

Replacement of Virgin Rubbers by Waste Ground Vulcanizates in Blends of Silicone Rubber and Fluororubber Based on Tetrafluoroethylene/Propylene/Vinylidene Fluoride Terpolymer

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ABSTRACT: This study reports the results of investigations on blends of silicone rubber and fluororubber based on tetrafluoroethylene/propylene/vinylidene fluoride terpolymer and the effects of replacement of silicone rubber and/or fluororubber in their 50/50 blend by the respective vulcanizate powders of known compositions. To simulate the aging condition of factory wastes, the silicone rubber or fluororubber vulcanizates were aged for 72 h at 200°C and then converted into powder by mechanical grinding. The fluororubber vulcanizate powder (FVP), mostly spherical in shape with average diameter varying between 2 and 10 μm , exists in a highly aggregated state displaying chainlike structures that, however, break down during blending with virgin rubbers. The silicone rubber vulcanizate powder (SVP) is irregular in shape, with larger particles in the range of 30–100 μm , and the smaller particles exist in highly aggregated chainlike structures, as in the case of FVP, which break down during milling to mostly spherical particles of 2–10 μm in diameter. Measurements of physical properties reveal that the blends of silicone rubber and fluororubber are technologically compatible. SEM photomicrographs of THF-etched samples show the biphasic structure of the blends, in which the fluororubber forms the dispersed phase in a continuous silicone rubber matrix of lower viscosity. Replacement of silicone rubber in the 50/50 silicone rubber/fluororubber blend by its vulcanizate powder (SVP) increases the Mooney viscosity, but replacement of fluororubber in the blend by its vulcanizate powder (FVP) has little effect on the Mooney viscosity. Monsanto rheometric studies reveal that replacement of silicone rubber by SVP or fluororubber by FVP in the 50/50 silicone rubber/fluororubber blend increases the minimum rheometric torque but decreases the maximum torque, and the effect is more pronounced in the case of SVP. Furthermore, the replacement of silicone rubber in the blend by SVP causes a decline in the physical properties (25% replacement causing about 10% decline in properties, for example), whereas even 75% replacement of fluororubber by FVP has little effect on the physical properties. When both silicone rubber and fluororubber are partially replaced by SVP and FVP in the same blend, properties of the resulting blend composition are controlled more by SVP incorporation, whereas fluororubber replacement has only a marginal effect on blend properties. It is evident from dynamic mechanical spectra that the blends are immiscible in all compositions and addition of SVP or FVP does not affect the glass–rubber transitions of the constituent polymers. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2326–2341, 2001

Key words: rubber recycling; ground rubber vulcanizates; silicone rubber; fluororubber; silicone rubber/fluororubber blend

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INTRODUCTION

The large-scale discarding of factory wastes and worn-out rubber products contribute to the mounting solid waste disposal problem. Research on recycling of waste rubbers has been undertaken by several researchers for both environmental and economic reasons. A potentially attractive method is to grind the vulcanized rubber and use the resultant powder as a compounding ingredient or as a replacement for raw polymer.^{1–3} Ground rubber powder can be produced by cryogenic grinding, ambient grinding, and wet ambient grinding. Rothermeyer⁴ discussed the effects of grinding and sieving methods on the particle size and structure of powders obtained from waste rubber as well as the effects of different powders on the physical properties of rubber vulcanizates. Improvement in physical properties can be attained by reduction of particle size of the powder and its surface modification.^{5,6}

Phadke et al.^{7–9} studied the effects of addition of cryoground rubber (CGR) powder in unfilled and carbon black-filled natural rubber (NR) compounds. Addition of CGR causes a decrease in Mooney scorch time, optimum cure time, and reversion time, and shows a detrimental effect on most of the vulcanizate properties such as tensile strength, flex, heat buildup, and set and abrasion resistance. The tear strength, however, is not adversely affected by CGR. Addition of reinforcing carbon black makes up the losses in physical properties. Naskar et al.¹⁰ studied the effect of ground rubber tire (GRT) particles of different sizes in a NR compound. Smaller particles contain less amounts of polymer but higher amounts of fillers (carbon black, silica) and metals (Cu, Mn, Fe). Accordingly, a NR compound containing smaller GRT particles shows enhanced physical properties but poorer aging characteristics. Fesus and Eggleton¹¹ described a proprietary product, Tirecycle, which is based on polymeric surface treatment of ground rubber that, when incorporated into cured rubber, enhances its ability to form a chemical bond with uncured rubber matrix during vulcanization. Surcrum is the trade name of a surface-activated crumb rubber developed by Vredestein Rubber Recycling.¹² The surface activation is done by two steps, grinding and activation. In the second step, a crosslinkable surface layer consisting of a polymer and a curing system is added to the rubber powder. The coating is specific to the base polymer. Surcrum is suitable for use as a compound substitute.

Han¹³ studied the effects of GRT on mixing behavior and curing characteristics of NR and SBR compounds and the physical properties of their vulcanizates. With increasing particle size and loading of GRT, the mechanical strength of the vulcanizates decreases. Gibala and Hamed¹⁴ observed a decrease in scorch time and maximum rheometer torque when ground vulcanizates were added to SBR compounds. Suma and Rani¹⁵ mixed butyl (IIR) tube reclaim (TR) with carbon black-filled NR compounds at various proportions and observed that the blend containing a low percentage of TR displayed improved aging resistance and improved processability without much reduction in mechanical properties. Aziz and Amu¹⁶ reported utilization of reclaimed rubber from latex gloves as replacement of virgin rubber. Fesus¹⁷ studied the use of ground scrap rubber from compounds based on specialty elastomers in compounds based on general-purpose rubber. Ghosh et al.¹⁸ reported that incorporation of silicone vulcanizate powder into virgin silicone rubber, even at a loading of 60 phr, caused marginal changes in physical properties.

This study reports the results of investigations on preparation of silicone rubber/fluororubber blend and replacement of the virgin polymers in the blend by the ground silicone rubber and/or fluororubber vulcanizates of known compositions. The fluororubber is based on tetrafluoroethylene/propylene/vinylidene fluoride terpolymer. The rubber vulcanizate powders were chosen as models for the corresponding waste rubbers.

EXPERIMENTAL

Materials

Details of the materials used are given in Table I.

Preparation of Silicone Rubber Vulcanizate Powder (SVP)

Silicone rubber was mixed with 2 phr of DCP according to the formulation silicone rubber/fluororubber, 100/0 (Table II) in a plasticorder (Brabender model PLE-330; Brabender OHG, Duisburg, Germany), at 80°C and a rotor speed of 60 rpm. First, silicone rubber was sheared in the plasticorder for 2 min. Then, DCP was added and mixed for 2 min. The 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

Table I Details of the Materials Used

Material	Abbreviated Names/Symbols	Specifications	Source
Terpolymer of tetrafluoro ethylene (40%), propylene (25%) and vinylidene fluoride (35%) (AFLAS 200)	Fluororubber	Specific gravity, 1.55; Mooney viscosity (ML_{1+4}) at 100°C, 85; light brown color	Asahi Glass Co., Yokohama, Japan
Poly dimethyl- <i>co</i> -methyl vinyl siloxane (grade, SE6075)	Silicone rubber	Specific gravity, 1.21; Mooney viscosity (ML_{1+4}) at 100°C, 60; appearance, transparent	GE Bayer Silicone (India) Pvt. Ltd., Bangalore, India
Dicumyl peroxide	DCP	Purity, 98%; melting point, 39–41°C	Aldrich Chemicals Company, Milwaukee, WI
2,4,6-Triallyloxy-1,3,5-triazine	TAC	Active, 97%	Aldrich Chemicals Company
Calcium hydroxide	Ca(OH) ₂	Laboratory grade	S.D. Fine Chemicals Ltd. Mumbai, India
Tetrahydrofuran	THF	Laboratory reagent; boiling point, 66°C; specific gravity, 0.89	S.D. Fine Chemicals Ltd., Mumbai, India
Fluororubber vulcanizate powder	FVP	Formulations given in Table II	Laboratory made
Silicone rubber vulcanizate powder	SVP	Formulations given in Table II	Laboratory made

MPa. The samples were then aged in an oven at 200°C for 72 h. Finally, SVP was prepared by grinding the thick rubber sheets over the silicone carbide wheel of diameter 150 mm, rotating at 2900 rpm, using a bench grinder (Type TG6; Ralli Wolf Ltd., Mumbai, India). The abraded rubber in the powder form was collected in a specially designed holder placed beneath the grinding wheel.

Preparation of Fluororubber Vulcanizate Powder (FVP)

Fluororubber vulcanizate powder was prepared according to the formulation silicone rubber/flu-

rorubber, 0/100 (given in Table II). First, fluororubber was sheared for 2 min in the Brabender plasticorder at 80°C and a rotor speed of 60 rpm. Then DCP, followed by the coagent (TAC) and Ca(OH)₂, were added and mixed for 3 min. The hot mix was sheeted out in a two-roll mill. The thick sheets (8.5 × 25 × 120 mm) were prepared by molding at 170°C for 15 min in a hydraulic press at a pressure of 5 MPa. The samples were then aged in an oven at 200°C for 72 h. Finally, FVP was prepared by using the same grinder and following the same procedure as discussed under the preparation of SVP.

Table II Formulations Showing Blends of Silicone Rubber and Fluororubber

Ingredients	Mix Symbol				
	Silicone Rubber/Fluororubber (Parts by Weight)				
	0/100	25/75	50/50	75/25	100/0
Silicone rubber	—	25	50	75	100
Fluororubber	100	75	50	25	—
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	—

Table III Formulations Showing Replacement of Silicone Rubber and Fluororubber in their 50/50 Blend by the Corresponding Vulcanizate Powders (SVP and/or FVP)

Ingredient	Mix Symbol								
	Silicone Rubber/SVP/Fluororubber/FVP (Parts by Weight)								
	100/0/100/0 ^a	75/25/100/0	50/50/100/0	25/75/100/0	100/0/75/25	100/0/50/50	100/0/25/75	100/0/0/100	50/50/50/50
Silicone rubber	100	75	50	25	100	100	100	100	50
SVP	—	25	50	75	—	—	—	—	50
Fluororubber	100	100	100	100	75	50	25	0	50
FVP	—	—	—	—	25	50	75	100	50
DCP	4.0	3.5	3.0	2.5	3.5	3.0	2.5	2.0	2.0
TAC	5.0	5.0	5.0	5.0	3.75	2.5	1.25	—	2.5
Ca(OH) ₂	5.0	5.0	5.0	5.0	3.75	2.5	1.25	—	2.5

^a Same as silicone rubber/fluororubber 50/50 blend of Table II.

Preparation of Blends

Silicone Rubber/Fluororubber Blends

Formulations used for preparation of the blends are given in Table II. The blending of fluororubber with silicone rubber was done in the Brabender plasticorder at 80°C and a rotor speed of 60 rpm. First, fluororubber was 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 mixed for another 3 min. After the mixing was over, the hot material was sheeted out in a two-roll mill at 25°C.

Replacement of Virgin Silicone Rubber in Blend by SVP

In the 50/50 silicone rubber/fluororubber blend, the virgin silicone rubber was replaced by SVP according to the formulations given in Table III. First, fluororubber was sheared in the Brabender plasticorder for 2 min at 80°C and a rotor speed of 60 rpm. Silicone rubber was then added and after 2 min SVP was mixed with the virgin rubbers. Finally, DCP, TAC, and Ca(OH)₂ were added and mixed for another 3 min. Then the hot material was sheeted out in a two-roll mill.

Replacement of Virgin Fluororubber in Blend by FVP

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

Replacement of Both Virgin Silicone Rubber and Fluororubber in Their 50/50 Blend by SVP and FVP

In the blend, both silicone rubber and fluororubber were replaced by SVP and FVP, respectively,

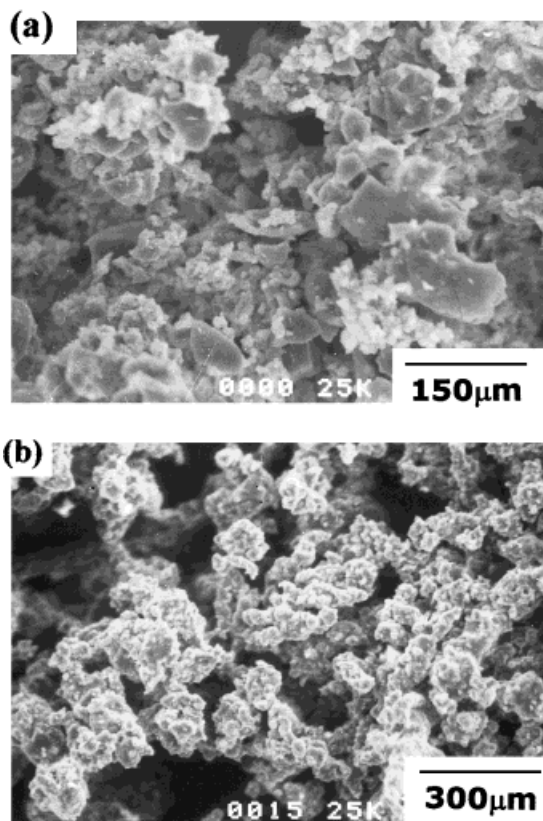


Figure 1 SEM photomicrographs of (a) silicone rubber vulcanizate powder and (b) fluororubber vulcanizate powder.

Table IV Results of Mooney Viscosity and Monsanto Moving Die Rheometric Studies of Silicone Rubber/Fluororubber Blends

Mix Symbol ^a	Mooney Viscosity Measurements at 120°C		Monsanto Rheometry (MDR 2000) at 170°C		
	Mooney Viscosity (ML ₁₊₄)	Mooney Scorch Time (min)	ΔTorque (dN · m)	Rate Constant of Curing (min ⁻¹)	Optimum Cure Time (min)
0/100	92	16	2.2	0.43	5.0
25/75	61 (76) ^b	8	5.5	0.73	3.2
50/50	42 (61) ^b	7	22.1	2.41	1.5
75/25	33 (45) ^b	8	25.0	3.76	1.0
100/0	29	11	18.8	3.88	1.0

^a Silicone rubber/fluororubber (parts by weight).

^b Values in parentheses stand for the calculated Mooney viscosity values.

according to the formulation silicone rubber/SVP/fluororubber/FVP, 50/50/50/50, as shown in Table III. First, the two masterbatches (i.e., silicone rubber with SVP and fluororubber with FVP) were prepared separately in the Brabender plasticorder at 80°C. Then the two masterbatches were mixed in the plasticorder at 80°C and a rotor speed of 60 rpm for 2 min. Finally, DCP, TAC, and Ca(OH)₂ were added and mixed for 3 min. The mix was sheeted out in a two-roll mill.

Determination of Particle Size and Shape

The particle size and shape of SVP and FVP were measured by a scanning electron microscope (Hitachi S-415, Japan) after gold coating.

Measurement of Mooney Viscosity and Mooney Scorch Time

Mooney viscosity (ML₁₊₄), and scorch time were determined at 120°C by using a Mooney viscometer (Negretti, Mark III; Negretti Automation Ltd., Buckinghamshire, UK) as per ASTM D 1646 (1997). Mooney scorch time (*t*₅) represents the time for 5 Mooney units to rise above the minimum torque.

Measurement of Curing Characteristics

The cure behavior of the samples was determined at 170°C, using a moving die rheometer (Monsanto model MDR 2000; Monsanto, St. Louis,

Table V Results of Mooney Viscosity and Monsanto Moving Die Rheometric Studies: Effect of Replacement of Constituent Rubber in 50/50 Blend of Silicone Rubber and Fluororubber

Mix Symbol ^a	Mooney Viscosity Measurements at 120°C		Monsanto Rheometry (MDR 2000) at 170°C		
	Mooney Viscosity (ML ₁₊₄)	Mooney Scorch Time (min)	ΔTorque (dN · m)	Rate Constant of Curing (min ⁻¹)	Optimum Cure Time (min)
100/0/100/0	42	7	22.1	2.41	1.5
75/25/100/0	65	7	16.5	2.24	1.5
50/50/100/0	89	8	11.6	1.59	1.8
25/75/100/0	115	10	8.1	0.88	3.5
100/0/75/25	43	6	22.8	2.31	1.3
100/0/50/50	44	6	17.9	1.85	1.5
100/0/25/75	47	7	14.7	1.75	1.5
100/0/0/100	50	7	10.2	2.56	1.7
50/50/50/50	92	9	10.2	2.24	2.3

^a Silicone rubber/SVP/fluororubber/FVP (parts by weight).

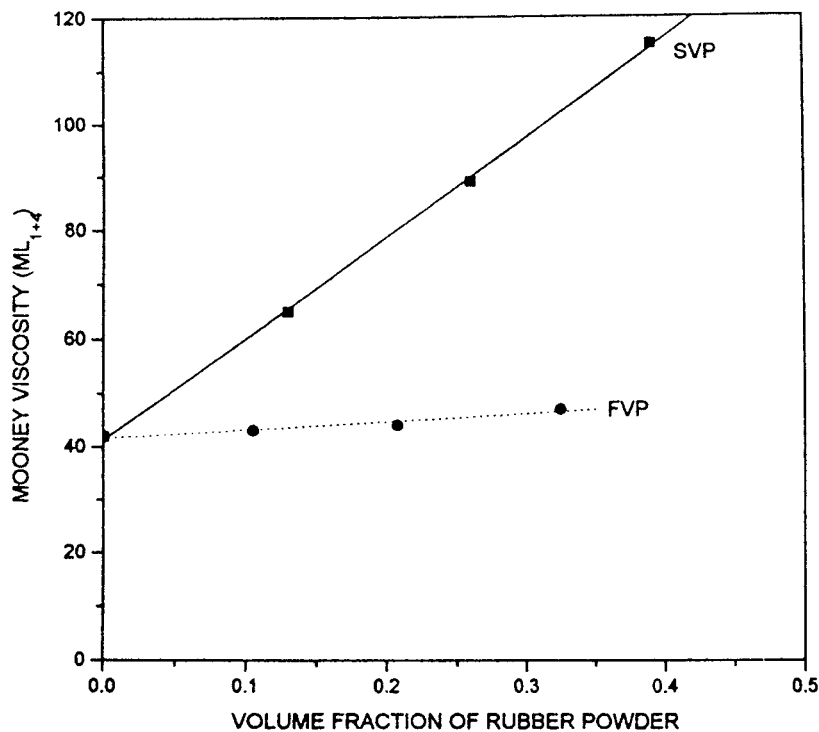


Figure 2 Plots of Mooney viscosity (ML_{1+4}) versus volume fraction of rubber vulcanizate powder at 120°C .

MO). The kinetics of the crosslinking reaction was studied from the changes in rheometric torque with time. For the first-order reaction,^{19,20}

$$\ln(M_{\alpha} - M) = -kt + \ln(M_{\alpha} - M_0) \quad (1)$$

where M , M_0 , and M_{α} are the torque at time t , the torque at zero time, and the maximum torque, respectively. For cure curves showing marching modulus, M_{α} was taken arbitrarily as the torque when the rise in torque was less than 1 unit in 5 min. At this stage it was assumed that the reaction almost came to an end. From the linear plot of $\ln(M_{\alpha} - M)$ versus time (t), the rate constant (k) of the crosslinking reaction was determined.

Molding

For physical testing, thin sheets of approximately 2 mm thickness were prepared by molding the samples according to the respective optimum cure times in a hydraulic press at 170°C and a pressure of 5 MPa. After molding, the samples were postcured at 200°C for 24 h.

Measurement of Physical Properties

The stress-strain properties were measured according to ASTM D412-98 using dumbbell-shape

test pieces in a Zwick Universal Testing Machine (UTM, model 1445; Zwick GmbH & Co., Ulm, Germany) at 25°C . The tear strength was determined according to ASTM D 624-98 using un-nicked 90° -angle test pieces in the Zwick UTM. The average of five measurements was taken for calculating the strength. The hardness was determined as per ASTM D2240 (1997) and expressed in Shore A units. The tension set at 100% elongation was determined as per ASTM D412 (1997) in the Zwick UTM. Hysteresis was determined under strain mode in the first cycle by stretching dumbbell-shape test pieces to a strain level of 100% in the Zwick UTM at 25°C and a rate of 500 mm/min.

Dynamic Mechanical Thermal Analyses

Dynamic mechanical thermal analyses were carried out in a dynamic mechanical thermal analyzer (DMTA, MK-II; Polymer Laboratory, Loughborough, UK). The testing was performed in bending mode at a frequency of 1 Hz and a strain amplitude of $64 \mu\text{m}$, (peak-to-peak displacement) over a temperature range of -120 to 100°C and a heating rate of $2^{\circ}\text{C}/\text{min}$. The data were analyzed by Compaq computer.

SEM Fractography

The samples were cryogenically fractured and the fracture surface was gold coated and then examined under a scanning electron microscope (JEOL JSM 5800; JEOL, Peabody, MA).

Blend Morphology

The morphology of the blends of silicone rubber/fluororubber was examined by a scanning electron microscope (JEOL JSM 5800). Thin sheets (approximate thickness 0.5 mm, diameter 10 mm) of the blends, not molded, were etched with THF for 7 days for removing the fluororubber phase and then dried for about 6 h at 80°C, followed by gold coating before examination under SEM.

RESULTS AND DISCUSSION

Size and Shape of Vulcanizate Powder Particles

The SEM photomicrographs of silicone rubber and fluororubber vulcanizate powders are shown in Figure 1. Both powders exist in aggregated chainlike structures. In the case of SVP, there is a mixture of both the larger particles, which are irregular in shape and of particle size varying from 30 to 100 μm , and the smaller particles, occurring in the highly aggregated state. In the case of fluororubber powder, the individual particles cannot be observed and it is believed that the small particles exist in highly aggregated chainlike structures. As discussed later under SEM fractography, the powder aggregates break down into mostly spherical particles (diameter 2–10 μm) during blending with virgin rubbers.

Mixing Behavior

Silicone rubber and the fluororubber can be conveniently blended in the plasticorder and sheeted on the two-roll mill. While replacing silicone rubber by SVP in the silicone rubber/fluororubber blend, no difficulty is encountered in mixing SVP in the blend up to 50% replacement of silicone rubber; however, at 75% replacement of silicone rubber, SVP can be mixed in the blend with difficulty (i.e., the compound crumbles in the Brabender plasticorder, which, however, can be sheeted in the subsequent milling operation in the two-roll mill). While replacing fluororubber by FVP in the silicone rubber/fluororubber blend, it is found that there is no difficulty in mixing FVP

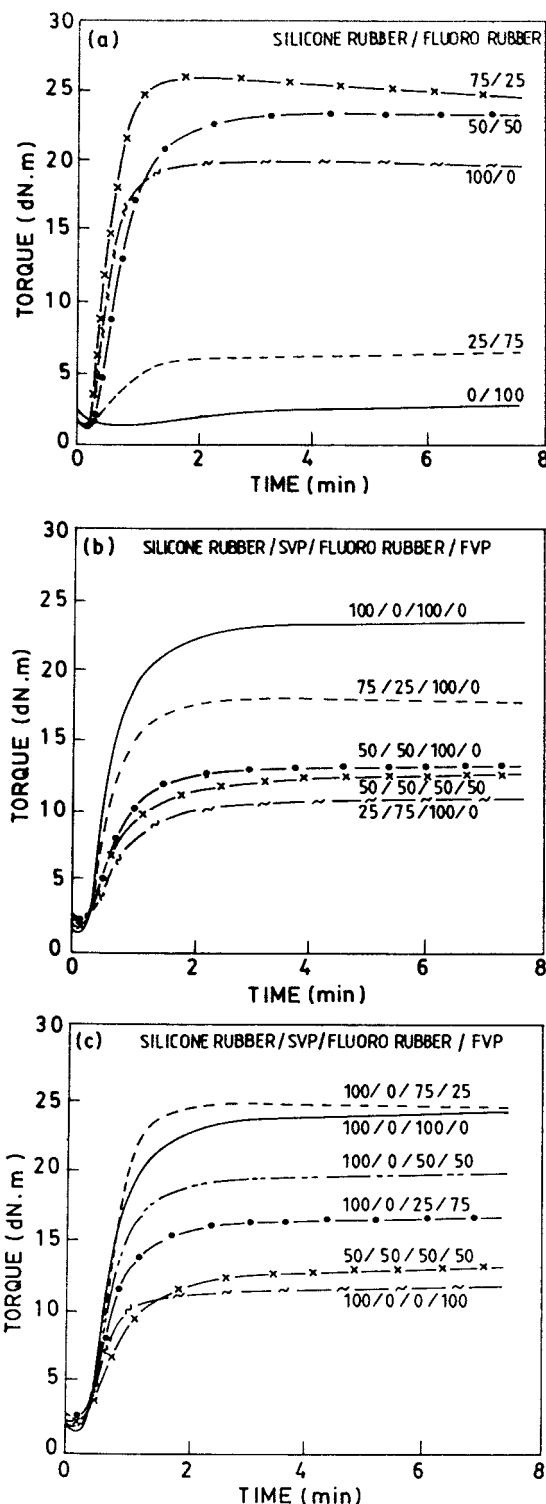


Figure 3 Monsanto rheographs at 170°C: (a) silicone rubber, fluororubber, and their blends; (b) 50/50 silicone rubber/fluororubber blend, in which silicone rubber is replaced by SVP; (c) 50/50 silicone rubber/fluororubber blend, in which fluororubber is replaced by FVP.

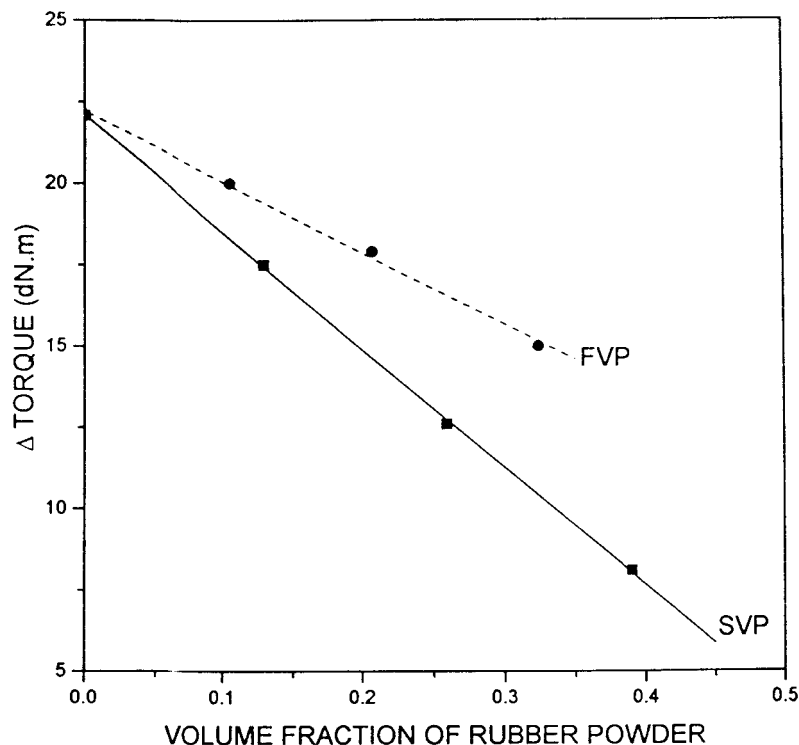


Figure 4 Plots of Δ torque versus volume fraction of rubber vulcanizate powder.

in the blend up to 100% replacement of fluororubber. When both silicone rubber and fluororubber in the same blend are replaced simultaneously by SVP and FVP, there is no difficulty in mixing at the replacement level of 50% of both rubbers by the respective rubber powders.

Mooney Viscosity Measurements

Mooney viscosity and Mooney scorch time for the base polymers and their blends are given in Table IV. It is evident that virgin fluororubber shows higher Mooney viscosity than that of virgin silicone rubber. In the case of blends, the Mooney viscosity decreases with an increase in silicone rubber content in the blends, and the decrease in Mooney viscosity is much greater than the calculated values, indicating the dominant role of silicone rubber in the blend, presumably by forming the continuous phase. Fluororubber shows higher scorch safety than silicone rubber. The blends are more scorchy than the virgin rubbers, which might result from the onset of interphase crosslinking of the two rubbers.

The results of Mooney viscosity measurements of the blends prepared by replacing virgin polymers with the ground vulcanizates are summa-

rized in Table V. Replacement of silicone rubber in the blend by irregular-shape SVP particles causes a sharp increase in Mooney viscosity, whereas replacement of fluororubber by mostly spherical FVP particles causes only a minor enhancement in Mooney viscosity. It is believed that the low viscous silicone rubber phase forms the continuous phase in the blend and therefore replacement of the fluororubber component by FVP does not alter the Mooney viscosity of the blend. However, replacement of the silicone rubber phase by SVP causes an increase in viscosity of the continuous phase, resulting in higher Mooney viscosity of the blend. Figure 2 shows the plot of Mooney viscosity versus volume fraction of SVP or FVP in the blend and the changes in the Mooney viscosity fit into the following equations.

In the case of SVP,

$$M_S = 42 + 187C_S \quad (2a)$$

and in the case of FVP,

$$M_F = 42 + 15C_F \quad (2b)$$

where M_S and M_F represent the Mooney viscosity for silicone rubber and fluororubber, respectively;

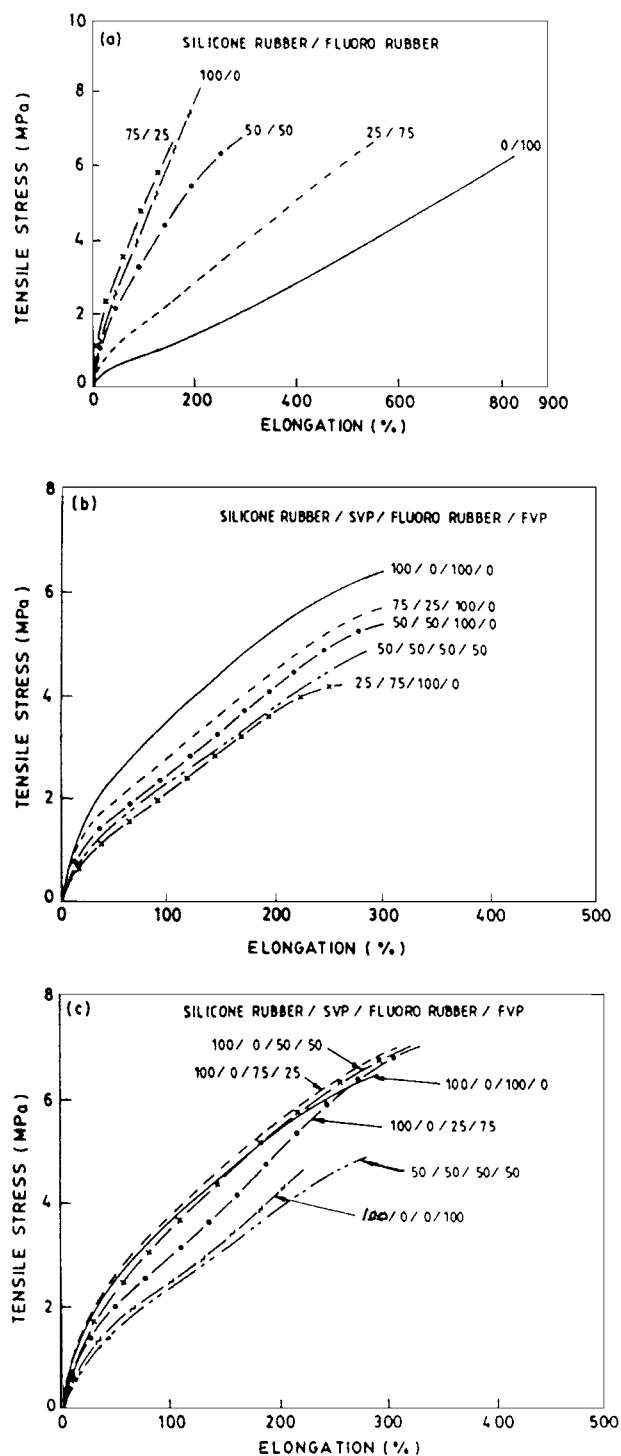


Figure 5 Stress-strain plots at 25°C: (a) silicone rubber, fluororubber, and their blends; (b) 50/50 silicone rubber/fluororubber blend, in which silicone rubber is replaced by SVP; (c) 50/50 silicone rubber/fluororubber blend, in which fluororubber is replaced by FVP.

C_S and C_F represent the volume fraction of SVP and FVP, respectively. Replacement of silicone rubber by SVP causes an increase in scorch time,

whereas replacement of fluororubber by FVP has little effect on the scorch time of the blends. Ghosh et al.¹⁸ observed an increase in scorch time while studying incorporation of SVP in virgin silicone rubber. It is also apparent that, when both silicone rubber and fluororubber are replaced in the same blend by SVP and FVP, changes in the Mooney viscosity and Mooney scorch time are controlled almost exclusively by the SVP, whereas FVP plays a less-dominant role. As discussed earlier, replacement of the continuous silicone rubber by SVP affects the viscosity, which is hardly affected by the replacement of fluororubber by FVP.

Cure Characterization

Monsanto rheographs of the blends along with control fluororubber and silicone rubber compounds at 170°C are shown in Figure 3. The results are summarized in Table IV. It is evident that the maximum rheometric torque of the blend progressively increases with increasing proportion of silicone rubber in the blend, whereas there is only a slight decrease in minimum torque on increasing silicone rubber in the blend. The difference between the maximum and minimum torques can be taken as a rough estimate of the degree of crosslinking, and the higher extent of crosslinking in the blends is presumably attributed to the onset of interphase crosslinking.

The effects of replacement of silicone rubber or fluororubber by SVP or FVP on the curing characteristics of the 50/50 silicone rubber/fluororubber blend are also shown in Figure 3. The results are summarized in Table V. The maximum torque and the rate of cure decrease when silicone rubber or fluororubber is replaced by SVP or FVP, presumably the result of migration of the curing agent from the virgin polymers to the vulcanizate powders. Similar observations on sulfur migration were made earlier by Phadke et al.⁹ in the case of cryoground rubber/natural rubber blend. This results in depletion of the curing agent in the polymer matrix and the effect is more pronounced in the case of silicone rubber replacement by SVP. It is also evident that, although fluororubber replacement by FVP has no effect on optimum cure times of the blends, silicone rubber replacement by SVP causes an increase in optimum cure time. Figure 4 shows the plots of Δ torque (difference between the maximum and minimum torque) versus volume fraction of the powder (SVP or FVP) in the blend and the variation can be fitted into the following equations.

Table VI Effect of Blend Ratio on the Physical Properties

Property	Mix Symbol				
	Silicone Rubber/Fluororubber (Parts by Weight)				
	0/100	25/75	50/50	75/25	100/0
Modulus at 100% elongation (MPa)	0.8	1.8	3.5	4.6	4.1
Modulus at 200% elongation (MPa)	1.3	2.8	5.5	—	7.6
Tensile strength (MPa)	6.3	6.6	6.6	6.6	7.9
Elongation at break (%)	834	549	302	164	212
Tear strength (kN/m)	23.2	28.4	28.3	26.5	24.1
Hysteresis loss at first cycle (J/m ²) × 10 ⁻⁶	0.010	0.031	0.077	0.095	0.060
Hardness (Shore A)	40	52	70	76	74
Tension set at 100% elongation (%)	8	8	8	6	4

In the case of SVP,

$$\Delta Q_S = 22 - 36C_S \quad (3a)$$

and in the case of FVP,

$$\Delta Q_F = 22 - 22C_F \quad (3b)$$

where ΔQ_S and ΔQ_F represent the torque difference in the case of silicone rubber compound and fluororubber compound, respectively; C_S and C_F represent the volume fraction of the corresponding rubber vulcanizate powders.

Physical Properties

Effects of blend ratio on the stress–strain behavior of silicone rubber/fluororubber blends are shown in Figure 5 and their physical properties are summarized in Table VI. Although there are marginal changes in tensile strength with change in blend ratio, the blends show synergism in modulus, tear strength, and hardness, in the sense that the experimental values are higher than those predicted by the additivity rule (Fig. 6). This is believed to be attributed to the formation of interphase crosslinking, resulting in an enhancement of properties. The interphase crosslinking causes a decrease in elongation at break and a marginal drop in tensile strength, although there is no significant change in tension set. On the basis of processing, curing characteristics, and final properties, it appears that silicone rubber, which is of much lower viscosity than that of the fluororubber, forms the continuous phase in the blend, particularly at silicone rubber concentrations of 50% and above. It is also evident that

synergism in properties becomes prominent at higher silicone rubber concentrations. Results of physical properties measurements reveal that the blends of silicone rubber and fluororubber are technologically compatible. The blends are thermodynamically immiscible, as discussed below under dynamic mechanical properties, the two T_g 's of the constituent polymers remaining unchanged in the blend. Technological compatibility means efficient stress transfer from one phase to another phase, resulting in improved physical properties as observed in the present case. If the blends were technologically incompatible, the physical properties would have fallen below the additivity line. SEM photomicrographs, discussed below, further reveal that the blends are homogeneously mixed and the degree of homogeneity increases with increase in silicone rubber concentration in the blend.

Effects of replacement of constituent rubbers in the 50/50 silicone rubber/fluororubber blend by SVP or FVP on the stress–strain properties are also shown in Figure 5. The physical properties of the blends are summarized in Table VII. Whereas incorporation of SVP in the blend causes deterioration in the properties, replacement of fluororubber by FVP causes only minor changes in properties. At 25% replacement of the virgin silicone rubber by SVP, the decline in properties is about 10% and a higher level of replacement causes a further decline in properties. On the other hand, even at 75% replacement of the fluororubber in the blend by FVP, there is no deterioration in properties. When the fluororubber in the blend is fully replaced by FVP, physical properties decline by about 25%. When both silicone rubber and

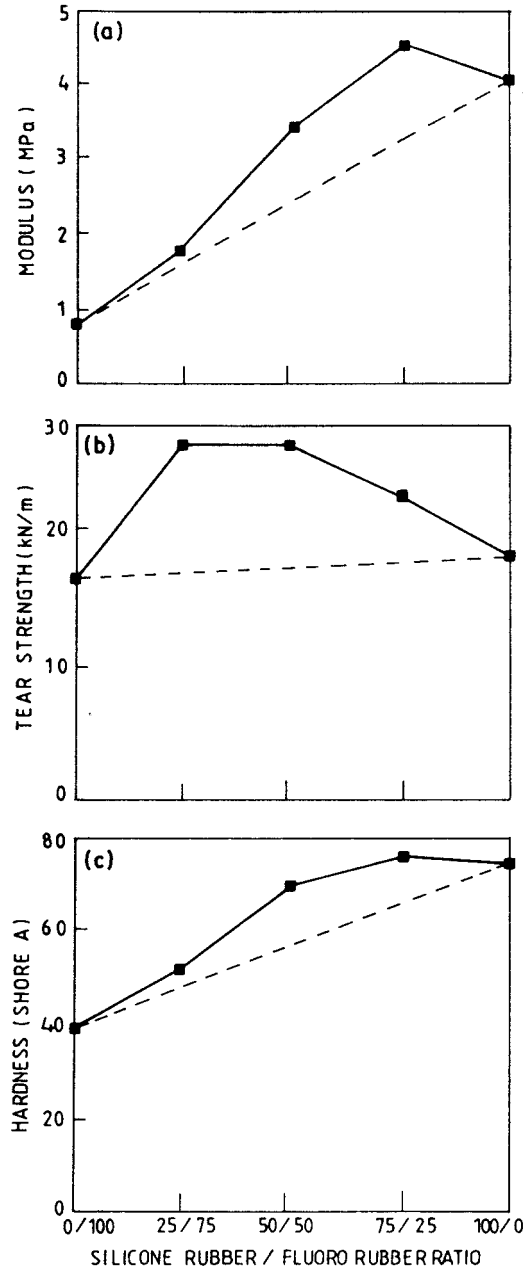


Figure 6 Physical properties of silicone rubber/fluororubber blends: (a) variation of modulus at 100% elongation with blend composition, (b) variation of tear strength with blend composition, (c) variation of hardness with blend composition. (Solid lines represent experimental values and dotted lines represent calculated values.)

fluororubber are simultaneously replaced by SVP and FVP, the decline in properties is about 25%. Ghosh et al.¹⁸ observed that addition of SVP up to 60 phr level into virgin silicone rubber caused a gradual decline in physical properties of the cor-

Table VII Effect of Replacement of Silicone Rubber and Fluororubber in Their 50/50 Blend by Ground Vulcanizates (SVP and/or FVP) on Physical Properties

Property	Silicone Rubber/SVP/Fluororubber/FVP (Parts by Weight)									
	100/0/100/0	75/25/100/0	50/50/100/0	25/75/100/0	100/0/75/25	100/0/50/50	100/0/25/75	100/0/0/100	50/50/50/50	50/50/50/50
Modulus at 100% elongation (MPa)	3.5	2.8	2.5	2.2	3.6	3.3	3.1	2.4	2.3	2.3
Modulus at 200% elongation (MPa)	5.5	4.7	4.3	3.8	5.6	5.6	5.2	4.3	4.1	4.1
Tensile strength (MPa)	6.6	5.9	5.4	4.5	7.4	7.6	7.5	5.1	5.0	5.0
Elongation at break (%)	302	302	301	263	307	313	318	240	287	287
Tear strength (kN/m)	28.3	30.0	27.2	24.4	28.0	26.0	26.1	20.5	23.5	23.5
Hysteresis loss at first cycle (J/m ²) × 10 ⁻⁶	0.077	0.061	0.050	0.041	0.069	0.064	0.055	0.041	0.042	0.042
Hardness (Shore A)	70	64	62	57	69	69	67	62	58	58
Tension set at 100% elongation (%)	8	8	7	8	8	8	8	8	8	8

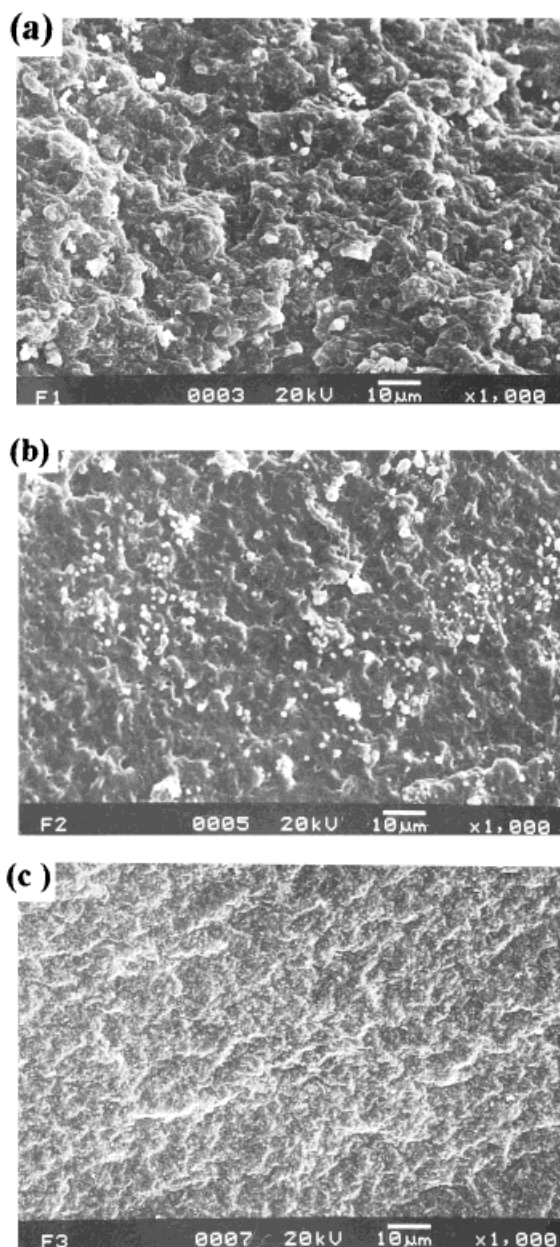


Figure 7 SEM fractographs of silicone rubber/fluororubber blends: (a) 25/75, (b) 50/50, and (c) 75/25.

responding vulcanizates, whereas incorporation of FVP into virgin fluororubber did not significantly change the physical properties of the corresponding vulcanizates, even at a level of 60 phr of FVP.²¹ It is apparent that changes in properties resulting from replacement of silicone rubber by SVP and fluororubber by FVP in the silicone rubber/fluororubber blend follow a pattern similar to that in formulations in which SVP or FVP is added as a filler to the respective single polymers (i.e., silicone rubber or fluororubber, respectively).

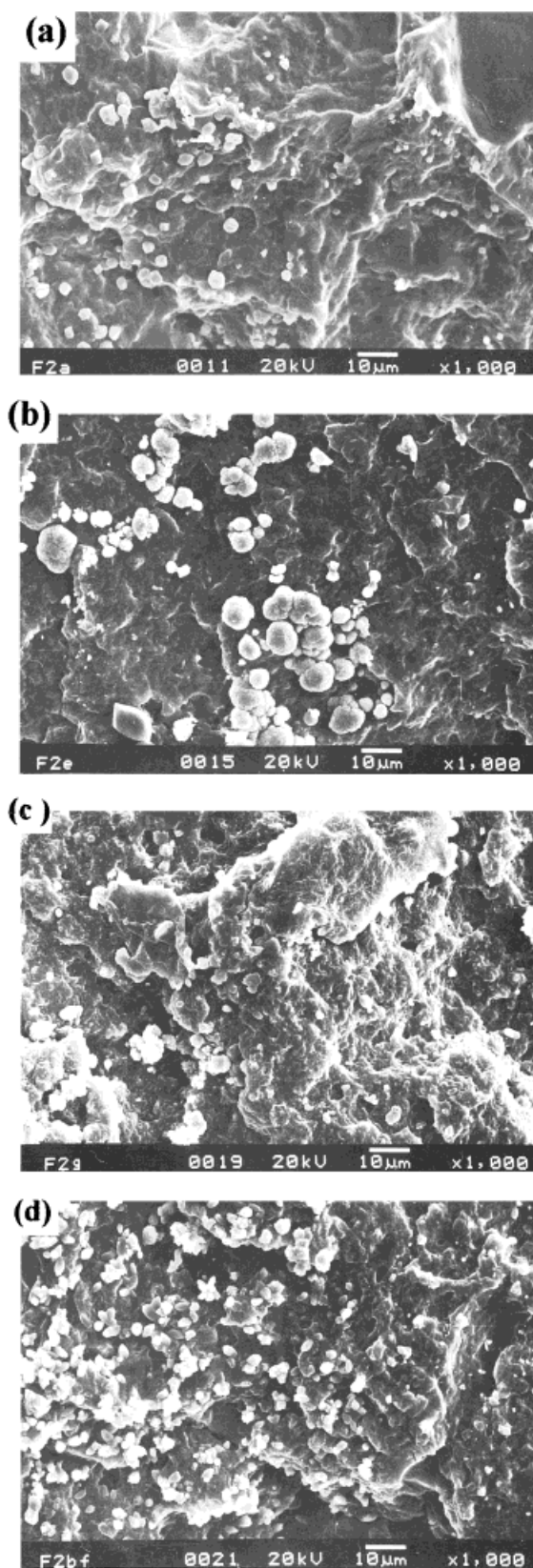


Figure 8 SEM fractographs of silicone rubber/SVP/fluororubber/FVP blends: (a) 75/25/100/0, (b) 100/0/75/25, (c) 100/0/25/75, and (d) 50/50/50/50.

Table VIII Results of DMTA Studies on Silicone Rubber, Fluororubber, and Their Blends

Mix Symbol ^a	Transition 1			Transition 2			Transition 3		
	Temp. (°C)	Log E' (Pa)	$\tan \delta$	Temp. (°C)	Log E' (Pa)	$\tan \delta$	Temp. (°C)	Log E' (Pa)	$\tan \delta$
0/100	—	—	—	—	—	—	4	8.06	1.87
25/75	-99.5	10.12	0.05	-55	9.88	0.06	2	8.34	1.14
50/50	-99.0	10.13	0.05	-36	9.37	0.09	3	8.48	0.67
75/25	-98.0	10.06	0.06	-32	8.85	0.14	1	8.42	0.39
100/0	-98.0	9.85	0.08	-37	8.45	0.16	—	—	—

^a Silicone rubber/fluororubber (parts by weight).

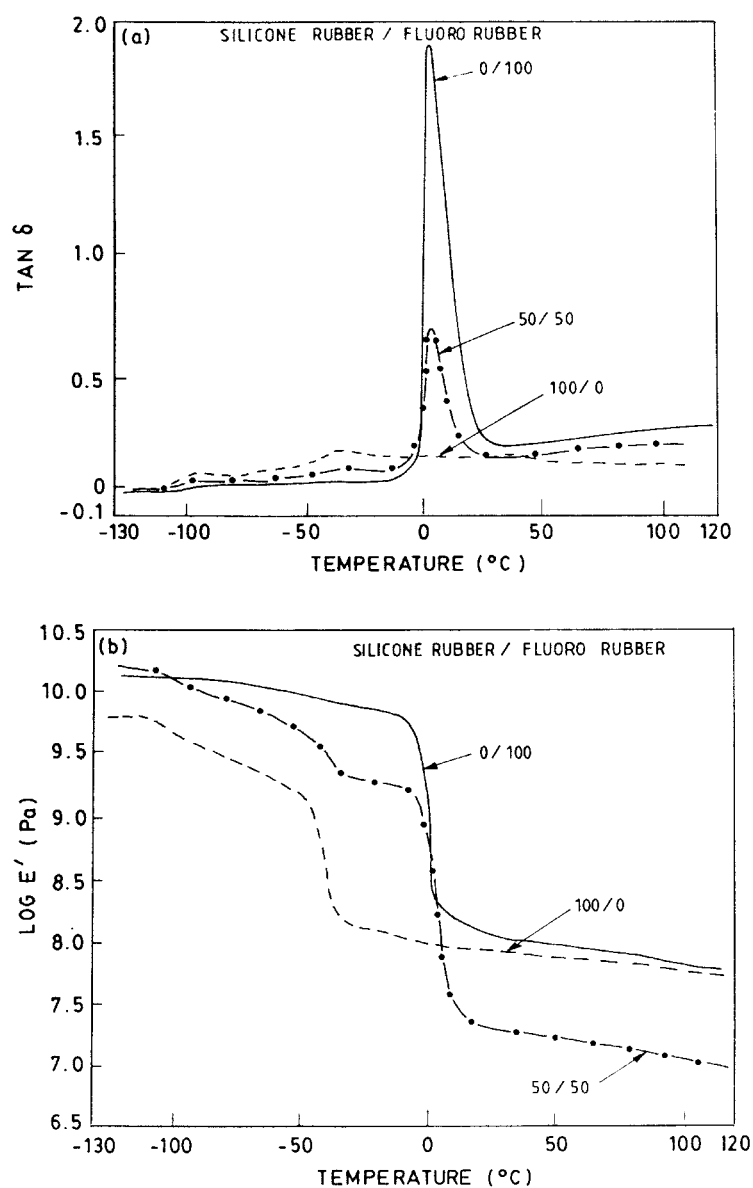


Figure 9 (a) Plots of $\tan \delta$ versus temperature and (b) plots of $\log E'$ versus temperature of silicone rubber, fluororubber, and 50/50 silicone rubber/fluororubber blend.

Table IX Results of DMTA Studies: Effect of Replacement of Constituent Rubber in 50/50 Blend of Silicone Rubber and Fluororubber

Mix Symbol ^a	Transition 1			Transition 2			Transition 3		
	Temp. (°C)	Log E' (Pa)	$\tan \delta$	Temp. (°C)	Log E' (Pa)	$\tan \delta$	Temp. (°C)	Log E' (Pa)	$\tan \delta$
100/0/100/0	-99.0	10.13	0.05	-36	9.37	0.09	3	8.48	0.67
50/50/100/0	-99.0	9.95	0.05	-39	9.43	0.06	1	8.40	0.71
100/0/50/50	-97.0	10.05	0.05	-37	9.35	0.09	2	8.44	0.66
50/50/50/50	-98.0	10.08	0.05	-39	9.43	0.08	3	8.35	0.73

^a Silicone rubber/SVP/fluororubber/FVP (parts by weight).

SEM Fractography

Figure 7 shows the SEM photomicrographs of typical blends. It is evident that the blends of silicone rubber and fluororubber are homogeneously mixed, which is substantiated by the physical properties of the blends that either follow the additivity line or show synergism. Figure 8 shows the SEM fractographs of the 50/50 silicone rubber/fluororubber blend, in which silicone rubber is replaced by SVP and fluororubber is replaced by FVP. At low degrees of substitution, the powder aggregates break down into particles that are mostly spherical with diameter varying from 2 to 10 μm . At a higher substitution level, breakdown of the powder aggregates occurs to a much lesser extent.

Dynamic Mechanical Thermal Analyses

The results of the dynamic mechanical thermal studies are summarized in Table VIII. Figure 9 shows the variation of $\tan \delta$ and storage modulus with temperature for silicone rubber, fluororubber, and their 50/50 blend. Fluororubber shows a peak at 4°C, which is its glass-rubber transition temperature, whereas silicone rubber displays two transitions: the peak at -98°C is ascribed to glass-rubber transition and the peak at -37°C is attributed to the cold crystallization. Only insignificant changes occur in the glass-rubber transition temperatures of the polymers in the blends, although Transition 2 (cold crystallization temperature) of silicone rubber drops in the case of 25/75 silicone rubber/fluororubber blend, reasons for which are not understood. The blends exhibit three transitions, two resulting from the silicone rubber phase and one resulting from the fluororubber phase. It is evident that the blends are immiscible at all compositions.

When silicone rubber and fluororubber are replaced by SVP and FVP, respectively, there are

only marginal changes in the transition temperatures of the blend, as shown in Table IX. Plots of $\tan \delta$ and dynamic modulus against temperature are shown in Figure 10. It is evident that the storage modulus at temperatures beyond glass-rubber transitions decreases on partial replacement of the silicone rubber or fluororubber by SVP or FVP, indicating that replacement of the constituent rubbers in silicone rubber/fluororubber blend causes adverse effects on the dynamic properties compared to that on the static properties.

Blend Morphology

Figure 11 shows the SEM photomicrographs of the THF-etched silicone rubber/fluororubber blend. Because THF removes the fluororubber phase from the blend (not cured), it is evident that the silicone rubber forms the continuous phase, consisting of fluororubber as the dispersed phase (shown as holes), in the 75/25 and 50/50 compositions of silicone rubber/fluororubber. At 25/75 composition the blend morphology could not be determined because of the removal of the major constituent (fluororubber phase, 75 parts) and the subsequent collapse of the silicone rubber matrix (minor constituent, 25 parts).

CONCLUSIONS

1. Blending of fluororubber with silicone rubber decreases its Mooney viscosity and Mooney scorch time. The replacement of silicone rubber in the 50/50 silicone rubber/fluororubber blend by SVP increases the Mooney viscosity, whereas the replacement of the fluororubber in the blend by FVP has little effect on the Mooney viscosity. Changes in Mooney scorch time of the blend are negligible when fluororubber is

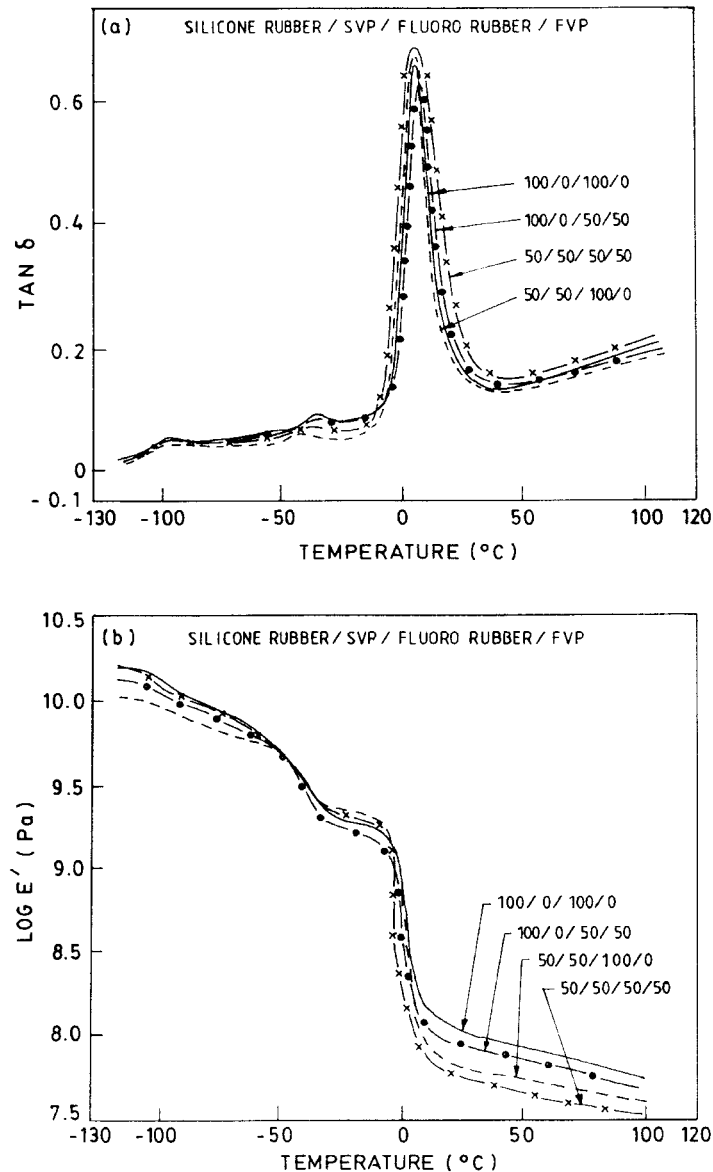


Figure 10 (a) Plots of $\tan \delta$ versus temperature and (b) plots of $\log E'$ versus temperature of 50/50 silicone rubber/fluororubber blend containing SVP and/or FVP.

- replaced by FVP, although the scorch time increases in the case of replacement of silicone rubber by SVP.
- When fluororubber is blended with silicone rubber, the minimum rheometric torque decreases slightly, whereas the rate constant for curing and maximum torque increase. On replacing silicone rubber by SVP or fluororubber by FVP in the 50/50 silicone rubber/fluororubber blend, the minimum torque increases and maximum torque and rate constant for curing decrease as the proportion of SVP or FVP increases.
 - The silicone rubber/fluororubber blends ex-

hibit higher modulus, tear strength, hysteresis, and hardness compared to the calculated values obtained by the additivity rule, whereas the tensile strength and tension set follow the additivity line. SEM photomicrographs reveal that the blends are technologically compatible. On replacing the silicone rubber in the 50/50 silicone rubber/fluororubber blend by SVP, the physical properties in general decrease. On the other hand, the physical properties do not change significantly by replacing the fluororubber in the blend by FVP. When both silicone rubber and fluororubber in

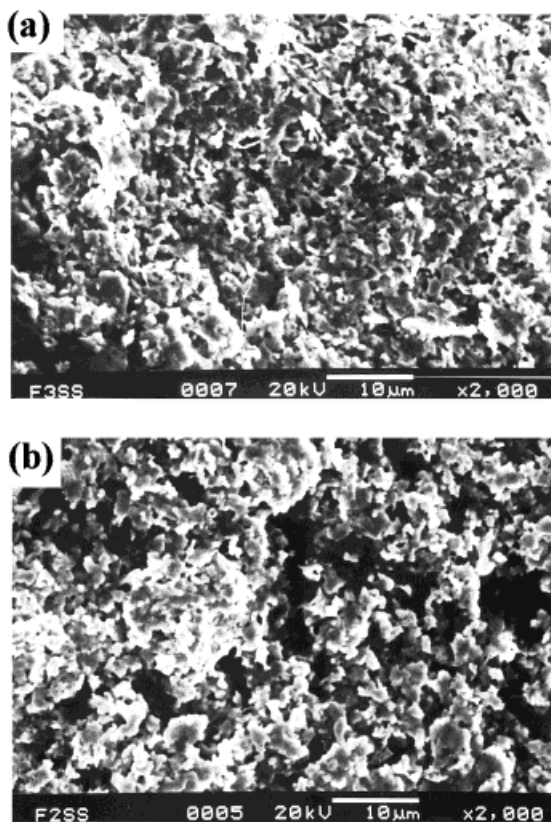


Figure 11 SEM photomicrographs of THF-etched silicone rubber/fluororubber blends: (a) 75/25 and (b) 50/50.

the blend are simultaneously replaced by SVP and FVP, the changes in physical properties are controlled by the SVP, whereas FVP has little effect.

4. Dynamic mechanical thermal analyses show that the blends of silicone rubber and fluororubber are thermodynamically immiscible in all compositions. It is also found that the vulcanizate powders have no effect on the glass-to-rubber transition temperatures of the constituent polymers and cold crystallization temperature of silicone rubber in the 50/50 silicone rubber/fluororubber blend. SEM photomicrographs of THF-etched samples reveal the biphasic structure of the blends, wherein the silicone rubber forms the continuous matrix with fluororubber as the dispersed phase.

In conclusion, silicone rubber and fluororubber form a technologically compatible blend. In the 50/50 blend of the two rubbers, 25% of the virgin silicone rubber can be replaced by the silicone vulcanizate powder and the decline in physical properties is about 10%. On the other hand, 75%

of the fluororubber in the blend can be replaced by the fluororubber vulcanizate powder, without significant loss in physical properties.

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