Crosslinking of Polyvinyl Alcohol (PVA) Fibrous Membranes with Glutaraldehyde and PEG Diacylchloride

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ABSTRACT: Polyvinyl alcohol (PVA) fibrous membranes were generated by elestrospinning 10% aqueous PVA solutions then rendered water insoluble by reactions with difunctional reagents. The as-electrospun PVA fibers were semicrystalline as evident by melting behavior ($T_m = 190°C$ $\Delta H_m = 39$ J/g) and wide angle x-ray diffraction (peak at $2\theta = 20°$). Chemical reactions with glutaraldehyde in either aqueous sodium sulfate (GA/Na_2SO_4) or ethanol (GA/EtOH) and polyethylene glycol (PEG) diacylchloride in 1 : 1 (v:v) toluene/pyridine produced crosslinked PVA with varied effects on the crystalline structure of the fibers. The fiber diameters remained in the submicrometer range. Among all crosslinking agents and conditions studied, reaction with shorter PEG at lower extent produced water-insoluble PVA fibrous membrane with least change to the interfiber porous structure.
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Key words: poly(vinyl alcohol); electrospun fibrous membrane; crosslinking; glutaraldehyde (GA); polyethylene glycol (PEG)

INTRODUCTION

Polyvinyl alcohol (PVA), a 1,3-diglycol polymer made from hydrolysis of polyvinyl acetate (PVAc), can be easily processed into fibers, films, and membranes with desirable hydrophilicity and biocompatibility. For most applications, PVA must be made insoluble in water by either crosslinking or grafting hydrophobic segments to the PVA hydroxyl groups. Crosslinking PVA by reactions using either difunctional or multifunctional reagents has led to other useful benefits. One such outcome is the formation of PVA hydrogels, which have been widely investigated for biomedical and biotechnological applications.[1] Crosslinking PVA membrane with glutaraldehyde (GA) has shown to be catalyzed by sulfuric acid[2] and effective in separating liquid mixtures, such as acetic acid–water mixture, in pervaporation.[3] The mechanical and thermal properties of PVA were improved when crosslinked with hexamethylene diisocyanate in DMSO/DMF mixture (1:1, v/v).[4] Crosslinking PVA with ethylene diamine tetra-acetic dianhydride that bears ionizable carboxylic acid groups led to polyelectrolyte hydrogels.[5] Crosslinking with boric acid produced PVA elastomer gels in dimethyl sulfoxide and water mixtures.[6] Epichlorohydrin can function as a bifunctional reagent toward hydroxyl groups of PVA in KOH solutions under basic conditions to form gels.[7]

PVA can be easily electrospun into ultra-fine fibrous membranes. To make electrospum PVA fibrous membranes water insoluble, gyoxal,[8] maleic anhydride,[9,10] or acryloyl chloride[11] have been added in the electrospinning solutions, then crosslinked by heat[8,9] or ultra violet light[10,11] post fiber formation. We have demonstrated that electrospinning of binary polymer mixtures followed by physical treatments is efficient to create new bicomponent nanofibers with unique chemical and physical features. Specifically, electrospinning aqueous PVA and poly(acrylic acid) (PAA) mixtures and followed by heat-induced esterification produced ultra-fine fibrous hydrogel membranes whose morphology and swelling behaviors could be easily tuned by varying the ratios of the two polymers.[12] Due to the ultrahigh specific surfaces of these nanofibers, the swelling responses of these fibrous membranes were instantaneous and could be tuned to pH and further expanded by electric fields.[13,14] Enzyme proteins have been successfully entrapped within the fibers via electrospinning of aqueous mixtures of lipase from *Candida rugosa* and PVA followed by crosslinking with glutaraldehyde (GA) in ethanol.[15]

This study aims to generate porous and hydrophilic PVA ultrafine fibrous membrane by postelectrospinning crosslinking reactions to render the obtained membrane water insoluble. This approach separates the fibrous membrane fabrication by

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electrospinning aqueous PVA solutions from the postelectrospinning crosslinking reactions and adds freedom and flexibility to couple crosslinking with other potential functionalization processes. Two crosslinking reagents, i.e., glutaraldehyde (GA) and polyethylene glycol (PEG) diacylchloride, were employed. With GA, the crosslinking reaction media (aqueous with sodium sulfate and ethanol) and conditions (crosslinker concentration and reaction time) on the membrane structure and properties were investigated. Reaction with PEG, a neutral polyether that exhibits attractive biological properties of being both protein rejecting and biocompatible,[16,17] was exploited by varying the chain lengths and molar ratios. We have previous successfully used PEG chains as spacers to tether enzyme proteins on the surfaces of cellulose nanofibers.[18] The tethered enzymes exhibited excellent catalytic activities while PEG spacers improved the enzyme stability in organic solvents or high temperatures. Reacting the PVA fiber surfaces with PEG diacylchloride should esterify the membranes to provide not only chemical crosslinks but also additional reactivity for further surface functionalization such as immobilization and binding of biomolecules.

EXPERIMENTAL

Materials

Polyvinyl alcohol (PVA, M_w = 124,000–186,000 Dalton, 87–89% hydrolysis, Aldrich), glutaraldehyde (GA, 50% aqueous solution, Acros) and sodium sulfate (Na_2SO_4, Arcos) and ethanol (EtOH, 95%) were used. Poly(ethylene glycol) bis(carboxylic acid), (HOOC-PEG-COOH, 250 and 600 Dalton, Aldrich), thionyl chloride ($SOCl_2$), toluene and pyridine were used without further purification. All aqueous solutions were prepared with purified water from Millipore Milli-Q plus water purification system.

Electrospinning of PVA

Ten percent PVA solution was prepared by dissolving PVA in water overnight under constant stirring. The aqueous PVA solution was fed through a horizontally placed pipette (Fisher, 0.5–10 μL) that serves as the capillary tip. Electrospinning was carried out by charging the solution at 20–25 kV with a power supply (Gamma High Voltage Research Inc.) and collecting the fibers on a grounded aluminum foil collector placed vertically and 8 inch from the capillary tip. The obtained fibrous PVA membranes were dried overnight in the air for characterization and further reactions.

Crosslinking of fibrous PVA membrane

The PVA fibrous membranes were crosslinked by reacting with either GA or PEG diacylchloride. The GA solutions were prepared by diluting 50% aqueous GA with either 0.5 *M* aqueous Na_2SO_4 or ethanol to 0.2 *M* GA concentration, both adjusted to pH 3.0 with 1 *M* H_2SO_4. Fibrous PVA membranes were immersed into aqueous GA/Na_2SO_4 or GA/EtOH solutions at ambient temperature for varying lengths of time from 20 min to 2 days. The membranes reacted with GA/Na_2SO_4 was rinsed with water while that with GA/EtOH was rinsed with EtOH, refreshed every half an hour over 5 h under constant stirring. The GA-reacted PVA membranes were dried under vacuum at 80°C for 12 h.

To prepare PEG diacylchloride, PEG bis(carboxylic acid) (HOOC-PEG-COOH) was acylated with thionyl chloride ($SOCl_2$) under N_2 purge and ambient temperature overnight. Excess $SOCl_2$ was removed by vacuum. The PEG diacylchloride was dissolved in 1/1 v/v toluene/pyridine mixture. Dried PVA fibers were added to ClOC-PEG-COCl solution under N_2 and constant stirring at ambient temperature for 2 days. The PEG-reacted PVA membranes were washed with methanol and vacuum dried at 80°C for 12 h and referred as PEG250-PVA-5, PEG600-PVA-5, and PEG600-PVA-10 to designate those reacted with 250 and 600 dalton PEGs at 5 and 10 COCl/OH ratios, respectively.

Quantification of ester and free carboxylic acid groups

The total acid (COOH) and ester (OCO) contents were quantified by saponification value and reaction with silver *o*-nitrophenolate as reported previously.[19] Saponification values were determined by hydrolyzing the esterified materials with 0.1 *N* NaOH at ambient temperature overnight, then titrating the excess NaOH with 0.1 *N* HCl to the phenolphthalein end point. The total acid (COOH) and ester (OCO) contents were derived from the difference between total and excess NaOH. The content of free acid was determined by the silver *o*-nitrophenolate method. The esterified samples were shaken in a saturated aqueous solution of silver *o*-nitrophenolate for two days. The amount of silver consumed was determined by potentiometric titration of an aliquot of the solution against 0.02 *N* HCl to a pH of 4.6.

Characterization

The morphology of PVA membranes was examined using a scanning electron microscope (SEM, International Scientific Instrument model DS 130) at 10 kV. All samples were sputtered with gold. Thermal

properties were profiled by heating under N_2 at 10°C/min to 500°C in a different scanning calorimeter (DSC) (Shimadzu DSC 60) and a thermogravimetric analyser (TGA) (Shimadzu TGA-50). The heat of melting (ΔH_m) was calculated from the peak area based on calibration and normalized by sample mass. The temperatures where initial weight loss (T_i), maximum decomposition (T_{max}), decomposition (T_d) occurred as well as the quantities of chars at 450°C were reported. The crystalline structure of the PVA membranes was discerned by wide-angle X-ray diffraction (WAXD) at 2θ between 10° and 35°. The interfiber pore volume (C_m) in a fibrous membrane was determined by pore saturation with a low surface tension and low viscosity liquid, i.e., hexadecane, to obtain the sample mass before (W_d) and after (W_m) and calculated as:

$$C_m = (W_m - W_d)/\rho W_d$$

where ρ is the density of hexadecane.

RESULTS AND DISCUSSION

Reaction with GA

Electrospinning of the 10% aqueous PVA solution generated fibrous membrane with 700 nm average fiber diameter [Fig. 1(a)]. The as-electrospun fibrous membranes are instantaneously soluble in water. Crosslinking with GA was performed in either aqueous sodium sulfate (Na_2SO_4) or ethanol (EtOH) solutions. EtOH is miscible with aqueous GA solution, but a non-solvent for PVA. The GA concentration was kept at the same 0.2 *M* or 2 CHO/OH for both systems.

Immersing PVA membranes in 0.5 *M* Na_2SO_4 aqueous solution alone for 1 h at ambient temperature caused fibers to swell considerably and merge with each other, but the fibrous form was still distinguishable [Fig. 1(b)]. The membrane appeared much less porous, but did not dissolve in the aqueous Na_2SO_4. Reaction with aqueous GA was conducted using 0.2 *M* GA in the presence of Na_2SO_4 at pH 3.0 under ambient temperature. With increasing length of reaction time, the fibrous membranes became more stable in water. Reactions that lasted up to 40 min prolonged the time taken to dissolve the membranes, but did not render the membranes insoluble. For the reactions lasted 20 or 40 min, the membranes turned soft and gel-like then fell apart after 20 or 50 min in water, respectively. The 1-h reaction turned the fibrous membrane into insoluble, but very soft, transparent, and gel-like material without its original membrane form. Lengthening the reaction to 1.5 h produced a still transparent, but firm and shape-retaining gel. Full retention of fibrous membrane form was observed on that reacted for 4 h. Prolonging the reaction to 48 h turned the membrane white and very rigid while in water. However, all these water exposed membranes lost their fibrous and porous structures to nonporous transparent film when dried, irrespective of their different forms in water. This indicates that reaction with GA in aqueous Na_2SO_4 did not produce sufficient crosslinking.

Reaction with the 0.2 *M* GA in ethanol resulted in well-preserved fibrous and porous morphology of PVA membrane [Fig. 1(c)]. The originally straight fibers became relaxed, slightly enlarged, packed more closely among the layers and merged in some areas (as indicated by the arrows). Most interfiber pores remained distinctly and could be clearly observed. Further exposing this GA/EtOH crosslinked PVA membrane to EtOH did not cause observable change in the fiber surface morphology nor packing. However, washing the GA/EtOH crosslinked PVA with water caused considerable fiber swelling and merging, resulting in film-like structure with fiber sihlouelle [Fig. 1(d)]. Although slightly better than the reaction in aqueous media, crosslinking with GA in ethanol still did not achieve full shape retention of the fibers nor the membrane.

The reactions between GA and PVA can be intramolecular (I) and/or intermolecular (II) crosslinks (Scheme 1), either should render PVA insoluble. In deed, the earlier results showed reactions with either aqueous GA (48 h) and ethanolic GA (12 h) could render the PVA fibrous membranes insoluble in water and had similar appearance [Fig. 1(b,d)]. Lengthening reaction time facilitated the diffusion of GA molecules in between and into the fibers and retained the membrane form better. The earlier observations showed such reactions with GA rendered PVA insoluble, indicating chemical crosslinks among PVA molecules to generate 3-D polymer network. Despite the lengthy reaction time, these reactions were insufficient to sustain the shape retention of the fibrous structure.

Reaction with PEG diacylchloride

Reactions of PVA fibrous membranes with PEG diacylchlorides were conducted using two PEG chain lengths and two COCl/OH ratios to produce PEG600-PVA-10, PEG600-PVA-5, and PEG250-PVA-5. The PVA membranes were reacted in toluene/pyridine and subsequently rinsed with methanol. In the reaction with the longer PEG chains and higher COCl/OH, or PEG600-PVA-10, the fibrous and porous structure was well retained [Fig. 1(e)]. Both the fibers and interfiber pores appeared to be enlarged [compared to Fig. 1(a)] and larger than that crosslinked with GA/EtOH.

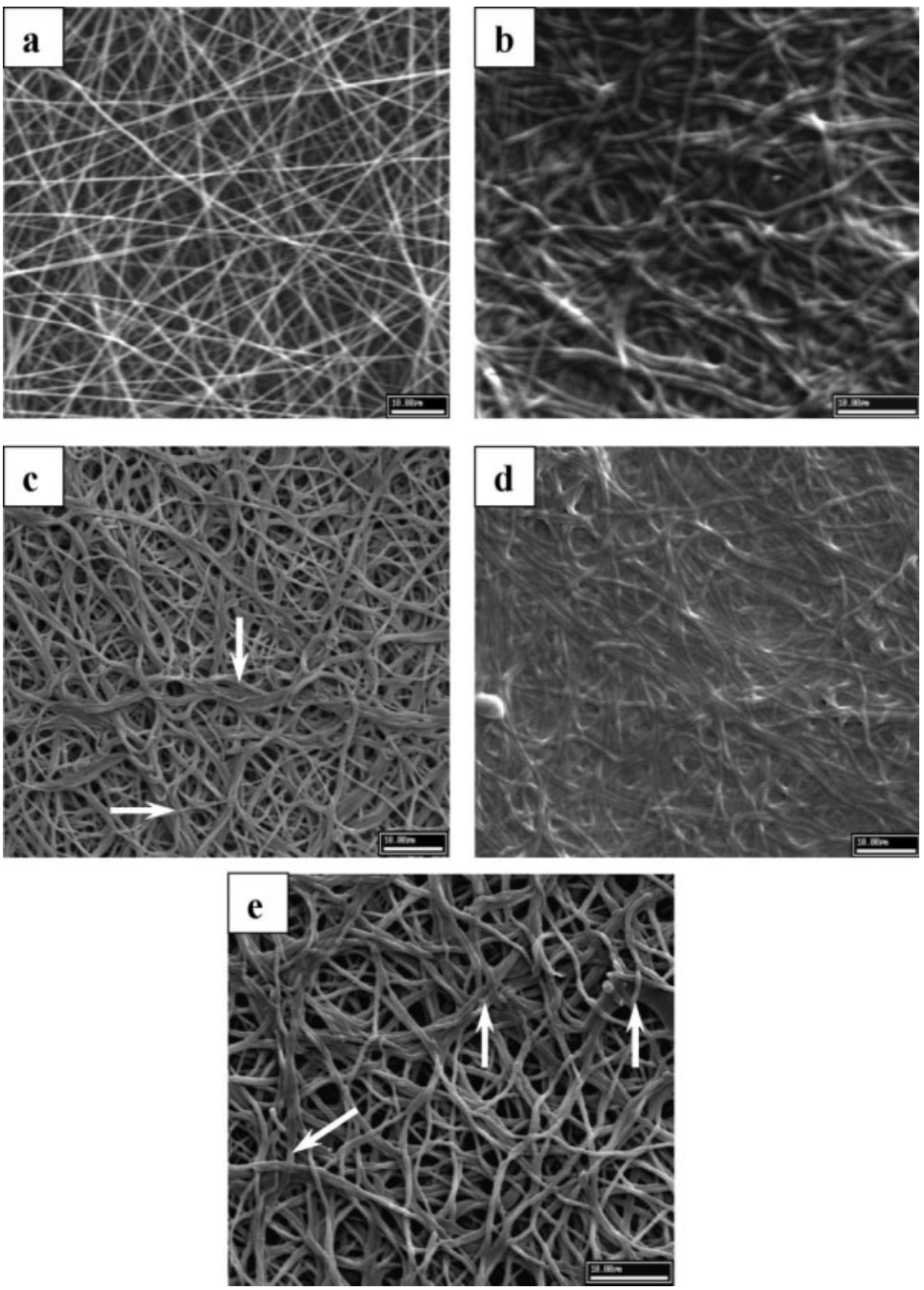
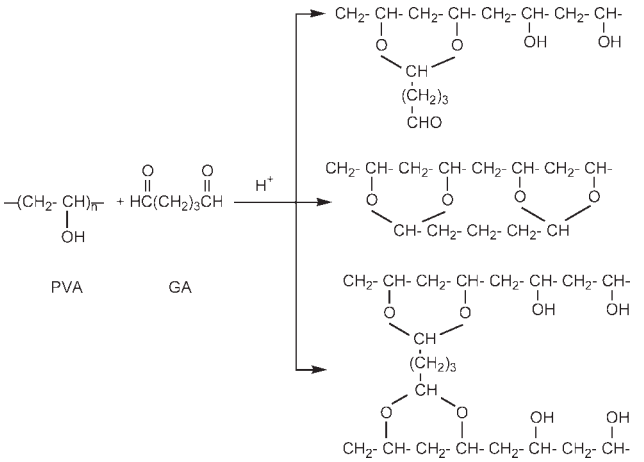


Figure 1 Morphologies of (a) PVA membrane; (b) PVA treated by 0.5 *M* Na_2SO_4 alone; crosslinked PVA membranes with 0.2 *M* GA/EtOH for 12 h; (c) sample in b washed with EtOH (d) sample in b washed with water; (e) PVA crosslinked with 600 *Da* PEG diacylchloride at COCl/OH of 10 (bar = 10 μm).

The reactions between PVA and PEG diacylchloride can proceed to form either PEG-modified PVA (pathway I) or PEG-crosslinks between the PVA hydroxyls (pathway II) (Scheme 2). To examine the extent by which the PEG chains crosslink PVA, the free acid chain ends COOH as well as the total ester OCO and COOH acid end groups were determined and their proportion analyzed. In this analysis, PEG diacylchloride moieties in the PEG-modified PVA were referred as COOH or COCl interchangeably because COCl could readily convert to COOH in the aqueous media during the quantification procedure. For PEG600-PVA-10, the total ester and free acid end groups was 5.89 mmol and free acid COOH was 0.13 mmol per g of fibrous membrane. Based on the fact that each PEG-crosslink contain two esters and each free acid bearing PEG also contain two esters, the PEG attached to PVA membrane in either form was calculated to be 3.01 mmol per g of membrane. Of which, only 0.13 mmol, or merely 4% of



Scheme 1 Reactions of PVA with GA

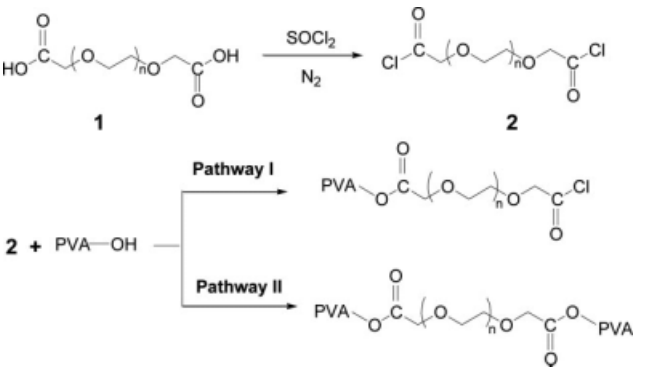
PEG involved in the reaction existed as free COOH end groups. This analysis suggests that esterification of PVA by PEG diacylchloride of 600 at COCl/OH of 10 takes place mainly via pathway II, forming inter- and/or intra-molecular ester linkages, as opposed to grafting reactions.

It is worthy of noting that reaction between electrospun cellulose membranes with PEG diacylchloride produced 4.0 mmol OCO/COOH and 1.0 mmol of COOH per g of cellulose.[17] In other words, in the similar reaction on cellulose, 60% proceeded via pathway I, which happened to serve the purpose of tethering enzyme proteins in the other work. This comparison suggests that the PVA hydroxyls are more accessible to PEG diacylchloride than the hydroxyls on the cellulose those chains are more rigid, highly crystalline and ordered.

The significance of this approach offers other benefits besides rendering the PVA membranes insoluble in water. The biocompatible PEG chains offer great prospects for biotechnological and biomedical applications. The reactive COCl end groups could also impart new functionalities.

Pore volume as affected by crosslinking and water exposure

The interfiber pore volume within the membranes characterized by maximum liquid retention (C_m) of a completely wetting liquid, i.e., hexadecane, showed the native PVA membrane had a C_m of 11 μL/mg. Generally, crosslinking with either GA or PEG significantly reduced the pore volumes of the PVA membranes as indicated by the much reduced C_m values (Fig. 2). This is consistent with the previous SEM observation (Fig. 1) that the crosslinking reactions cause the fibrous structure to be more compacted with reduced porous structure. Exposure to water (24 h) also further reduced the interfiber pore volumes.



Scheme 2 Reactions of PVA with PEG diacylchloride

Among the crosslinkers and reaction conditions, aqueous GA reaction reduced the total interfiber pore volume most substantially from 11 to 1.8 μL/mg or by 84% while the shorter PEG at a lower ClO/OH ratio of 5 (PEG250-PVA-5) caused the least (~ 19%) pore volume reduction. Either lengthening the PEG chains (PEG600-PVA-5) or increasing the extent of crosslinker (PEG600-PVA-10), caused further pore volume reduction of the membranes to 5.0 or 2.3 μL/mg (by 55% or 81%), respectively (Figure 2, open bars). Among the PEG crosslinking reactions, the compaction of fibers was less with either lower PEG chain lengths or lower ClO/OH ratio. Both are consistent with the higher degree of crosslinking produced by longer and higher contents of PEG diacylchloride in the reaction.

Exposing the crosslinked PVA membranes to water also further reduced the total pore volume. Water exposure reduced the pore volume of the GA/EtOH crosslinked membrane from 5.7 to 1. 8 μL/mg, a nearly 69% loss. This is believed to be due to the ability of water to swell the hydrophilic

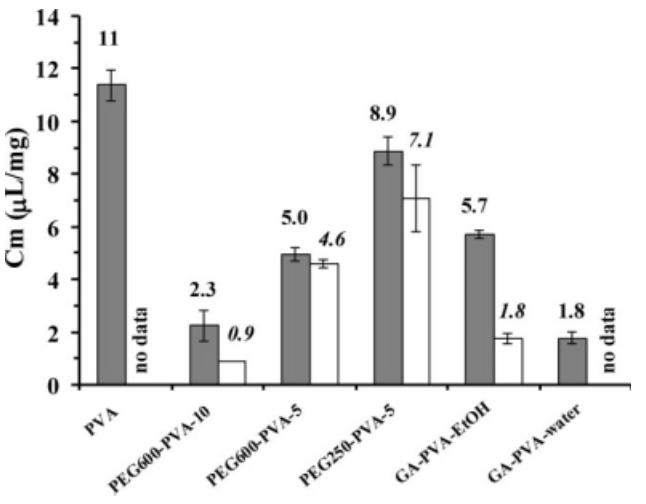


Figure 2 Pore volume by maximum liquid retention (C_m) of as-electrospun (grey) and GA and PEG diacylchloride modified (open) PVA membranes.

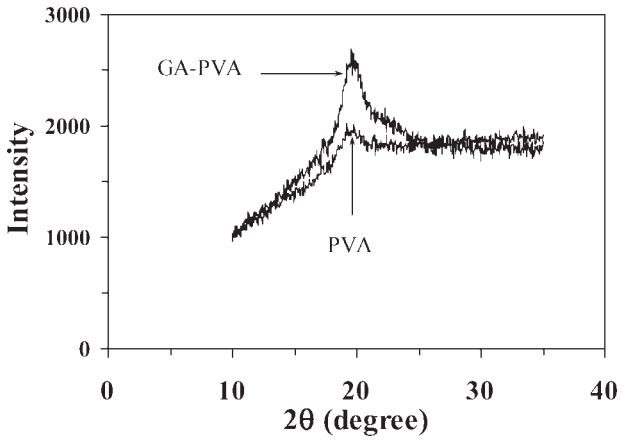


Figure 3 WAXD of as-electrospun PVA fibers and PVA crosslinked with 0.2 *M* GA/EtOH for 12 h and subsequently washed with EtOH.

fibrous membranes and reducing the interfiber pore spaces. The PEG-crosslinked PVA fibrous membranes tended to change less in their total pore volumes, i.e., by 20, 8, and 61% for PEG250-PVA-5, PEG600-PVA-5 and PWG600-PVA-10, respectively.

The overall porosity of the fibrous membranes depends on the arrangement and packing density of fibers and is critical to their performance and applications. The pore volume reduction can be results of compaction of interfiber spaces and/or fiber enlargement. The observations above showed reduced porosity was due to compaction of fiber structure in terms of chemical crosslinking reactions and fiber swelling in the cases with water exposures.

Crystalline and thermal properties

The wide-angle X-ray diffraction of the electrospun PVA membrane showed one small peak at 20° 2θ (Fig. 3), suggesting the presence of crystalline microstructure in the as-electrospun PVA fibers. The crystalline structure was also evident by the melting peak (T_m) at around 190°C with a melting enthalpy (ΔH_m) of 39 J/g, followed by a decomposition endothotherm at around 318°C. Both X-ray diffraction peak and melting endotherm support the notion that electrospinning alone induces some levels of order, being crystalline and/or oriented, in the fibers (Table II). Evidence of crystalline structure in electrospun fibers has been reported on those from polyamide-6,[20] polylactide[20] as well as PVA.[21]

Crosslinking with GA/Na_2SO_4 lowered both T_m and ΔH_m and the extent of both decreased with increasing CHO/OH ratios from 0.5 to 2, i.e., T_m from 173°C to 165°C and ΔH_m from 24 J/g to 14 J (Table II). These T_m and ΔH_m decreases indicate the diminution of crystallinity and perfection of the crystal structure in PVA fibers as a result of increasing crosslinking. Similar diminishing WAXD peaks in PVA fibers have also been reported from crosslinked with glyoxal ranging from 2 to 10 wt %[19]. Extending crosslinking time raised T_m yet decreased ΔH_m slightly while imposing little on the decomposition behavior.

The WAXD of GA/EtOH-crosslinked PVA membrane showed a peak in the same 20° position yet was stronger in comparison to the uncrosslinked membrane, indicating that the PVA crystalline microstructure was enhanced upon crosslinking with GA in EtOH which may have enhanced the crystallinzation and/or perfection of crystals of PVA fibers.. The GA/EtOH (2 CHO/OH, 25°C) crosslinked PVA had unaltered T_m at 190°C with a slightly higher ΔH_m of 41 J/g, which agrees with the improved crystalline microstructure by WAXD (Fig. 4).

On the contrary, none of the PEG-crosslinked membranes showed PVA melting at any PEG lengths or COCl/OH molar ratios (Fig. 4), indicating loss of crystalline structures upon reaction and/or exposure to the organic media. The PVA fibrous membrane reacted with the short PEG chain and lower PEG content exhibited a significantly reduced PVA decomposition endotherm whereas those reacted with longer PEG chains e.g., PEG600-PVA-10 and PEG600-PVA-5, showed new and intense exothermic peaks at 410°C. These observations clearly showed the significant impact of PEG on the decomposition behavior of PVA.

In the TGA thermogram, the PVA membrane lost about 4% mass at temperatures up to 80°C due to the evaporation of absorbed moisture (Fig. 5). The decomposition of PVA began around 280°C and lost half of its mass at 340°C, leaving merely 4% residue

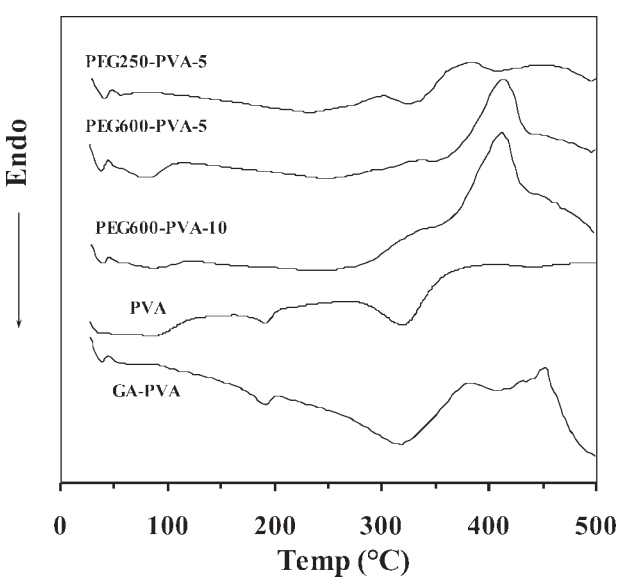


Figure 4 DSC of PVA and modified PVA with GA and PEG diacylchloride.

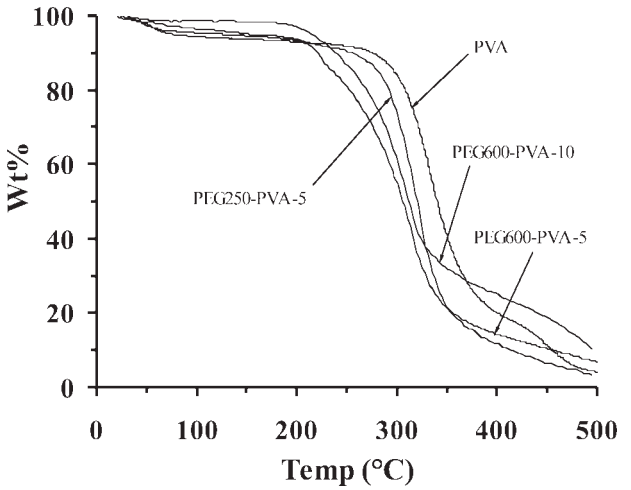


Figure 5 TGA of PVA and modified PVA GA and PEG diacylchloride.

at 500°C. The PEG-reacted membranes showed slightly lowered moisture absorption as well as onset temperature of decomposition while leaving slightly more char. The extent of lowered moisture absorption and onset decomposition temperature of decomposition were generally increased with longer PEG chain lengths and higher PEG contents, consistent with altered decomposition behavior observed by DSC.

CONCLUSION

Electrospinning of aqueous PVA solutions followed by crosslinking the as-electrospun fibrous membranes with difunctional reagents, i.e., glutaraldehyde (GA) and PEG diacylchloride, was proven to be effective in fabricating water-stable hydrophilic PVA fibrous membranes. The as-electrospun PVA fibers were partially crystalline (T_m = 190°C, ΔH_m = 39 J/g, 2θ peak at 20°) and such ordered structure was affected by the crosslinkers and reactions differently. Crosslinking with GA/EtOH enhanced the crystalline structure in PVA membranes whereas that with GA in aqueous Na_2SO_4 solutions reduced crystallinity and crystalline structure in PVA fibers. On the contrary, crosslinking with PEG diacylchloride in toluene/pyridine caused complete loss of crystalline structure. The crosslinking reactions generally caused the fibrous structure to become more compacted with reduced interfiber pore volume. Aqueous GA reaction caused the most (84%) while the shorter PEG at a lower ClO/OH ratio caused the least (~ 19%) pore volume reduction. Exposing the crosslinked PVA membranes to water further reduced the pore volume, again more with the GA-crosslinked than PEG-crosslinked ones. The observed pore volume reduction appeared to be due to compaction of fiber structure in terms of chemical crosslinking reactions and fiber swelling in the cases with water exposures. Among all crosslinking agents and conditions studied, reaction with shorter and lower extent of PEG produced water-insoluble PVA fibrous membrane with least change to the interfiber porous structure. The biocompatible PEG chains offer great prospects for biotechnological and biomedical applications. The reactive COCl end groups could also impart new functionalities.

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