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**Elastomers obtained by crosslinking of α,ω -bis(glycidylether)
poly(dimethylsiloxane) as versatile platforms for functional materials**

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ABSTRACT

Elastomers with an interesting set of properties were synthesized by crosslinking α,ω -bis(glycidylether)poly(dimethylsiloxane,PDMS), using two different strategies. The first one was the anionic homopolymerization of terminal epoxy groups initiated by 4-dimethylaminopyridine (DMAP); the second strategy was the crosslinking with a polyoxypropylenediamine (Jeffamine D2000). Reaction conditions were selected to achieve complete conversion of epoxy groups. Resulting soft elastomers (*PDMS-Homop* and *PDMS-D2000*) were transparent materials with gel fractions higher 95 %. *PDMS-D2000* exhibited an outstanding damping capacity (maximum $\tan \delta > 2$) in a temperature range located between -50 °C and -75 °C, assigned to a high viscous dissipation during the relaxation of polyoxypropylene blocks. *PDMS-Homop* showed also good damping properties in a broader low-temperature range. A significant property of both elastomers was the capacity to re-organize their nanostructures, as shown by SAXS spectra and contact angle measurements, in response to the hydrophilic or hydrophobic nature of the liquid in contact. Hydroxyl groups present in the chemical structure of *PDMS-D2000* could be used as reducing agents for the in situ generation of gold nanoparticles from an infused Au(III) compound. The synthesis was also performed using a sacrificial template to provide macroporosity to the resulting materials. These macroporous elastomers were used to remove organic components from water. Magnetic nanoparticles were infused and stabilized inside the macroporous structure to allow magnetic separation of the materials after use.

Keywords: elastomer, α,ω -bis(glycidylether) poly(dimethylsiloxane), nanostructured network, damping, amphiphilicity.

Introduction

Due to its chemical inertness and outstanding elastic, gas permeation and dielectric properties, poly(dimethylsiloxane) (PDMS) has been the choice of many strategies leading to the synthesis of polymer networks with special properties. Most of these approaches have been focused in the decrease of the extreme hydrophobicity of PDMS with the aim of avoiding protein adsorption and biofouling. These are main drawbacks of this material for biomedical applications [1-2]. In most of proposed strategies to confer amphiphilicity to PDMS, poly(ethylene oxide) (PEO) has been used as the hydrophilic segment due to its excellent biocompatibility, high hydrophilicity and exceptional resistance to protein adhesion [2]. PEO can be attached to PDMS by physical/chemical adsorption methods, direct covalent attachment, and graft copolymerization. As an example, branched PEO-silanes, with varying siloxane tether lengths, were synthesized and used in a crosslinking reaction with α -bis(Si-OH)PDMS for the synthesis of amphiphilic silicones with increased protein resistance and water-induced increase of surface hydrophilicity [3]. UV photo-crosslinking copolymerization of poly(dimethylsiloxane), polyoxyethylene and perfluoroalkyl (meth)acrylate (macro)-monomers was also used to obtain networks with interesting properties for marine anti-biofouling [4]. Highly resilient hydrogels were synthesized by using the thiol-norbornene chemistry to cross-link PEO and PDMS. These materials showed excellent mechanical energy storage efficiency (resilience) at high strains, comparable with one of the most resilient materials known, natural resilin[5].

Here, we propose the use of a simple, solvent-free approach for the synthesis of PDMS crosslinked networks based on the use of a commercial PDMS oligomer terminated in epoxy groups, α -bis(glycidylether)PDMS (Fig. 1a). Taking advantage of the versatility of epoxy chemistry we used two different crosslinking schemes. The first

one was an anionic homopolymerization of the epoxy groups initiated by 4-dimethylaminopyridine (DMAP), Fig. 1b [6]. The second one was a typical stepwise polymerization involving epoxy-amine reactions, employing a polyoxypropylenediamine (Jeffamine D2000, Fig. 1c).

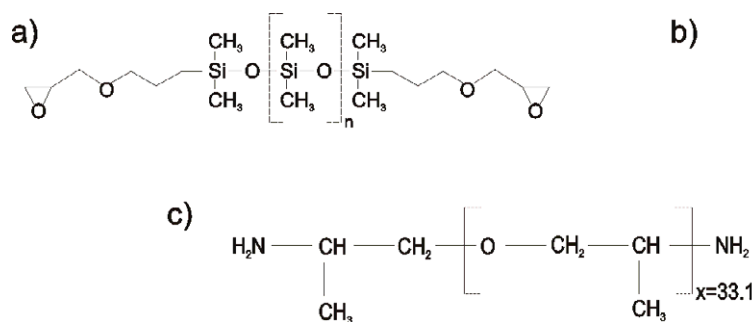


Figure 1: Chemical structures of: (a) α -bis(glycidylether)PDMS; (b) 4-dimethylaminopyridine (DMAP); (c) polyoxypropylenediamine (Jeffamine D-2000).

Both selected strategies lead to the generation of elastomers with different nanostructures and properties. The homopolymerization of terminal epoxy groups generates short polyether chains [6] covalently bonded to PDMS chains (Fig. 2a and 2b). This reaction can be regarded as a threading of a few PDMS chain ends generating a cluster. The reaction occurs also at the other end of the chains. However, the threading can involve the formation of new clusters as shown in Fig. 2a. The nanostructure percolates throughout the material generating the cross-linked amphiphilic elastomer (hydrophilic polyether chains and hydrophobic PDMS clusters). The large fraction of intramolecular cycles present in this structure leads to a low fraction of effective crosslinks related to a low elastic modulus of the material.

The second strategy gives a completely different nanostructure as shown in Fig. 2c and 2d. Large hydrophobic polyoxypropylene (PPO) blocks alternate with hydrophobic

PDMS blocks. However, the crosslinks composed of a tertiary amine with neighboring hydroxyl groups are highly hydrophilic.

The particular nanostructure of both elastomeric networks produces a set of interesting properties that might be useful for practical applications. Our aim is to discuss the synthesis, characterization and significant properties of both materials.

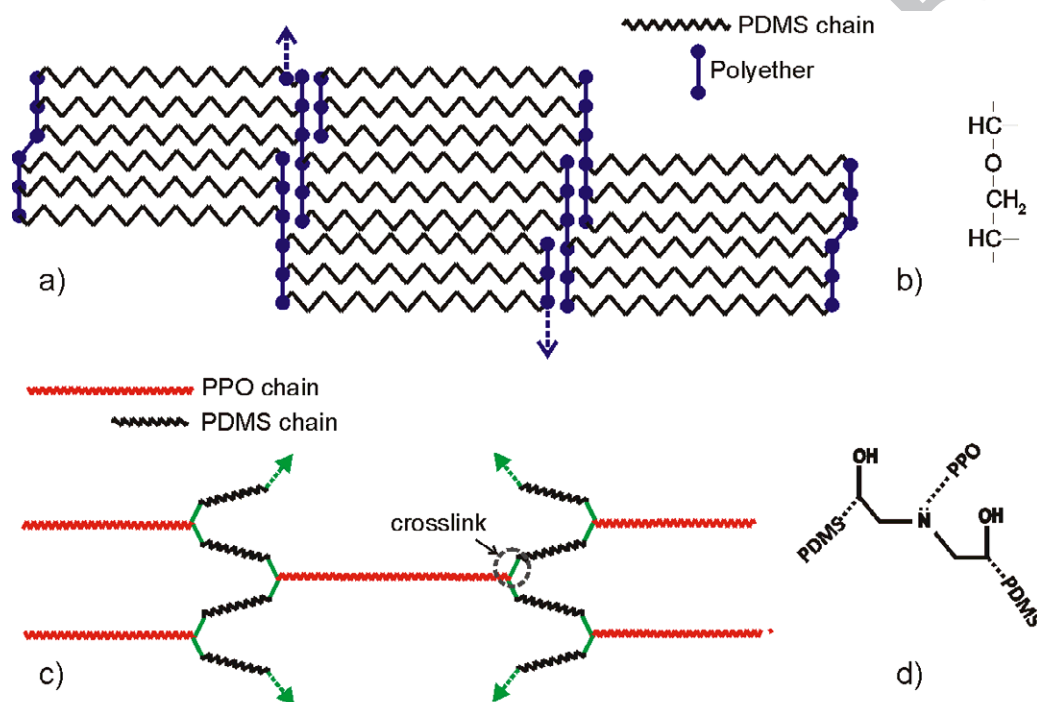


Figure 2: (a) Scheme of the nanostructure produced by the homopolymerization of α,β bis(glycidylether)PDMS; (b) Chemical structure of a polyether chain; (c) Scheme of the nanostructure produced by reaction with polyoxypropylenediamine; (d) Chemical structure of a crosslink.

Experimental Section

Materials

The α -bis(glycidylether)PDMS had a weight per epoxy group equal to 490 g/mol ($n \sim 8$ in the chemical structure shown in Fig. 1a), and was provided by Aldrich; 4-dimethylaminopyridine (DMAP) was also provided by Aldrich. Jeffamine D2000 was provided by Huntsman. Its molar mass was 2470 g/mol, as determined by titration of terminal amine groups. Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 49 wt% as Au), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and ammonium hydroxide were provided by Aldrich. All organic solvents were P.A. grade.

Synthesis of the elastomers

The homopolymerization of α -bis(glycidylether)PDMS was performed at 85 °C for 96 h, employing a molar ratio DMAP/epoxy groups equal to 0.08 (equal to the one found optimum in another system [6]). The reaction with a stoichiometric amount of Jeffamine was performed at 120 °C for 48 h. Under these conditions both systems attained complete conversion as will be discussed in next section. The generation of porous elastomers and the modification with gold or magnetite nanoparticles will be described in the Results and Discussion section.

Methods

Middle-infrared spectra of samples were obtained with a Thermo Scientific Nicolet 6700 spectrometer, employing a resolution of 4 cm^{-1} . Measurements were carried out both in transmission and attenuated total reflectance modes (smartOrbit ATR accessory).

Gel fractions were determined gravimetrically from samples cut in squared pieces (weight close to 100 mg) and dried in an oven at 50 °C for 24 h (initial weight = W_0).

After 96 h immersion in tetrahydrofuran (THF) at room temperature, the supernatant was removed and slices blotted with filter paper and weighed in a stoppered vial (weight = W_s). Samples were then dried at 50 °C to constant weight (weight = W_d). The gel fraction was defined by the ratio $(W_d/W_0) \times 100$. To determine the swelling degree of gels in different solvents, a similar procedure was carried out by immersion of the samples at room temperature by 48 h. The swelling degree was calculated as: $[(W_s - W_d)/W_d] \times 100$.

The contact angle (CA) was measured at room temperature using 5 μ L droplets of liquid (motor oil SAE20 or MiliQ water) by gently depositing it on the substrate using a micropipette. A goniometer Ramé Hart 500, provided with DROP Image Advanced Software was used for the measurements. Tests were repeated at least three times with a final precision within 1.5°.

Rheological measurements were carried out using an Anton Paar Physica MCR 301 rheometer. Specimens of rectangular cross-section (15 mm height x 6 mm width x 2mm thickness), were tested under torsion mode with a distance between clamps equal to 12 mm. Dynamic mechanical analysis (DMA) tests were performed at a heating rate of 5°C/min from -80 to 100°C with a fixed frequency of 1 Hz.

Both scanning (SEM) and transmission (TEM) electron microscopy were employed to characterize morphologies. SEM images were obtained using a JEOL JSM-6460 LV instrument. Samples were cryo-fractured by a previous immersion in liquid N₂ and coated with gold before testing. TEM images of samples cut with a cryo-ultramicrotome, were obtained with a JEOL JEM-1011 microscope operated at 100 kV.

Small-angle X-ray scattering (SAXS) measurements were taken at room temperature at the beam line SAXS 1 of the National Laboratory of Synchrotron Light (LNLS, Campinas, Brazil). The scattering intensity (in arbitrary units) was recorded as a

function of the scattering vector $q = (4\pi/\lambda) \sin\theta$ where λ is the light wavelength (1.55 Å) and 2θ the scattering angle.

Results and Discussion

Synthesis of the elastomers

The conversion of epoxy groups was monitored by FT-NIR spectroscopy, following the characteristic absorption band at 4530 cm^{-1} (conjugated epoxy CH_2 deformation band with the aromatic CH fundamental stretch) [7]. The complete disappearance of this band was observed after 96 h in the homopolymerization reaction (Fig. 3) and after 48 h in the epoxy-amine reaction (Fig. 4).

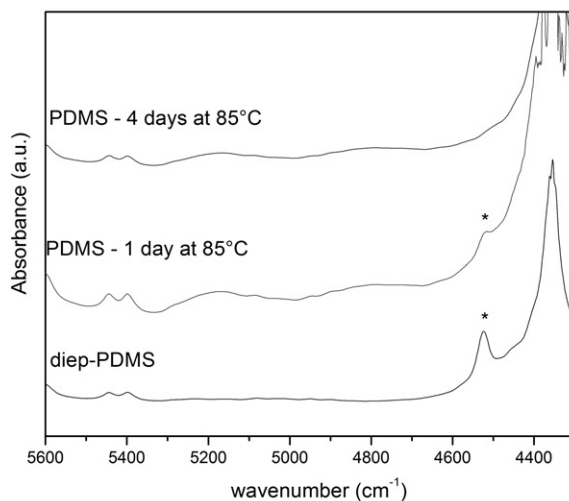


Figure 3: FT-NIR spectra during the homopolymerization of α,ω -bis(glycidylether)PDMS.

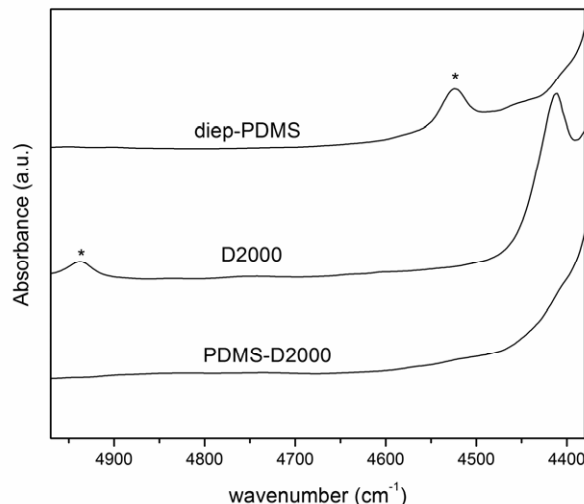


Figure 4: FT-NIR spectra of α -bis(glycidylether)PDMS, Jeffamine and the reaction product, after 48 h at 120 °C.

Characterization of the elastomers

In what follows, the synthesized elastomers will be denoted as *PDMS-Homop* and *PDMS-D2000*. Both were soft, highly elastic and transparent materials. Gel fractions were 96.6 % for *PDMS-Homop* and 95.2 % for *PDMS-D2000*.

The presence of a nanostructure was searched by SAXS. Fig. 5 shows SAXS spectra of both elastomers. While no peaks were present in the spectrum of *PDMS-D2000*, a broad band appeared in the spectrum of *PDMS-Homop*, at q close to 2 nm^{-1} . This corresponds to a characteristic distance of 3.1 nm that might be assigned to an average separation among PDMS clusters (Fig. 2a).

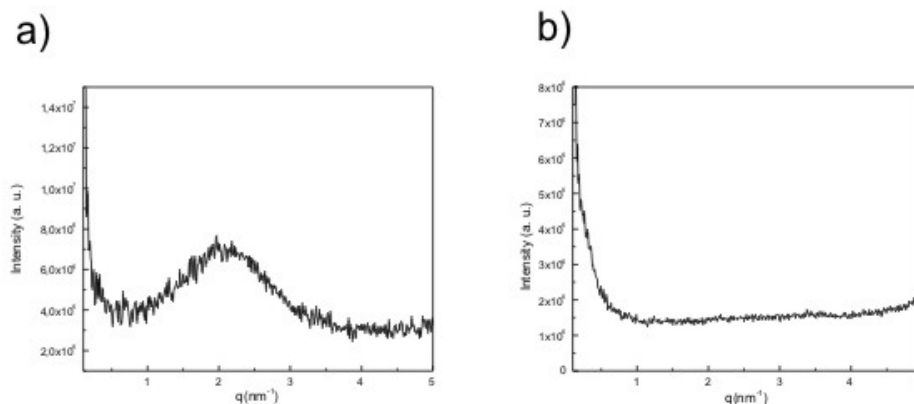


Figure 5: SAXS spectra of (a) *PDMS-Homop* and (b) *PDMS-D2000*.

The rheological behavior was monitored in the -80 °C to 100 °C range. This temperature range was much higher than the one needed to observe the relaxation of PDMS chains but was adequate to characterize the relaxation of polyether chains. Figure 6 shows this relaxation for both elastomers.

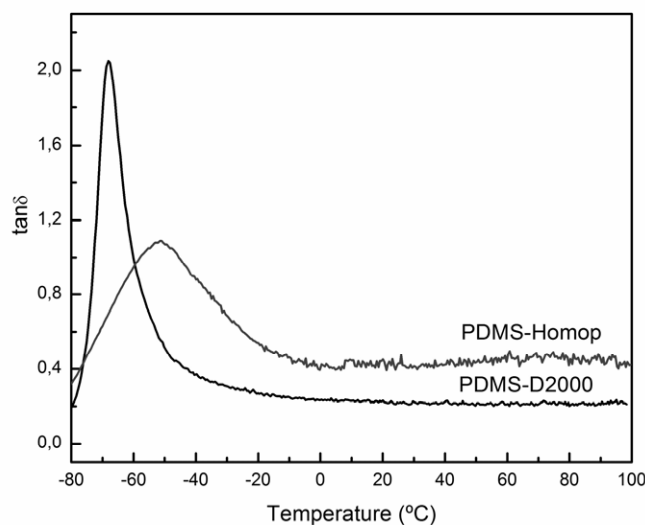


Figure 6: $\tan \delta$ vs. temperature for *PDMS-Homop* and *PDMS-D2000*.

For the case of *PDMS-D2000*, this relaxation is sharp with a maximum at -68.1 °C. For *PDMS-Homop*, the relaxation is broad with a maximum at -51.3 °C. The maximum

value of $\tan \delta (> 2)$ for *PDMS-D2000* is surprising for a cross-linked elastomer. This corresponds to a loss modulus (G'') higher than the storage modulus (G'), which is characteristic of a liquid state present in a cross-linked solid! This behavior was reproducible and characteristic of this material. The explanation is that the relaxation of polyoxypropylene blocks occurs with a large viscous dissipation, giving the elastomer excellent damping properties in the $-50\text{ }^{\circ}\text{C}$ to $-75\text{ }^{\circ}\text{C}$ temperature range. The relaxation peak of the other elastomer, *PDMS-Homop*, indicates good damping characteristics in a broader temperature range. A value of $\tan \delta$ in the order of 0.4 is still adequate to provide good damping properties at room temperature, with technological relevance in applications like noise reduction and attenuation of vibration.

The values of the storage moduli at $25\text{ }^{\circ}\text{C}$ were 48 kPa for *PDMS-Homop* and 282 kPa for *PDMS-D2000*. The very low elastic modulus of *PDMS-Homop* is directly related to the low concentration of effective crosslinks, as previously discussed (Fig. 2a).

Figure 7 shows the swelling of both elastomers in solvents with different values of the solubility parameter.

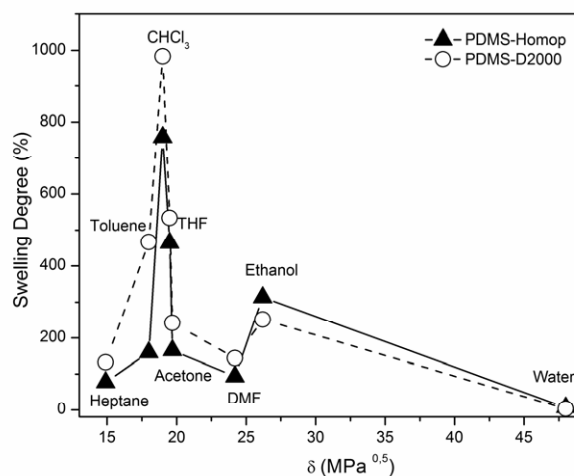


Figure 7: Swelling degrees of *PDMS-Homop* and *PDMS-D2000* in different solvents.

For both elastomers, a maximum swelling was observed for CHCl_3 . THF was also an excellent solvent while water did not produced any significant swelling, as expected

(6.7 % for *PDMS-Homop* and 2.9 % for *PDMS-D2000*). The moderate swelling in ethanol could be related with the existence of strong hydrogen bonds between ethanol and ether groups present in the networks.

Response to water

In spite of the main hydrophobic character of both elastomers, the presence of water produced significant re-arrangements of their nanostructures. Figs. 8 and 9 show a comparison of SAXS spectra for the dry elastomers and those swollen with the equilibrium amount of water.

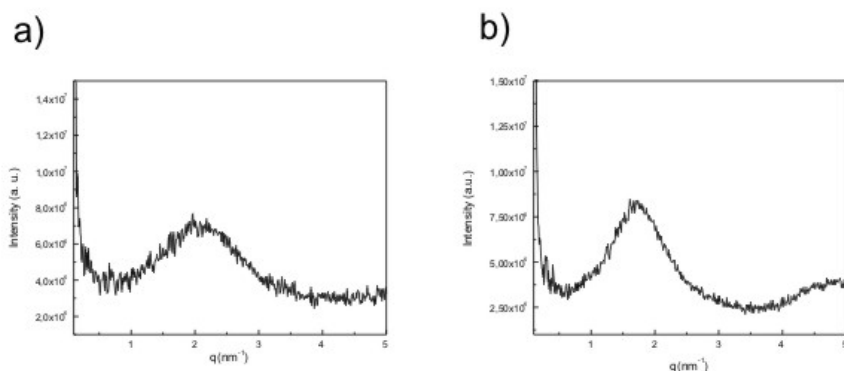


Figure 8: SAXS spectra of dry (a) and water-swollen (b) *PDMS-Homop* elastomer.

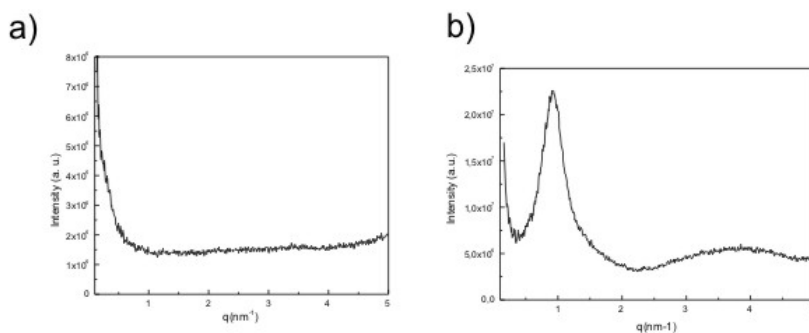


Figure 9: SAXS spectra of dry (a) and water-swollen (b) *PDMS-D2000* elastomer.

For *PDMS-Homop* the broad scattering peak shifts from about 2 nm^{-1} to 1.7 nm^{-1} , indicating a small increase in the average distance among PDMS clusters from 3.1 nm

to 3.7 nm. This might be assigned to the swelling of the hydrophilic polyether chains present at the boundaries of the *PDMS* clusters. For *PDMS-D2000*, the small amount of absorbed water produced a re-arrangement of the network that generated a sharp scattering peak at $q \approx 0.9 \text{ nm}^{-1}$ ($d = 7 \text{ nm}$), followed by a smaller and broad peak centred at $q \approx 3.8 \text{ nm}^{-1}$ ($d = 1.65 \text{ nm}$). The high mobility of both hydrophobic blocks produced a clustering that generated the scattering peak as a response to the presence of water. However, the nature of the objects (clusters) scattering SAXS radiation could not be determined.

Static water contact angles were measured on the free surface of both elastomers. For *PDMS-Homop*, the initial contact angle was 98° , indicating the material surface was hydrophobic. However, after two minutes of contact between the water droplet and the surface, this angle changed to 60° and kept this value. This proves that the surface has the ability to restructure in response to environmental changes. In order to minimize surface energy, hydrophobic *PDMS* clusters are expected to concentrate at the air-sample interface, providing hydrophobicity to the exposed surface. In the presence of water, a fast re-arrangement of the superficial nanostructure takes place, partially replacing hydrophobic clusters by hydrophilic polyether chains. This produced a significant decrease of the water contact angle. Samples previously immersed in water showed an initial contact angle of 60° . When they were dried at 50°C for 3 h, the initial contact angle changed to 95° . In this case, the re-arrangement of the superficial nanostructure proceeded in the opposite direction, proving the reversibility of this transformation.

For *PDMS-D2000*, the transformation of the nanostructure at the surface took place at a fast rate. The high contact angle expected for this hydrophobic elastomer could not be

detected. Instead, the initial measured value was 70° that decreased rapidly and stabilized at 65° .

Hydrophobic surfaces that become hydrophilic in contact with water might have applications as antifogging materials [8].

Response to oil

In order to evaluate the oleophilic behavior of the elastomers, contact angles were also measured using commercial motor oil SAE20 as probe liquid. Initial contact angles were 60° for *PDMS-Homop* and 62° for *PDMS-D2000*. In about 2 minutes, these values were reduced to 38° and 49° , respectively. In both cases, the surface was enriched with hydrophobic segments / clusters in response to the hydrophobic environment. Therefore, these materials adapt their contact surface to either hydrophilic or hydrophobic environments through re-arrangements of their nanostructures.

Dispersion of gold nanoparticles

A transparent coating containing a dispersion of gold nanoparticles can be heated by irradiation with light with a wavelength close to the maximum of the plasmon band of the nanoparticles [9-12]. The location of the maximum depends on the size and shape of nanoparticles. For application of these elastomers as antifogging materials, the possibility of drying by light irradiation might be of interest. Conferring this property needs to produce a dispersion of gold nanoparticles inside the material. Here, we show how to generate such dispersion in *PDMS-D2000*.

In a first step, a sample of *PDMS-D2000* was put in contact with a 1:6 water/THF solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (6mM). Due to the high swelling in THF, the gold compound was rapidly infused as confirmed by the yellow color acquired by the elastomer. Presumably, Au(III) was complexed / stabilized by tertiary amines and hydroxyl groups

present in the structure of the elastomer. After 24h of immersion, the elastomers became colorless, a fact explained by the room-temperature reduction of Au(III) to Au(I) produced OH groups[13]. The sample was then removed from the solution and heated at 100 °C for 1 h. The color turned to a dark red, evidencing the reduction of Au(I) to Au(0). TEM images (Fig. 10) show the presence of a distribution of gold nanoparticles with an average diameter of 17 nm.

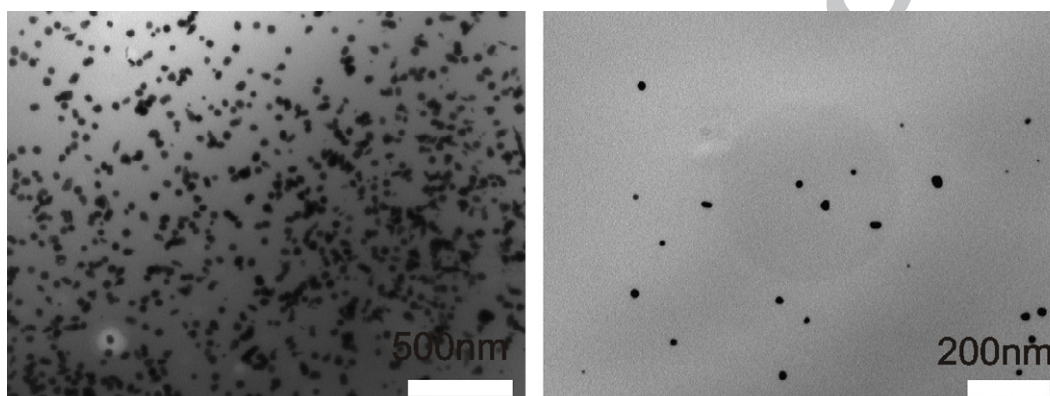


Figure 10: TEM images showing the dispersion of Au nanoparticles in *PDMS-D2000*.

Macroporous Elastomers

In order to use *PDMS-Homop* or *PDMS-D2000* to absorb oils dispersed in water, it is convenient to generate macroporosity to increase the exposed surface per unit volume. Elastomeric sponges were obtained by applying a sugar-template with an approach similar to that used by Choi et al [14]. Sponges were replicated from commercially available cube sugars by infiltration of the monomers followed by polymerization using the curing schedules previously described. After reaction, sugar was eliminated by immersion in water and sonication for several hours. SEM images (Fig. 11) of cryogenically fractured samples showed the presence of macroporous structures with a broad pore size distribution (ranging between 200-400 μm).

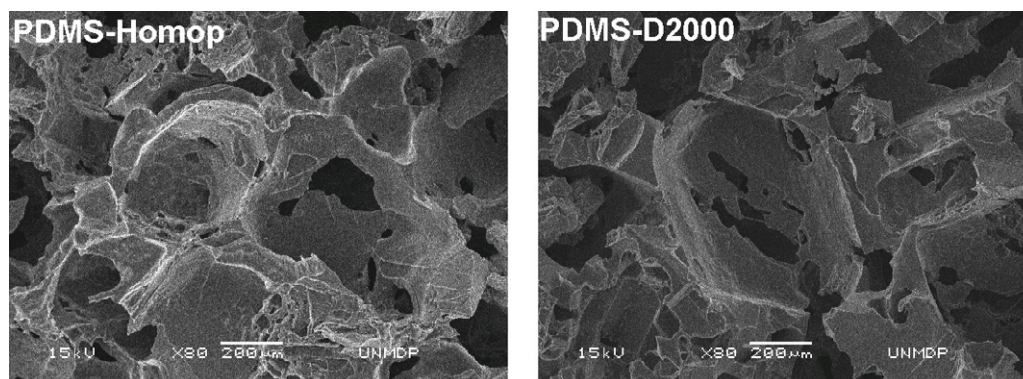


Figure 11: SEM images of macroporous *PDMS-Homop* and *PDMS-D2000*.

Bulk densities of porous samples were 0.26 g/cm^3 for *PDMS-Homop*, and 0.38 g/cm^3 for *PDMS-D2000*. The feasibility to use these sponges to separate heptane or chloroform from water is shown in Fig. 12. As the solvents are retained both in the bulk of the materials (producing swelling) and inside the macropores, the efficiency of solvent removal is very high. For macroporous *PDMS-Homop* the weight % of absorbed heptane was 233 % while for chloroform, it was 589 %. For *PDMS-D2000*, corresponding values were 296 % and 2251 %, respectively.

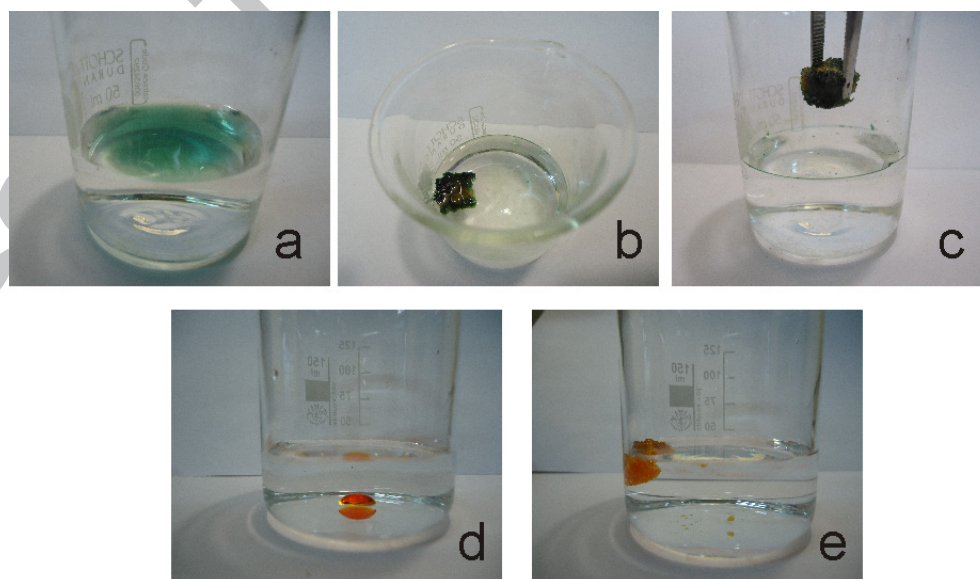


Figure 12: Photographs of samples immersed in water/organic solvents mixtures. The organic solvent was colored using organic dyes for better visualization. a) Heptane (green) in water; b) absorption of heptane by the *PDMS-Homop* sponge; c) *PDMS-Homop* sponge containing the solvent. d) Chloroform (orange) in water and e) *PDMS-D2000* sponge containing the solvent.

The dispersion of magnetic nanoparticles inside the sponges can help to recuperate the materials by magnetic separation. Magnetite nanoparticles stabilized by oleic acid were synthesized using a procedure described in the literature [15]. They were dispersed in chloroform and the sponges were immersed into this dispersion for 24 h. When removed, sponges had a dark-brown color, conferred by the infused nanoparticles. The color was not lost after a new immersion in pure chloroform for 24 h, evidencing that the interaction of oleic acid with hydrophobic domains was strong enough to avoid the re-dispersion of nanoparticles in the solvent. Sponges containing the magnetic nanoparticles adhered to a permanent magnet, as shown in Fig. 13.

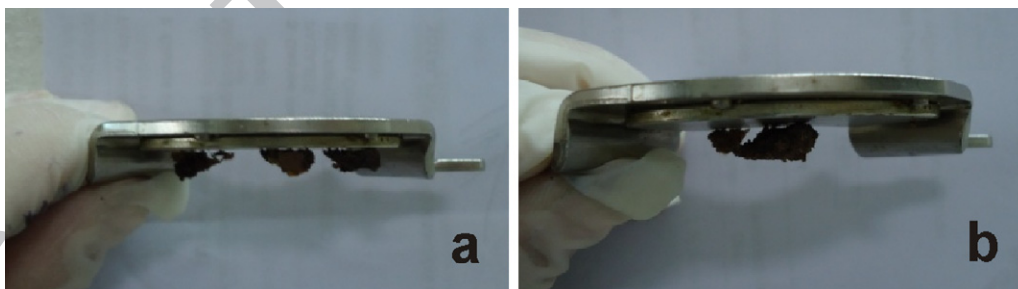


Figure 13: Magnetic sponges attracted by a permanent magnet a) *PDMS-D2000* Sponge; b) *PDMS-Homop* Sponge.

CONCLUSIONS

Elastomers with interesting properties were synthesized by crosslinking α,ω -bis(glycidylether)PDMS using two different strategies. The first one was the anionic homopolymerization of terminal epoxy groups and the second one was the crosslinking with a polyoxypropylene diamine. Resulting soft elastomers (*PDMS-Homop* and *PDMS-D2000*) were transparent materials with gel fractions higher than 95 %. *PDMS-D2000* exhibited an outstanding damping capacity (maximum $\tan \delta > 2$) in a temperature range located between -50 °C and -75 °C, assigned to a high viscous dissipation during the relaxation of polyoxypropylene blocks (a liquid-like behavior of segments in a cross-linked material). *PDMS-Homop* showed also good damping properties in a broader low-temperature range. At room temperature, the value of $\tan \delta$ was still adequate (about 0.4), for applications requiring damping capacity.

A significant property of both elastomers was the capacity to re-organize their nanostructures, as shown by SAX spectra and contact angle measurements, in response to the hydrophilic or hydrophobic nature of the liquid in contact. Hydroxyl groups present in the chemical structure of *PDMS-D2000* could be used as reducing agents for the in situ generation of gold nanoparticles from an infused Au(III) compound. This can allow remote heating of the elastomer by exciting the plasmon band of the nanoparticles with visible light of an adequate wavelength. The ability to turn the surface from hydrophobic to hydrophilic in contact with water, combined with the possibility of drying by light irradiation, opens applications in the area of antifogging materials.

The synthesis was also performed using a sacrificial template to provide macroporosity to the resulting materials. These macroporous elastomers were used to remove organic components from water making use of their high absorption capacity. Magnetic nanoparticles were infused and stabilized inside the macroporous structure. This would allow magnetic separation of the materials after use.

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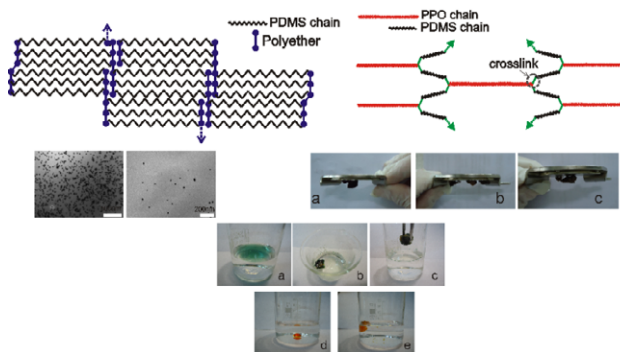
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Graphical abstract

Elastomers obtained by crosslinking of α,ω -bis(glycidylether) poly(dimethylsiloxane) as versatile platforms for functional materials

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Highlights

PDMS elastomers obtained by different strategies / Elastomer with outstanding damping capacity / Capacity to re-organize their nanostructures depend on the medium hydrophilicity /Elastomers as reducing agents for the in situ generation of gold nanoparticles / Macroporous elastomers were used to remove organic components from water.