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Large-scale synthesis of polydimethylsiloxane as vitreous replacement applications

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ABSTRACT

Polydimethylsiloxane (PDMS) is a polymer that can be used as a vitreous substitute. To fulfill the need for PDMS on a large scale, synthesis of PDMS in a large number is also needed. Therefore, intensive research is needed to produce PDMS in large quantities. This study reported that the result of the synthesis of PDMS on a scale three and five times larger than the lab-scale using a ring-opening polymerization method with octamethylcyclotetrasiloxane (D4) as a monomer and hexamethyldisiloxane as a chain terminator by increasing the volume of raw materials and reactors. The viscosity of PDMS obtained is in the ranges of 1000–3700 mPa.s for lab-scale, 1130–3590 mPa.s for three times scale-up, and 1270–4320 for five times scale-up. The obtained refractive index ranges from 1.3982 to 1.4008 and the surface tension ranges from 20 to 21 mN/m. From FTIR measurements, the synthesized PDMS from lab-scale and scale-up had structural and functional groups similar to commercial PDMS, showing that PDMS has been successfully synthesized.

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Introduction

Vitreous humour (VH) is transparent fluid with 98% water content, making up around two-thirds of the eye's volume [1–3]. It fills the eyes' cavity, located in the posterior between the lens and retina which functions to stabilize the volume of the eyeball and as a pathway to delivering nutrients to the lens and retina [4]. VH can experience physical characteristic damage and changes which can lead to retinal detachment that causes poor vision and blindness [3,5]. The treatment of retinal detachment is pars plana vitrectomy which involves the replacement of VH through the injection of VH substitute [6].

One of the vitreous substitutes is polydimethylsiloxane (PDMS) or silicone oil [7,8]. PDMS, $(CH_3)_3SiO–[Si(CH_3)_2O]n–Si(CH_3)_3$, is a siloxane with methyl as a side group and is one of the repeat units from polymer that can be utilized in various industries, including biomedical field [7,9–11]. PDMS has significant characteristics such as being chemically inert, optically clear, and thermally stable [12,13]. Because of the limited availability of PDMS and its expensive cost, the production of PDMS is conducted. Previous research studies have reported that PDMS was successfully synthesized through various syntheses, including ring-opening polymerization (ROP) and hydrolysis condensation [14–17]. For the ROP method, octamethylcyclotetrasiloxane (D4) is used as a monomer, and hexamethyldisiloxane (HMDS) is used as a chain terminator [14,18]. As for the condensation hydrolysis method, dichlorodimethylsilane (DCMS) and dichloromethane (DCM) are used as synthesis materials [17]. The ROP method is well-established research, with a clear synthesis route and defined parameters. The PDMS that has been produced on a laboratory lab-scale using the ROP method has three groups of viscosity category, including low viscosity ranges from 940 to 1350 mPa.s, medium viscosity ranges from 1800 to 2600 mPa.s, and high viscosity that lies at the value of 3650 mPa.s which is close to the value of commercial PDMS [14,19,20].

To fulfill the high demand for PDMS, the formulation of synthesis of PDMS needs to be developed on a large scale (scale-up) to be produced with good quality comparable to lab-scale PDMS. Synthesis of PDMS at a scale two times larger than the lab-scale was successfully conducted with the result of the viscosity of PDMS ranges from 1700 to 2920 mPa.s [21]. However, the information about the scale-up PDMS synthesis at

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a larger scale, resulting in a wider range of viscosity, has not been reported in detail. In this study, the synthesis of scale-up PDMS was carried out at a scale three and five times larger than the lab-scale to obtain PDMS with viscosity ranges from 1000 to 4500 mPa.s that is usually utilized as fluid for a vitreous substitute in vitreoretinal surgery.

Materials and methods

Materials

Octamethylcyclotetrasiloxane ($C_8H_{24}O_4Si_4$) (D4) with a purity of >98% from Alfa Chemical, hexamethyldisiloxane ($C_6H_{18}OSi_2$) (HMDS) with purity of 99.5% from Sigma–Aldrich, and potassium hydroxide (KOH) from Merck were used in the synthesis process. While chloroform ($CHCl_3$) and Milli-Q water were used in the purification step.

Methods

PDMS was synthesized through the ROP method with the process that has been reported in the previous publication [21]. Synthesis of PDMS includes three parts, those are synthesis of lab-scale PDMS, synthesis of three times scale-up PDMS, and synthesis of five times scale-up PDMS. For the synthesis of lab-scale PDMS, 7.8 mL of D4 monomer, 3 mL of HMDS chain terminator, and 0.6 M of potassium hydroxide (KOH) catalyst were stirred at a speed of 300 rpm at a temperature of 150℃ in a 50-mL volume of reactor. The polymerization time ranges from 15 to 21 min to get PDMS with viscosity ranges from 1000 mPa.s to 3700 mPa.s. After the polymer was formed, 1:1 chloroform was added to the mixture. Then, purification using milli-Q water in a ratio of 2:1 was performed until the aqueous phase of the sample reached a pH of 7. The evaporation step was then conducted to remove residual chloroform.

To produce PDMS on a scale three and five times larger than the lab-scale, the polymerization step was conducted by modifying the volume of raw materials and the reactor. Hence, 23.4 mL of D4, 9 mL of HMDS, and 0.105 mL of KOH were used to produce three times scale-up PDMS. While 39 mL of D4, 15 mL of HMDS, and 0.175 mL of KOH were used to produce five times scale-up PDMS. A reactor with 100 mL was used for the polymerization step at the same stirrer speed and temperature conditions. The polymerization time ranges from 32 to 39 min to obtain three times scale-up PDMS with viscosity ranges from 1130 to 3590 mPa.s. While the polymerization time ranges from 59 to 68 min to obtain five times scale-up PDMS with viscosity ranges from 1270 to 4320 mPa.s.

Purified PDMS samples were then characterized by measuring the value of viscosity through SEKONIK VISCOMATE viscometer model VM-10A0MH, surface tension through surfgauge, refractive index through AS ONE 1–500 refractometer (Brix 0–90%), and functional group through Perkin Elmer Spectrum 100 FTIR spectrometer. According to the previous report [22], the additional diopters were determined by Equation (1):

$$\left(\frac{N_s - N_v}{AL - ACD}\right) \times 1000 = \text{Additional diopters} \qquad (1)$$

N_s is the refractive index value of PDMS, N_v is the refractive index value of VH (1.3348), AL is axial length (23.35), and ACD is anterior chamber depth (3.06 mm).

Result and discussion

In Table 1, the comparison of synthesis parameters between lab-scale PDMS, three times, and five times scale-up PDMS is presented. The synthesis of PDMS at a scale three and five times larger than the lab-scale was achieved by increasing the volume of raw materials by three and five times, respectively. Additionally, the reactor volume was increased to 100 mL while the polymerization temperature and stirrer speed were same as PDMS polymerization at a lab-scale. The synthesized PDMSs were transparent, as shown in Figure 1.

In Table 2, the viscosity (η), surface tension (γ), refractive index (n), and additional diopters of synthesized PDMS are presented. The viscosity ranges from 1130 to 3590 mPa.s for PDMS scale-up three times larger than the lab-scale. Samples of PDMS-1 lab-scale

Table 1. Synthesis parameters of lab-scale, three times, and five times scale-up PDMS.

Synthesis parameter	Lab-scale	Three times scale-up	Five times scale-up
Volume of D4 (mL)	7.8	23.4	39
Volume of HMDS (mL)	3	9	15
Volume of KOH (mL)	0.035	0.105	0.175
Reactor volume (mL)	50	100	100
Polymerization time (min)	15–21	32–39	59–68
Polymerization temperature (℃)	150	150	150
Stirrer speed (rpm)	300	300	300
Chloroform ratio	1:1	1:1	1:1
Milli-Q water ratio	2:1	2:1	2:1

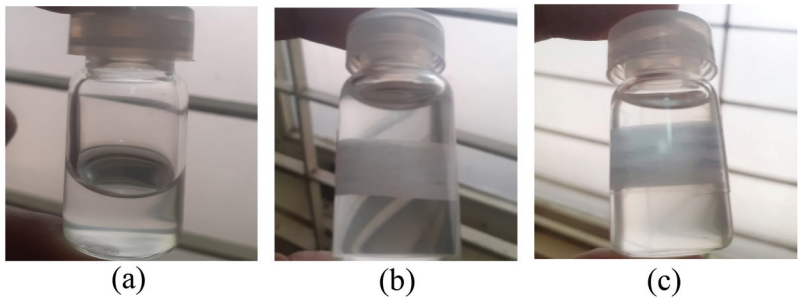

Figure 1. Synthesized PDMS: (a) lab-scale, (b) three times scale-up, and (c) five times scale-up.

Table 2. Characterization results of viscosity, surface tension, refractive index, and additional diopters for PDMS with lab-scale, three times scale-up, and five times scale-up.

Sample	Time (min)	η (mPa.s)	γ (mN/m)	n	Yield (%)	Additional diopters
PDMS-1 lab-scale	15	1000	20.0	1.3982	50	3.12
PDMS-2 lab-scale	19	2410	20.0	1.3989	46	3.16
PDMS-3 lab-scale	21	3700	20.0	1.3997	63	3.20
PDMS-1 3× scale-up	32	1130	21.0	1.3982	51	3.12
PDMS-2 3×scale-up	37	1740	20.0	1.3986	74	3.14
PDMS-3 3× scale-up	39	3590	21.0	1.4005	67	3.24
PDMS-1 5× scale-up	59	1270	20.0	1.3986	70	3.14
PDMS-2 5× scale-up	60	2490	20.0	1.3993	70	3.18
PDMS-3 5× scale-up	68	4320	21.0	1.4008	65	3.25
Commercial lowviscosity	-	1080	20.0	1.4044	-	-
Commercial high viscosity	-	3550	19.0	1.4040	-	-

with three timesand five times scale-up were classified as low viscosity PDMS. Samples of PDMS-2 were in the range of medium viscosity and samples of PDMS-3 were categorized as high viscosity. Commercial PDMS as a vitreous substitute has a low viscosity range of 931–1800 mPa.s, medium viscosity range of 1800–3420 mPa.s, and high viscosity range of 3420–5500 mPa.s [22–25]. Low-viscosity PDMS is easy to inject into the eye but tends to undergo emulsification more quickly. Previous research indicated that PDMS with medium viscosity was successfully obtained and tends to undergo less emulsification compared to high-viscosity PDMS. On the other hand, high-viscosity PDMS tends to experience less emulsification, but it is hard to inject into the eyes [23,26,27]. The refractive index value ranges from 1.3982 to 1.4008. The difference between the refractive index value of PDMS and VH may lead to additional diopters ranges from + 3.12 D to +3.25 D, as shown in Table 2. The additional diopters are still in the range of allowable value. The value of surface tension ranges from 20 to 21 mN/m. PDMS with a surface tension of 21 mN/m has a higher surface tension than commercial PDMS. PDMS used as a vitreous substitute must have high surface tension to avoid easy emulsification and to maintain the shape of PDMS so that it remains intact in the eye [7]. The value of yield is up to 70%. It represents the effectiveness of the production of PDMS. Overall, the synthesis of the PDMS scale-up three times and five times larger than the lab-scale took between 32–39 min and 59–68 min, respectively, while the lab-scale synthesis took between 15 and 21 min. This indicates that the synthesis of three times and five times scale-up PDMS required more time than the lab-scale. The longer the polymerization time, the higher the viscosity. The effect of polymerization time on viscosity of PDMS is represented in Figure 2.

Figure 3 represents the FTIR characterization results of lab-scale PDMS (a), three times scale-up PDMS (b), five times scale-up (c), and commercial PDMS (d). Table 3 displays functional groups at specific wavenumbers. In the lab-scale PDMS, there were vibration of Si–C at 804 cm^{-1}, Si–O–Si at 1084.4 cm^{-1}, asymmetric deformation CH_3 of Si–CH_3 at 1264.9 cm^{-1}, symmetric deformation CH_3 of Si–CH_3 at 1411.9 cm^{-1}, and CH of CH_3 at 2905.4–2965.1 cm^{-1}. Three times scale-up PDMS showed vibration of Si–C at 852.10 cm^{-1}, Si–O–Si at 1032.26 cm^{-1}, asymmetric deformation of CH_3 of Si–CH_3 at 1264.35 cm^{-1}, asymmetric deformation CH_3 of

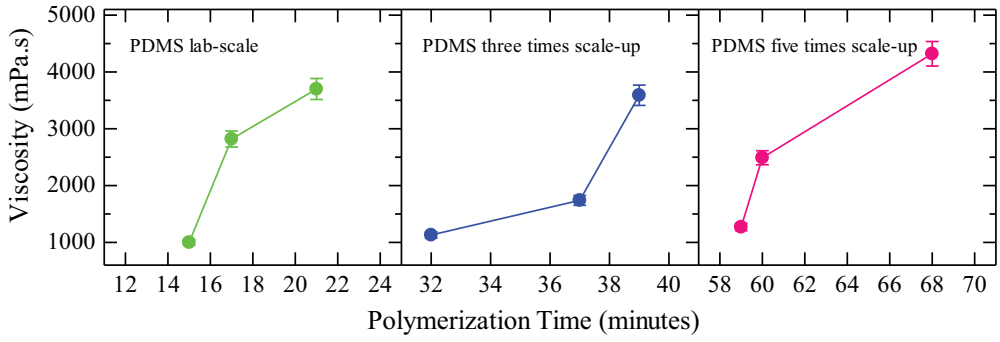

Figure 2. Effect of polymerization time on viscosity of PDMS.

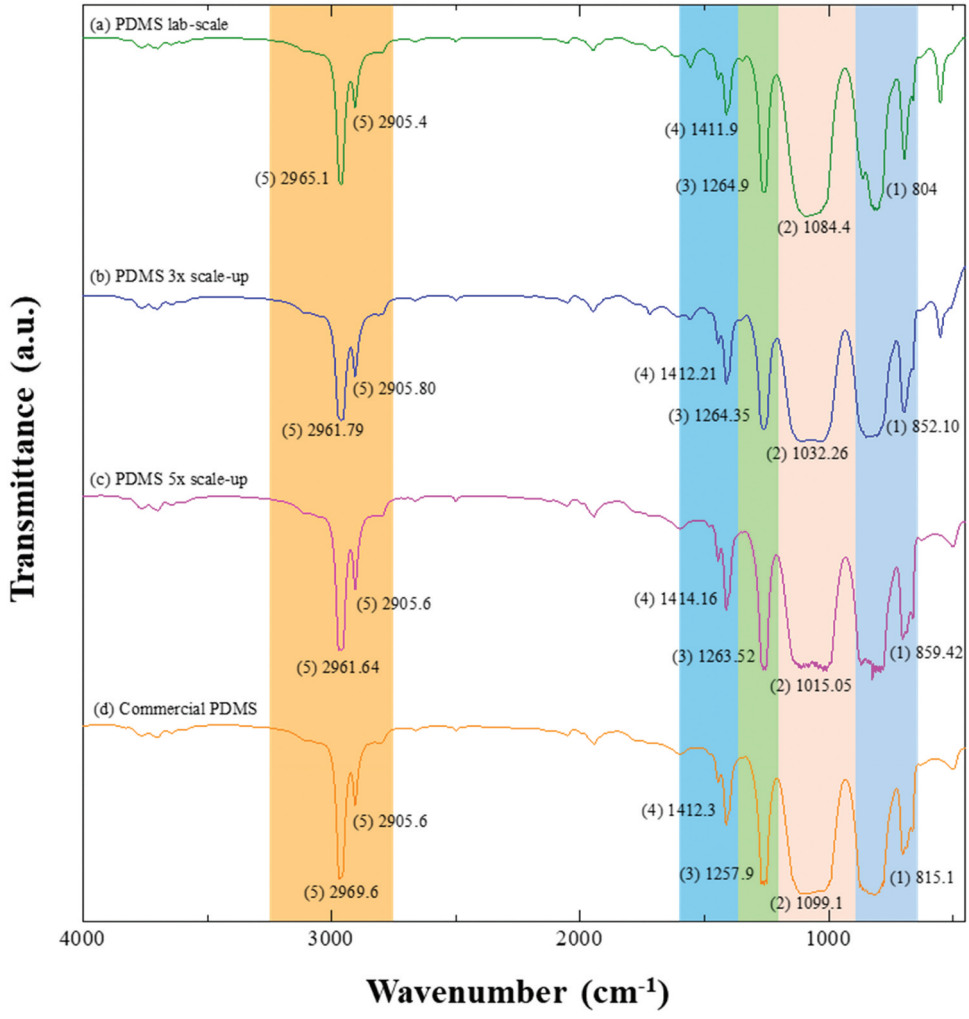

Figure 3. Result of FTIR characterization of (a) lab-scale PDMS, (b) three times scale-up PDMS, (c) five times scale-up PDMS, and (d) commercial PDMS.

Si–CH_3 at 1412.21 cm^{-1}, and CH of CH_3 at 2905.80–2961.79 cm^{-1}. Five times scale-up PDMS showed vibration of Si–C at 859.42 cm^{-1}, Si–O–Si at 1015.05 cm^{-1}, asymmetric deformation of CH_3 of Si–CH_3 at 1263.52 cm^{-1}, asymmetric deformation CH_3 of Si–CH_3 at 1414.16 cm^{-1}, and CH of CH_3 at 2905.6–2961.64 cm^{-1}. It was found that PDMS samples from both lab-scale and scale-up had the same functional groups as commercial PDMS with a slight shift in the wave numbers.

Table 3. Functional groups of lab-scale, three and five times scale-up PDMS.

Functional group	Wavenumber (cm^{-1})			
	Lab-scale PDMS	Three times scale-up PDMS	Five times scale-up PDMS	Commercial PDMS
(1) Si–C stretching and CH_3 rocking	804	852.10	859.42	815.1
(2) Si–O–Si stretching	1084.4	1032.26	1015.05	1099.1
(3) CH_3 symmetric deformation of Si–CH_3	1264.9	1264.35	1263.52	1257.9
(4) CH_3 asymmetric deformation of Si–CH_3	1411.9	1412.21	1414.16	1412.3
(5) CH stretching of CH_3	2905.4; 2965.1	2905.80; 2961.79	2905.6; 2961.64	2905.6; 2969.6

Conclusions

The synthesis of three times and five times scale-up PDMS has been successfully conducted through ROP by changing the volume of raw materials D4, HMDS, catalyst KOH, and the reactor with stirrer speed and polymerization temperature the same as the lab-scale. Synthesis of scale-up PDMS requires more polymerization time than the lab-scale PDMS. The viscosity of synthesized PDMS is 1000, 2410, and 3700 mPa.s for lab-scale, which can be categorized as low viscosity, medium viscosity, and high viscosity. The viscosity of synthesized PDMS for three times scale-up is 1130, 1740, and 3590 mPa.s and the viscosity of synthesized PDMS five times scale-up is 1270, 2490, and 4320 for which can be categorized as low viscosity, medium viscosity, and high viscosity. The values of surface tension, refractive index, and additional diopters are within the expected values. The results of FTIR characterization indicate that the functional groups of synthesized PDMS are similar to those of commercial PDMS, proving that PDMS with three times and five times scale-up has been successfully obtained.

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Disclosure statement

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