

Video Article

Synthesis of Hydrogels with Antifouling Properties As Membranes for Water Purification

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Abstract

Hydrogels have been widely utilized to enhance the surface hydrophilicity of membranes for water purification, increasing the antifouling properties and thus achieving stable water permeability through membranes over time. Here, we report a facile method to prepare hydrogels based on zwitterions for membrane applications. Freestanding films can be prepared from sulfobetaine methacrylate (SBMA) with a crosslinker of poly(ethylene glycol) diacrylate (PEGDA) via photopolymerization. The hydrogels can also be prepared by impregnation into hydrophobic porous supports to enhance the mechanical strength. These films can be characterized by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) to determine the degree of conversion of the (meth)acrylate groups, using goniometers for hydrophilicity and differential scanning calorimetry (DSC) for polymer chain dynamics. We also report protocols to determine the water permeability in dead-end filtration systems and the effect of foulants (bovine serum albumin, BSA) on membrane performance.

Video Link

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Introduction

There is a great need to develop low cost and energy efficient technologies to produce clean water in order to meet the increasing demand. Polymeric membranes have emerged as a leading technology for water purification due to their inherent advantages, such as their high energy efficiency, low cost, and simplicity in operation¹. Membranes allow pure water to permeate through and reject the contaminants. However, membranes are often subjected to fouling by contaminants in the feed water, which can be adsorbed onto the membrane surface from their favorable interactions^{2,3}. The fouling can dramatically decrease water flux through the membranes, increasing the membrane area required and the cost of water purification.

An effective approach to mitigate fouling is to modify the membrane surface to increase the hydrophilicity and thus decrease the favorable interactions between the membrane surface and foulants. One method is to use thin-film coating with superhydrophilic³ hydrogels. The hydrogels often have high water permeability; therefore, a thin-film coating can increase the long-term water permeance through the membrane due to the mitigated fouling, despite the slightly increased transport resistance across the whole membrane. The hydrogels can also be directly fabricated into impregnated membranes for water purification in osmotic applications⁴.

Zwitterionic materials contain both positively and negatively charged functional groups, with a net neutral charge, and have strong surface hydration through electrostatic-induced hydrogen bonding^{5,6,7,8,9}. The tightly bound hydration layers act as physical and energy barriers, preventing foulants from attaching onto the surface, thus demonstrating excellent antifouling properties¹⁰. Zwitterionic polymers, such as poly(sulfobetaine methacrylate) (PSBMA) and poly(carboxybetaine methacrylate) (PCBMA), have been used to modify the membrane surface by coating^{11,12,13,14,15,16,17,18} to increase surface hydrophilicity and thus antifouling properties.

We demonstrate here a facile method to prepare zwitterionic hydrogels using sulfobetaine methacrylate (SBMA) via photopolymerization, which is crosslinked using poly(ethylene glycol) diacrylate (PEGDA, $M_n = 700$ g/mol) to improve the mechanical strength. We also present a procedure to construct robust membranes by impregnating the monomer and crosslinker in a highly porous hydrophobic support before the photopolymerization. The physical and water transport properties of the freestanding films and impregnated membranes are thoroughly characterized to elucidate the structure/property relationship for water purification. The prepared hydrogels can be used as a surface coating to enhance membrane separation properties. By adjusting the crosslinking density or by impregnating into hydrophobic porous supports, these materials can also form thin films with sufficient mechanical strength for osmotic processes, such as forward osmosis or pressure-retarded osmosis⁴.

Protocol

1. Preparation of the Prepolymer Solutions

1. Preparation using water as a solvent

1. Add 10.00 g of deionized (DI) water to a glass bottle with a magnetic stir bar.
2. Measure 2.00 g of SBMA and transfer it to the glass bottle containing the water. Stir the solution for 30 min, until the SBMA is completely dissolved.
3. In a separate bottle, add 20.00 g of PEGDA ($M_n = 700$ g/mol).
4. Add 20.0 mg of 1-hydroxycyclohexyl phenyl ketone (HCPK), a photo-initiator, to the PEGDA solution. Let the solution stir for at least 30 min.
5. Using a disposable pipette, transfer 8.00 g of the PEGDA-HCPK solution to the SBMA aqueous solution. Continuously stir the mixture until the solution is homogenous.

2. Preparation using water/ethanol mixtures as solvents

1. Add 6.00 g of DI water and 4.00 g of ethanol to an amber glass bottle with a magnetic stir bar. Stir the solution to allow thorough mixing.
2. Add 2.00 g of SBMA to the water/ethanol mixture. Stir the solution and allow the SBMA to completely dissolve.
3. Use a pipette to transfer 8.00 g of the PEGDA-HCPK solution to the SBMA mixture. Stir to mix the solution thoroughly.

2. Preparation of the Freestanding Films

1. Place two spacers with known thicknesses on a clean quartz disc; the thickness of the spacers controls the thickness of the obtained polymer films¹⁹.
2. Transfer a small amount (~1.0 mL) of the prepolymer solution to the quartz disc using a disposable pipette.
3. Place another quartz disc on top of the liquid and ensure that there are no bubbles in the liquid film.
4. Place the sample in an ultraviolet (UV) crosslinker and irradiate for 5 min using UV light with a wavelength of 254 nm¹⁹.
NOTE: Alternative irradiation times and wavelengths can be used depending on the type of photoinitiator.
5. Separate the polymer film from the quartz discs using a sharp blade. Use tweezers to transfer the film to a DI water bath. Change the water twice during the first 24 h to remove the solvent, unreacted monomer/crosslinker, and sol from the film.
NOTE: The polymer film should be kept in the DI water to preserve the pore structure, if there is any.
6. Prepare dried films for ATR-FTIR and DSC analysis.
 1. Remove the film from the water bath and allow it to air dry for 24 h.
 2. Place the film in a vacuum oven at 80 °C to dry overnight under vacuum.

3. Preparation of the Impregnated Membranes

1. Place a sheet of porous support onto a quartz disc.
2. Using a foam brush, coat each side of the support twice with the prepolymer solution based on the water/ethanol mixture⁴.
NOTE: Since the support is hydrophobic, the prepolymer solution containing ethanol can easily wet the support.
3. Place another quartz disc on top of the support.
4. Place the sample in a UV crosslinker and irradiate for 5 min using UV light with a wavelength of 254 nm.
5. To remove the impregnated membrane from the quartz discs, immerse the whole assembly in a DI water bath for 5 min and carefully remove the membrane using a sharp blade and tweezers.
6. Keep the membrane in DI water. Change the water twice to remove the solvent, the unreacted monomer/crosslinker, and the sol from the membrane.
7. Prepare dried, impregnated membranes for ATR-FTIR and DSC analyses.
 1. Remove the membrane from the water bath. Allow the membrane to dry at ambient conditions for 24 h.
 2. Dry the membrane in a vacuum oven overnight at 80 °C under vacuum.

4. Characterization of the Freestanding Films and Impregnated Membranes

1. ATR-FTIR analysis

1. Prepare a sample of the prepolymer solution, as stated in step 1.1, for FTIR analysis.
2. Perform a background scan before scanning the sample. Set the wavenumber range from 600 cm⁻¹ to 4,500 cm⁻¹ at a 4-cm⁻¹ resolution of measurement.
3. Place the sample in the FTIR machine for analysis.
4. Remove the sample. Clean the crystal and the tip with an appropriate solvent.
5. Repeat steps 4.1.1 - 4.1.4 for the following samples: porous support, prepolymer solution, dried freestanding films, and dried impregnated membranes.

2. Differential scan calorimetry (DSC)

1. Place a DSC pan and lid in a weighing balance and record their weight.

2. Place a small amount of sample (5-10 mg) inside the pan and close it with the lid.
3. Weigh the pan containing the sample. From the weight difference between the occupied pan and lid and the unoccupied pan and lid, calculate the weight of the sample.
4. Using a press, hermetically seal the sample inside the pan.
5. Place the sealed pan inside the DSC cell in which the inert reference is located.
6. Enter the weight of the unoccupied pan and lid and the weight of the sample in the program.
7. Scan with the DSC from -80 °C to 160 °C at a heating rate of 10 °C/min.
8. Perform the DSC analysis using the manufacturer's protocol.
9. Repeat the DSC experiments for different samples following the aforementioned steps.

3. Measurement of contact angles using a pendant drop method

1. Cut a rectangular strip of the membrane sample (approximately 30 mm by 6 mm).
2. Soak this strip in DI water for 10 min and then dry it for 5 min.
3. Place the dried sample on the sample holder.
4. Submerge the sample holder in a transparent environmental chamber containing the DI water²⁰.
5. Using a microliter syringe with a stainless steel needle, dispense drops of *n*-decane (approximately 1 µL) onto the membrane sample.
6. Leave the setup undisturbed for 2 min to ensure the stabilization of the droplets.
7. Use an appropriate image analysis software to determine the contact angle of the samples by measuring the angles of the dispensed droplets on the membrane surface.
8. Take the average of the contact angle values obtained for various droplets.

4. Characterization of water permeability using a dead-end filtration system

1. Use a hammer-driven hole punch with an appropriate diameter to cut coupons of freestanding films and impregnated membranes.
2. Place a prepared coupon on the porous support inside a dead end filtration cell.
3. Place the O-ring on top of the sample. Screw the two halves of the permeation cell together.
4. Add approximately 50 mL of DI water to the permeation cell. Screw on the cap and place the permeation cell on a magnetic stirrer. Set the stirring rate between 300 and 900 rpm.
5. Place a covered beaker on a balance to collect the permeate water. Tare the balance.
6. Open the valve on the gas cylinder. Turn the pressure regulator valve clockwise until the desired pressure is reached (45 psig for freestanding films and 35 psig for impregnated membranes).
7. Open the release valve to deliver the pressure to the permeation cell.
8. Monitor and record the weight of the beaker with time.
9. Calculate the water permeance (A_w) and permeability (P_w) with the solution-diffusion model shown below^{4,21}

$$A_w = \frac{1}{\rho_w A \Delta p} \frac{\Delta m}{\Delta t}$$

$$P_w = A_w \cdot l$$

where A_w is the water permeance (L/m²hbar or LMH/bar), P_w is the water permeability (LMH cm/bar), ρ_w is the water density (g/L), A is the effective area of the membrane (m²), Δm is the change in the mass of water permeate (g) over a time period Δt (h), Δp is the pressure difference across the membrane (bar), and l is the thickness of the swollen film (cm).

10. Use a BSA solution containing 0.5 g/L BSA in a phosphate-buffered saline (PBS) solution with pH = 7.4 to evaluate the antifouling properties and rejection rates of the membranes.
11. Repeat steps 4.4.5 - 4.4.10 to determine the water flux in the presence of BSA. Calculate the BSA rejection rate with the following equation²²

$$R_{BSA}(\%) = \left(1 - \frac{C_P}{C_F}\right) \times 100\%$$

where R_{BSA} is the BSA rejection rate of the membrane (%), C_P is the concentration of BSA in the permeate (g/L), and C_F is the concentration of BSA in the feed (g/L); the concentration of BSA can be determined via UV spectroscopy.

Representative Results

Freestanding films prepared with the prepolymer solutions specified in steps 1.1 and 1.2 are referred to as **S50** and **S30**, respectively. Detailed information is shown in **Table 1**. The prepolymer solution specified in step 1.2 was also used to fabricate impregnated membranes, which are denoted as **IMS30**. Because the porous support is made of hydrophobic polyethylene, only the prepolymer solution containing ethanol can be impregnated into the support and form transparent films, as shown in **Figure 1**⁴.

The conversion of (meth)acrylate groups in PEGDA and SBMA was confirmed by ATR-FTIR spectroscopy. **Figure 2** presents the IR spectra of the porous support, prepolymer solution, dried polymer films (S50 and S30), and dried impregnated membrane (IMS30). The spectrum of porous support (a) shows a characteristic peak around $1,460\text{ cm}^{-1}$, which is associated with bending deformation²³. The IR spectrum of the prepolymer solution (b) shows three peaks characteristic of acrylate group at 810 , $1,190$, and $1,410\text{ cm}^{-1}$ ^{19,21}. These peaks disappear in the IR spectra of the S50 film (c), the S30 film (d), and the IMS30 membrane (e), indicating the complete conversion of the (meth)acrylate. Additionally, a characteristic peak at $1,035\text{ cm}^{-1}$ for the vibration of the SO_3^- group in SBMA appears in all IR spectra, except for the spectrum of the porous support.

Figure 3 compares the DSC results of the dried S50 film (a), the S30 film (b), and the IMS30 membrane (c). The DSC curves are utilized to determine the glass transition temperature (T_g) of each sample. The T_g values are consistent and slightly lower than the literature value (*i.e.*, -33°C) for films with similar SBMA and PEGDA content⁷. The DSC curve for IMS30 also shows a melting peak for high-density polyethylene at 132°C , which is comparable to the value reported in the literature²⁴.

The water contact angles are presented in **Figure 4** and are used to elucidate the surface hydrophilicity. Lower contact angles suggest greater hydrophilicity. The porous support has a contact angle of 92° , which is much higher than the value of 26° for the S50 film, 18° for the S30 film, and 37° for the IMS30 membrane. This result indicates that the films and impregnated membrane are much more hydrophilic than the porous support.

Table 1 summarizes physical properties and water transport properties of the S50 film, S30 film, and IMS30 membrane, as well as the composition of the prepolymer solutions used to fabricate the films and membrane. The water permeance was calculated, and the film thickness was measured using a digital micrometer. The SM50 film with a $471\text{-}\mu\text{m}$ thickness has a water permeance of 0.085 LMH/bar . The thinner SM30 film exhibits a water permeance of 0.16 LMH/bar , and the IMS30 membrane, with a thickness similar to the SM30 film, also shows a comparable water permeance of 0.15 LMH/bar . The uncertainty shown in the thickness measurement is the standard deviation of multiple measurements.

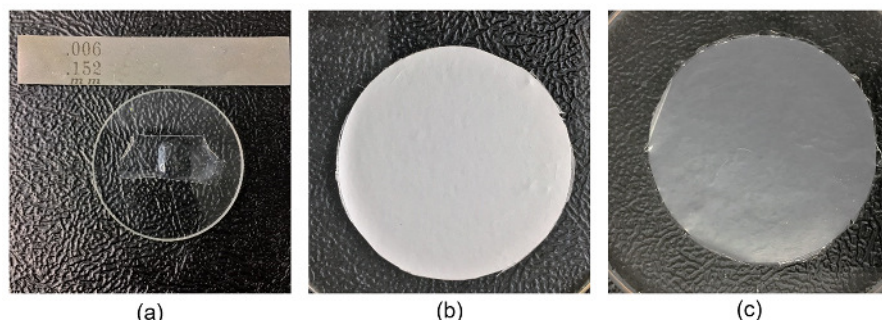


Figure 1: Photographs of (a) a freestanding film (S30, thickness = $152\text{ }\mu\text{m}$) (b) a porous support, and (c) an impregnated membrane (IMS30). [Please click here to view a larger version of this figure.](#)

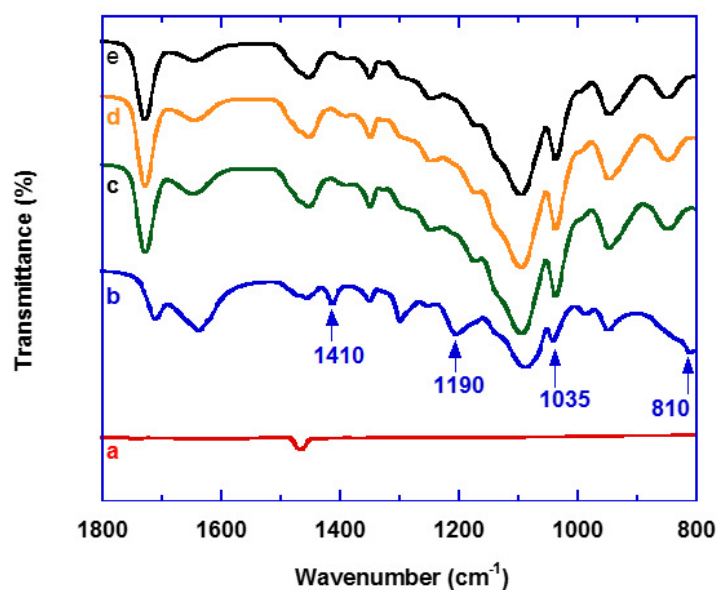


Figure 2: Comparison of ATR-FTIR spectra of (a) the porous support, (b) the prepolymer solution, (c) the S50 freestanding film, (d) the S30 freestanding film, and (e) the IMS30 impregnated membrane.

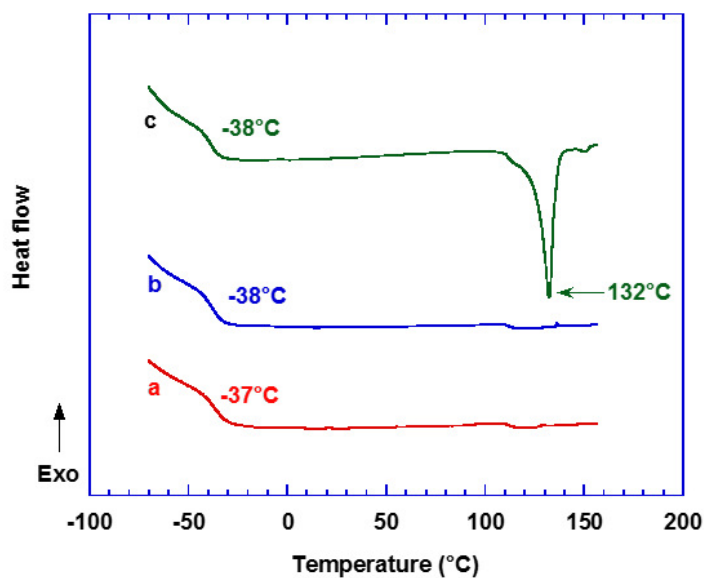


Figure 3: DSC curves for (a) the S50 freestanding film, (b) the S30 freestanding film, and (c) the IMS30 impregnated membrane.

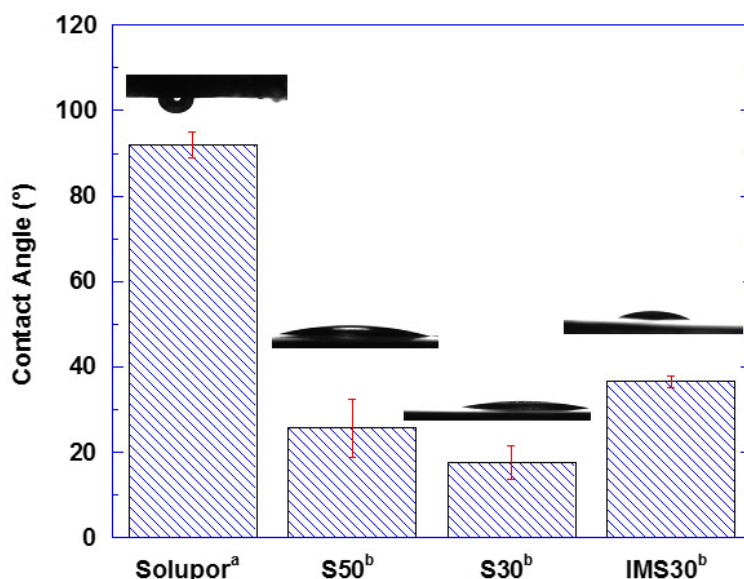


Figure 4: Contact Angle Measurements and Pictures of Water Droplets on the Surface of the Porous Support, Freestanding Films, and Impregnated Membrane. The error bar is the standard deviation of multiple measurements. Note: ^a Pendant drop method²⁵, ^b Normal drop method²⁵.

Sample	Prepolymer Solution Content (wt.%)				T_g (°C)	Thickness (μm)	Water Permeance (LMH/bar)	Water Permeability (cm^2/s)
	SBMA	PEGDA	H ₂ O	EtOH				
S50	10	40	50	0	-37	471 ± 3	0.085 ^a	1.5×10^{-6}
S30	10	40	30	20	-38	110 ± 7	0.16 ^a	6.6×10^{-5}
IMS30	10	40	30	20	-38	94 ± 11	0.15 ^b	5.3×10^{-5}

^a Water flux was measured at 45 psi with a stirring rate of 350 rpm.

^b Water was measured at 35 psi with a stirring rate of 350 rpm.

Table 1: Summary of the physical and Water Transport Properties of the Freestanding Films and Impregnated Membrane.

Discussion

We have demonstrated a facile method to prepare freestanding films and impregnated membranes based on zwitterionic hydrogels. The disappearance of three (meth)acrylate characteristic peaks (*i.e.*, 810, 1,190, and 1,410 cm^{-1}) in the IR spectra of the obtained polymer films and impregnated membrane (**Figure 2**) indicates the good conversion of the monomers and crosslinker^{4,19,21}. Additionally, the appearance of the SO_3^- vibrational peak in the spectra for the films and membrane confirms that the zwitterionic groups have been successfully incorporated into the hydrogels. The obtained copolymers have negligible sol fractions, indicating that the copolymer compositions are very similar to those of the prepolymer solutions⁷.

The T_g values of S30 and S50 are similar, suggesting that the solvent type in the prepolymer solutions has minimal effect on the T_g . For the impregnated membrane, the melting peak is ascribed to the porous support (polyethylene), which suggests the promise of this membrane to sustain high temperature and high pressure across the membrane.

The contact angle measurement via the pendant drop method was only applicable to the porous support. This method could not be used for the freestanding films and membranes fabricated in this work because the samples detached themselves from the sample holder when submerged in the water chamber. Therefore, the contact angle measurements for these samples were measured by simply dropping a small droplet of water (1.0-5.0 μL) on top of the sample surface. The contact angle for the support is much higher than those of the freestanding films and impregnated membrane, which confirms the greater hydrophilicity in these zwitterionic hydrogels.

The water permeance of each sample was determined by dead-end filtration systems. Hydrated S50 film with a thickness of 471 μm exhibits the lowest water permeance (0.085 LMH/bar), while S30 film and IMS30 membrane show higher water permeance.

This paper describes a facile method to fabricate hydrogel-based freestanding films and impregnated membranes via photopolymerization for water purification. Hydrogels containing PEGDA and SBMA with hydrophilicity are synthesized, and they can enhance the hydrophilicity of the porous support in impregnated membranes. This report provides practical guidance in preparing these materials and characterizing their physical properties, including water transport properties. The method and materials can also be used to prepare membranes for gas separation, such as CO₂ capture.

Disclosures

The authors declare that they have no competing financial interests.

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