



## Full silicone interpenetrating bi-networks with different organic groups attached to the silicon atoms



Codrin Tugui, Maria Cazacu\*, Liviu Sacarescu, Adrian Bele, George Stiubianu, Cristian Ursu, Carmen Racles

*"Petru Poni" Institute of Macromolecular Chemistry Iasi, Aleea Grigore Ghica Voda 41A, 700487, Romania*

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### ABSTRACT

Mixed silicone interpenetrating networks have been prepared using two groups of siloxane polymers and copolymers as precursors in different combinations. Each combination chosen, after a good mixing in solution with cross-linking agents was processed into film, which has been stabilized through sequential crosslinking using separate chemical pathways: condensation with tetraethyl orthosilicate at room temperature for the first network and addition (hydrosilylation) at higher temperatures in the case of the second one. The morphology of the resulted materials was studied by scanning electron microscopy (SEM). The mixing degrees of the two networks were estimated on the basis of the differential scanning calorimetry (DSC) traces as well as by small angle X-ray scattering (SAXS). The obtained films were characterized from point of view of the properties of interest for electromechanical applications by mechanical testing, dielectric spectroscopy and electrical breakdown measurements. The influence of the nature and content of the polar groups attached on the silicon on these characteristics was discussed.

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## 1. Introduction

Since they have been discovered, the dielectric elastomers (DE's), show a continuous interest due to the wide field of applications including their use as actuators in biomedical engineering, artificial muscles, haptic screens or for energy harvesting [1,2]. Besides acrylic elastomers, silicones occupy a top position in this research area due to their special properties derived from unique characteristics of the siloxane bond: shortness and large angle, accounted either to  $(p \rightarrow d)\pi$  back-bonding or to ionic character [3]. These lead to high intramolecular bond energy and flexible polymer chain. The presence of the organic nonpolar groups attached to the silicon atoms, as in PDMS for example, is the reason for weak intermolecular forces [4]. Silicones show a unique flexibility, with shear modulus  $G$  values between 100 kPa and 3 MPa and loss tangent values,  $\tan \sigma \ll 0.001$  [5–6]. On the other hand, the tensile strength is higher than for most organic elastomers at elevated temperatures. In addition, silicone elastomers can operate in a wide range of temperature, without being affected by the moisture, are resistant to oxygen, ozone and sunlight irradiation,

have a good dielectric strength and no toxicity, which make them suitable for a large number of applications [6–10]. However, as concerning the electromechanical applications, silicones have the disadvantage of a low dielectric permittivity. Therefore, a significant research effort was focused to improve the dielectric permittivity by incorporating various fillers in the polymer matrix or by attaching polar groups to the polymer network [11–25]. However, by these approaches, the mechanical properties of these materials could be damaged [26]. As for most electroelastomers, mechanical prestrain is generally required to obtain high electromechanical strain and high elastic energy density although the prestrain causes a reduction in certain parameters of the actuators. An interesting approach is to create and maintain prestrain by interpenetrating polymer networks (IPNs) [27]. In the literature there are a number of polysiloxane-organic polymers interpenetrated networks, those reported before 2000 being excellently reviewed in Ref. [28] It is highlighted the difficulty of obtaining homogeneous networks due to well-known incompatibility of the silicones with almost any organic component. These silicone-containing networks generally have been found useful as pervaporation membrane in gears, for medical aims (silicone rubber–nylon or PU with trade name Rimplast), in drug release (poly(vinyl alcohol) – polydimethylsiloxane hydrogels), for high temperature damping (polydimethylsiloxane – polyacrylates – polymethacrylates), or sound and vibration

\* Corresponding author.

E-mail address: [mcazacu@icmpp.ro](mailto:mcazacu@icmpp.ro) (M. Cazacu).

damping (polysiloxanes - poly(methyl methacrylate)) [29–33]. The use of interpenetrating polymer networks (IPN) as dielectric elastomers is a less addressed attempt to improve both dielectric and mechanical properties [34,35]. Only recently the electroactive interpenetrating networks that to deform easily under the influence of an electric field became of interest. In general, these are constructed by generating a network in the presence of a basic, already formed one [34]. To increase the actuation strain, the primary network is usually prestrained [32]. As electroactive elastomers, IPNs based on VHB and poly(1,6-hexanediol diacrylate) or trimethylolpropane trimethacrylate (TMPTMA) as well as IPNs of silicone and 3M VHB 4910 have been prepared [34–36]. The interpenetrating polymer networks are formed in the highly prestrained VHB acrylic elastomer network [35].

Brochu et al. used a commercial kit consisting in soft room temperature vulcanizing (RTV) silicone as the host elastomer and a more rigid high temperature vulcanizing (HTV) silicone as a guest to prepare IPN. Prestrain was applied to the crosslinked RTV silicone host material, after that the HTV silicone was cured locking the host network in this state [37–39].

Prompted by the Brochu works, our approach consists in the preparation of siloxane–siloxane networks on the basis of several available, in house prepared polymers as network precursors [37]. The two networks differ by the nature of the substituents at the silicon atom, by the molecular masses of the precursors and also by the crosslinking path. Polar groups (phenyl, trifluoropropyl, 3-cyanopropyl) were attached to the silicon belonging to one of the networks in order to increase the dielectric permittivity. In this case, a big challenge is to find a good compatibility between networks, mainly when one network is more polar than the other, because a phase separation may occur. Further, the interpenetration of two networks with high value of dipole moment can lead to a significant decrease of the breakdown strength. The samples were processed as thin films, which have been stabilized through sequential cross-linking using two separate chemical pathways, without prestrain: one is condensation of OH-terminated siloxane copolymers containing various percents of polar groups (phenyl or trifluoropropyl) along the chain and cured by condensation (used as main network), and the second one is addition of  $\alpha,\omega$ -bis(vinyl)polydimethylsiloxane to  $\alpha,\omega$ -bis(trimethylsiloxy)poly(dimethylsiloxane-co-methylhydrosiloxane) or  $\alpha,\omega$ -bis(trimethylsiloxy)poly(methylcyanopropylsiloxane-co-methylhexylsiloxane-co-methylhydrosiloxane)s. The mechanical and dielectric properties, morphology and thermal behaviour of the resulting IPNs were studied.

## 2. Experimental

### 2.1. Materials

$\alpha,\omega$ -Bis(trimethylsiloxy)poly(methylhydrosiloxane),  $M_w = 2200$  g mol<sup>-1</sup>, octaphenylcyclotetrasiloxane ( $D_4^{Ph}$ ),  $\geq 98\%$ , n-hexene, octamethylcyclotetrasiloxane ( $D_4$ ), dibutyltin dilaurate (DBTDL), 95%, and hexachloroplatinic(IV) acid hydrate,  $\geq 99.9\%$  trace metals basis, Sigma–Aldrich, Germany, were used as received. 1,3,5-Trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)cyclotrisiloxane, 97%, tetraethylorthosilicate (TEOS), 99.9%, supplied by Alfa Aesar, Germany were used as such.

Polydimethylsiloxane- $\alpha,\omega$ -diol (PDMS) with  $M_n = 377,300$  g mol<sup>-1</sup>, as determined by gel permeation chromatography (GPC), was prepared by cationic ring-opening polymerization of octamethylcyclotetrasiloxane ( $D_4$ ) catalysed by sulphuric acid, according to an already reported procedure [40]. Poly(dimethylsiloxane-co-diphenylsiloxane)- $\alpha,\omega$ -diol, PDMDPhS, with  $M_n = 104,500$  g mol<sup>-1</sup> was prepared by bulk anionic ring opening copolymerization of the

octamethylcyclotetrasiloxane ( $D_4$ ) and octaphenylcyclotetrasiloxane ( $D_4^{Ph}$ ), using tetramethylammonium hydroxide as catalyst and a Lewis base (DMF) as promoter, according to procedure described in Ref. [41]. The content in phenyl groups estimated on the basis of <sup>1</sup>H NMR was 18.4 mol% (Fig. 1).

Poly[dimethylsiloxane-co-methyl(3,3,3-trifluoropropyl)siloxane]- $\alpha,\omega$ -diol, PDMTFS,  $M_n = 64,800$  g mol<sup>-1</sup>, was prepared by ring-opening copolymerization of  $D_4$  with 1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)cyclotrisiloxane in the presence of cation-exchanger, Purolite CT-175. The content of trifluoropropyl groups estimated from <sup>1</sup>H NMR spectrum was 15.4 mol% (Fig. 1). The  $\alpha,\omega$ -bis(trimethylsiloxy)poly(dimethylsiloxane-co-methylhydrosiloxane), PDMMHS, was synthesized by equilibrium copolymerization of  $D_4$  with  $\alpha,\omega$ -bis(trimethylsiloxy)poly(methylhydrosiloxane) homopolymer in the presence of Purolite CT-175 [40]. The molecular mass of the resulted copolymer determined by GPC was  $M_n = 17,800$  g mol<sup>-1</sup>. Based on <sup>1</sup>H NMR spectrum it has been estimated a content of 19.2 mol% Si–H groups (Fig. 1). This copolymer was used as a precursor to generate Net B, or in general the second networks, by hydrosilylation with another one containing vinyl group (see below  $V_{12}$ PDMS). The  $\alpha,\omega$ -bis(trimethylsiloxy)poly(methylcyanopropylsiloxane-co-methylhexylsiloxane-co-methylhydrosiloxane)s, PMCyMHS<sub>1</sub> and PMCyMHS<sub>2</sub>, with 3-cyanopropyl/hexyl/hydro contents 9.2/82.9/8.9 and 62.1/26.9/11 and  $M_n = 4600$  and 4200, respectively were prepared by co-hydrosilylation reactions of the commercial  $\alpha,\omega$ -bis(trimethylsiloxy)poly(methylhydrosiloxane) with found molecular weight  $M_n$  of 2200 g mol<sup>-1</sup>, with allylcyanoide and n-hexene [23].  $\alpha,\omega$ -Bis(vinyl)polydimethylsiloxane,  $V_{12}$ PDMS, was synthesized by an equilibrium cationic ring-opening polymerisation of  $D_4$  in presence of 1,3-bis(vinyl)tetramethyldisiloxane used to block the chains ends [42]. The resulted polymer had  $M_n = 40,200$  g mol<sup>-1</sup> as determined by GPC and was used in the addition reaction to achieving the second network of IPN. The percentages of the polar units contained in copolymers were calculated from <sup>1</sup>H NMR spectra (Fig. 1).

### 2.2. Equipments

The Fourier transform infrared (FTIR) spectra were recorded in KBr pellets and ATR mode with Bruker Vertex 70 FTIR instrument, at room temperature. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer, using CDCl<sub>3</sub> as solvent. The molecular mass of the polymers was determined by gel permeation chromatography (GPC) in CHCl<sub>3</sub> on a PL-EMD 950 chromatograph/evaporative mass detector instrument. The morphology of the films was studied by scanning electron microscope (ESEM) type Quanta 200 operating at 20 kV with secondary and backscattering electrons in low vacuum mode. DSC measurements were performed with a DSC 200 F3 Maia (Netzsch, Germany). About 10 mg of sample was heated in pressed and punched aluminium crucibles at a heating rate of 10 °C min<sup>-1</sup>. Nitrogen was used as inert atmosphere at a flow rate of 100 ml min<sup>-1</sup>. Small angle X-ray scattering (SAXS) measurements were carried out using a Bruker NanostarU instrument equipped with a X-ray I $\mu$ S microsource with copper anode and a three-pinhole collimation system. A high sensitive 2D detector, Vantec-2000, having 68  $\mu$ m resolution was used to record the scattered intensity. The scattered intensity  $I(q)$  is measured as a function of the momentum transfer vector  $q = 4\pi\sin\theta/\lambda$ , where  $\lambda$  is the wavelength of the X-rays (Cu K $\alpha$  radiation, 1.54 Å), and  $\theta$  is half the scattering angle. The sample-to-detector distance was 107 cm allowing measurements with  $q$  values between 0.008 Å<sup>-1</sup> and 0.3 Å<sup>-1</sup>. The angular scale was calibrated by the scattering peaks of a silver behenate standard. The samples to be analysed have been prepared by cutting small square pieces of about 5 × 5 mm of thin

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