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Melt blown polypropylene nanofiber template for homogenous pore channels monoliths

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Abstract. Monoliths are an important technology for filtration, liquid chromatography, and protein purification. A template commonly uses to produce porous monolith. However, it is a challenge to produce a monolith with a homogenous porous structure due to the arrangements of pores within the monolith are often uneven and sometimes closed, causing pressure to accumulate and increase within the monolith which reduce the efficiency of the monoliths. Therefore, an appropriate template is needed to produce a monolith with homogenous porous structure. Nanofiber is a potential alternative as a template due to its high porosity and interconnectivity. Therefore, this research aimed to investigate the potential of polypropylene melt blown nanofiber fabricated at various operating condition to fabricate monolith by assessing the monolith morphology. Nanofibers templates were produced using a melt blowing technique at various motor speeds, air pressures, and die-to-collector distance (DCD) between 30 and 50 Hz, 0.30 and 0.50 Mpa, and 20 and 50 cm respectively, design by Response Surface Methodology. The nanofibers were characterized for its morphology and melting point using scanning electron microscope (SEM) and molten point analysis instrument respectively. The findings show that the polypropylene nanofiber diameter was in the range of 3.58 to 11.00 x 10³ nm. Meanwhile, melting point obtained were in the range of 121.0 to 128.8 °C. Subsequently macropores monoliths were successfully fabricated at 0.45 Mpa air pressure, 40 Hz motor speed and 60.23 cm die-to-collector distance. It can be concluded that, melt blown polypropylene nanofiber can be potentially applied as a template for monolith fabrication.

1.0 Introduction

Recently, monoliths have emerged as an important technology for separation/adsorption matrix in biomedical and environmental fields, high performance liquid chromatography [1], filtration [2], protein purification [3] and in enzymatic bioreactor for bioprocessing [4]. A monolith is a material with porous structure and has a significant amount of interconnected pores that allow substances to flow through the column at low pressure [5].

Porous structure monoliths enable high fluid flow at low pressure drop [6]. For biomolecule separation and purification, the high mobile phase flow enables a high separation capacity [7]. Furthermore, monolith can simultaneously act as an enzyme carrier and a reactor for a continuous bioreaction process therefore increase the reactor productivity[3].

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The porous structures inside the monolith are formed using a template usually biodegradable polymers or the supramolecular aggregate. Free radicals and toxic additives such as porogens, cross-linkers and other compounds able to form porous distributions within the monolith [4]. However, current monolith preparation technologies have limitations, including “wall channel effect”, low dissipation of heat, weak mechanical strength and uneven pore distributions [4]. The uneven pore distributions within the monolith can lead to a pressure build up within the material. Therefore, to create homogeneous and well-structured pore distributions within the monolith, it is important to identify an appropriate template for the monolith fabrication.

Nanofiber can act as a template due to its precise control over porous structure. The properties of nanofiber can be altered so that it can be easily removed and creating a well-structured pore channels. Nanofiber is a material that has many desired characteristics, including high surface area, high porosity and interconnectivity, possess self-assembling behavior as well as able to establish a homogenous dispersion in liquid phase [7].

Melt blowing technique, produce nanofibers by co-extrusion of a high force ejection of polymer melts through a very small opening and a stream of cooling fluid such as air [9,10]. In this research, a melt blowing technique will be used to produce good quality nanofibers. However, there are some challenges to consider such as choosing the right operating parameters such as air pressure, polymer flow rate and die-to-collector distance (DCD) to produce a desired nanofibers. It is important to know the range of these parametric conditions in order to obtain good quality of nanofiber to form a homogenous pore distribution across a monolith structure.

To the best of our knowledge, the study on using nanofibers as monolith template has never been done before. Hence, this study will facilitate a better understanding on how the melt-blowing operating conditions affect the quality of nanofiber as a template to fabricate monolith. This information obtained from this research can be used to tackle some of the challenges faced in the fabrication of monolith.

2.0 Methodology

2.1 Experimental Design and Statistical Analysis

The experimental design was performed by using Response Surface Methodology (RSM) using Design Expert V.7.0.0 software as used in other studies [11,12]. The operating parameters such as air pressure (A), polymer flowrate (B) and DCD (C) were selected. The ranges were then set between 0.3 and 0.6 Mpa, 30 and 50 Hz and 20 and 50 cm for A, B and C respectively. A total runs of 20 experiments were designed with responses include the nanofiber diameter, melting point and heterogeneity.

2.2 Production of polypropylene nanofiber by melt blowing

Polypropylene (PP, Sun Allomer) was used as the precursor to produce nanofiber using melt blowing system (Japan Zetta Co. Ltd.). The PP was melted gradually at three stages at 200, 250 and 300°C respectively to avoid thermal degradation. The air temperature was set at 450°C. The other parameters were then set in accordance to experimental design by RSM. The solidified nanofibers then collected using an aluminium foil-surface collector.

2.3 Preparation of Polymethacrylate Monolith

2.3.1 Preparation of Polymethacrylate Monolith Solution and incorporation and removal of nanofiber template.

A 1% v/v of azobisisobutyronitrile (AIBN) was dissolved in 5 ml of solution containing 3 mL of porogen, 1.4 ml of glycidyl methacrylate (GMA) and 0.6 ml of ethyl dimethacrylate (EDMA). The GMA-EDMA was added in the ratio of 7:3 for the purpose of monolith preparation. 5 ml of the monolith solutions were mixed with 100 mg of nanofibers in a centrifuge tube and prepared each for nanofibers of samples A1-A3. Another 5 ml monolith solution was prepared without the addition of nanofibers as a control sample. The solution was subsequently mixed using a sonicator for 20 minutes and later heated in a water bath at 60°C for 3 hours. The solid monolith was next washed with methanol and left overnight. Afterwards, it was washed with distilled water and kept at room temperature prior to calcination process using a furnace (Thermolyne 46100) at 150°C for 30 minutes to burn off the nanofiber template from the nanofiber-monolith assembly.

2.3.2 Physicochemical Characterization of Nanofiber and Monolith.

The surface morphology and diameter of nanofiber and monolith samples were observed using Scanning Electron Microscopy (SEM, Hitachi S-3400N) and melting point analysis instrument (Bibby Stuart Scientific Melting Point SMP1) was used to analyze the melting point of the nanofiber samples.

3.0 Results and discussion

3.1 Nanofiber mean diameters and melting point

The diameter sizes of the nanofibers were found to be in the range of between 3.58 and 11.0 x 10³ nm. The morphological structure of each sample observed under SEM are presented in Figure 1. Samples 1, 8, 14, 16 and 19 showed unfavorable structure due to the insufficient separation between the fibers. This may due to low values of both air pressures and DCD, therefore lack of driving force to split the individual fibers [12]. Fused fibers, found in samples 11 and 13, may due to a sudden cooling by surrounding air [13].

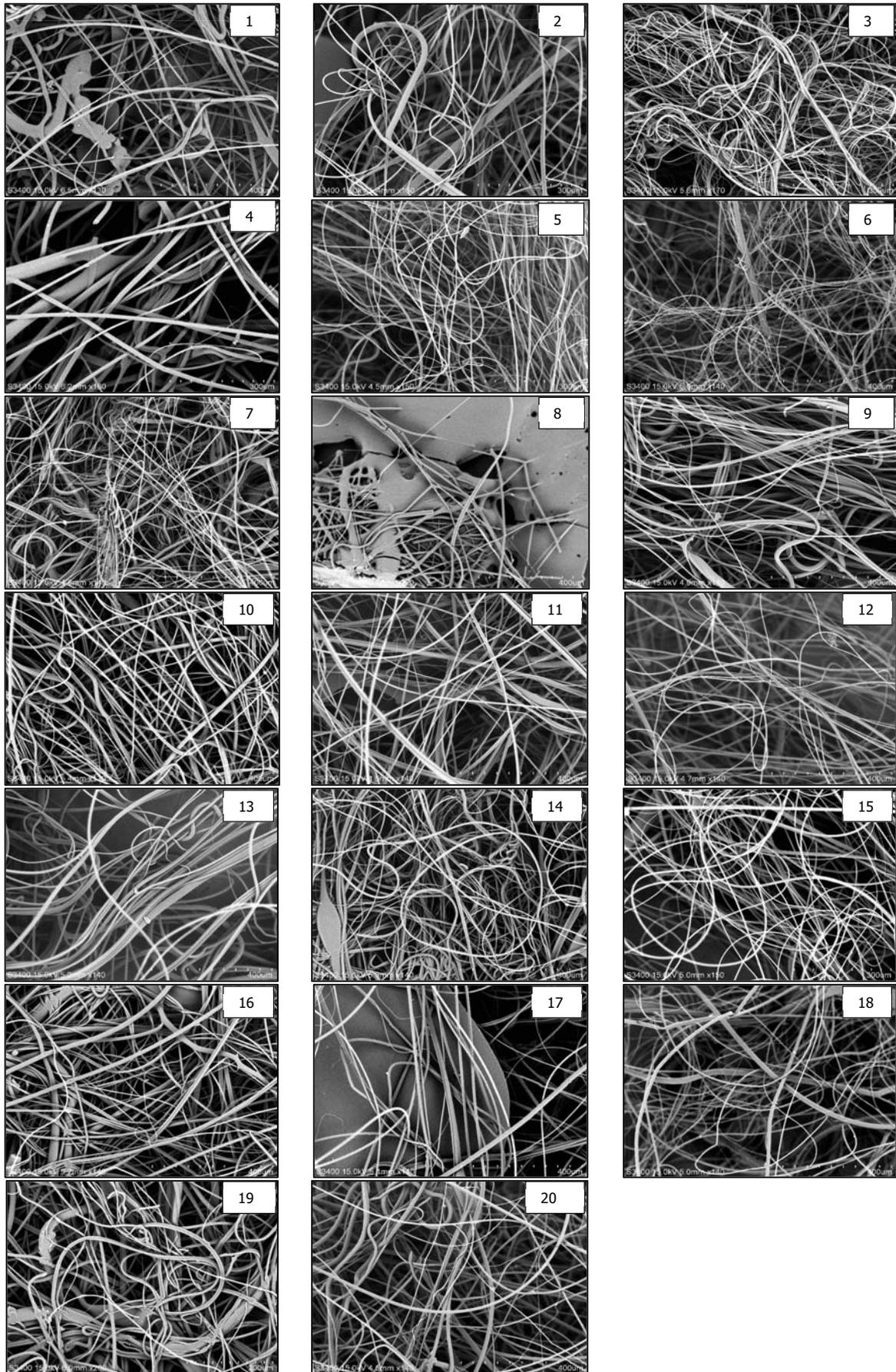


Figure 1. SEM images of the produce melt blown nanofibers.

The standard deviations of the average diameters of the nanofibers samples were plotted in Figure 2. Samples 1, 2, 4, 8, 12, 13, 18, and 20 demonstrated fiber size heterogeneity, however their average diameters were found to be above 6.0×10^3 nm. In contrast, samples 5, 6 and 15 which have a smaller diameter, were observed to have a low standard deviation. Based on Figure 2, sample 4 have the largest fiber diameter of 11.0×10^3 nm and sample 3 has the smallest diameter of 3.58×10^3 nm which is comparable with previous studies [14–18].

The melting point of the polypropylene granule was found at 139.3°C and the melt blown polypropylene nanofibers melting points were in the range of between 121 and 128.8°C . The result shows that, the melting properties of nanofibers were not significantly affected by the melt blowing process, but its melting point has slightly reduced in comparison with the polypropylene granule.

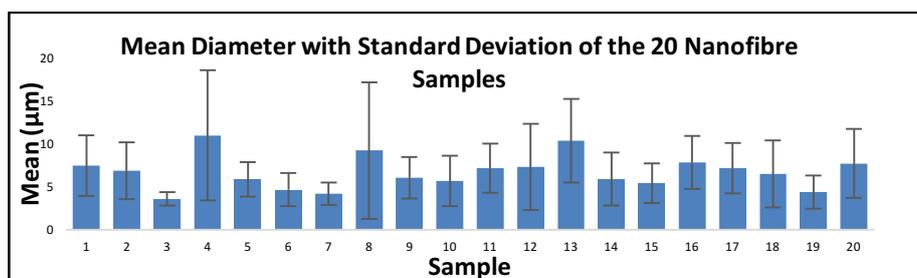


Figure 2. Mean diameter with standard deviation of nanofiber samples.

3.2 Selection of Nanofiber Template

Sample 5, 6 and 15, which later denoted as A1, A2 and A3 respectively, were chosen based on their morphological structures, mean diameters, and melting point as templates. Although a small amount of beads were present, most of the fibers were finer, forming homogenous fiber mats and continuous shown by SEM images. The average fiber diameter for A1, A2 and A3 samples were 5.89 , 4.68 and 5.43×10^3 nm, respectively. Samples A1-A3 were produced at various points across the ranges for air pressure (0.6 , 0.3 , 0.45 Mpa) and motor speed (30 , 50 , 40 Hz), but at a higher range of DCD (50 , 50 and 60.23 cm) respectively.

3.3 Incorporation of Nanofiber Template into Monolith and removal of Nanofiber Template from Monolith

After 3 hours of immersion in a water bath at 60°C , the mixtures of nanofibers samples and monolith solutions, solidified into white solid and nanofiber could be observed on sample A1, A2 and A3 while none was observed on controlled sample (Figure 3). After washing the samples with methanol to remove unreacted monomeric reagents, inert porogen and droplets of condensed water [19] and later washed with distilled water, the samples looked firmer and more solid and were left to dry. The samples were eventually harden when fully dried and subsequently, subjected to a calcination process to remove the nanofiber-template from the nanofiber-monolith assembly.

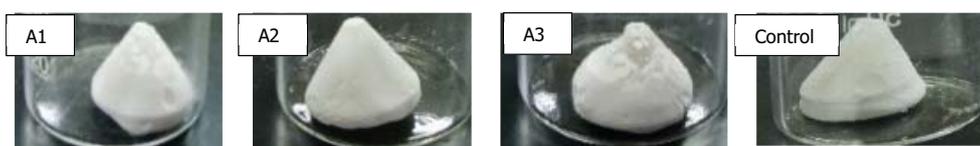


Figure 3. Samples A1-A3, and a control sample before being washed with methanol.

After the calcination process, sample A1 and A3 shows several holes on the top part meanwhile sample A2 shows intact top part (Figure 4). For bottom part all samples show some cracks on the bottom part. Unlike sample A1, A2 and A3, the control sample shows intact top and bottom part. This was due to there was no nanofiber incorporated in the control sample, making the porous properties contributed only by the porogen.

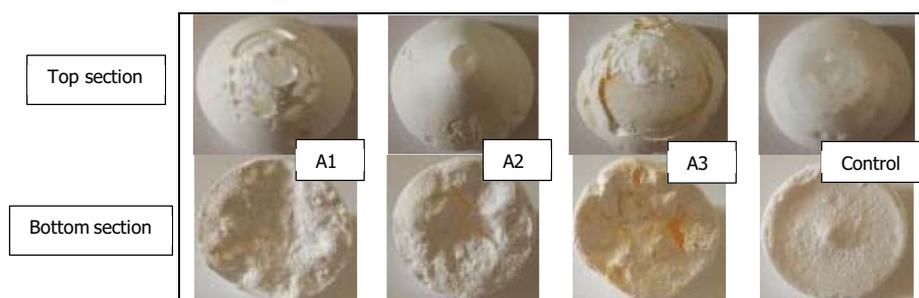


Figure 4. Top and bottom part of sample A1- A3, and control sample after calcination.

3.4 Characterization of Monolith after Calcination

Microscopic analysis by SEM shows that, monolith sample of A1, A2 and A3 tend to be isotropic in structure as shown in Figure 5. These results are similar with monolith fabricated by [20] using similar method. Sample A1, A2 and A3 show different porous structures from each other and have larger pore structures than the control sample.

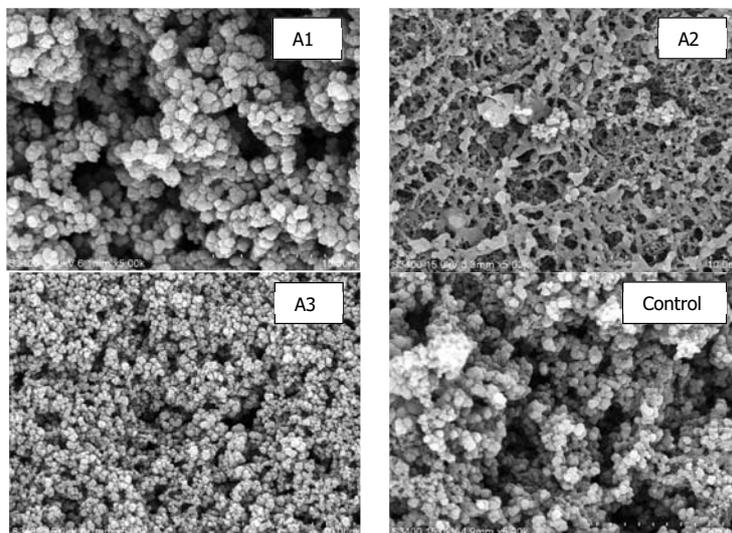


Figure 5. SEM images of samples A1-A3 and control sample after calcination.

Sample A1 demonstrated uneven pores and the largest pores sizes compared to other samples. This might be due to the larger diameter of the nanofibers template compared to the rest of the sample. Sample A2, was found to possess smaller and more homogenous pores. However, the sample did not show the formation of globular structures as a normal pore morphology of polymethacrylate monoliths [21]. Furthermore, foreign substances were observed covering the monolith surface may due to the remaining of dry porogenic crust or the nanofiber template itself [19]. Meanwhile, sample A3 indicated comparable pores to the control sample. From the perspective of homogeneity, A3 sample was found more homogenous than A1 and A2 samples. The pores formed within the monolith samples were mostly macropores having sizes of more than 50 nm [22]. The nanofiber templates were removed from the monolith structure via calcination process, leaving porous channels inside the monolith as evident by the formation of finer pores in the nanofiber-template monolith samples in comparison with the sample without nanofiber template.

4.0 Conclusion

Polypropylene nanofibers were successfully synthesized using melt blowing technique with diameters in the range between 3.58 and 11.0 x 10³ nm with melting points ranging from 121.0 to 128.8 °C. Macropores monoliths were successfully synthesized as shown by sample A1, A2 and A3. As evident in SEM images, the nanofiber template was successfully removed by heating above its melting point and a porous structure monolith was obtained after nanofiber template removal. A3 sample produce at both midpoints of the ranges for air pressure and motor speed which were at 0.45 Mpa and 40 Hz respectively, and the highest length of the DCD at 60.23 cm, shows a comparable monolith structure to control sample indicating the potential use of nanofiber produced by melt blowing technique as monolith template. The finding of this study offers useful guidelines for monolith fabrication with homogenous pore using nanofiber as a template.

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