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Polymeric micro-filter manufactured by a dissolving mold technique

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Abstract
For filtration applications, we developed a process involving a 'dissolving mold technique' to fabricate polymeric filter membranes which have high aspect ratio pores with narrow pore size distribution. The dissolving mold technique has some advantages over the existing membrane microfabrication methods. Firstly, it resolves thoroughly the demolding problem by dissolving an interim polymer pillar mold, and secondly, it solves the membrane-folding (curling) problem upon releasing the membrane from the mold by integrating a support mesh bonding layer before dissolving of the interim pillar mold. This process is capable of fabricating filter membranes having micrometer and potentially nanometer pore sizes. The fabricated membranes have good mechanical properties, high porosity, smooth surface and uniform pore size distribution.

1. Introduction

Nowadays, filter membranes are being used in a wide range of industrial applications, such as particle and biological sample collections, gas separation, pervaporation, waste water treatment and desalination. The ultimate aim of membrane microfiltration is to achieve a low flow resistance and a well-controlled pore size distribution of the membrane in order to obtain a high operational flux, long life and maximum dirt-holding capacity [1]. Drawbacks of commercial filters such as rough surface, tortuous pore path, low pore density and high coefficient of variation [2] (CV $>$ 20%) are the major factors that compromise their efficiency and throughput in microfiltration. So far, the best homogeneity in terms of pore size distribution and pore shape in commercial membranes can be found in track-etched polymeric membranes (normally made of polycarbonate), but irregular distribution of pores on the membrane surface, low porosity and also pore angle with the surface, limit the membrane strength and flow rate, fabrication yield and batch-to-batch performance repeatability during mass production. In addition, these filters are hard to clean completely with a single backflush step, and therefore, they are normally employed in single-use laboratory analysis [3].

In the last few decades, different methods have been proposed for producing membranes with micro/nano cylindrical pores, high porosity and good mechanical strength. For instance, optical lithography has been employed to fabricate silicon nitride membranes with a pore size around 0.1 μm. Identical and uniform pore diameter and smooth pore surface allow the filtration membrane to have low transmembrane pressures and large flux, but the restriction in membrane material (limited to nitride) and small thickness of the silicon nitride film ($<$1 μm), which allows only low working pressure ($<$2 bar), limit the application of this type of filtration membrane [4]. The fabrication of the polymeric through-hole membrane using high aspect ratio metal molds with hole diameters of as little as hundreds of nanometers based on alumina templates was also investigated by Yanagishita *et al* [5]. A major impediment in the fabrication of the membrane with this method is demolding of the membrane, because peeling off the membrane from a mold often results in membrane damage and failure. Also, the choices of pore size and pore density are restricted due to the use of alumina templates. In another study, polymeric sieves have been fabricated using aperture array lithography [6]. In this method, aperture array lithography and reactive ion etching (RIE) techniques are combined to obtain polymeric membranes with a homogeneous pore diameter on the scale of hundreds of

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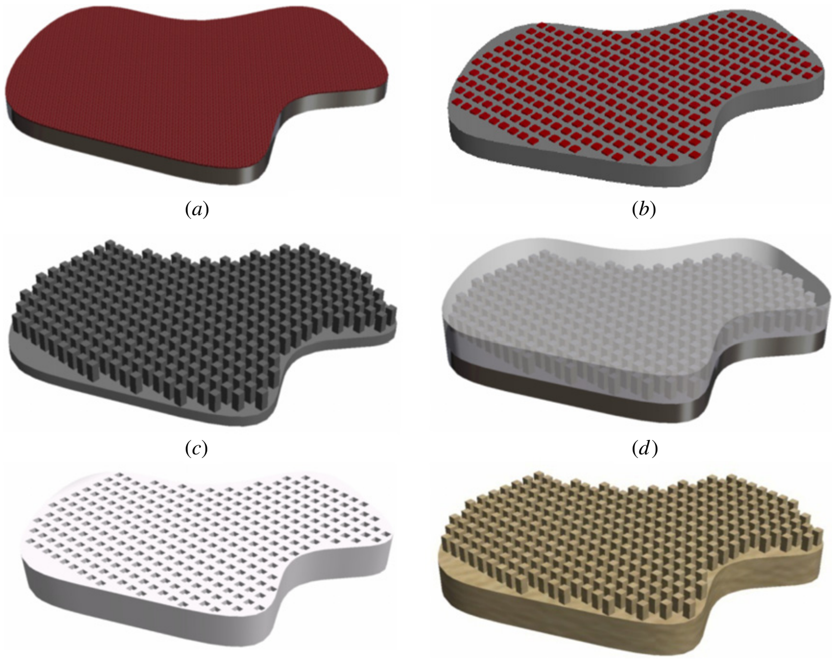

Figure 1. Schematic representation of the fabrication process for the dissolvable polymer pillar mold, (*a*) spin coating of photoresist, (*b*) photolithography, (*c*) Si micro pillar mold, (*d*) dispensed PDMS on the Si pillar mold, (*e*) PDMS interim blind-hole mold, and (*f*) dissolvable polymer pillar mold.

nanometers, but it is a costly process which is not appropriate for large-scale production. More recently, polymeric membranes were obtained by phase separation micromolding [7]. In spite of the capability of this method to employ a variety of polymers for filter design, some major problems such as enlargement of pore size during the shrinkage stage, fragility of the mold and folding (or failure) of the membrane during the release stage are associated with this method. Submicrometric sieves with the SU-8 resist were also fabricated by UV interference lithography [8]. Even though SU-8 is a biocompatible material and possesses good mechanical properties, a small thickness of the fabricated membranes (i.e. of the order of hundreds of nanometers) with this method makes them unsuitable for producing filter membranes that require the application of pressure across the membrane.

In this paper, we describe a 'dissolving mold technique' for the fabrication of polymeric filter membranes, which comprises the following steps: (1) fabrication of a silicon micro pillar mold, (2) fabrication of a dissolvable polymer pillar mold, (3) UV embossing of a polymer membrane using a dissolvable mold, (4) bonding of the membrane with a support grid, and (5) dissolving of the polymer pillar mold to obtain the final filter membrane with a support grid. This method has a few advantages over existing methods. Firstly, it resolves thoroughly the demolding problem in existing membrane fabrication methods [4–7] by dissolving the polymer pillar mold. Secondly, folding (curling) of the membrane upon release from the mold is also solved with this method by bonding the membrane initially to a support grid and then dissolving the polymer pillar mold. Furthermore, obtained membranes have features such as identical pore-diameter, high porosity and a smooth surface.

2. Experimental details

2.1. Fabrication of the dissolvable polymer pillars mold

Figure 1 schematically illustrates the process for the fabrication of the dissolvable polymer pillar mold. Firstly, a silicon wafer was cleaned in the piranha solution (98% H_2SO_4 + 30% H_2O_2 in a ratio of 3:1) for 20 min at 120 °C to remove any organic contamination and then submerged in a buffered oxide etchant (BOE) for 3 min. Afterwards, a 3 μm thick positive photoresist layer (AZ7220, Clariant Corporation) was spin coated on the wafer surface (figure 1(*a*)). Photolithography was carried out on a mask aligner (Karl-Suss MA6), and a resist dot array with a dot diameter of 2 μm and a space of 2.5 μm was patterned on the silicon wafer (figure 1(*b*)). The patterned resist was used as an etching mask and silicon etching was then conducted on an STS deep reactive ion etching (DRIE) system to form high aspect ratio micro-pillars with about 2 μm diameter and 20 μm height (figure 1(*c*)). If molecular filters with sub-micro or nano hole diameter are required, the diameter of the pillars can be further reduced by thermal oxidation followed by an HF etching method. After stripping off the resist and processing a passivation treatment, the silicon pillar mold can be used as a master mold for the fabrication of the interim blind-hole mold by means of soft lithography. Figure 2 shows a scanning electron microscopy (SEM) image of the silicon micro pillar mold. It can be seen that a perfectly ordered array of uniform-sized silicon pillars was formed after the process.

In order to fabricate the dissolvable polymer pillar mold, a PDMS (polydimethylsiloxane) interim blind-hole mold was first replicated from the silicon master pillar mold. For this

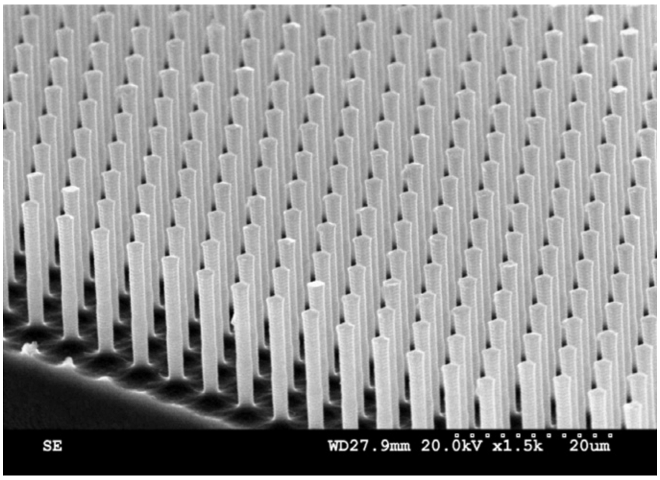

Figure 2. An SEM image of a silicon micro pillar mold.

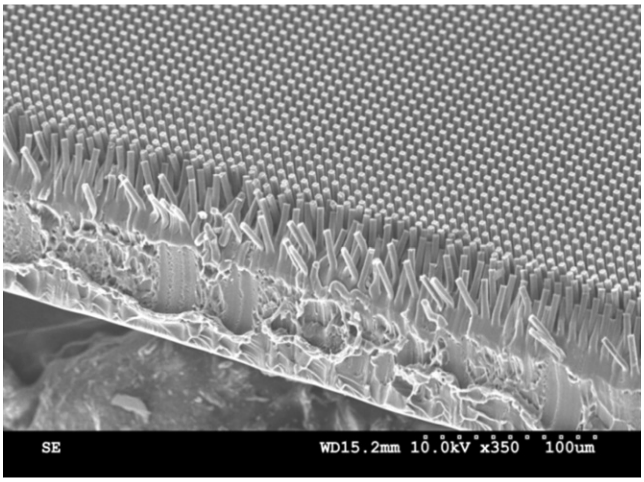

Figure 3. An SEM image of a dissolvable polymer pillar mold.

purpose, PDMS (Sylgard®184, Dow Corning) was prepared according to the manufacturer's instructions (mixing 10:1 elastomer to curing agent by weight) and then cast onto the silicon mold (figure 1(*d*)). After degassing in a vacuum chamber, the PDMS prepolymer was kept inside an oven for 3 h at 85 °C for curing, and subsequently the PDMS mold was obtained by peeling it off from the silicon master mold (figure 1(*e*)). To obtain the dissolvable polymer pillar mold, a PVA (polyvinyl alcohol, Sigma-Aldrich®) solution was prepared (mixing 9:1 water to PVA granules by weight) and then dispensed on the PDMS interim blind-hole mold. After degassing in a vacuum chamber for 2 h, it was left at room temperature for 24 h and finally the dissolvable polymer pillar mold was obtained by peeling it off from the PDMS mold (figure 1(*f*)).

The material for making the dissolvable polymer pillar mold should be curable (e.g. UV curable, hot curable, etc) and also dissolvable in a solvent such as water or acetone. PVA, polyimide (PI), polymethyl methacrylate (PMMA) and photoresist can be used to fabricate the dissolvable polymer pillar mold. In the present work, PVA was used because of its good mechanical properties and dissolvability in water. Figure 3 shows an SEM image of a dissolvable polymer pillar mold made of PVA. Similar to the silicon master pillar mold, a perfectly ordered array of PVA pillars were obtained after the replication process.

2.2. Fabrication of the polymer through-hole membrane

In order to obtain the through-hole polymeric membrane, a UV curable resin such as polyurethane (PU), SU-8 or other epoxies can be employed to cast on the solvable polymer pillar mold. In this study, we used PU (polyurethane, Sigma-Aldrich®) because it is a versatile polymer material with a wide variety of physical and chemical properties [9]. UV curable PU is typically composed of three basic components [10]: (i) a resin (i.e. an oligomer or a prepolymer), (ii) a reactive diluent and (iii) a photoinitiator capable of absorbing UV radiation. First, the PU solution was prepared (mixing oligomer, reactive diluents and photoinitiator by weight in a ratio of 70:20:10) and then dispensed onto the PVA mold. Afterwards, a glass plate was pressed onto the uncured resin to spread it between the pillars, and finally the PU was exposed under UV light (I line) for 90 s (figure 4(*a*)). A passivated transparent plastic sheet was placed between the glass plate and the UV curable resin to prevent their adhesion. After exposure and detaching the passivated sheet and the glass plate from the cured resin, oxygen plasma dry etching was carried out to remove the residual resin layer that remained on the top of the pillars. To strengthen the PU membrane and to avoid curling of the membrane during subsequent processes and handling, a piece of stainless steel mesh was bonded to the PU membrane by UV curable glue (UV Cure, IllumaBond™) (figure 4(*b*)). Subsequently, the entire membrane was immersed into DI water (60 °C over night) to dissolve the polymer pillar mold to obtain the through-hole membrane (figure 4(*c*)). Last, another piece of steel mesh was bonded to the backside of the through-hole membrane to complete the process of making a filter with micro pores supported with two steel meshes (figure 4(*d*)). Figure 5 shows an SEM image of a polymeric microfabricated membrane that is obtained by this method. This image confirmed that the uniform-sized holes are arranged at uniform intervals. An SEM image of the membrane bonded to steel meshes is illustrated in figure 6. Steel meshes with a variety of aperture sizes can be used as a support layer, but the mesh apertures should be 50- to100-fold larger than the membrane pore size so that the mesh does not affect the hydraulic resistance [6].

3. Result and discussion

3.1. Membrane morphology and properties

By employing a UV embossing method and the dissolving mold technique, we demonstrated a process for the fabrication of micro-filters. The process has the potential to be low cost and high yield. The process is suitable for mass production because the silicon master pillar mold can be used many times to produce the PDMS interim blind-hole mold, which can be used many times to produce the dissolvable polymer pillar mold.

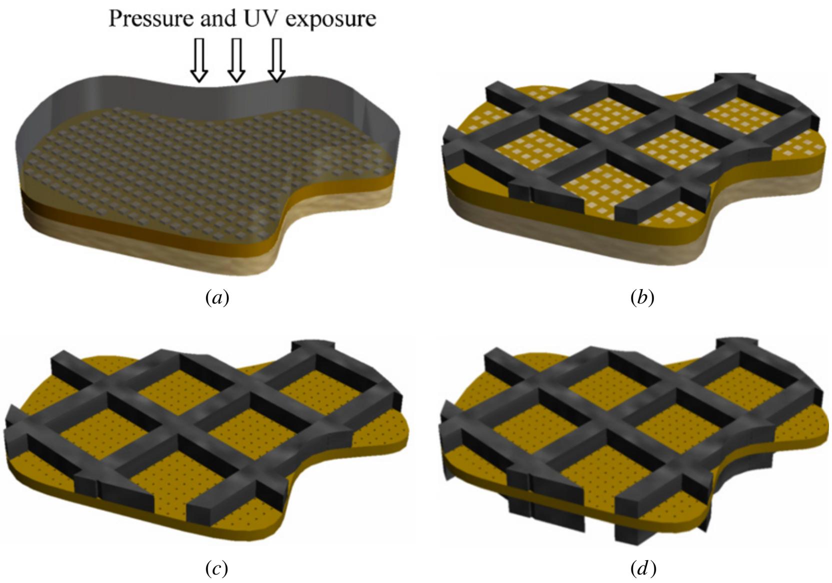

Figure 4. Schematic representation of the fabrication process of the filter membrane with micro pores and support meshes, (*a*) dispense UV curable resin on the polymer pillar mold, press the resin with the glass plate, and expose the assembly to UV, (*b*) bond a support mesh to the cured polyurethane on the dissolvable pillar mold, (*c*) dissolve the polymer pillar mold to obtain the through-hole membrane bonded to the support mesh, and (*d*) the final micro-filter with support meshes on both sides.

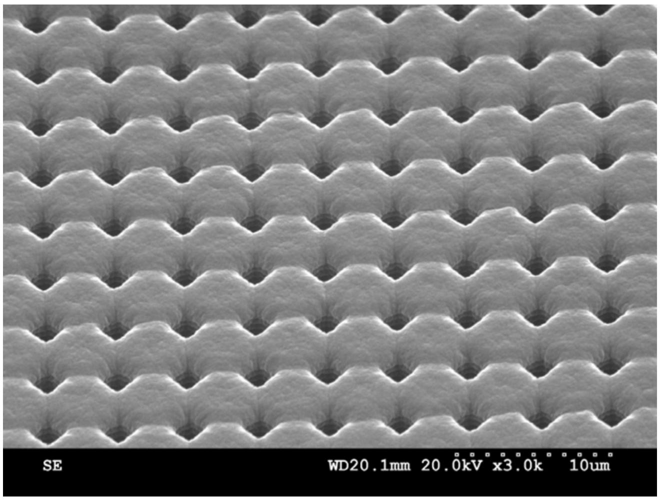

Figure 5. An SEM image of a polymer though-hole membrane.

The mechanical strength of the membrane obtained depends on the thickness of the membrane, the Young modulus of the membrane, the intrinsic tensile stress, the shape and distribution of the pores, and the distance between the bars of support mesh [4]. With this process, through-hole membranes with different thicknesses depending on the size of pillars of the silicon master mold can be produced. Also, as stated earlier, a variety of UV curable resins can be employed for the fabrication of the polymeric membrane according to their physical and chemical properties and their applications (e.g. SU-8 as a biocompatible material). In addition, the distance between the bars of support mesh can be controlled by using meshes that have different aperture sizes. Hence, with this technique, micro-filters with different strengths according to the required pressure for the microfiltration process can be fabricated.

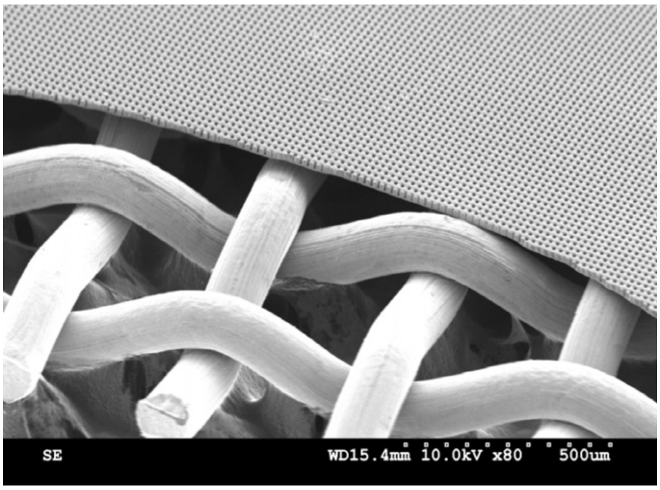

Figure 6. An SEM image of a microfabricated filter membrane bonded to a support mesh.

The measurement of the pore-size distribution of the polymeric membrane was carried out using digitalized images from a HITACHI S3500 scanning electron microscope, which is equipped with an 'in-built dimension measurement' module and an image analysis program (SEMICAPS 2200, SEMICAPS PTE LTD). The mean pore diameter (M) and standard deviation (σ) of the pores are 2 μm and 80 nm, respectively, and the corresponding coefficient of variation (CV $= \sigma / M$) is 4%. The CV represents the dispersion which is about five times lower than track-etched membranes which present a CV of about 20% [11]. The histogram of analyzed samples is illustrated schematically in figure 7. In the present work, we fabricated more than 80 membrane filters with 13 mm^2 and 47 mm^2 effective filtration areas. Figure 8 shows four distinct regions with different porosities. The pitch sizes in different regions are (a) 12 μm, (b) 8 μm, (c) 6 μm and (d) 4 μm,

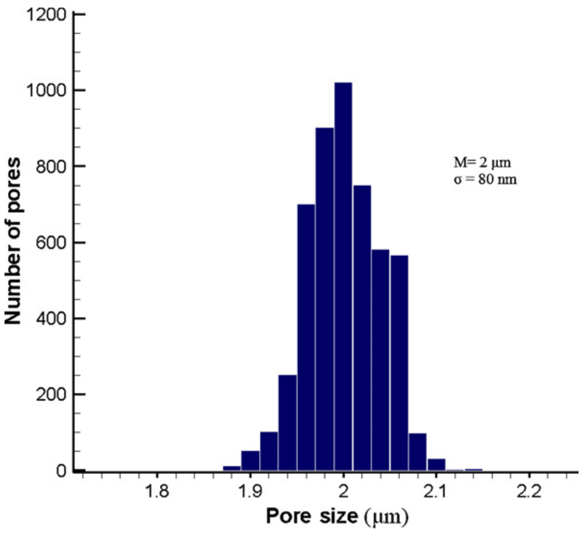

Figure 7. Pore size distribution of a 2 μm microfabricated membrane filter.

respectively. In the dense region, the membrane presents a pore density of about 7×10^7 pores cm^{-2}, which is much higher than the polymeric track-etched membranes that have an average pore density of around 2×10^5 pores cm^{-2}. It should also be noted that increasing porosity considerably decreases the strength of the membrane. Therefore, required flow rate for the filtration process can be a criterion for choosing optimum pore density.

3.2. Pillars failure and membrane occlusion

In the fabrication of the silicon master micro/nano pillar mold, increasing the length of the pillars excessively will lead to a pillar failure upon detaching the PDMS interim blind-hole mold from the silicon master mold. Therefore, finding the optimum aspect ratio for the silicon pillar mold according to the desired size of the pores is an important issue in the fabrication process. Furthermore, passivation of the silicon mold before casting PDMS on it will help to release the PDMS mold without difficulty.

Another important issue in the fabrication of the polymeric micro-filter is the required time for dissolving the polymer pillar mold in a solvent. In this stage, if the membrane with the mold was not kept for an adequate period of time in a solvent (e.g. water in this study), some pores may remain closed because of incomplete dissolution of the pillars.

3.3. Reusability

Commercial filters are generally not designed to be reusable, and they can hardly retain their initial filtration properties after each filtration and the back-flushing process. In contrast, microfabricated filters are able to retain their original condition with simple back-flushing or a lateral shaking process. Therefore, a long lifetime and the ability to be cleaned easily make the microfabricated filters a good option for large-scale applications where conventional filters must be replaced frequently, such as in the water purification industry or in breweries.

3.4. Application

The unique properties of our polymeric microfabricated filter, such as uniform pore size, high porosity, smooth surface and diversity in material choice, make it appropriate for different applications. For instance, in the water industry it can be used for the fast detection, capture and recovery of waterborne pathogens such as *Cryptosporidium* oocysts and *Giardia* in very dilute suspensions. For this purpose, we need to isolate a small amount of oocysts in a large volume of water with high

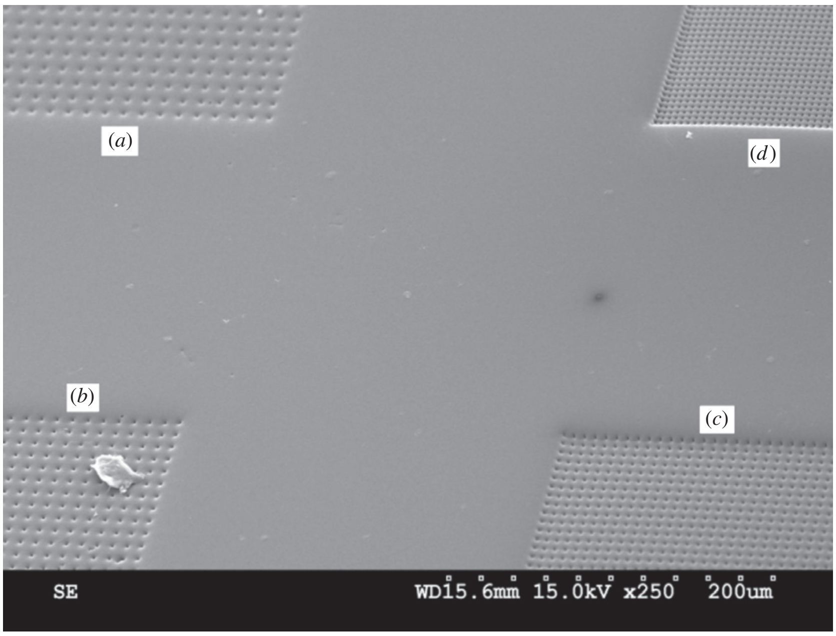

Figure 8. An SEM image of the microfabricated membrane with four different pore densities.

flux. In our preliminary test for this purpose, our polymeric microfabricated filter shows a recovery ratio of around 95% to 99% from a 10 L tap water sample, which is much higher than commercial filters with a recovery ratio of around 50% [2]. Separation of milk fat globules from raw milk, filtration of white blood cells (leukocytes) from blood–cell concentrations, cytology and cell culture, detection of microorganisms and air monitoring can be other applications of the polymeric microfabricated filter [12].

4. Conclusion

In this paper, we described a 'dissolving mold technique' for the fabrication of a polymeric through-hole membrane by means of UV embossing, which has some advantages over existing methods. Firstly, it resolves thoroughly the demolding problem in existing membrane fabrication methods. Secondly, folding (curling) of the membrane upon release from the mold is solved by bonding the membrane initially to a support grid and then dissolving the pillar mold. Because of the unique characteristics obtained, such as identical pore diameter, smooth surface and high porosity, the microfabricated filter presents higher flow rate, higher recovery ratio and longer life in comparison with commercial micro-filters. The technique can be used to fabricate membranes with various polymeric materials, which makes it appropriate for many applications such as blood filtration, cell analysis, bacterial and yeast harvesting, microorganism analysis and healthcare.

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