Preparation of Flexible, Self-Extinguishing Silicone Foams

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ABSTRACT: Flexible, self-extinguishing silicone foams (SFs) with a relatively low density (0.25–0.45 g/cm^3) were obtained from a mixture of α,ω-(dihydroxy)poly-dimethylsiloxanes, water, flame retardants (melamine and/or expanded graphite), and polyisocyanates [poly(di-phenylmethane isocyanate)]. These compositions were crosslinked at room temperature with branched poly-methylhydrosiloxanes with the structure $(MeSiO_{1.5})_3$ $(MeHSiO)_{102}(Me_3SiO_{0.5})_5$ in the presence of tin octoate as a catalyst. The SFs were modified by the addition of linear or graft carbofunctional polysiloxanes containing γ-hydroxypropyl groups. Only the SFs prepared by means of a dehydrocondensation reaction had a good homogeneity of pores, whereas the foams formed with two kinds of blowing agents (hydrogen and carbon dioxide, generated in the reaction of water with isocyanate groups) had lower densities but a poor homogeneity of pores. Unmodified SFs showed a tensile strength of 20 kPa or less, whereas the foams formed with the addition of poly(diphenylme-thane isocyanate) and water had a tensile strength of 23–25 kPa. The SFs with 15 and 30% contents of melamine or expanded graphite had tensile strengths in the ranges 38–45 and 51–54 kPa, respectively. All of the prepared SFs were combustible materials. The SFs without the addition of flame retardants had a limiting oxygen index of approximately 21%, whereas the SFs with a 30% content of fire retardant had self-extinguishing properties and a limited oxygen index of 41–43%. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1696–1703, 2011

Key words: crosslinking; elastomers; flame retardance; modification; silicones

INTRODUCTION

Expanded silicone rubbers present very interesting advantages in comparison with polyurethane foams, the most important elastomers with a cellular structure. The superior thermal properties, the good chemical and electric stability, and the excellent resistance of silicone polymers against ozone and ultraviolet irradiation permit their use over a considerably wider temperature range compared to many conventional polymer foam materials. Thermal, acoustic, and electrical insulators; mechanical shock absorbers in the aerospace industry; and the aircraft and transportation industries are the major applications of siloxane foams.[1–5] The biocompatibility of siloxane foams permit their application in medicine as superior dressings for deep, open, granulating wounds.[6]

α,ω-(Dihydroxy)polydimethylsiloxanes (PDMSs) are the basic components of flexible silicone foams (SFs). The production of foamed silicone rubber includes two parallel processes: crosslinking reactions and foaming. In general, two conventional methods of silicone elastomer and rubber (SR) crosslinking are known: high-temperature vulcanization and room-temperature vulcanization.[7] The crosslinking of high-temperature vulcanization SR systems occurs according to a radical reaction mechanism, and a polymer network is formed by ethylene bridges between the polysiloxane chains. In this method, it is necessary to use peroxides at elevated temperatures (>100°C). In the case of room-temperature vulcanization systems, crosslinking agents, such as silanes, siloxanes, or polysiloxanes, with different functional groups (hydroxyl, acetoxy, alkoxy, and hydrogen atoms) bound to silicon atoms are required. At room temperature and in the presence of catalysts (mainly platinum or tin compounds), polycondensation and polyaddition reactions occur between PDMS and the crosslinking agents; new siloxane or carbosilane linkages form a polymer network in the crosslinking silicone material. One of the processes for crosslinking with room-temperature vulcanization for SRs is based on dehydrocondensation, which takes place between the silanol groups of the hydroxyl-terminated PDMS and the Si—H groups of the crosslinking agents; it is accompanied by the evolution of hydrogen.[7] Gaseous

volatile products formed in the crosslinking reactions or by the decomposition of porophors (e.g., 2,2′-azobisisobutyronitrile)[8] play the role of blowing agents.[2,9–20] In the case of the manufacturing of polyurethane foams, low-boiling additives (e.g., fluorocarbons, pentanes, methylene chloride, liquid carbon dioxide) are often used as physical blowing components.[21] Usually, during the preparation of SFs, the crosslinking and foaming processes progress simultaneously. A new dehydrocarbocondensation reaction of poly(hydrogen methylsiloxane) (PMHS) with multifunctional alkoxysilanes, for example, $MeSi(OEt)_3$ catalyzed by $(C_6F_5)_3B$, give SFs as well.[22] Methods for the manufacturing of SFs in which foaming occurs in previously vulcanized polymers are very rare.[23] In a closed-cell foam, the gas is dispersed as discrete bubbles, and a polymer matrix forms a continuous phase.

The major disadvantage of most polymers is their combustibility. This weakness especially limits the application of foamed plastics, which have a very outspread surface of contact of a gaseous phase. The cellular structure of polymers facilitates the ignition and burning of such materials. To increase the fire resistance of SFs, the addition of flame retardants to plastics is necessary. Most flame retardants contain in their structures the following elements: nitrogen, phosphorus, boron, aluminum, or fluorine.[24–27] An advantageous effect of inorganic fillers, and especially of crystalline silica, on the improvement of the ignition resistance of SFs has also been observed.[28–31]

Although SFs are commercially available, mostly in the form of sheets, it seems quite important to study further modifications of their properties and, especially, to improve the procedures used for the manufacturing of nonflammable and self-extinguishing materials. The aim of this study was the preparation of flexible, self-extinguishing SFs with a relatively low density (0.3–0.45 g/cm^3). They were obtained from mixtures of PDMSs, which were crosslinked at room temperature with branched polymethylhydrosiloxanes, in the presence of tin octoate (TO) as a catalyst.[32] Some compositions were modified by the addition of linear or graft carbofunctional polysiloxanes (CFPSs). Moreover, aromatic polyisocyanates, water, and flame retardants (melamine and expanded graphite) were used in some compositions. The influence of each component and the order of their addition to the reaction mixture during the preparation of SFs were tested. Some properties of the prepared materials, including the density, ability to self-extinguish, limiting oxygen index (LOI), tensile strength (TS), and elongation at break (E_b)], were determined. The size and homogeneity of pores were preliminarily evaluated.

EXPERIMENTAL

Materials

Three kinds of polysiloxanes were used for the preparation of SFs:

1. PDMSs with the formula $HO(SiMe_2O)_nOH$ (dynamic viscosity = 1812 cP, number-average molecular weight = 25 800 g/mol, weight-average molecular weight = 43 340 g/mol, weight-average molecular weight/number-average molecular weight = 1.68; Polastosil M-2000, Chemical Plant Silikony Polskie, Nowa Sarzyna, Poland).
2. CFPSs [i.e., α,ω-bis(hydroxypropyl)polydimethylsiloxanes] with the formula $HO(CH_2)_3(SiMe_2O)_nSi(CH_2)_3OH$, which were prepared from Polastosil M-2000 by multistep synthesis.[33,34]
3. Carbofunctional (in side chains) polysiloxanes with the general formula $Me_3SiO\{[SiMe_2O]_x[(HOCH_2CH_2CH_2)Si(Me)O]_{10}\}_zSiMe_3$. D-17 was the product with $x = 17$, and D-66 was the polysiloxane with $x = 66$. The method of preparation of these copolymers has already been presented.[33,34]

A polymethylhydrosiloxane with a branched, random structure (T-3) was used as the crosslinking agent; its general formula was $T_3D^H_{102}M_5$ (where T is $MeSiO_{1.5}$, D^H is MeHSiO, and M is $Me_3SiO_{0.5}$).[35]

Most of the SF samples were prepared in the presence of polyisocyanates and a small amount of water. We used poly(diphenylmethane isocyanate) (PMDI; Alfapur ISO FM 3900, Alfa Systems, Brzeg Dolny, Poland), which was a composition containing greater than 50% 4,4′-diphenylmethane diisocyanate, greater than 25% isomers and homologs of 4,4′-diphenylmethane diisocyanate, greater than 10% 2,4′-diphenylmethane diisocyanate, and greater than 10% modified diphenylmethane diisocyanate. Distilled water or silicone–water emulsion Sarsil ME-25, containing 25 wt % methylsilicone oil (Silikony Polskie, Nowa Sarzyna, Poland) were used as foaming reagents.

Crosslinking and foaming processes were catalyzed by TO (Kosmos 29, Goldschmidt). Melamine (Nitrogen Works, Puławy S.A., Poland) and expanded graphite Nordmin 251 (Nordmann Rassmann, Poland) were used as flame retardants.

Method of preparation of the SFs

The SFs were prepared at room temperature in cylindrical, open, polyethylene vessels with a volume of 50 cm^3. The polysiloxanes (Polastosil M-2000, CFPS, and D-17 or D-66, 5.0 g) were weighed in the vessel; thereafter, other components were added. After the addition of each ingredient, the mixture was stirred with a metal spatula for 30–45 s. PMDI was always added to the reaction mixture as the last

TABLE I
Chemical Compositions of the SFs

Foam no.	Polysiloxanes (g)	Flame retardants (g)	Water (mL)	T-3 (mL)	Catalyst TO (mL)	PMDI (mL)
F1	PDMS (5.0)			0.2	0.06	
F2	PDMS (5.0)	Melamine (0.75)		0.2	0.06	
F3	PDMS (5.0)	Melamine (1.5)		0.2	0.06	
F4	PDMS (5.0)			0.3	0.12	1.05
F5	PDMS (4.0) CFPS (1.0)	Melamine (0.75)		0.2	0.06	
F6	PDMS (4.0) CFPS (1.0)	Melamine (0.75) Graphite (0.75)		0.2	0.06	
F7	PDMS (2.5) CFPS (2.5)			0.2	0.06	1.05
F8	PDMS (2.5) CFPS (2.5)	Melamine (0.75) Graphite (0.75)		0.2	0.06	1.05
F9	PDMS (2.5) CFPS (2.5)	Melamine (1.0) Graphite (1.0)		0.2	0.06	1.05
F10	PDMS (3.33) CFPS (1.67)			0.3	0.06	1.05
F11	PDMS (3.33) CFPS (1.67)	Melamine (0.75) Graphite (0.75)		0.3	0.06	1.05
F12	PDMS (5.0)		H_2O (0.07)	0.2	0.06	1.0
F13	PDMS (5.0)	Melamine (0.75) Graphite (0.75)	H_2O (0.07)	0.2	0.06	1.0
F14	PDMS (5.0)	Melamine (0.75) Graphite (0.75)	Sarsil (0.07)	0.2	0.06	1.0
F15	PDMS (3.33) CFPS (1.67)		Sarsil (0.07)	0.2	0.06	1.0
F16	PDMS (3.33) CFPS (1.67)	Melamine (0.75)	Sarsil (0.07)	0.2	0.06	1.0
F17	PDMS (3.33) CFPS (1.67)	Melamine (0.75) Graphite (0.75)	Sarsil (0.07)	0.2	0.06	1.0

component. After careful mixing of all of the substrates, intensive growth of SFs was observed within 3–5 min. Measurements of the density, gelation time, and flammability were conducted for the prepared materials. The densities of the SFs were determined after a conditioning period exceeding 24 h. The LOI and mechanical properties (TS and E_b) were determined for the SFs prepared on a scale 25 times larger in polystyrene vessels with a volume of 0.7 dm^3. In this case, the ingredients were stirred with a mechanical mixer operating at 1000 rpm.

The compositions of the SFs are presented in Tables I and II.

Characterization of the SFs

Determination of the gelation times of the SFs

The gelation times were measured from the moment of the intermixing of all of the components until the moment when any adhesion of the mixture to a metal spatula was observed.

Determination of the density of the SFs

The density of the SFs (d) was calculated as follows:

$$d = m/V$$

where m is the mass of a cylindrical sample of the SF and V is the sample volume. V was calculated as follows:

$$V = h(\pi d^2/4)$$

where h is the height of the sample and d is the diameter of the sample.

Preliminary determination of the combustibility of the SFs

We prepared the samples for the flammability test by cutting off the top parts (1 cm thick) of cylindrical SFs. These samples were put into the flame of a gas burner for a period of 15 s, and after their removal from the flame, the times of burning and glowing were measured or the disappearance of the burning of the samples was observed. Self-extinguishing samples were qualified for the determination of LOI.

Determination of LOI

The LOI flammability test were carried out according to the standard method PN-EN ISO 4589-2

TABLE II
Chemical Compositions of the SFs

| Foam no.	Polysiloxanes (g)	Flame retardants (g)	Water (mL)	T-3 (mL)	Catalyst TO (mL)	PMDI (mL)
F18	PDMS (3.33) CFPS (1.50) D-17 (0.17)		H_2O (0.07)	0.2	0.06	1.0
F19	PDMS (3.33) CFPS (1.50) D-17 (0.17)	Melamine (0.75)	H_2O (0.07)	0.2	0.06	1.0
F20	PDMS (3.33) CFPS (1.50) D-17 (0.17)	Melamine (0.75) Graphite (0.75)	H_2O (0.07)	0.2	0.06	1.0
F21	PDMS (3.33) CFPS (1.50) D-17 (0.17)	Melamine (0.75) Graphite (0.75)	Sarsil (0.07)	0.2	0.06	1.0
F22	PDMS (3.33) CFPS (1.50) D-66 (0.17)		H_2O (0.07)	0.2	0.06	1.0
F23	PDMS (3.33) CFPS (1.50) D-66 (0.17)	Melamine (0.75)	H_2O (0.07)	0.2	0.06	1.0
F24	PDMS (3.33) CFPS (1.50) D-66 (0.17)	Melamine (0.75) Graphite (0.75)	Sarsil (0.07)	0.2	0.06	1.0

(1999), which is similar to ASTM methods D 2863-74 and E 662.

Determination of TS and relative E_b

TS and E_b were measured according to the standard method PN-ISO 37 (1998).

RESULTS AND DISCUSSION

The SFs were prepared during simultaneously progressing crosslinking and foaming processes. The crosslinking process was based on the dehydrocondensation of hydroxyl-terminated PDMS with the Si—H groups of the crosslinking agent T-3 (a branched PMHS), and it was catalyzed by TO[7,32,36,37] as follows:

$$\equiv Si - OH + H - Si \equiv \xrightarrow{Sn(II)} \equiv Si - O - Si \equiv \\ + H_2 \uparrow \quad (1)$$
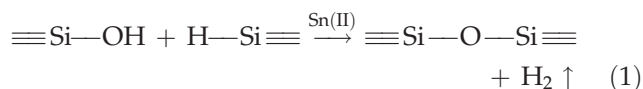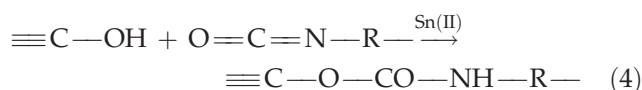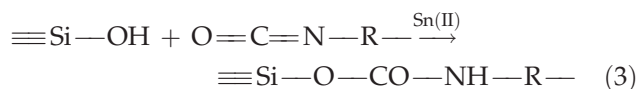
New siloxane linkages formed in this reaction led to a polymer network in a silicone rubber, and gaseous hydrogen acted as a blowing agent. In this way, the pure, unmodified SFs F1–F3 were obtained. The densities of these foams were in the range 0.41–0.42 g/cm³.

In the polysiloxane mixtures of PDMS and CFPS, the gelation process was based on the reaction [eq. (1)] between the Si—OH groups of PDMS and the Si—H groups of T-3 and the dehydrocondensation reaction of the carbinol groups of CFPS with the Si—H groups of T-3[33,34,38]:
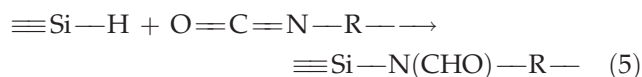
$$\equiv C - OH + H - Si \equiv \xrightarrow{Sn(II)} \equiv C - O - Si \equiv \\ + H_2 \uparrow \quad (2)$$
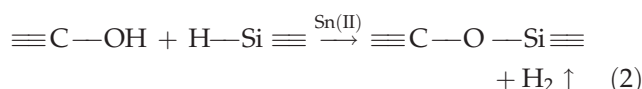
In both eqs. (1) and (2), the hydrogen is liberated.

In the presence of isocyanate groups, addition reactions take place as follows:

$$\equiv Si - OH + O = C = N - R - \xrightarrow{Sn(II)} \\ \equiv Si - O - CO - NH - R - \quad (3)$$

$$\equiv C - OH + O = C = N - R - \xrightarrow{Sn(II)} \\ \equiv C - O - CO - NH - R - \quad (4)$$

Of course, the addition of Si—H groups to isocyanate groups is also possible:[39]

$$\equiv Si - H + O = C = N - R - \longrightarrow \\ \equiv Si - N(CHO) - R - \quad (5)$$

Reactive hydrogen atoms are consumed in the addition reactions [eqs. (3)–(5)], so the densities of the SFs prepared from the mixtures of PDMS, CFPS, T-3, TO, and PMDI were higher (0.53–0.60 g/cm³) than the densities of the pure SFs (0.41 g/cm³).

The water used for the preparation of the SFs had an important effect on their properties. The density of the foams obtained in the presence of water (or a silicone-water emulsion) were in the range 0.24–0.28 g/cm³. The considerably lower density of SFs F12–F24 (Table III) was caused by the evolution of a new blowing agent, carbon dioxide, which was

formed in the addition reaction of water to isocyanate groups, according to eq. (6):

$$H_2O + O{=}C{=}N{-}R{-}\xrightarrow{Sn(II)}{-}R{-}NH_2$$
$$+ CO_2 \uparrow \quad (6)$$
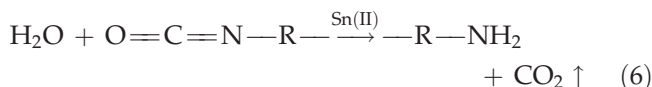
Intermediate primary amines react with the isocyanate groups of PMDI [see eq. (7)] approximately 10^3 times faster than Si—OH and C—OH groups do.[21]

The lowest density (0.24–0.25 g/cm^3) was determined for the foams F18 and F22, which were prepared from the mixture of three kinds of polysiloxanes: PDMS, CFPS, and D-17 or D-66. The addition of the carbofunctional polysiloxanes D-17 or D-66, containing in their structures statistically 10 hydroxypropyl groups, gave the possibility of the formation of a polymer network with a much higher crosslinking density in comparison with the network formed from a composition including only the difunctional polysiloxanes PDMS and CFPS. In this latter case, the density of the foams F12 and F15 was only slightly higher (0.28 g/cm^3).

The density of the SFs increased with the growing amount of flame retardants. Materials containing 15 wt % flame retardants had densities in the range 0.29–0.31 g/cm^3 (foams F19 and F23), whereas SFs with a 30 wt % content of flame retardants (F20 and F24) had densities of 0.32 and 0.49 g/cm^3, respectively.

Crosslinked silicone rubbers show markedly worse mechanical parameters than conventional rubber goods. One of the methods of the elimination of this drawback is a chemical modification. In the case of the SFs, we decided to add to the polysiloxanes a mixture of liquid polyisocyanates (PMDI). The results of our studies proved this assumption. We noticed that PMDI could be crosslinked with PMHS in the presence of TO within 1–2 days, depending on the stoichiometry of the substrates and the concentration of TO. This reaction was very slow in comparison with the crosslinking reaction of PDMS with PMHS and the foaming reaction of PMDI with water. During the conditioning time of the SFs, nonreacted Si—H groups of PMHS may have reacted with the remaining NCO groups of PMDI, and this process should have strengthened the structure of the foams. The presence of aromatic rings in crosslinked materials may improve their mechanical strength. The mechanical properties of the SFs depended on the contents of the fire retardants, CFPSs, and PMDI. Pure SFs without PMDI segments in their structures reached TS ≤ 20 kPa. The worst values of TS were obtained for foams without the addition of PMDI and/or fire retardants (TS =

18 kPa for SF F1 and TS = 23 kPa for SF F15). A substantial increase in TS was observed for the SFs containing CFPS and flame retardants; for example, for SF F22, prepared with participation of PMDI and the graft (hydroxypropyl)polysiloxane D-66, TS = 35 kPa. Foaming materials composed of PDMS and CFPSs (2 : 1 w/w) with 15 wt % melamine had TS values in the range 38–45 kPa. The best mechanical properties (TS = 51–54 kPa, E_b = 31–34%) were reached for SFs F17, F21, and F24, which contained mixtures of PDMS with CFPSs, 15 wt % melamine, 15 wt % expanded graphite, and PMDI. Maximum values of E_b (41–42%) and middle values of TS (35–38 kPa) were obtained for foams F16 and F22, which were based on mixtures of PDMS, CFPSs, PMDI, and water. The foam F16 contained 15 wt % melamine, and SF F22 was crosslinked with the graft (hydroxypropyl)polysiloxane D-66. It was quite obvious that the addition of melamine gave SFs with better mechanical properties. This improvement of the properties of the SFs was probably caused by the addition reaction of the amine groups of 2,4,6-triamine-1,3,5-triazine to isocyanate groups, which gave ureas linkages, according to eq. (7):

$$\equiv C{-}NH_2 + OC{=}N{-}R{-}\xrightarrow{Sn(II)}$$
$$\equiv C{-}NH{-}CO{-}NH{-}R{-} \quad (7)$$
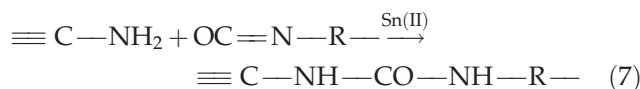
Apparently, the formed urea moieties improved the homogeneity of the crosslinked materials. Polyurea linkages were also formed in the reactions of PMDI with water [eq. (6)] and the subsequent reaction of amine groups with NCO groups. The microphase separation of the silicone and polyurea phases could not be avoided, although the addition of melamine, which reacted with PMDI and led to an interpenetrating network system, should have decreased the tendency toward microphase separation. It seemed that the application of CFPSs with γ-hydroxypropyl groupings should have helped as well to minimize the tendency toward the microseparation of different phases.

The sequence of addition of the components was also very essential to the preparation of the SFs. After many experiments, we noticed that the best procedure was the addition of the components in the following order: water, curing agent, catalyst, and PMDI to the mixtures of polysiloxanes and flame retardants. This procedure ensured a suitable rate of crosslinking and foaming processes and made possible the formation of materials with stable, cellular structures.

The size of the pores and their homogeneity were dependent on the amounts of blowing agents. The foams prepared by the dehydrocondensation processes with the evolution of hydrogen (but without

TABLE III
Characteristics of the SFs

Foam no.	Gelation time (min)	Density (g/cm³)	Combustibility		TS (kPa)	E_b (%)	Porosity	
			Burning time (s)[a]	LOI (%)			Pore size[b]	Homogeneity[c]
F1	5	0.41	85		18	20	Very small	Very good
F2	5	0.42	43				Very small	Very good
F3	5	0.42	0 (S)				Very small	Very good
F4	1	0.53	105				Middle	Moderate
F5	2	0.54	33				Middle	Moderate
F6	3	0.62	0 (S)				Middle	Moderate
F7	2	0.60	103				Middle	Moderate
F8	1	0.62	0 (S)				Middle	Moderate
F9	1	0.66	0 (S)				Middle	Moderate
F10	1	0.53	92				Middle	Moderate
F11	1	0.57	0 (S)				Middle	Moderate
F12	7	0.27	110				Middle and large	Moderate
F13	8	0.38	0 (S)				Middle and large	Moderate
F14	10	0.33	0 (S)	43.3	34	22	Large	Small
F15	15	0.28	108	21.3	23	39	Middle and large	Small
F16	7	0.32	47	25.7	38	41	Large	Moderate
F17	4	0.36	0 (S)	41.1	51	31	Middle and large	Moderate
F18	8	0.24	109				Large	Small
F19	8	0.29	49				Large	Small
F20	9	0.32	0 (S)				Large	Small
F21	12	0.49	0 (S)	41.5	54	32	Large	Small
F22	6	0.25	120	20.9	35	42	Large	Small
F23	8	0.31	26	25.2	45	27	Large	Small
F24	8	0.40	0 (S)	41.3	51	34	Large	Small

[a] Time of burning and glowing after a sample was removed from the flame (at which it was kept for 15 s). S = self-extinguishing foam.
[b] *Very small* indicates a pore diameter less than 0.4 mm, *middle* indicates a pore diameter less than 1 mm, and *large* indicates a pore diameter greater than 1 mm.
[c] *Very good* indicates an identical diameter for 95% of the pores, *moderate* indicates an identical diameter for 80% of the pores, and *small* indicates an identical diameter for less than 50% of the pores.

the addition of PMDI and water) had very homogeneous pores with diameters below 0.4 mm (Fig. 1), whereas materials foamed by hydrogen and carbon dioxide had a very small number of homogeneous pores with diameter even up to 3 mm (Fig. 2). Most of the prepared SFs had pores with diameters of about 1 mm (see Fig. 3). In the case of the application of a double-foaming system, on the basis of dehydrocondensation reactions of PDMS with PMHS and the reaction of PMDI with water, large pores were formed, presumably because of the very fast reaction of NCO functional groups with water, which led to the formation of CO_2. On the basis of our studies, it was difficult to estimate unequivocally the effects of the applied flame retardants on the size of pores and their homogeneity. Further studies are in progress.

Combustibility of the SFs

All of the prepared SFs were combustible materials in the flame of a gas burner. SFs without addition of flame retardants burned over a period of 80 s after

Figure 1 SF F1 (Tables I and III).

their removal from the flame. The addition of 15 wt % flame retardant shortened by almost twice the time of the samples' combustibility after they were removed from the flame. SFs containing 30 wt % flame retardant burned in the flame, but outside the flame, they went out immediately. Thus, the prepared foamed composites of silicone rubbers with fire retardants were considered self-extinguishing materials of the first class of combustibility among polymers.[40] The results of the LOI flammability test led us to the same conclusion. The polymers with LOI $\geq 28\%$[40] belonged to the first class of polymer combustibility. The SFs without the addition of flame retardants had LOI $\approx 21\%$, the foams with a 15 wt % content of melamine or/and expanded graphite had LOI = 25.2–25.7%, and foams with a 30 wt % content of fire retardants had LOI = 41.1–43.3%.

CONCLUSIONS

SFs were prepared by the dehydrocondensation of polydimethylsiloxane-α,ω-diols with polymethylhydrosiloxanes, accompanied by the evolution of hydrogen; this provided porous silicone rubbers (foams F1–F11), characterized by densities greater than 0.40 g/cm^3 and small, homogeneous pores.

It was shown that to prepare the SFs at room temperature with densities less than or equal to 0.40 g/cm^3 from mixtures of polysiloxanes crosslinked with branched polymethylhydrosiloxanes in the presence of tin catalyst, it was necessary to use water and isocyanates. The modification of the foam-
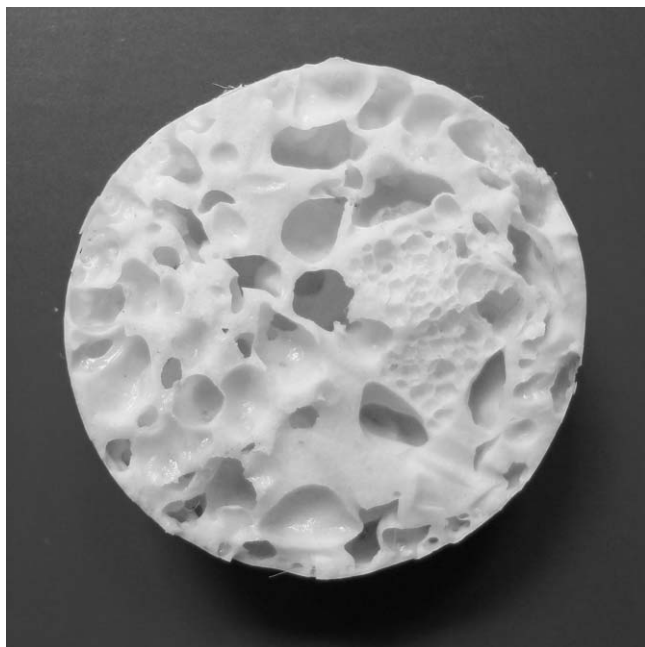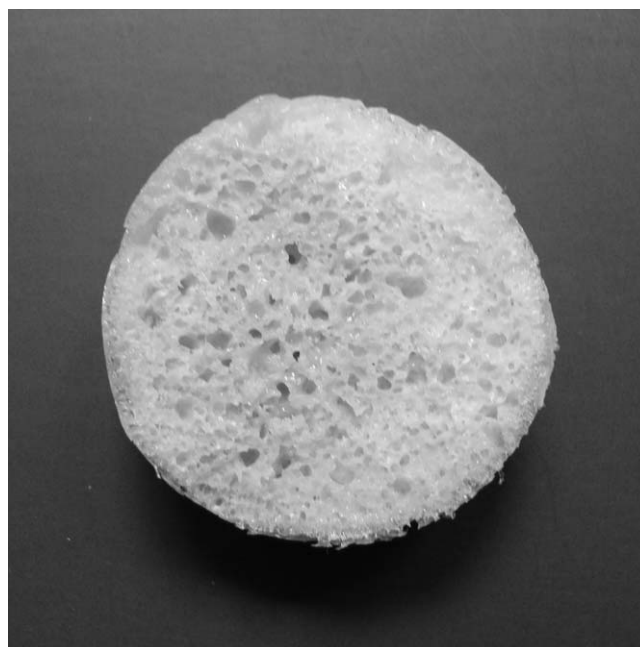

Figure 3   SF F12 (Tables I and III).

ing process by the application of a second blowing agent, carbon dioxide, generated in the reaction of water with isocyanate groups, gave more expanded silicone rubbers with lower densities. Materials foamed by hydrogen and carbon dioxide usually had a poor homogeneity of pores.

The modification of the chemical composition of the SFs by the use of PMDI and CFPS caused the improvement of the mechanical properties of these materials.

The best values of TS = 51–54 kPa and middle values of E_b = 31–34% were reached for the SFs containing mixtures of PDMS with CFPSs, 30 wt % melamine and expanded graphite (1 : 1 w/w), and PMDI. The maximum values of E_b (41–42%) and middle values of TS (35–38 kPa) were obtained for foams F16 (with 15 wt % melamine) and F22 (with the addition of $\sim$ 3.4 wt % D-66), which were based on mixtures of PDMS, CFPSs, and PMDI.

All of our SFs were combustible materials in the flame of a gas burner. The addition of fire retardants (melamine or/and expanded graphite) markedly decreased the flammability of SFs and enabled us to obtain self-extinguishing materials. Self-extinguishing SFs with a very high LOI of approximately 41% were prepared by the addition of 30 wt % of the flame retardants.

Figure 2   SF F19 (Tables II and III).

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