Property Optimization in Nitrile Rubber Composites via Hybrid Filler Systems

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ABSTRACT: Nitrile rubber–PVC composites having carbon black and mica fillers in different compositions as hybrid reinforcements were studied. The effect of the silane treatment of mica, the degree of replacement, and the molecular architecture of nitrile rubbers on static-dynamic mechanical, swelling, and curing behavior of the resultant composites are discussed. The results showed that an increase in unsilanized and silanized mica total filler resulted in increased toughness values and decreased swelling in organic solvents together with increased vibrational damping capacity for all types of nitrile rubber composites, depending on the polyacrylonitrile content. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 366–374, 2001

Key words: nitrile rubber; mica/carbon black hybrid reinforcement; swelling behavior; tensile strength; toughness; vibrational damping; composite

INTRODUCTION

Addition of filler materials to improve the mechanical, electrical, thermal, optical, and processing properties of polymers, while reducing their cost, has become a popular field of research. More than 100 different types of reinforcing materials, both organic and inorganic, have been reported in the literature. However, among these, only a few have been commercialized and used extensively. Depending on the type of reinforcement provided, fillers are often divided into three classes: one-dimensional (fibers, whiskers, etc.) ; two-dimensional (flakes, platelets, etc.), and three-dimensional (beads, spheres, etc.).[1] When optimum reinforcement is desired, the well-known filler surface area-to-filler volume ratio (A/V) should be maximized. Fibers and platelets are two main classes of reinforcing particles which allow for this maximization. Use of these particles maximizes the particle–matrix interaction through the interface. The success of mineral platelet reinforcement is due to their desirable combination of cost and properties such as (i) price per unit mass, which is typically less than one-fifth of the common plastics, (ii) stiffness and strength, both of which are greater than those of plastics, and (iii) anisotropic alignment providing reinforcement in all directions, in contrast to uniaxially aligned fibers that enhance properties in one direction only.

Mica refers to a group of minerals whose chemical composition is $KAl_2(OH)_2(AlSi_3O_{10})$ and crystals exhibit a high degree of basal cleavage, which allows them to be split into very thin sheets that are strong, flexible, chemically inert, and transparent.[2] Mica has been used as a sheetlike filler for plastics due to its low cost, easy availability,

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and outstanding electrical, thermal, and chemical resistance.

In the area of rubber reinforcement with mica, there are some patent studies conducted on siloxane rubber compositions with good weatherability and quiet operation of wiper blades[3] and good shock-absorbing and vibration-damping properties.[4] Among other rubbers, polyurethane[5,6] and polyurethane–epoxy composites[7] may be listed as mica-reinforced rubbers, which are especially important for their good damping properties. Szentivanyi et al.[8] published a study on rubber hoses based on nitrile rubber–mica composites for fuel-line systems in which swelling, permeability, and low-temperature properties were optimized by selection of the mica filler without any surface treatment. A study on 1,2-polybutadiene and natural rubber composites as odorless and vibration-damping sheets having mica-group minerals as fillers was patented.[9] Debnath et al.[10] reported the effect of a silane coupling agent on vulcanization conditions, network structure, polymer–filler interaction, physical properties, and failure mode of mica-filled styrene butadiene rubber.

Recently, our laboratory reported the physical properties of mica-reinforced linear (LPB) and star-branched polybutadiene (SPB) composites with special reference to the effect of the silane coupling agent, the degree of crosslinking, the degree of mica loading, as well as the molecular architecture of the polybutadienes.[11] Effective damping regions were determined in terms of frequency and temperature.

Carbon black, on the other hand, is the name given to wide variety of finely divided black pigments composed mainly of elemental carbon.[1] The commercial carbon blacks are spherical particles with diameters of the order 15–50 nm and tend to exist in fused chainlike agglomerates which are referred to as the structure.[13] The presence of carbon black in vulcanized rubber enormously enhances such properties as tensile strength, elastic modulus, and abrasion resistance as well as the stabilization against UV light, coloring, opacifying, cost reduction as a filler, and electrical and thermal conductivity.[14]

At the present time, the effects of individual fillers on the properties of components are relatively well known. For example, as a general rule, tensile strength can usually be improved by fibrous fillers, provided that the adhesion is sufficient. Rigidity can be increased by sheetlike fillers and improvement depends on the aspect ratio of the filler.[15] Impact strength cannot usually be improved by mineral fillers.[16] On the other hand, multicomponent compounding, where two or more different filler types are used, produces so-called hybrid structures where effects of the different components are combined. Recent investigations on composites having multicomponent filler systems have focused mainly on thermoplastics and thermosets. Multicomponent reinforcing has been used in fiber-reinforced composites, for the elimination of the low impact strength carbon fiber-reinforced composites by adding glass or aramide fibers.[17] The simultaneous compounding of polypropylene with several mineral fillers selected on the basis of their size and shape such as spherical (glass beads), sheetlike (mica), or fibrous (wollastonite) was investigated by Jarvela and Jarvela.[18] Superior mechanical properties were attained by the simultaneous use of two or more fillers. Chand and Gautam[19] studied the effect of the variation of load and sliding distance on the abrasive behavior of fly ash/glass fiber polyester composites. Wear loss was minimum in the case of highest fly ash-loaded hybrid system. The effect of replacement of sand with fly ash on the tensile-strength properties of polyester mortar (PM) using resins based on recycled poly(ethylene terephthalate) was evaluated by Rebeiz et al.[20] The results showed that the best mix design for PM, optimized for tensile strength and economy, is 40% by weight of fillers, of which 50% by weight is sand and 50% by weight is fly ash.

This article reports a study on nitrile rubber–poly(vinyl chloride) (PVC) composites having carbon black and mica fillers in different compositions as hybrid reinforcement. The effect of silane treatment of mica, the degree of replacement with carbon black, and the molecular architecture of nitrile rubber on both the static-dynamic mechanical and swelling behavior of the resultant composites are discussed. The results are compared with those of composites having only FEF carbon black. It is good to mention here that composites having only FEF as a reinforcing filler exhibit a higher hardness difference after high-temperature aging, high swelling in the fuel medium, and higher price than those of mica as drawbacks. Partially replacing carbon black with a cheaper and naturally abundant mica is expected to improve the engineering properties of the rubbers under investigation. Additionally, since these rubbers are working under specified vibrational mediums (under hood applications in cars), the composites were evaluated in terms of their vibrational-damping properties.

Table I Formulation of NBR Composites

	Mica in Total Filler (%)										
Components	0	30	47	60	75	100	30S	47S	60S	75S	100S
NBR/PVC	100	100	100	100	100	100	100	100	100	100	100
DOP	16	16	16	16	16	16	16	16	16	16	16
Zinc oxide	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6
Stearic acid	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Mica	0	20.4	32.0	40.8	51.0	68	20.4	32.0	40.8	51.0	68
Carbon black	68	47.6	36	27.2	17.0	0	47.6	36	27.2	17.0	0
Polyvest	—	—	—	—	—	—	0.4	0.64	0.82	1.02	1.36
CBS	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
TMTD	2	2	2	2	2	2	2	2	2	2	2
DCP	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48
Wax	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
IPPD	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
TMQ	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2

EXPERIMENTAL

Materials Used

Nitrile rubbers blended with 30% PVC (Perbunan NT/VC) and having 28, 34, and 43% acrylonitrile contents are coded as 2870 NBR, 3470 NBR, and 4370 NBR, respectively. They were supplied from Bayer (Leverkusen, Germany). The Muscovite mica (30 μm) used for this study was supplied by the Sabuncular–Mica Trading Corp. (Ayd'n, Turkey). Carbon black with an average particle diameter of 44 nm (FEF N550) was manufactured by Continental Carbon (Akron, OH). Other compounding ingredients such as dicumyl peroxide (DCP), stearic acid, zinc oxide, wax, cyclohexylbenzothiozole sulfenamid (CBS), tetramethylthiuram disulfide (TMTD), *N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine (IPPD), and 1,2-dihydro-2,2,4-trimethylquinoline (TMQ) were of commercial grade. The silane coupling agent, Polyvest 25, trimethoxysilane having an oligomeric polybutadiene matrix selective group, was supplied by Union Carbide (Danbury, CT). Tetrahydrofuran (THF) was the product of Merck (Darmstadt, Germany) and was used as received. N liquid, which is a mixture of 50% isooctane and toluene, was used for the swelling experiments.

Sample Preparation: Application of the Coupling Agent

The silane coupling agent was added to THF to give a 2% solution. Solid mica was mixed with the coupling agent solution for 2 h and then filtered with a Buchner filter. The solvent was removed at 120°C overnight, where a complete condensation reaction occurred.

All composites were prepared using silanized/unsilanized mica and carbon black to give 0, 30, 47, 60, 75, and 100 weight percentages of mica in total filler. 3470 NBR composites with, for example, 30% unsilanized and silanized mica, are designated as 3470 NBR 30 and 3470 NBR 30S, respectively. Total filler content of rubber was kept at 33%. A typical formulation is given in Table I.

Mixing was achieved on an open two-roll mill with a nip gap of 0.25 mm. The optimum cure time at 175°C was determined using rheograms taken with a Monsanto rheometer R-100.

Vulcanization was done in an electrically heated press at 175°C in 2-mm-thick steel molds. The samples were conditioned for 24 h at 20°C before testing. All properties were measured along the machine direction.

Physical Testing of the Samples

Swelling Measurements

Strips of dimensions 0.2, 0.5, and 2 cm were immersed in N liquid at room temperature for 3 days. The length changes were measured in the immersed state by a traveling microscope (Gaertner 7109-C-46) with an accuracy of 0.001 cm. Measurements were repeated for three samples in each case and the results were averaged. Swelling degrees were reported in terms of the swelling ratio $q = v_2^{-1}$, where v_2 is the volume fraction of

Table II Curing Characteristics of the 4370 NBR Composites at 175°C

Mica in Total Filler (%)	Minimum Torque (dNm)	Maximum Torque (dNm)	Optimum Cure Time (min)
0	6.3	18.8	3.32
30	4.4	15.2	3.45
(30S)	(4.5)	(12.5)	(3.57)
47	3.6	12.9	3.50
(47S)	(3.6)	(12.2)	(4.0)
60	3.1	12.0	3.59
(60S)	(3.2)	(11.2)	(3.98)
75	2.9	11.4	4.07
(75S)	(2.9)	(10.3)	(4.15)
100	2.5	10.8	4.18
(100S)	(2.5)	(8.8)	(4.19)

the polymer in the swollen network at a given time during the course of the experiment. v_2 is found from the ratio of the dry network volume to the swollen network volume at a given time.

Mechanical Experiments

Mechanical experiments were performed under two loading conditions: (1) quasi-static mechanical tests, carried out at room temperature and a crosshead speed of 50 cm/s in the static mode of a Zwick 1464 machine equipped with an incremental extansiometer, and (2) dynamic mechanical tests, carried out on a Polymer Laboratories dynamic mechanical testing analyzer (DMTA) at a temperature range of $-60°\mathrm{C} < T < 120°\mathrm{C}$ at a frequency of 1 Hz. Tests were also performed at room temperature at frequencies of 1, 3, 5, and 10 Hz with the samples having dimensions of about $16.0 \times 8.0 \times 2.0$ mm.

RESULTS AND DISCUSSION

Curing Characteristics of Composites

Rheometric data related to the 4370 NBR composite having different amounts of both silanized and unsilanized mica in carbon black are given in Table II. The values in parentheses in the table are for silanized samples. As can be seen from the table, the optimum cure time increases with the addition of unsilanized mica and further increases in the case of silanized mica.

Composites having both unsilanized and silanized mica content show a significant decrease in minimum viscosity (ML) values. It is known that a drastic viscosity reduction of a highly filled system can be achieved only by breaking up the aggregates of the filler.[21] Changing the surface energetics of the filler is the alternative way of breaking these aggregates. Here, a gradual decrease in viscosity can be attributed to the solvent effect of mica on carbon black. This appears as a major benefit of platelet hybridization of spherical fillers in terms of easy processing of rubber composites. All other physical properties of the NBR types are summarized in Tables III–V.

Swelling of Composites

The general effect of introducing mica is observed to decrease swelling. In Figure 1, swelling ratios as a function of the silanized mica content are shown. Only the results for 3470 NBR and 4370

Table III Physical Properties of Hybrid–reinforced 2870 NBR Composites

	Mica in Total Filler (%)					
Measurement	0	30	47	60	75	100
Tensile strength (MPa)	12.4	12.9	13.3	12.0	10.9	8.0
Elongation at break (%)	405	509	627	652	698	764
Swelling ratio (q)	1.564	1.5371	1.358	1.352	1.439	1.523

Table IV Physical Properties of Hybrid-reinforced 3470 NBR Composites

		Mica in Total Filler (%)				
Measurement	0	30 (30S)	47 (47S)	60 (60S)	75 (75S)	100 (100S)
Tensile strength (MPa)	14.5	15.8	15.0	15.0	14.7	8.3
		(16.2)	(14.4)	(15.4)	(13.7)	(8.2)
Elongation at break (%)	357	483	394	422	668	695
		(570)	(556)	(607)	(704)	(742)
Swelling ratio (q)	1.540	1.360	1.389	1.360	1.3617	1.287
		(1.342)	(1.330)	(1.345)	(1.348)	(1.261)

NBR are shown. Due to the relatively smaller resistivity to the solvents than that of the others because of the low content of acrylonitrile, 2870 NBR was excluded from the silanization experiments. The straight lines are obtained by least-squares fit to the data points.

It is well known that a polymer network filled with a filler swells to a much lesser extent than does the unfilled network. This is due to the contribution of the filler to the elastic activity of the network and is fully an entropic one, resulting from the constraining action of the filler on the fluctuations of the polymer chains.[22] In the present experiments, increase in the mica content in the total filler induces a further decrease in swelling. Within the composites, as the acrylonitrile content increases, swelling decreases at each filler composition, which is due to the inherent solvent-resistant property of the polyacrylonitrile segments.

Static Mechanical Properties of Composites

Figure 2 shows the variation of tensile strength as a function of unsilanized filler composition of three types of nitrile rubber composites. The straight lines are obtained by least-squares fit to data points.

The nitrile rubber composite having 43% acrylonitrile without any mica replacement exhibits higher tensile strength due to the beneficial effect of a higher amount of thermoplastic acrylonitrile content. The general effect of increasing the mica content in the filler is to decrease the tensile srength as seen from the figure. The effect of bridging via silanization on reinforcement is observed by a small increase in tensile strength (Table III–IV). This improvement in the ultimate properties is attributable to the Polyvest, which again improves the dispersion and reduces the number of failure-initiating stress concentrations. It is also well known that if there is adhesion between the polymer and the filler, the tensile strength of the composite increases. If there is no or weak adhesion, tensile strength decreases.[23]

Figure 3 presents elongation-at-break values of the composites. Similar to the behavior observed for the polybutadiene composites,[11] addition of mica increases the ductility of the samples. Sim-

Table V Physical Properties of Hybrid-reinforced 4370 NBR Composites

		Mica in Total Filler (%)				
Measurement	0	30 (30S)	47 (47S)	60 (60S)	75 (75S)	100 (100S)
Tensile strength (MPa)	15.0	14.6	12.9	13.9	13.1	9.8
		(14.8)	(13.0)	(14.1)	(13.5)	(9.0)
Elongation at break (%)	303	446	441	534	576	605
		(465)	(534)	(553)	(583)	(632)
Swelling ratio (q)	1.511	1.345	1.232	1.298	1.295	1.277
		(1.321)	(1.210)	(1.267)	(1.258)	(1.243)

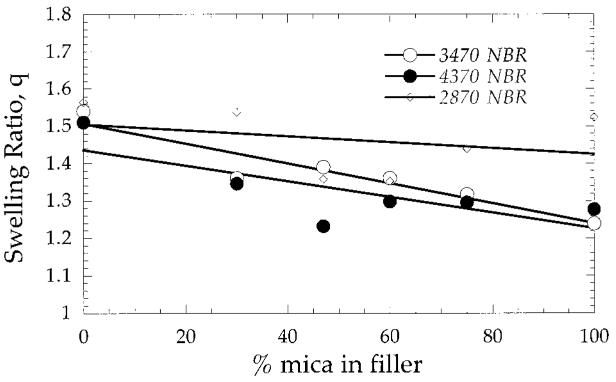

Figure 1 Plot of swelling ratios of NBR composites having different amounts of acrylonitrile content as a function of unsilanized mica in total filler.

ilar to our observations, Khanh and Denault[24] observed that with the addition of two-dimensional fillers such as mica in the polypropylene matrix mica-reinforced polypropylene becomes more and more ductile, leading to higher elongation. Here, in the same manner (Tables III–V), elongation increases with the surface treatment of mica, which allows a decrease of surface energy of the filler, reduction in agglomeration, and improvement in flake alignment.[25]

The stress–strain curves of the 3470 NBR composites with only carbon black (a) and optimum compositions with (b) unsilanized and (c) silanized mica are given in Figure 4. The area under these curves is a measure of the toughness and is equal to the energy absorbed by the specimen up to fracture. Our results are similar to results on polypropylene–mica composites.[24] Here, toughness is maximum for the composition having 47% both unsilanized and silanized mica in the total filler.

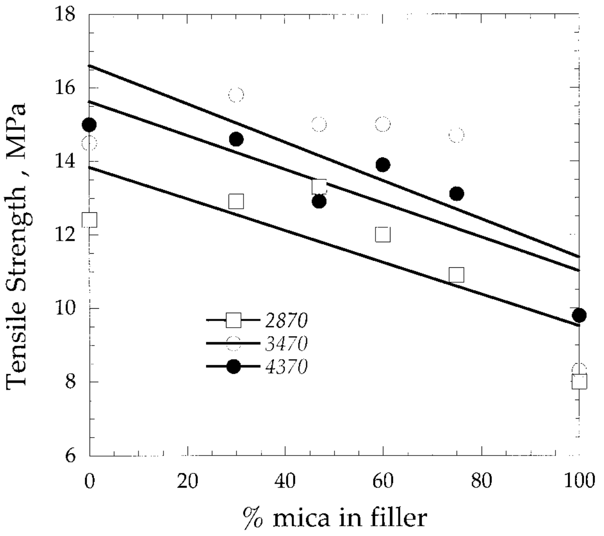

Figure 2 Variation of ultimate tensile strength with concentration of unsilanized mica in total filler for NBR composites having different amounts of acrylonitrile content.

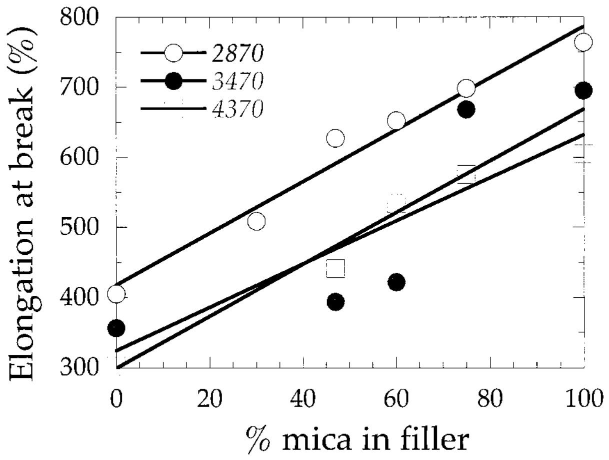

Figure 3 Variation of elongation at break with concentration of unsilanized mica in total filler for NBR composites having different amounts of acrylonitrile content.

Dynamic Mechanical Properties of Composites

Dynamic mechanical behavior of the composite is of great interest and important in structural application. Figure 5 show dynamic mechanical spectra of (a) only carbon black, (b) 47% mica in the total filler, and (c) 47% silanized filler-reinforced 3470 NBR.

One can observe that both E' (storage modulus) and E'' (loss modulus) increase with increas-

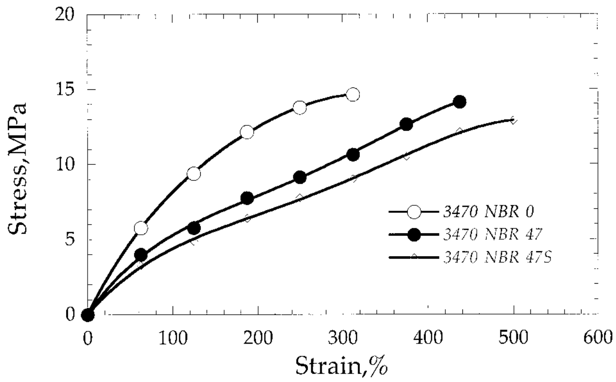

Figure 4 Stress–strain diagram for (a) 3470 NBR 0, (b) 3470 NBR 47, and (c) 3470 NBR 47S composites.

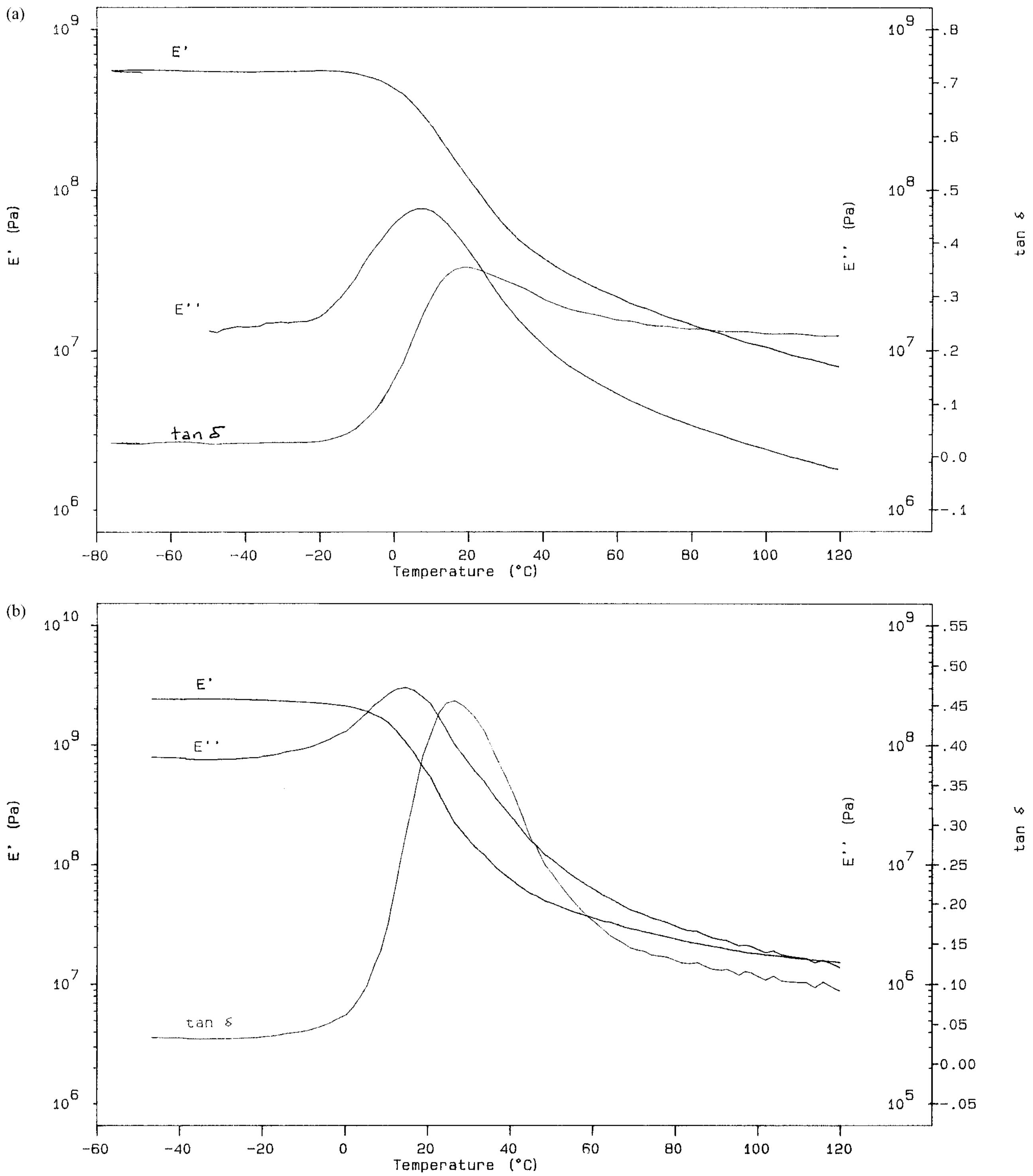

Figure 5 Dynamic moduli and tan δ (damping) versus temperature plots of (a) 3470 NBR 0, (b) 3470 NBR 47, and (c) 3470 NBR 47S composites.

ing silanized and unsilanized mica content at a frequency of 1 Hz. Another feature observed from the figure is that the glass transition temperature (T_g) of the sample with carbon black reinforcement is only 17°C. In the presence of about 47% mica as a replacer, the T_g of the composite in-

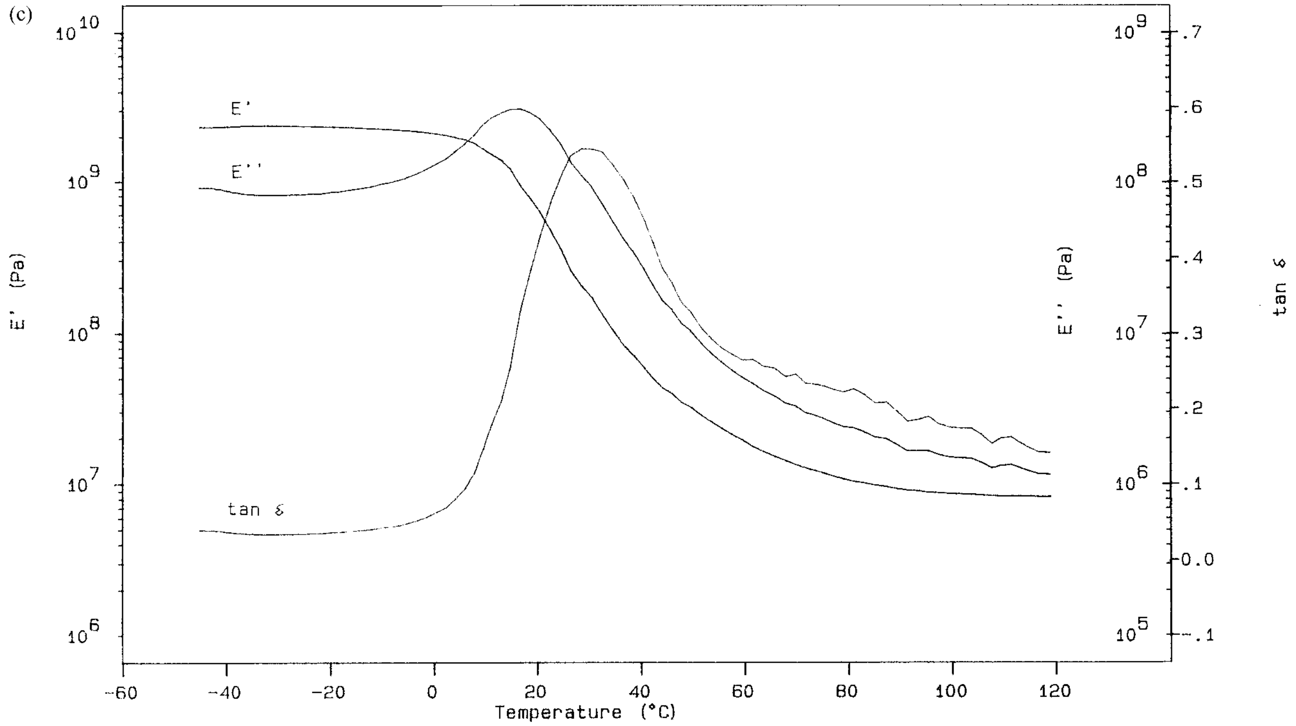

Figure 5 (*Continued from the previous page*)

creases to 22°C and the damping peak becomes broader. Although the mica is inert at this temperature range, the dynamic mechanical properties of the composite are different from the carbon black-reinforced polymer due to the effect of the mica–matrix interphase. Moreover, silane treatment also causes an additional broadening of the tan δ peak. We believe that a slight upshift of the glass transition temperature, the broader damping peak, and the increased dynamic modulus are due to the extra bonding between the matrix and the mica, as well as to the optimum packing of the two different sized and shaped fillers. Tan δ values, measured at a large temperature range (−60–120°C) and a frequency of 1 Hz, increase from 0.35 to 0.45 and, finally, to 0.54 for the composites having only carbon black, 47% unsilanized mica, and 47% silanized mica in the total filler, respectively.

CONCLUSIONS

Replacement of unsilanized mica with carbon black marginally decreases the swelling of the composites' organic solvents and increases toughness values. Silanization of the mica surface by using Polyvest 25, trimethoxysilane having the oligomeric polybutadiene matrix selective group, substantially improves the ultimate strength, indicating an enhanced polymer–filler interaction and increases both the elongation and toughness and causes a decrease in swelling. Dynamic mechanical properties show that the moduli E' and E'' increase with replacement of mica with carbon black and the composite can act as a better vibration damper at a wider temperature range.

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