Biogenic Silica Short Fibers as Alternative Reinforcing Fillers of Silicone Rubbers

V. P. Silva, M. C. Gonçalves, I. V. P. Yoshida

Instituto de Química, Universidade Estadual de Campinas, CP 6154, 13083–970, Campinas, São Paulo, Brazil

ABSTRACT: The performance of biogenic opaline silica short fibers, natural (NF) or modified with vinyltrimethoxysilane (MF), as primary or secondary fillers in an elastomeric matrix of poly(dimethylsiloxane), PDMS, was evaluated in this work. Compounding was carried out on a two-roll mill, and the PDMS matrix was peroxide crosslinked by compression molding. Characterization of these fibers was performed by BET surface area, X-ray fluorescence, infrared spectrum, X-ray diffractometry, field emission scanning electron microscopy, and Bayer's test. The obtained rubbers were characterized by thermogravimetric analysis, field emission scanning electron microscopy, swelling measurements in cyclohexane, dynamic mechanical analysis, and tensile tests. As primary filler, NF and MF increased the thermal stability of the PDMS matrix, and MF also restricted the swelling of this matrix in cyclohexane. For the rubbers containing NF or MF as secondary filler, the swelling restriction was caused by both fibers. Silica short fibers were also efficient as primary filler in PDMS with regard to Young's modulus and tensile strength, and as secondary filler, NF and MF were effective reinforcing fillers in relation to storage and Young's modulus, resulting on an increase in the stiffness of the rubbers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 290–299, 2006

Key words: biogenic silica short fibers; fillers; reinforcement; silicone; rubbers

INTRODUCTION

Siloxane polymers, particularly high molecular weight poly(dimethylsiloxane), PDMS, exhibit some properties, such as high flexibility and mobility of chains, that make them suitable for use in the rubber technology. However, PDMS-based rubbers generally have poor mechanical properties, in the absence of fillers, such as low tensile strength.[1] Appropriate strengths are obtained by incorporating suitable reinforcement agents, such as silica particulates (fumed silica, precipitated silica, and quartz), which are the most widely used reinforcing fillers in silicone rubbers.[2] Although particulate filler reinforcement still dominates the rubber industry, sisal, and cellulose fibers,[3–5] and also synthetic short fibers[6–11] have been incorporated into elastomeric matrices to improve or modify mechanical properties or for cost reduction.

Filled polymers are the simplest type of composite polymeric materials. Their mechanical properties depend on the characteristics of the polymeric matrix and of the fillers, as well as on the adhesion at the filler-matrix interface.[5,7,12] Interactions at the interface can be enhanced by treating the filler surface with suitable coupling agents, such as those based on silane chemistry.[5,7,13] Coupling agents can create covalent bonds between the reactive groups of the polymeric matrix and those on the filler surface, which increase the stress transfer efficiency at the interface and, consequently, improve the mechanical properties of the composite.[13]

Biogenic silica short fibers are found in high amounts in sediments of lake beds together with clay, sand, and organic matter, in some regions of Brazil. They represent the inorganic material of the internal supporting structure of sponges (Demospongiae),[14] and because of the siliceous nature, these silica short fibers are potentially nonexpensive reinforcing fillers in polymeric composites. In this study, natural and modified biogenic silica short fibers were used as primary or secondary filler in PDMS matrix, and the effect of these fibers on the thermal, mechanical, and swelling properties of the silicone matrix was analyzed.

EXPERIMENTAL

Materials

Natural silica short fiber (NF), with average diameter and length of 10 and 200 μm, respectively, was kindly

supplied by Cerâmica São Caetano Ltd. (Belo Horizonte, MG, Brazil). Tetrahydrofuran (THF) and n-butyl titanate catalyst were purchased from Carlo Erba (Rodano, MI, Italy) and E. I. Du Pont de Nemours and Company (Wilmington, DE), respectively. Vinyltrimethoxysilane (VTMS), used to modify the natural silica short fiber surface, and poly(dimethylsiloxane) gum (PDMS-gum), with an average molecular weight of $\sim 10^6$ g mol^{-1} and $(SiCH_3CH = CH_2O):(Si(CH_3)_2O) < 1:1000 M$ ratio, used as matrix for the rubbers, were supplied by Dow Corning do Brazil Ltd. (Hortolāndia, SP, Brazil). The same PDMS-gum previously mixed with $\sim 27\%$ (w/w) of nanometric fumed silica (S), which was named S-PDMS, was also used in the preparation of the rubbers. The 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane used as a radical initiator agent was obtained from Akzo Nobel Polymer Chemicals (Amersfoort, AE, The Netherlands). Cyclohexane was acquired from Vetec Química Fina Ltd. (Rio de Janeiro, RJ, Brazil).

Surface treatment of the natural silica short fiber

Natural short fiber surface was modified with previously hydrolyzed VTMS at a molar ratio VTMS: H_2O of 1:1, using THF as solvent and n-butyl titanate as catalyst, 2% (w/w) in relation to the silane amount. The solution of THF containing VTMS and catalyst was mechanically stirred for 3 h at 25°C. Afterwards, NF was transferred to the reaction flask and this mixture was then mechanically stirred for 24 h at 25°C, under argon atmosphere. After the reaction, the resulting modified silica short fiber (MF) was filtered and washed with THF, and this procedure was repeated for three times to eliminate the physically adsorbed silane on the fiber surface. MF was then dried at 60°C for 48 h prior to the characterization.

Compounding procedure

The rubbers were prepared by using 20 phr (parts per hundred parts of rubber, by weight) of NF or MF and 0.65 phr of peroxide, which were added to PDMS-gum or to S-PDMS. By mixing PDMS-gum or S-PDMS with peroxide, two reference samples were also prepared, which were called unfilled rubber (UR) and fumed silica rubber (S-rubber), respectively. Compounding of all the samples was carried out in a COPÉ open two-roll mill for 20 min at 25°C. The rotors were operated at a speed ratio of 1:1.4. To obtain sheets with low degree of silica short fiber orientation, the mixtures were passed through the mill at least eight times in a random way and the mill parameters were kept constant. The compounds were compression molded in a Parabor PL350 compression molding machine at 175°C and 22 MPa of pressure for 10 min, followed by post cure treatment in a vacuum oven at 120°C for 8 h.

The samples were molded as $150 \times 150 \times 2$ mm^3 sheets.

Characterization

BET surface area of NF and MF was measured in a Micromeritics FLOW SORB II-2300. Elementar composition of these fibers was determined by energy dispersive X-ray fluorescence (XRF) in a Shimadzu EDX-700, with a rhodium tube, and a detector of Si(Li). For this purpose, samples were analyzed as powder, under vacuum and with a collimator of 10 mm.

Fourier transform infrared (FTIR) spectra of NF and MF were obtained in a Bomem MB-SERIES spectrometer, collecting 256 scans in the range from 4000 to 400 cm^{-1}, in KBr pellets, with a resolution of 4 cm^{-1}. X-ray diffraction (XRD) measurements of these fibers were carried out in a Shimadzu XRD6000 equiped with CuKα radiation ($\lambda = 0.15418$ nm), 30 mA of current, and 40 kV of voltage.

The short fibers were also submitted to the qualitative Bayer's test, with the main purpose of determining the presence of vinyl groups on the MF surface. This test consists on the oxidation reaction of double bonds by permanganate giving rise to MnO_2 brown precipitate.[15] For this reaction, some drops of an aqueous solution of $KMnO_4$ (1%, w/w) were added to $\sim 1\%$ (w/w) of MF in water. The formation of brown precipitate indicated the presence of double bonds.

The morphology of the silica short fibers and rubbers was investigated by field emission scanning electron microscopy (FESEM), performed in a JEOL JSM-6340F microscope operated at 3 kV. For this purpose, samples of NF and MF were pulverized on an appropriate support and sputter-coated with very thin carbon and gold layers in a Bal-Tec MED 020 instrument. Rubber samples were cryogenically fractured and the fracture surface was also sputter-coated with very thin carbon and gold layers, before scanning.

Swelling measurements were performed in cyclohexane, following ASTM D471.[16] Rubber strips with dimensions of $30 \times 10 \times 2$ mm^3 were weighed and immersed in 25 cm^3 of the solvent, and, at regular intervals, the surface of the swollen strip was gently dried with a filter paper, and the weight of the sample was registered. The earlier mentioned procedure was repeated until a constant swollen weight was obtained. Afterwards, samples were dried in a vacuum oven at 50°C, for 24 h, and weighed again. For each rubber, three specimens were tested and the average results were reported.

Thermal stability of the rubbers was analyzed by thermogravimetric analysis (TGA) in a TA 2950 thermobalance, TA Instruments, from 25 to 1000°C, at a heating rate of 20°C min^{-1}, under argon flow (100 cm^3 min^{-1}, 99.999%).

Dynamic mechanical analysis (DMA) of the rubbers was carried out in a DTMA V, Rheometric Scientific, in a temperature range between −135°C and 40°C, at a frequency of 1 Hz, and at a heating rate of 2°C min⁻¹. Tensile tests were performed in an Instrom 4464, according to ASTM D412–98a,[17] at 25°C and a rate of grip separation of 500 mm min⁻¹. For this purpose, seven specimens were tested for each rubber and the average results were reported.

RESULTS AND DISCUSSION

Characterization of the silica short fibers

The surface of the natural silica short fiber (NF) was modified by the reaction with VTMS prehydrolysed oligomeric species. According to Plueddemann,[18] silane oligomers are more effective than monomers as modifier agents. Hypothetical scheme for the modification reaction is illustrated as following:

The incorporation of vinyl groups on the NF surface, giving rise to the modified silica short fiber (MF) with higher hydrophobic character than NF, could be qualitatively shown by the nonwettability of MF in water. This hydrophobic characteristic facilitated the incorporation of MF into the hydrophobic PDMS-gum. In addition, the vinyl groups on the fiber surface can be active centers for peroxide induced reactions, allowing the formation of covalent bonds between the MF surface and the PDMS matrix.[19,20]

NF and MF showed very low surface areas, 0.95 m² g⁻¹ and 0.04 m² g⁻¹, respectively. Chemical composition of these fibers, obtained by XRF, expressed as percentage of oxides, can be seen in Table I. They are composed essentially of silica (~95%), as expected, and with small concentration of Al_2O_3 and other oxides.

Similar FTIR spectra (not shown) were obtained for NF and MF, characterized by absorptions related to Si—O—Si groups: a doublet with maxima at 1104 and 981 cm⁻¹, corresponding to the asymmetrical stretchings; an absorption at 793 cm⁻¹, related to the symmetrical stretching; and another absorption at 471 cm⁻¹, characteristic of siloxane cyclic structure vibrations. Other absorptions at 3433 and 1640 cm⁻¹, associated to the adsorbed water, were also observed. The band at 3433 cm⁻¹ may also have some contributions

from associated Si—OH stretching. These spectra were characteristic of opal or opaline silica.[21–23]

X-ray difractograms of NF and MF showed only a very broad and intense halo at ~22° (2θ), with a correlation distance of ~4 Å, characteristic of amorphous opaline silica, containing cristobalite nanocrystallites.[22–25]

Silica short fibers showed a cylindrical needle shape, with polydisperse sizes and a cylindrical void parallel to the fiber axis that may contribute to a mechanical anchorage of the matrix [Fig. 1(a) and (b)].

TABLE I
Chemical Composition of Natural and Modified Silica Short Fibers (NF and MF)

Chemical composition (% w/w)	NF	MF
SiO_2	95.5 (0.1)	95.9 (0.1)
Al_2O_3	3.08 (0.04)	2.70 (0.04)
$SO_3{}^a$	1.02 (0.01)	1.08 (0.01)
CaO^a	0.140 (0.003)	0.153 (0.004)
TiO_2	0.104 (0.004)	0.073 (0.003)
Fe_2O_3	0.102 (0.002)	0.097 (0.002)
CuO	0.025 (0.001)	0.025 (0.001)

Standard deviation are given in parentheses
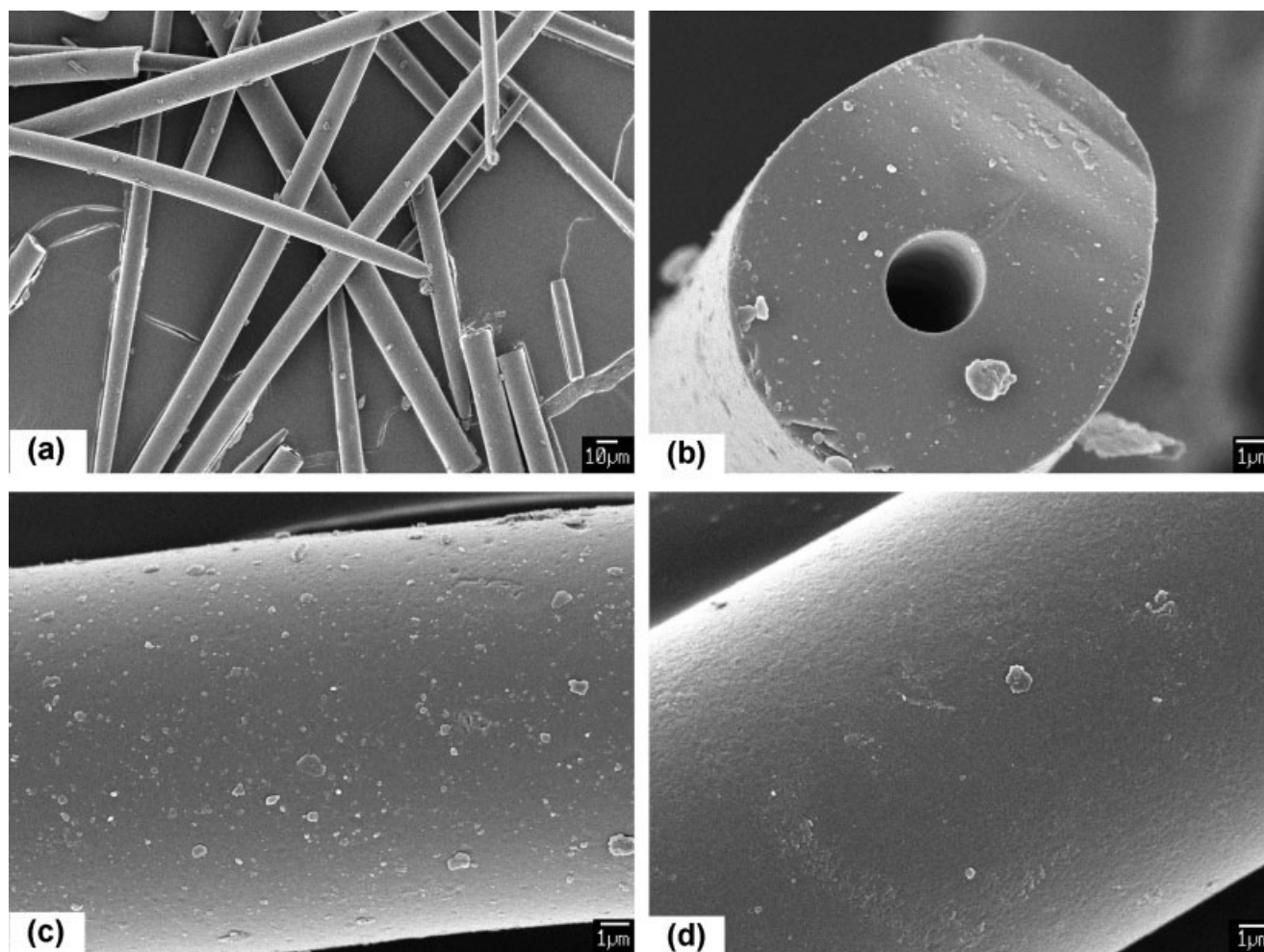[a] Obtained from the equipment. It does not correspond to the real compound.

Figure 1 FESEM micrographs of (a–c) NF and (d) MF.

In addition, Figure 1(c) showed the relatively smooth and nonporous surface of this fiber, containing few aggregated particles, which agrees with the low BET surface area value. The micrograph of the MF surface [Fig. 1(d)] showed a discrete smoothing effect on the surface, when compared to NF, which was attributed to the loss of aggregated particles in the modification reaction.

Characterization of the rubbers

Thermal stability of the rubbers was evaluated by TGA and the thermogravimetric curves for PDMS-gum, UR, NF-rubber, and MF-rubber can be seen in Figure 2(a). The degradation profiles of these samples were similar, with one thermal decomposition step, characteristic of PDMS-gum.[5] The percentages of residues correspond to the amount of filler added to the PDMS matrix. As can be seen, UR presented a higher initial weight loss temperature (T_i), compared to PDMS-gum, because of the crosslinking of the PDMS chains. Moreover, the presence of fibers in NF-rubber

and MF-rubber contributed to an increase in the T_i values, in relation to UR, and also in the maximum weight loss rate temperature (T_{max}) of these rubbers. These results suggested that the thermal stability of the PDMS matrix was increased by two factors: the crosslinking of PDMS chains and the introduction of NF or MF in the matrix. Both factors restricted the mobility of the chains, hindering the well-known inter and intramolecular rearrangements of the PDMS chains, characteristic of the thermal degradation of silicones.[26–29]

For the rubbers with short fibers as secondary filler, NF/S-rubber and MF/S-rubber, T_i and T_{max} values decreased in relation to those of S-rubber. As these short fibers are biogenic, they are found together with clay, sand, and organic matter, and bring traces of ions as contaminants, as verified by XRF. Thus, these ions, particularly Al^{3+} and Ti^{4+}, could catalyze nucleophilic attacks from the residual Si—OH groups of the fumed silica to the PDMS chains, creating volatile species that were eliminated from the material.[27] Moreover, during the compounding of the rubbers, the interfacial
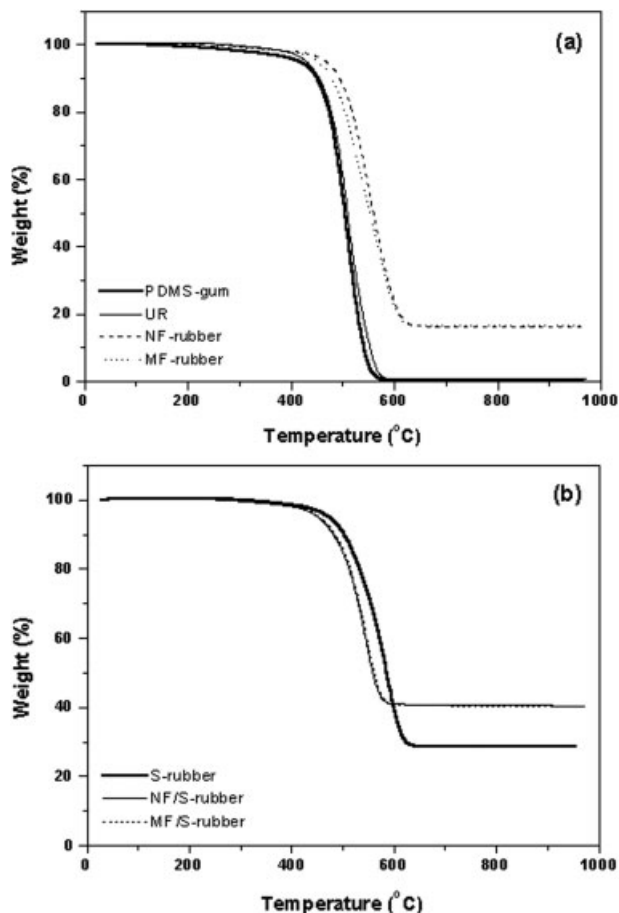
Figure 2 TGA curves for (a) PDMS-gum, UR, NF-rubber, and MF-rubber; (b) *S*-rubber, NF/S-rubber and MF/S-rubber.

shear stress between silica short fibers and fumed silica could decrease the size of the fumed silica agglomerates, which could result in a better dispersion of this last filler in the matrix and in new interactions of fumed silica particles with the PDMS chains, decreasing the thermal stability of the PDMS matrix. It is
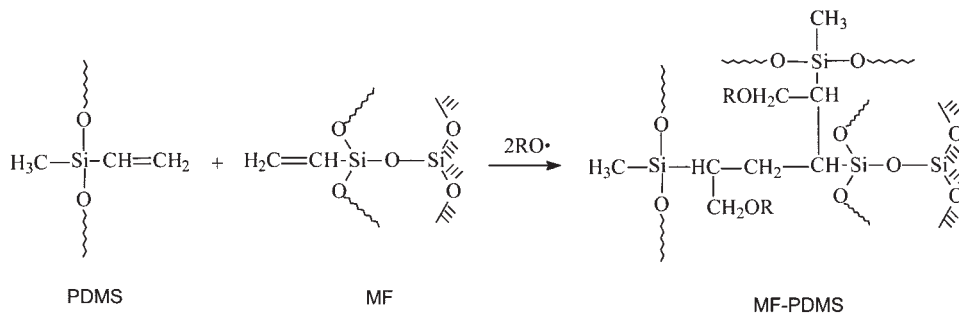
important to mention that fumed silica are aggregates of spherical and monodisperse particles, and that agglomerates are "clusters" of aggregates joined by physical interactions.[30]

From Figure 3, a uniform distribution of the silica short fibers in the PDMS matrix, with a tendency of orientation, was observed for NF-rubber and also for MF-rubber in micrographs (a) and (c), respectively. Few holes and regions with fiber pull-out were also observed for these filled rubbers. Micrographs (b) and (d) showed good adhesion at the fiber-matrix interface for both rubbers, where NF and MF were still covered by the PDMS matrix, suggesting strong interfaces.

In S-rubber, the silica particles were homogeneously dispersed in the PDMS matrix, with some agglomerates expressed by white points, as can be seen in Figure 4(a). Micrographs (b) and (d) showed uniform dispersions of NF or MF in the matrix. However, when NF acts as a secondary filler, in NF/S-rubber, micrographs (b) and (c) showed few debonding points at the fiber-matrix interface and the natural short fibers were not covered by the matrix, contrary to what was observed for NF-rubber. This fact could be explained by the greater viscosity of the S-PDMS mixture, as compared with the pure PDMS-gum, which made more difficult the spreading of the matrix on the NF surface and consequently induced failure in the fiber-matrix interaction at the interface, when this rubber was fractured. On the other hand, for MF/S-rubber, good adhesion at the fiber-matrix interface was observed in Figure 4(e). This could be attributed to the higher hydrophobicity of the MF surface that increased the compatibility between MF and PDMS matrix. In addition, the presence of vinyl groups on the MF surface allowed the formation of covalent bonds at the MF-PDMS interface, during the cure reaction of the matrix induced by peroxide, as shown in the following reaction scheme.

The effect of the silica short fibers on the swelling properties of the studied PDMS rubbers was evaluated. The equilibrium swelling ratio is determined by the balance between the osmotic pressure of the sol-

vent, which force the polymeric chains to take an elongated conformation, and the stretching of the polymeric network. Thus, the greater the crosslinking density of the network, the smaller the average mo-
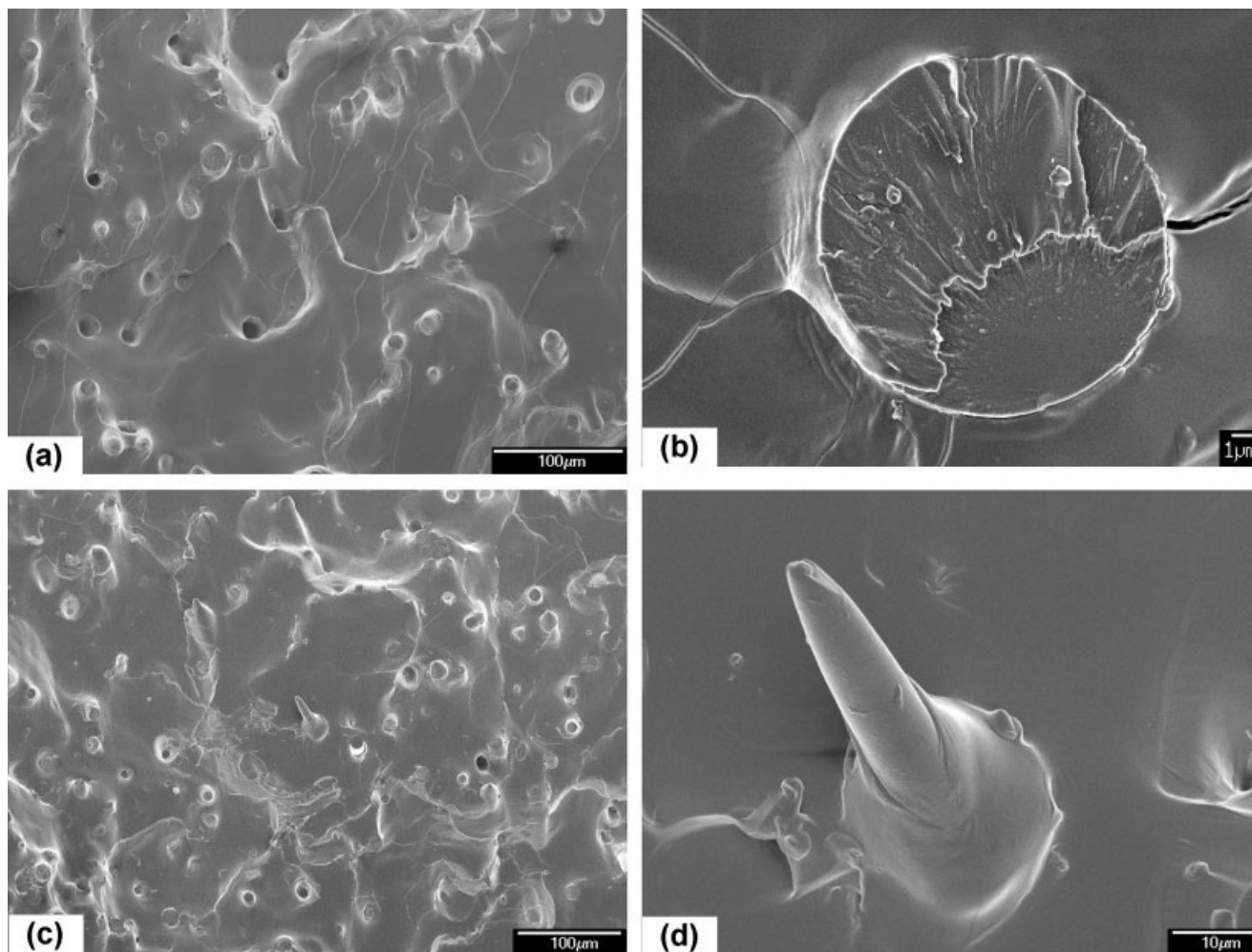
Figure 3 FESEM micrographs of (a,b) NF-rubber and (c,d) MF-rubber.

lecular weights between crosslinking points and the smaller the swelling. In filled rubbers, when the filler is covalently connected to the elastomeric network, the polymeric matrix cannot sustain an isotropic extension. In this situation, the matrix remains connected to the filler and the filler-matrix interactions also increase the crosslinking density of the elastomeric matrix in the vicinity of the filler. Thus, the swelling of a filled rubber is restricted, in relation to an unfilled one, particularly at the filler-matrix interphase. The more effective the interaction between filler and matrix, the greater the restriction.[31]

Swelling measurements of the studied rubbers were performed in cyclohexane, because of its solubility parameter ($\delta = 8.2$ (cal cm^{-3})$^{1/2}$) being close to that of PDMS ($\delta = 7.5$ (cal cm^{-3})$^{1/2}$).[32] The swelling ratio (S_R) was calculated by using eq. (1). Because the filler does not swell, the swelling ratio of the polymeric matrix alone was calculated discounting the amount of filler in each sample.[33]

where m_s is the weight of the swollen sample at equilibrium, m_d is the weight of the dried sample after swelling, and α_{filler} and α_{pol} are the filler and polymer weight fractions, respectively. The curves of S_R, as a function of time, can be seen in Figure 5.

As compared to UR, a smaller equilibrium swelling ratio ($S_{R(\text{eq})}$) for MF-rubber was observed. However, this swelling restriction effect was not caused by NF as primary filler in the rubber. Whereas, both silica short fibers, as secondary filler, promoted a smaller swelling of the matrix in cyclohexane, with no significant differences related to the modification of the fiber surface. A decrease in the equilibrium swelling ratio of the matrix was also observed for S-rubber when compared to UR.

The average molecular weight between crosslinking points (M_C) was calculated by using the Flory–Rehner equation [eq. (2)] for a tetrafunctional polymeric network.[34]

$$S_R = \frac{[m_s - (\alpha_{\text{filler}} m_d)]}{[\alpha_{\text{pol}} m_d]} \quad (1)$$

$$M_C = \frac{[-d_{\text{pol}} V_{\text{sol}}(\phi_{\text{pol}}^{1/3} - \phi_{\text{pol}}/2)]}{[\ln(1 - \phi_{\text{pol}}) + \phi_{\text{pol}} + \chi \phi_{\text{pol}}^2]} \quad (2)$$
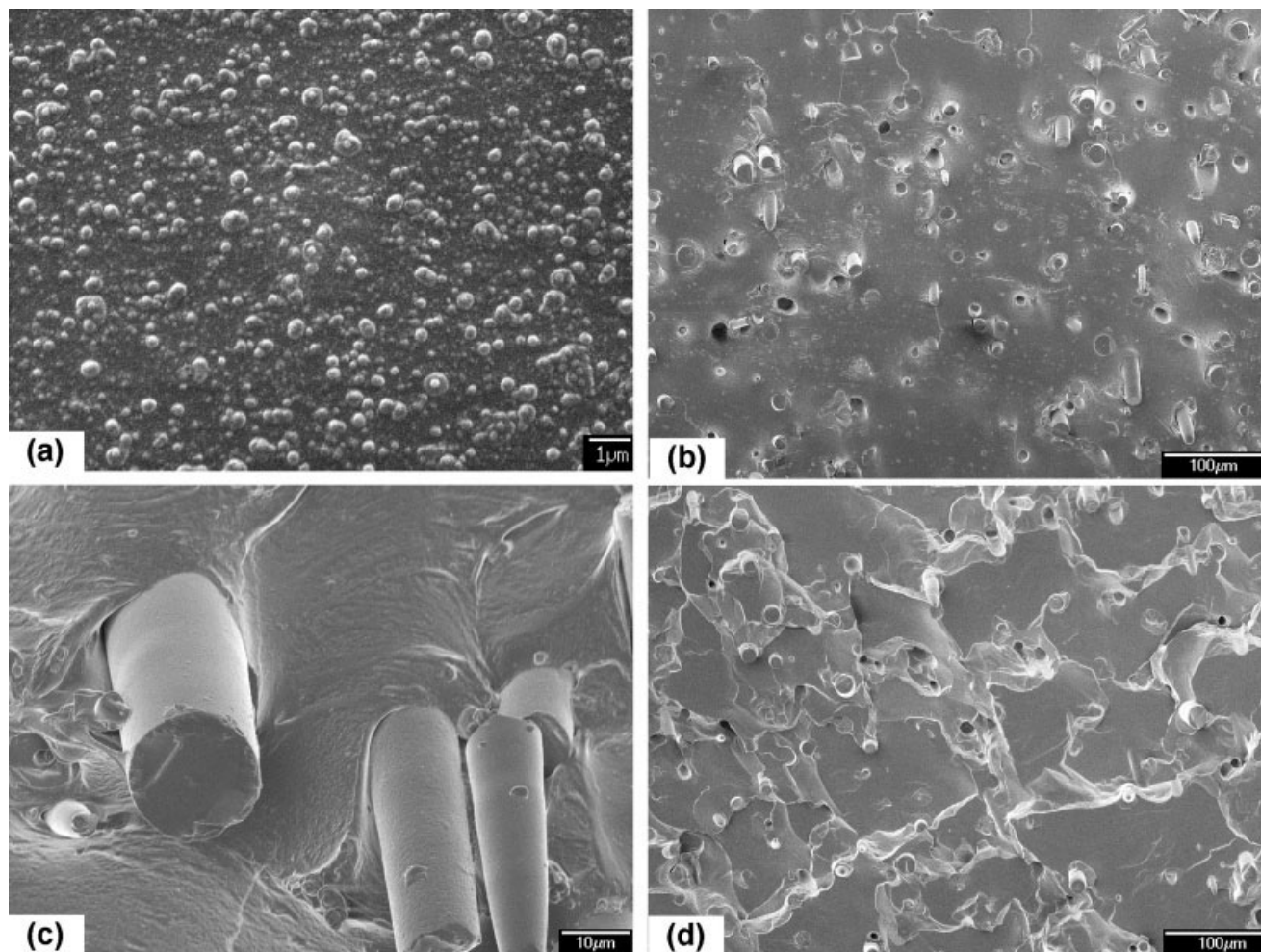
Figure 4 FESEM micrographs of (a) S-rubber, (b,c) NF/S-rubber and (d-e) MF/S-rubber.

where d_{pol} is the density of PDMS-gum, V_{sol} is the molar volume of cyclohexane, ϕ_{pol} is the volume fraction of the polymer in the swollen sample at equilibrium, and χ is the Flory–Huggins polymer-solvent interaction parameter. ϕ_{pol} was calculated by eq. (3).[35]

$$\frac{1}{\phi_{pol}} = 1 + S_{R(eq)}\frac{d_{pol}}{d_{sol}} \tag{3}$$

where d_{sol} is the density of cyclohexane at 40°C.[36] The Flory–Huggins interaction parameter, χ, was determined by eq. (4).[35,37]

$$\chi = \frac{(\delta_{sol} - \delta_{pol})^2}{RT}V_{sol} \tag{4}$$

where δ_{sol} and δ_{pol} are the solubility parameters of solvent and polymer, respectively, R is the gas constant, and T the absolute temperature. With the M_C values obtained for each sample, the crosslinking density of the polymeric network (n^{FR}) was calculated by using eq. (5).[38]

$$n^{FR} = \frac{d_{pol}}{M_C} \tag{5}$$

The $S_{R(eq)}$, M_C, and n^{FR} values calculated from swelling measurements of the samples in cyclohexane are presented in Table II.

According to the obtained results, the addition of MF to PDMS promoted an increase in the crosslinking density of this matrix, which contributed to a decrease in the M_C and $S_{R(eq)}$ values. This fact confirmed the formation of a covalent MF-PDMS interface. The swelling results also suggested that the interaction of NF with the PDMS matrix was not enough to result in a significant increase in the crosslinking density of the matrix due to the very low surface area of this fiber, which is characteristic of its morphology. However, when NF or MF were added to the matrix as secondary filler, the shear stress from the compounding of the rubbers could disaggregate fumed silica clusters, which favored the interaction of fumed silica particles with the PDMS matrix, increasing the crosslinking density of the matrix in the vicinity of the fumed silica
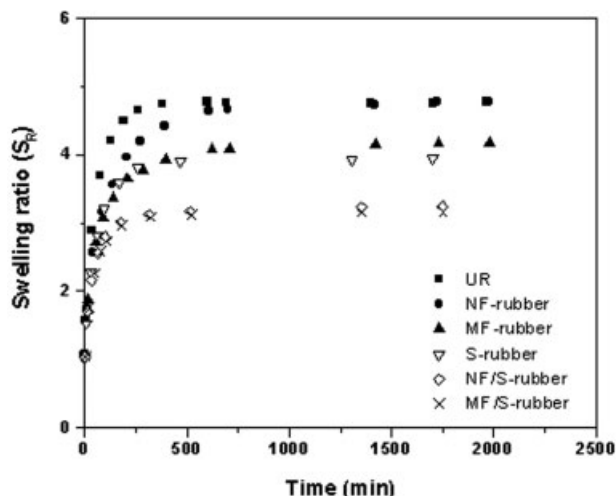
Figure 5 Variation of swelling ratio (S_R) with time for swelling of UR, NF-rubber, MF-rubber; S-rubber, NF/S-rubber and MF/S-rubber in cyclohexane.
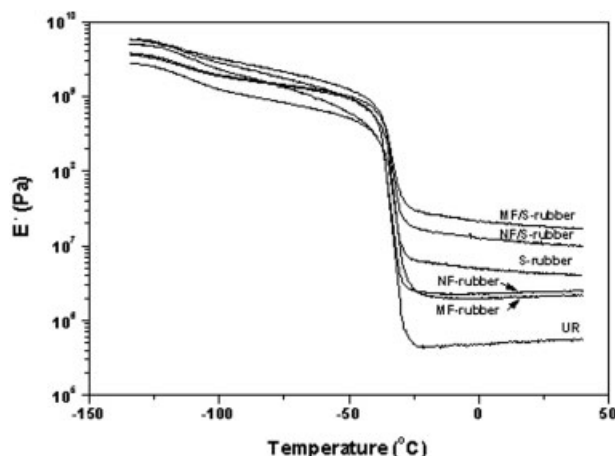

Figure 6 Variation of storage modulus (E') with temperature for (a) UR, NF-rubber and MF-rubber, (b) S-rubber, NF/S-rubber and MF/S-rubber.

particles. There were no differences between the values of $S_{R(eq)}$, M_c, and n^{FR} obtained for the rubbers with NF or MF as a secondary filler.

DMA showed the stiffening effect promoted by the short fibers. Higher storage modulus (E') values at room temperature were observed for the rubbers with NF or MF as primary filler, when compared to UR, and for the rubbers with NF or MF as secondary filler, compared to the S-rubber, as can be seen in Figure 6. Moreover, as primary filler in the PDMS matrix, MF contributed to a higher E' at room temperature, as compared to NF. It is known that the increase in stiffness promoted by an active filler added to an elastomer is a consequence of the inclusion of rigid particles and also of an increase in the crosslinking density arising from the polymer-filler bonding.[33] Thus, the greater stiffening effect promoted by MF as a primary filler in PDMS, as compared to NF-rubber, agrees with the greater crosslinking density of the MF-rubber determined by the swelling measurements.

From the stress–strain curves obtained for the rubbers, Young's modulus, tensile strength, and elongation at break were determined (see Fig. 7 and Table III).
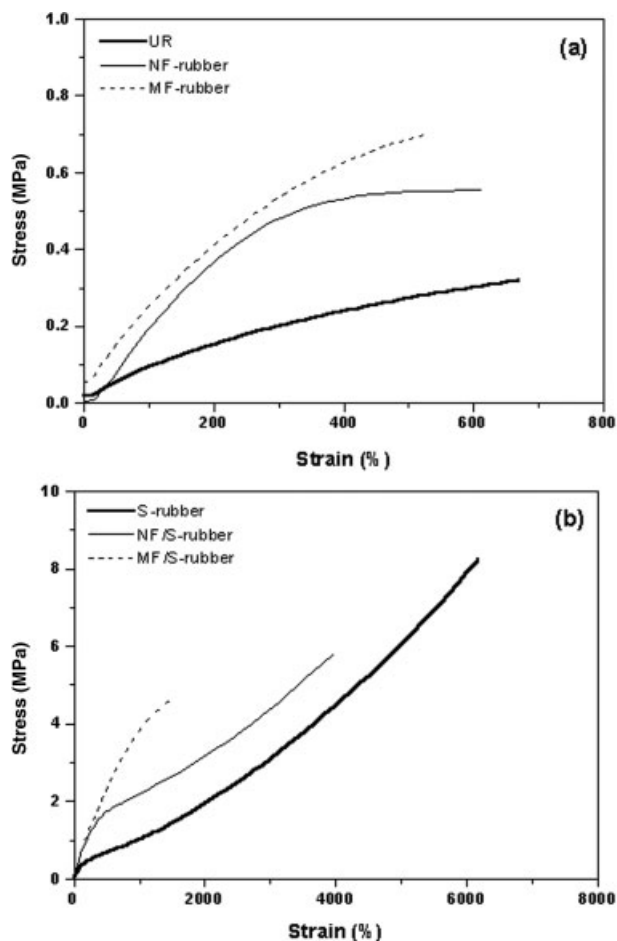
TABLE II
Equilibrium Swelling Ratio ($S_{R(eq)}$), Crosslinking Density (n^{FR}) and Average Molecular Weight (M_C) Between Crosslinking Points, for Swelling of the Rubbers in Cyclohexane

Sample	$S_{R(eq)}$	n^{FR} (10^{-4} mol cm^{-3})	M_C (g mol^{-1})
UR	4.77 (0.15)	3.0	2431
NF-rubber	4.78 (0.03)	3.0	2431
MF-rubber	4.18 (0.02)	3.7	1973
S-rubber	3.94 (0.01)	4.1	1790
NF/S-rubber	3.24 (0.01)	6.4	1141
MF/S-rubber	3.16 (0.01)	6.4	1141

Standard deviation are given in parentheses.

Figure 7 Stress–strain curves for (a) UR, NF-rubber and MF-rubber, (b) S-rubber, NF/S-rubber and MF/S-rubber.

TABLE III
Young's Modulus, Tensile Strength, and Elongation at Break Values for the Rubbers

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
UR	0.07 (0.01)	0.29 (0.06)	620 (213)
NF-rubber	0.20 (0.01)	0.55 (0.02)	639 (108)
MF-rubber	0.18 (0.01)	0.67 (0.05)	579 (50)
S-rubber	0.11 (0.01)	8.3 (0.6)	6133 (311)
NF/S-rubber	0.36 (0.04)	6.0 (0.4)	3991 (328)
MF/S-rubber	0.47 (0.07)	7.2 (0.7)	1572 (197)

Standard deviation are given in parentheses.

As primary filler, both silica short fibers acted as reinforcing fillers in relation to Young's modulus and tensile strength, and no significant differences were found between the behaviors of NF-rubber and MF-rubber. A reinforcement effect with regard to tensile strength can be achieved by an efficient matrix-fiber stress transfer, which can be obtained by a good adhesion at the fiber-matrix interface.[39] Therefore, the reinforcement effect provided by the silica short fibers as primary filler, in relation to tensile strength, could be attributed to good adhesion at the interface, in both cases, as observed in the micrographs, which promoted an efficient distribution of stress through the PDMS matrix.

NF and MF also increased Young's modulus of S-rubber when added as secondary filler. For S-rubber, an excellent performance was observed in relation to the tensile strength and elongation at break values, when compared to UR. However, the fumed silica presented a small influence on the Young's modulus of S-rubber, and, in this case, the addition of a secondary reinforcing filler that acts on this property, as the studied short fibers did, becomes essential to satisfy some specific applications. However, the addition of NF or MF to the PDMS matrix, as secondary filler, resulted in a decrease of the tensile strength and elongation at break values, in relation to S-rubber. This fact could be attributed to the shear stress between the silica short fibers and the fumed silica that increased the crosslinking density of the matrix, as was shown by swelling measurements. The smaller value of elongation at break for MF/S-rubber could also be due to the good adhesion at the MF–PDMS interface, observed in the micrographs.

CONCLUSIONS

The effect of biogenic silica short fibers, NF and MF, as primary or secondary fillers in an elastomeric matrix of PDMS was studied. As primary filler, both silica short fibers increased the thermal stability of the matrix, and MF restricted the PDMS swelling in cyclo-hexane. For the rubbers with silica short fibers as secondary filler, the swelling restriction was caused by both fibers. Silica short fibers were also efficient as primary filler in PDMS with regard to Young's modulus and tensile strength, and as secondary filler, NF and MF were effective reinforcing fillers in relation to storage and Young's modulus, resulting in an increase in the stiffness of the rubbers. These facts together with the abundance of the biogenic silica short fibers suggest the possibility of using NF or MF as primary or secondary reinforcing fillers in PDMS, with the main objectives of increasing the thermal stability of the matrix, restricting the swelling in solvents, stiffening and also decreasing the price of the PDMS rubbers.

References

1. Cochrane, H.; Lin, C. S. Rubber Chem Technol 1993, 66, 48.
2. Elvers, B.; Hawkins, S.; Russey, W.; Schulz, G. Ulmann's Encyclopedia of Industrial Chemistry, 5th ed.; VCH: New York 1993; Vol. A24, Chapter 4.
3. Manchado, M. A. L.; Arroyo, M. Polym Compos 2002, 23, 666.
4. Agarwal, K.; Setua, D. K.; Mathur, G. N. Defence Sci J 2002, 52, 337.
5. Redondo, S. U. A.; Radovanovic, E.; Gonçalves, M. C.; Yoshida, I. V. P. J Appl Polym Sci 2002, 85, 2573.
6. Clarke, J.; Harris, J. Plast Rubber Compos 2001, 30, 406 .
7. López, M. M. A.; Arroyo, M. Polymer 2000, 41, 7761.
8. Varghese, S.; Kuriakose, B.; Thomas, S.; Koshy, A. T. J. Adhesion Sci Technol 1994, 8, 235.
9. Pecorini, T. J.; Hertzberg, R. W. Polym Compos 1994, 15, 174.
10. Weber, M. E.; Kamal, M. R. Polym Compos 1992, 13, 133.
11. Rueda, L. I.; Antón, C. C.; Rodriguez, M. C. T. Polym Compos 1988, 9, 198.
12. Chawla, K. K. Composite Materials: Science and Engineering, 2nd ed.; Springer: New York, 1998; Chapter 4.
13. Metin, D.; Tihminlioglu, F.; Balköse, D.; Ülkü, S. Compos A 2004, 35, 23.
14. Esper, J. A. M. M. Masters Thesis, Universidade Federal de Minas Gerais: Belo Horizonte, 2000.
15. Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Engel, R. G. Introduction to Organic Laboratory Techniques—A Microscale Approach, 3rd ed.; Saunders College Publishing: Philadelphia, 1994; Part 1.
16. ASTM D 471–986°. Standard Test Method for Rubber Property—Effect of Liquids, Annu Book of ASTM Standards, 1998.
17. ASTM D412–98ª. Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension, Annu Book of ASTM Standards, 1998.
18. Plueddemann, E. P. Silane Coupling Agents, 2nd ed.; Plenun Press: New York, 1991; Chapter 6.
19. Zhao, S.; Feng, S. J. Appl Polym Sci 2002, 83, 3123.
20. Xu, C.; Feng, S. J Appl Polym Sci 2000, 76, 1554.
21. Wilson, M. J. Clay Mineralogy: Spectroscopic and Chem Determinative Methods, 1st ed; Chapman & Hall: London, 1994; Chapter 2.
22. Graetsch, H. Rev Miner 1994, 29, 209.
23. Graetsch, H.; Gies, H.; Topalovic, I. Phys Chem Miner 1994, 21, 166.
24. Wilding, L. P.; Drees, L. R. Clays Clay Miner 1974, 22, 295.

25. Graetsch, H.; Mosset, A.; Gies, H. J. Non-Cryst. Solids 1990, 119, 173.
26. Dvornic, P. R.; Lenz, R. W. High Temperature Siloxane Elastomers; CIP: New York, 1990; Chapter 2.
27. Clarson, S. J.; Semlyen, J. A. Siloxane Polymers; PTR Prentice Hall: New Jersey, 1993; Chapter 5.
28. Camino, G.; Lomakin, S. M.; Lazzari, M. Polymer 2001, 42, 2395.
29. Camino, G.; Lomakin, S. M.; Lageard, M. Polymer 2002, 43. 2011.
30. Aranguren, M. I.; Mora, E. C.; Macosko, W. J. Colloid Interface Sci 1997, 195, 329.
31. Berriot, J.; Lequeux, F.; Montes, H.; Pernot, H. Polymer 2002, 43, 6131.
32. Yerrick, K. B.; Beck, H. N. Rubber Chem Technol 1964, 37, 261.
33. Bokobza, L. J Appl Polym Sci 2004, 93. 2095.
34. Hauser, R. L. C.; Walker, A.; Kilbourne, F. L. Ind Eng Chem 1956, 48, 1202.
35. Sobhy, M. S.; Mahdy, M. M. M.; El-Fayoumi, M. A. K.; Abdel-Bary, E. M. Polym Test 1997, 16, 349.
36. Yoo, J. S.;. Kim, S. J.; Choi, J. S. J Chem Eng Data 1999, 44, 16.
37. Barton, A. F. M. CRC Handbook of Solubility Parameters and Other Cohesion Parameters, 3rd ed.; CRC Press: Florida, 1985; Chapter 13.
38. Sereda, L.; Visconte, L. L. Y.; Nunes, R. C. R.; Furtado, C. R.; Riande, G. E. J Appl Polym Sci 2003, 90, 421.
39. Kelly, A.; Zweben, C. Comprehensive Composite Materials, 1st ed.; Elsevier: Oxford, 2000; Vol. 2, Chapter 9.