Effects of Blend Ratio and Vulcanizate Powders on the Processability of Silicone Rubber/Fluororubber Blends

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ABSTRACT: While silicone rubber has a much lower shear viscosity than that of fluororubber, the viscosity of silicone rubber/fluororubber blends is closer to that of silicone rubber. All rubber compositions show pseudoplastic behavior. While the viscosity of a 50/50 silicone rubber/fluororubber blend increases on replacement of the silicone rubber by silicone rubber vulcanizate powder (SVP), the effect of fluororubber replacement by the corresponding fluororubber vulcanizate powder (FVP) on the shear viscosity is less pronounced. The difference in viscosity between SVP-replaced silicone rubber and FVP-replaced fluororubber becomes less prominent at higher shear rates. Fluororubber exhibits a higher extrudate die swell than that of silicone rubber. The die swell of the silicone rubber/fluororubber blends is higher than are the figures obtained by the additivity rule. Replacement of constituent rubbers in the blend by the corresponding vulcanizate powders causes an increase in the die swell. While the silicone rubber extrudate surface is smooth, the fluororubber extrudate shows melt fracture. The extrudate surfaces of the silicone rubber/fluororubber blends are similar to that of the silicone rubber extrudate. Replacement of constituent rubbers by the corresponding vulcanizate powders increases the roughness of the extrudate surface, which is more prominent in the case of silicone rubber replacement by SVP. SVP can replace 50% of silicone rubber and FVP can replace 75% of fluororubber in the 50/50 silicone rubber/fluororubber blend. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2377–2387, 2003

Key words: blends; fluoropolymers; silicones; recycling; processing

INTRODUCTION

Waste rubber recycling is of great interest for both environmental and economic reasons. Utilization of waste rubber in virgin rubber depends on the processing characteristics of the rubber compounds, in addition to the final properties of the resulting vulcanizates. Phadke et al.[1] studied the effect of carbon black-reinforced cryoground rubber (CGR) on the melt viscosity of a natural rubber compound. Bhattacharya et al.[2] observed the rheological properties of ground rubber tire (GRT)-filled low-density polyethylene (LDPE). Munstedt[3] investigated the effect of rubber particles on the rheological properties of styrene–acrylonitrile and poly(vinyl chloride). Hamed et al.[4] observed an increase in the Mooney viscosity of a styrene–butadiene rubber (SBR) compound on incorporation of ground rubber. Jacob et al.[5] studied the effect of the addition of ground EPDM vulcanizate on the processability of EPDM compounds.

In contrast to tire rubbers, specialty rubbers have received little attention in regard to waste rubber utilization. In an earlier communication,[6] it has been reported that the constituent polymers in a blend of silicone rubber and fluororubber based on tetrafluoroethylene/propylene/vinylidene fluoride can be partially replaced by the respective vulcanizate powders, where the deterioration in properties is within acceptable limits (say, 10%). For example, in the 50/50 blend of the two polymers, 50% of the silicone rubber and 75% of the fluororubber can be replaced by the corresponding ground vulcanizates. The rubber vulcanizates were chosen to simulate the waste rubbers.

The objective of the present work was to investigate the effects of the blend ratio and replacement of the constituent rubbers on the processability of the 50/50 blend of silicone rubber and fluororubber by the corresponding ground vulcanizates of known compositions. While processability of polymer blends has been studied by several workers,[7–11] there has been no report on the processability of rubber blends where the blend constituents are partially replaced by the respective ground waste rubbers.

EXPERIMENTAL

Materials

Details of the materials used are given in Table I.

Mixing procedure

The blends were prepared in a plasticorder (Brabender Model PLE-330; Brabender OHG, Duisburg,

TABLE I
Details of the Materials Used

Materials	Abbreviated names/symbols	Specifications	Source
Terpolymer of tetrafluoroethylene (40%), propylene (25%), and vinylidene fluoride (35%) (AFLAS 200)	Fluororubber	Specific gravity, 1.55; Mooney viscosity (ML_{1+4}) at 100°C, 85	Asahi Glass Co. (Yokohama, Japan)
Poly(dimethyl-*co*-methyl vinyl siloxane) (grade, SE6075)	Silicone rubber	Specific gravity, 1.21; Mooney viscosity (ML_{1+4}) at 100°C, 60	GE Bayer Silicone Pvt. Ltd. (Bangalore, India)
Dicumyl peroxide	DCP	Purity, 98%; melting point, 39°C	Aldrich Chemical Co. (Milwaukee, WI)
2,4,6-Triallyloxy-1,3,5-triazine	TAC	Active, 97%	Aldrich Chemical Co.
Calcium hydroxide	$Ca(OH)_2$	Laboratory grade	S.d. Fine Chem. Ltd. (Mumbai, India)
Fluororubber vulcanizate powder	FVP	Formulation given in Table II	Laboratory-made
Silicone rubber vulcanizate powder	SVP	Formulation given in Table II	Laboratory-made

Germany) at 80°C and at a rotor speed of 60 rpm. The volume capacity of the plasticorder is 0.06 L. After completion of the mixing, the resulting hot material was sheeted out by passing through the close nip-gap of a two-roll mill at 25°C.

Preparation of blends

The formulations used for the preparation of the blends of silicone rubber and fluororubber are given in Table II. Fluororubber was first charged and sheared for 2 min and then silicone rubber was added and mixed for an additional 2 min. Finally, DCP, TAC, and $Ca(OH)_2$ were added and the mixing was continued for another 3 min.

Preparation of vulcanizate powders

Silicone rubber vulcanizate powder (SVP) was prepared according to the formulation under the silicone rubber/fluororubber blend ratio of 100/0 in Table II. First, silicone rubber was charged and sheared in the plasticorder for 2 min. Then, DCP was added and

TABLE II
Formulations: Blends of Silicone Rubber and Fluororubber

	Mix symbol				
	Silicone rubber/fluororubber (parts by weight)				
Ingredients	0/100[a]	25/75	50/50	75/25	100/0[b]
Fluororubber	100	75	50	25	—
Silicone rubber	—	25	50	75	100
DCP	2.0	2.0	2.0	2.0	2.0
TAC	5.0	3.75	2.5	1.25	—
$Ca(OH)_2$	5.0	3.75	2.5	1.25	—

[a] Formuation for FVP.
[b] Formuation for SVP.

mixed for another 2 min. Next, the resulting hot material was sheeted out in a two-roll mill. Thick sheets (8.5 × 25 × 120 mm) were then prepared by molding at 170°C for 10 min in a hydraulic press at a pressure of 5 MPa. The molded samples were aged for 72 h at 200°C in an air oven. Finally, SVP was prepared by grinding the aged rubber sheets over a silicone carbide wheel of diameter 150 mm, rotating at 2900 rpm, using a bench grinder-type TG 6 (Ralli Wolf Ltd. Mumbai, India). The abraded rubber in the powder form was collected in a specially designed holder placed beneath the grinder wheel.

Fluororubber vulcanizate powder (FVP) was prepared according to the formulation under the silicone rubber/fluororubber blend ratio of 0/100 in Table II. Fluororubber was first charged and sheared for 2 min. Then, DCP followed by TAC and $Ca(OH)_2$ were added and mixed for 3 min. The hot material was sheeted out in a two-roll mill. Finally, FVP was prepared using the same procedure as described above for SVP preparation.

Particle-size distribution

The particle-size distribution and the average particle size of the vulcanizate powders were measured using a light optical microscope (LOM)–ultrasonic technique. The particles were suspended in hexane and subjected to ultrasonic dispersion and examined under an Olympus BH-2 LOM at a magnification of 200×. Images of representative areas were transmitted to an on-line Olympus Cue 2 automated image analysis system (IAS). The individual particles were identified and their respective sizes were measured.

Replacement of silicone rubber in the 50/50 blend by SVP

In the 50/50 silicone rubber/fluororubber blend, silicone rubber was replaced by SVP, according to for-

TABLE III
Formulations: Replacement of Silicone Rubber and Fluororubber in Their 50/50 Blend
by the Corresponding Vulcanizate Powders (SVP or FVP)

	Mix symbol					
	Silicone rubber/SVP/fluororubber/FVP (parts by weight)					
Ingredients	100/0/100/0[a]	75/25/100/0	50/50/100/0	100/0/75/25	100/0/50/50	100/0/25/75
Fluororubber	100	100	100	75	50	25
FVP	—	—	—	25	50	75
Silicone rubber	100	75	50	100	100	100
SVP	—	25	50	—	—	—
DCP	4.0	3.5	3.0	3.5	3.0	2.5
TAC	5.0	5.0	5.0	3.75	2.5	1.25
Ca(OH)$_2$	5.0	5.0	5.0	3.75	2.5	1.25

[a] Same as 50/50 silicone rubber/fluororubber blend in Table II.

mulations given in Table III. First, fluororubber was charged in the plasticorder for 2 min and then silicone rubber was added. After 2 min, SVP was added, followed by DCP, TAC, and Ca(OH)$_2$, and the mixing was continued for another 3 min.

Replacement of fluororubber in the 50/50 blend by FVP

Virgin fluororubber in the 50/50 silicone rubber/fluororubber blend was replaced by FVP according to formulations given in Table III. The mixing procedure was similar to that described above under replacement of silicone rubber in the blend by SVP.

Measurements of rheological properties

The rheological properties of the constituent polymers and their blends were measured using a Monsanto processability tester Model 83077 (Monsanto Co., USA), which is a microprocessor-based automated and programmable capillary rheometer. The measurements were carried out using a capillary having a length-to-diameter ratio of 30:1 and the barrel diameter was 19.06 mm, and length, 100 mm. The melt was allowed to enter into the round capillary die having multiple entry angles of 45° and 60°, which minimize the pressure drop. Thus, the Bagley[12] correction can be assumed to be negligible and, therefore, the apparent shear stress can be taken as equal to the true shear stress. The preheat time used for each sample was 5 min for uniform temperature attainment. The rate of shear variation was performed by autoprogrammimg, by changing the speed of the plunger after a preselected time interval. The extrusion studies were carried out at three different temperatures (viz., 90°, 100°, and 110°C) and at four different shear rates (viz., 919.5, 1226, 1839, and 2145.5 s^{-1}).

The apparent shear stress (τ), apparent shear rate ($\dot{\gamma}$), and apparent shear viscosity (η) were calculated using the following equations[13]:

$$\tau = d_c \Delta P / 4 l_c \tag{1}$$

$$\dot{\gamma} = 32Q / \pi d_c^3 \tag{2}$$

$$\eta = \tau / \dot{\gamma} \tag{3}$$

where ΔP is the pressure drop across the length of the capillary; d_c and l_c, the diameter and length of the capillary, respectively; and Q, the volumetric flow rate of the material.

Flow behavior index and consistency index

The flow behavior index (n) and consistency index (k) were calculated by using the appropriate power law model[13]:

$$\tau = k \, \dot{\gamma}^n \tag{4}$$

where τ and $\dot{\gamma}$ are the shear stress and shear rate, respectively.

Extrudate die swell

After leaving the MPT capillary, the extrudate was allowed to pass a scanning laser device, which mea-
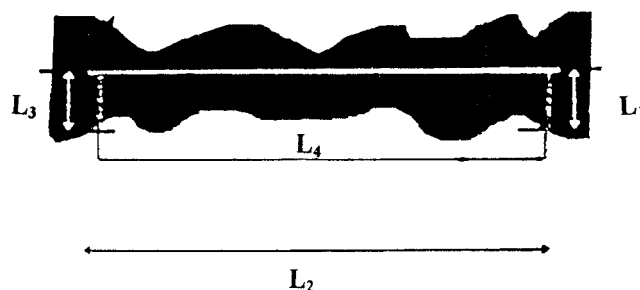

Figure 1 Schematic drawing for the measurement of extrudate roughness.
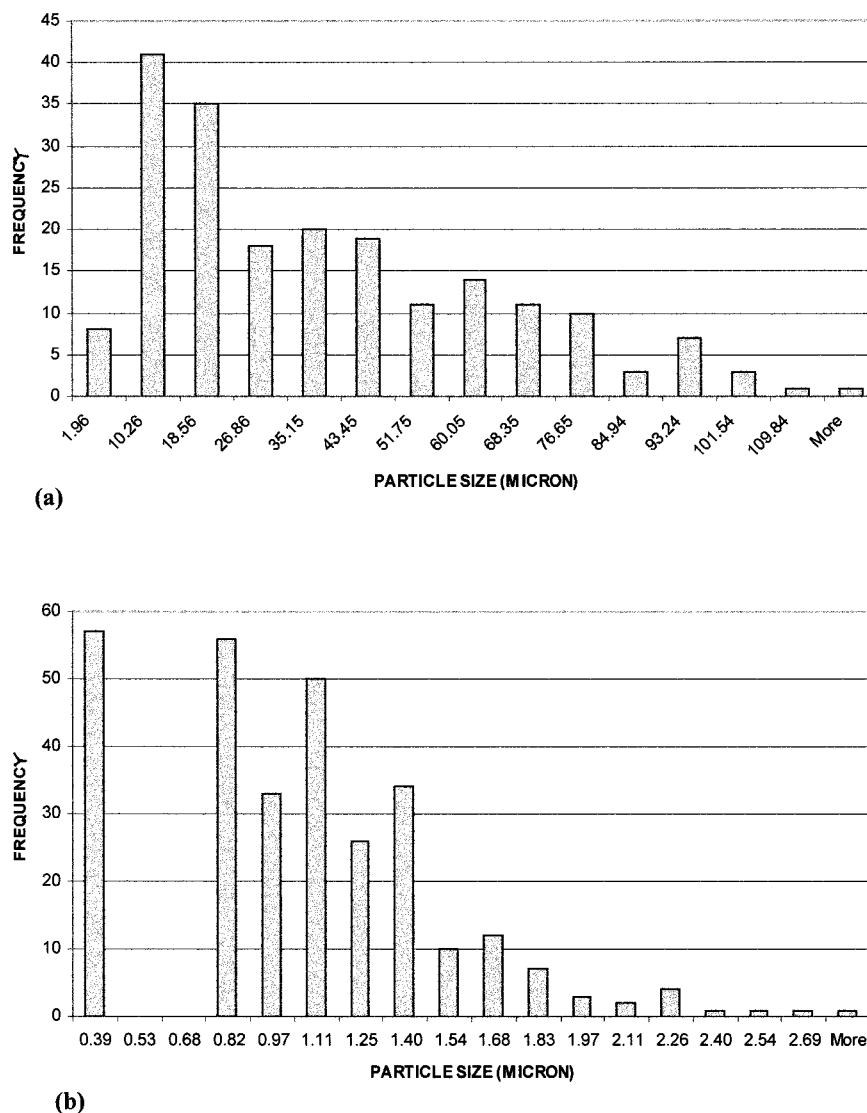
(a)

(b)

Figure 2 Particle-size distribution of (a) SVP and (b) FVP.

sured its average diameter as a percentage of the capillary diameter:

$$\% \text{ Die swell} = 100 \times (d_e - d_c)/d_c \qquad (5)$$

where d_e and d_c are the diameter of the extrudate and capillary, respectively. The swelling index is defined as d_e/d_c.

Extrudate surface morphology

The extrudate surface morphology was examined under a scanning electron microscope (JEOL JSM 5800; JEOL, Peabody, MA), using gold-coated samples. The surface roughness of the extrudate was measured using the technique of Schaal and Coran.[14] The extrudates obtained at 90°C and a shear rate of 919.5 s^{-1} were photographed at 100× magnification, using an optical microscope, Leitz Metallux-3 (Leitz Wetzlar,

Germany). Using an image analysis technique (using the free UTHSCSA Imagetool program developed at The University of Texas Health Science Center at San Antonio, TX), the length (L_2), breadth (L_1 and L_3), perimeter (P), and rough length (L_4) of the extrudate surface were measured:

$$L_4 = P - L_2 - L_1 - L_3 \qquad (6)$$

The extrudate roughness (ER) is defined as

$$\text{ER} = L_4/L_2 \qquad (7)$$

In each case, this procedure was repeated three times in different places over the length of the extrudate and an average extrudate roughness was estimated. The standard deviation of the extrudate roughness measurements was within 0.015. A typical observation of
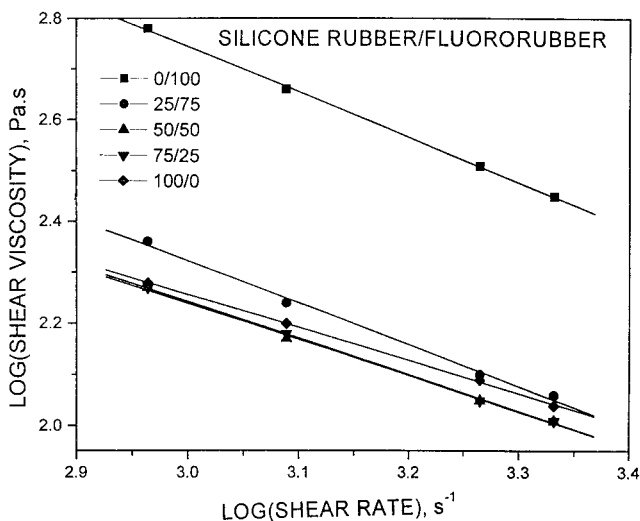
Figure 3 Representative plots of log(shear viscosity) versus log(shear rate) of silicone rubber, fluororubber, and silicone rubber/fluororubber blends at 90°C.
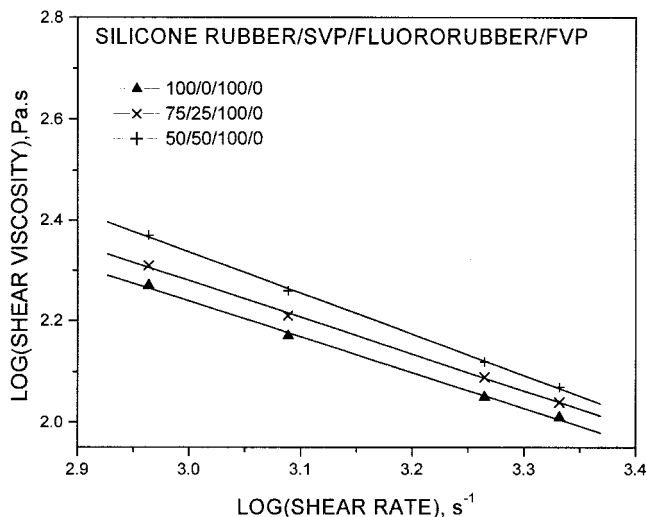

Figure 4 Representative plots of log(shear viscosity) versus log(shear rate) of silicone rubber/SVP/fluororubber/FVP blends, 100/0/100/0, 75/25/100/0, and 50/50/100/0, at 90°C.

an extrudate using the optical microscope is shown in Figure 1.

RESULTS AND DISCUSSION

Particle-size distribution of vulcanizate powders

The particle-size distribution of SVP and FVP are given in Figure 2. It can be seen that the particle-size distribution is broader in the case of SVP, ranging from approximately 2 to 110 μm with the average particle size of 33 μm. FVP produces finer particles with a particle-size distribution varying between 0.4 and 2.7 μm and the average particle size being 1.0 μm.

Non-newtonian behavior

Figures 3–5 show the representative log–log plots of shear viscosity versus the shear rate at 90°C. It is believed that the blend compositions follow the power law model . The shear viscosity decreases with an increasing shear rate, showing the pseudoplastic nature of all compositions. The n and k values are summarized in Table IV. The n value of the non-Newtonian fluids is less than 1. Therefore, a higher value of n indicates a less pseudoplastic behavior or a more Newtonian nature of the polymer melt. The n value of neat silicone rubber is higher than that of neat fluororubber. The n value of silicone rubber/fluororubber blends increases (i.e., pseudoplasticity decreases) with an increasing silicone rubber content in the blend. Replacement of silicone rubber by SVP and fluororubber by FVP in the 50/50 silicone rubber/fluororubber blend has little effect on the n values, except at higher temperatures and a higher level of replacement (i.e., 50% replacement of silicone rubber

by SVP and 75% replacement of fluororubber by FVP) when the n values show a decreasing trend. The k value of neat fluororubber is much higher than that of neat silicone rubber and the temperature has an insignificant effect on k. It is observed that the k values of the silicone rubber/fluororubber blends are closer to silicone rubber and it decreases with an increasing silicone rubber content in the blend. Replacement of silicone rubber and fluororubber in the blend by SVP and FVP, respectively, increases the k values, but the effect is less pronounced in the case of fluororubber replacement. It is apparent that the processability of the blend is controlled more by the silicone rubber
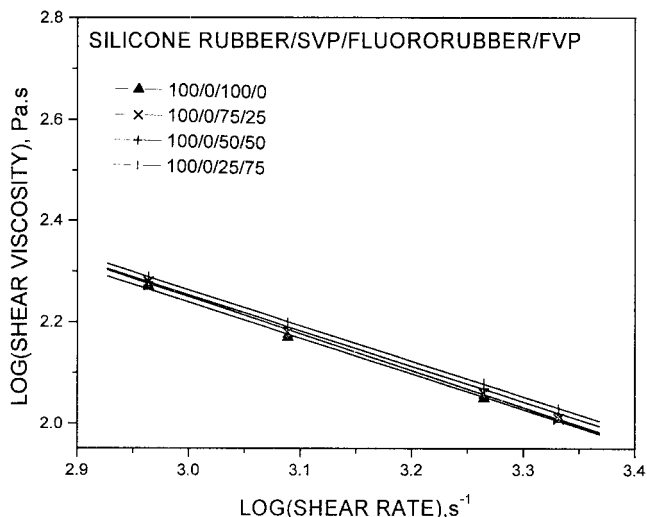

Figure 5 Representative plots of log(shear viscosity) versus log(shear rate) of silicone rubber/SVP/fluororubber/FVP blends, 100/0/100/0, 100/0/75/25, 100/0/50/50, and 100/0/25/75, at 90°C.

<div align="center">

TABLE IV
Values of Flow Behavior Index (n) and Consistency Index (k)

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Mix symbol	n			k (kPa), $\times 10^{-4}$		
	90°C	100°C	110°C	90°C	100°C	110°C
0/100[a]	0.11	0.10	0.10	25.7	27.04	26.42
25/75[a]	0.18	0.18	0.17	5.89	5.40	4.89
50/50[a] or 100/0/100/0[b]	0.29	0.26	0.25	2.25	2.69	2.76
75/25[a]	0.31	0.30	0.30	2.42	2.07	1.72
100/0[a]	0.36	0.34	0.34	1.56	1.58	1.55
75/25/100/0[c]	0.28	0.22	0.21	5.53	4.02	2.84
50/50/100/0[c]	0.26	0.20	0.18	6.41	8.13	5.97
100/0/75/25[c]	0.28	0.25	0.24	2.96	2.89	2.65
100/0/50/50[c]	0.30	0.29	0.24	3.10	2.31	2.28
100/0/25/75[c]	0.30	0.27	0.22	3.71	2.72	2.33

[a] Silicone rubber/fluororubber (parts by weight).
[b] 50/50 silicone rubber/fluororubber blend is same as 100/0/100/0 silicone rubber/SVP/fluororubber/FVP blend (parts by weight).
[c] Silicone rubber/SVP/fluororubber/FVP (parts by weight).

component, as compared to the fluororubber component.

Fluororubber has much higher shear viscosity than that of the silicone rubber at all shear rates and temperatures. Figure 3 represents the variation of shear viscosity with the shear rate at 90°C. The silicone rubber/fluororubber blends possess shear viscosity closer to that of silicone rubber. At a lower shear rate (e.g., 919.5 s^{-1}), the blends containing a high proportion (i.e., 50 and 75%) of silicone rubber show the same shear viscosity as that of silicone rubber and it is marginally less than that of silicone rubber at higher shear rates (>919.5 s^{-1}). But at a low shear rate level, the shear viscosity of the blend is higher than that of silicone rubber, which is supported by the k values as discussed earlier and the Mooney viscosity measurements, reported earlier.[6] However, at all shear rates and temperatures, the shear viscosity of the blend is less than the values calculated by the additivity rule. The negative deviation indicates that there is little interaction between the two rubber phases.

It was reported earlier[6] that the blend morphology consists of a continuous silicone rubber matrix with the fluororubber acting as the dispersed phase. The results of the shear viscosity measurements are also in conformity with these observations. When the silicone rubber in the blend is gradually replaced by SVP, the shear viscosity increases with an increasing SVP loading at all shear rates (Fig. 4). SVP consists of both chainlike aggregated structures consisting of smaller particles as well as larger particles, which, however, do not form an aggregated structure.[6] Replacement of the low viscous silicone rubber, acting as the continuous phase, by SVP causes reduction of the proportion of the continuous matrix and results in higher viscosity. It was observed that beyond 50% replacement of silicone rubber by SVP mixing becomes difficult. Furthermore, the physical properties of the rubber vulca-

nizates decrease substantially beyond 50% replacement of silicone rubber by SVP.[6] It is interesting to note that with an increasing shear rate (from 919.5 to 2145.5 s^{-1}) the shear viscosities of different compositions become closer to each other.

When fluororubber is replaced by FVP, there is a marginal increase in the shear viscosity with FVP loading (Fig. 5). Similar observations were also made in the case of Mooney viscosity measurements.[6] It is believed that the aggregated chainlike structure of FVP breaks down into smaller aggregates and single particles during blending. Highly viscous fluororubber in the blend exists as the dispersed phase and partial replacement of the dispersed phase by the corresponding vulcanizate powder has little effect on the viscosity, the continuous silicone rubber phase remaining unaffected.

Dependence of the viscosity of the blends on the volume fraction of the respective vulcanizate powders
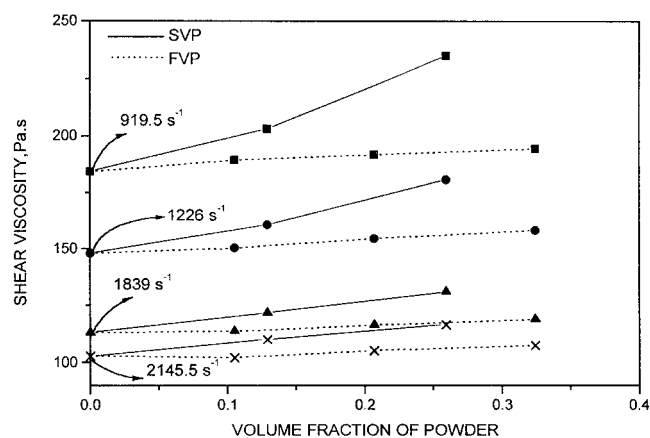

Figure 6 Representative plots of shear viscosity versus volume fraction of vulcanizate powder in the 50/50 silicone rubber/fluororubber blend at 90°C.
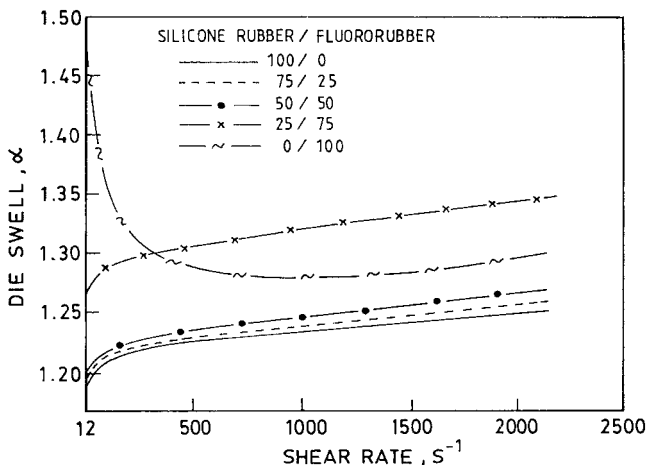
Figure 7 Plots of die swell versus shear rate of silicone rubber, fluororubber, and silicone rubber/fluororubber blends at 100°C.

TABLE V
Dependence of $\Delta\alpha$ on Blend Compositions

Mix symbol[a]	$\Delta\alpha$ 90°C	100°C	110°C
0/100	—	—	—
25/75	1.086	1.075	1.083
50/50	1.042	1.036	1.030
75/25	1.021	1.013	1.012
100/0	—	—	—

[a] Silicone rubber/fluororubber (parts by weight).

at four different shear rates and at 90°C is shown in Figure 6. It is apparent that the increase in the shear viscosity is sharp in the case of silicone rubber replacement and it is more prominent at lower shear rates. At higher shear rates, the increase in the shear viscosity in the case of silicone rubber replacement is less pronounced. When fluororubber is replaced by FVP, the shear viscosity marginally increases and the shear rate has little effect. It is also apparent that at high shear rates the shear viscosity of the blend containing SVP becomes closer to that containing FVP and this is true at all temperatures (90, 100, and 110°C). Expectedly, the shear viscosity of all the compositions decreases with an increasing temperature.

Extrudate die swell

Measurements of the extrudate die swell at different shear rates provide valuable information in under-

standing the processability of rubber compounds. It was reported earlier that the die swell of gum and filled EPDM rubber compounds loaded with ground EPDM waste at a low concentration increases with the shear rate up to the critical shear rate, beyond which the die swell decreases with increase in the shear rate.[5]

Figure 7 shows that neat silicone rubber and neat fluororubber differ from each other in the variation of the die swell with the shear rate used in the study (i.e., in the range between 12.26 and 2145.5 s^{-1}). Silicone rubber is a low viscous material and its die swell slowly increases with the shear rate, but the maximum in the die swell is not reached even at 2145.5 s^{-1}, implying that the critical shear rate is >2145.5 s^{-1} and it could not be determined in the range of the shear rate used. But for the higher viscous fluororubber, the die swell decreases with a shear rate from 12.26 s^{-1} onward, implying that the critical shear rate is <12.26 s^{-1}. The die swell of the silicone rubber/fluororubber blends increases with the shear rate, from 12.26 s^{-1} onward, but beyond a certain shear rate level (i.e., ~10^3 s^{-1}), the changes of the die swell with the shear rate are marginal. Thus, the critical shear rate of the blends also could not be determined in the range of the shear rate used. At all shear rates, fluororubber
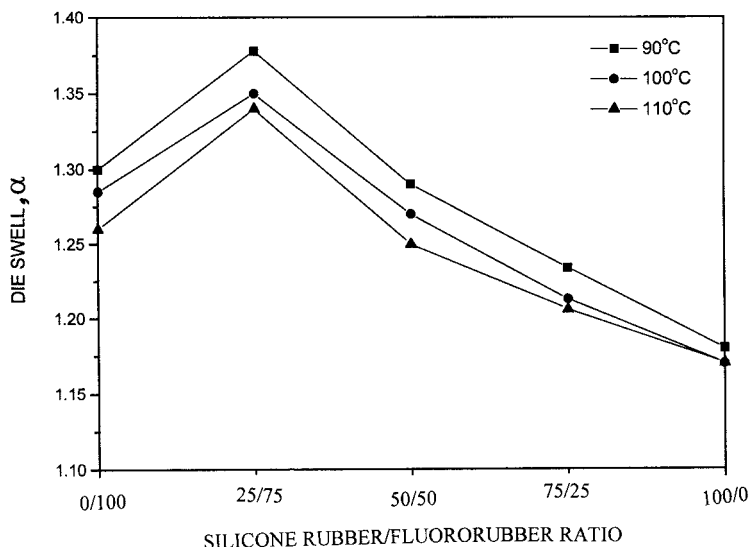

Figure 8 Plots of die swell versus silicone rubber/fluororubber ratio in the blend at (a) 90°C, (b)100°C, and (c) 110°C.
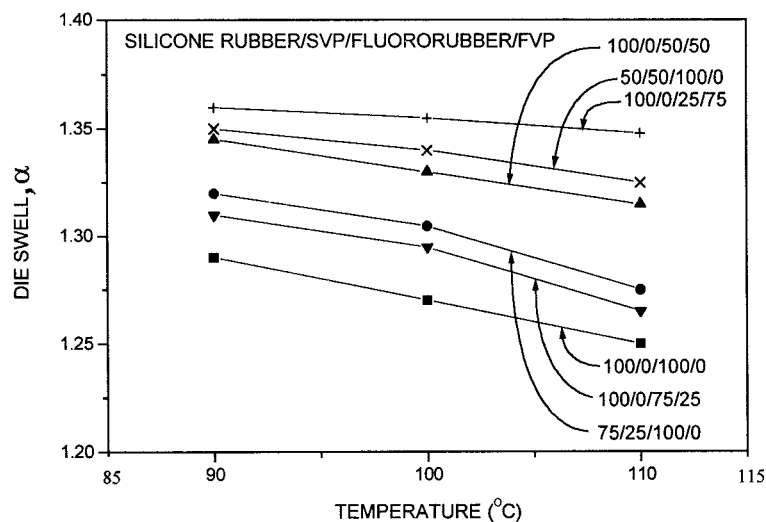
Figure 9 Plots of die swell versus temperature at a shear rate of 919.5 s^{-1}.

shows a higher die swell than that of the silicone rubber. The effect of the shear rate in the range of 919.5 to 2145.5 s^{-1} on the die swell of all compositions is insignificant.

Figure 8 shows the effect of the blend ratio on the die swell of the silicone rubber/fluororubber blend at three different temperatures and at a shear rate of 919.5 s^{-1}. It was found that the die swell (α) of the blends is much higher than are the values calculated by the logarithmic additivity rule:

$$\ln \alpha_{\text{cal}} = \sum_{i=1}^{2} w_i \ln \alpha_i \qquad (8)$$

where w and α are the weight fraction and swelling index of the constituent polymers, respectively. The deviation in the swelling index of the blends, $\Delta\alpha$, as compared to the logarithmic additivity rule can be expressed as

$$\ln \Delta\alpha = (\ln \alpha_{\text{expt}} - \sum_{i=1}^{2} w_i \ln \alpha_i) \qquad (9)$$

$\Delta\alpha$ values are also given in Table V. The occurrence of the positive deviation in the die swell may be explained in terms of the morphology of the blends. Both rubber phases in a blend are viscoelastic in nature and, therefore, they store part of the energy supplied to them as they enter the capillary. However, during flow, the dispersed phase would dissipate less energy than would the continuous phase, which wets the passage wall. Therefore, the total recoverable energy in a two-phase system containing deformable particles would be greater than in a single-phase system or a two-phase system containing barely deformable particles.[15] It has been shown earlier that, in the blend of silicone rubber and fluororubber, fluororubber is dis-

persed in a continuous matrix of silicone rubber at all compositions. The volume fraction of deformable particles increases with an increasing fluororubber content in the blend. The higher the volume fraction, the higher is the elastic energy stored during capillary flow. For this reason, the 25/75 silicone rubber/fluororubber blend exhibits a maximum positive deviation in the die swell than that of the other compositions.

With increasing replacement of silicone rubber and fluororubber in the 50/50 silicone rubber/fluororubber blend by the respective vulcanizate powders, the proportion of the elastic component in the blend increases, which results in a higher die swell of the blends. At a similar replacement level, the die swell for silicone rubber replacement is higher than that for fluororubber replacement. In the case of silicone rubber replacement, the low viscous phase is substituted

TABLE VI
Dependence of ER on Blend Composition

Mix symbol	ER
0/100	1.34
25/75[a]	1.21
50/50[a] or 100/0/100/0[b]	1.07
75/25[a]	1.07
100/0[a]	1.08
75/25/100/0[c]	1.22
50/50/100/0[c]	1.43
100/0/75/25[c]	1.21
100/0/50/50[c]	1.25
100/0/25/75[c]	1.30

[a] Silicone rubber/fluororubber (parts by weight).
[b] 50/50 silicone rubber/fluororubber blend is same as 100/0/100/0 silicone rubber/SVP/fluororubber/FVP blend (parts by weight).
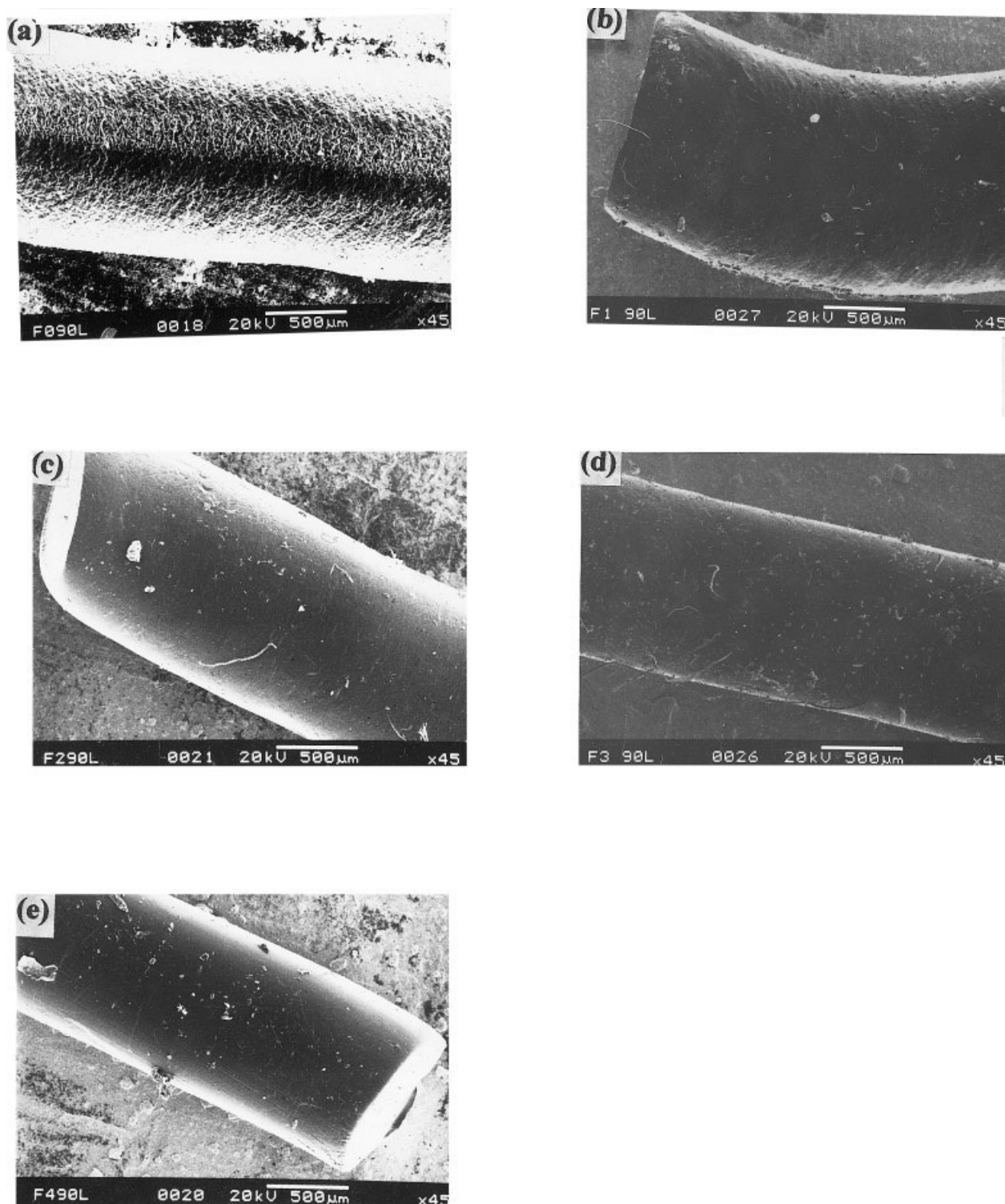[c] Silicone rubber/SVP/fluororubber/FVP (parts by weight).

Figure 10 SEM photomicrographs ($\times$45) of extrudate surfaces of silicone rubber/fluororubber blends: (a) 0/100; (b) 25/75; (c) 50/50; (d) 75/25; (e) 100/0. Extrusion done at a shear rate of 919.5 s^{-1} and 90°C.

by the elastic SVP component, whereas in the case of fluororubber replacement, the highly viscous fluororubber is substituted by the elastic FVP component. For silicone rubber replacement, the proportion of the continuous matrix diminishes and, consequently, the volume fraction of deformable particles increases with an increasing level of replacement, but in the case of fluororubber replacement, the proportion of the continuous matrix remains unchanged. With increasing temperature, the die swell decreases marginally (Fig. 9) for all compositions. The changes of the die swell in the shear-rate range of 919.5 to

2145.5 s^{-1} are insignificant. Jacob et al.[5] reported that the temperature and shear rate had little effect on the die swell of EPDM compounds containing a high loading of ground EPDM waste.

Extrudate surface morphology

Table VI shows the ER based on image analysis, with a higher ER corresponding to a greater extent of roughness. The results are in conformity with the SEM photomicrographs discussed below.

Figures 10–12 show typical SEM photomicrographs of the extrudate surfaces of different compositions. Figure 10 shows that silicone rubber forms a smooth extrudate surface, while the fluororubber forms a rough extrudate surface. The blend extrudates, in general, show the characteristics of the silicone rubber extrudate surface. However, at a high fluororubber content (i.e., 25/75 silicone rubber/fluororubber), the blend shows a tendency for melt fracture. The extrudate surface of 50/50 and 75/25 silicone rubber/fluororubber blend compositions are smooth as silicone
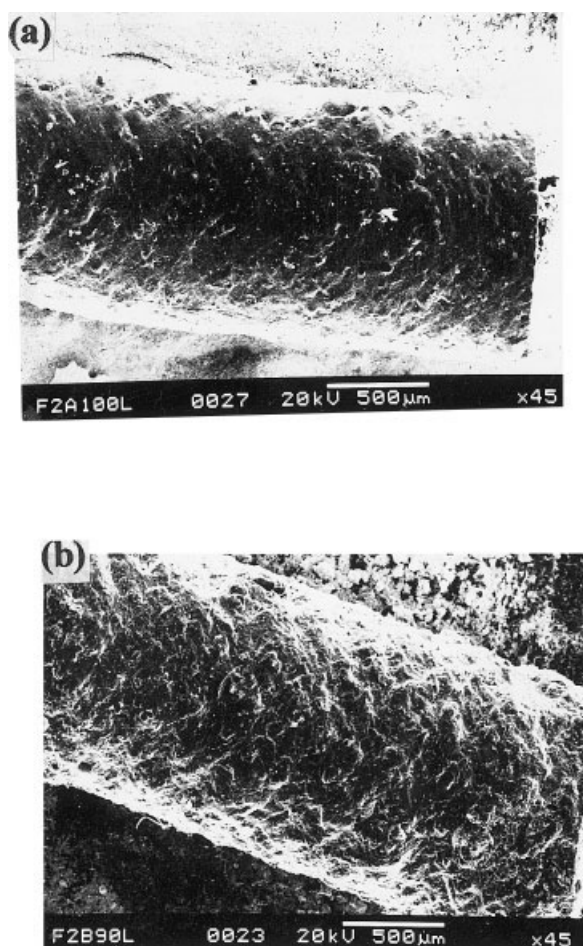

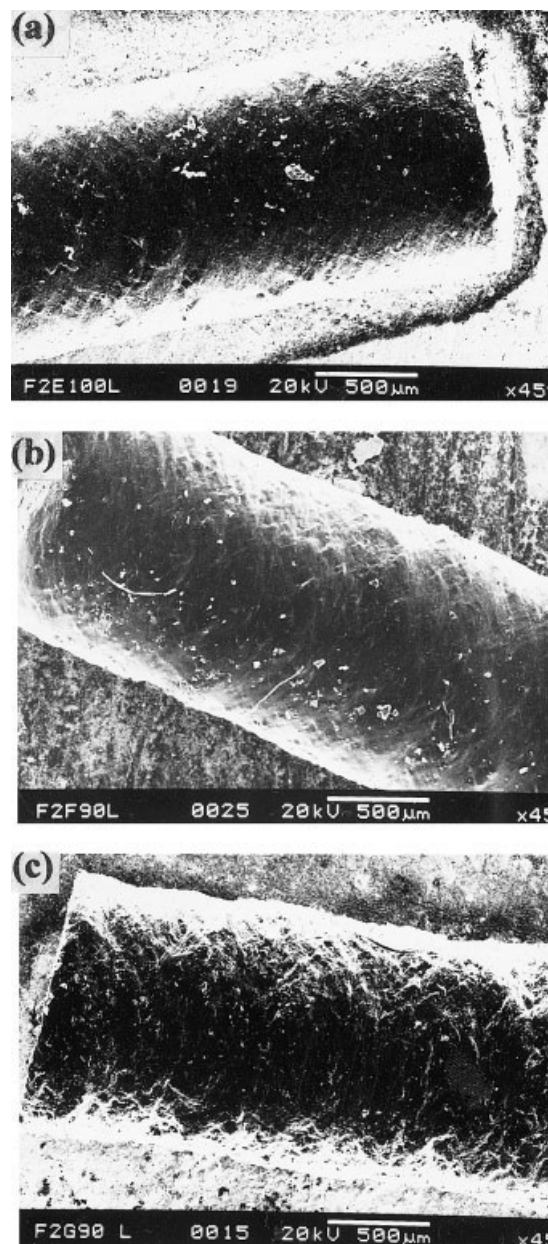**Figure 12** SEM photomicrographs (×45) of extrudate surfaces of silicone rubber/SVP/fluororubber/FVP blends: (a)100/0/75/25; (b)100/0/50/50; (c) 100/0/25/75. Extrusion done at a shear rate of 919.5 s^{-1} and 90°C.

rubber extrudate and devoid of melt fracture. It is believed that melt fracture occurs in the case of fluororubber since the experimental shear rate is above the critical shear rate. This type of distortion of the extrudate surface of fluororubber can be eliminated by blending with silicone rubber, when the experimental shear rate falls below the critical shear rate.

Figure 11 shows that the replacement of silicone rubber in the 50/50 blend of silicone rubber and fluororubber by SVP makes the extrudate surface rougher, the degree of roughness increasing with an increasing level of replacement. Figure 12 shows that

Figure 11 SEM photomicrographs (×45) of extrudate surfaces of silicone rubber/SVP/fluororubber/FVP blends: (a) 75/25/100/0; (b) 50/50/100/0. Extrusion done at a shear rate of 919.5 s^{-1} and 90°C.

the extrude surface becomes rougher on increasing of the fluororubber replacement by FVP, but the extent of roughness is less prominent in the fluororubber replacement, as compared to the silicone rubber replacement by SVP and the effect is prominent at a higher level of replacement. As discussed earlier, in the case of the fluororubber replacement, the proportion of the continuous matrix remains unchanged, while it decreases in the case of the silicone rubber replacement by SVP.

CONCLUSIONS

1. Silicone rubber has much lower shear viscosity than that of fluororubber. The shear viscosity of the 50/50 silicone rubber/fluororubber blend is closer to that of silicone rubber. The shear viscosity of the blend increases with an increasing level of silicone rubber replacement by SVP. The effect of fluororubber replacement in the blend by FVP on the shear viscosity is marginal. All the compositions are pseudoplastic in nature.

2. The fluororubber shows a higher die swell than that of silicone rubber. The extrudate die swell of silicone rubber/fluororubber blends are higher than the values calculated by logarithmic additivity rule. On increasing the level of replacement of the constituent rubbers in the 50/50 blend by the respective vulcanizate powders, the die swell increases. The increase in the die swell is more prominent in the case of silicone rubber replacement by SVP, as compared to fluororubber replacement by FVP.

3. The results of image analysis of the extrudate surface and SEM photomicrographs reveal that the extrudate surfaces of silicone rubber/fluororubber blends are smooth and are similar to that of the silicone rubber extrudate. The fluororubber extrudate surface shows roughness and melt fracture. With increasing replacement of the virgin rubber in the 50/50 blend by vulcanizate powder, the smoothness of the extrudate

surface decreases, and this effect is more prominent in the case of silicone rubber replacement by SVP.

In conclusion, the processability of fluororubber can be improved on blending with silicone rubber. A high level of replacement of virgin rubbers in the blend by the corresponding vulcanizate powders causes difficulty in processing and this effect is more pronounced in the case of silicone rubber replacement by SVP than in fluororubber replacement by FVP.

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