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ORIGINAL PAPER

Polydimethyldiphenylsiloxanes/silica interconnected networks: preparation and properties evaluation

Maria Cazacu · Angelica Vlad · Mihaela Alexandru · Petru Budrugeac · Carmen Racles · Felicia Iacomi

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Abstract A series of copolymers, polydimethyldiphenylsiloxane-α,ω-diols, differing by compositions and molecular masses has been prepared by equilibrium anionic ring-opening copolymerization of octamethylcyclotetrasiloxane with octaphenylcyclotetrasiloxane in presence of tetramethylammonium hydroxide as a catalyst. These copolymers were used as matrix for the in situ developing silica networks. The crosslinking of the copolymers concomitantly occurs by reaction between the ending silanol groups and tetraethoxysilane, thus the polydiorganosiloxane network interconnects with the silica one. The resulted materials processed as films (thickness 0.25–1.50 mm) were investigated by various techniques in order to evaluate morphology, optical properties, and thermal behavior. The results were compared with those obtained by model samples based on polydimethylsiloxanes/silica.

Keywords Polydimethyldiphenylsiloxanes/silica composites · Networks · Morphology · Optical properties · Thermal stability

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M. Cazacu (✉) · A. Vlad · M. Alexandru · C. Racles
“Petru Poni” Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A,
700487 Iasi, Romania
e-mail: mcazacu@icmpp.ro

P. Budrugeac
National Institute for Research and Development in Electrical Engineering ICPE-CA,
Splaiul Unirii 313, 030138 Bucharest, Romania

F. Iacomi
Faculty of Physics, “Al. I. Cuza” University, Blvd. Carol I 11, 700506 Iasi, Romania

Introduction

Polydimethylsiloxane (PDMS) consisting in alternating Si and O atoms with two methyl groups attached to each Si atom is the most representative for silicones and exhibits a variety of properties combinations: highly flexible backbone, small dielectrically constant, stability towards atomic oxygen, high permeability for different gases, hydrophobic and antiadhesive behavior, chemical and physiological inertness, etc. Silicone polymers containing organic groups other than methyl, i.e. long alkyl, phenyl, fluoro- or cyano-alkyl, vinyl, H, received considerable attention from the beginning of the silicones. Such substituents tend to modify the properties of the parent PDMS, improving certain properties as resistance to heat, oxidation, solvents, and/or radiation, adhesivity to the certain substrates, lubricity, compressibility, shear resistance, etc. [1–3]. As phenyl groups replace methyl groups in a polysiloxane, several changes occur. Some studies on the effect of the phenyl groups content on the degradation behaviour have been recently performed [3–5]. The diphenyl homopolymer has mechanical properties that are measurably different than those of PDMS. Therefore, in general only a limited amount of PDPS can be blended into a PDMS formulation, to maintain mechanical integrity. Copolymers of the two materials exhibit properties somewhere between the two pure materials [3]. The flexibility of the polysiloxane backbone decreases by methyl groups replacing with bulky phenyl ones [6]. When substitution exceeds 75 mol%, the polymers are solid [7]. Poly(diphenylsiloxane) (PDPS) has a much higher glass transition temperature and viscosity than PDMS, due to the limited mobility of the bulky phenyl groups. In particular, the viscosity change rate is significantly higher for polymer containing high phenyl content. PDPS is a polymer with liquid-crystalline properties, which can form a mesomorphic phase above its melting temperature [2]. The solubility parameter of the polydimethylsiloxane is increased by the presence of the phenyl groups. The solubility parameters of dimethyl, methyl–phenyl, and diphenyl substituted polysiloxanes are 7.5, 9.0, and 9.5 $(\mathrm{cal/cm}^3)^{1/2}$ respectively. As a result, the miscibility of polyorganosiloxanes with organic polymers improves when the solubility parameter increases [7].

The polysiloxanes, either homopolymers or copolymers, have two major drawbacks: (a) poor mechanical properties; (b) high costs. In order to minimize these disadvantages two approaches are generally used: (a) the crosslinking of the siloxane backbone; (b) the incorporation of inorganic powders, as reinforcing and/or bulking fillers, in the siloxane matrix. Fumed silica is the common additive used as optimal reinforcing material to improve insulating properties, mechanical strength or thermal stability of the polysiloxanes. However, the effects of the silica on the properties of the composites depend on the preparation method. In 1980s Mark et al. first applied a method specific for inorganic chemistry, the sol–gel technique, to prepare polydimethylsiloxane (PDMS) networks containing in situ precipitated silica [8, 9]. The major advantage of the network filling by this in situ approach is the avoidance of the problems associated with mechanical blending [9]. In addition, in the case of in situ reinforcement some properties of the resulted materials are improved, as compared to those obtained by classical methods. Certain applications of the filled polysiloxanes, such as protective masks, contact lenses, medical and industrial tubing, and light guides require transparency. Small domain sizes relative to the wavelength of light are necessary in order to obtain a high transparency. If the filler is a powder, then the primary particles themselves must be small and their aggregation should be eliminated or minimized. The in situ generation of silica by sol–gel procedure proved to be a good approach to obtain unusually transparent polydimethylsiloxane nanocomposites [9].

In this study we applied this method to obtain such composites based on silanol-terminated polydimethyldiphenylsiloxane copolymers. The effects of the generated silica content as well as diphenylsiloxane unit's content on the properties were investigated by different techniques: UV–Vis, fluorescence, XRD, AFM, ESEM and EDX, TGA, and differential scanning calorimetry (DSC) measurements.

Experimental

Materials

Octamethylcyclotetrasiloxane, $[(CH_3)_2SiO]_4$ (D_4), supplied by Fluka AG with the following characteristics: b.p. = 175 °C; $n_D^{20} = 1.396$; $d_4^{20} = 0.955$, purity >99% (GC) was dried over Na wire and freshly distilled before use.

Octaphenylcyclotetrasiloxane, $[(C_6H_5)_2SiO]_4$ (Ph_4), supplied by ABCR, purity 98%.

Tetramethylammonium hydroxide pentahydrate, $(CH_3)_4NOH \cdot 5H_2O$ was isolated in solid state from solution 25 wt% in water (Fluka), by the solvent removal in vacuum direct in the polymerization vessel just before use.

Dimethylformamide (Fluka AG) was dried over calcium hydride and distilled under vacuum before use.

Tetraethyl-orthosilicate (TEOS), purchased from Fluka (purity >98%, b.p. = 163–167 °C, $d_4^{20} = 0.933$) was used as received.

Dibuthyltin dilaurate (DBTDL) was received from Merck-Schuchardt, $d_4^{20} = 1.055$ and was used as received.

Equipment

The ^{1}H-NMR spectra were recorded on a BRUKER Avance DRX 400 spectrometer, using $CDCl_3$ as a solvent.

Gel permeation chromatographic analyses (GPC) were carried out on a PL-EMD 950 Evaporative Mass Detector instrument by using chloroform as eluant, after calibration with standard polystyrene samples.

Fourier transform infrared (FT-IR) spectra were obtained on a Bruker Vertex 70 FT-IR analyzer. Analyses were performed on the films in reflectance mode (ATR), in the 600–4,000 cm^{-1} range, at room temperature with 2 cm^{-1} resolution and accumulation of 32 scans.

X-ray diffraction was performed by using a DRON-2 diffractometer with CoKα, $\lambda = 0.1789$ nm and CuK$_\alpha$, $\lambda = 0.154$ nm radiation.

A home-made atomic force microscope (AFM, noncontact mode) was used to evaluate the morphology and surface roughness of the films (10 × 10 μm AFM images).

UV–Vis transmittance measurements on the films were performed by using a SPECORD M42 spectrophotometer.

Fluorescence spectra were obtained by using a Perkin Elmer LS55 luminescence spectrometer on films. The samples were excited at 380 nm. The excitation and emission slits were set at 2.5 and 10 nm, respectively.

Thermogravimetric measurements were performed with STA–Luxx apparatus produced by NETZSCH GERATEBAU GMBH—Germany, in static air atmosphere, in the temperature range 25–1,000 °C, and a heating rate of 10 K min^{-1}.

DSC analysis was performed on Diamond Perkin Elmer equipment between -150 and 0 °C with a heating rate of 20 °C/min, in nitrogen.

Microscopic investigations were performed on an Environmental Scanning Electron Microscope (ESEM) type Quanta 200 operating at 30 kV with secondary and backscattering electrons in high vacuum mode. Before analysis, the investigated films were covered with a thin layer of gold by sputtering (EMITECH K550X). The coupled dispersive X-ray spectroscope (EDX) permitted to perform the elemental analysis on the film surface.

Procedure

Synthesis of the dimethyldiphenylsiloxane copolymer

A pre-established quantity of TMAH solution (in order to result 0.1/100 g monomers) was introduced in a three-necked flask having inert gas inlet and reflux condenser with $CaCl_2$ protection. An excess of benzene was added and refluxed for about 0.5 h. Then, the solvents were completely removed by vacuum distillation. The promoter (0.01 wt% DMF) and cyclosiloxane co-monomers (D_4 and Ph_4) in pre-established molar ratios were added and the reaction vessel was equipped with a mechanical stirrer.

All glassware was dried in flame. The reaction mixture was stirred under a steady stream of nitrogen at 80 °C for 90 min. Then the temperature was increased to 150 °C for 1 h to decompose the catalyst. Finally, the polymer was vacuumed at room temperature for degasation and then at 150 °C to remove the eventually equilibrium cycles. The composition, and molecular masses of the resulted copolymers (Table 1) were evaluated by ^{1}H-NMR, and GPC, respectively.

Polymer filling in situ by sol–gel procedure

Ten grams PDPS were introduced in a Teflon dish and mixed with pre-established amounts of TEOS, according to Table 1. After about 10 min of stirring, 0.17 mL of DBTDL was added and the stirring continued for another 10 min. The resulted mixture was used to obtain films by pouring on a Teflon foil. The films were maintained at room temperature for 48 h and another 24 h in vacuum at 50 °C. The obtained colorless and transparent films (with 0.25–1.50 mm thickness) were easily

Table 1 The prepared composites

Sample	Mol% diphenylsiloxane units in copolymer	GPC data			Designed polymer/silica weight ratio[a]
		Mn	Mw	I	
PC1	0/P0	167,045	237,477	1.422	0.620
PC2	0/P0	167,045	237,477	1.422	0.232
PC3	4.2/P1	95,558	192,184	2.010	0.635
PC4	4.2/P1	95,558	192,184	2.010	0.621
PC5	6.7/P2	114,817	245,802	2.141	1.070
PC6	6.7/P2	114,817	245,802	2.141	0.639
PC7	12.4/P3	144,105	316,890	2.199	0.930
PC8	12.4/P3	144,105	316,890	2.199	0.744
PC9	18.4/P4	104,535	214,160	2.049	0.930
PC10	18.4/P4	104,535	214,160	2.049	0.620

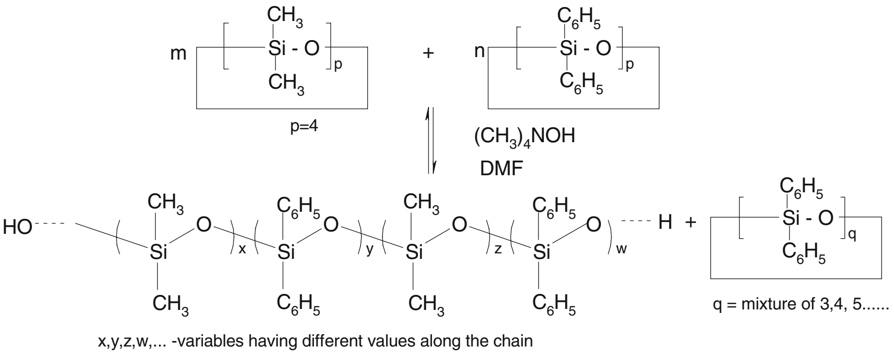
[a] According to feed ratio polymer/TEOS

peeled off from the substrate. The films were then kept in the laboratory environment about two months before investigations. The tests revealed that after this time the mass of the samples is stabilized.

Results and discussion

Copolymerization of the proper cycles (dimethyldiphenyl or methylphenyl mixed cycles or mixture of dimethylcyclosiloxanes and diphenylcyclosiloxanes, trimers or tetramers) catalyzed by bases (alkaline or onium hydroxides and organometalls, in principal) is the main procedure to synthesize phenyl-substituted polysiloxanes [5, 10]. In this paper, the synthesis of the linear dimethyldiphenylsiloxane (PDPS) copolymers was achieved by the adapted literature method [11, 12], as have already been reported [13]: bulk anionic ring opening copolymerization of the octamethylcyclotetrasiloxane (D_4) and octaphenylcyclotetrasiloxane (Ph_4), using tetramethylammonium hydroxide as catalyst and a Lewis base (DMF) as promoter. The reaction occurs according to the Scheme 1, being thermodynamically controlled one as already was established for the case when such a catalyst is used [6, 14]. A base was chosen as catalyst because it is very difficult to open octaphenyltetrasiloxane cycle in the presence of usual acid catalysts. In addition, tetramethylammonium hydroxide can be easily removed in the end by increasing temperature of the reaction mixture to 150 °C when the catalyst is decomposed in volatile compounds (trimethylamine and methanol) [15]. Dimethylformamide as promoter was added in order to increase the reaction rate by counter ion complexation and hindering the ion pair's formation [14].

The molecular weights of the obtained polymers were determined by GPC. The compositions of the copolymers (Table 1) were determined on the basis of ^{1}H-NMR spectra (Fig. 1) taking into account the peaks corresponding to the protons in the



Scheme 1 The simplified scheme for the synthesis of polydimethyldiphenylsiloxane

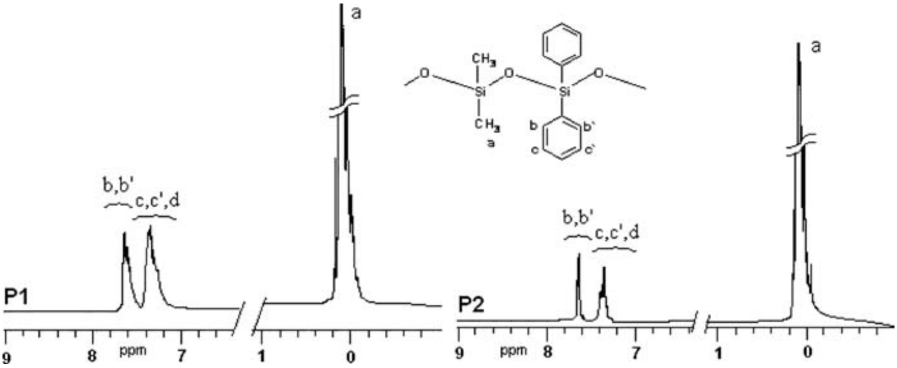
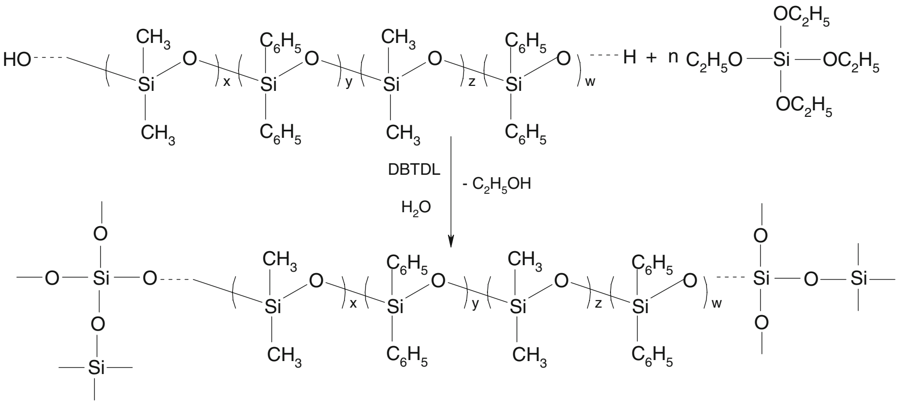


Fig. 1 ^{1}H-NMR spectra for the dimethyldiphenylsiloxane copolymers P1 (4.2 mol% diphenylsiloxane units) and P2 (6.7% diphenylsiloxane units)

methyl (0.15 ppm) and phenyl (7.0–7.6 ppm) groups, respectively. It is known that the dimethyldiphenylsiloxane copolymers obtained by ring-opening polymerization in the presence of such a catalyst (alkaline or onium hydroxides) that we used, are randomly [6, 14, 16].

The synthesized copolymers were mixed in different ratios with TEOS (Table 1) as in situ generating silica network precursor in presence of DBTDL as a catalyst. No water was added as hydrolysis agent, except for that absorbed by the sample from the atmosphere. The crosslinking of the polymers by their Si–OH end groups is also possible to occur concomitantly (Scheme 2). Thus, poly(dimethyldiphenylsiloxane)s/silica interconnected networks resulted that were processed as films cast before crosslinking.

The method used for the samples preparation is based on the same principle with the room temperature vulcanization silicone (RTV) preparation, when the crosslinking of the polydimethylsiloxane-α,ω-diols occurs by polycondensation reactions in the presence of the environmental humidity, needing a few days to process ending. Water must to diffuse in deep of the film, while low molecular condensation



Scheme 2 Simplified scheme for the polymer crosslinking and silica generating

compounds (i.e. alcohol) migrates outside. Therefore, the films were kept in the laboratory environment about 2 months before investigations, when the weighting revealed the mass stabilization.

Although it should be expected as the presence of diphenylsiloxane units in the copolymers to induce some crystallinity in the resulted material, the XRD patterns presented in Fig. 2 rather show an increasing in amorphous character. It is possible that the presence of the random diphenylsiloxane units to create a higher disorder degree, disrupting the symmetry [7].

The AFM images (Fig. 3) reveals in general the formation of the surfaces having low roughness. Thus, the samples having prescribed polymer/silica ratio of about 0.6 but differing by the copolymer composition (4.2%—PC4 and 6.7%—PC6) have very closely values for the surface roughness, RMS (1.37 and 1.30 nm, respectively). However, at higher polymer/silica ratio, the sample based on copolymers with high diphenylsiloxane units (18.4% mole) proved to show a slight increased RMS (38.70 nm). This can be hypothesized by polymer segregation on the surface.

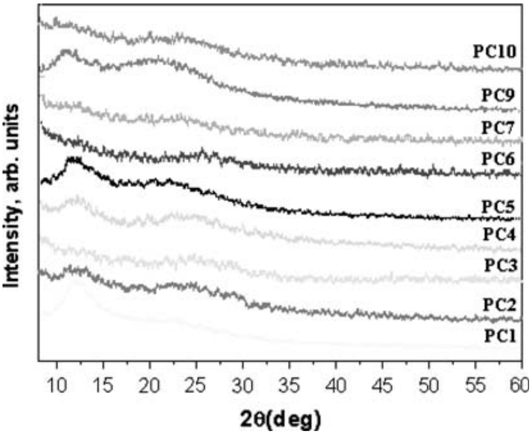


Fig. 2 XRD patterns of the prepared polyorganosiloxane/silica samples


PC4, 10x10μm, RMS = 1.37 nm

PC6, 10x10μm RMS = 1.30 nm

PC9, 20x20μm RMS = 38.70 nm

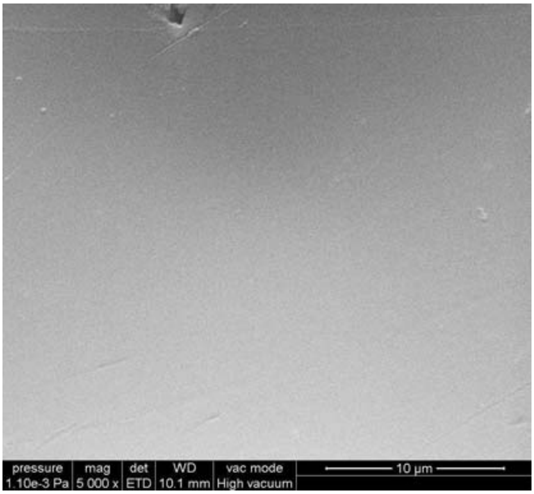
Fig. 3 Comparative 3D AFM images of some composite films

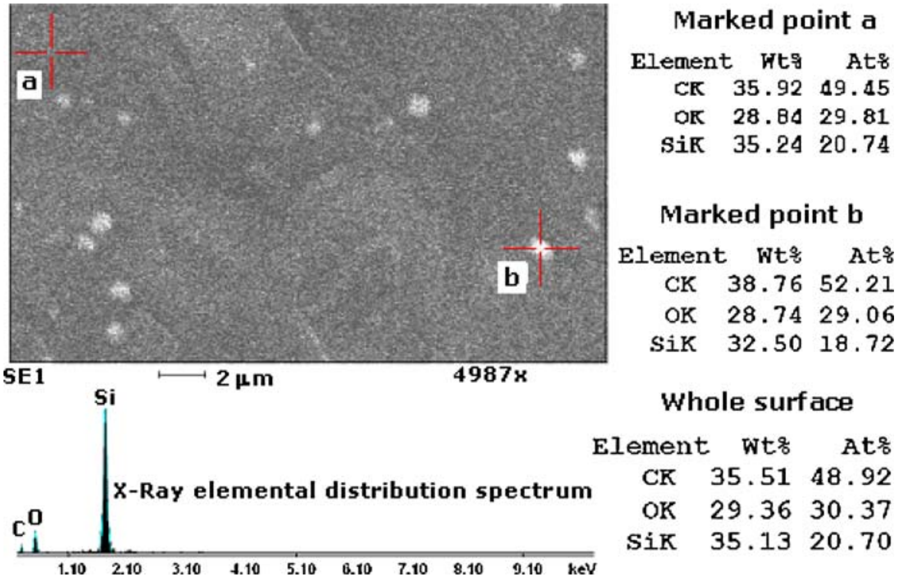
The images taken with ESEM technique by using backscattering electrons detector (BSD) when the analysis is performed at 500 nm to 5 μm depth from the surface reveal a homogeneous enough structure without emphasizing the presence of any silica domains (Fig. 4).

The EDX method able to identify the nature of the atoms present in the sample at a depth of 100–1,000 nm from the surface also reveals in general a uniform distribution of the C, O and Si. The rare visible domains proved to be formed by copolymer, according to the elemental composition (Fig. 5).

The quantitative UV–Vis transmittance spectra for relatively thick films based on polydimethyldiphenylsiloxanes reinforced with different in situ silica percents and two polydimethylsiloxanes reinforced in the same conditions were registered. All samples as films with different thickness showed good transmittance (around 80–90%) with some deviation resulted from the interplay between the polymer composition and silica content influences (Fig. 6). It was already established [7] that at 15–20 mol% phenyl concentrations, the refractive index matches that of amorphous silica and transparent compounds may be prepared. This can be due to the better compatibility between silica and polymer matrix at such a ratio.

Fig. 4 ESEM image of the PC5 film surface





Marked point a

Element	Wt%	At%
CK	35.92	49.45
OK	28.84	29.81
SiK	35.24	20.74

Marked point b

Element	Wt%	At%
CK	38.76	52.21
OK	28.74	29.06
SiK	32.50	18.72

Whole surface

Element	Wt%	At%
CK	35.51	48.92
OK	29.36	30.37
SiK	35.13	20.70

Fig. 5 EDX analysis results for the sample PC5

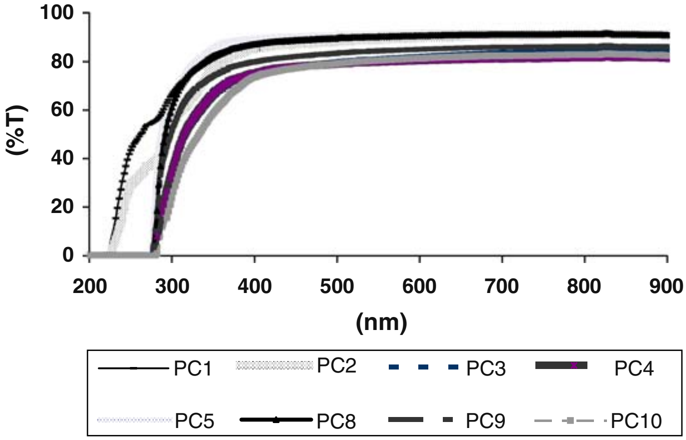


Fig. 6 UV–Vis transmittance curves for the investigated samples as films

It is known [17] that methylphenylsiloxane as well as diphenylsiloxane polymers exhibit characteristic UV absorption bands due to the $\pi \rightarrow \pi^*$ transition of phenyl chromophores. Such materials usually emit fluorescence both in solution and in glassy matrices. Our investigated samples proved indeed to show fluorescence as in Fig. 7. The fluorescence intensity generally should increase by diphenylsiloxane unit's content. However, other parameters such as diphenylsiloxane unit's distribution in the chain or copolymer amount in composite also influence fluorescence. Therefore, it is difficult to establish a correlation between spectra intensity and copolymer composition.

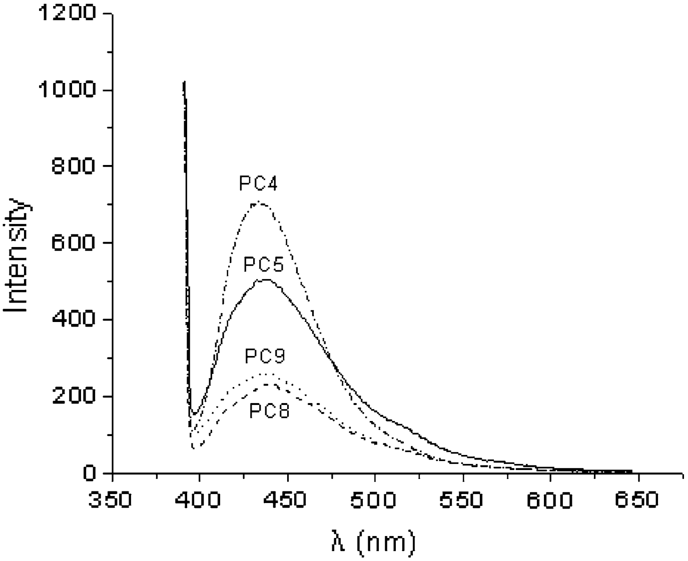


Fig. 7 Fluorescence emission spectra for some dimethyldiphenylsiloxane/silica samples. The excitation and emission slits were set at 2.5 and 10 nm, respectively

It is known that replacing methyl with phenyl groups improves the thermal and oxidative stability when compared to polydimethylsiloxane [1]. This occurs because of the inherent stability of the phenyl ring and also because the phenyl group strengthens the siloxane bond by increasing $d\pi$–$p\pi$ contribution [7].

The thermogravimetrical analysis shows that the thermo-oxidative processes of our dimethyldiphenylsiloxane/silica composites are more complex ones. The three peaks from DTG curves (Fig. 8) led to the conclusion that by progressive heating of every sample three successive global processes occur. The first process is endothermic one and consists in volatile compounds emitting, water probably, as a result of the residual groups hydrolysis-condensation. This process is succeeding by two exothermic thermo-oxidative processes. Finally, a white solid residue remains, SiO_2 probably.

Some parameters of the thermal decomposition processes are presented in Table 2.

The decreasing thermal stability order is the order of $\%\Delta m_{300}$ increasing or $T_{10\%}$ decreasing as can be seen in Fig. 9 [18–20].

Thus, based on $\%\Delta m_{300}$ criteria the thermal stability decreasing order is:

$$\text{PC2} > \text{PC1} > \text{PC3} > \text{PC4} > \text{PC8} > \text{PC6} > \text{PC7} > \text{PC5} = \text{PC10} > \text{PC9},$$

being very closely to that established based on $T_{10\%}$ criterion:

$$\text{PC2} > \text{PC1} > \text{PC4} > \text{PC3} > \text{PC8} > \text{PC6} > \text{PC7} > \text{PC10} > \text{PC5} > \text{PC9}.$$

Unexpectedly, the thermal stability of the samples based on polydimethyldiphenylsiloxanes decreased as compared with those based on PDMS.

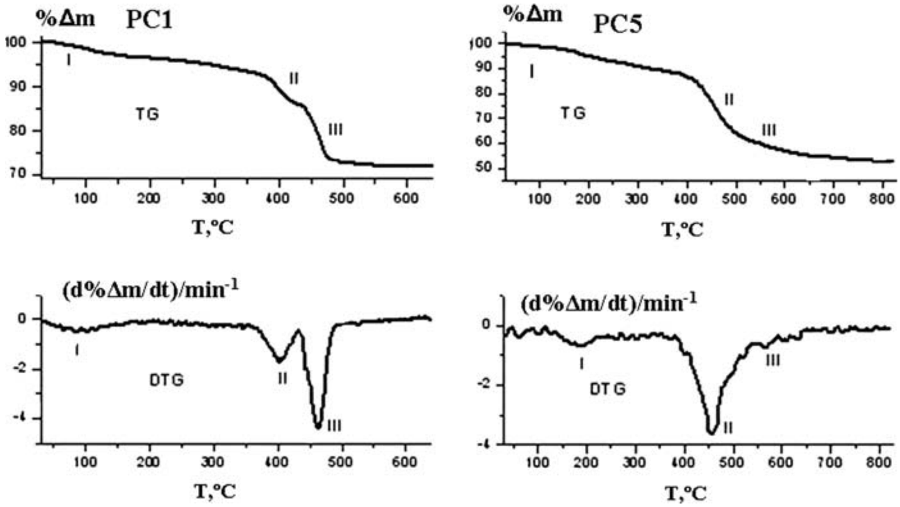


Fig. 8 Illustrative TG and DTG curves for two composites, PC1 and PC5

Table 2 Some non-isothermal parameters of thermo-oxidative degradation determined by TGA

Sample	$T_{10\%}$ (°C)	$\%\Delta m_{300}$	$\%\Delta m_t$
P0	350	5	55.0
P4	370	5	70.0
PC1	400	5.4	71.7
PC2	420	4.9	77.1
PC3	358	7.4	70.9
PC4	360	7.8	56.1
PC5	307	9.0	52.3
PC6	330	8.6	54.2
PC7	327	8.9	53.8
PC8	352	8.5	48.6
PC9	300	9.7	57.4
PC10	320	9.0	54.4

One explanation for this would be the presence of the acid catalyst trace (DBTDL) in the material that affects mainly diphenylsiloxane units. Our hypothesis is based on the fact that, as was already proved [21, 22], different from the Si–CH_3, the Si–C_{aryl} bond is very susceptible to the electrophilic agents attack with benzene removing. The thermogravimetrical analysis results of the samples P0 and P4 are expected ones: copolymer has increased thermal stability as compared with homopolymer. However, both polymers have thermal stability increased as compared with some of the crosslinked composites (i.e., PC5–PC10). This supports the hypothesis that the thermal decomposition is accelerated by the presence of the DBTDL traces in samples.

Instead, slight improvements of the considered thermal stability parameters ($\%\Delta m_{300}$ and $T_{10\%}$) with the silica content increasing it can be observed, when

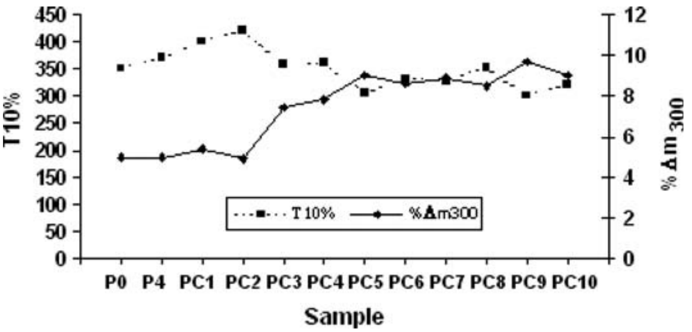


Fig. 9 Graphical representation of two parameters (%Δm_{300} and $T_{10\%}$) concerning to the thermal stability for the investigated samples

compared the samples based on the copolymers having the same compositions (i.e., PC1 with PC2, PC3 with PC4, PC5 with PC6, PC7 with PC8 or PC9 with PC10).

Taking into account the high flexibility of the siloxanes, in general, the DSC traces were registered in low temperature range (−150 to 0 °C) (Fig. 10).

It can be seen that Tg of about −123 °C in the case of samples PC1 and PC2 based on polydimethylsiloxane slowly shifted to increased values as diphenylsiloxane content increases. So, at the highest diphenylsiloxane content (18.4%) Tg value can be seen around −75 °C. In addition, the composite based on polydimethylsiloxane with low silica content (PC1) shows a crystallization exotherms and a melting endotherm at about −60 and −40 °C. In the case of PC2 sample having a high silica content no crystallization happens due to polymer embedding in the dense silica network.

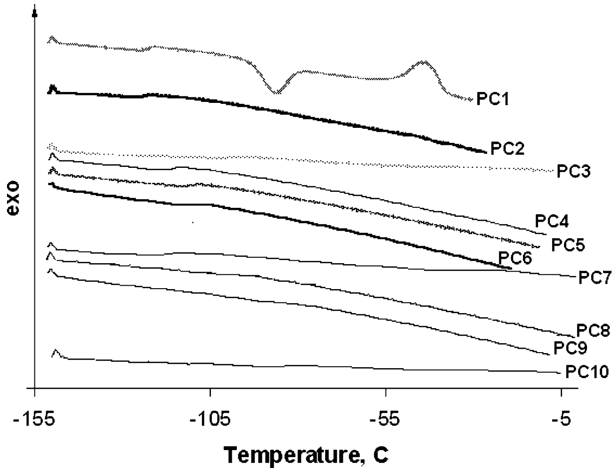


Fig. 10 DSC scans (second heating) for the prepared samples

Conclusions

Some dimethyldiphenylsiloxane copolymers have been prepared and used as matrix for in situ generation of the silica in various ratios. The resulted materials processed as films, proved to be amorphous as was emphasized by DSC, and XRD, and having good UV transparence as well as fluorescence. ESEM and EDX investigations revealed homogeneous materials without visible silica domains. While the thermo-oxidative stability is improved by the silica presence, the diphenylsiloxane units proved to have not the expected effect. The presence of the acid catalyst trace in material is supposed to be responsible for this.

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