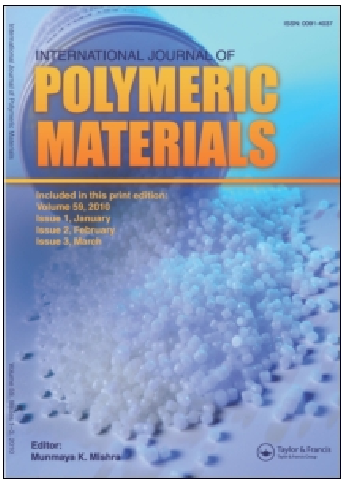

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Polydimethylsiloxane Composites Reinforced by Fumed Silica/Mica Hybrid Reinforcers

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In this study, physical properties of fumed silica and mica hybrid reinforced polydimethylsiloxane composites have been investigated with special reference to the effect of loading composition, degree of cross-linking, and silanization. The composites were prepared *via* milling technique and were examined in terms of static and dynamic mechanical properties as well as swelling behaviour. Swelling ratio of the composites was found to decrease as mica content increased. Silanization of mica gives rise to a further decrease in swelling. Static mechanical properties of the composites, such as elongation at break, stress at break, and work up to fracture were also found to be enhanced by the addition of mica. Dynamic mechanical spectra were obtained, and the effects of filler and silanization as well as frequency on E', E'', and tan δ values were all discussed. In light of this study, we found that, by tailoring the compositions of the composites, it is possible to obtain structures that are resistant to solvents, have good static and dynamic mechanical properties. And also, by adjusting the compositions, composites can become effective dampers in the frequency and temperature range of interest.

Keywords: Polydimethylsiloxane composites; Fumed Silica; Mica; Hybrid reinforcement

INTRODUCTION

Polymer science and technology seek new routes to improve the performance of the filled plastic materials while reducing their costs. At the present time the effects of individual fillers on the properties of components are relatively known. For example tensile strength can

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usually be improved by fibrous fillers, provided that adhesion is sufficient and rigidity can be improved by sheet like fillers, and the improvement depends on the aspect ratio of the filler [1].

Multi-component compounding, on the other hand, produces so called hybrid-structures where the effects of two or more components are combined to yield composites that have better physical properties than those of single-component compounds [2]. Multi-component compounding is also an effective way to reduce the amount of an individual component in a composite.

Recently, the investigations on composites having multi-component filler systems were mainly focused on some thermoplastics and thermosets [2–5]. Jarvela *et al.* [2] reported that multi-component compounding of polypropylene with several mineral fillers, glass beads (spherical), mica (sheet-like), and wollastonite (fibrous) gave better results than what could be obtained with single component compounding. Rebeiz *et al.* [3] published an article about multi-component compounding of PET based unsaturated polyester filled with fly ash and sand filler. In this study, it was found that the tensile strength increased with increasing sand with up to 50 per cent by weight of fly ash, but the tensile modulus decreased with increasing fly ash since fly ash has lower stiffness than sand.

Varughese *et al.* [4], have prepared unsaturated polyester based polymer concretes by the use of fly ash and river sand as fine aggregates and granite as a coarse aggregate. Properties such as cure time, flexural strength, and resistance to water absorption were studied by varying the level of fly ash.

Recently, the physical properties of mica and fly ash hybrid reinforced unsaturated polyester composites in both uncured and cured state have been investigated by Nugay *et al.* [5]. Results were discussed with a special reference to effect of hybrid reinforcement on curing characteristics, viscosity, sedimentation rate of uncured liquid polyester composites as well as on mechanical, swelling, and vibrational damping properties of resultant cured composites.

Although some recent investigations on composites having multi-component filler systems were Mentioned in the literature, studies for rubber matrixes are limited. Recently, Nugay and Erman [6] investigated the swelling behaviour, static mechanical properties, and dynamic mechanical properties of nitrile rubber having both carbon black and mica hybrid filler system. In this study which is an example for multi-component compounding, beneficial effects of using mica as a second filler on the properties examined, have been reported.

An aim of this study is to improve the static and dynamic mechanical properties, as well as swelling behaviour of fumed silica reinforced polydimethylsiloxane composites *via* hybrid reinforcement with mica particles. It is well known that mica refers to a group of minerals whose crystals exhibit a high degree of basal cleavage, which allows them to be split into very thin sheets that are strong, flexible, slippery, chemically inert and transparent. Fumed silica's, on the other hand, are fluffy white powders of amorphous structure. Because of their extremely small particle size and spherical morphology, high surface area, unique surface chemistry, and high purity, these products are used in a multitude of applications.

In this study, the effect of composition of these fillers, degree of cross-linking, and silane treatment of mica on the final performance of the resultant composites are all discussed.

EXPERIMENTAL

Materials Used

Polydimethylsiloxane (PDMS-Silopren HTV) having 40 per cent fumed silica as filler was supplied from Bayer, Germany. Muscovite mica ca 45 μm used for this study was supplied by Sabuncular-Mica Trading Corporation, Turkey, Çine. Tetrahydrofuran (THF) was the product of Merck and used as received. Dicumyl peroxide is supplied by Bayer and the silane coupling agent methacrylsilane is a product of Hülls.

Preparation of the Composites

All composites were prepared using silanized and unsilanized mica to give 0, 2, 5, 10, 15 weight per cent of mica with respect to polydimethylsiloxane and were cross-linked to three different extents; 0.5, 1.0, 1.5 phr dicumyl peroxide. The following nomenclature is used. Composition of siloxane composite without mica and 0.5 phr DCP is indicated as SC0-0.5. Compositions having 2, 5, 10, 15 weight per cent mica and 0.5 phr DCP are designated as SC2-0.5, SC5-0.5, SC10-0.5, SC15-0.5 respectively. The numbers appended to the two letter words denote the amount of mica in per cent and the number following the line denotes the amount of DCP used in phr. The same notation is used for silanized samples also, where an 'S' follows the number indicating the amount of mica. 1.0 and 1.5 phr DCP containing compositions having 5 per cent mica are indicated as SC5-1 and SC5-1.5 and for the silanized analogues of the same composition an 'S' is added after the number denoting mica per cent, SC5S-1 and SC5S-1.5, respectively.

Mixing was achieved on an open two-roll mill with a nip gap of 0.25 mm. Optimum cure time at 175°C was determined using rheograms taken with Monsanto Rheometer R-100. Vulcanization was done in an electrically heated press at 175°C in two mm thick steel moulds. The samples were post-cured at 200°C for six hours and conditioned for 24 hours at 20°C before testing.

Application of the coupling agent was done as follows. The silane coupling agent, methacrylsilane was added to a mixture of distilled water and ethanol previously adjusted to pH 5.5. Solid mica was mixed with the coupling agent solution for two hours and then filtered on a Buchner filter and dried.

Physical Testing of the Samples

For swelling experiments, strips of dimensions $0.2 \times 0.5 \times 2$ cm were immersed in THF at room temperature for three days and the length changes were measured in the immersed state by a travelling microscope, Gaethner 7109-C-46, with an accuracy of 0.001 cm. Swelling degrees were reported in terms of swelling ratio, which is expressed as, $q = [L_{swollen} / L_{unswollen}]^3$ [7].

Mechanical experiments were performed under two loading conditions: a) Dynamic mechanical tests, carried out on a Polymer Laboratories Dynamic Mechanical Thermal Analyser (DMTA) at room temperature for frequencies 1, 10, 100 Hz with the samples having dimensions of $16.0 \times 8.0 \times 2.0$ mm. b) Quasi-static mechanical tests, were carried out at room temperature and cross-head speed of 50 cm/min in the static mode of a Zwick 1464 Universal Testing Machine equipped with an incremental extensometer. Samples are dumbbell shaped and the dimensions are 0.70 mm. width and 2 mm thickness.

RESULTS AND DISCUSSION

All physical properties of the composites are given in Table I.

Figure 1 shows the variations of the swelling ratios with both silanized and unsilanized mica loading to fumed silica containing PDMS.

It is evident from the figure that the general trend followed by the composites by the addition of mica is exhibited as a decrease in the swelling ratio. This decrease is much more pronounced for silanized mica composites especially after five per cent addition. For the samples with silanized mica, swelling decreases about forty per cent up to ten per cent mica loading and remains unchanged beyond this value with about twenty per cent decrease. These results can be safely attributable to the enhanced polymer filler interaction, which inhibits the solvent diffusion into the network.

It can also be concluded that the optimum composition for best swelling properties can be achieved after five per cent mica loading. The explanation of the decrease in swelling ratios by the addition of mica for both silanized and unsilanized mica composites probably lies in the mechanism by which fumed silica particles settled between the mica particles affects the structure. Mica has sheet-like particles and they tend to orientate strongly along the machine direction. Fumed silica particles are ordered to a much lower degree than mica particles.

TABLE I Physical properties of the composites

	Stress at break N/mm^2	*Elongation at break %*	*Work up to fracture N.mm*	*Swelling ratio*
SC0-0.5	6.40	210.84	4.63	3.11
SC2-0.5	5.8	208.01	4.96	3.53
SC5-0.5	4.6	201.21	4.40	2.845
SC10-0.5	3.65	266.32	6.85	2.41
SC5-1.0	5.46	171.27	4.10	2.47
SC5-1.5	6.00	187.12	4.75	2.40
SC15-0.5	5.06	243.55	6.56	2.33
SC2S-0.5	6.13	250.46	6.16	2.48
SC5S-0.5	5.83	226.80	5.46	2.51
SC10S-0.5	4.83	272.32	6.70	2.05
SC15S-0.5	6.80	241.10	7.33	1.88

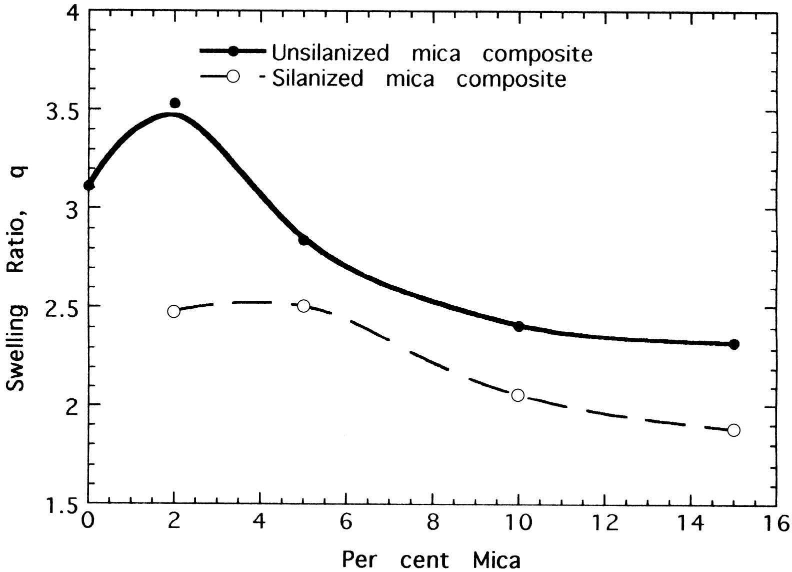

FIGURE 1 Variations of the swelling ratios of the composites with both silanized and unsilanized mica loading.

Thus, fumed silica particles will be situated in between the mica particles resulting in uniform distribution of cross-linker and effective cross-linking probably *via* providing optimum packing. In their studies on carbon black and mica hybrid reinforced nitrile rubber composites, Nugay and Erman [6] determined the specific compositions at which composites have maximum dimensional stability in solvent by using the beneficial effect of mica on the other.

Additionally, PDMS composites having more cross-links also exhibit a decrease in swelling when both silanized and unsilanized mica is used, owing to the decrease of the diffusion of solvent molecules into the polymer structure caused by the cross-links. On the other hand, the composite having unsilanized mica and low degrees of cross-linking (SC5-0.5) shows higher swelling ratio than the same composite with higher degree of cross-linking (SC5-1 and SC5-1.5), as given in Table I. In another words, polydimethylsiloxane composite having low degree of cross-linking also exhibits a decrease in swelling when silanized mica is used as reinforcer, which is a major benefit in terms of practical application.

Stress at break values of the composites decreases when mica content increases up to ten per cent loading. But beyond that point stress at break increases rapidly. The decrease in stress at break values is probably due to the viscous drag of small amount of mica particles with the help of small fumed silica particles showing somewhat solvent effect for platelet mica in the matrix. In this way platelet mica can easily move between spherical fumed silica particles, like rolling on balls. This gives rise to a decrease in stress at break values for mica content till ten per cent. But after that, the rise of stress at break indicates that mica reaches optimum amount and orientates along the direction of the applied force which results in higher tensile strength. The orientation effect of mica in the same composite was also determined by infrared and birefringence measurements [8]. Results are also given in Figure 2 as the change of stress at break by the addition of mica to fumed silica reinforced PDMS.

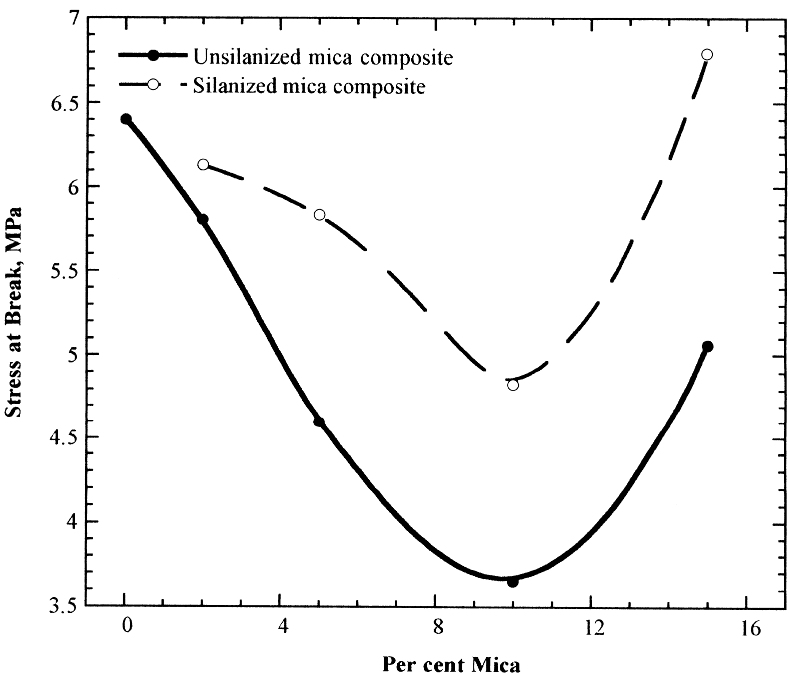

FIGURE 2 Change of stress at break of the composites with mica %.

The effect of bridging *via* silanization on reinforcement is also observed by an increase in tensile strength. Similar results are given in the literature [5, 9]. This improvement in the ultimate properties is attributable to the silane coupling agent, methacrylsilane, which improves the dispersion and reduces the number of failure-initiating stress concentrations by means of enhancing polymer-filler interaction. It is also well known that if there is adhesion between polymer and filler, the tensile strength of the composite increases. If there is no or weak adhesion, the tensile strength decreases.

Table I also indicates that, stress at break values are enhanced when the degree of cross-linking increases. This result is expected since the flexing of the matrix is prevented by increasing the amount of cross-links. When a larger amount of DCP is used it is possible to obtain a much more cross-linked and thus more rigid and stiff network structure.

On the other hand, addition of mica in fumed silica reinforced PDMS does not make the composites brittle, as is evident from the higher percentage of elongation at break values of composites having increased mica loading. This behaviour is given as the plot of elongation versus mica per cent in Figure 3.

Composites have high elongation at break values at especially ten and fifteen per cent mica loading. Similarly elongation increases with surface treatment of mica, which allows a decrease in surface energy of filler, reduction in agglomeration and improvement in flake alignment. Nitrile rubber composites that have carbon black and mica hybrid filler system, were found to exhibit enhanced elongation, in the study of Nugay and Erman [6], when the composites were further filled with both unsilanized and silanized mica particles.

It is also clear from Table I that elongation at break decreases when DCP phr increases. This means, when the amount of cross-links increase, composites become much more stiffer and cross-links prevent the flexing of the polymer and thus elongation decreases.

It is well known that the area under stress-strain curves is a measure of the toughness and gives an idea about the energy absorbed by the specimen or, in short, how the matrix dissipates energy in the case of damage or fracture of the composite. Toughness of the composites is observed in Figure 4 as work up to fracture *versus* mica loading.

It is obvious that the amount of energy observed by the specimen to break, *i.e.*, toughness of the fumed silica reinforced PDMS, increases

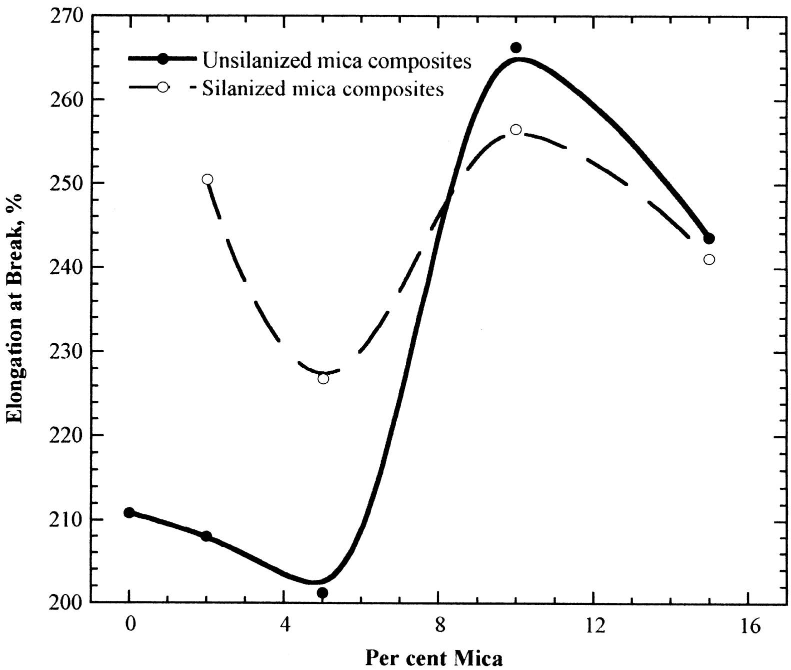

FIGURE 3 Change of elongation of the composites with mica %.

when mica content increases. Especially composites having ten and fifteen per cent mica exhibit the maximum toughness due to the inherent high elongation and tensile strength of these compositions.

Nugay *et al.* [5, 6] also stated an increase in toughness of nitrile rubber and polyester composites having carbon black/mica and fly ash/mica hybrid filler systems, respectively, in case of higher mica loading.

When cross-linking increases, the ability of the composites to absorb energy till fracture is enhanced. In other words, composites exhibit higher toughness values if they are cross-linked to higher extents (Tab. I).

Dynamic mechanical data, such as E′, EE″, and tan δ values of fumed silica and mica hybrid filler containing PDMS composites were examined, first at constant temperature and 1, 10, 100 Hz frequencies. The results are given in Table II.

It is evident from the table that the E′, EE″, values increase when the frequency increases. When the frequency increaes the period of

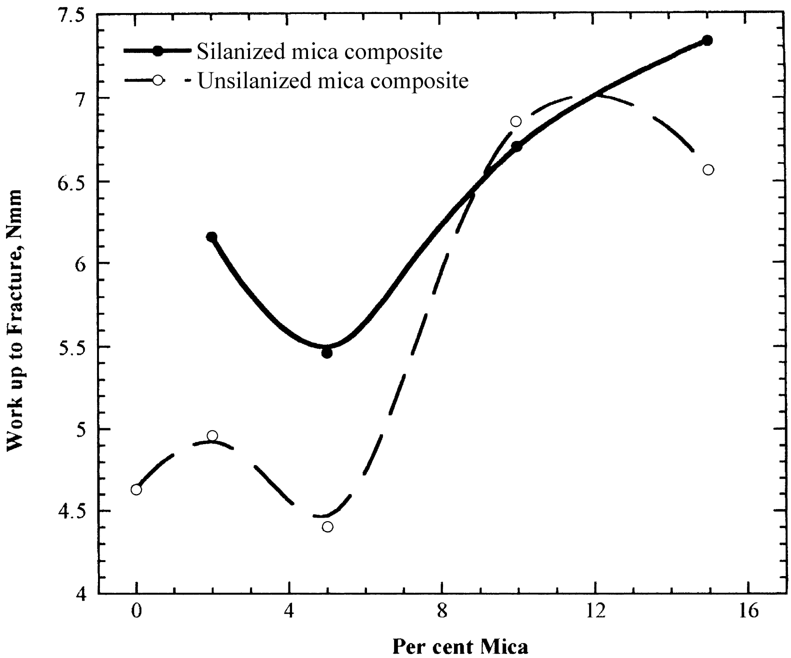

FIGURE 4 Variation of work up to fracture of the composites with mica %.

oscillation shortens, so possible configurational changes and rearrangements of macromolecules through an entropy change becomes difficult. E′ shows small increment, whereas the change in E″ is relatively higher. This zone may be characterized as the plateau zone where E″ changes little with frequency and E″ values increases due to the sufficient time (moderate or low frequency) network strands between coupling points have to rearrange their configurations and store elastic energy through an entropy change as stated above.

The loss factor, tan δ, is one of the damping parameters since it is a measure of the ability of the polymer to convert mechanical energy into heat at a temperature and frequency of interest. Variation of tan δ values with increasing frequency and mica content is given in Figure 5.

Since this value is simply the ratio of E″ to E′, ($\tan\delta = E''/E'$), and E″ of composites increase more, with respect to E′, it is logical to expect an increase in tan δ values with increasing frequencies.

TABLE II Dynamic mechanical data of the composites

Sample Code	*SC*0-0.5	*SC*2-0.5	*SC*5-0.5	*SC*10-0.5	*SC*15-0.5	*SC*5-1	*SC*5-1.5	*SC*2*S*-0.5	*SC*5*S*-0.5	*SC*10*S*-0.5	*SC*15*S*-0.5	*SC*5*S*-1	*SC*5*S*-1.5
100HZ													
tan delta;	0.1434	0.1476	0.2058	0.1953	0.1980	0.1555	0.1506	0.1376	0.1428	0.1945	0.2008	0.1404	0.1807
E' GPa	6.8580	6.7090	8.9495	9.1040	9.0790	7.3250	8.8950	6.6950	8.9460	6.833	8.126	6.899	7.002
E'' GPa	0.9843	0.9888	1.8740	1.7800	1.7980	1.1360	1.3390	0.9217	1.2780	1.327	1.633	0.9681	1.265
10 Hz													
tan delta;	0.1212	0.1299	0.1211	0.1334	0.1382	0.1305	0.1150	0.1233	0.1140	0.1297	0.1318	0.1251	0.1264
E' GPa	6.1200	5.8200	7.9190	7.8430	7.9600	6.5980	7.8360	5.8330	7.8390	6.826	7.222	6.181	6.125
E'' GPa	0.7418	0.7563	0.9588	1.0530	1.0990	0.8621	0.8997	0.7191	0.8942	0.8856	0.9511	0.7739	0.7739
1 Hz													
tan delta;	0.1150	0.1189	0.1113	0.1215	0.1291	0.1236	0.1090	0.1185	0.1073	0.1236	0.1231	0.1194	0.1216
E' GPa	5.4380	5.2180	7.0840	7.1620	7.1840	5.8430	7.0350	5.2150	7.0650	6.078	6.559	5.557	5.487
E" GPa	0.6249	0.6204	0.8007	0.8688	0.9275	0.7328	0.7711	0.6184	0.7579	0.7512	0.8073	0.6636	0.6675

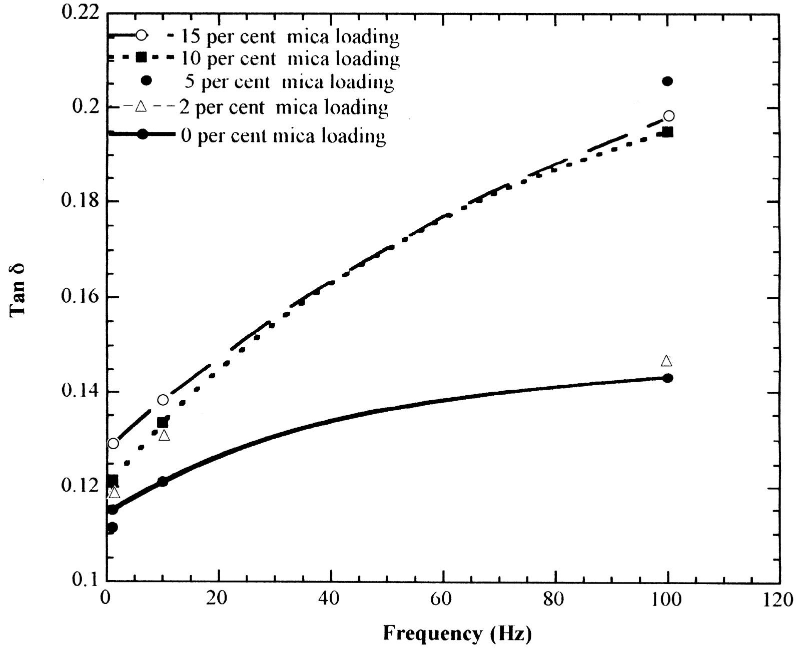

FIGURE 5 Variation of tan δ with frequency and mica %.

It can be concluded that, since the composites in this study exhibit reasonably high tan δ values at especially ten and hundred Hz frequency range and especially for ten and fifteen per cent mica loading, these materials have good damping properties for the given range and compositions. This may result from the fact that in optimum filler state in which the distribution of the filler in the matrix is perfect, the internal friction among macromolecule segments and fillers increases much more to convert the mechanical energy into heat. The increase of the internal friction increases the mechanical dissipation and enhances vibration damping. This result was also observed in the studies of Nugay and Erman [6] in which nitrile rubber has been hybrid reinforced *via* carbon black/mica particles.

If the results of dynamic mechanical thermal analysis at one Hz frequency and -140 to 60°C temperature range are considered (Fig. 6), it can be concluded that addition of mica increases the

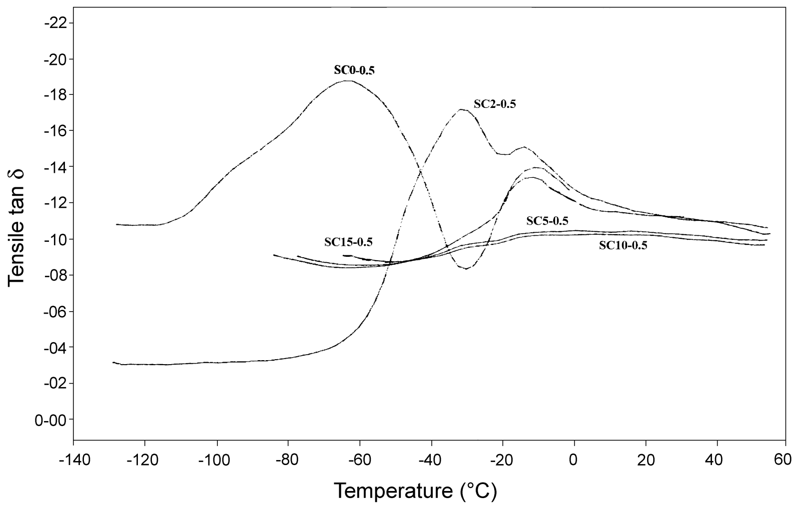

FIGURE 6 Variation of tan δ of the composites at a termperature range.

stiffness of the composites, since it has a higher modulus than the matrix, and gives rise to the increase of interaction between fillers and macromolecules, and as a result $\tan\delta$ peak shifts to higher temperatures and broadens.

For the composite having only fumed silica as filler, tan δ peak is observed near $-60°C$. There seems to be some heterogeneity in the structure, probably because of a different molecular weight portion or inhomogeneous distribution of fumed silica particles, since another peak is observed nearly at $-10°C$. On the other hand, by the addition of mica to the fumed silica containing PDMS, $\tan\delta$ peak shifts to higher temperature and heterogeneity seems to be less. Here a beneficial effect of hybridisation in getting homogeneous structures still exist. That is, by changing the compositions of the composites, it is possible to adjust the $\tan\delta$ peak range of composites, so that they become an effective damper at that temperature or frequency range of interest.

Silanization does not only cause the $\tan\delta$ peak shift to higher temperatures but also, makes the composites exhibit broader tan δ peaks than their unsilanized counter parts.

CONCLUSIONS

The results of the study can be outlined as follows:

- Swelling of composites decreased significantly in case of mica loading and higher extent of cross-linking. Also, silanization of mica gave rise to a further decrease in swelling ratios as a result of improved interfacial properties and adhesion *via* silane coupling agent. Especially, SC15S-0.5 and SC5S-1 seem to be optimum compositions that have more resistance to solvent. Composites having low degree of cross-linking also exhibited a decrease in swelling when silanized mica was used as reinforcer, which is a major benefit in terms of practical application.
- Stress at break of the composites decrease when mica content increases up to ten per cent. But after ten per cent loading, stress at break increases, which is an indication of the optimum packing and orientation of platelet mica in the direction of applied force. Stress at break also increases when degree of cross-linking increases, as a result of decreasing flexibility of the structure. On the other hand, addition of mica does not make the composites brittle as is evident from higher elongation at break values in case of more mica incorporation. Elongation at break decreases when composites are cross-linked to higher extent, which is attributable to the more rigid and stiffer structure of the composites *via* cross-links.
- Static mechanical tests also revealed that toughness increases when mica loading increases. Especially, composites having ten and fifteen per cent mica exhibit the maximum toughness.
- Dynamic mechanical properties of the composites are also observed to be enhanced by the incorporation of platelet mica and a further enhancement was seen in case of silanization of the filler. E' and E'' values of both silanized and unsilanized composites increased with increasing frequency and mica content. Cross-linking to higher extents and silanization also enhances these values. E'' of composites increase more, with respect to E' values. Since composites exhibit reasonably high tan δ values at especially ten and hundred Hz frequency range and especially for ten and fifteen per cent mica loading, materials have good damping properties for the given range and compositions. Addition of mica gives rise to a shift of tan δ peak

to higher temperatures together with a broadening effect. Silanization does not only cause the tan δ peak shift to higher temperatures but also, makes the composites exhibit broader tan δ peaks than their unsilanized counter parts.

- All these studies have revealed that hybridisation of fumed silica reinforced PDMS composites with ten and fifteen per cent mica particles can lead to a real enhancement in final performance, in terms of maximum dimensional stability in organic solvent, maximum toughness, and maximum vibrational damping capacity within quite reasonable temperature and frequency ranges. By changing the compositions of the composites, here by adding ten and fifteen per cent mica to fumed silica reinforced PDMS composites, it is possible to adjust the composite structures, so that they become an effective damper at the temperature or frequency range of interest. In other words, tailoring the compositions results in good vibration damping properties.

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