

## DEVELOPMENT OF METHODS FOR THE PRODUCTION OF SILICONE MEMBRANES

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Received: 18.01.2023

A simple method for the preparation of highly transparent hydrophobic thin silicone membranes using Floating-on-Water (FoW) technology has been proposed. The centrifugation method was also used to obtain homogeneous and transparent silicone membranes. A new approach to the one-step synthesis of Janus-type membranes has been proposed.

Ref.5, fig. 4, tabl. 3.

**Key words:** silicone membranes, FoW technology, spin-coating, RTV catalyst, TEOS crosslinker.

### 1.Introduction

It is known that silicone polymers (polysiloxanes) show such properties as high heat resistance, elasticity, high hydrophobicity, low surface activity, non-toxicity, biocompatibility, which allow their wide application in practice both at low and high temperatures [1, 2].

The properties of the silicone matrix (elasticity, swelling ability, sorption capacity/desorption ability) significantly depend on the topology of the polymer network and the morphology of the silicone system, which are also largely responsible for the adsorption of biologically active substances and their release. The crosslinked/cured polydimethylsiloxanes are prepared from linear silicones in the presence of various catalysts of curing. As room

temperature vulcanization catalysts primary amines, e.g. bis-aminopropyl terminated polydimethylsiloxane (PDMSNH<sub>2</sub>) were used in the synthesis of silicone elastomers [3]. Tin based catalysts are also widely used as room temperature vulcanization catalysts (RTV). We use small amount of the tin catalyst (0.02%) for room temperature vulcanization of hydroxyl terminated polydimethylsiloxane (PDMSOH) allowing to obtain silicone matrices of different sizes and shapes using different molds.

The aim of this study is to develop methods for obtaining highly transparent thin silicone membranes based on hydroxyl terminated polydimethylsiloxane (PDMSOH).

## 2. Experimental

Tetraethoxysilane (TEOS, Aldrich), hydroxyl terminated polydimethylsiloxane (PDMSOH) and aminopropyl-terminated polydimethylsiloxane (PDMSNH<sub>2</sub>) (Gelest Inc.), dibutyltin dilaurate (DBTDL, Aldrich), tin (II) 2-ethylhexanoate (Aldrich), PEG 200 and PEG 1000 (Aldrich) are used as received. Ethanol (96%) and ethyl acetate (99%) were purchased from Medisar LLC (Armenia).

TG-MS analysis was performed with “Netzsch STA 449 F5 Jupiter” thermoanalyzer coupled with mass-spectrometer. BET surface area and porosity were analyzed by ASAP 2020 Plus Physisorption Analyzer. Contact angles were measured by contact angle and surface tension meter CAM 101 (KSV instruments Ltd., Finland).

Molecular masses of the initial linear silicones (PDMSOH) and their viscosity are important parameters for elastomers formation. For preparation of crosslinked/cured silicone elastomers initial linear silicone PDMSOH with molecular masses 26,000 (viscosity 1000 cSt), 36,000 (viscosity 2000 cSt), 43,500 (viscosity 3500 cSt), and 49,000 (viscosity 5000 cSt), supplied by Gelest Inc. were tested.

Hydroxyl terminated polydimethylsiloxane (PDMSOH) of different molecular masses, commercially available tetraethoxysilane (TEOS) as cross-linker and tin catalyst (dibutyltin dilaurate or tin (II) 2-ethylhexanoate)- the most active RTV catalyst for PDMSOH curing were used for preparing the initial batch composition in fabrication of silicone elastomeric membranes. The compositions of the batch solutions are discussed in the next section.

## 3. Results and discussions

A method to fabricate a thin (<10  $\mu\text{m}$ ) silicone membrane by placing liquid PDMS solution on the surface of water and curing the PDMS solution was disclosed in paper [4]. This membrane fabrication method, utilizing the characteristics of the two-phase immiscible fluids (water and PDMS), is

referred to as the floating-on-water (FoW) method. The production process done by using a hot plate. Briefly, after filling a Petri dish with water, the PDMS solution is dropped and heated at 40-80 °C for 1h to obtain various membranes with thicknesses of a few to tens of micrometers. The two-component Sylgard 184 (Dow Corning, USA) silicone kit (S184), comprising divinyl-terminated polydimethylsiloxane (PDMS), a crosslinker and Pt catalyst, were used in these studies. Though this method can be used to produce thin PDMS membranes without the need of expensive equipment, however, the method requires multicomponent composition and high crosslinking/ vulcanization temperature.

In the framework of the present work, we have developed a simple method of production silicone elastomeric membranes with various thicknesses by room temperature crosslinking/vulcanization of hydroxyl terminated polydimethylsiloxane (PDMSOH) on water surface using the (FoW) technology.

Thus, we propose a novel FoW method to produce a silicone elastomeric membrane on a water surface with various thicknesses under different production conditions. The thickness of the membrane depends on the amount of PDMSOH used. Thus, it is easy to prepare membranes with various thickness using only PDMSOH and water. In addition, the membrane produced by FoW is significantly easier to handle, as water serves as the substrate and the produced membrane floats on the water surface. This reduces the preparation time. In addition, the FoW method is not limited to producing flat mono-layer hydrophobic membranes. For example, it is possible to manufacture the alternative membrane structures, such as the multi-layer membranes, or Janus type membranes.

Studies have shown that when tetraethoxysilane (TEOS) is used a crosslinker and DBTDL a catalyst, the best results have been obtained when PDMSOH with molecular mass 26,000 (viscosity 1000 cSt) was used as a silicone base. It readily spreads on the water surface forming homogeneous and uniform coating. Using silicones with molecular mass 36,000 (viscosity 2000 cSt) and above results in poor spreading and formation of clumps. Thus, the optimum molecular mass of the base silicone is 26,000. The scheme of the reaction is given below (Fig.1).



We have further developed and optimized the conditions of the silicone elastomeric membranes preparation for finding possibility of preparing membranes using PDMSOH of various molecular weights, using dibutyltin dilaurate and tin (II) 2-ethylhexanoate as RTV tin catalysts and determining the optimum amounts of the RTV catalyst and crosslinking agent (TEOS) for producing high quality elastomeric membranes.

It has been found out that **ethyl acetate** is an appropriate solvent for preparing the batch solutions of linear silicones with different molecular masses. It was used to obtain less viscous and more fluid batch mixtures with good spreading on water surface. During films curing, ethyl acetate completely evaporated. The resulting films were smooth and uniform in thickness. Compositions of the synthesized hydrophobic films is given in Table 1.

The membranes were prepared by stirring the components and dropwise pouring the batch solution onto surface of water filled in a Petri dish of 9 cm in diameter, which was placed in a strictly horizontal surface. The next day, a smooth uniform disc-shaped film was formed.

**Table 1.**

**Composition of the silicone films**

<b>PDMSOH</b>	<b>TEOS, g</b>	<b>Ethyl acetate, ml</b>	<b>DBTDL, mg</b>
3.56g (viscosity 1000 cSt, M <sub>w</sub> 26,000)	0.5	1	20
3.56g (viscosity 2000 cSt, M <sub>w</sub> 36,000),	0.5	1	20
3.56g (viscosity 3500 cSt, M <sub>w</sub> 43,500)	0.5	1.3	20
3.56g (viscosity 5000 cSt, M <sub>w</sub> 49,000)	0.5	1.3	20

In the case of higher molecular weight PDMSOH (3500 cSt, M<sub>w</sub> 43500 and 5000 cSt, M<sub>w</sub> 49.000) the amount of ethyl acetate was increased from 1ml up to 1.3 ml to obtain good spreadable batch solution, and as a result uniform and high quality transparent membrane was produced by FoW technology.

Thickness of the prepared films is 0.15-0.2 mm. By changing concentrations of the PDMSOH in ethyl acetate solution, it is possible to vary thickness of the produced membranes over a wide range.

**Contact angles  $\Theta$  measured:**

Water-  $\Theta$  -103  $\pm$  5<sup>0</sup>, Toluene-  $\Theta$ - 44  $\pm$  6<sup>0</sup>

The contact angles were measured with silicone membranes prepared from 26,000 (1000 cSt) and 36,000 (2000 cSt) PDMSOH, as well as by increasing the amount of TEOS from 0.5 *ml* to 1.0 *ml* (PDMSOH - 3.56 g; TEOS-05 *ml* (1.0 *ml*); DBTDL- 20 *mg*).

Regardless of the method of obtaining the membranes, contact angles were the same - for water 107.5° and for toluene - 42.5°.

Further we were trying to substitute dibutyltin dilaurate RTV catalyst by less toxic tin (II) 2-ethylhexanoate (tin(II) octoate). The experiments have shown that the use of FoW technology for preparing silicone membranes with this catalyst results in the formation of shrunk polymer material on water surface. Presumably, difference between these two silicone RTV catalysts accounts for laurate fragment of DBTDL, which can play the role of surfactant uniformly distributing the corresponding batch solution on water surface. However, excellent films with tin (II) 2-ethylhexanoate are formed by dry spin coating method. Recipes of the silicone membrane preparation with tin (II) 2-ethylhexanoate catalyst and water contact angles of the prepared membranes are given in Table 2.

**Table 2**

**Silicone membranes preparation by spin-coating method with tin (II) 2-ethylhexanoate catalyst.**

<b>MB 1</b>			<b>MB 2</b>			<b>MB 3</b>		
Components	Content, g	%	Components	Content, g	%	Components	Content, g	%
PDMSOH M <sub>w</sub> 26,000 1000 cSt	2.6	73.09	PDMSOH M <sub>w</sub> 36,000 2000 cSt	3.6	79.0	PDMSOH M <sub>w</sub> 43,500 3500 cSt	3.6	78.99
TEOS	0.5	14.06	TEOS	0.5	10.97	TEOS	0.5	10.97
tin (II) 2-ethylhexanoate	0.0072	0.2	tin (II) 2-ethylhexanoate	0.0072	0.16	tin (II) 2-ethylhexanoate	0.0072	0.16
ethyl acetate	0.45	12.65	ethyl acetate	0.45	9.87	ethyl acetate	0.45	9.87
	<b>3.557</b>	100		<b>4.5572</b>	100		<b>4.5573</b>	100
Contact angle Θ <sup>0</sup> , water		<b>102.2</b>	Contact angle Θ <sup>0</sup> , water		<b>103.6</b>	Contact angle Θ <sup>0</sup> , water		<b>103.1</b>

This Sn-catalyst is very reactive, so it was first mixed with ethyl acetate, and then added to the mixture of PDMSOH and TEOS in order to increase the time before crosslinking/curing and to have enough time to pour the mixture into a plastic Petri dish. Film formation occurs within 10-15 *min*. MB1-MB3 films are transparent, elastic, and easily removable from a plastic surface. In case of using PDMSOH with MW 49,000 (viscosity 5000 cSt)

the film formed is not uniform, brittle, and with opaquer streaks. MB1 film thickness - 0.3 mm, thickness of MB2 and MB3 films are within the range of 0.5-0.55 mm.

Measurement of BET surface area has shown that the silicone membranes prepared both with dibutyltin (II) dilaurate and tin (II) 2-ethylhexanoate do not contain sorption pores.

#### ***A new approach for synthesis of Janus type membranes***

Janus membranes with entirely different properties on two faces show big advantages when compared with homogeneous materials due to their high selectivity. Potential applications of Janus membranes are as follows: emulsification and demulsification processes, nanofiltration, osmosis energy harvesting, aeration, fog harvesting, batteries design, use as catalytic contactors, etc. [5].

To obtain two-layer Janus type membrane, polyethylene glycol (PEG) of different molecular masses (PEG 200 and PEG 1000) was added to the composition used for preparation of hydrophobic membrane: PDMSOH - 3.56 g (viscosity 1000 cSt,  $M_w$  26000), TEOS - 0.5 g, DBTDL -20 mg. First we tried to produce the membrane using FoW technology, however, after curing, the resulting film significantly shrunk (the diameter decreased from 5-6 cm to 1.5 cm), the edges of the film were bent upward, apparently due to different internal stresses of different layers, and the resulting film in the bottom part ("hydrophilic" adjacent to water) was inhomogeneous. Further on, the membranes were obtained using spin-coating method. PEG was preliminarily dissolved in 1 ml of ethyl acetate and added to the batch solution of PDMSOH and TEOS, then the catalyst- dibutyltin dilaurate was added and, after thorough stirring, the mixture was poured into plastic PE Petri dish and rotation of 100-120 rpm for 20-30 sec was applied to spread the layer. When PEG 200 was used in an amount of 1g it resulted in droplets formation emerging from the bottom side of the film; the addition of 0.5 g of PEG 200 resulted in the formation of smaller amount of droplets; the addition of 0.3 g of PEG 200 resulted in the formation of uniform membrane, and the same uniform membrane was obtained when using 0.3 g of PEG 1000. Contact angles measured for these films showed that there were small differences ( $\Theta^0=15-16^0$ ) between top and bottom parts of the membrane. Twofold decrease in the amount of DBTDL RTV catalyst down to 10 mg per batch didn't change this contact angles difference.

For producing next series of Janus type bilayer membranes tin (II) 2-ethylhexanoate was used as a catalyst. To prepare the membranes the required amount of the Sn-catalyst was quickly mixed with ethyl acetate for further adding into the composite mixture. For preparing the composite mixture PDMSOH was mixed with TEOS, stirred for 2-3 minutes, then ethyl acetate was added (minus the amount used for dissolving Sn-catalyst), then

PEG 200 was added. The mixture thoroughly mixed up for 40 *min*, then the catalyst solution was added, and the resulting mixture was mixed for 30 – 60 *sec* and poured into a plastic Petri dish.

It is quite possible that the performance difference of these two Sn catalysts at the films forming, here also can be explained by presence of laurate fragment of DBTDL, which can play the role of surfactant uniformly distributing hydrophilic PEG in the batch solution. Table 3 shows the recipes for preparing membranes and water contact angles of top and bottom of the synthesized membranes.

The biggest difference in contact angles (water) between top (hydrophobic) surface and bottom (hydrophilic) surfaces was observed in case of **Membrane 3**. The membrane thickness- 0.45 *mm*.

**Table 3**

**Silicone membranes synthesis**

<b>Membrane 1*</b>			<b>Membrane 2**</b>			<b>Membrane 3***</b>		
Components	Content, g	%	Components	Content, g	%	Components	Content, g	%
PEG 200	0.3	5.67	PEG 200	0.3	5.69	PEG 200	0.3	5.70
PDMSOH			PDMSOH			PDMSOH		
1000 cSt	3.56	67.30	1000 cSt	3.56	67.50	1000 cSt	3.56	67.58
TEOS	0.5	9.45	TEOS	0.5	9.48	TEOS	0.5	9.49
Sn-cat	0.03	0.57	Sn-cat	0.014	0.27	Sn-cat	0.0075	0.14
ethyl acetate	0.9	17.01	ethyl acetate	0.9	17.06	ethyl acetate	0.9	17.09
	<b>5.29</b>	100.00		<b>5.274</b>	100.00		<b>5.2675</b>	100.00
Contact angle $\Theta^0$ , water								
Top/bottom	Curing in 10 <i>min</i>	73/83		Curing in 25 <i>min</i>	100/37.5		Curing in 45 <i>min</i>	108/13

\*) It was not possible distributing mixture uniformly, as it cured very quick (10 *min* after adding the catalyst).

\*\*) The membrane with reduced amount of catalyst by half, the mixture cured in 25 *min*, and after an hour the resulting film easily came off from the plastic surface.

\*\*\*) The membrane with reduced amount of catalyst by four times, the mixture cured in 45 minutes. The film was easily removed next day from the plastic dish.



Fig. 3 show photos of hydrophobic membrane (a) and **Membrane 3** (b)

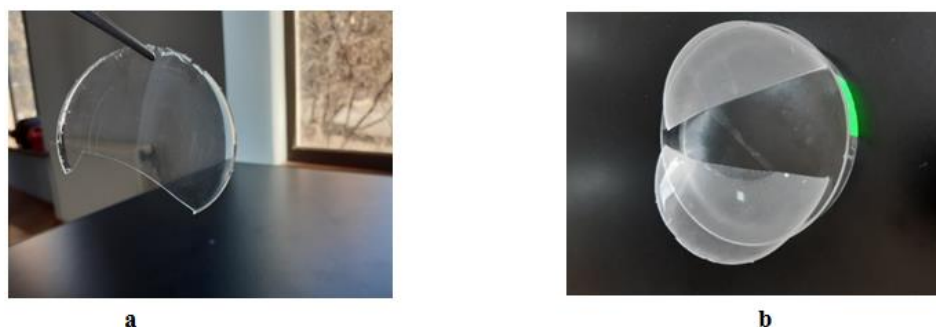
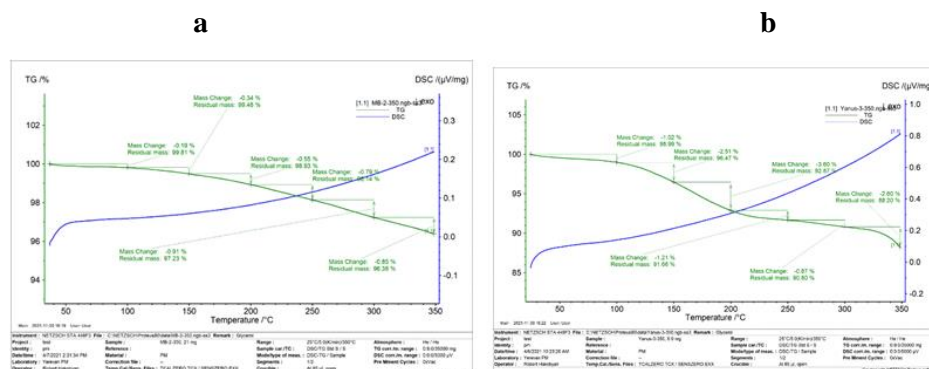


Fig. 3. Membranes pictures.

Measurement of BET surface area has shown that the **Membrane 3** also doesn't contain sorption pores.



**Fig. 4.** TG-DSC data of the silicone membrane (a) (RTV catalyst - tin (II) 2-ethylhexanoate) and **Membrane 3** (b)

Fig. 4a shows TGA-DSC data of the silicone membrane (RTV catalyst - tin (II) 2-ethylhexanoate). From the figure follows that at 150 °C the weight loss of sample is 0.5%, at 200 °C it makes up 1.07%, and at 300 °C - 2.77%.

Fig. 4b shows TGA-DSC data of the **Membrane 3** from which follows that at 150 °C the weight loss of sample is 3.5%, at 200 °C it makes up 7.13%, and at 300 °C - 8.34%. Comparison of these data showed that **Membrane 3**, containing PEG as hydrophilic additive (Fig. 4b) is less thermostable than the hydrophobic matrix not containing PEG (Fig. 4a).

From the data on synthesis of “Janus type” membranes follow that contact angles difference of hydrophobic and hydrophilic sides depend on quite many factors: thickness of the membrane, its curing time, ambient temperature of curing, amounts of crosslinker and RTV catalyst, PDMSOH concentration in ethyl acetate solution; dependency on molecular weights of PDMSOH and PEG here is also possible. Our further research will be focused on finding reproducible and optimum conditions of producing this type of membranes and studies the potential fields of their application.

## Conclusion

A simple production method for producing hydrophobic transparent membranes was proposed using hydroxyl terminated polydimethylsiloxane (PDMSOH) as a base silicone, tetraethoxysilane (TEOS) as crosslinker and tin catalyst for room temperature vulcanization (curing) using Floating-on-Water (FoW) technology. In some cases, for producing uniform and transparent silicone membranes spin-coating method was also used. Novel approach to one-pot synthesis of Janus type membranes has been put forward.

## ACKNOWLEDGMENT

This work was financially supported by Philip Morris Armenia LLC.

## ՍԻԼԻԿՈՆԵ ԹԱՂԱՆԹՆԵՐԻ ՍՏԱՑՄԱՆ ՄԵԹՈԴՆԵՐԻ ՄՇԱԿՈՒՄ

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*Առաջարկվում է բարձր թափանցիկ հիդրոֆոբ բարակ սիլիկոնե թաղանթների արտադրության պարզ մեթոդ՝ օգտագործելով Floating-on-water (FoW) տեխնոլոգիան: Յենտրիֆուգացման մեթոդը կիրառվել է նաև համասեռ և թափանցիկ սիլիկոնե թաղանթներ ստանալու համար: Առաջարկվում է Յանուսի տիպի թաղանթների միաստիճան սինթեզի նոր մոտեցում:*

## РАЗРАБОТКА МЕТОДОВ ИЗГОТОВЛЕНИЯ СИЛИКОНОВЫХ МЕМБРАН

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Предложен простой способ изготовления высокопрозрачных гидрофобных тонких силиконовых мембран с использованием технологии Floating-on-Water (FoW). Для получения однородных и прозрачных силиконовых мембран использовался также метод центрифугирования. Предложен новый подход к одностадийному синтезу мембран типа Януса.

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