

Polysiloxane Networks

Synthesis and thermo-mechanical characterization

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The polysiloxane networks have been prepared by means of hydrosilylation reaction of poly(dimethyl, hydrogen-methyl)siloxanes (H₂PDMS) containing Si-H groups and siloxane copolymers named V₂PDMS and V₄PDMS containing Si-CH=CH₂ functional groups. The structure of the siloxane copolymers was determined from ¹H-NMR and FT-IR spectra analyse and the characterization of the siloxane copolymers was performed by gel permeation chromatography (GPC), viscosity and determination of the content of functional groups. The mechanical properties of the newly obtained networks were determined by physico-mechanical measurements, dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC).

Keywords: polysiloxane, hydrosilylation crosslinking, polymer networks

Although silicone technology has been around for over five decades, this unique material continues to be used in new and various applications.

Introduction of new functions on both siloxane main chain or at its end is known to modify the properties of the silicones opening new and various possibilities for applications in different fields. By adequate substitution of polysiloxanes new materials with different utilities from catalysts, active ligand polymers for transition metals, materials for chromatography, electrolytic polymers, adhesives, liquid crystals, crosslinking agents, conductive and electroluminescent polymers, non-linear optic materials, bactericides, permselective membranes, resistive fittings for fuels, inert implant devices, covers for atomic oxygen protection and for contact lenses, etc were obtained [1-4]. Additionally, functional siloxanes could be mixed with organic polymers in order to improve their properties and performances.

The variety of side groups determines the ability of polysiloxanes to be used in a wide array of applications, due to different properties as thermal stability (-115 to 260 °C) was increased, fuel resistance, optical clarity (with refractive indexes as high as 1.60), low shrinkage 2%), and low shear stress determined by specific side groups [5,6].

From all known polysiloxanes only a few are directly used as technical products. Almost all polysiloxanes must be treated, must be „manufactured” to give a useful technical end product varying from vulcanized rubber, resins and varnish to emulsions [7].

Crosslinked siloxane products, unlike mixtures, present chemical bonds between polymer sequences with the same (siloxane) or different nature (siloxane and organic) that hinder the basic phase separation.

Crosslinked silicon materials can be obtained by addition reaction, catalyzed by Pt or Rh, or by condensation reaction with peroxides or oximes in the presence of Sn catalysts. Other chemists presented the crosslinking process of silicones by means of condensation with acetoxi groups, method known as hydrolisis reaction at room temperature with acetic acid elimination [7].

The curing reaction is a hydrosilylation reaction, which is an addition that proceeds, almost entirely (> 95 %), in an anti-Markovnikov way. The reaction is run optimally in

the presence of the Karstedt platinum catalyst, which is a complex of platinum with 1, 3-divinyltetramethyldisiloxane with high solubility in prepolymers [8-10].

The reaction can be also conducted in the presence of Speiers catalyst (PtH₂Cl₆), known for the hydrosilylation reaction. Unfortunately, the Speiers catalyst is not stable in the presence of alcohols. The hexachloroplatinic acid (PtH₂Cl₆) reacts with a hydroxyl group (e.g. Si-OH) [8-10] producing HCl, which causes a lowering of the concentration of active catalyst, making the curing reaction uncontrollable and unpredictable.

The cross-linking process is significant because it prevents the possible presence of any secondary products or toxins. The cross-linking by hydrosilylation does not need post-curing, it is irreversible and non-blocked.

This paper deals with the synthesis and characterization of a series of polysiloxanes with Si-H and Si-CH=CH₂ functional groups and crosslinked siloxane materials by hydrosilylation reaction. The evolution of their physical structure as a function of temperature was followed by differential scanning calorimetry (DSC). In order to facilitate comparison, the dynamic mechanical modulus has been analyzed upon an analogous temperature scanning by dynamic mechanical analysis (DMA).

Experimental part

Materials and methods

Octamethylcyclotetrasiloxane (D₄) 98%, linear hydrogenmethylsiloxane (L-31), with: 1.364 % H hexamethyldisiloxane (HMDS), 99.5 %, 2,4,6,8-tetramethyl-tetramethylcyclotetrasiloxane (V₄) ≥ 97%, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, in xylene, Karsted's catalyst, AEROSIL® 380 - hydrophilic fumed silica with a specific surface area of 380 m²/g, average primary particle size = 7 nm, SiO₂ = 99.8% were used without any purification.

Styrene-divinylbenzene copolymer with sulfonic groups was used after conditioning which consisted in washing with water, followed by 4% NaOH solution, regeneration with a 4% HCl solution, and final washing with water and subsequent dehydration by azeotrope distillation with toluene. The cation-exchanger had the following characteristics: active group, SO₃H; volumic exchange

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capacity, 1.8 meq/mL; gravimetric exchange capacity, 4.2 meq/g; specific surface, 35 m²/g (Romanian product).

Infrared spectra (FT-IR) were obtained using a Nicolet 60 SX FT-IR under dry air, at room temperature, on KBr pellets, in the range of 4000–400 cm⁻¹.

¹H-NMR spectra were recorded on a Bruker Avance 400 spectrometer in CDCl₃.

Gel permeation chromatographic analyses (GPC) were carried out on a PL-EMD 950 evaporative mass detector instrument using chloroform as the eluent, after consequent calibration with standard polystyrene samples.

The determination of the active hydrogen content from polysiloxanes with Si-H functional groups is based on the reaction of this group with alkaline bases [11].

Physico-chemical measurement were made on a TITRA-TEST 2161 device with a elongation speed of 1.242 mm/s, at room temperature.

The hardness was determined with a TIP 1 Durometer (scale 0 ÷ 100 Shore).

Differential scanning calorimetry (DSC) data were obtained using a Perkin Elmer Diamond USA device. Each sample was exactly weighted in an aluminium pan and heated at a rate of 10°C/min from -150 to +20°C, under nitrogen gas flow.

Dynamic mechanical analyses (DMA) were performed on a Perkin Elmer Diamond apparatus, in tension mode, at a frequency of 1 Hz. The temperature scans were between -150 and +250°C at 2°C/min. The films (A: 10 x 9.7 x 2.21 mm; B: 10 x 8.83 x 2.11 mm; C: 10 x 9.54 x 2.54 mm) were longitudinally deformed by small sinusoidal stress and the resulting strain was measured. The value of the storage modulus (E'), the loss modulus (E'') and the tension loss tangent (tan δ = E''/E') as functions of temperature were obtained. For each network, the following events were identified [12; 13]:

- a mechanical relaxation associated with a first order transition (melting or crystallization).

- a mechanical relaxation associated with the glass transition (T_g), named the "dynamic" glass transition (T_g).

Synthesis of poly(dimethylhydrogen-methyl)siloxane copolymers (H₁PDMS)

Poly(dimethyl hydrogen-methyl)siloxane copolymers (H₁PDMS) [14], were obtained through polymerization - equilibration reaction of a mixture of octamethylcyclotetrasiloxane (D₄), hydrogenmethylsiloxane oligomer (L-31) and hexametyldisiloxane (HMDS) in the presence of an exchange ion resin (PUROLITE CT 175) as catalyst (scheme 1).

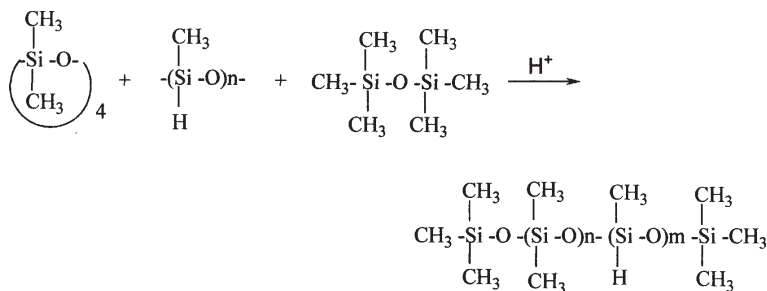
The molecular weight of these copolymers was adjusted by the disiloxane amount added and the number of Si-H groups varied with (CH₃)₂Si/HSiCH₃ units introduced in reaction.

Synthesis of α,ω-trimethylsiloxy poly(methyl-vinyl, dimethyl)siloxane copolymers (V₁PDMS)

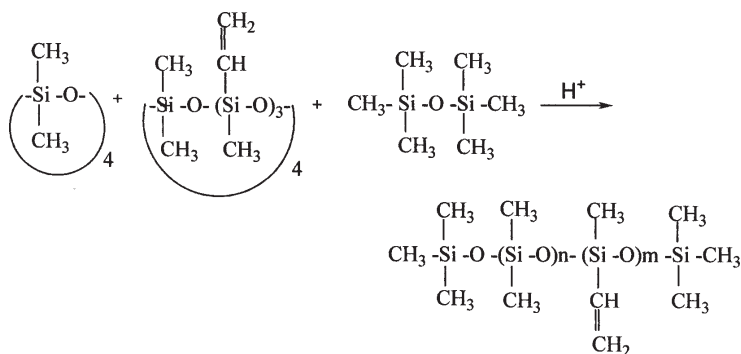
The α,ω-trimethylsiloxy poly(methyl-vinyl dimethyl)siloxane copolymers (V₁PDMS) [15] were obtained by the copolymerization reaction of octamethylcyclotetrasiloxane (D₄) and tetramethyltetravinylcyclo tetrasiloxane (V₄) mixture in the presence of hexamethyldisiloxane (HMDS) as end-blocker and mass regulator (scheme 2). The ion exchange compound (PUROLITE CT 175) was used as catalyst.

Synthesis of α,ω-vinyl-dimethylpolysiloxane (V_cPDMS)

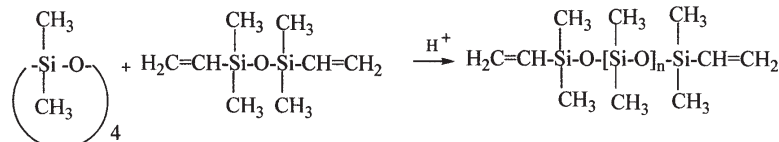
The α,ω-vinyl-dimethylpolysiloxane (V_cPDMS), were obtained through the polymerization - equilibration reaction of a mixture of octamethylcyclotetrasiloxane (D₄) and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane in the presence of an exchange ion resin (PUROLITE CT 175) as catalyst (scheme 3).



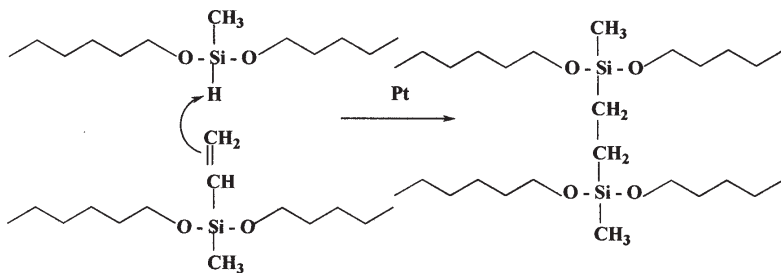
Scheme 1. Synthesis of the H₁PDMS copolymers



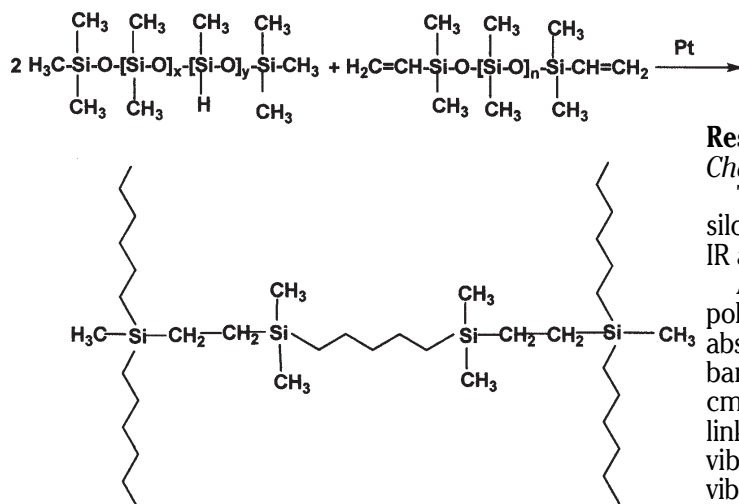
Scheme 2. Synthesis of the V₁PDMS copolymers



Scheme 3. Synthesis of the V_cPDMS polymers



Scheme 4. Synthesis of the siloxane networks connected by ethylene bridges



Scheme 5. Synthesis of the siloxane networks connected by diethylene-polysiloxane bridges

Synthesis of polysiloxane networks

The crosslinking of H₁PDMS with V₁PDMS and V_cPDMS copolymers in order to obtain polysiloxane networks was achieved by hydrosilylation reaction, in the presence of the Karstedt catalyst, in quantities of 50 ÷ 100 ppm. The reaction was conducted for 5 ÷ 10 h at room temperature or 30 ÷ 60 min at a temperature of 60 ÷ 80°C. Polysiloxane networks are formed by the two siloxanic chains linked together by ethylene (scheme 4) or diethylene - polysiloxane bridges (scheme 5).

The mixtures for obtaining polysiloxane networks

A mixing vessel masticator type was filled with 20g V₁PDMS, 2g H₁PDMS-1 and 2g Aerosil 380, as active material for obtaining a homogeneous paste, which flows. 0,1mL (90 ppm Pt) Karstedt catalyst was also added, and the paste was poured into a mould (10x10x2 mm) and exposed to vacuum in order to eliminate the air incorporated by mixing. The crosslinking reaction was conducted for 10 h at room temperature. A siloxane membrane with almost 2 mm thickness was obtained.

In the above described masticator 2g poly (dimethylsiloxane) (PDMS) (η²⁵, [cSt] =139) as inactive polymer was added, in order to obtain an homogenous material.

The crosslinking polymers were introduced into a vessel-type blender. For that 7g V_cPDMS with two vinyl groups on the polymer chain end and 8g H₁PDMS-2 were used. The two components were mixed until a fluid homogenous paste was obtained. After that 0.1 mL (0.90 ppm) the Karstedt catalyst was added and the final product was put in a matrix (10x10x2 mm) and crosslinked after air removal in a vacuum dessicator. The crosslinking was conducted at room temperature for 10 h (scheme 5).

Results and discussions

Characteristics for H₁PDMS copolymers

The structure of poly (dimethyl, hydrogen-methyl) siloxane (H₁PDMS) copolymers was determined from FT-IR and ¹H-NMR spectra analyzes.

As presented in figure 1, the FT-IR spectra of H₁PDMS polysiloxanes indicate the presence of the characteristic absorption bands of Si-H bond at 2127 cm⁻¹. Also, absorption bands characteristic for the siloxanic chain (at 2963 cm⁻¹ the asymmetric stretching vibration of -CH₃ group linked to silica, at 2905 cm⁻¹ the symmetrical stretching vibration of -CH₃ group, at 1261 cm⁻¹ the symmetrical vibration deformation of the -CH₃ group) were observed. In the range 1093-1027 cm⁻¹, the characteristic asymmetric stretching vibration of the Si-O-Si bond from siloxanic chain can be also identified.

From ¹H-NMR spectrum of H₁PDMS copolymer the protons from Si-H δ appearing at 4.7 ppm and Si-CH₃ protons at 0.14 ppm can be easily identified.

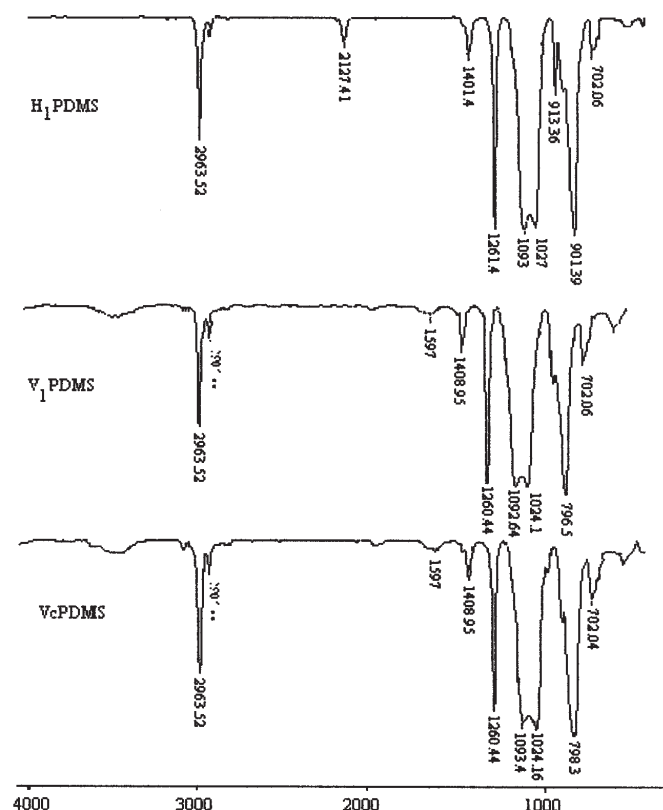


Fig. 1. FT-IR spectra of the H₁PDMS, V₁PDMS and V_cPDMS

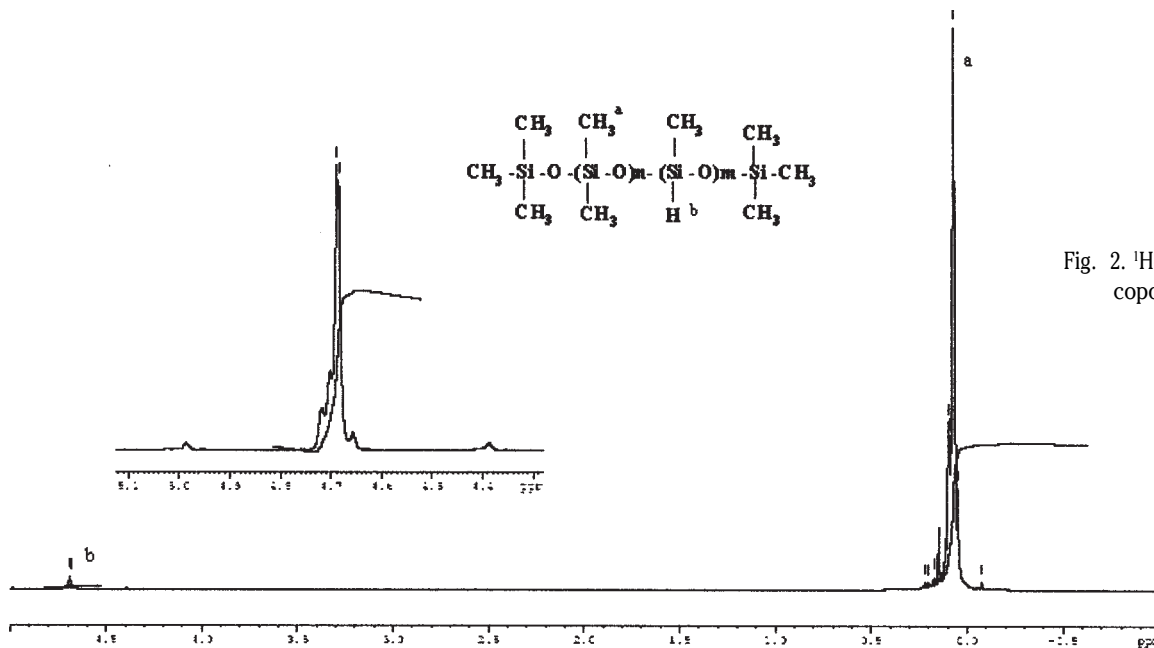


Fig. 2. ¹H-NMR spectra of the copolymer H₁PDMS

Sample	D ^H /D	H ^a [%]	η ²⁵ [cSt]	M _v ^b	GPC		
					M _n	M _w	M _w /M _n
H ₁ PDMS-1	1:8.4	0.1393	78	7000	6250	11187	1.79
H ₁ PDMS-2	1:10	0.1312	63	4000	3583	5750	1.6

Table 1
THE CHARACTERISTICS OF H₁PDMS
COPOLYMERS

^a As determined by modified Zerewitinoff metode [16];

^b $\lg \eta^{25} = 1 + 0.0123M^{0.5}$ [17].

In table 1 the specific characteristics of H₁PDMS copolymers are presented. The ratio between CH₃ (H) SiO/(CH₃)₂SiO (D^H/D) was determined from the integrals of the corresponding protons signals for the above mentioned groups in the ¹H-NMR spectrum.

Characteristics for V₁PDMS and V_cPDMS copolymers

The characteristics of the V₁PDMS and V_cPDMS copolymers are presented in table 2. The ratios CH₂=CHSi/(CH₃)₂SiO- (V/D), calculated according to the quantities of the two components introduced in reaction are presented.

The structure of the V₁PDMS and V_cPDMS copolymers was initially determined by FT-IR spectroscopy.

Figure 1, that presents the FT-IR spectrum of the polysiloxanes with vinyl functional groups (V₁PDMS and V_cPDMS), indicates the presence of the characteristic absorption bands: one at 3052 cm⁻¹ attributed to -Si-CH-CH₂ group, the second one at 1597 cm⁻¹ characteristic to the C=C bond and another one at 1408 cm⁻¹ determined by =CH₂ grouping.

Sample	V/D ^a initial	Conversie [%]	M _v ^b	GPC		
				M _n	M _w	M _w /M _n
V ₁ PDMS	1:70	78	95.500	50.677	104.753	2.067
V _c PDMS	1:8	85	594	1366	1853	1.357

^a V/D = CH₂=CHSi/(CH₃)₂SiO-

^b $\lg \eta^{25} = 1 + 0.0123M^{0.5}$ [17].

Table 2
THE CHARACTERISTICS OF
V₁PDMS AND V_cPDMS
COPOLYMERS

In the ¹H-NMR spectrum (fig.4) of V_cPDMS copolymer the characteristic peaks of -CH₃ methyl protons linked to Si atom (at 0.1-0.2 ppm) and the peaks characteristic of protons from the double bond -Si-CH=CH (at 5.7-6.2 ppm) can be observed.

The presence of vinyl groups from V₁PDMS copolymers could not be the evidence of ¹H-NMR technique due to the small number of vinyl groups in the structure of copolymers.

Thermo-mechanical characterisation for polysiloxane networks

The physico-mechanical properties (table 3) of the crosslinked polymers related to the molar ratio of the -Si-CH=CH₂/-Si-H reactive groups were studied.

As depicted in table 3 the values of the physico-mechanical parameters are quite low, but typical for silicon elastomers [18].

The dependence of the physical properties of the corresponding siloxanes on temperature was studied by differential scanning calorimetry (DSC) (fig. 4).

The glass temperature T_g (around -118°C) and ΔC_p obtained were characteristic for an amorphous phase. Around -48°C an endothermic peak associated with the

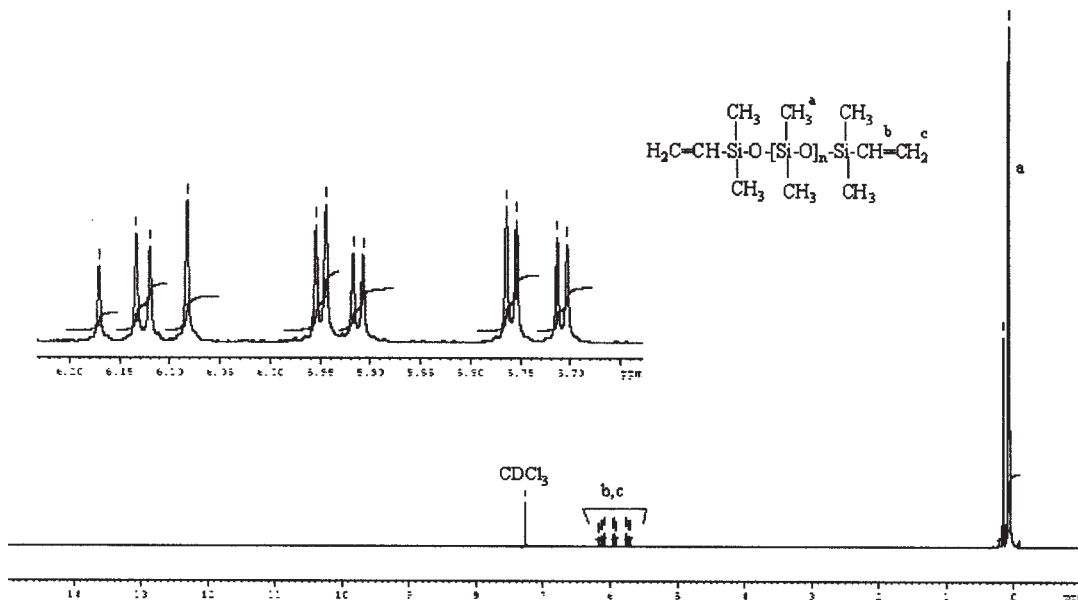


Fig. 3. ¹H-RMN spectra of the V_c PDMS copolymer

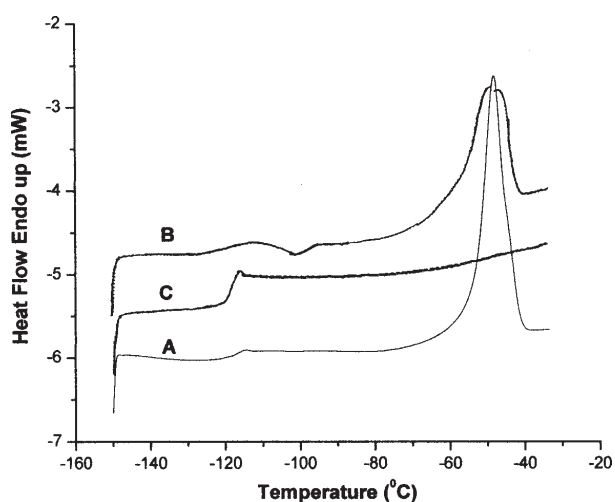


Fig.4. DSC thermograms of polysiloxane networks (A, B, C)

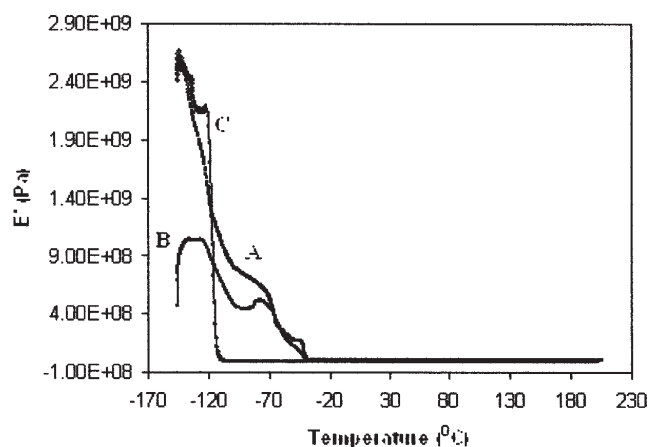


Fig. 5. Storage modulus as function of temperature plots for the probe: A, B and C

Sample	Hardness [°Shore]	Tensile strength [MPa]	Elongation at break [%]
A	60	5.776	143.6
B	38	2.834	332.5
C	20	2.137	85

Table 3
PHYSICO-MECHANICAL
PARAMETERS OF POLYSILOXANE
NETWORKS

melting temperature for the A and B samples (table 4) was also observed.

The glass temperature T_g around -123°C and the crystallization temperature T_c around -100 °C specific for PDMS chain (added to mixture B) was correlated with the existence of long PDMS segments not included in the siloxane network (fig.6, curve B).

A special situation was encountered for the C sample. The crystallization process did not occur during the cooling scan as indicated by the absence of the melting peak on the DSC thermogram (fig. 4, curve C). The crosslinking rate is so high that the bound rubber increment renders into the immobility of the network that inhibits any crystallization. As a consequence, the polymer was frozen in the disordered glassy state. This result can be explained by the chemical structure of this crosslinked polymer,

which presents a regular structure with methyl groups and diethylene - polysiloxane bridges.

The characteristic parameters of transitions are listed in table 4.

The dynamic mechanical modulus of the siloxanes was analyzed by dynamic mechanical analysis (DMA) in order to facilitate comparison.

The DMA thermograms (fig.5-7) emphasize different mechanical relaxations associated with transitions. The mechanical behaviour can be foreseen for each crosslinking at different temperatures.

It was observed that the samples had a viscoelastic behaviour (fig.5) All samples had a glassy region (T<-130°C) with a storage modulus (E') higher than 10⁹Pa, excepting the sample B that had a storage modulus under 10⁹Pa. The abrupt descent of the storage modulus up to -

Table 4
THE MAIN PARAMETERS OF DSC AND DMA CURVES

Sample	T _g	T _g	ΔC _p	T _c	ΔH _c	T _m	T _m	ΔH _m
	(DSC)	(DMA)	(DSC)	(DSC)	(DSC)	(DSC)	(DMA)	(DSC)
	[°C]	[°C]	[J/g. °C]	[°C]	[J/g]	[°C]	[°C]	[J/g]
A	-118.59	-107.56	0.181	-	-	-48.10	-52.91	24.308
B	-123.39	-118.3	0.036	-100.88	-1.0855	-49.63	-62.47	17.3496
	-117.51	-105.82	0.033	-	-	-46.61	-43.1	17.3496
C	-118.58	-109.04	0.392	-	-	-	-	-

-T_g, glass transition temperature evaluated from DSC curves.
 -T_g, glass transition temperature evaluated from DMA curves (read as tan δ peak)
 -ΔC_p, heat capacity evaluated from DSC curves.
 -T_c, crystallization temperature evaluated from DSC curves.
 -ΔH_c, crystallization enthalpy evaluated from DSC curves.
 -T_m, melting temperature evaluated from DSC curves.
 -T_m, melting temperature evaluated from DMA curves (read as tan δ peak).
 -ΔH_m, melting enthalpy evaluated from DSC curves.

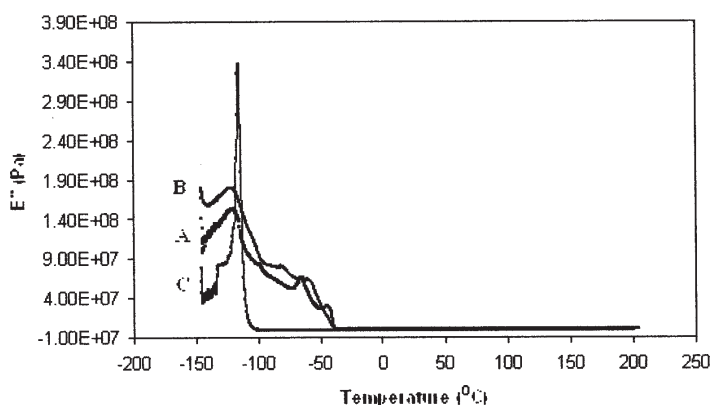


Fig. 6. Plot of loss modulus as a function of temperature for the samples: A, B and C

90°C (a mechanical relaxation associated with glass transition) for all samples followed by another one up to -50°C (characteristic for a viscoelastic behaviour) was observed instead of a plateau zone with a specific modulus value for each sample.

At temperatures above -50°C, PDMS networks exhibits a good thermal stability up to +180°C temperatures (experimental temperature limit) despite the small value of E' (A: 7.52 x10⁸ Pa; B: 3.52x10⁸PA; C: 1.59x10⁶PA) featured by silicone rubber.

The plot of loss modulus (E'') as a function of temperature (fig.6) indicates a glass transitions of the samples occurring around -120°C.

The temperature of -110°C (A:-107.56°C; B:-105.82°C; C:-109.04°C) corresponding to the tan δ loss factor maximum was considered as the mechanical relaxation temperature (fig.7). The melting temperature can be uncovered around -45°C (A: -52.91°C; B:-43.1°C) corresponding with the tan δ loss factor maximum. The tan δ values are constant above -45°C.

The mechanical relaxation temperatures, associated with glass transition T_g and melting T_m recorded by isochronal DMA at 1Hz (fig.7), have comparable values with the glass and melting temperatures T_g and T_m recorded by DSC (table 4). The molecular mobility resulted from the breaking of physical interactions at the glass transition is responsible for the corresponding mechanical relaxation.

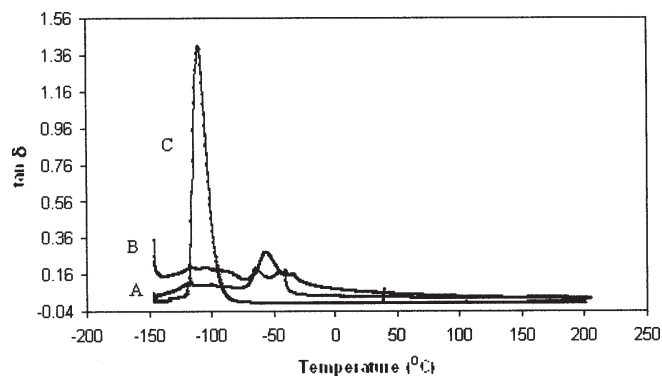


Fig. 7. Plots of tan δ as function of temperature for the samples: A, B and C

The physico-mechanical parameters and thermal stability in the positive temperature interval of both A and B networks, suggests that SiO₂ acts as a reinforcing agent.

Conclusions

Siloxane copolymers with different functional groups (Si-H and Si-CH=CH₂) were synthesized and characterized. These copolymers were cross-linked by hydrosilylation using a platinum catalyst and the obtained siloxane membranes were characterized from a physico-mechanical point of view.

The mechanical relaxation temperatures associated with glass transition and melting recorded by DMA have comparable values with the glass and melting

temperatures recorded by DSC. The direct relationship between physical structure and mechanical properties allows the deep understanding of the mechanical behaviour around the working temperature. For temperatures higher than the melting temperature, the storage modulus of polysiloxanes is constant: this is a characteristic of the elastic rubbery plateau.

The cross-linked polymers with siloxane sequences have in general good yield and physical properties in elastomers and silicon gels. The end product properties depend on the nature of polymer chain, cross-linking bridges and on cross-linking density. This cross-linked siloxane networks can be used for medical and pharmaceutical purposes like matrices for drugs inclusion with controlled release abilities and for durable covering due to high predictable stability.

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