Silicone rubber membranes: Influence of the electric field of medium frequency on the dielectric properties

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In this paper, we prepare porous membranes based on a solution consisting of silicone rubber, stearic acid and silicone oil. For volume fractions of 5%, 10% and 20% of catalyst, after polymerization (~24 h) we obtain membranes with dimensions 110x100x0.42 mm^3. The average pore diameters range from 4.43 μm to 4.99 μm. We fabricate plane capacitors based on the obtained membranes. Using electric capacitance and dissipation factor measurements of the plane capacitors in a medium electric field of frequencies between 10 kHz and 200 kHz, we obtain the dispersion and absorption characteristics. We present and discuss the obtained results.

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1. Introduction

Membranes are media through which is established the contact between two liquid phases, with a minimum amount of energy. Inspired from biological membranes, a new type of artificial membranes („membrane materialis“) have been produced in Ref. [1]. They are fabricated using a large variety of materials [2], such as metals or ceramics [3-5], homogeneous films (polymers), heterogeneous solids (polymeric mixes, mixed glasses) [6, 7] and liquids [8].

The selective transport from one phase into another can be realized due to the concentration gradient, pressure difference or due to an electric field [9]. The transport of substance through membranes takes place by diffusion, as described in Ref. [11]. In porous membranes, the pore diameters and the liquid viscosity [12] determine the selective transport process. For nanoporous membranes (with diameters smaller than 2 nm) and mesoporous membranes (with diameters between 2 nm and 50 nm), diffusion is the leading transport mechanism [13].

Regardless of their transport mechanism, an increased interest has been focused on production of polymeric membranes with applications in various areas [1, 6, 7,9,11, 13], such as in:

- Desalination and production of ultrapure water through reverse osmosis;
- Blood detoxification plasma separation in medical devices;
- Fabrication of sterile filters by microfiltration;
- Separation and purification of natural gases etc.

Following this trend and knowing that dielectric [14, 15] and electric [16] properties of the membranes can be used for fabrication of devices with membranes based on polymers, in this paper we describe the production process of microporous membranes (with pores having average diameters between 4.43 μm and 4.99 μm) based on silicone rubber. We show the influence of the catalyst on the dispersion and absorption characteristics of the membrane in an electric field between 10 kHz and 200 kHz

The obtained results can be used for fabrication of liquid filtration systems using electric field of medium frequency.

By fixing the frequency, we can choose an optimal value for the dispersion characteristic of the electric field, so that the electric polarization of the membrane to allow additional electric charge on some components from the liquid phase, thus blocking them in the membrane. Thus, it takes place the transport of the desired component through the polymeric membrane. For other frequencies of the electric field, as it is shown here, it takes place a lowering of the electric charge quantity, followed by the membrane heating (maximum dissipation). In this way there are created new possibilities for membrane clogging and selective transport from one side to another.

2. Membrane preparation

2.1 Materials

The obtained elastomeric membranes are based on the following constituents:

- Silicone rubber (SR), from Bluestars-Silicones (RTV-3325 type) in the form of a white paste with viscosity 35000 mPa*s at 296 K [17];
- Catalyst (C), from Rhone-Poulenc (6H-type). It became polymerized with 25% SR. At 296 K, the gelation time is 50 - 60 minutes and polymerization time is about 6 h [18];
- Silicone oil (SO) from Merk has density 1040 kg/m^3 at 293 K and ignition temperature of 733 K;
- Stearic acid (SA), from Merk [19], in the form of a white powder has density between 400 - 500 kg/m^3 and the melting point between 333 K and 343 K.

2.2 Methods

We prepare a mixture with a total volume of $5 * 10^{-6} m^3$ containing $96\ \%\ vol. SO$ and $4\ \%\ vol. C$. Then the mixture is heated up to $\sim 350\ K$, and after $\sim 300\ s$ it becomes homogeneous. This homogeneous misture is called SAS and it has the property that it is in liquid phase down to $\sim 300\ K$, and crystallizes at lower temperatures.

A volume of $5 * 10^{-6} m^3$ of SR is heated up to $\sim 450\ K$, when a volume of $1 * 10^{-6} m^3$ of SAS (at $\sim 330\ K$) is added. The temperature is controlled by using an infrared thermometer, $AX - 6520$ type. Then, the mixture is homogenized for $\sim 600\ s$, and when the temperature drops below $300\ K$, we add C. The final mixture is again homogenized for $\sim 300\ s$. Depending on the volume of C added, the obtained solutions are denoted by: S_1 (sol. with $0.3 * 10^{-6} m^3$ C), S_2 (sol. with $0.6 * 10^{-6} m^3$ C) and S_3 (sol. with $1.2 * 10^{-6} m^3$ C).

Each liquid and viscous solution is poured between two plane and parallel plates. The sides of the plates, which are in contact with the solution, are plated with a layer of Cu with the thickness 0.00015 m and they are provided with conductors having the diameter of 0.02 m and length 0.25 m. The mobile plate is fixed at 0.0042 m ± 5% from the fixed one. The excess solution eliminated by pressing the mobile plate is collected in the pawls mounted on the edge of the ensemble formed by the two plates.

After 24 h the solution between the plates becomes polymerized. Thus, one fabricate three plane capacitors having between plates the membranes S_1 with 5% vol. of C, S_2 with 10% vol. of C, and S_3 with 20% vol. of C.

3. Results and Discussions

The plane condensers C_i, which are connected, in turn, to the RLC programmable bridge, $HM - 8118$ type [20]. We measure the capacitance and the dissipation factor as a function of the frequency of an external electric field, for each condenser. The obtained results are shown in Fig. 1a and Fig. 1b. The capacitance Cp of the plane condenser (Fig. 1a) increases linearly with f and is influenced by the volume concentration of catalyst. Thus, at f=10 kHz:

- C_p = 237.016 pF for S_1, with C = 5% vol.;
- C_p = 308.034 pF for S_2, with C = 10% vol.;
- C_p = 401.840 pF for S_3, with C = 20% vol.

However, for f=200 kHz one obtains:

- C_p = 243.584 pF for S_1, with C = 5% vol.;
- C_p = 317.511 pF for S_2, with C = 10% vol.;
- C_p = 412.41 pF for S_3, with C = 20% vol.

Variation of dissipation factor D with f (Fig. 1b) ia also significantly influenced by the catalyst concentration. Thus, in an electric field with f = 10 kHz one obtains:

- 10^4 x D = 0.44866 for S_1 with C = 5% vol.;
- 10^4 x D = 4.3562 for S_2 with C = 10% vol.;
- 10^4 x D = 8.11553 for S_3 with C = 20% vol.

The dissipation factor increases with increasing the frequency f of the electric field, and it reaches the maximum 10^4 x D_{max} = 5.97548 at f = 54.1414 kHz for S_1 with 5% , and 10^4 x D_{max} = 7. 60501 at f = 40,70707 kHz for S_2 with 10%. Starting with f = 54.1414 kHz, D decreases with increasing the frequency and has a minimum (10^4 x D_{min} = 5.74566 at f = 82.92929 kHz). Then, with further increasing of f, D starts to increase up to 10^4 x D = 40.49629 at f =200 kHz, for S_1 with C = 5% vol.

However, for S_2 with C = 10% vol., D decreases with increasing f and it reaches 10^4 x D_{min} = 7.56367 at f = 54.1414 kHz. With further increasing of f, D increases up to 10^4 x D = 56.30208 la f = 200 kHz. Increasing the vol. concentration of the catalyst, D for S_3 increases, thus at f = 200 kHz one obtains 10^4 x D = 66.49913.

Thus, the membranes S_i (i = 1, 2, 3) are materials with dielectric loss when is applied an external electric field with frequencies between 10 kHz and 200 kHz. It is known [21, 22] that they show a complex dielectric permittivity, namely

$$\epsilon^* = \epsilon' - j\epsilon'', \qquad (1)$$

where ϵ' and ϵ'' are relative dielectric permittivity and respectively the dielectric loss factor, and $j = \sqrt{-1}$.

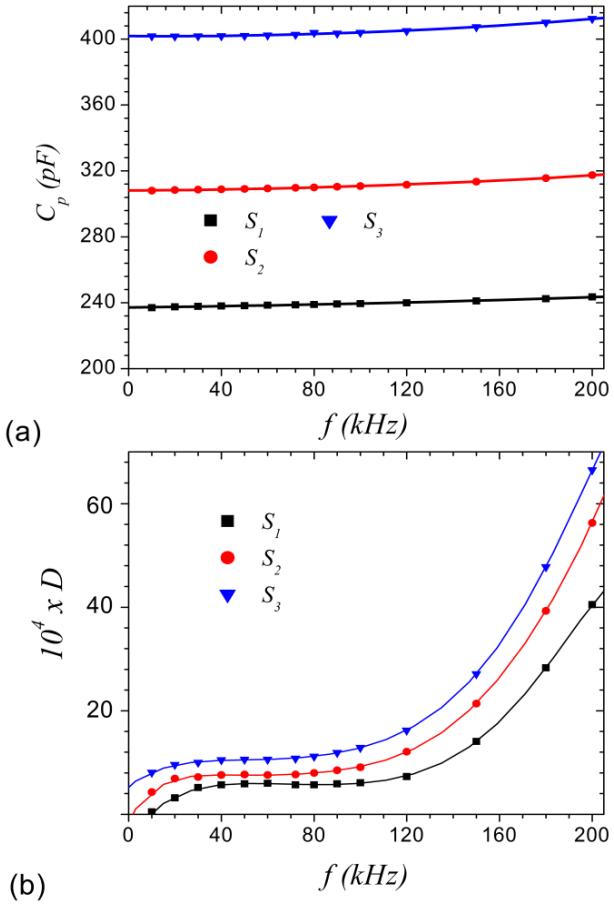

Fig. 1 Variation of the capacitance (a) and of dissipation factor (b) with the frequency f of the electric field, for the plane capacitors having as dielectric material the membranes S_i (i = 1, 2, 3).

By neglecting the edge effects and using the equation for the capacitance of the plane condenser [21, 22] one obtains

$$\epsilon' = \frac{C_p d}{\epsilon_0 L l}, \qquad (2)$$

where C_p is the electrical capacitance of the capacitor, L, l, and d are the length, width and height of the dielectric, and ϵ_0 is the dielectric permittivity of the vacuum. For d = 0.00042 m, L = 0.11 m, l = 0.10 m, $\epsilon_0 = 8.85\ 10^{-12}\ F/m$, and using Eq. (2) one obtain:

$$\epsilon' = 0.0043\ C_p\ (pF), \qquad (2')$$

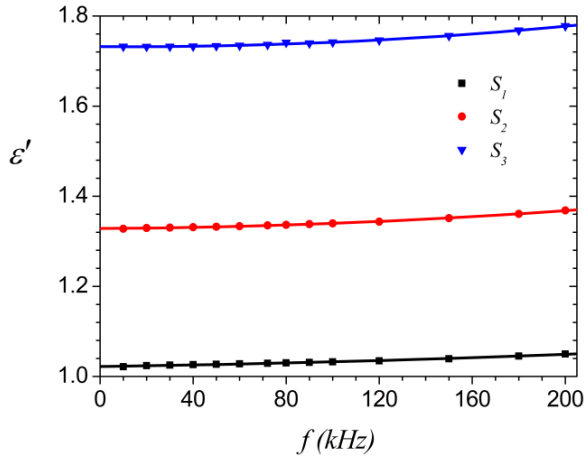

Fig. 2 Variation of the relative dielectric permittivity ϵ' with the frequency f of the electric field for the membranes S_i (i = 1, 2, 3).

The values of C_p from Fig. 1a are introduced into Eq. (2') and we obtain $\epsilon' = \epsilon'(f)$ as shown in Fig. 2.

Variation of ϵ' with f is called the dispersion characteristic of the membranes S_i in an electric field of medium frequency. As expected (Fig. 1a) the characteristics are linear, thus the elastomeric membranes are linear dielectrics. For a fixed f (Fig. 2), ϵ' is significantly influenced by the volume concentration of the catalyst. It is known [21, 22] that

$$\epsilon'' = \epsilon' D, \qquad (3)$$

and thus, from D=D(f) shown in Fig. 1b and $\epsilon' = \epsilon'(f)$ (Fig. 2) one obtains the absorption (dissipation) characteristic of the membranes (Fig. 3). They depend also on the volume concentration of the catalyst, thus, for C = 5% vol., ϵ'' increases from 0.000045 (at f = 10 kHz) up to $\epsilon''_{max} = 0.0006139$ (at f = 54.1414 kHz), called resonance frequency. Starting with value, ϵ'' decreases with increasing f. For f = 82.92959 kHz one obtains $\epsilon''_{min} = 0.00059051$ and then ϵ'' increases with increasing f.

By increasing the catalyst concentration, the shape of absorption characteristic is changed. For 10 < f (kHz) < 200, the resonance phenomenon is missing for membranes S_2 and S_3. Instead there can be seen minima values for ϵ'' at high ranges of f, namely $\epsilon'' = 0.0010$ for 33.03 < f (kHz) < 61.82 (for S_2) and $\epsilon'' = 0.0018$ (for S_3).

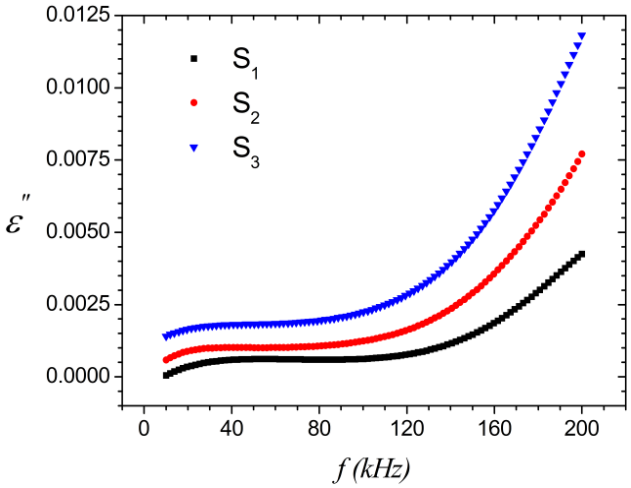

Fig. 3 Variation of the dielectric loss factor ϵ'' with the frequency f of the electric field for the membranes S_i.

Pore distribution of the elastomers has been determined by using AFM for four random scanned areas of $40 * 40\ \mu m^2$. The acquisition and analysis of the images were performed using the NanoScope 531r1 software and SPIP 5.1.11 analysis software [23].

One can see that the samples posses very similar topographical characteristics (Fig. 4). The relative frequency of the pores as a function of their diameter is shown in Fig. 5, where we can observe that the diameter increases with increasing the catalyst concentration. Considering the membrane S_1 (with C = 5 % and diameter $d_m = 4.43\mu m$) as a reference, we can see that by increasing C twice, the average diameter increases with 1.81 % (d_m 4.51 μm) for S_2. Further, by increasing C with 400%, the average diameter increases with 12.64 %, up to $d_m = 4.99\mu m$.

During homogenization, inside the liquid mixtures S_i, air diffuses. The air molecules together with catalyst vapours become condensed [24] at various points of the liquid membranes and thus forming growth sites of a new phase, which is an air bubble. This becomes stable when its radius is at least equal with critical radius [25]

$$R_{cr} = 2\gamma / p\ (s^m - 1), \qquad (4)$$

where γ is the liquid-gas surface contact tension, p is the liquid-gas equilibrium pressure, S is supersaturation, m depends on the type of gas and is called power of volatile concentration [25].

Air bubbles move to the membrane surface due to the Archimedes' force when this is much bigger than the resistance force appeared due to the bubble weight and viscous force. By increasing C, the viscous force increases and thus, for the air bubble to move to the surface, it is necessary that their diameter to be large enough so that Archimedes' force to dominate. Therefore, the resulting pore distributions for the three membranes have the shapes shown in Fig. 5.

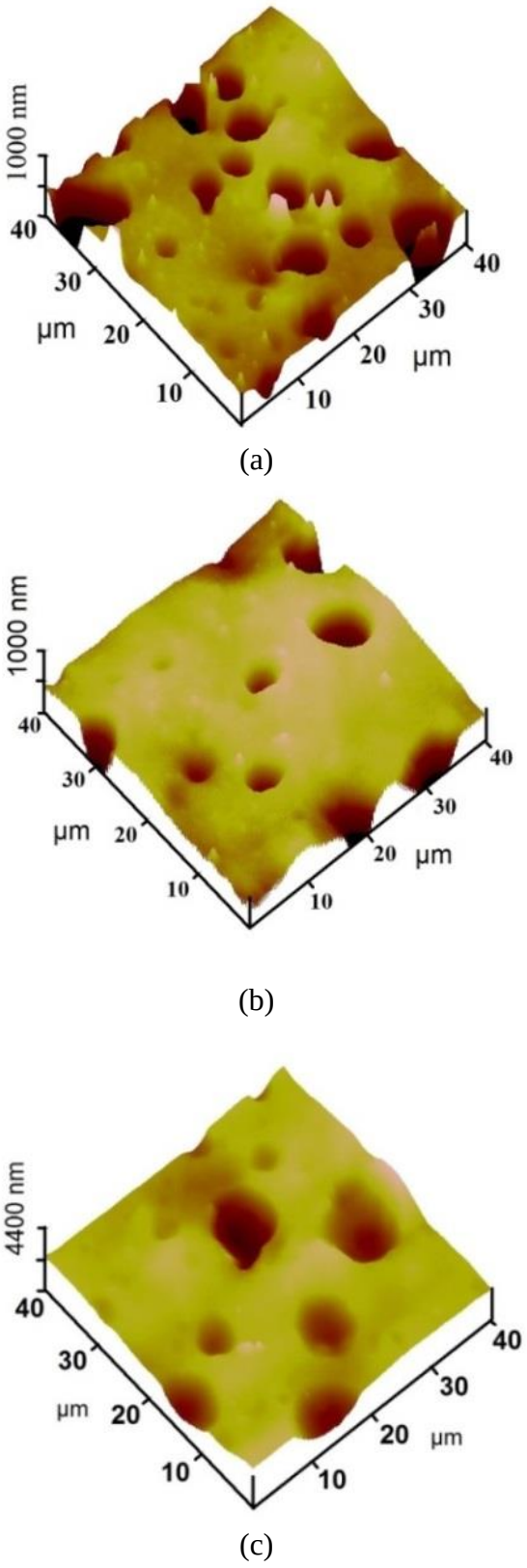

Fig. 4. AFM of the four types of elastomers. (a) S_1; (b) S_2; (c) S_3;

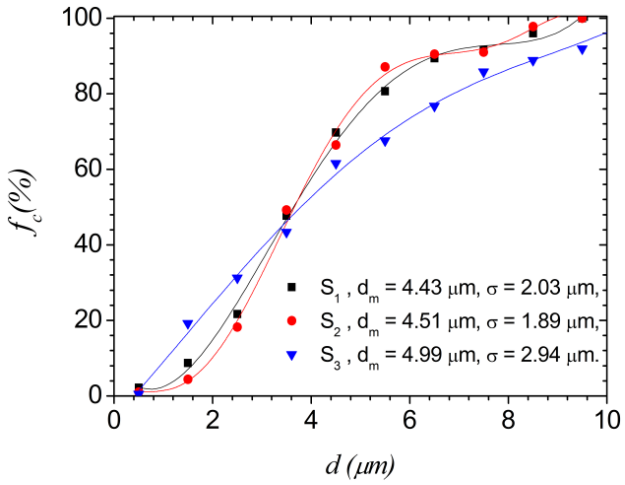

Fig. 5 Relative frequency f_r versus pore diameter d. d_m is the average diameter and σ is relative variance.

4. Conclusions

We have obtained porous membranes consisting of silicone rubber, stearic acid solution at various volume concentrations of catalyst. We have shown that the absorption and dispersion characteristics, pore distribution and their average diameter are significantly influenced by the volume concentration of the catalyst.

This effect can be used for phase separation using electrical methods. Here, by choosing the frequency and the intensity of the electric field to the membrane, one can perform selective separation of solid phases from a liquid matrix.

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