

Melt Rheology and Elasticity of Natural Rubber—Ethylene–Vinyl Acetate Copolymer Blends

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SYNOPSIS

The melt rheology of blends of natural rubber (NR) and ethylene–vinyl acetate copolymer (EVA) has been studied with reference to the effects of blend ratio, cross-linking systems, shear stress, and temperature. When EVA formed the dispersed phase, the viscosity of the blends was found to be a nonadditive function of the viscosities of the component polymers at lower shear region, i.e., a positive deviation was observed. This behavior has been explained based on structural buildup of dispersed EVA domains in the continuous NR matrix. The effect of the addition of silica filler on the flow characteristics of the blends has been investigated. The melt elasticity parameters such as die swell, principal normal stress difference, recoverable shear strain, and elastic shear modulus of NR–EVA blends were also evaluated. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, blending of two or more polymers to produce the required combination of properties for specific end uses is gaining industrial importance. Knowledge of flow behavior of polymer blends is of paramount importance to optimize processing operations. In polymer blends, the viscosity of individual components plays a critical role in the flow and forming of compounds. Several investigations have been made to understand the complicated rheological behavior of polymers in view of its relevance to processing.^{1–4} The melt flow behavior of polymer blends and that of polymers containing cross-linked particles have been studied by different research groups.^{5–10} Danesi and Porter¹¹ studied the rheological behavior of polypropylene and ethylene propylene rubber. They explained how the state of dispersion is affected by conditions of blend preparation and extrusion. Utracki and Samut¹² studied the flow properties of various polyethylene blends. Kuriakose and De¹³ and Thomas et al.¹⁴ studied the

flow behavior of thermoplastic elastomer blends. Recently, Varughese¹⁵ studied the rheological behavior of poly(vinyl chloride)/epoxidized natural rubber (PVC/ENR) blends. All these studies indicated that the dispersed phase in an immiscible blend is deformable and may give rise to wide range of sizes and shapes during processing. This, in turn, determines the morphology of the system. The melt rheology is particularly sensitive to morphology.

Blends of ethylene–vinyl acetate copolymer (EVA) and natural rubber (NR) are now being used in many applications such as in cables and footwear. These materials combine the superior mechanical properties of NR and the excellent aging properties of EVA. Recently, we have examined the miscibility, morphology, mechanical properties, and aging characteristics of these blends.^{16–19} However, the rheological behavior of these blends has not been studied. This paper examines the rheological characteristics of NR–EVA blends by capillary rheometry. The effects of blend ratio, cross-linking system, and silica on the viscosity of the blends have been studied. In addition, the morphology of extrudate has been examined to understand the influence of blend morphology on flow characteristics.

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EXPERIMENTAL

Materials Used

NR used for the study was ISNR-5 grade (light color) and EVA copolymer used was EVA-Exxon 218, manufactured by Exxon Chemical Co., USA. The vinyl acetate content of EVA was 18% by weight, and its melt flow index and density, 1.7 g/10 min and 0.939 g/cm³, respectively. All other ingredients used were of rubber chemical grade.

Preparation of Blends

Blends were prepared in a laboratory model intermix (Shaw Intermix KO) set at a temperature of 80°C and a rotor speed of 60 rpm. NR was masticated for 2 min and then blended with EVA for 2.5 min. The final temperature of the blend inside the intermix was in the range of 110–128°C, depending upon the blend ratio. The blends contained 0, 10, 20, 30, 40, 50, 60, 70, 80, and 100% of EVA and were designated as A, B, C, D, E, F, G, H, I, and J, respectively. The blends were compounded in a two-roll laboratory mill as per test recipes given in Table I. The compounds containing sulfur as curative are designated as A₁, B₁, C₁ . . . , etc., and those containing the dicumyl peroxide (DCP) cross-linking system are designated as A₂, B₂, C₂ . . . , etc. Compounds containing a mixed cure system consisting of sulfur and DCP are designated as A₃, B₃, C₃ . . . , etc. The corresponding silica-filled blends are designated as A₃S₀ . . . A₃S₁₅ . . . A₃S₃₀ . . . , etc.

Rheological Measurements

The shear viscosity of the blends was determined using a capillary rheometer attached to a Zwick UTM Model 1474. The capillary used was made of tungsten carbide and has an l/d ratio of 40 and angle

of entry of 180°. The sample for testing was placed inside the barrel of the extrusion assembly and forced down to the capillary with a plunger attached to the moving crosshead. After a warming up period of 3 min, the melt was extruded through the capillary at preselected speeds of the crosshead, which varied from 0.5 to 500 mm min⁻¹. The forces corresponding to specific plunger speeds were recorded using a strip chart recorder assembly. The force and crosshead speed were converted into apparent shear stress (τ_w) and shear rate ($\dot{\gamma}_w$) at the wall, respectively, using the following equations involving the geometry of the capillary and the plunger:

$$\tau_w = \frac{F}{4A_p \left(\frac{lc}{dc} \right)} \quad (1)$$

$$\dot{\gamma}_w = \frac{(3n' + 1)}{4n'} \times \frac{32Q}{\pi dc^3} \quad (2)$$

where F is the force applied at a particular shear rate; A_p , the cross-sectional area of the plunger; l_c , the length of the capillary; and d_c , the diameter of the capillary. Q is the volume flow rate and was calculated from the velocity of the crosshead and the diameter of the plunger. n' is the flow behavior index defined by

$$n' = \frac{d(\log \tau_w)}{d(\log \dot{\gamma}_{wa})} \quad (3)$$

and was determined by regression analysis of the values of τ_w and $\dot{\gamma}_{wa}$ obtained from the experimental data. $\dot{\gamma}_{wa}$ is the apparent wall shear rate calculated as $32Q/\pi dc^3$. The shear viscosity, η , was calculated as

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} \quad (4)$$

Extrudate Swell

The extrudates were carefully collected as they emerged from the capillary die, taking care to avoid any deformation. The diameter of the extrudate was measured after 24 h of extrusion using a binocular stereomicroscope. The die swell was calculated as the ratio of the diameter of extrudate to that of the capillary (d_e/d_c).

Extrudate Morphology

The morphology of the uncross-linked blend was studied by the solvent-etching technique. For this,

Table I Formulation of the Mixes

Ingredients	Sulfur (1)	DCP (2)	Mixed (3)
Polymer	100.0	100.0	100.0
Zinc oxide	5.0	5.0	5.0
Stearic acid	1.5	1.5	1.5
Styrenated phenol	1.0	1.0	1.0
Dibenzothiazyl disulfide	0.8	—	0.8
Dicumyl peroxide (40% active)	—	4.0	4.0
Sulfur	2.5	—	2.5

cryogenically fractured extrudate was kept immersed in benzene, for preferential extraction of NR, for about 48 h. These samples were then dried at 40°C in an air oven without disturbing the extracted surface and this surface was examined under a scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Effect of Blend Ratio and Shear Stress on Viscosity

The effect of blend ratio and shear stress on the viscosity of uncross-linked NR/EVA blends at 120°C is shown in Figure 1(a) and (b). It can be

seen that the viscosity of all the blends decreased with increase in shear stress, indicating pseudoplastic behavior.

The pseudoplastic behavior is due to the fact that at zero shear the molecules are extensively entangled and randomly oriented. Under the application of shear, the molecules become oriented and become disentangled, as a result of which the viscosity decreases.

It is interesting to note that at the low shear stress region ($< 3 \times 10^5$ Pa), when EVA content is less than 50% [Fig. 1(a)], the viscosity of the blends is a nonadditive function of the viscosities of the component polymers. NR exhibits slightly higher viscosity than does EVA and the viscosity of the blends

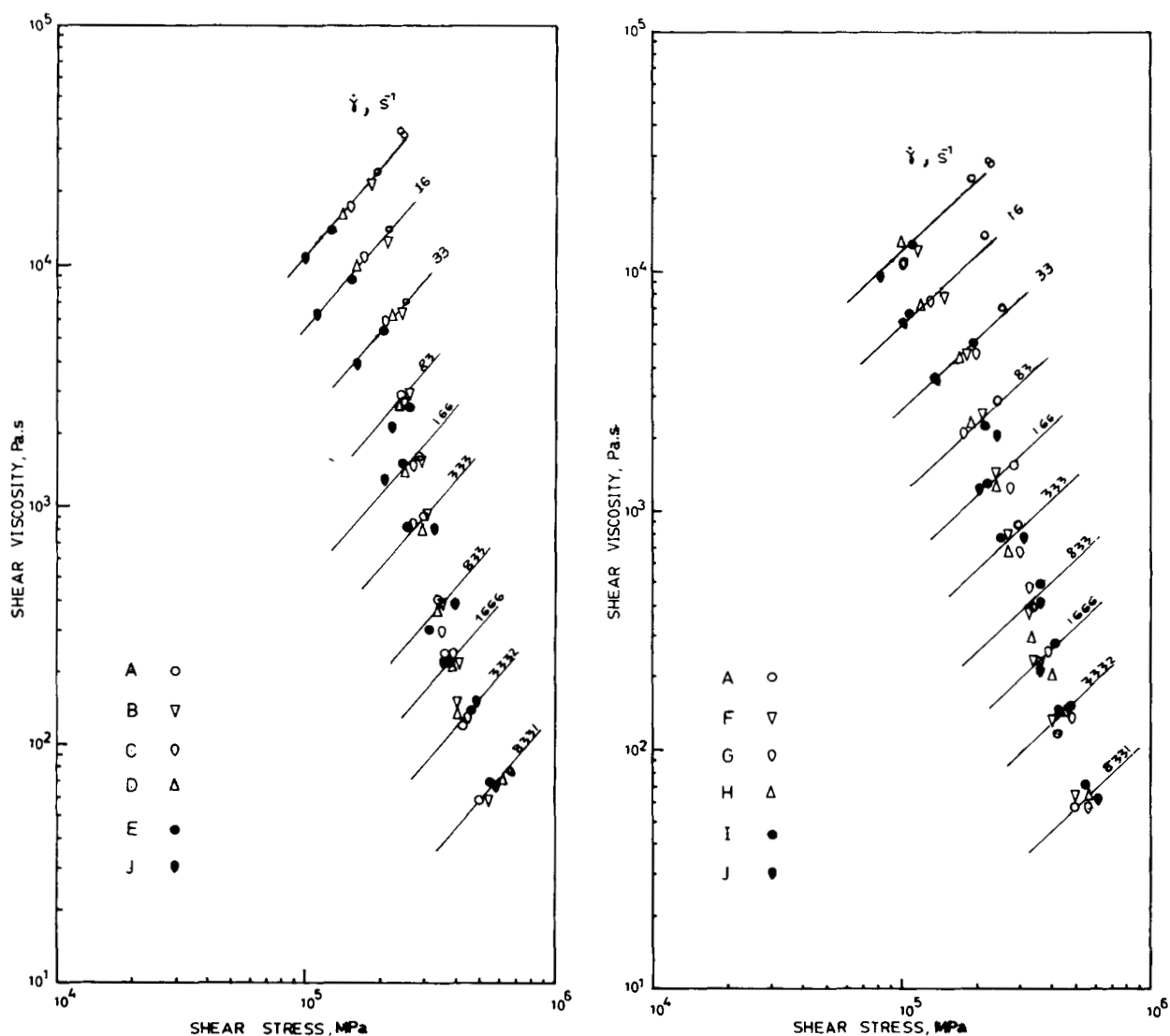


Figure 1 Shear viscosity-shear stress plots for the NR-EVA blends at 120°C. The numbers on the solid lines indicate the approximate shear rate range at which the viscosity is calculated.

is higher than that of the components. This is clear from Figure 2, where the viscosity of the blends at low and high apparent shear rate is plotted as a function of the weight percent of EVA. It can be seen that this phenomenon is observed only at the lower shear region and also at lower proportions of the EVA where it formed the dispersed phase in the continuous NR matrix. In this context, it is important to mention that our earlier studies¹⁹ on the morphology of NR-EVA blends indicated that the EVA remained as dispersed domains in the continuous NR matrix at lower proportions, but as the proportion of EVA is increased to 40% or more, this phase also formed a continuous matrix. The non-additive nature in the viscosity function of NR/EVA blends at the low shear stress region can be explained as follows:

At the low shear stress region, there would be little deformation of the EVA domains and strong interactions among domains can be expected due to the reported clustering of the acetate groups.⁵ Therefore, such a state of interaction can give rise to the structural buildup of EVA domains in the NR matrix. This can lead to a bulk viscosity greater than that of the constituent components. As the level of shear stress is increased, the structure breaks down

and the chances of interactions between the domains are reduced. Some support for such a model can be drawn from the scanning electron micrographs in Figure 3(a) and (b), which show the morphology of 20/80 and 30/70 EVA/NR blend, respectively, extruded at a low shear rate. These figures show aggregates of EVA domains resting on the NR surface. It is also important to note that the increase in viscosity at the low shear stress region is more pronounced at a lower proportion of EVA in the blend (Fig. 2) where the domain size is minimum. This is because smaller domains give rise to strong structure buildup and, as the proportion of EVA increases, the domain size increases and tends to become a continuous phase. It is seen that when the EVA phase becomes fully continuous, the anomaly disappears completely [Fig. 1(b)]. This sort of positive deviation in the viscosity of polymer blends has been reported by many researchers.^{5,20-23} Lee²⁰ and Munstedt²¹ noticed an increase in viscosity at a lower shear region in the case of elastomer-modified thermoplastics. They have argued that agglomeration and network formation by the rubber domains is the cause for the existence of yield stress. Ablanova²² reported that the viscosity vs. composition curve of polyoxymethylene (POM)/copoly-

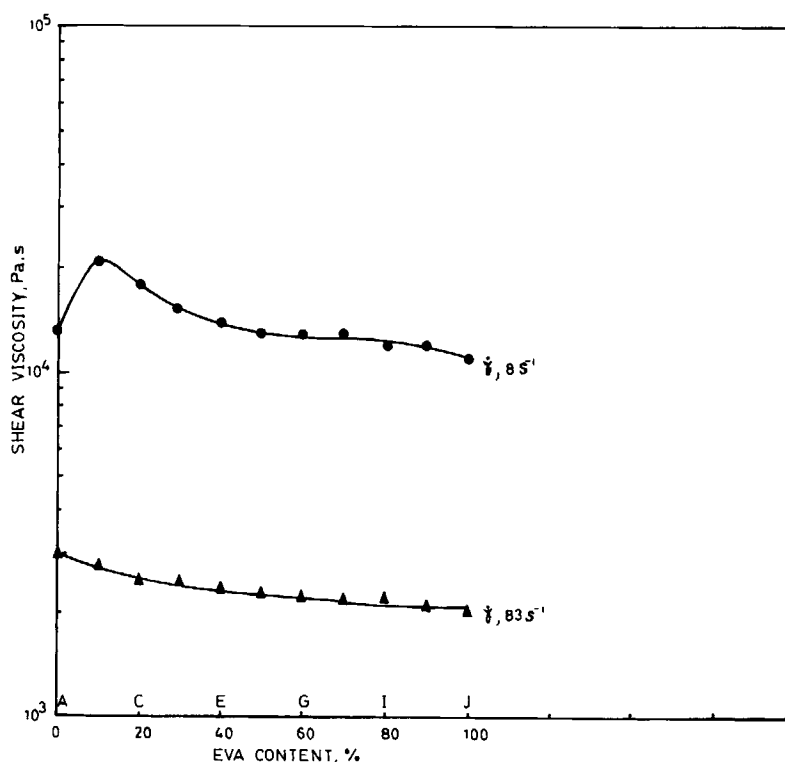


Figure 2 Variation of shear viscosity with EVA content of the blends at low and high shear rates.

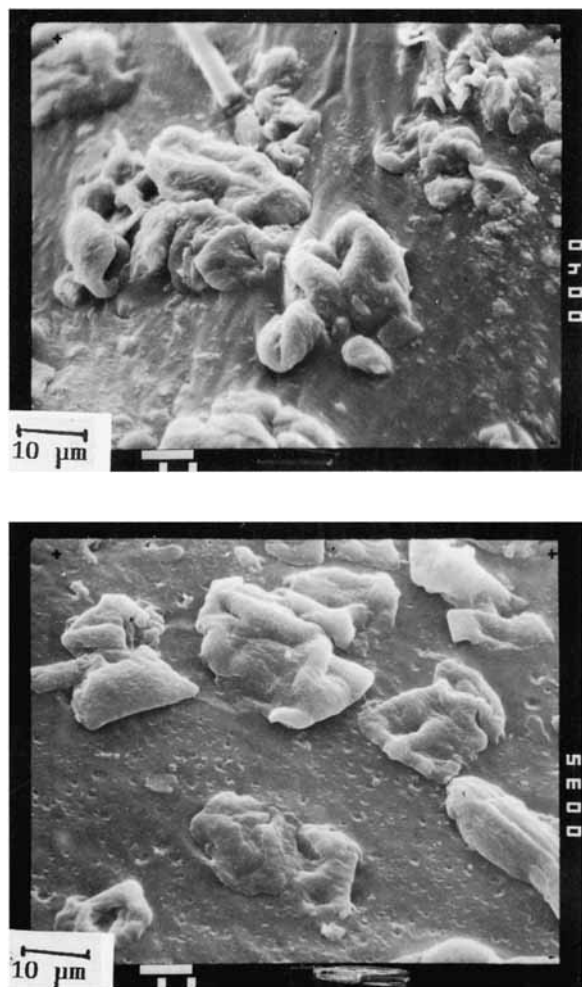


Figure 3 SEM photomicrographs of extrudates of blends C and D at low shear rate.

amide (CPA) goes through a maximum at low shear stress levels and through a minimum at high stress levels. Fujimura and Iwakura²³ reported on the zero-shear viscosity vs. blending ratio for blends of EVA copolymer and high-density polyethylene (HDPE). It is seen that in most cases the viscosities of HDPE/EVA blends are greater than those of the constituent polymers.

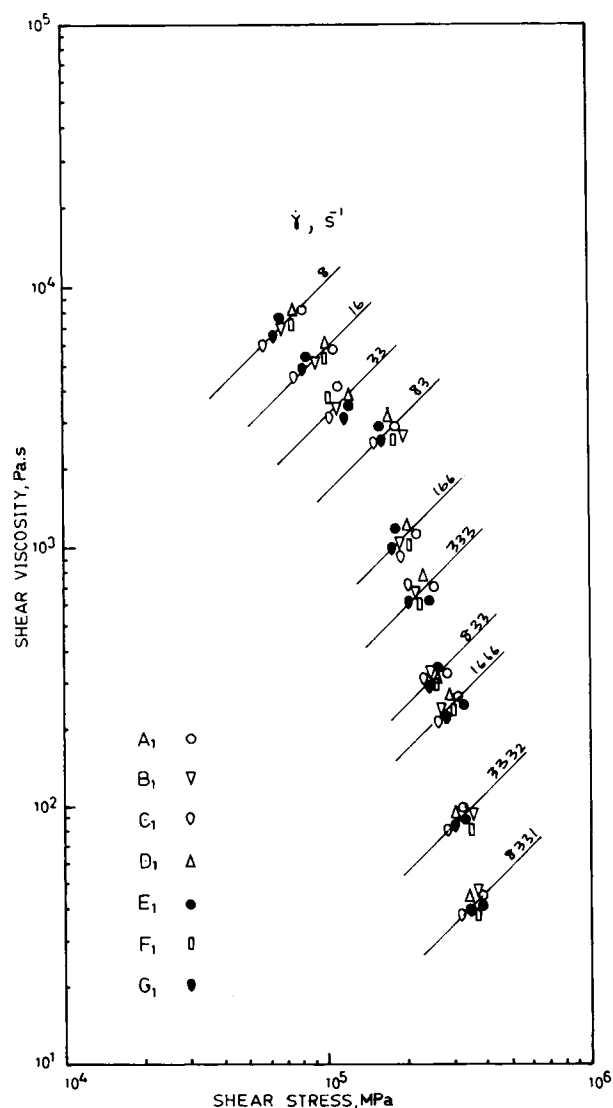
Effect of Cross-linking System on Viscosity

The viscosity of NR/EVA blends containing three vulcanizing systems, namely, sulfur, peroxide, and a mixed one, at different shear stress, is given in Figures 4, 5(a and b), and 6(a and b), respectively. Since the experiment was conducted at 120°C, no cross-linking reaction is expected to take place during extrusion. Therefore, the flow behavior of these

compounds is similar to that of unvulcanized blends. However, slight variation is observed in certain cases due to the presence of compounding ingredients.

Effect of Precipitated Silica on Viscosity

The effect of precipitated silica (INSIL VN₃) on the viscosity of NR/EVA blends at three shear rates is shown in Figure 7. It is seen that the filled systems exhibit higher viscosity than do the pure polymers at all shear rates. This is an expected trend especially in polymer systems containing reinforcing-type fillers. The decrease in viscosity at high shear rates is



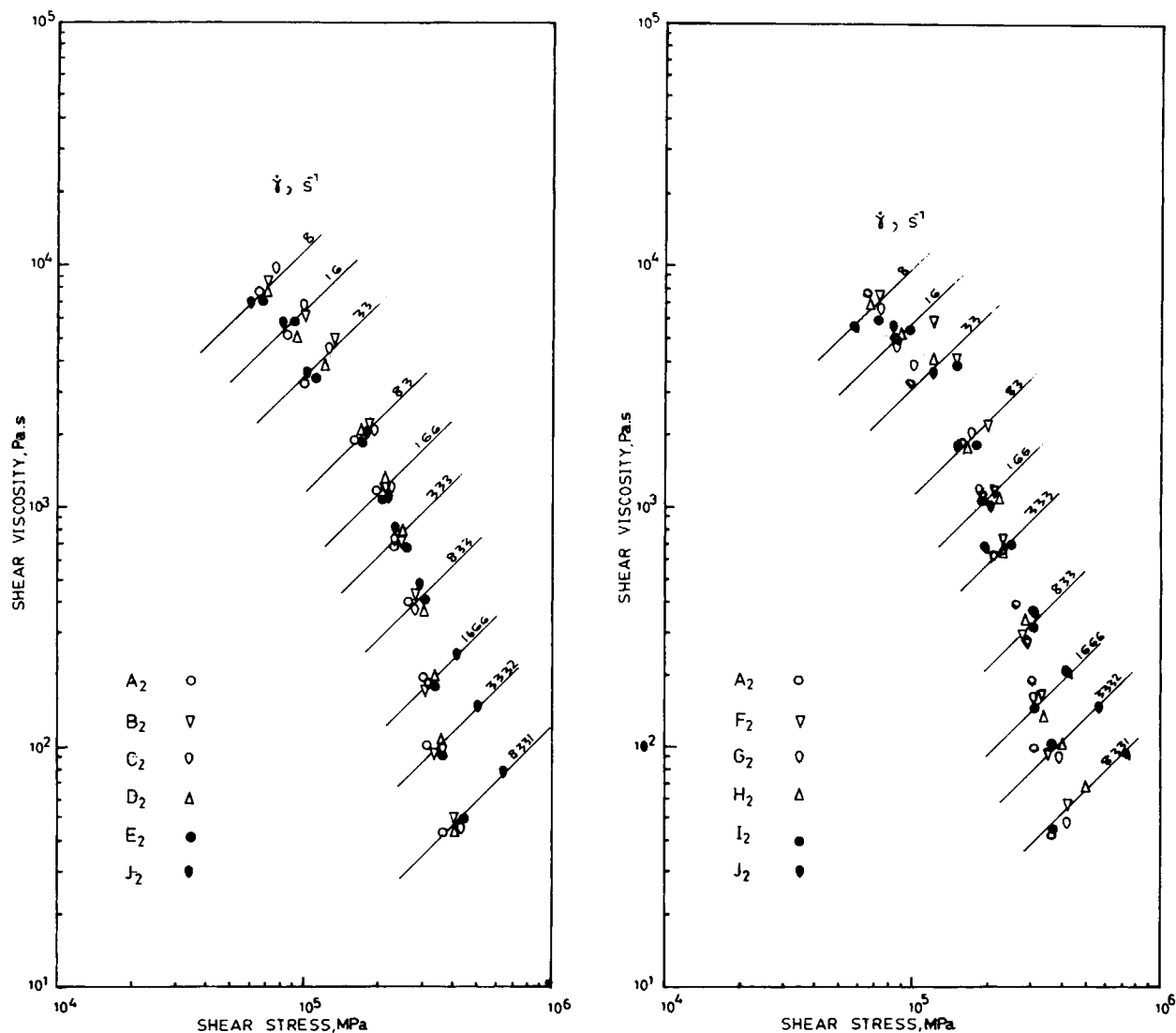


Figure 5 Shear viscosity–shear stress plots for NR–EVA blends having a peroxide cross-link system, at 120°C. The numbers on the solid lines indicate the approximate shear rate at which the viscosity is calculated.

due to the orientation of polymer chains in the direction of shear. In the presence of filler, this alignment becomes more restricted. Therefore, the viscosity increases as filler loading is increased.

Effect of Temperature on Viscosity

Figure 8 illustrates the effect of temperature on the viscosity of NR/EVA blends at different shear rates. As expected, the viscosity decreased with the increase of temperature for all the blends. However, at the low shear rate region, the decrease in viscosity is more predominant than that at the high shear

rate. This may be due to the high residence time of the melt in the barrel of the extruder at low shear rates. It is seen that temperature has a marginal effect on the viscosity at high shear rates.

To further understand the influence of temperature on the viscosity of the blends, Arrhenius plots at a constant shear rate were made (Fig. 9). In this figure, the logarithm of viscosity is plotted as a function of reciprocal temperature. It can be noticed that the points for all the systems lie on straight lines. The activation energies of flow, calculated from the slopes of these lines, are given in Table II. The activation energy of a material provides valuable

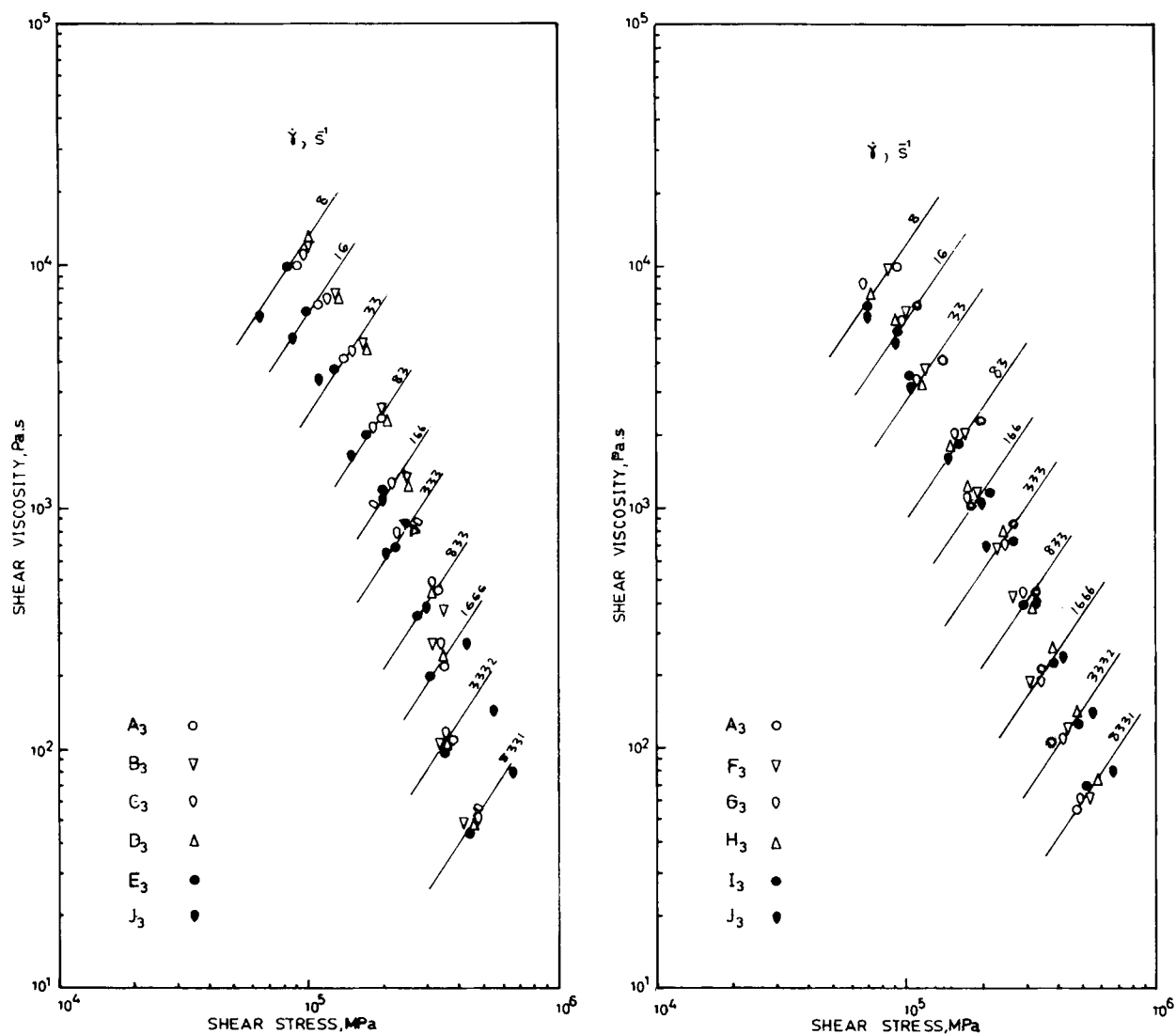


Figure 6 Shear viscosity–shear stress plots for NR–EVA blends having a sulfur cross-link system, at 120°C. The numbers on the solid lines indicate the approximate shear rate range at which the viscosity is calculated.

information on the sensitivity of the material toward the change in temperature. The higher the activation energy, the more temperature-sensitive the material will be. Such information is highly useful in selecting the processing temperature during the shaping process. It can be noticed from Table II that EVA has the maximum value of activation energy and that it is unaffected by the addition of small quantities of NR that remained as domains. However, when the proportion of NR in the blend is more than 40%, where it formed a continuous phase, the activation energy decreased sharply. Therefore, it can be concluded that the viscosity of EVA-rich blends exhibits

greater temperature dependence than do those blends having a higher proportion of NR, especially at higher shear rates.

Flow Behavior Index (n')

The effect of temperature and blend ratio on the flow behavior indices of the samples is given in Table III. The extent of non-Newtonian behavior of polymeric materials can be understood from n' values. Pseudoplastic materials are characterized by n' below 1. Therefore, a high value of n' shows a low pseudoplastic nature of the material. The results in-

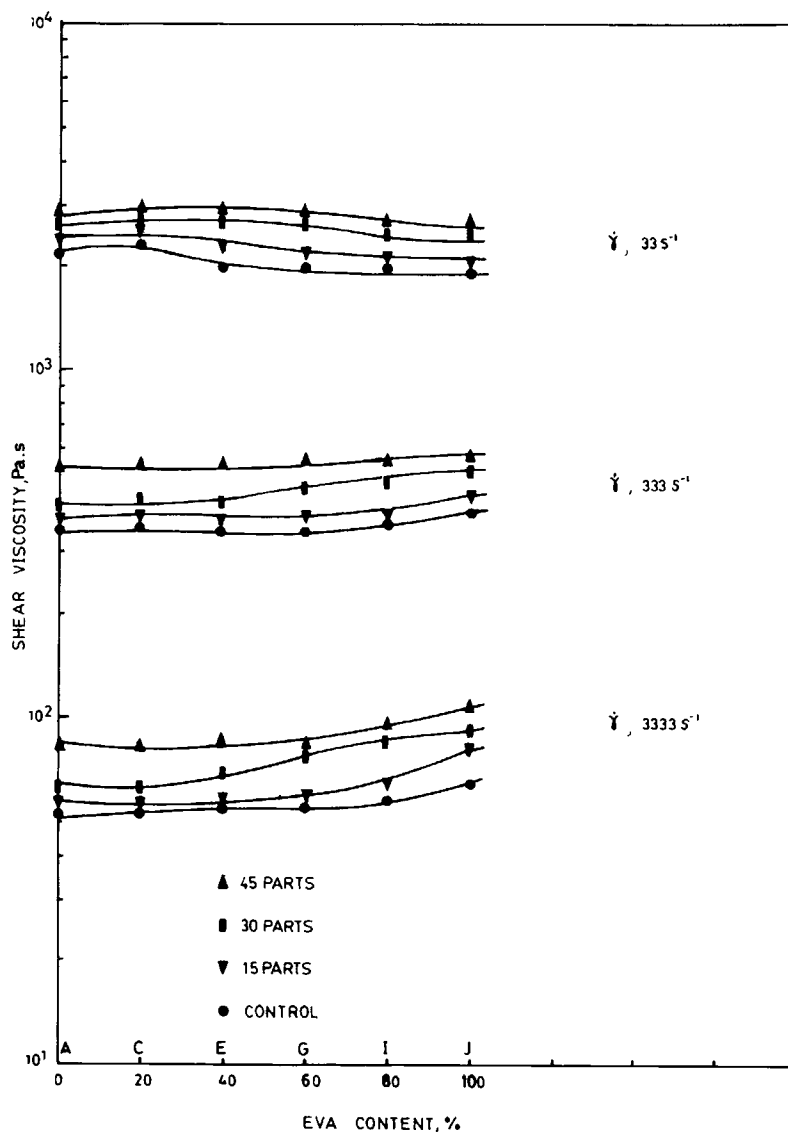


Figure 7 Effect of silica on shear viscosity of NR-EVA blends at three shear rates, at 120°C.

indicate that as the proportion of EVA in the blend is increased n' values also are increased. It can also be noted that in all cases n' values increased with the increase of temperature and this effect is predominant in the case of pure EVA and high EVA blends. Therefore, it can be concluded that the pseudoplastic nature of NR/EVA blends decreased with temperature and that the high EVA blends are more Newtonian than are low EVA blends.

The effect of addition of silica filler on the n' value is given in Table IV. The results show that in all cases the increase of filler loading decreased the n' values. However, the decrease is pronounced in the

case of high EVA blends. This is because silica has more affinity toward the EVA phase.

Melt Elasticity

Properties such as extrudate swell, principal normal stress difference ($\tau_{11} - \tau_{22}$), recoverable shear strain (S_R), and elastic shear modulus (G) characterize the elasticity of polymer melts.

The principal normal stress difference ($\tau_{11} - \tau_{22}$) was calculated from the extrudate swell values and shear stress according to Tanner's equation²⁴:

$$\tau_{11} - \tau_{22} = 2\tau_w [2(de/dc)^6 - 2]^{1/2} \quad (5)$$

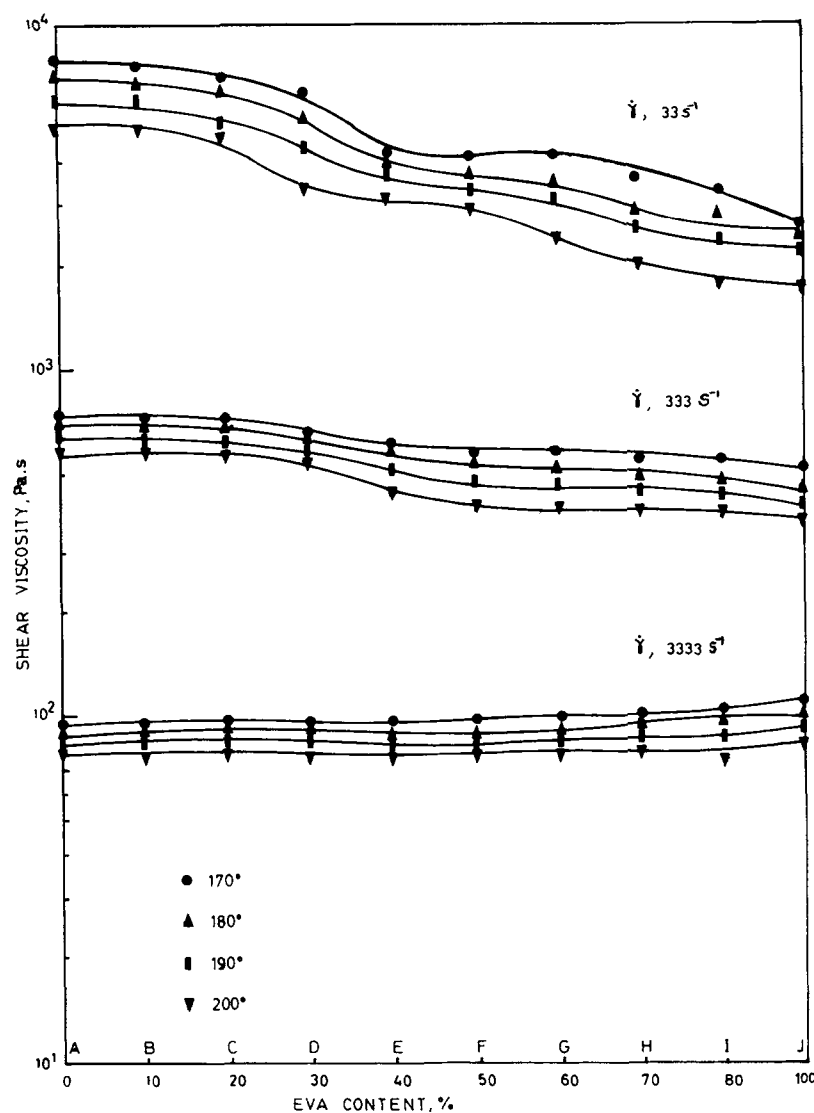


Figure 8 Effect of temperature on shear viscosity of NR-EVA blends at three shear rates.

Recoverable shear strain (S_R) and the apparent shear modulus (G) were calculated from the following equations:

$$S_R = (\tau_{11} - \tau_{22}) / 2\tau_w \quad (6)$$

$$G = \tau_w / S_R \quad (7)$$

Extrudate Swell

As molten polymer flows through the capillary, orientation of the polymer chains occurs due to shear. When the melt emerges from the die, polymer molecules tend to recoil, leading to the phenomenon of

die swell or extrudate swell. This is a relaxation effect due to the recovery of the elastic deformation imposed in the capillary. Factors such as chain branching, stress relaxation, cross-linking, and the presence of fillers and plasticizers control the elastic recovery.

Table V shows the die swell values of uncross-linked NR/EVA blends extruded at 120°C at two shear rates. It can be noticed that EVA shows the lowest die swell due to its low elastic recovery and the addition of NR increases the die swell of the blend. It can also be noted that for a given blend die swell increased with shear rate. This is because at high shear rates the residence time of the material

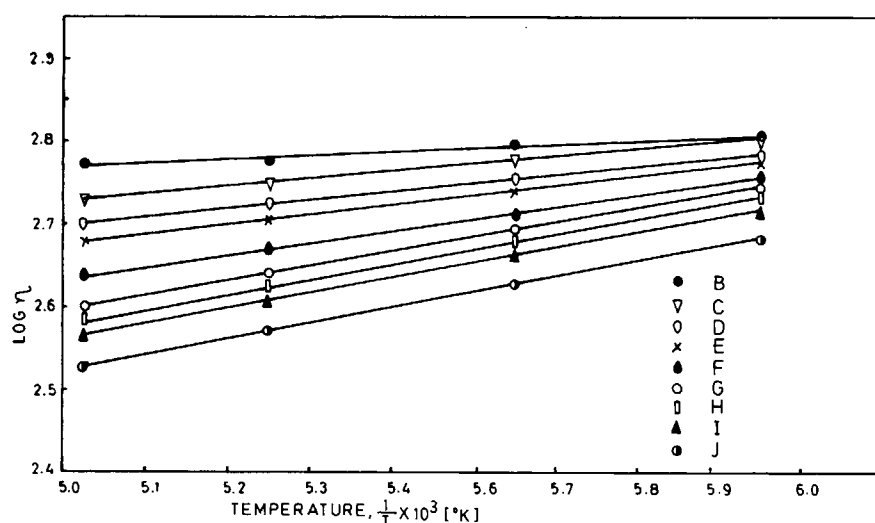


Figure 9 Plots of $\log \eta$ vs. reciprocal of temperature.

in the capillary decreases and, hence, more elastic energy is stored by the polymer. This results in an increase in the die swell. The die swell values of silica-filled blends containing mixed cure systems, extruded at 120°C at a shear rate of 330 s^{-1} , is given in Table VI. It is seen that, in general, die swell decreased with filler loading. Silica filler increases the rigidity and stiffness of the polymer chain. This results in low mobility of the polymer chains under the influence of applied shear stress. Hence, the elastic recovery and, consequently, the die swell decreases with the increase of filler loading.

Deformation of Extrudates

Figure 10 shows the photograph of the blends extruded at two different shear rates. At low shear

rates, most of the extrudates have smooth surfaces. However, at high shear rates, extrudate surfaces exhibit a different extent of distortion. These extrudates have rough surfaces and are of nonuniform diameter. This is associated with melt fracture that occurs at high shear forces where the shear stress exceeds the strength of the melt. The effect of silica filler on the deformation of the cross-linkable extrudate can be understood from Figure 11. It is seen that the addition of silica decreased the deformation of the extrudates.

Principal Normal Stress Difference ($\tau_{11} - \tau_{22}$)

Table VII shows the principal normal stress difference of the blends extruded at a shear rate of 330

Table II Activation Energy for Flow of the Blends

Sample No.	Blend Ratio (NR : EVA)	$\Delta E \times 10^{-3}$ (kcal/mol)
B	90 : 10	0.4145
C	80 : 20	0.4606
D	70 : 30	0.5066
E	60 : 40	0.5066
F	50 : 50	0.6440
G	40 : 60	0.8751
H	30 : 70	0.9212
I	20 : 80	0.9212
J	0 : 100	0.9212

Table III Flow Behavior Index (n') of Blends at Different Temperatures

Sample No.	120°C	170°C	180°C	190°C	200°C
A	0.165	0.195	0.220	0.220	0.237
B	0.171	0.208	0.221	0.230	0.244
C	0.183	0.208	0.238	0.261	0.354
D	0.188	0.218	0.240	0.270	0.360
E	0.194	0.239	0.248	0.275	0.376
F	0.223	0.245	0.270	0.280	0.382
G	0.233	0.309	0.303	0.314	0.398
H	0.245	0.327	0.362	0.358	0.437
I	0.296	0.358	0.360	0.415	0.439
J	0.289	0.371	0.436	0.452	0.484

Table IV Effect of Silica on Flow Behavior Index of NR/EVA Blends at 120°C

Sample No.	Silica Loading (phr)			
	0	15	30	45
A	0.166	0.155	0.142	0.131
C	0.198	0.192	0.175	0.168
E	0.239	0.211	0.174	0.164
F	0.249	0.239	0.194	0.144
G	0.282	0.271	0.260	0.149
I	0.318	0.308	0.279	0.143
J	0.344	0.312	0.281	0.152

s^{-1} . The temperature of extrusion was 120°C. EVA showed the lowest value of principal normal stress difference. Addition of NR increased the normal stress difference of EVA. The higher value of $\tau_{11} - \tau_{22}$ implies higher elasticity of the blends. This is reflected in higher die swell values (Table V).

Recoverable Elastic Shear Stress (S_R)

It has been reported²⁵ that when the stored elastic strain energy of a polymer melt exceeds a critical value the excess amount may be converted into surface free energy yielding distortion to the extrudates. Table VII shows the S_R value of the blends at a shear rate of 330 s^{-1} . The S_R values of the blends increase with the increase in NR content.

Elastic Shear Modulus (G)

The elastic shear modulus of the blends as shown in Table VII indicated that the melt elasticity of EVA is increased by the addition of NR. The elastic

Table V Die Swell of NR/EVA Blends at 120°C

Sample No.	Shear Rate (s^{-1})	
	3330	330
A	1.46	1.19
B	1.61	1.43
C	1.46	1.35
D	1.40	1.26
E	1.36	1.26
F	1.26	1.25
G	1.26	1.24
H	1.25	1.23
I	1.24	1.23
J	1.08	1.03

Table VI Effect of Silica on Die Swell at 120°C and at a Shear Rate of 330 s^{-1}

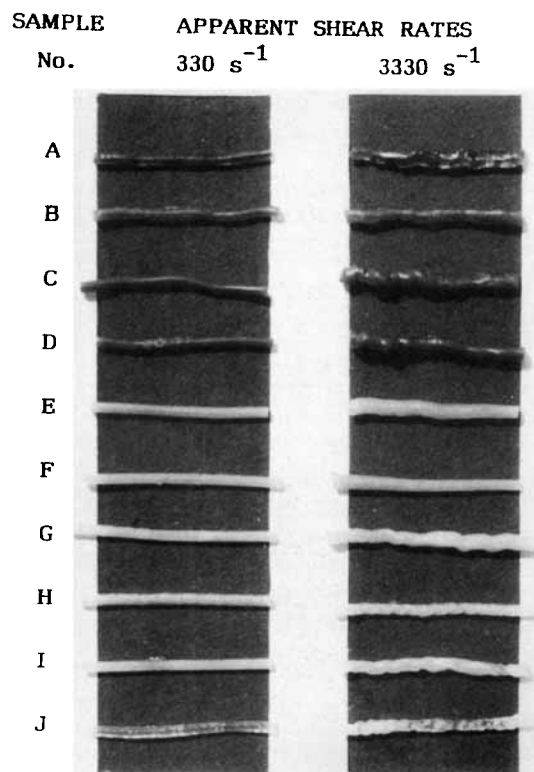
Sample No.	Silica Loading (phr)		
	15	30	45
A ₃ S	1.07	1.06	1.05
C ₃ S	1.07	1.05	1.04
E ₃ S	1.06	1.00	1.00
F ₃ S	1.22	1.12	1.01
G ₃ S	1.12	1.12	1.01
I ₃ S	1.12	1.11	1.01
J ₃ S	1.07	1.06	1.01

shear modulus of the blends containing a higher proportion of EVA was much higher than that in the blends having a lower proportion of EVA.

CONCLUSION

Melt flow studies indicated that NR/EVA blends exhibit pseudoplastic behavior. At the low shear

TEMPERATURE OF EXTRUSION, 120°C

**Figure 10** Extrudate distortion of NR-EVA blends at 120°C, extruded at 330 and 3330 s^{-1} shear rates.

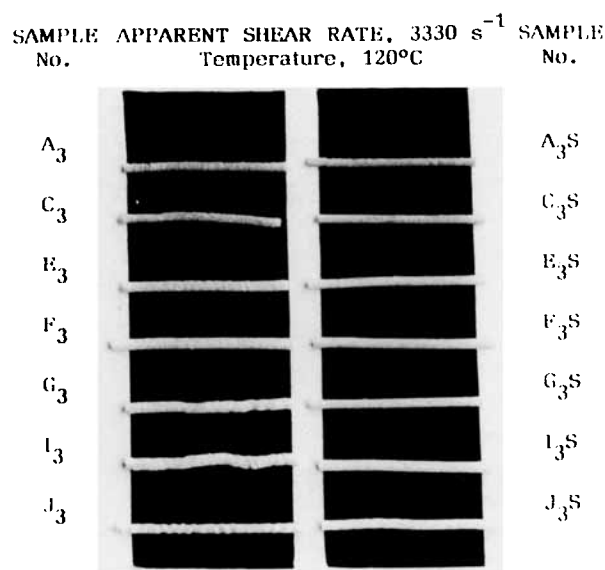


Figure 11 Effect of silica on extrudate distortion of NR-EVA blends, at 3330 s^{-1} shear rate and at 120°C .

stress region, when the content of EVA is less than 40%, the viscosity of the blends showed a positive deviation that is associated with strong interactions among EVA domains. Morphological findings support this view. Addition of silica filler increased the viscosity of the blends. The activation energy of flow of EVA is reduced by the addition of NR. The flow behavior index of the blends decreased with the in-

Table VII Melt Elasticity of NR/EVA Blends Extruded at a Shear Rate of 330 s^{-1} and at 120°C

Sample No.	Parameters		S_R
	$\tau_{11} - \tau_{22}$ (Nm^{-2})	G (Nm^{-2})	
B	23.98×10^5	0.80×10^5	3.86
C	18.47×10^5	0.94×10^5	3.13
D	14.06×10^5	1.17×10^5	2.44
E	13.66×10^5	1.14×10^5	2.44
F	12.68×10^5	1.15×10^5	2.33
G	12.41×10^5	1.18×10^5	2.28
H	12.02×10^5	1.22×10^5	2.21
I	12.01×10^5	1.22×10^5	2.21
J	3.35×10^5	4.38×10^5	0.62

crease of EVA. Addition of natural rubber to EVA increased the melt elasticity of the system.

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