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Dielectric properties of blends of silicone rubber and tetraflouroethylene/propylene/vinylidene fluoride terpolymer

Arun Ghosh, Amit K. Naskar, D. Khastgir, S.K. De*

Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, West Bengal, India

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Abstract

Dielectric studies show that the blends of silicone rubber and fluororubber based on tetrafluoroethylene/propylene/vinylidene fluoride terpolymer are immiscible. Dielectric loss factor at any temperature increases with increase in concentration of the fluororubber phase in the blend composition. The activation energy of the relaxation of the vinylidene fluoride segment of the fluororubber is influenced by the presence of silicone rubber in the composition. The higher the concentration of silicone rubber in the composition, the higher is the activation energy of the fluorine-containing segment of the fluororubber. The interfacial polarization of the blends is dependent on the domain size of the fluororubber dispersed in the silicone rubber matrix. Higher degree of polarization at fine dispersion of fluororubber in the blend composition of 75/25-silicone rubber/fluororubber makes the dielectric constant higher than that of the neat silicone rubber and raises the energy barrier for the free rotation of vinylidene fluoride segment, causing maximum activation energy for the dipolar relaxation. © 2001 Published by Elsevier Science Ltd.

Keywords: Dielectric loss; Dielectric constant; Fluororubber

1. Introduction

Fluororubber based on tetrafluoroethylene/propylene/vinylidene fluoride terpolymer is used as a specialty polymer in a variety of applications such as seals, o-rings, tubes, hose and cables [1]. One disadvantage of this material is its lack of low temperature resistance. Blending of the fluororubber with a polymer like silicone rubber might enhance the low temperature properties. Silicone rubber itself is used as a dielectric material for high temperature cable. In a previous communication, it has been shown that blends of silicone rubber and fluororubber are technologically compatible, silicone rubber forming a continuous phase wherein fluororubber forms the dispersed phase [2]. Mechanical properties of the blends either follow the additive rule or show synergism, indicating co-crosslinking and consequent technological compatibility. It is worth mentioning in this connection that both silicone rubber and fluororubber are vulcanizable by peroxide.

Since polymers and polymer blends find wide applications as insulating materials in electrical appliances due to their low dielectric loss; dielectric analysis of polymers and their blends might provide useful information. Reports on dielectric relaxation studies on fluoropolymers are available [3,4]. Dielectric studies of blends based on silicone rubber with EPDM have also been made [5]. The present investigation deals with dielectric properties of the blends of silicone rubber and fluororubber.

2. Experimental

2.1. Materials

Details of the materials used are given in Table 1.

2.2. Preparation of silicone rubber/fluororubber blends

Formulations used for preparation of the blends are given in Table 2. The blending of fluororubber with silicone rubber was done in a Brabender Plasticorder PLE 330 at 80°C and at a rotor speed of 60 rpm. First, the 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 made into sheets in a two-roll mill at 25°C.

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* Corresponding author. Tel.: +91-3222-83188; fax: +91-3222-55303.
E-mail address: skde@rtc.iitkgp.ernet.in (S.K. De).

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Table 1
Details of the materials used

Materials	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-co-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°C	Aldrich Chemicals Company, Inc., USA
2,4,6-Triallyloxy-1,3,5-triazine	TAC	Active, 97%	Aldrich Chemicals Company, Inc., USA
Calcium hydroxide	$Ca(OH)_2$	Laboratory grade	S.d.fine. Chem. Ltd, Mumbai, India
Tetrahydrofuran	THF	LR grade, boiling point 66°C	S.d.fine. Chem. Ltd, Mumbai, India

2.3. Molding

Sheets of rubber blends of desired thickness were prepared by molding the samples according to the respective optimum cure times, as measured by a Monsanto Moving Die Rheometer, MDR 2000, in a hydraulic press at 170°C and at a pressure of 5 MPa. The molded samples were post-cured at 200°C for 24 h.

2.4. Morphology of the blends

Blends of the two rubbers, prior to molding, were treated with tetrahydrofuran (THF) at 50°C for 24 h, in order to remove the fluororubber phase from the blends. The THF-etched blends were dried, then gold coated and examined under a scanning electron microscope (JEOL JSM 5800).

2.5. Measurement of electrical properties

The dielectric constant (ϵ') and the loss factor (ϵ'') of fluororubber, silicone rubber and their blends were measured in a dielectric analyzer DEA-2970 coupled with a temperature controller 2000 (TA Instruments Inc., USA) using the compression molded specimens of 0.3–0.6 mm thickness. The measurements were done in the frequency range of 1–10^5 Hz and at the heating rate of 3°C/min, using parallel plate sensors.

Table 2
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	5.00	3.75	2.5	1.25	–
$Ca(OH)_2$	5.00	3.75	2.5	1.25	–

3. Results and discussion

Fig. 1 shows the variation of dielectric constant (ϵ') of blends of different compositions against temperature at 10^3 Hz. Neat silicone rubber vulcanizate exhibits a peak in ϵ' around −116°C, due to transition from glassy to the rubbery state, beyond which there is an increase in the specific volume leading to a decrease in dipole density and hence the decrease in dielectric constant. In addition, silicone rubber shows a secondary relaxation transition around −50°C, where a change in slope of the ϵ' versus temperature plot is observed, presumably due to melting of small crystallites formed by cold crystallization. Neat fluororubber vulcanizate, on the other hand, exhibits two transitions. The broad β-transition in the temperature region −100 to −25°C, is due to the onset of flexibility caused by the propylene and tetrafluoroethylene segments and the

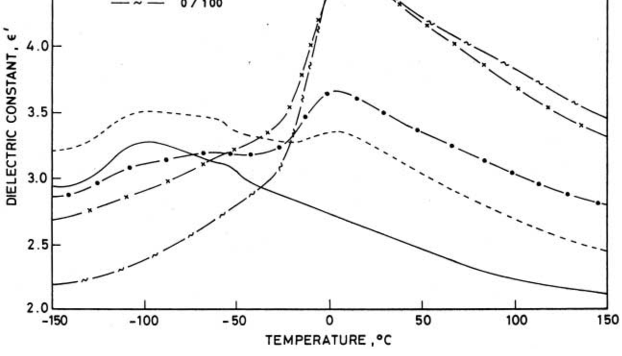

Fig. 1. Temperature dependence of dielectric constant of the blend compositions at 10^3 Hz.

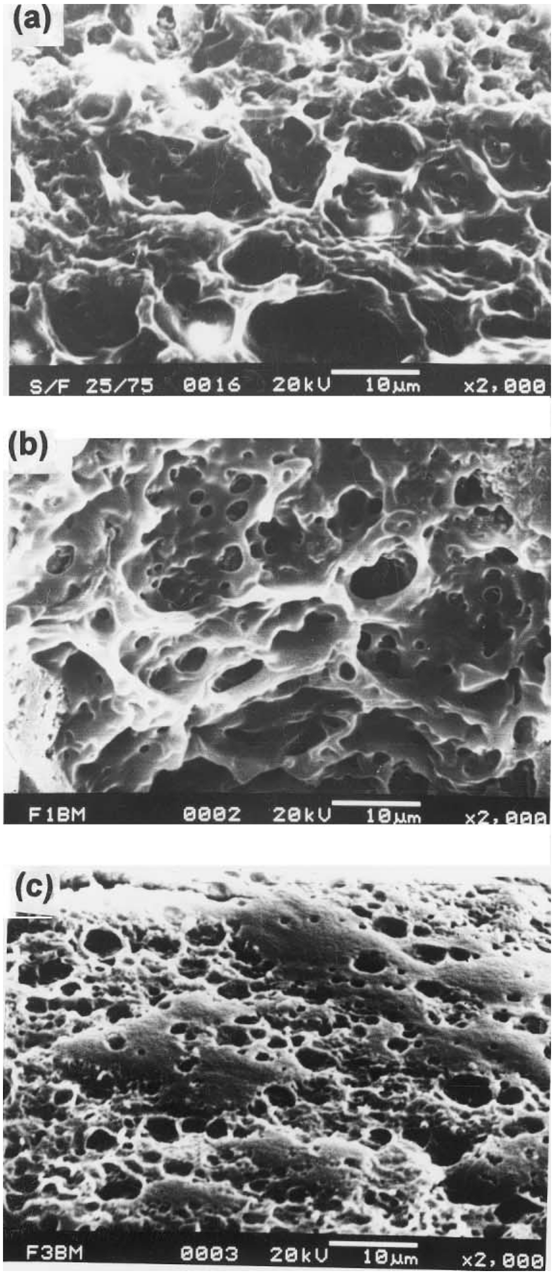

Fig. 2. SEM photomicrographs of the blend compositions where from fluororubberhas been etched out: (a) 25/75-silicone rubber/fluororubber, (b) 50/50-silicone rubber/fluororubber, (c) 75/25-silicone rubber/fluororubber.

sharp α-transition occurs in the temperature region −25 to 0°C, which is ascribed to the glass–rubber transition of the relatively rigid and polar fluorine containing segments (that is, vinylidene fluoride) of the terpolymer. The dielectric signal of vinylidene fluoride segment is significantly stronger than that for other segments because of stronger dipoles. Kojima and co-workers investigated the fluoroelastomer based on alternating copolymer of propylene and tetrafluoroethylene (AFLAS 100) and observed a single glass transition temperature by differential scanning calorimetry [6]. Like silicone rubber, fluororubber also shows a decrease in ϵ' at a temperature higher than the α-transition of the fluororubber. The blends of silicone rubber and fluororubber exhibit characteristic dielectric relaxations of the two elastomeric phases. Neat fluororubber having the highest $C^{+\delta}$–$F^{-\delta}$ dipole density amongst different elastomeric vulcanizates shows the maximum dielectric relaxation strength (difference between low temperature unrelaxed dielectric constant and relaxed dielectric constant at T_g). As the concentration of the fluororubber in the blend increases, dielectric relaxation strength increases. Beyond the glass–rubber transition, dielectric constant of the blends increases with increase in fluororubber component in the composition. On the other hand, in the low temperature region (−150 to −50°C), with increase in concentration of silicone rubber in the blend composition, ϵ' gradually increases, due to enhanced flexibility in the low temperature region by the silicone rubber component. But the 75/25-silicone rubber/fluororubber blend shows a higher dielectric constant than that of the neat silicone vulcanizate. This indicates that the presence of a small quantity of fluororubber in the silicone rubber enhances the extent of polarization in the low temperature region. In this temperature range, propylene and vinylidene fluoride segments of fluororubber phase remains rigid, and a higher degree of interfacial polarization between relatively rigid fluororubber and soft silicone rubber occurs. Higher degree of interfacial polarization at this composition is possibly due to the morphology of the blend. Fig. 2a–c show the SEM photomicrographs of the 25/75, 50/50 and 75/25 silicone rubber/fluororubber blend compositions, respectively, wherefrom the fluororubber has been etched out by treating with THF. It is apparent that at all the compositions, low viscous silicone rubber forms the continuous matrix, containing spherical and/or elliptical domains of the highly viscous fluororubber. The domain size is small at very low concentration of the fluororubber in the blends. In other words, the 75/25-silicone rubber/fluororubber blend exhibits smaller domain size than that of the 25/75-silicone rubber/fluororubber blend. Though the concentration of fluororubber is low in the 75/25-silicone rubber/fluororubber blend, smaller domain size contributes to higher interfacial area. A homogenized dispersion of fluororubber phase raises the dielectric constant of the 75/25-silicone rubber/fluororubber blend at T_g of silicone rubber due to contribution of interfacial polarization.

Fig. 3a shows the variation of dielectric loss factor (ϵ'') of blends of different compositions against temperature at 10^3 Hz. It is observed that the characteristic loss maxima due to the two constituent phases are retained in the spectra of the blend compositions, indicating immiscibility of the two rubber components. Silicone rubber exhibits very low dielectric loss factor at T_g. With increase in fluororubber content in the composition, dielectric loss factor (ϵ'') at any temperature increases, due to permanent dipoles from the fluororubber. The variation of dielectric loss factor at different blend ratios at 25°C is shown in Fig. 3b. It is clear

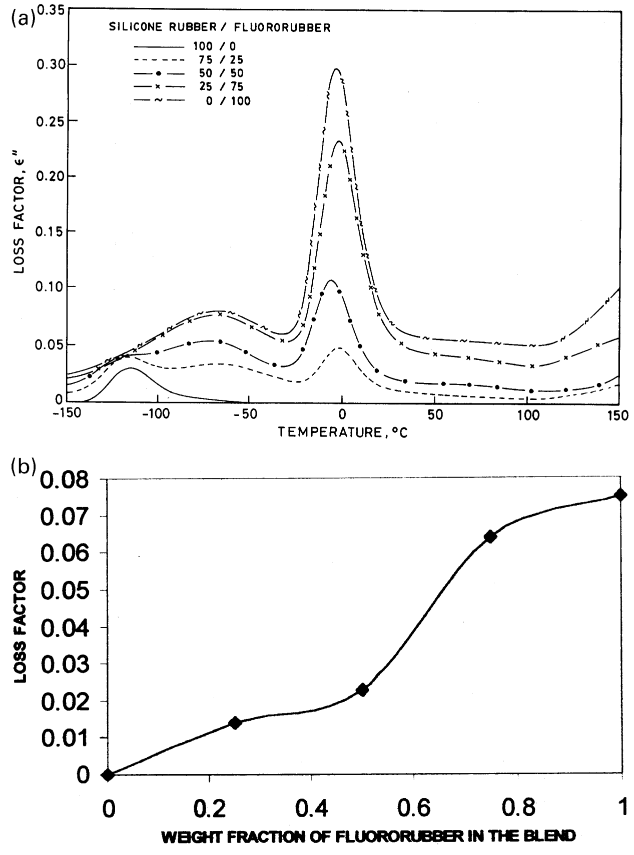

Fig. 3. (a) Temperature dependence of dielectric loss factor of the blend compositions at 10^3 Hz. (b) Variation of loss factor of the blend at 25°C with weight fraction of fluororubber at 10^3 Hz.

that loss factor of the blends is closer to that of the silicone rubber when the blend contains 50% or more silicone rubber. At lower proportion of silicone rubber (that is, 25/75-silicone rubber/fluororubber), the loss factor is closer to that of the fluororubber. At higher proportion of silicone rubber in the blend, the silicone rubber matrix controls the properties. But at higher proportion of the fluororubber, though silicone rubber forms the matrix due to its low viscosity, larger fluororubber domains contribute to the loss factor to a greater extent.

Fig. 4a,b shows the effect of frequency on the variation of loss factor against temperature for neat fluororubber and a representative blend (that is, 50/50 blend). The characteristic loss peak temperatures of the rubber components are summarized in Table 3.

Fig. 4a shows that both loss maximum of the primary transition (α-transition) and the secondary transition (β-transition) of the fluororubber shift to the high temperature region with increase in frequency. The half width of the loss maximum also increases with increase in frequency, due to overlapping of the relaxation processes of different segments. At 10^5 Hz, the β-relaxation is partially merged with the α-relaxation. At higher frequencies, the loss factor at high temperature is lowered due to restriction on the segmental mobility.

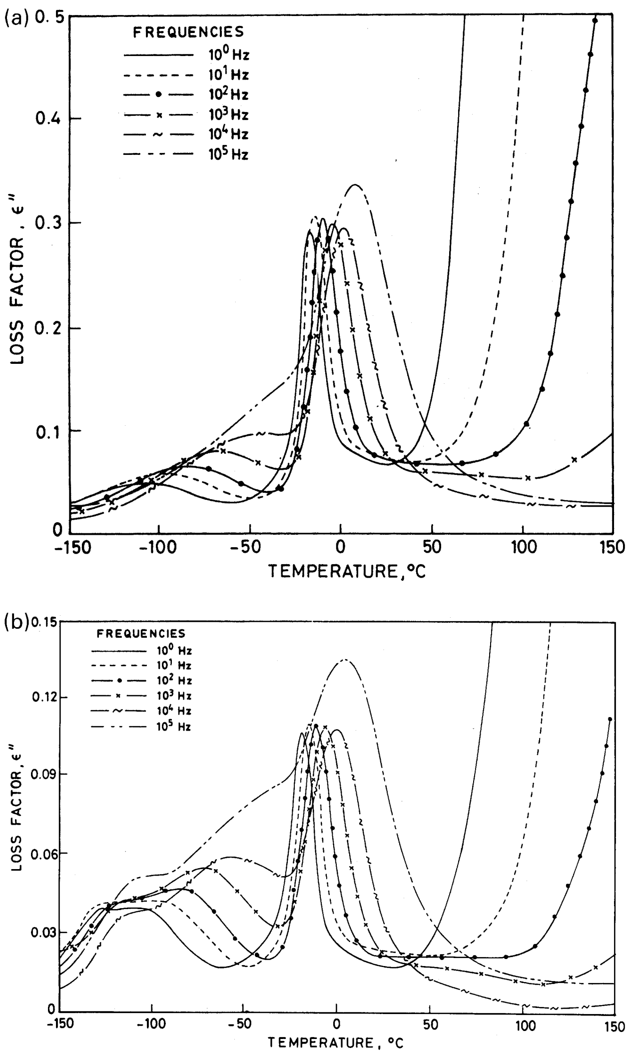

Fig. 4. Frequency dependence of dielectric loss factor of the compositions against temperature: (a) neat fluororubber and (b) 50/50-silicone rubber/fluororubber blend.

Fig. 4b shows that for the 50/50 blend of silicone rubber and fluororubber, all the relaxation transitions of the constituent rubbers are prominent. With increase in frequency, the peak positions shift to the higher temperature showing an increase in half width of the peak. At 10^5 Hz, a very broad dielectric relaxation is observed as the relaxation regions of the two rubber phases partially overlap.

Measurement of loss factor at different frequencies enables one to calculate the activation energy for dielectric relaxation with the help of Arrhenius equation [7]. The calculated activation energies for the dielectric relaxations of different segments are summarized in Table 4. It is observed that the activation energy of the β-transition of the fluororubber is not significantly changed with change in blend composition, as the β-transition is due to mobility of the polypropylene and tetrafluoroethylene segments of fluororubber, which do not involve relaxation of any strong dipole. Similarly, the activation energy of the relaxation of

Table 3
Temperatures (°C) corresponding to the relaxation transitions of the blend compositions at different frequencies

Frequency (Hz)	Primary relaxation temperature (or T_g) of silicone rubber phase					Secondary (β) relaxation temperature of the fluororubber phase					Primary (α) relaxation temperature of the fluororubber phase				
	Silicone rubber/fluororubber (parts by weight)					Silicone rubber/fluororubber (parts by weight)					Silicone rubber/fluororubber (parts by weight)				
	100/0	75/25	50/50	25/75	0/100	100/0	75/25	50/50	25/75	0/100	100/0	75/25	50/50	25/75	0/100
1	−124	−126	−127	–	–	–	−99	−109	−104	−107	–	−14	−19.3	−16	−17
10	−123	−123	−123	–	–	–	−97	−100	−97	−96	–	−10	−15	−12	−14
10^2	−119	−120	−118	–	–	–	−81	−85	−82	−83	–	−7	−11	−8	−9
10^3	−116	−117	−116	–	–	–	−67	−72	−69	−68	–	−2	−7	−3	−4
10^4	−112	−112	−112	–	–	–	−55	−57	−47	−43	–	3	−1	3	2
10^5	−107	−108	−107	–	–	–	−29	−30	–	–	–	5	3	9	8

Table 4
Activation energies of the dielectric relaxations of silicone rubber/fluororubber blends

Types of dielectric relaxation	Activation energies (in kJ/mol)				
	Blend composition (silicone rubber/fluororubber, by weight)				
	100/0	75/25	50/50	25/75	0/100
β-relaxation in fluororubber	–	53.2	47.4	49.9	45.8
α-relaxation in fluororubber	–	332.3	291.6	282.4	263.4
Primary α transition in silicone rubber	120.6	123.6	122.3	–	–

silicone rubber segments does not vary significantly with change in blend composition. However, the activation energy of the relaxation of the highly polar vinylidene fluoride segment of fluororubber increases with increase in silicone rubber content in the composition (Table 4). It has been already mentioned earlier that the morphology of the blend plays a key role in electrical properties. The 75/25-silicone rubber/fluororubber composition exhibits fine dispersion of the fluororubber domains in the silicone rubber matrix, wherein the interfacial polarization involved during the relaxation of silicone rubber segments is high. So a large number of dipoles from the fluororubber, which are attached with silicone rubber at the interface by co-crosslinking, are involved in such polarization. Thus, motion of these dipoles is partially restricted, or in other words, energy barrier to rotation of these dipoles is higher in the blend.

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