; E/P = 80/20
Elvax-460, 18% VA, MFI = 2.8
Levaprene-450, 45% VA, ML_{1+4} at 100°C = 22 ± 2

and Royalene-501 (E/P = 57/43) from Uniroyal Co., U.S.A. EVAs were Elvax-460 and Levaprene-450 from DuPont, U.K. and Bayer, Germany, respectively. Nine different shear rates and three different temperatures were selected for the study of rheological parameters. The non-Newtonian index (n) and the consistency index (k) were determined by regression analysis of the experimental data of the shear stress and shear rate.

Swelling ratios (α) were determined from the extrudate samples with the help of a microscope fitted with a micrometer. Viscoelastic parameters such as

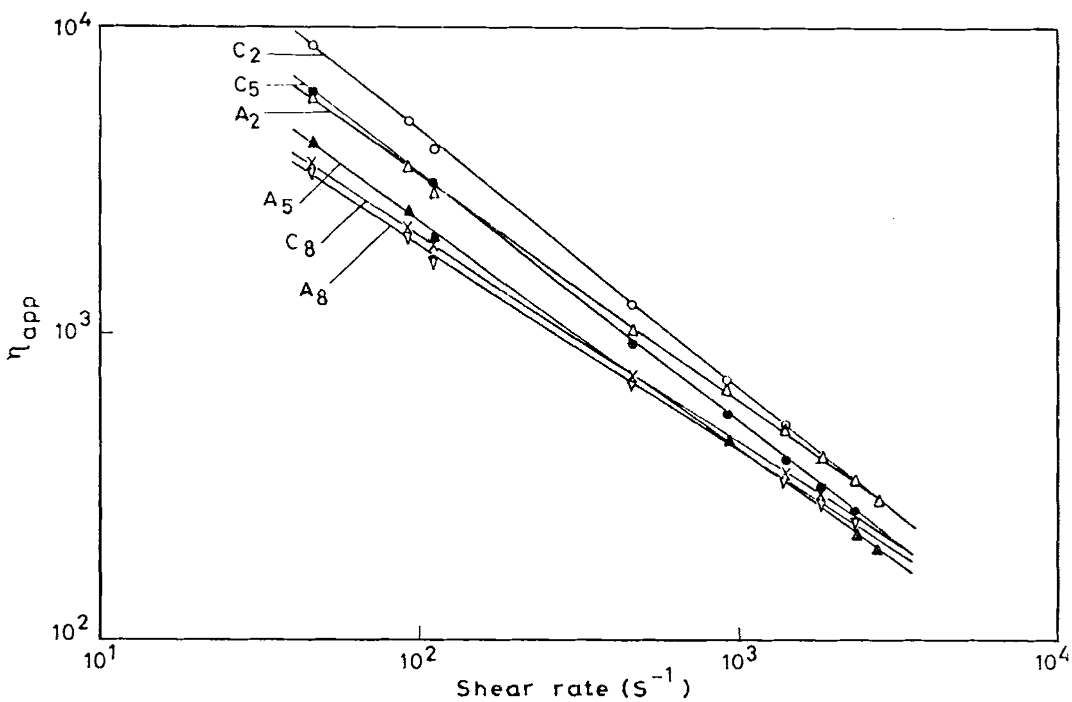

Figure 1 Variation of apparent viscosity with shear rate for the blends at 150°C.

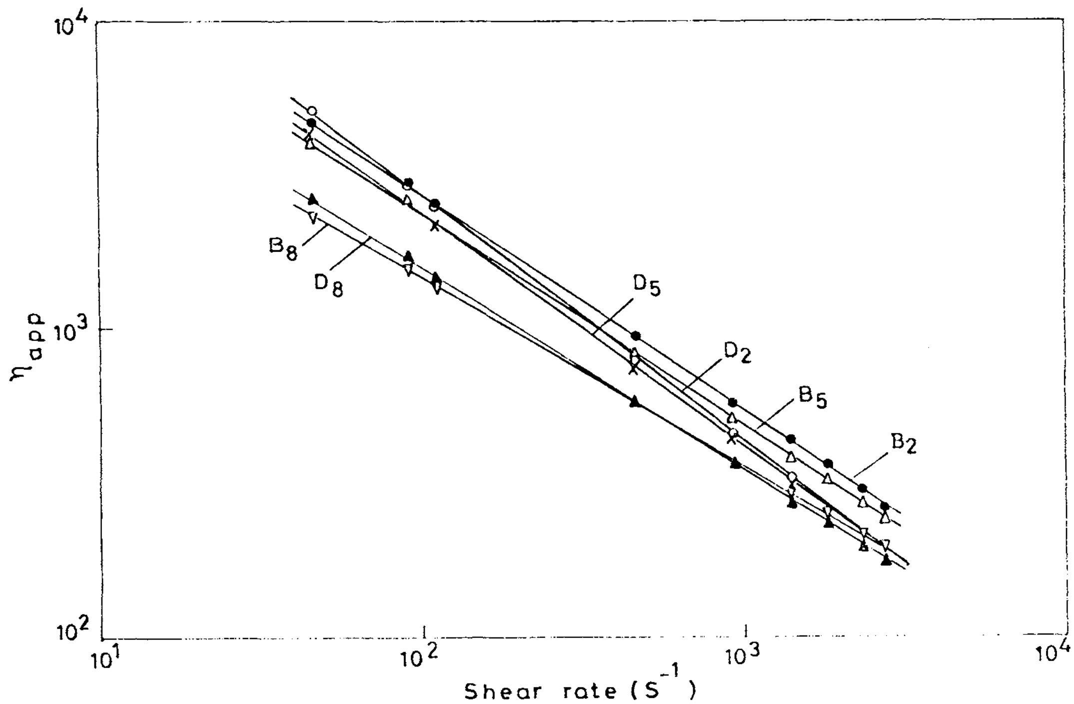

Figure 2 Variation of apparent viscosity with shear rate for the blends at 150°C.

stored elastic energy (W), recoverable deformation (γ_m), shear modulus (G), relaxation time (t_R), and modified Weissenburg number (W'_N) were determined using the mathematical model previously developed by Das and co-workers[15-16] as given below:

$$\gamma_m = \sqrt{1/2C(\alpha^4 + 2\alpha^{-2} - 3)}$$

where $C = (3n + 1)/4(5n + 1)$, γ_m is recoverable deformation.

$$W = C\gamma_m\tau$$

$$G = \frac{2W}{\alpha^4 + 2\alpha^{-2} - 3}$$

$$t_R = [1/\tau^{(1-n)/n}][(n \cdot k^{1/n})/ G(1 - n)]\{\exp[(1 - n)/n] - 1\}.$$

Extrudate morphology and melt fracture were studied with the help of an M45 WILD Autophotomat.

RESULTS AND DISCUSSION

Melt Viscosity

Variation of melt viscosity at 150°C as a function of shear rate is graphically represented in Figures 1 and 2. The melt viscosity decreases logarithmically with the shear rate for all the blends. At a particular shear rate, viscosity decreases as the EPDM/EVA ratio decreases. This trend is unaffected in the case of both high and low E/P ratio EPDMs and it is independent of VA content of EVA. For high E/P ratio EPDM, the viscosity is higher irrespective of the VA content of EVA. At low shear rates, differences in viscosity are comparatively wide, but straight line plots tend to converge at the higher shear rates. In the case of blends for fixed E/P ratio of EPDM, the EVA with low VA content renders the blend more viscous than the EVA with high VA content.

Variation of melt viscosity with the blend composition for all the blends, both EPDM rubbers in the blend with both EVAs having different VA content, are shown as a logarithmic plot of viscosity against blend composition at a particular shear rate (Fig. 3). As observed the viscosity increases as the EPDM content in the blend. The extent and pattern of variation depends on the E/P ratio of EPDM and on the VA content of EVA. Viscosity is found to be more in the case of high E/P ratio EPDM in the blend. EVA with high VA content renders the blend less viscous than the EVA with low VA content. A steady increase in viscosity for both E/P ratio EPDMs is observed with two distinct steps in the case of low VA containing EVA. The rate of

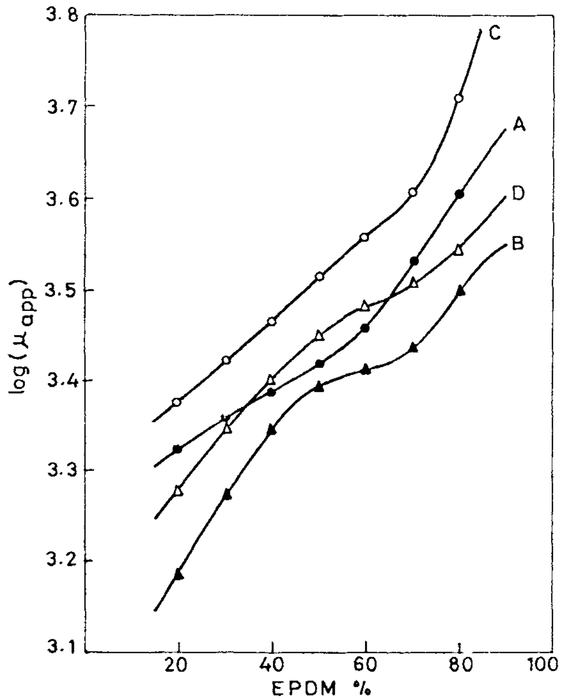

Figure 3 Variation of viscosity (at 130°C, 92.16 s^{-1}) with blend ratio. (●) E : P = 57 : 43, VA = 18%; (▲) E : P = 57 : 43, VA = 45%; (○) E : P = 80 : 20, VA = 18%; (△) E : P = 80 : 20, VA = 45%.

increase in viscosity with the increase in EPDM content is more for high E/P ratio EPDM. However, the point of inflection occurs at around 55–60% of EPDM in the case of low E/P ratio EPDM and 65–70% of EPDM for high E/P ratio EPDM in the blend. For low VA content EVA, there are three distinct stages in the curve (Fig. 3). Initially, there is a rapid rise in the viscosity with the increase in EPDM content, followed by a comparatively slow rise at the intermediate composition followed by once again a rapid rise. The intermediate region spreads over a composition range and their onset points depend on the E/P ratios of EPDM. A wider range (50–70% EPDM) is observed in the case of low E/P ratio EPDM. However, a comparatively narrow range (60–70% EPDM) is observed in the case of high E/P ratio EPDM and in this case the onset point shifts slightly toward the higher EPDM side.

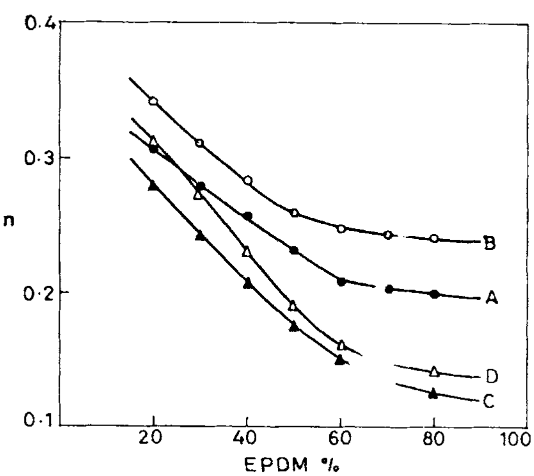

Figure 4 Variation of non-Newtonian index (n) with blend ratio. (●) E : P = 57 : 43, VA = 18%; (○) E : P = 57 : 43, VA = 45%; (▲) E : P = 80 : 20, VA = 18%; (△) E : P = 80 : 20, VA = 45%.

Table II Values of Consistency Index (k) at 130°C

Blend No.	$k \times 10^{-4}$	Blend No.	$k \times 10^{-4}$
A_2	15.00	C_2	25.10
A_4	9.54	C_4	15.80
A_5	8.12	C_5	13.18
A_6	6.76	C_6	10.20
A_8	4.90	C_8	5.62
B_2	10.00	D_2	16.98
B_4	7.58	D_4	13.18
B_5	6.91	D_5	10.71
B_6	5.62	D_6	2.08
B_8	2.95	D_8	4.36

Law Indices

The non-Newtonian index n as determined by regression analysis is plotted against the percent EPDM in Figure 4 for all the blends. As observed, n decreases as the EPDM/EVA ratio increases. But the rate of decrease depends on the E/P ratio of EPDM and VA content of EVA in the blend. A rapid decrease is observed for the high E/P ratio EPDM

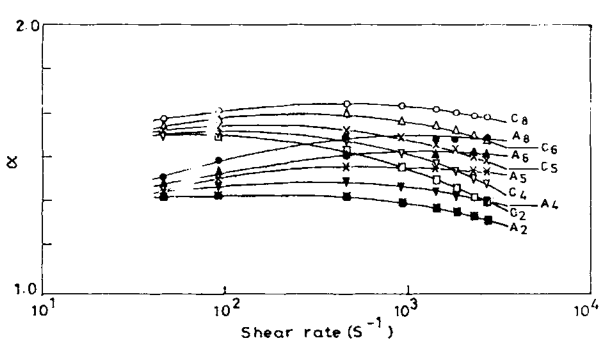

Figure 5 Variation of extrudate swell (at 150°C) with shear rate for the blends.

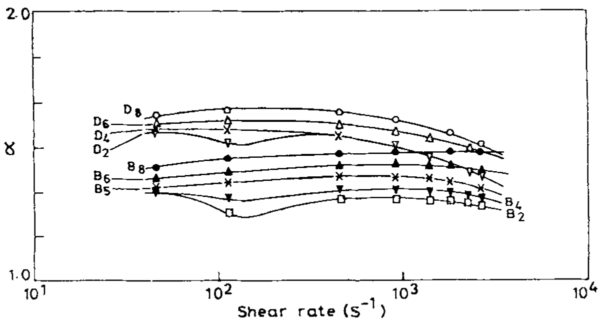

Figure 6 Variation of extrudate swell (at 150°C) with shear rate for the blends.

in the case of both high and low VA content EVAs. The plot shows two distinct stages: a rapid decrease in n values followed by a slow decreasing stage. For high E/P ratio (80 : 20) EPDM, the transition between these two stages appears to be at a higher EPDM level (70%) than the low E/P ratio EPDM in the blend (60%) with low VA content EVA. This trend is the same for high VA content EVA where transition occurs at 50% EPDM for low E/P ratio EPDM and 60% for high E/P ratio EPDM. An increase in processing temperature and VA content increases the non-Newtonian index for all the blend systems maintaining the transition points at the same level. The consistency index (k) decreases as the EPDM/EVA ratio increases (Table II). k-Values are found to be higher for EPDM having a higher E/P ratio in the blend.

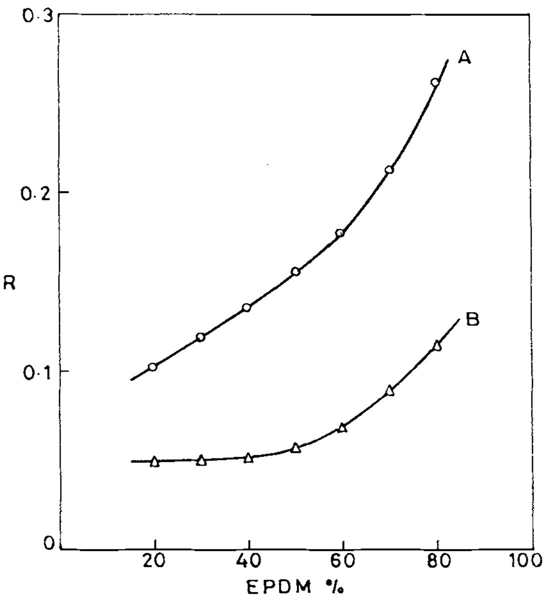

Figure 7 Variation of relaxation time (at 130°C, 92.16 s^{-1}) with blend ratio. (○) E : P = 57 : 47, VA = 18%; (△) E : P = 57 : 43, VA = 45%.

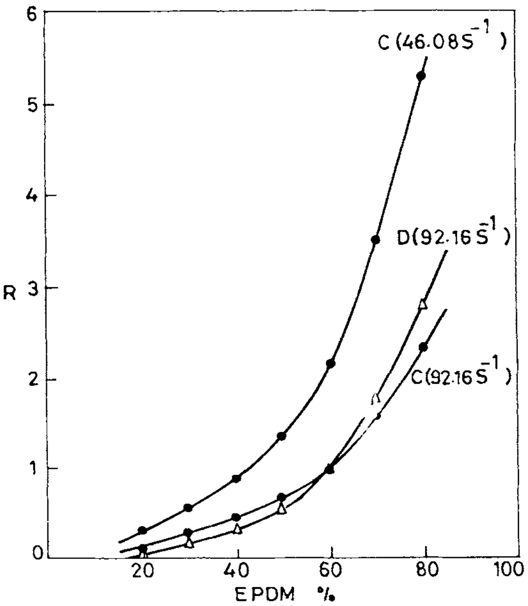

Figure 8 Variation of relaxation time (at 130°C) with blend ratio. (●) E : P = 80 : 20, VA = 18%; (△) E : P = 80 : 20, VA = 45%.

Swelling Ratio

A representative example of the extrudate swell behavior of the blends is shown in Figures 5 and 6 as a function of shear rate. The general trend is a slow rise of swelling with the shear rate at the low shear rate region and then decreases at high shear rates. An increase in EVA content increases the swelling ratio for either of the EPDMs in the blend irre-

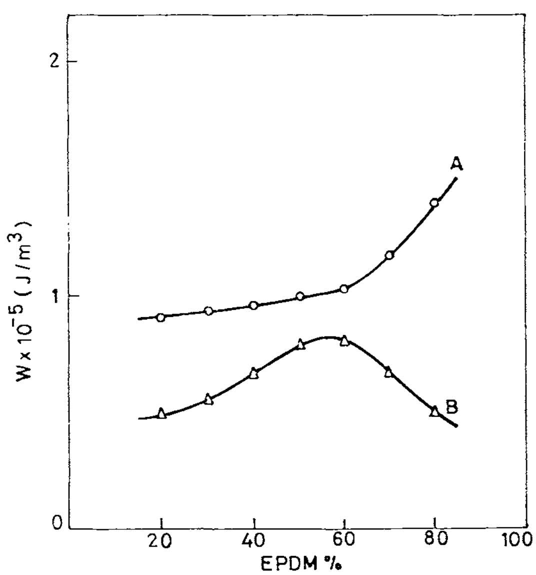

Figure 9 Variation of stored elastic energy (at 130°C, 92.16 s^{-1}) with blend ratio. (○) E : P = 57 : 43, VA = 18%; (△) E : P = 57 : 43, VA = 45%.

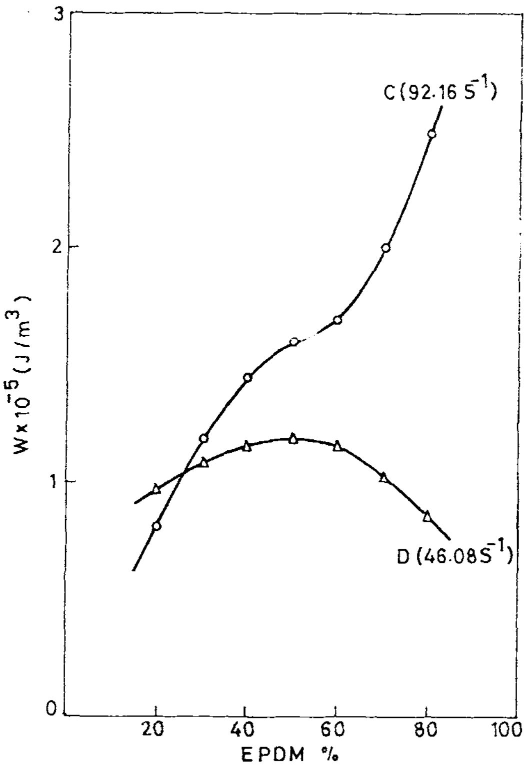

Figure 10 Variation of stored elastic energy (at 130°C) with blend ratio. (○) E : P = 80 : 20, VA = 18%; (△) E : P = 80 : 20, VA = 45%.

spective of the VA content in EVA. It is also more prominent at the high shear rate region. EPDM with high E/P ratio renders higher swelling than the EPDM with low E/P ratio for low VA content EVA. EVA with high VA content renders lower swelling irrespective of E/P ratios of EPDM. An increase in extrusion temperature decreases the swelling ratio for low E/P ratio EPDM irrespective of the VA content in EVA. However, a reverse trend is observed in the case of high E/P ratio EPDM.

Rheological Parameters

Rheological parameters such as relaxation time, shear modulus, and stored elastic energy are determined by fitting the extrudate swell and stress–strain data to the mathematical model developed earlier by Das et al.[16] The variation of these parameters with blend composition for all the blends are shown in Figures 7–12. Figures 7 and 8 depict that EPDM with low E/P ratio causes lower relaxation times than the one with high E/P ratio. This pattern holds true for both EVAs in the blend. These figures also reveal that at a fixed level of E/P ratio, EVA with high VA content is accompanied by low t_R when

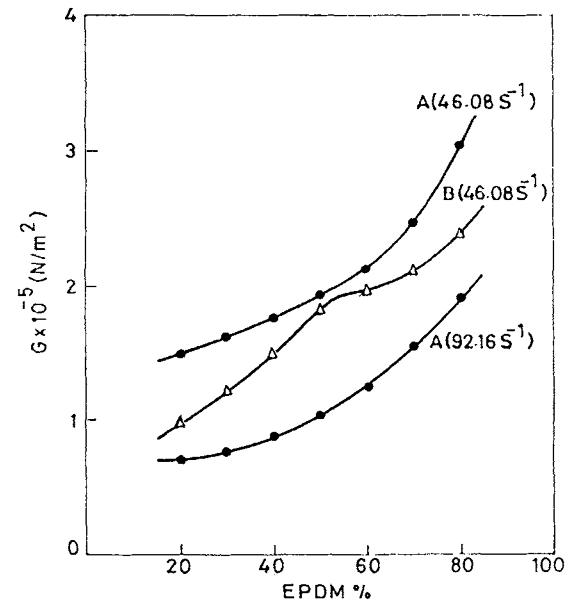

Figure 11 Variation of shear modulus (at 130°C) with blend ratio. (●) E : P = 57 : 43, VA = 18%; (△) E : P = 57 : 43, VA = 45%.

compared at a particular shear rate. As observed, there are two distinct steps in increasing the relaxation time with increasing EPDM content. Inflection point, however, depends on the E/P ratio and the VA content. The inflection point shifts toward the lower EPDM side as the VA content of EVA

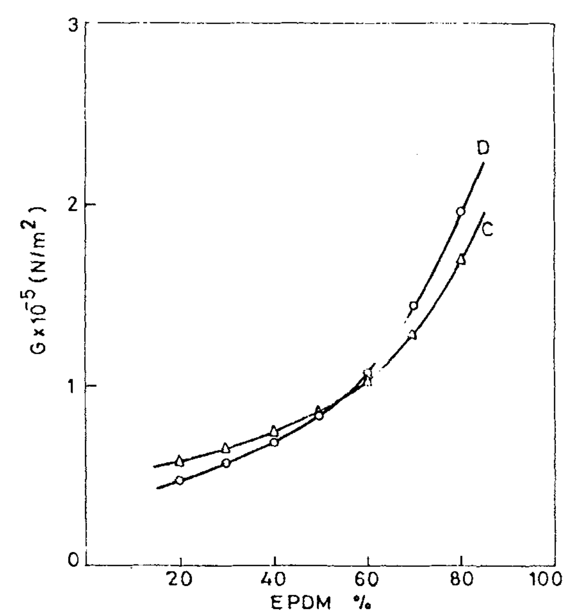

Figure 12 Variation of shear modulus (at 130°C, 46.08 s^{-1}) with blend ratio. (△) E : P = 80 : 20, VA = 18%; (○) E : P = 80 : 20, VA = 45%.

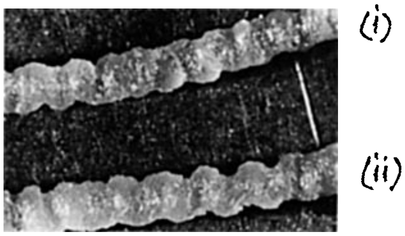

Figure 13 Photographs of the extrudates (i) blend A_2 at 130°C and 46.08 s^{-1}, (ii) blend A_2 at 130°C and 460 s^{-1}.

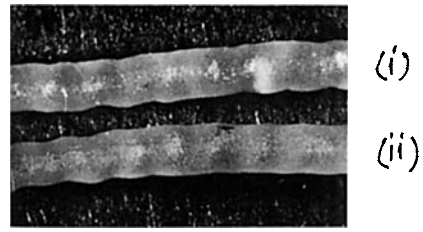

Figure 15 Photographs of the extrudates (i) blend A_8 at 130°C and 1382 s^{-1}, (ii) blend A_8 at 130°C and 2764 s^{-1}.

increases. This holds true for both types of EPDM having different E/P ratios.

Stored elastic energy (Figs. 9 and 10) also increases with the increases in EPDM content in the blend except for EVA with high VA where it increases at lower shear rates and then decreases at the high shear rate region. A blend of EPDM with high E/P ratio and low VA content EVA exhibits a rapid increase in stored elastic energy at the initial shear rate region. However, a change in the pattern is observed at around 40–45% of EPDM after which it increases only slightly up to 60% and then increase sharply in the case of the blend of high E/P ratio EPDM with EVA having low VA content. For EVA with high VA content, there is an increase in *W* for both low and high E/P ratio EPDMs. But there is a change in pattern. The change is observed around 50% EPDM content for high E/P ratio (80 : 20) EPDM and 55–60% EPDM content for low E/P ratio EPDM beyond which level stored elastic energy decreases for both types. Shear modulus (Figs. 11 and 12) increases with the increase in EPDM content in the blend. Lower E/P ratio EPDMs show higher shear modulus. Up to 55–60% of EPDM addition, shear modulus is higher for high E/P ratio EPDM with low VA content EVA in the blend beyond which the trend changes. Shear modulus is higher for EVA with high VA content as the EPDM content increases beyond 60% in the case of high E/P ratio EPDM. Shear modulus increases with increasing shear rate except for the blend containing low E/P ratio EPDM and low VA content EVA. In general, shear modulus decreases with increase in extrusion temperature.

Melt Fracture Studies of Extrudates

Photographs of the different extrudates are shown in Figures 13–19 for various blends under different experimental conditions. Figures 13 and 14 reveal that as the shear rate increases (for low E/P ratio EPDM, Blend A_2) the extrudate surface becomes smoother at the higher level of EPDM content of the blend with EVA (low VA content). However, as the EVA/EPDM ratio increases (Fig. 15, Blend A_8) smooth extrusions result. As the E/P ratio of the EPDM rubber increases (Figs. 13 and 16, blend nos. A_2 and C_2) the melt fractures appears. This surface tearing tends to diminish at a high shear rate region (Fig. 17). An increase in extrusion temperature diminishes the surface tearing further (Figs. 17 and 18) especially in the case of high E/P ratio EPDM. At the same EPDM level, the increase in VA content of EVA gives rise to smooth extrudate (Figs. 18 and 19, Blend Nos. C_2 and D_2). A higher amount of surface wrinkling in the case of low E/P ratio EPDM may be due to the presence of larger globules of the EPDM present in the

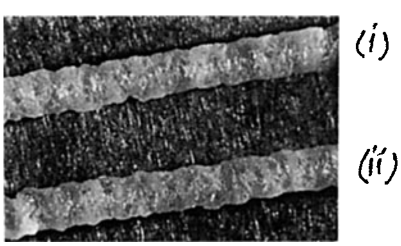

Figure 14 Photographs of the extrudates (i) blend A_2 at 130°C and 1382 s^{-1}, (ii) blend A_2 at 130°C and 2764 s^{-1}.

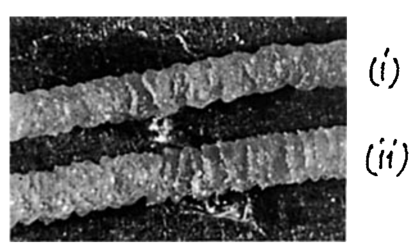

Figure 16 Photographs of the extrudates (i) blend C_2 at 130°C and 46.08 s^{-1}, (ii) blend C_2 at 130°C and 460 s^{-1}.

Figure 17 Photographs of the extrudates (i) blend C_2 at 130°C and 1382 s^{-1}, (ii) blend C_2 at 130°C and 2764 s^{-1}.

Figure 19 Photographs of the extrudates (i) blend D_2 at 150°C and 46.08 s^{-1}, (ii) blend D_2 at 150°C and 460 s^{-1}.

blend.[17] The shark skin behavior as observed in the case of high E/P ratio EPDM probably results from the rod-like EPDM phase in the blend[17] that tends to diminish at high temperature of extrusion because of probable easy orientation. High VA content elastomeric EVA gives rise to smoother extrudates. This may be due to an even distribution of the blend partners.

CONCLUSION

Flow behavior of EPDM/EVA blend depends on the E/P ratio of the EPDM and VA content of EVA used and their relative response toward shear rate and extrusion temperature. High E/P ratio EPDM is accompanied by higher swelling at a low level of VA content. High E/P ratio EPDM makes the blend more pseudoplastic. This pseudoplasticity increases as the VA content decreases. The phase inversion point changes toward the higher EPDM content as the E/P ratio of the EPDM increases. However, this inversion spreads over a wide blend ratio as the VA content decreases.

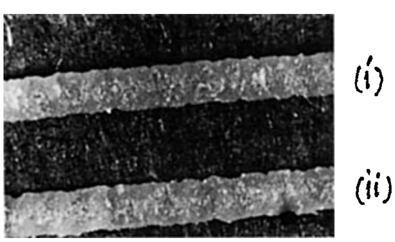

Figure 18 Photographs of the extrudates (i) blend C_2 at 150°C 1382 s^{-1}, (ii) blend C_2 at 150°C and 2764 s^{-1}.

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