The Ultrafast and Continuous Fabrication of a Polydimethylsiloxane Membrane by Ultraviolet-Induced Polymerization

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Abstract: The polydimethylsiloxane (PDMS) membrane commonly used for separation of biobutanol from fermentation broth fails to meet demand owing to its discontinuous and polluting thermal fabrication. Now, an UV-induced polymerization strategy is proposed to realize the ultrafast and continuous fabrication of the PDMS membrane. UV-crosslinking of synthesized methacrylate-functionalized PDMS (MA-PDMS) is complete within 30 s. The crosslinking rate is three orders of magnitude larger than the conventional thermal crosslinking. The MA-PDMS membrane shows a versatile potential for liquid and gas separations, especially featuring an excellent pervaporation performance for *n*-butanol. Filler aggregation, the major bottleneck for the development of high-performance mixed matrix membranes (MMMs), is overcome, because the UV polymerization strategy demonstrates a freezing effect towards fillers in polymer, resulting in an extremely high-loading silicalite-1/MA-PDMS MMM with uniform particle distribution.

Concerns towards carbon dioxide emissions and associated climate warming instigate an accelerated research and production of renewable energy sources.^[1] Biobutanol is considered a competitive and efficient substitute of fossil fuels, because 1) its energy content is 30% higher than that of ethanol and is closer to gasoline; 2) its low vapor pressure facilitates its application in existing gasoline supply channels, and 3) it can be mixed with gasoline in any proportion.^[2] Similar to the improved fermentative production of bioethanol,^[3] the downstream pervaporation unit is a crucial process item in the high-efficiency biobutanol production by fermentation^[4] necessitating high-

performance pervaporation membranes. However, the large-scale industrial fabrication of the most widely used and representative PDMS membrane^[5] is seriously limited due to the required discontinuous and highly polluting thermal fabrication process (**Figure S7**).^[6]

Specifically, three key challenges hamper the continuous fabrication of PDMS membrane (**Scheme 1a**). (i) The coating layer must be dry before winding up onto a take-up roll. Since the length of a commercial-scale applicator is usually 30 m with a maximum coating velocity of 1.5 m min⁻¹,^[7] the crosslinking must be completed within 20 min to avoid the sticking of adjacent membranes after winding up. Unfortunately, the thermal crosslinking process typically lasts for > 180 min (**Table S1**). (ii) The coating solution in the groove must keep its fluidity, which is difficult to achieve since its viscosity increases rapidly after the addition of catalyst, resulting in the formation of a gel and hence prevents the continuous coating operation. (iii) The organic solvents in the coating solution need to be avoided or minimized due to their flammable and hazardous properties. Large amounts of organic solvents are commonly used to dissolve the polymer materials (**Table S2**), of which the volatilization not only increases the operation difficulty and production costs but also threatens the environment and operators.^[8] Obviously, the above key limiting issues imply the development trend in membrane fabrication technology, namely fast curing, controllable reaction and free-solvent process.

Scheme 1. Fabrication processes of PDMS membrane via (a) conventional thermal-crosslinking approach and (b) UV-polymerization approach.

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Hughes et al.^[9] reported the photocurable thiol-acrylate hydrogels, which are fully cured within 0.5–1 min after UV light exposure. Doyle et al.^[10] studied a functionalized hydrophilic polymer with a UV-polymerizable group, poly-(ethylene glycol) diacrylate, which achieves fast polymerization within seconds under UV irradiation. Previous studies also demonstrate the fast nature of UV-polymerization in the preparations of accommodating intraocular lens^[11] and polymer electrolyte membranes.^[12] However, such relevant studies were not expanded to the fabrication of pervaporation membrane. Since UV-polymerization displays the advantages of solvent-free and ambient conditions,^[13] especially shorter processing time as well as lower energy consumption than thermal-driven processes,^[14] it opens a new avenue for achieving continuous fabrication.

Herein, we proposed, for the first time, to use the UV-polymerization technology to adequately and simultaneously solve the above three key issues. The ultrafast (< 30 s) and continuous approach for the fabrication of the PDMS membrane was easily realized in an atmospheric environment (**Video S1**) via the UV-polymerization of the synthesized methacrylate-functionalized polydimethylsiloxane (MA-PDMS) (**Scheme 1b**). Additionally, the fillers aggregation is the biggest bottleneck for the development of mixed matrix membranes (MMMs) with outstanding pervaporation performance, which restricts the increase of particle loading (in most reports < 30 wt%).^[15] Interestingly, the fast curing of MA-PDMS provides a “freezing effect” towards fillers in MA-PDMS layer, which extremely minimizes filler aggregation and further results in a high-performance membrane with 45 wt% particle loading.^[16]

To provide PDMS with methacrylate groups (i.e. MA-PDMS), 3-methacryloxypropylmethyldimethoxysilane (KH571) was employed. The functionalization of PDMS and polymerization of MA-PDMS were confirmed by FT-IR and photo-rheology measurement. Compared with PDMS, the new peaks at 1730 and 1637 cm^{-1} separately belongs to the stretching vibrations of C=O and C=C,^[17] which are consistent with the spectrum of KH571 (**Figure 1a**).^[18] The peak at 1637 cm^{-1} disappeared in the spectrum of MA-PDMS membrane, revealing that the C=C participates in the UV-polymerization. Additionally, the transformation of MA-PDMS from liquid to solid was confirmed by the low value (close to 0) of tan delta (**Figure 1b**).^[19]

The UV-crosslinking rate of MA-PDMS was investigated by real-time infrared spectroscopy and photo-rheology, respectively.^[20] The degree of double bond conversion (DBC) and the polymerization rate (R_p) were obtained by monitoring the decay of the methacrylate double bond peak at 1637 cm^{-1} (**Figure 1c**). Results show that the eventual DBC reaches the highest value at around 80% within 30 s, while the maximum R_p appears at 4.7 s. Thus, the MA-PDMS system exhibits an excellent UV-polymerization efficiency. We also observed a fast increase in storage modulus G' and a sharp decrease in tan delta value (~ 0) within 30 s. This rate is increased by three orders of magnitude compared with the conventional thermal crosslinking rate (20000 s) (**Figure S8**). The polymerization rate is expected to further increase under oxygen-free^[21] or by decreasing the system viscosity^[22] using solvent, however, which is practically difficult for industrial continuous fabrication. The membrane has to pass through the irradiation area continuously, determining it a semi-closed space containing both inlet and outlet slots, which must be

larger enough to avoid contacting the new coating layer and damaging its structure. Additionally, the use of solvent should be avoided according to the green principle mentioned above. More importantly, the 30 s (< 20 min) curing time definitely meets the requirement of production process.

Figure 1. (a) FT-IR spectra of PDMS, MA-PDMS coating solution and MA-PDMS membrane. (b) Photo-rheometer curve of MA-PDMS coating solution: the light was automatically turned on after 100 seconds. (c) Double bond conversion and UV-polymerization rate of MA-PDMS coating solution: the corresponding absorbance at 1637 cm^{-1} over time is shown in **Figure S9**.

The MA-PDMS membrane has a smooth and homogeneous morphology (**Figure 2a and 2b**). It shows a slightly lower total flux but a higher separation factor than conventional thermal-crosslinked PDMS (CT-PDMS) membrane for separating 1.5 wt% *n*-butanol aqueous solution at 55 °C (**Figure S10**). This is attributed to its higher crosslinking density, which results in a lower free volume and chain mobility (**Table S3 and Table S4**).^[23] Importantly, the MA-PDMS membrane exhibits a better separation performance than other reported PDMS membranes for *n*-butanol (**Table S5**).

To further improve the pervaporation performance of PDMS membrane, inorganic porous particles are often introduced into the selective layer.^[24] However, the particles easily aggregate within the polymer matrix during the long duration thermal crosslinking, leading to forming non-selective voids (**Figure 2c**). In contrast, the particles are highly loaded and uniformly distributed in MA-PDMS matrix without apparent voids (**Figure 2d and Figure S11**), exhibiting a “freezing effect” towards particles and extremely improving their dispersibility. The resulting MA-PDMS layer allows the permeant molecules to preferentially pass through the nanoporous fillers rather than the non-selective voids.^[6a, 25] In addition, the significantly increased particle loading enhances the membrane surface roughness (**Figure S12**), which favors its hydrophobicity (**Figure S13**) and the dissolution of permeant molecules into membrane.^[26] As a result, the separation factor increases from 47 to 70, and the *n*-butanol permeability from 14.60×10^4 Barrer increase to 16.69×10^4 Barrer (**Figure 3a and Table S6**).

Figure 2. (a) Photograph and (b) SEM images of the surfaces of MA-PDMS membrane (Inset is the cross-section of fabricated MA-PDMS membrane). SEM images of the surfaces of (c) silicalite-1/CT-PDMS MMM (20000 s) and (d) silicalite-1/MA-PDMS MMM (30 s) with 45 wt% particle loading.

Figure 3. (a) *n*-Butanol permeability and separation factors and (b) radii of the free volume of MA-PDMS membrane and silicalite-1/MA-PDMS MMMs with different silicalite-1 amount.

The performance improvement in the UV-polymerized MMM can also be understood from the free volume variation of polymer and pore structure of silicalite-1.^[27] The free volume is the finely tuned result of r_3 (smaller pore from the cross-linked site) and r_4 (larger pore from networks clusters as well as the polymer-filler interface) (**Table S7 and Figure 3b**).^[28] r_3 increases as the silicalite-1 amount increases, because the well-dispersed silicalite-1 effectively disrupts the MA-PDMS chain packing.^[29] Meanwhile, r_4 increases since the weak interaction between silicalite-1 and MA-PDMS causes a loose chain packing and an increased chain mobility in the interface (**Tables S8**).^[27, 30] Simultaneous increases in r_3 and r_4 allow the feed molecules to easily pass through the free volume cavities and further facilitate an enhanced permeability. The increment in r_3 and decrement in r_4 imply the partial pore blockage of silicalite-1 by polymer chains^[31], hence leading to the decrease of free volume. In addition, the water transport is influenced by the interactions between water and the channel surface.^[32] The hydrogen bonding between hydroxyl groups in the pore structure of silicalite-1 and water restricts the water transport in silicalite-1, which contributes to the decrease in water permeability and the increase in *n*-butanol separation factor.^[33]

In addition, we measured the gas separation performance of our MA-PDMS membrane using single gas permeation at 35 °C and 1 bar. The high CO₂, N₂ and CH₄ permeabilities were obtained with effective ideal selectivity of CO₂/CH₄, CO₂/N₂ and CH₄/N₂ (**Figure S14**), thus confirming the versatile ability of MA-PDMS membrane.

In summary, the proposed UV-polymerization strategy realizes the ultrafast and continuous fabrication of a PDMS membrane, making its large-scale high-efficient industrial fabrication possible and solving the most important bottlenecks of MMMs development. The synthesized MA-PDMS was rapidly polymerized under UV irradiation within 30 s, three orders of magnitude faster than that of the conventional thermal approach. The resulting MA-PDMS membrane exhibits outstanding pervaporation performance for *n*-butanol. The UV-polymerization strategy demonstrates a “freezing effect” towards fillers in the polymer, which results in an extremely high-loading silicalite-1/MA-PDMS MMM with uniform particle distribution. Considering the universality and operability of UV-polymerization approach, it shows great potential for fabrication of various polymer membranes and polymer-based MMMs.

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Conflict of Interest

The authors declare no conflict of interest.

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The ultrafast (< 30 s, three orders of magnitude faster than conventional method) and continuous fabrication of a polydimethylsiloxane membrane was realized by an ultraviolet-induced polymerization strategy. The “freezing effect” towards fillers in the polymer results in an extremely high-loading of silicalite-1/MA-PDMS MMM with uniform particle distribution.

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