Effect of KOH concentration on characteristics of polydimethylsiloxane synthesized by ring opening polymerization method

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Abstract. Polydimethylsiloxane (PDMS) that widely known as silicone oil is commonly used as vitreous humour substitutes in vitreoretinal surgery. PDMS is needed to be produced in Indonesia and should be provided with sufficient quantity and quality for domestic needs. We synthesized PDMS using ring-opening polymerization method from octamethylcyclotetrasiloxane as monomer, hexamethyldisiloxane as chain terminator, and KOH as catalyst. KOH concentrations are varied from 0.5 M to 2.5 M to study the effect of KOH concentration on characteristics of PDMS. PDMS We successfully synthesized PDMS with a yield in between 39.73% and 65.30% and various viscosities in the range between 0.58 Pa.s and 9.36 Pa.s. From FTIR spectroscopy, it is found that all synthesized samples have structure and functional groups similar with that of commercial PDMS. From UV-Vis and refractometer measurements, all samples have transparency almost 100% and refractive indexes in the range of 1.3989 to 1.4039. The effect of KOH concentration on the synthesized PDMS gel is on its viscosity, the higher concentration of KOH, the higher viscosity of the obtained PDMS.

1. Introduction

Eyes are optical system, which is very important to support our daily activities. The largest part of human eyes is a liquid called vitreous humour. Disorders of some parts of human eyes in vitreous humour is commonly occurred. One of disorders in vitreous humour is a damage causes retinal detachment. In that case, the retinal neurosensory layer is separated from the epithelium pigment. Same factors that usually cause retinal detachment are acute posterior vitreous detachment (PVD), myopi, afakia, and trauma [1]. A treatment of the retinal detachment can be done by using artificial replacement fluid to replace the vitreous humour in the human eyes. The artificial replacement fluid is known as vitreous substitutes or tamponade agents. An ideal vitreous substitutes is a liquid that has high surface tension, optically clear, and biologically inert [1].

One of liquids that commonly used as vitreous substitutes in vitreoretinal surgery is polydimethylsiloxane (PDMS) known as silicone oil. The aims of replacement of vitreous humour are to restore a normal retinal position in the eyes, to restore the volume of vitreous cavity, and to assist
surgeons in the membrane surgery [2]. The study of optical and structure properties of commercial PDMS before and after vitreoretinal surgery in Indonesia has been performed and found that some additional functional groups were observed after a few months of vitreoretinal surgery [3]. It causes commercial PDMS should be replaced several times. There are limitations in availability of commercial PDMS in Indonesia, PDMS is needed to be produced and should be provided with sufficient quantity and quality for domestic needs.

There are many polymerization methods in synthesis PDMS such as addition polymerization, condensation polymerization, and ring opening polymerization. We studied a synthesis of PDMS as a vitreous substitute for domestic production. Previous works reported synthesis of PDMS by ring-opening polymerization method [2, 4]. In this work, a cyclic chain of monomer is breaking into a linear chain by applying high temperature treatment. A catalyst needed in this polymerization technique. Some catalyst such as tetramethylammonium silanolate, tetramethylphosphonium-siloxanolate, tetramethylammoniumsiloxanolate, alkaline metal hydroxides are frequently used in the ring opening polymerization [2]. We used KOH as one of alkali metal hydroxides since this chemical is readily available.

2. Experiment
The polymerization process was initiated by mixing 7.8 ml octamethyleneoctamersiloxanone (D4) as monomer and 3 ml hexamethylenebisiloxane (MM) as chain terminator. The mixture was stirred using a magnetic stirrer at 300 rpm in oil bath at a temperature 170°C. The oil bath was used to maintain temperature stability during polymerization process. Then, 0.06 ml KOH catalyst with a certain concentration was added slowly into the solution. The solution was further stirred for 45 minutes to form a thick and clear gel. The various concentrations of KOH were performed with value in between 0.5 M and 2.5 M.

In order to remove residual monomers and a residual KOH from the PDMS gel, the synthesized PDMS was purified by using solvent extraction method. The purification process was started by dissolving the synthesized PDMS with chloroform with volume ratio of 1:1. The solution was mixed until it became homogeneous. Mili-Q water was added into the PDMS solution with ratio of 1:2. The mixture was stirred and then waited for about 10 minutes until form a two phase mixture of the solution. The bottom phase is a PDMS solution in chloroform and the upper phase is mili-Q water containing KOH and residuals of monomer. The PDMS solution was separated from the aqueous phase and the pH of the aqueous was checked. If the pH of the aqueous phase is not 7, some mili-Q waters were added again into the PDMS solution. The process was repeated until the pH of the aqueous phase is 7. The PDMS solution in chloroform was stirred and heated at 50°C to remove the chloroform solvent to obtain a transparent PDMS gel.

All samples were characterized using viscometer to measure viscosity, FTIR spectroscopy to identify its functional groups, refractometer to determine refractive index and UV-Vis spectrophotometer to measure transparency.

3. Results and Discussion
The synthesized PDMS gel obtained using ring opening polymerization method is thick and transparent. After purification, the synthesized gel seem more clear as compare to the condition before purification. A yield of PDMS calculating from different amount of monomer and resulted polymer is shown in table 1. The highest yield was obtained in sample with 1 M KOH and the smallest yield was obtained in sample using 0.5 M KOH. From yield value, it is found that optimal concentration of KOH was 1 M.

The highest yield obtained in this synthesis is 65 % which is still relatively small. It is might be due to the high polymerized temperature causing some monomers to be evaporated during the polymerization process.

Viscosity of the synthesized PDMS was displayed in table 1. The value of viscosity of PDMS obtained using 2.5 M KOH was 8.66 Pa.s, while the sample using 0.5 M KOH was 0.58 Pa.s. The
viscosity of synthesized PDMS was significantly increased with increasing concentration of KOH from 0.75 M to 1 M KOH. The viscosity slightly decreased when KOH concentration increased larger than 2 M KOH. Liquids with short polymer chains (low molecular weight) have low viscosity, and liquids with long polymer chains (high molecular weight) have high viscosity. This suggests that increasing of KOH concentration affects propagation of the polymer chain and resulted increasing of molecular weight. The longer PDMS chain formed, the thicker viscosity and the higher PDMS molecular weight. Synthesized PDMS using 0.75 M KOH has viscosity that very close with the viscosity of commercial PDMS of 3.55 Pa.s.

| Table 1. The yield of synthesized PDMS at varied concentrations of KOH. |
|---------------------------------------------------------------|
| **Concentration of KOH (M)** | **Mass of Monomer (gr)** | **Mass of Polymer (gr)** | **Yield (%)** | **Viscosity (Pa.s)** |
| 2.50 | 10.28 | 5.35 | 52.04 | 8.66 |
| 2.00 | 10.33 | 5.80 | 56.20 | 8.36 |
| 1.00 | 10.46 | 6.83 | 65.30 | 9.36 |
| 0.75 | 10.13 | 4.59 | 45.29 | 3.65 |
| 0.50 | 10.15 | 4.03 | 39.73 | 0.58 |

In vitreoretinal surgery, when low-viscosity tamponade agents or liquid was used, it will be readily reabsorbed in short time. Conversely, PDMS that has high viscosity is expected to be durable as a tamponade agent.

Figure 1 shows FTIR spectra of all synthesized PDMS. For comparison, the spectrum of commercial PDMS was also displayed in figure 1(f). It is found that all samples had functional groups of PDMS. The FTIR spectra of the commercial PDMS have vibration of C – H bond in the ranges of 2905 cm\(^{-1}\) and 2962 cm\(^{-1}\), Si – \(\text{CH}_3\) bond in the range of 1262 cm\(^{-1}\), Si – O – Si bond in the range of 1099 cm\(^{-1}\) and 1025 cm\(^{-1}\), Si – C bond in the range of 800 cm\(^{-1}\), and \(\text{CH}_3\) bond in the range of 1412 cm\(^{-1}\). FTIR spectra of all synthesized PDMS using various KOH concentrations show identical frequency of C-H bond in the range of 2897 – 2969 cm\(^{-1}\) dan 2897 – 2906 cm\(^{-1}\), Si – \(\text{CH}_3\) bond in the range of 1262 – 1264 cm\(^{-1}\), CH\(_3\) bond in the range of 1407 – 1418 cm\(^{-1}\), Si – O – Si bond in the range of 1091 – 1098 cm\(^{-1}\) and 1019 – 1026 cm\(^{-1}\) and Si – C bond in the range of 799 – 805 cm\(^{-1}\). This indicates that all synthesized PDMS samples have same structure which is similar with commercial PDMS.

Table 2 shows the value of refractive index for PDMS with various KOH concentrations. The refractive index measurements were carried out at a maintained room temperature of 20° C. The value refractive index was observed in the range of 1.3989 – 1.4036. The differences in refractive index is not significant but still in the range of the values.

| Table 2. The refractive index of PDMS synthesized with various KOH concentrations at 20°C. |
|---------------------------------------------------------------|
| **Concentration of KOH (M)** | **Refractive Index** |
| 2.50 | 1.4036 |
| 2.00 | 1.4034 |
| 1.00 | 1.4030 |
| 0.75 | 1.4008 |
| 0.50 | 1.3989 |
Figure 1. FTIR spectra of synthesized PDMS (a) KOH 2.5 M, (b) KOH 2 M, (c) KOH 1 M, (d) KOH 0.75 M, (e) KOH 0.5 M and (f) commercial PDMS.

Figure 2. Transmittance spectra of the synthesized PDMS in the UV wavelength range.
The refractive index of PDMS is higher compared to the refractive index of actual vitreous humour which is in the range of 1.3345 to 1.3348 [5]. Significant differences of refractive index values can cause complications of myopia to vitreoretinal surgical patients. Changes in refractive index values result in the adhesion of silicone oil to intraocular lenses [6]. Since the refractive index of PDMS measured at outside the human body, there is a possibility of refractive index value of PDMS changed when PDMS gel is injected into the eye. It is because the value of refractive index is highly depend on the ambient temperature.

Transparency of synthesized PDMS was measured in transmittance mode. PDMS samples synthesized using KOH with concentration of 0.5 M and 0.75 M were measured in the range of 190 nm to 400 nm as representation of absorption of PDMS gel in the UV range. Through visual observation, PDMS gel with KOH concentration of 0.5 M is more clear than the one synthesized with KOH concentration of 0.75 M. The quantitative transmittance of both PDMS samples is shown in figure 2.

![Transmittance spectra of synthesized PDMS gel at the visible range.](image)

The PDMS gel with KOH concentration of 0.5 M has a 100% transmittance value and the transmittance decrease at 249.8 nm. The decreasing transmittance indicates that PDMS gel sample was being absorbed at UV wavelength. While the PDMS synthesized with KOH concentration of 0.75 M has a low transmittance in the UV range and start to decrease at of 249.9 nm. These data shows that PDMS was absorbed the UV wavelength.
The synthesized PDMS samples were measured in the visible wavelength in the range of 380 nm to 1100 nm are shown in figure 3. From the spectra, it can be seen that all transparencies of PDMS gel are almost 100%. PDMS synthesized using 0.5 M KOH is 100%. Other PDMS samples have a transmittance slightly below 100 %. The transparency corresponds to visual observation that PDMS gel synthesized with 0.5 M KOH seem more clear than PDMS synthesized with other concentration of 0.75 M, 1 M, 2 M, and 2.5 M.

4. Conclusion
We have succeeded to synthesis PDMS gel using ring-opening polymerization method using octamethylcyclootetrasiloxane (D4) as monomer, hexamethyldisiloxane (MM) as chain terminator at various concentrations of KOH. The synthesized PDMS gel are transparent, viscous and has yield in the range of 40 % to 65 0% with various viscosities in the range between 0.58 Pa.s and 9.36 Pa.s. The synthesized PDMS gel has similar structure as commercial silicone oil with refractive index value in the range of 1.3989 - 1.4036. All transparency properties of PDMS gel are almost 100%. The KOH concentration strongly affect the viscosity of the PDMS, the higher concentration of KOH, the higher viscosity of synthesized PDMS.

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