

Parametric Studies of Polymethacrylate-based Monolith Fabrication

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ABSTRACT Polymethacrylate monoliths (PM) have interconnected pores that allow physical form of filtration whereby particles that are smaller than the pore size can flow through while particles that are larger than the pore size are unable to pass through. The size of the pores determines the effectiveness of PM in filtering certain particles. Larger pore size means more void spaces within the structure of a monolith which affects its mechanical strength. Besides that, pore size also affects the flow rate and energy required to push a liquid sample through for filtration. Therefore, information regarding parameters that affect the pore size formation of a fully polymerized PM is important not only for the targeted particle size, but also for the structural strength and operating energy requirement of the intended filters. Among the parameters investigated were thickness of monolith, percentage of porogen, percentage of initiator and polymerization temperature. Higher polymerization temperature yield PM with smaller pore size. The increase of percentage initiator and porogen used were observed to increase the pore size of the PM formed. Finally, the pore size of PM becomes bigger as the monolith becomes thicker (observed from 1 mm to 5 mm thickness).

KEYWORDS: Polymethacrylate monolith; Pore size; Monolithic membrane; Polymerization; Parametric Studies

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INTRODUCTION

Monolithic polymer membranes consist of single structures with many interconnected pores. The interconnected pores are thin, vertical, parallel channels, separated from each other by walls. The geometry of the monolith channels is usually rectangular; however, hexagons or more complex geometries also exist (William, 2001). One important characteristic of polymethacrylate-based monolith fabrication is that its functional group, shape and size of pore can be readily altered by modifying the type and ratio of monomer/s, porogenic solvent and ligands (e.g., enzymes and ion exchange groups) to target the different components in wastewater (e.g., suspended solid particles, virus, microbes, organic and inorganic compounds).

Chemicals needed in the production of polymethacrylate monolith are the initiator (2,2'-azobisisobutyronitrile, AIBN), the functional monomer (GMA), cross-linker (EDMA) and porogen (cyclohexanol/dodecanol), which were thoroughly mixed. Sparging of the mixture to remove oxygen is sometimes required especially if it was produced in a large batch before poured inside a mold. Polymerization was then done at a temperature where the initiator decomposes to start the reaction in no less than 2 hours. Initially, the mixture will be a clear liquid and slowly solidifies into a single porous white monolithic structure as the process comes into completion (Mihelič *et. al.*, 2001). Finally, the porogen within the void region of the polymethacrylate monolith was flushed out using methanol.

The polymerization of a polymethacrylate monolith is a heat-based free radical reaction process. When heat is supplied, the initiator will start to decompose which in turn form free radicals that attack the carbon bond of the monomers thus forming polymer (Danquah & Forde, 2008). The decomposition of the initiator into free radicals will produce exothermic heat. Interaction between the free radicals and the monomer will form gel-like species known as nuclei which acts as the seeding nucleus in the development of microglobules. The lack of solubility of the polymer in porogenic solvent and the crosslinking of polymer chains result in phase separation. Polymerization

process continues within the nuclei due to the higher concentration of monomers compared to that in the surrounding solution (Buchmeiser, 2007). As the polymerization progresses further, polymer chains that are branched or cross-linked in the solution continue to grow inside and outside the nuclei until all become connected thereby forming a single interconnected porous material (Arrua *et al.*, 2009). The shape and structure of a polymethacrylate monolith are highly affected by the conditions of its polymerization process which opens up possibilities to tailor their morphology in accordance to their needs (Jungbauer & Hahn, 2008).

METHODOLOGY

Materials

Azobisisobutyronitrile (AIBN), glycidyl methacrylate (GMA) 97%, ethylene glycol dimethacrylate (EDMA) 98%, cyclohexanol 99% and methanol AR grade $\geq 99.5\%$.

Preparation of polymethacrylate monolith sample at different conditions

A typical polymethacrylate monolith was prepared via free radical co-polymerization of cross-linker EDMA and GMA as functional monomers. EDMA/GMA mixture was combined with an alcohol-based porogenic solvent in a different proportion depending on the percentage of porogen used. The initiator, AIBN (in % weight used with respect to monomer), was added to initiate the polymerization reaction. The polymer mixture was sonicated for 20 min. The mixture was then transferred into 15 mm diameter and 120 mm height Econo column (BIORAD) sealed at the bottom end. The top end was sealed with a parafilm sheet and placed in a water bath for 3 h at 60 °C. The standard setting for the polymerization process apart from the parameter tested (refer Table 1) were, 5.66 mm monolith thickness, 60% porogen, 1% initiator and 60 °C polymerization temperature.

Table 1. Experimental setup

Parameters tested/ Independent variables	Percentage of porogen (%) (30, 40, 50 & 60)	Percentage of initiator (%) (1, 2, 3 & 4)	Polymerization temperature (°C) (50, 60, 70 & 80)	Monolith thickness (mm) (1.42, 2.83, 4.25, 5.66)
Controlled variables	Thickness : 5.66 mm % of initiator : 1%	Thickness : 5.66 mm % of porogen : 50%	Thickness : 5.66 mm % of porogen : 50%	% of porogen : 50% % of initiator : 1%
Dependent variables	Polymerization temperature : 60°C	Polymerization temperature : 60°C	% of initiator : 1%	Polymerization temperature : 60°C
Pore sizes of polymethacrylate monolith (microns)				

SEM sample analysis

Polymethacrylate monolith was removed from the column and transferred into a 250-ml conical flask filled with 100 ml of methanol. It was then placed inside an incubator shaker overnight at 100 rpm and 35 °C. The methanol was then replaced with 100 ml of deionized water and placed inside the incubator shaker under similar conditions for 5 h. Prior to analysis, the monolith was oven dried at 70 °C overnight. High resolution scanning electron microscope (Hitachi S-3400N, Japan) was used to analyze the sample at 15 kV according to the manufacturer's instructions. The images captured from SEM were then measured using Image J software in order to determine the pore size of the monolith.

RESULT AND DISCUSSION

Effects of different parameters on pore size of polymethacrylate monolith

The effects of 4 parameters on pore size of polymethacrylate monolith were tested. These parameters were the thickness of the monolith, the percentage of porogen, the percentage of initiator and the initial polymerization temperature.

Effect thickness on the pore size of polymethacrylate monolith

Figure 1 shows the effect of thickness of polymethacrylate monolith on pore size. At 2.83 mm and below, no formation of pore was observed as the whole polymethacrylate was crystalized, while at 4.25 mm and 5.66 mm there was an increase in pore size. Thicker monolith results in poorer heat transfer which affects the kinetic of polymerization process. However, this data is only valid up to 5.66 mm thickness

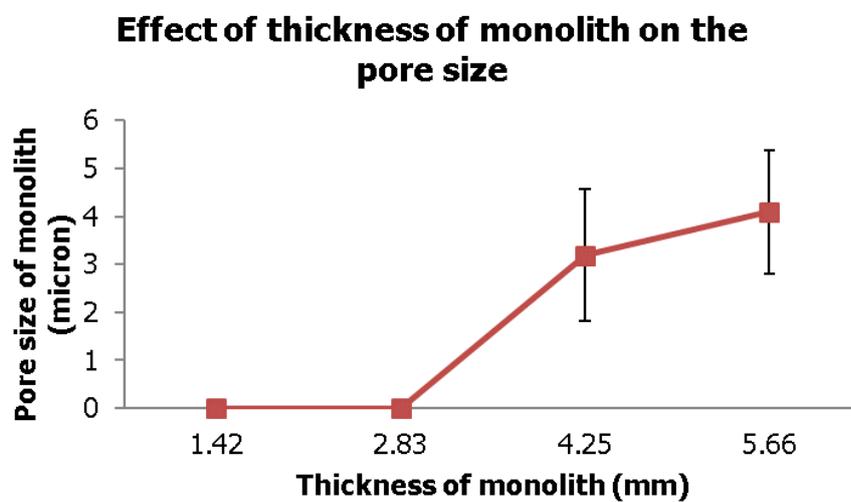


Figure 1. Effect of the thickness of monolith on the pore size of the polymethacrylate monolith

Effects of percentage of porogen on pore size of polymethacrylate monolith

Figure 2 represents the effect of percentage of porogen on the pore size of polymethacrylate monolith. The regulation of porogen content is the most common approach to control the pore size of monolithic membrane. As expected, the higher the percentage of porogen used, the bigger the pore size formed. An increase in the porogen content leads to less cross-linked nuclei. This will increase their swelling causing higher concentration of the monomers in the swollen gel nuclei compared to that in the solution. Consequently, the chances of newly formed nuclei adsorbed by the macro pre-formed globules by coalescence of nuclei in abundance will be greatly increased. The increase in local concentration of monomer increases the size of the globules which in the end results in increased pore size.

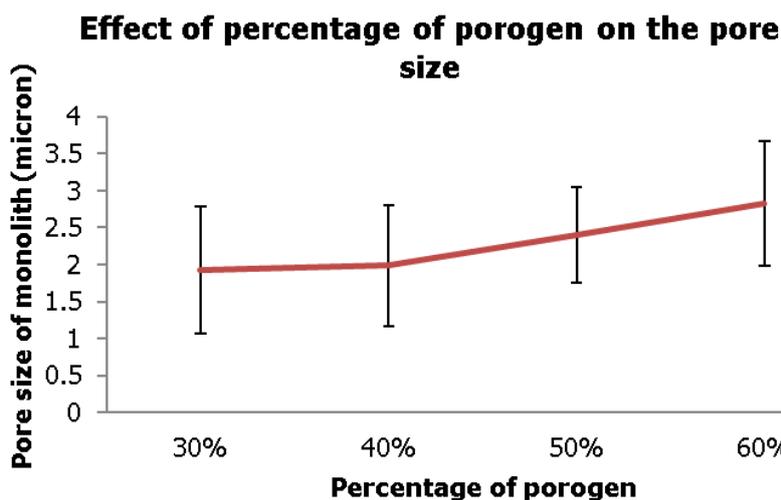


Figure 2. Effect of percentage of porogen used on pore size of polymethacrylate monolith

Effects of percentage of initiator used on pore size of polymethacrylate monolith

The effects of percentage of initiator used on the pore size of monolith membrane can be seen in Figure 3. Under normal polymethacrylate monolith polymerization process, 1% of initiator (1% weight with respect to total monomers) was used. In this study, the effects of increasing the amount of initiator on pore size were tested. Based on the result in Figure 3, higher initiator content resulted in bigger pore size. This could be attributed to polymethacrylate monolith shrinkage during the drying process. According to Alves *et al.*, (2013), an increase in the amount of initiator would result in an increased degree of crosslinking thus reduced shrinkage after drying process.

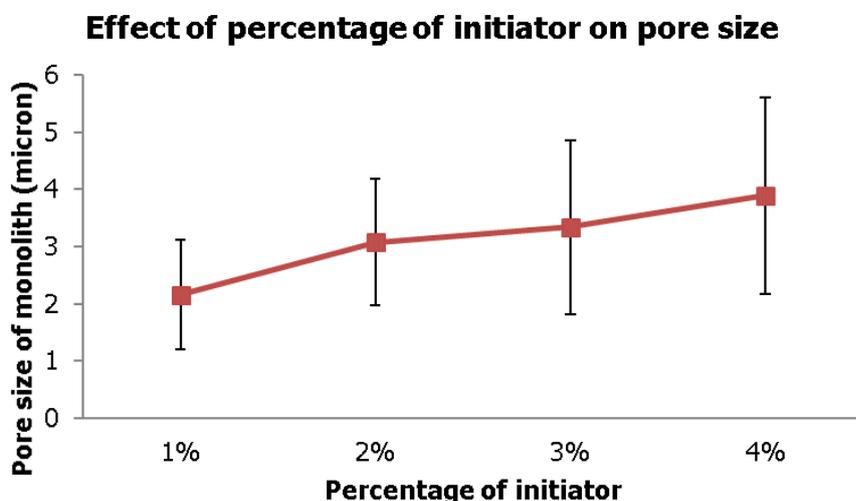


Figure 3. Effect of percentage of initiator used on pore size of polymethacrylate monolith

Effects of initial polymerization temperature on pore size of polymethacrylate monolith

Figure 4 depicts the effect of initial polymerization temperature on the pore size of polymethacrylate monolith. In heat-induced polymerization process, temperature dictates the kinetic energy of the process. It affects the rate of decomposition of an initiator into free radical, phase separation and nuclei growth. At low temperatures, the monomers in the pre-polymerized mixture receive a small amount of energy. The formation of free radicals occurs at a slow rate allowing for gradual phase transition from micro-globules to long inter-connected polymer chains hence bigger pore size. At high temperatures, whereby the kinetic energy is also high, the phase

transition occurs at a much faster rate resulting in short inter-connected polymer chains hence smaller pore size (Bisjak *et al.*, 2007). The increase in pore size at 60°C is regarded as an anomaly.

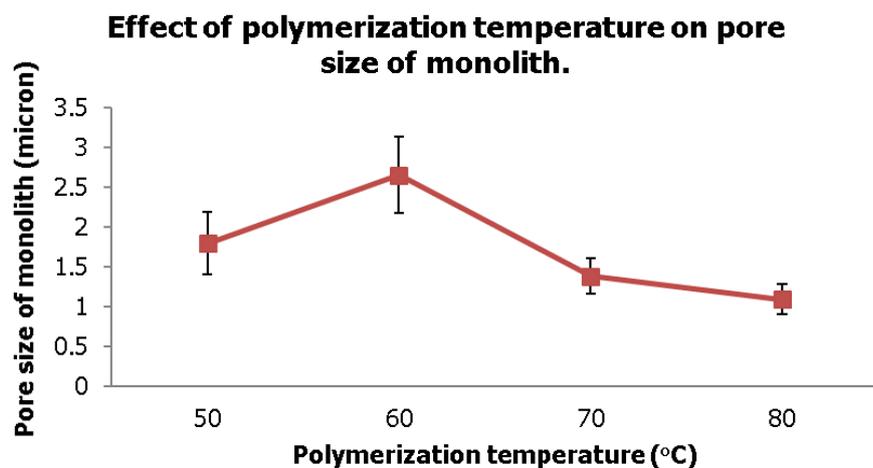


Figure 4. Effect of polymerization temperature on pore size of polymethacrylate monolith

CONCLUSION

Parameters that affect the pore size of polymethacrylate monolith comprise thickness of monolith, polymerization temperature, percentage of porogen used and percentage of initiator used. Current findings show that the percentage of porogen and initiator are directly proportional to the pore size of monolith. For the effect of monolith thickness, the increase in thickness resulted in increased pore size; however, data were limited up to only 5.66 mm thickness. As for the effect of polymerization temperature, the pore size decreased with temperature. The pore size reading at 60°C was regarded as an anomaly.

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