Engineering novel polyelectrolyte complex membranes with improved mechanical properties and separation performance

Journal:	*Journal of Materials Chemistry A*
Manuscript ID:	TA-ART-11-2014-006477.R1
Article Type:	Paper
Date Submitted by the Author:	15-Feb-2015
Complete List of Authors:	Wang, Xue san; Key Laboratory of Macromolecular Synthesis and Functionalization (Ministry of Education), Polymer Science and Engineering Ji, Yan-Li; Key Laboratory of Macromolecular Synthesis and Functionalization (Ministry of Education), Polymer Science and Engineering Zheng, Pei-Yao; Key Laboratory of Macromolecular Synthesis and Functionalization (Ministry of Education), Polymer Science and Engineering An, Quan fu; Key Laboratory of Macromolecular Synthesis and Functionalization (Ministry of Education), Polymer Science and Engineering Zhao, Qiang; Key Laboratory of Macromolecular Synthesis and Functionalization (Ministry of Education),, Lee, Kueir-Rarn; Chung Yuan University, Chemical Engineering Qian, Jin wen; Key Laboratory of Macromolecule Synthesis and Functionalization, (Ministry of Education), Polymer Science and Engineering Gao, congjie; Zhejiang University, Department of Chemical & Biological Engineering

Journal of Materials Chemistry A

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Engineering novel polyelectrolyte complex membranes with improved mechanical properties and separation performance

Xue-San Wang,[a] Yan-Li Ji,[a] Pei-Yao Zheng,[a] Quan-Fu An,*[a] Qiang Zhao,[a] Kueir-Rarn Lee,[b] Jin-Wen Qian[a] and Cong-Jie Gao[c,d]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Polyelectrolyte complexes (PECs) commonly suffer from poor processability owing to their ionic crosslinking nature, a problem which spurs increasing interest in processable PECs. New processing technologies have been exploited to render PECs processable, but usually at the expense of compromising their mechanical properties. Through a conceptually novel strategy of "complexation-sulfation", here we engineer solution-processable PECs derived from strong polyacid, in the pursuit of high mechanical strength combined with exceptional separation performance. Effects of chemical structures and compositions on mechanical properties of these PEC membranes were studied. It was found that the mechanical properties of these PEC membranes based on strong "ion-pairs" were substantially enhanced, with their tensile strength and elongation at break reaching as high as 108.3 MPa and 5.0 %, respectively. In addition, PEC membranes exhibited a high performance in separating water-ethanol mixtures. For example, the flux and water content in permeate for PEC membranes was 2100 g/m^2 h and 99.58 wt%, respectively, in dehydrating 10 wt% water-ethanol mixture at 70 ^{o}C.

Introduction

Polyelectrolyte complexes (PECs) are formed by electrostatic interactions between positively and negatively charged polymers, whereas the entropy gain associated with the release of counter-ions is the major driving force for PEC formation.[1] Attributed to their multi-component nature and the ionic complexation structures, PECs have found applications ranging from papermaking,[2] functional coatings and films,[3-5] to gene delivery vehicles,[6] coacervates and smart materials.[7] Very recently, bio-inspired PEC nanocomposites with supreme mechanical strength are being actively explored, with higher quality and practical durability attained.[8-10] Moreover, PECs are known to be straightforward in preparation, as exemplified by the layer-by-layer (LbL) assembly and the solution mixing of oppositely charged polyelectrolytes.[11-14] While the LbL method usually produces thin films with tailored structures and thickness,[11,12] the solution mixing method commonly yields agglomerates and precipitates.[13,14] Nevertheless, PEC materials prepared in both methods suffer from the low processability as a result of their electrostatic cross-linking structures, i.e., the acquired PEC bulks are notoriously known as insoluble and infusible.[13]

As such, increasing efforts are being directly paid toward improving the processability of PECs, in the faith that processability is the premise for functionality of bulk PECs. For example, Schlenoff et al. exploited the concept of "saloplastic PECs", which improved the processability of bulk PECs by salts doping.[15-17] These authors were able to prepare bulk PECs with different shapes (rod, tapes, and tubes) via conventional processing methods such as extrusion.[18] Yet, the presence of external salts in the saloplastic PECs would weaken the ionic bonding, leading to the poor tensile strength (lower than 20 MPa).[18] Recently, our group introduced an "acid-protection" method which conferred solution processability to bulk PECs,[19] giving rise to a variety of PEC membranes with improving performance in pervaporation and desalination.[20] While the success of this method inevitably relies on the utilization of weak polyelectrolytes containing carboxylic acid groups, the mechanical strength of these membranes is not satisfactory (~30 MPa tensile strength for the pristine PEC membranes).[21,22] The tensile strength could be improved to be 65 MPa and 110 MPa with the incorporation of carbon nanotubes and graphene oxides,[21,23] respectively, however, their membranes' permeability would be reduced. As such, the optional combination of PECs' processability and mechanical strength remains an unresolved problem, which necessitates new strategies that could go beyond the current dilemma and confer higher mechanical strength to processable PEC bulk materials. In particular, the mechanical improvement without incorporating external nanofillers or salts is sought after, so that the properties (e.g. molecular separation) of pristine PECs could be largely preserved.[24]

In this study, we set out to tackle the above mentioned problem by incorporating strong polyelectrolytes into the system, as it has been hinted that the strength of the ionic interactions between strong polyelectrolytes is larger than that between weak ones.[25] However, every coin has two sides; the processability of PECs based on strong polyacid is even more challenging. For example, our previous "acid-protection" strategy no longer applies to strong polyelectrolytes systems, and higher ionic strength is required in order to shield the complexation force.[26] To this end we exploit a new concept of "complexation-sulfation", which unlike previous strategies, relies on the post chemical modification to confer the beneficial processability to PEC systems. In detail, chitosan (CS) and dextran sulfate sodium (DSS) (strong polyacid) are solution-mixed to prepare their PECs. Subsequently, through the sulfation of residual NH_2 groups on CS, the PECs are made solution-processable without affecting their ionic compelxation structures. In doing so, high mechanical strength (the tensile strength up to be 108 MPa) is combined with high separation performance.

Experimental section and characterization

Materials

Chitosan (CS) (Mn = 200,000 g/mol, deacetylation degree = 90 %) was purchased from Yuhuan Chemical Company, Zhejiang, China. Dextran sulfate sodium (DSS) solids (Mw≈40,000) was all acquired from Aldrich, and used as received. Sodium carboxymethyl cellulose (CMCNa) (degree of substitution: 0.85) was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. The chemical structures of these materials are shown in Fig. S1. Trim-ethylamine-sulfur trioxide complex ($(CH_3)_3N{\bullet}SO_3$) was obtained from Aldrich and utilized without further treatment. All organic solvents used in this work including alcohols (ethanol, isopropanol and n-butanol), dimethyl sulfoxide (DMSO), diethyl ether (DEE) and dichloromethane (DCM) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further treatment. Hydrochloric acid (HCl), acetic acid, sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) were analytical reagents. Polysulfone ultra-filtration membranes were kindly provided by the Development Centre of Water Treatment Technology, Hangzhou, China, which were employed as membrane substrates for pervaporation dehydration. In all experiments, de-ionized water with a resistance of 18 MΩ cm was utilized.

Preparation of sulfated PECs (S-PECs) and their membranes

S-PECs were prepared with complexation-sulfation strategy (Fig. 1). First, 0.01 M CS was dissolved in 400 mL aqueous solution at pH 4.0 with HCl, and then the solution pH value was tuned up to be 6.15 with NaOH. Subsequently, 0.01 M DSS solutions (pH = 6.15) were dropped into CS solutions under vigorous stirring (600 rpm), producing DSS/CS PEC precipitates when CS was adequately neutralized (Fig. S2). The obtained DSS/CS PECs were washed thoroughly and dried at 50 °C for 6 h. Subsequently, the sulfation step was conducted to render these PECs soluble. This sulfation reaction was N-sulfation of NH_2 groups, which transferred the NH_2 group in CS into $NHSO_3^-$ groups, by using trim-methylamine-sulfur trioxide complex ($(CH_3)_3N{\bullet}SO_3$) as the sulfation agent.[27] In detail the dried DSS/CS PECs (0.8 g) were dispersed in a Na_2CO_3 aqueous solution (60 mL), and then $(CH_3)_3N{\bullet}SO_3$ was added. This dispersion was maintained at pH 9.0 by varying the molar ratio of Na_2CO_3 to $(CH_3)_3N{\bullet}SO_3$, and was kept at 60 °C for 5 h for the sulfation reaction. Afterwards a homogeneous solution was obtained (Fig. S2), and was precipitated in ethanol to obtain sulfate DSS/CS (S-DSS/CS) PECs. The acquired S-DSS/CS complexes were dispersed in 80 mL water, and precipitated in ethanol, collected and then washed three times with an ethanol-water 80 % (v/v) mixture to get rid of the residual salts. The obtained S-DSS/CS PECs were dried (50 °C, 12 h), and their chemical compositions were controlled by tuning the mole ratio of $(CH_3)_3N{\bullet}SO_3$ to the monomer unit of CS. The mole ratio of $(CH_3)_3N{\bullet}SO_3$ to the monomer unit of CS in DSS/CS complexes was denoted by X, and the corresponding complex was designated as S-DSS/CS-X. The degree of sulfation (DS) was designated as follows:

$$\mathrm{DS}=\left(\frac{[\mathrm{S}]_S}{[\mathrm{N}]_S}-\frac{[\mathrm{S}]_0}{[\mathrm{N}]_0}\right)\times 100\%$$

$[S]_0$ and $[N]_0$ were denoted as the concentrations of S and N atoms in the pristine PEC, $[S]_S$ and $[N]_S$ were presented the concentrations of S and N atoms in S-PECs, respectively.

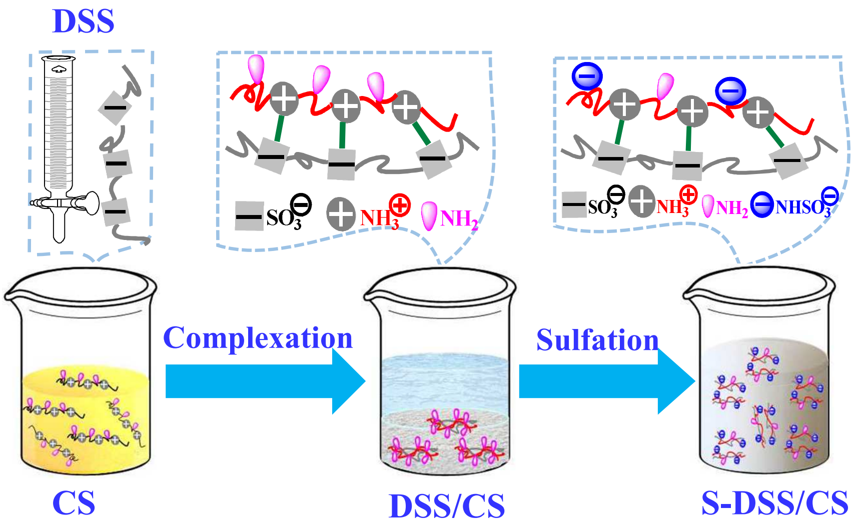

Fig. 1 Schematic fabrication of solution-processable S-DSS/CS PECs based on strong polyacid.

The degree of sulfation for S-DSS/CS complexes was given in Table 1. For membrane preparation S-PECs were dispersed in water (2 wt %, pH 7.0). S-PEC membranes were fabricated by casting this solution on the polysulfone ultra-filtration supporting membranes, followed by two steps drying (35 ^{o}C for 24 h, plus 60 ^{o}C for 2 h) to remove any residual solvent. The thickness of S-PEC membrane active layer was kept at ca. 2.5 μm.

Characterization

Fourier transform infrared spectroscopy (FT-IR) for solid PECs was obtained using a BRUKER VECTOR 22 FT-IR spectrometer (Germany). PECs were dispersed in KBr and made into pellets. The size and zeta potential of PEC particles were examined with 0.02 wt% dispersion solution (pH 7.0) pre-filtrated with a microfiltration membrane (pore size: 2 μm) by using dynamic light scattering (DLS, 90 Plus/BI-MAS, USA). The particle morphologies of PEC (0.005 wt% aqueous solution) and cross-sectional morphologies of PEC membranes were observed with a Hitachi S4800 field emission scanning electron microscopy (SEM, SIRION-100, USA).. Attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR) measurement for a membrane was performed using a Nicolet FT-IR/Nexus 470 spectrometer, which was equipped with an ATR accessory (ZnSe crystal, 45^{o}). Stretching tests of a membrane were employed on a universal testing machine (SANS CMT4204, Shenzhen, China) at a stretching rate of 1 mm min^{-1} as previously reported.[21] Tensile data of a membrane (20×10 cm, thickness 12 to 15 μm) was averaged by testing five samples, whereas the atmosphere relative humidity for stretching tests was maintained at 30 %. All membrane samples for tensile tests and ATR-FTIR were dried under vacuum (35 ^{o}C, 24 h) to constant weight, and then equilibrated with the atmosphere humidity of 30 % for *ca.* 6 h. The concentrations of S, O, and N atoms in PECs were analyzed by X-ray photoelectron spectroscopy (XPS, PerkinElmer PHI 5300 ESCA) with Mg/Al Dual Anode Hel/Hell ultraviolet source (400 W, 15 kV, 1253.6 eV). Pervaporation experiment was employed to characterize the separation performance of these homogenous S-PEC membranes. This was performed on the same apparatus as the previous report.[19] Permeation flux (J) and water content in permeate were used to evaluate the pervaporation performance of a measured membrane.

Table 1 Compositions of DSS/CS and their S-PECs determined by XPS.

Sample	Molar ratio (sulfate agent:CS)	S (At. %)	N (At. %)	S:N	DC [a]	DS [b]
DSS/CS	-	0.97	2.31	0.42	0.42	-
S-DSS/CS-1	1	1.21	2.08	0.58	-	0.16
S-DSS/CS-2	2	1.36	1.94	0.70	-	0.28
S-DSS/CS-3	3	1.42	1.59	0.89	-	0.47

DC [a]: Degree of complexation; DS [b]: Degree of sulfation.

Results and discussion

First we tested the solubility of as prepared PECs (before sulfation) in various solvents under different conditions (Fig. S3). DSS/CS PECs appear fairly insoluble in four representative solvents of DMSO (electron acceptor), ethanol (proton donor), DCM (dipole-dipole interaction) and DEE (proton acceptor), respectively (Fig. S3a). Though PECs are dispersible in 4.5 M NaCl aqueous solution under vigorous stirring at 30 ^{o}C for 24 h, the presence of high centration salts severely weakens or breaks the ionic bonding (Fig. S3b).[18,24] Moreover, as shown in Fig.2, the weight of the PECs before and after being soaking in various organic solvents (30 ^{o}C, 24 h) and hot water (80 ^{o}C, 24 h) was changed less than 5 wt% weight loss. Given these results, a conclusion could be drawn that PECs based on strong polyacid (before sulfation) are insoluble in most of solvent conditions, which is a common feature of normal PECs.[28]

Thus we apply the sulfation reaction to DSS/CS PECs for imparting processability to the insoluble materials without severely disrupting their ionic complexation structures. Indeed, we found that the PECs after sulfation reaction were easily dispersed in pure water at 25 ^{o}C, without the need for either additional salts or organic solvents in the system. Importantly, the obtained solution is stable even after 100 d (Fig. S2), implying a good dispersibility of the sulfated PECs in water. The chemical structures of S-DSS/CS PECs was characterized by FTIR (Fig. 3).

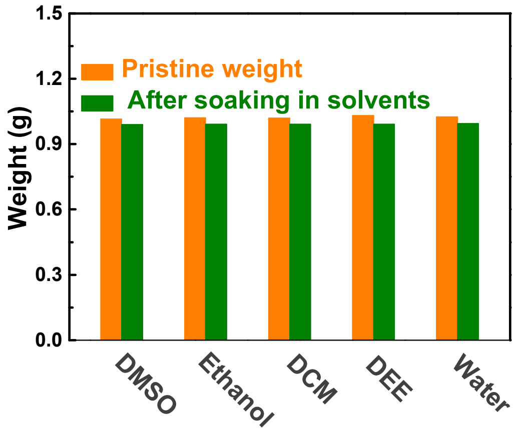

Fig. 2 Weight variation of DSS/CS after being soaked in different solvents (DMSO, ethanol, DCM and DEE) at 30 ^{o}C for 24 h, and water at 80 ^{o}C for 24 h. All samples were dried at 60 °C under vacuum to constant weight.

On the basis of Fig. S3 (CS and S-CS), the net decrease in the intensity of the peak at 1590 cm^{-1} (NH_2),[29] and the appearance of a large shoulder at 1125 cm^{-1} (O=S=O),[27] as well as the absence of the peak at 800 cm^{-1} (C-O-S symmetric vibration) are observed,[30] which indicates that a selective sulfation occured with

NH_2 groups but not the hydroxygroups. This result corresponds with the doccumented result in the literature.[31] The virations of these peaks are also seen in S-DSS/CS compared with DSS/CS complexes as shown (Fig. 3), which indicates S-DSS/CS PECs are sucessfully sulfated. From Fig. 3 it is also seen that the characrteristic peaks of sulfate groups for S-DSS/CS are at 720 cm^{-1} and 625 cm^{-1} reveals, while the characrteristic peak of sulfate groups for sulfated CS is at 625 cm^{-1} alone. The absorption peak at 625 cm^{-1} is ascribed to the free sulfate (i.e. $NHSO_3^-$) groups, which are exisisted in both sulfated CS and S-DSS/CS. The absorbtion band at 720cm^{-1} is associated with the complexed sulfonate groups, which is in presence of S-DSS/CS and DSS/CS complexes formed by sulfonate groups on DSS chains and NH_3^+ groups on CS chains. Meanwhile, the dextran characteristic peaks of DSS and CS at 1240 cm^{-1} and 889 cm^{-1} are also seen in the FT-IR spectra of S-DSS/CS and DSS/CS complexes.[32,33] These obervations indicate that S-DSS/CS complexes are formed without breaking their ionic-complexation and the dextran main-chain structure. Morover, the absorption intensity at 625 cm^{-1} (free sulfate groups) for S-DSS/CS PECs increases with increasing the amount of the sulfate agent, indicative of the tunable compositions of S-DSS/CS PECs.

The S-DSS/CS dispersion is milk-white (Fig. S2). Thus it is rational to expect that the dispersion is composed of colloidal particles, which is confirmed by the dynamic light scattering and SEM (Fig. 4). From Fig. 4a and b, as-prepared S-DSS/CS PEC particles appear as needle-shaped nanostructures, which are PEC aggregates as a result of the binding between polyacid and CS chains via ionic interaction. The morphologies of PEC nanoparticles can be either needle-shaped or round, as previously reported.[34] These needle-shaped morphologies of DSS/CS complexes are typical for charged PEC parties,[35] which are probably due to the rigid and extended conformation of both CS and DSS polyelectrolyte chains before mixing.[36,37] Additionally, the zeta potential characterizations (Fig. 4c) confirm that they are negatively charged. It is also observed that the negative potential of S-DSS/CS complex increases with increasing the degree of sulfation, which indicates that the free sulfate groups are incorporated into S-DSS/CS PECs in a tunable fashion. Moreover, the depositing of S-PEC aggregates in Fig.4b is shown as the fibriform and seems some tortuous. This is because the molecular chain conformation of CS and DSS within S-PEC particles was changed with increasing the hydrophilicity and electrostatic repulsive effect via incorporating the sulfate groups into S-PECs. All of above observations are in good agreement with the FTIR and XPS results (Fig. 3, Table 1). It is seen from Fig. 4d that the size of S-PEC particles ranges from 450 to 600 nm, which increases with increasing the degree of sulfation. This observation is ascribed to the formation of more expanded polyelectrolyte chains in S-DSS/CS PEC particles and higher hydration ability, owing to the increasing charge density of their chains arising from free SO_3 groups.[38] Thus Fig. 4 verifies that S-PEC particles based on strong polyacid containing free strong-acid groups are prepared.

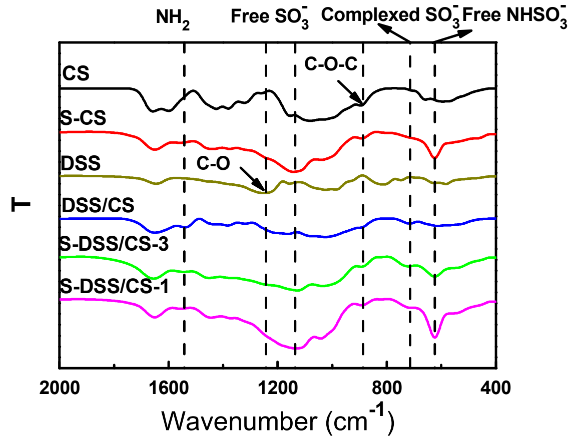

Fig. 3 FT-IR spectra for CS, sulfated CS (S-CS), DSS, DSS/CS complex and their S-DSS/CS PECs.

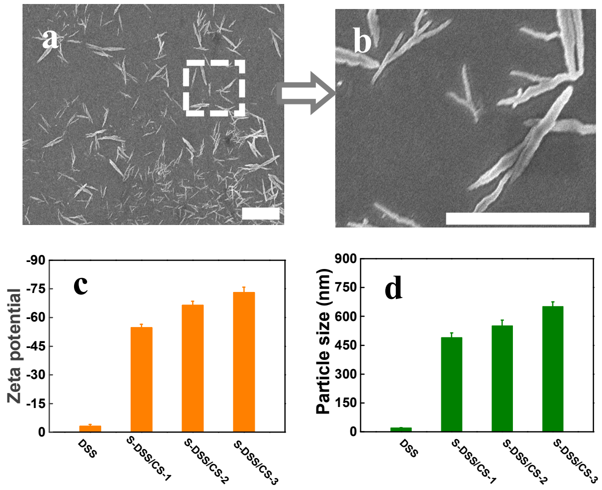

Fig. 4 (a, b) SEM micrographs of S-DSS/CS-3, (c) zeta potential and (d) DLS size (number average) of S-PECs and DSS. The scale bars in SEM are 1 μm.

Fig. 5 provides the optical micrographs of S-DSS/CS-1 membranes and SEM cross-sectional pictures of membranes for tensile testing. From Fig. 5a, it is seen that S-DSS/CS PEC membranes appear homogenous and transparent. Moreover, S-DSS/CS PECs possess good membrane form ability, and these membranes in a large scale (12×10 cm) can be easily fabricated (Fig. 5a). These membranes are also endowed with good flexibility (Fig. 5b). As such, S-PECs based on strong polyacid are solution-processable. The thickness of S-PEC membranes utilized for tensile testing is controlled at ca. 13 μm (Fig. 5c and d), which is comparative with the PECMs prepared with layer-by-layer.[1,12,21]

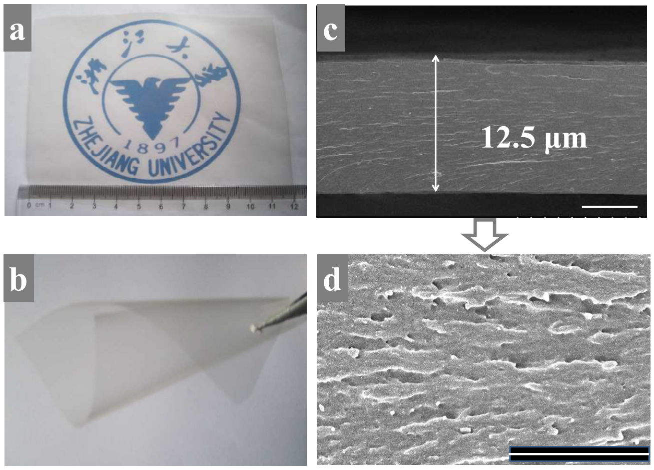

Fig. 5 (a, b) Optical micrograph and (c, d) SEM cross-section of the S-DSS/CS-1 membranes. The scale bars are 5μm.

Subsequently the mechanical properties of PEC membranes were investigated under controlled humidity (e.g. 30 %) as reported in many literatures [39,40] (Fig. 6). It is clearly seen that the tensile strength of PECMs is highly enhanced by the incorporation of strong ion-pairs. It should be mentioned that the ionic cross-linking degrees of these membranes are maintained at ca. 0.42 (Table S1 and S4). The chemical structures of DSS and CMC have similar cyclic ester and hydroxyl groups but different ion groups (Fig. S1). The tensile strength and elongation at break for S-DSS/CS-1 membrane based on only strong acid groups are 108.3 MPa and 5.0 %, both of which are much higher than those for CMC/CS membrane (31.2 MPa, 1.5%) based on weak acid groups. This result indicates that the strong ion-pairs could simultaneously improve the strength and flexibility of their membranes, which is understandably because the sulfonate groups on DSS chains and ammonium groups on CS chains form strong ion pairs.[14] In detail, the difference in free energy of association of an ammonium group with a sulfonate group and a carboxylate group is as large as 15 KJ mol^{-1} for PECMs.[22] On basis of Fig. S5, S6 and Table S2, it can be seen that the higher content of bound water exists in S-DSS/CS in comparison with SCMC/CS (Fig .S3) and CMC/CS, which is due to the super-high hydrophilicity of strong-ion groups in PECMs as described in Fig. 7. It is this bound water that serves as a plasticizer enhancing both free volume and lubricity between PEC chains,[41] and thus the elongation at break for PECMs is improved. As shown in Fig. 6, the tensile strength decreases with increasing the degree of sulfation of S-DSS/CS PEC and vice versa for the elongation at break increases. It is readily anticipated that the NH_2 groups are reduced with increasing the degree of sulfation in S-DSS/CS membranes. The hydrogen bond formed by NH_2 groups is weakened, reducing the tensile strength for S-DSS/CS membranes. The hydration ability of S-DSS/CS membranes tends to increase with increasing the degree of sulfation (Table S2), thus the elongation at break for S-DSS/CS membranes increases accordingly.[41] In conclusion, mechanical properties of PECMs are effectively improved via the incorporation of strong ion-pairs.

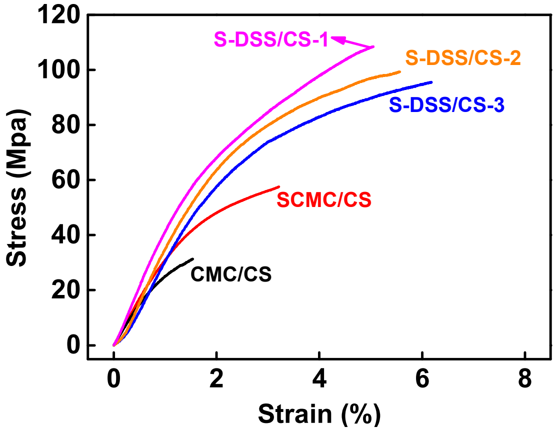

Fig. 6 Stress–strain curves of PEC membranes with different types of ion-pairs.

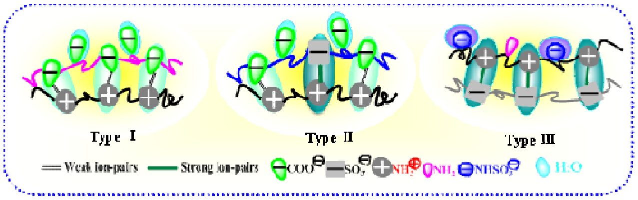

Fig. 7 Schematic diagram of hydration state in PEC membranes.

Mechanical properties of S-DSS/CS membranes are compared with the vairous polyelectrolytes films reported previously (Table 2),. The mechanical properties of as-prepared S-PEC membranes virtually outperform other PEC membranes based on weak-acid groups,[8,21,42-45]. Mechanical strength of the S-DSS/CS membrane is thought to be a cumulative product of many factors,[22,23,46] e.g., macroscale defect free with homogeneity distribution of the oppositely charged polyelectrolytes, rigidity of the polysaccharide molecular chains, strong interfacial attraction from strong ion pairs, and the plasticization of the super-hydrophilic sulfonate groups. It is observed that the S-DSS/CS membranes are also stronger than the assembled PEC membranes prepared with layer-by-layer method.[1,47,48] Moreover, S-PEC membranes containing no nanofillers show mechanical properties competitive with the hybrid films.[12,21,23,49]

In addition to the mechanical properties, we are also interested in how the “strong ion pair” structures will influence its membrane separation performance. Pervaporation for the dehydration of alcohols is energy-saving, easy manipulation and low cost in comparison with the traditional distillation or adsorption.[50] As such there is great interest in the pervaporation dehydration of aqueous ethanol solutions by using PEC membranes. All these PEC membranes show improved pervaporation performance in comparison with the CS membranes (Fig. 8), due to their hydrophilic properties and ionic cross-linking membranes. structures.[11] S-DSS/CS membranes exhibit higher flux and selectivity than the homogenous CMC/CS membranes based on weak polyacid, which is attributed to the higher hydrophilic property for strong-acid groups than that for weak-acid groups.[26] As shown in Fig. 8, both the flux and selectivity increases substantially with increasing the degree of sulfation for S-DSS/CS PEC membranes. This result is attributed to the sulfate groups which attract water molecules while repel organic molecules.[26,51] As such the pervaporation performance of S-DSS/CS membranes is effectively improved by the free sulfate groups. In the dehydration of a 10 wt% water-ethanol mixture at 70 °C, both of the flux and water content in permeate for S-DSS/CS-3 membranes maintain at 2100 g/m^2 h and 99.58 wt% in the continuous operation of 60 h (Fig. S7). From Table S3 S-DSS/CS-3 membranes exhibit ultra-high permeation flux and selectivity in comparison with poly(vinyl alcohol) and other polyelectrolyte membranes.[19,51-55] Additionally, S-DSS/CS-3 membranes show high pervaporation performance in the dehydration of both butanol and isopropanol aqueous solutions (Fig. S8). This exceptional separation performance of S-PEC membranes is probably because they combine the compact structures contributed by complexed strong-acid groups and the enhanced hydrophilicity associated with free strong-acid groups.[22,37] In addition to S-DSS/CS solution-processable PECs, in the same method we also prepare solution-processable S-PSS/CS and S-PVS/CS, both of which also exhibit good mechanical properties and pervaporation dehydration performance (Fig. S9). Given that both of the two PECs are based on strong polyacid, this indicates the relatively broad applicability of the strategy.

Table 2 Comparison of mechanical properties of the S-PEC membranes in this work with the results of other PECs and their nanocomposite films.

Membrane	Tensile strength	Elongation at break	Modulus	Reference
S-DSS/CS-1	108.3 MPa	5.0 %	4.3 GPa	This work
PAA/CS	13 MPa	4.0 %	-	42
PC/PA	23 MPa	-	-	33
CMC/Gelatin	40 MPa	-	-	34
Gelatin/CS	58.8 MPa	-	-	45
CMC/PVAm	60 MPa	3.5 %	2.1 GPa	8
CMC/PDDA	33.5 MPa	1.9 %	1.6 GPa	21
PAA/PEI LbL film	9 MPa	4.2 %	40.0 GPa	47
PSS/PDADMA LbL film	19 MPa	4.0 %	-	1
PSS/PDDA LbL films	24.1 MPa	5.0 %	0.6 GPa	48
MMT/PDDA LbL films	109 MPa	10 %	13.0 GPa	12
GO/CS LbL film	130 MPa	2.1 %	8.2 GPa	49
CNT/PEC	65.4 MPa	3.4 %	2.8 GPa	21
GO/PEC	115 MPa	6.1 %	3.5 GPa	23

Abbreviations: PAA: Poly(acrylic acid), CS: Chitosan, PC: Carboxymethylated poly(vinyl alcohol), PA: Aminoacetalized poly (vinyl alcohol), CMC: Carboxymethyl cellulose, PVAm: Polyvinylamine, PDDA: Poly(diallyldimethylammonium chloride), PEI: Polyethyleneimine, PSS: Sodium Polystyrenesulfonate, PDADMA: Poly(diallyldimethylammonium), MTM: Montmorillonite, CNT: Carbon Nanotubes, PEC: PDDA/CMC, GO: Graphene oxide.

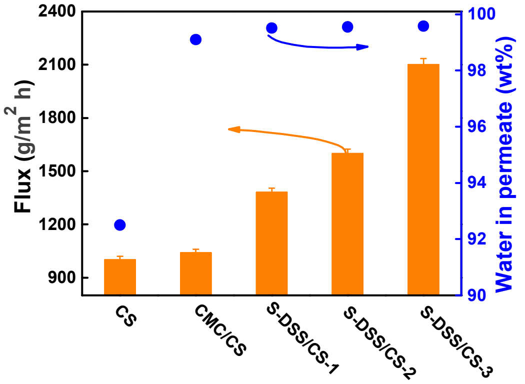

Fig. 8 Pervaporation performance of PEC membranes with different types of ion-pairs in the dehydration of 10wt% water-ethanol mixtures at 70 °C.

Conclusions

Solution-processable S-PECs containing strong polyacid were fabricated through a "complexation-sulfation" strategy, and their homogenous membranes were prepared. Chemical structures and compositions of S-PECs were controlled by varying PEC components and the sulfation processes. SEM, DLS and zeta potential of S-PEC dispersions demonstrated that these complexes contain free sulfate groups without breaking ionic-complexation were successfully synthesized. Stretching test results revealed that the mechanical properties of S-PEC membranes based on strong "ion-pairs" were enhanced to a level that could compete with hybrid films. For instance, the tensile strength and elongation at break of S-DSS/CS-1 membranes were 108.3 MPa and 5.0 %, respectively. In addition, S-DSS/CS membrane exhibited a high separation performance in the dehydration of aqueous ethanol solutions. For example, in dehydrating 10 wt% water-ethanol mixture at 70 °C, high pervaporation performance for S-DSS/CS-3 membranes was achieved, with flux and water content in permeate being 2100 g/m^2 h and 99.58 wt%, respectively. These unique properties of S-PEC membranes were associated with the ionic-complexation features and free sulfate groups, which render compact structures and high hydration ability.

Acknowledgment

This research was financially supported by the NNSFC (NO. 51173160, 21376206), the General Financial Grant from the China Postdoctoral Science Foundation (NO. 2013M531460), the National Basic Research Program of China (NO. 2015CB655300), and Zhejiang University K.P.Chao's High Technology Development Foundation.

Notes and references

a MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China. Fax: +86-571-87953780. Tel.: +86-571-87953780; E-mail: anqf@zju.edu.cn.

b R&D Center for Membrane Technology, Department of Chemical Engineering, Chung Yuan University, Chung-Li 32023, Taiwan.

c Department of Chemical Engineering and Bioengineering, Zhejiang University, Hangzhou 310027, China *d The Development Center of Water Treatment Technology, Hangzhou 310012, China*

† Electronic Supplementary Information (ESI) available: [Some characterizations are presented].

1. C. B. Bucur, Z. J. Sui and J. B. Schlenoff, *J. Am. Chem. Soc.,* 2006, **128**, 13690-13691.
2. C. Ankerfors and L. Wågberg, *Adv. Polym. Sci.,* 2014, **256**, 1-24.
3. L. P. Xu, J. Peng, Y. Liu, Y. Wen, X. Zhang, L. Jiang and S. Wang, *ACS Nano*, 2013, **7**, 5077-5083.
4. N. Joseph, P. Ahmadiannamini, R. Hoogenboom and I.F. Vankelecom, *Polym. Chem.*, 2014, **5**, 1817-1831.
5. Q. Zhao, J. W. C. Dunlop, X. L. Qiu, F. H. Huang, Z. B. Zhang, J. Heyda, J. Dzubiella, M. Antonietti and J. Y. Yuan, *Nat. Commun.,* 2014, **5**, 4293.
6. H. P. Yap, X. J. Hao, E. Tjipto, C. Gudipati, J. F. Quinn, T. P. Davis, C. B. Kowollik, M. H. Stenzel and F. Caruso, *Langmuir,* 2008, **24**, 8981-8990.
7. Q. Zhao, M. J. Yin, A. P. Zhang, P. Simon, M. Antonietti, and J. Y. Yuan, *J. Am. Chem. Soc,,* 2013, **135**, 5549-5552.
8. X. Feng, R. Pelton and M. Leduc, Ind. Eng. *Chem. Res.,* 2006, **45**, 6665-6671.
9. P. Shao and R. Y. M Huang, *J. Membr. Sci.,* 2007, **287**, 162-179.
10. L. Dähne and C. S. Peyratout, *Angew. Chem. Int. Ed.,* 2004, **43**, 3762-3783.
11. Q. Zhao, T. P. Fellinger, M. Antonietti, J. Y. Yuan, *Macromol. Rapid Commun.,* 2012, **33**, 1149−1153.
12. Z. Tang, N. A. Kotov, S. Magonov and B. Ozturk, *Nat. Mater.,* 2003, **2**, 413-418.
13 A. F. Thünemannl, M. Müller, H. Dautzenberg, J. F. Joanny and H. Löwen, *Adv. Polm. Sci.,* 2004, **166**, 113-171.
14. Q. Zhao, P. F. Zhang, M. Antonietti and J. Y. Yuan, *J. Am. Chem. Soc.,* 2012, **134**, 11852-11855.
15. C. H. Porcel and J. B. Schlenoff, *Biomacromolecules,* 2009, **10**, 2968-2975.
16. A. Reisch, P. Tirado, E. Roger, F. Boulmedais, D. Collin, J. C. Voegel, B. Frisch, P. Schaaf and J. B. Schlenoff, *Adv. Funct. Mater.,* 2013, **23**, 673-682.
17. H. H. Hariri and J. B. Schlenoff, *Macromolecules,* 2010, **43**, 8656-8663.
18. R. F. Shamoun, A. Reisch and J. B. Schlenoff, *Adv. Funct. Mater.,* 2012, **12**, 1923-1931.
19. Q. Zhao, J. W. Qian, Q. F. An, C. J. Gao, Z. L. Gui and H. T. Jin, *J. Membr. Sci.,* 2009, **333**, 68-78.
20. Q. Zhao, Q. F. An, Y. L. Ji, J. W. Qian and C. J. Gao, *J. Membr. Sci.,* 2011, **379**, 19-45.
21. Q. Zhao, J. W. Qian, M. H. Zhu and Q. F. An, *J. Mater. Chem.,* 2009, **19**, 8732-8740.
22. S. T. Dubas and J. B. Schlenoff, *Langmuir,* 2001, **17**, 7725-7727.
23. Q. Zhao, Q. F. An, T. Liu, J. T. Chen, F. Chen, K. R. Lee and C. J. Gao, *Polym. Chem.,* 2013, **4**, 4298-4302.
24. D. V. Pergushov, A. H. E. Müller and F. H. Schacher, *Chem. Soc. Rev.,* 2012, **41**, 6888-6901.
25. P. M. Biesheuvel and M. A. C. Stuart, *Langmuir,* 2004, **20**, 2785-2791.
26. S. I. Semenova, H. Ohya and K. Soontarapa, *Desalination,* 1997, **110**, 251-286.
27. K. R. Holme and A. S. Perlin, *Carbohydr. Res.,* 1997, **302**, 7-12.
28. A. S. Michaels, Ind. Eng. Chem., 1965, 57, 32-40.
29. C. Zhang, Q. N. Ping, Y. Ding, Y. Cheng and J. Shen, *J. Appl. Polym. Sci,* 2004, **91**, 659-665.
30. S. Vogt, D. Klemm and T. Heinze, *Polym. Bull.,* 1996, **36**, 549-555.
31. C. Viton, A. Domard and T. Delair, *Biomacromolecules,* 2005, **6**, 1642-1647.
32. A. Pawlak and M. Mucha, *Thermochim. Acta,* 2003, **396**, 153-166.
33. Y. Boonsongrit, B. W. Mueller and A. Mitrevej, *Eur. J. Pharm. Biopharm.,* 2008, **69**, 388-395.
34. M. Müller, T. Reihs and W. Ouyang, *Langmuir,* 2005, **21**, 465-469.
35. Q. Zhao, J.W. Qian, Q. F. An, B.Y. Du, *J. Mater. Chem.,* 2009, 19, 8448-8455.
36. Q. Zhao, J. W. Qian, Z. L. Gui, Q. F. An and M. H. Zhu, *Soft Matter,* 2010, **6**, 1129-1137.
37. Q. Zhao, Q. F. An, Z. W. Sun, J. W. Qian, K. L. Lee, C. J. Gao and J. Y. Lai, *J. Phys. Chem. B,* 2010, **114**, 8100-8106.
38. A. V. Dobrynin and M. Rubinstein, *Prog. Polym. Sci.,* 2005, **30**, 1049-1118.
39. H. J. Bai, H. Q. Zhang, Y. K. He, J. D. Liu, B. Zhang and J. T. Wang, *J. Membr. Sci.,* 2014, **454**, 220-232.
40. Z. Y. Tang, N. A. Kotov, S. Magonov and B. Ozturk, *Nat. Mater.,* 2002, **1**, 190-194.
41. H. H. Hariri, A. M. Lehaf and J. B. Schlenoff, *Macromolecules,* 2012, **45**, 9364-9372.
42. S. Y. Nam and Y. M. Lee, *J. Membr. Sci.,* 1997, **135**, 161-171.
43. M. Hosono, S. Sugii, R. Kitamaru and Y. M. Hong, *J. Appl. Polym. Sci.,* 1977, **21**, 2125-2134.
44. S. H. Lee, *Polym. J.,* 2000, **32**, 716-721.
45. Y. J. Yin, K. D. Yao, G. X. Cheng and J. B. Ma, *Polym. Int.,* 1999, **48**, 429-433.
46. P. Podsiadlo, Z. Y. Tang,| B. S. Shim and N. A. Kotov, *Nano Lett.,* 2007, 7, 1224-1231.
47. A. A. Mamedov, N. A. Kotov, M. Prato, D. M. Guldi, J. P. Wicksted and A. Hirsch, *Nat. Mater.,* 2002, **1**, 190-194.
48. Z. L. Gui, J. W. Qian, Q. F. An, Q. Zhao, H. T. Jin and B. Y. Du, *J. Mater. Chem.,* 2010, **20**, 1467–1474.
49. D. D. Kulkarni, I. Choi, S. S. Singamaneni and V. V. Tsukruk, *ACS Nano,* 2010, **4**, 4667-4676.
50. L. Y. Jiang, Y. Wang, T. S. Chung, X. Y. Qiao and J. Y. Lai, *Prog. Polym. Sci.,* 2009, **34**, 1135-1160.
51. X. S. Wang, Q. F. An, Q. Zhao, K. R. Lee, J. W. Qian and C. J. Gao, *J. Membr. Sci.,* 2012, **415-416**, 145-152.
52. M. L. Gimenes, L. Liu and X. S. Feng, *J. Membr. Sci.,* 2007, **295**, 71-79.
53. V. T. Magalad, G. S. Gokavi, M. N. Nadagouda and T. M. Aminabhavi, *J. Phys. Chem. C,* 2011, **115**, 14731-14744.
54. C. H. Zhao, H. Wu, X. S Li, F. S. Pan, Y. F. Li, J. Zhao, Z. Y. Jiang, P. Zhang, X. Z. Cao and B. Y. Wang, *J. Membr. Sci.,* 2013, **429**, 409-417.
55. J. J Shieh and R. Y. M. Huang, *J. Membr. Sci.,* 1997, **127**, 185-202.

Graphic Tabe of Content