

Preparation and High Performance of Cellulose Acetate Films by Grafting with Imidazole Ionic Liquid

Shuangping Xu, Hailiang Zhou, Hongge Jia,* Jingyu Xu,* Liqun Ma, Yu Zang, Pengfei Jiang, Wenqiang Ma, Yushu Zhang, Wenwen Zhao, Xintian Wang, Shijun Zhao, Yonglan Zou, and Yuxin Zha

Cite This: *ACS Omega* 2021, 6, 12500–12506

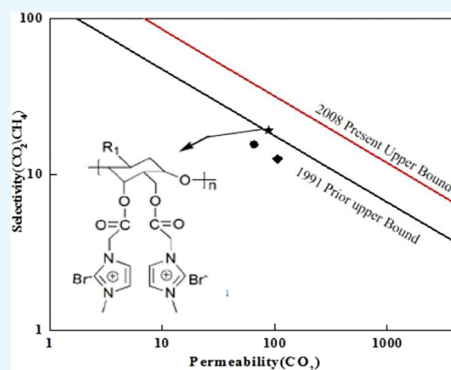
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: Cellulose acetate (CA) grafted with imidazole ionic liquids (CA-ILs) was synthesized by reacting CA with imidazole ionic liquids ([HO₂CMmim]Cl, [HO₂CEtmim]Cl, and [HO₂CMmim]Br) by using tetrahydrofuran (THF) as the solvent and pyridine as the catalyst. The CA and CA-IL films were fabricated by using the casting solution method. The CA-IL films exhibited good film forming ability and mechanical properties. The successful grafting of CA with imidazole ionic liquids was confirmed by Fourier transform infrared (FTIR), ¹H NMR, scanning electron microscopy (SEM), and elemental analysis, and the grafting degrees were 2.24, 2.45, and 3.30%, respectively. The CO₂ permeation properties of the CA-IL films were 65.5, 105.6, and 88.3 Barrer, increased up to 2.0, 3.2, and 2.7 times, respectively, as compared to pure CA (32.6 Barrer). The CO₂/CH₄ selectivities of the CA-IL films were 15.6, 12.6, and 19.2, increased up to 1.7, 1.4, and 2.1 times, respectively, as compared to pure CA (9.26). Therefore, it can be concluded that the imidazole ionic liquids are immensely useful for improving the gas separation performance of CA films.



1. INTRODUCTION

Gas film separation technology is an important research part in the field of gas separation, and compared with the traditional gas separation technology (such as amine absorption, pressure swing adsorption, cryogenic separation, etc.), it has a great application prospect with low-energy consumption, without phase change, high efficiency, and environmental friendliness in oxygen or nitrogen concentration, oil refining, chemical production, carbon dioxide capture, and other fields.^{1–3} As the core of gas film separation technology, the film materials with high permselectivity are the purpose of researchers.⁴ Polymeric films have some applicable advantages, such as good film forming ability, low cost of raw materials, environmental resistance, and simple operation.^{1,2} In this case, a variety of materials have been used for gas separation films in the past few decades. Among these films, polymeric films have been applied in industrial gas separations for decades,^{5–7} the main ones being polyimide (PI),⁸ poly(vinylidene fluoride) (PVDF),⁹ poly(dimethyl siloxane) (PDMS),¹⁰ polysulfone (PSF),¹¹ polyetherimide (PEI),¹² and cellulose derivatives.^{13,14} In addition to the advantages of polymeric films, these films have an inevitable limitation in the field of gas separation applications, which is called the tradeoff of permeability and selectivity.^{15,16} Nonetheless, polymeric films are still good candidates for gas separation, but more points of view are

necessary to enhance the gas permselectivity above the tradeoff.¹⁷

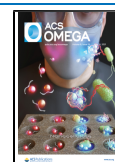
Cellulose-based materials have become a necessary part of the gas separation because they have a moderate chain structure, high mechanical strength, and good flexibility.^{18–22} All kinds of cellulose derivatives, such as ethyl cellulose (EC), cellulose acetate (CA), trifluoroacetylated cellulose, and silyl cellulose, have been prepared to be used for the gas separation film materials.^{23–25} Of those film materials, CA was found to be the most suitable and most widely developed membrane material for gas separation and enrichment.²³ As such, there is always a tradeoff between gas permeance and selectivity. Surprisingly, gas separation performance of film materials could be realized by chemical or physical modification to change their microstructure, such as ionic liquids (ILs) as grafting agents and inorganic materials as additives, or by blending with other polymers in the CA polymeric matrix.^{24–31}

Ionic liquid is a kind of liquid ionic compound consisting of organic cations and organic (inorganic) anions with the

Received: December 31, 2020

Accepted: April 9, 2021

Published: May 3, 2021



melting point at room temperature or near room temperature. It was developed as a new green reaction medium in various industrial fields.³² Because of the good solubility and selectivity of ionic liquids for CO₂, ionic liquids are mainly used for the separation of CO₂ in the gas separation film technology; especially, the ionic liquids containing functional imidazole groups are more remarkably effective.^{33,34} Authors such as Nikolaeva et al. reported a new poly(diallyldimethyl ammonium)-bis-(trifluoromethylsulfonyl)imide (P(CA)-(Tf₂N)) membrane for CO₂ separation; the ideal CO₂/N₂ adsorption selectivity of (P(CA)(Tf₂N)) was constantly up to 10 bar. The mixed gas permeation tests showed that the P[CA][Tf₂N]-based film with a 5 μm-thick selection layer had a 2-fold higher CO₂ flow than conventional CA.³⁵ These results present that the successfully modified CA with IL did not only improve the permeance but also enhance the process stability in a wide range of pressures and concentrations of CO₂/CH₄ and CO₂/N₂ gas mixtures.

In this paper, we continue to work on predicting gas separation in the EC blended ionic liquids and EC grafted with ionic liquids.³⁶ Based on the CA as a good gas separation film with good flexibility and mechanical strength and imidazole ionic liquids as a good additive with good solubility and selectivity for CO₂, the CA grafted with imidazole ionic liquids films was fabricated. The molecular structure of graft CA, morphology, mechanical properties, and CO₂ separation performance of membranes were studied subsequently.

2. EXPERIMENTAL SECTION

2.1. Materials. Cellulose acetate (CA) and ionic liquids were purchased from Chembee (Shanghai), and Greenchem ILs (Lanzhou) were used as reactants. Cellulose acetate (the acetyl content was 32.0 wt %; the hydroxyl content was 8.7 wt %) was different from the purity and type of cellulose acetate used in the literature, resulting in a certain deviation from the literature. Tetrahydrofuran, pyridine, and methanol were purchased by Kaitong Chemical Reagent Co. Ltd. (Tianjin) and were employed after distillation.

2.2. Synthesis of CA-ILs. Cellulose acetate grafted with imidazole ionic liquids (CA-IL1, CA-IL2, and CA-IL3) was synthesized by reacting cellulose acetate with imidazole ionic liquid (IL1: [HO₂CMmim]Cl, IL2: [HO₂CEtmim]Cl, and IL3: [HO₂CMmim]Br), according to Scheme 1.

Cellulose acetate (2.00 g, 0.04 mmol) was placed into a flask under the protection of N₂. Then, pyridine (2.0 mL, 24.8 mmol) and THF (50 mL) were added into the flask at room temperature. Subsequently, imidazole ionic liquid (IL1:

[HO₂CMmim]Cl) (3.66 g, 20.7 mmol) was injected dropwise into the above solution, and it was stirred at 70 °C for 48 h. After the reaction solution was cooled to room temperature, it was poured into a large amount of methanol (1000 mL) for a week. The formed precipitate was concentrated by centrifugal separation and filtered, and the obtained solid was dried in vacuo at 50 °C to give a white solid (CA-IL1) (yield: 78.1%). The CA-IL2 and CA-IL3 were obtained by a similar method with yields of 79.3 and 73.3%, respectively. The yield was calculated using the following equation (eq 1)

$$\text{yield} = \frac{M}{M_{\text{CA}} + M_{\text{IL}}} \times 100\% \quad (1)$$

where M_{IL} is the added mass of ionic liquid, M_{CA} is the added quantity of CA, and M is the mass of the obtained graft product.

2.3. Preparation of Gas Separation Films. The corresponding homogeneous membranes of CA and CA-ILs were prepared through the coating solution method (concentration of 5 wt % in THF) on clean glass plates and evaporating solvents at room temperature. Finally, the obtained films (thickness: 120.7–134.6 μm) were dried under vacuum at 25 °C for 12 h. The thickness of the films was measured by a thickness gauge (the thickness gauge was purchased from Shanghai Liuling Instrument Factory, the model was a CH-1-B hand-type millimeter thickness gauge, the graduation value was 0.001 mm, the measurement range was 0–1 mm, and the error was about ≤0.007 mm).

2.4. Characterization of the CA and CA-IL Films. A Fourier transform infrared spectrometer (Spectrum Two, PE company, Waltham, Massachusetts, USA) was used to characterize the molecular structures of CA and CA-ILs. The ¹H NMR (400 MHz) spectra were recorded on a JEOL LEOLEX-400 spectrometer with 16 scans in DMSO-*d*₆ (LEOLEX-400, JOEL Japan). The content of the nitrogen element in the grafted CA was measured using an organic elemental analyzer (PE2400 SERIES II CHNS/O, PerkinElmer, Waltham, Massachusetts, USA). The microstructures of the pure CA and CA-IL films were studied by scanning electron microscopy (SEM) (JSM-6490, JOEL Japan). Mechanical properties of the pure CA and CA-IL films were tested by a film tensile testing machine (XLW(PC)-500 N, Sumspring, Jinan, China) at 25 °C.

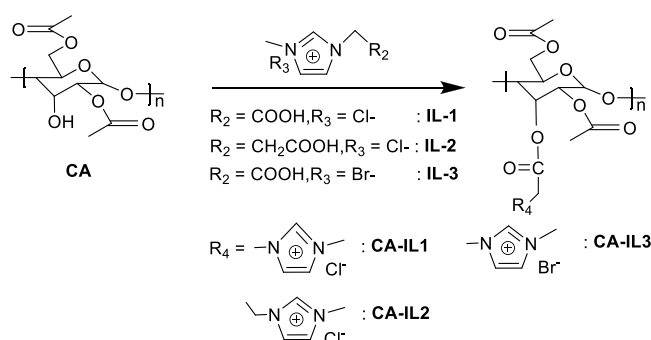
2.5. The Grafting Degrees of CA-IL Films. The organic elemental analyzer was used to mark the content of the nitrogen element in the grafted CA, and then, the mass fraction of the ionic liquid in CA was calculated using the following formula (eq 2)³⁶

$$d = \frac{1}{2} \text{N}\% \times \frac{M_{\text{IL}}}{M_{\text{N}}} 100\% \quad (2)$$

where d is the grafting degree of ILs in CA. N% is the mass fraction of N, which was determined by using an elemental analyzer. The content of the nitrogen element is expressed in wt %. M_{IL} and M_{N} are the molecular weights of the ionic liquid and N element, respectively.

2.6. Gas Separation. The test of mixed gas permeation was performed using a differential pressure gas transmission instrument (GTR-11MH type, GTR TEC Corporation, Kyoto, Japan; the test area was 0.785 cm². The instrument test temperature was 34 °C, the test pressure was maintained at 49 kPa, the content of the mixed gas was the same, and the test

Scheme 1. Synthesis of CA Grafted with Imidazole Ionic Liquids (CA-IL1, CA-IL2, and CA-IL3)



pressure was 0.1 MPa. The carrier gas was H₂, and the pressure was 0.5 MPa). The permeability coefficients of the mixed gases were measured by the gas chromatographic method using the differential pressure gas transmission instrument (GTR-11MH type), and the gas permeability coefficient P was calculated using the following relation (eq 3)

$$P = \frac{q \times K \times l}{a \times p \times t} (\text{mL} \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}) \quad (3)$$

where q is the transmission volume (mL), K is the auxiliary positive coefficient (the fixed value is 2); it is the setting point instrument by factory, l is the film thickness (cm), p is the permeability pressure (cmHg), t is the measurement time (s), and a is the area of the gas permeation film (the fixed value is 0.785 cm²).

In this experiment, the gas separation factor was calculated using the following relation (eq 4)

$$\alpha = \frac{P_A}{P_B} \quad (4)$$

where P_A and P_B correspond to single gases A and B, respectively, and they can be calculated from eq 3.

3. RESULTS AND DISCUSSION

3.1. Characterization of CA and CA-ILs. The final desired CAs grafted with ionic liquids (Scheme 1; CA-IL1, CA-IL2, and CA-IL3) were synthesized through an esterification reaction from the carboxyl groups in imidazole ionic liquid reaction with hydroxyl groups in CA under the protection of N₂ at 70 °C for 48 h in THF. The mechanism of pyridine-catalyzed esterification can be seen in the previous research.

The molecular structures of the CA and CA-ILs were characterized by FTIR. As shown in Figure 1 (CA, CA-IL1,

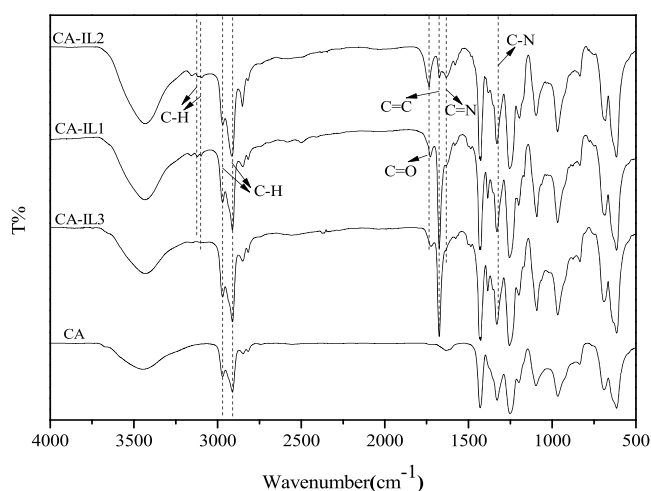


Figure 1. FTIR spectra of CA, CA-IL1, CA-IL2, and CA-IL3.

CA-IL2, and CA-IL3), the absorption peak at 1760 cm⁻¹ was credited to the C=O bond stretching vibration of the ester group by esterification reaction from the hydroxyl groups in CA reaction with the carboxyl groups in imidazole ionic liquid; the two peaks around 1620 and 1640 cm⁻¹ were ascribed to the C=N and C=C bond stretching vibrations of imidazole groups in ionic liquid, respectively. The two weak peaks around 2960 and 2860 cm⁻¹ can be ascribed to the C-H bond

stretching vibration of methyl and methylene in CA, respectively. Similarly, the peaks at 3080, 3020, and 1400 cm⁻¹ were attributed to the C-H bond stretching vibration in the imidazole-based double bond in ionic liquid. In addition, the observed peaks at 1470, 1250, and 1348 cm⁻¹ were attributed to the C-N bond stretching vibrations of the imidazole group. For the analysis based on IR spectra, the obtained products were tentatively concluded that they are the grafted products.

¹H NMR spectra were used to elucidate the molecular structures and evaluate the distribution of graft groups of the as-prepared CA-ILs. The typical spectra of ¹H NMR of pure CA and the prepared CA-ILs are shown in Figure 2. In the case

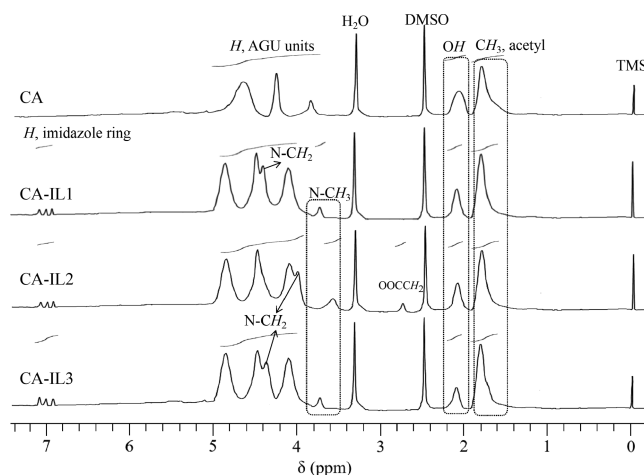


Figure 2. ¹H NMR spectra of CA, CA-IL1, CA-IL2, and CA-IL3.

of pure CA, the broad peaks from 3.9 to 4.9 ppm are attributed to the proton resonance on the AGU units. The signal at 2.1 ppm was ascribed to protons of OH. The strong signal at 1.8 ppm was assigned to methyl protons of acetyl. Compared with the pure CA, in the case of the CA-ILs, in addition to having the peaks of CA, the CA-ILs also have the peaks of corresponding ionic liquids. Most obviously, there are no signals from the carboxyl hydrogen of ionic liquids. At the same time, the peak areas have decreased at 2.1 ppm from the protons of OH in the CA-ILs, and this is due to the esterification reaction from the carboxyl groups in imidazole ionic liquid reacted with hydroxyl groups in CA. Based on the observed peak assignments and the corresponding integrals, the chemical structure factors of the CA-ILs, there is a reason to believe that the CA grafted with ionic liquids was prepared successfully.

The microeconomics of films were observed by SEM. Figures 3 and 4 show the surface and cross-sectional photographs, respectively, of (Figures 3a and 4a) the pure CA film and (Figures 3b–d and 4b–d) CA-IL films. From the SEM image, (Figures 3b–d and 4b–d) CA-IL films are very similar to the CA film (Figures 3a and 4a), and all of them clearly demonstrate a smooth, non-porous, and dense morphology. In addition, the cross-sectional images have also given similar phenomena. This indicated that CA-ILs are grafting products but not blended products. In combination with the IR analysis, we can validate that the CA grafted with ionic liquids was synthesized successfully.

In this experiment, the final products were washed with large methanol at room temperature for 1 week; its purpose is to

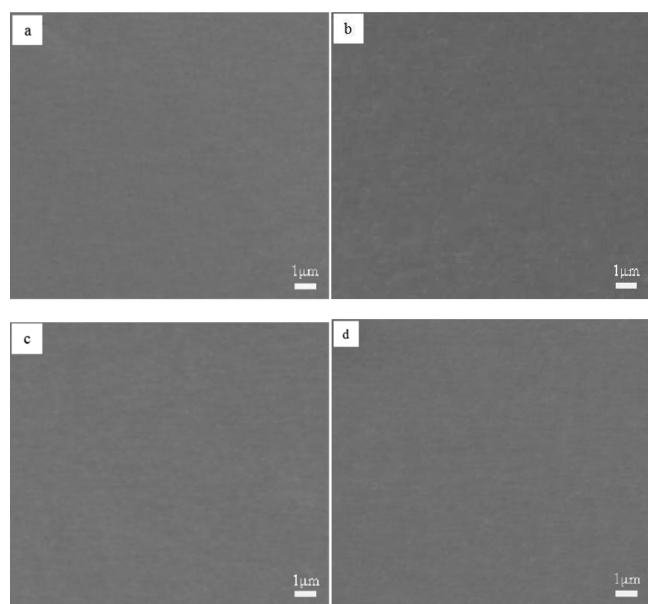


Figure 3. Surface SEM photographs of CA (a), CA-IL1 (b), CA-IL2 (c), and CA-IL3 (d).

wash the raw ionic liquid to the methanol solution. The yields and grafting degrees of the final products are summarized in Table 1 (CA-IL1, CA-IL2, and CA-IL3), and the yields were about 73.3–79.3%, respectively. The grafting degrees of CA-

Table 1. Yields, Grafting Degrees, and the N Element Contents of CA-ILs

| sample | yield (%) | N element content (%) | grafting degree (%) |
|--------|-----------|-----------------------|---------------------|
| CA-IL1 | 78.1 | 0.37 | 2.34 |
| CA-IL2 | 79.3 | 0.36 | 2.45 |
| CA-IL3 | 73.3 | 0.42 | 3.30 |

ILs were about 2.34–3.30%, which further indicated that the grafted CA was successfully synthesized.

3.2. Mechanical Properties of Films. Since the obtained films will be used in the gas separation, the mechanical properties were tested. As shown in Table 2, given the test data

Table 2. Mechanical Properties of CA and CA-IL Films^a

| sample | thickness (μm) | elongation (%) | elastic modulus (MPa) | tensile strength (MPa) |
|--------|----------------|----------------|-----------------------|------------------------|
| CA | 125.5 | 37.8 | 104 | 52.7 |
| CA-IL1 | 134.6 | 25.1 | 174 | 43.8 |
| CA-IL2 | 128.5 | 26.4 | 163 | 42.9 |
| CA-IL3 | 120.7 | 28.4 | 167 | 47.5 |

^aTested at 5.00 mm/min speed. The standard spline had a length of 50 mm and a width of 10 mm.

of the CA and CA-IL films, although the tensile strength and elongation at break of the CA-IL films have decreased slightly from being pure, the elasticity moduli of the CA-IL films

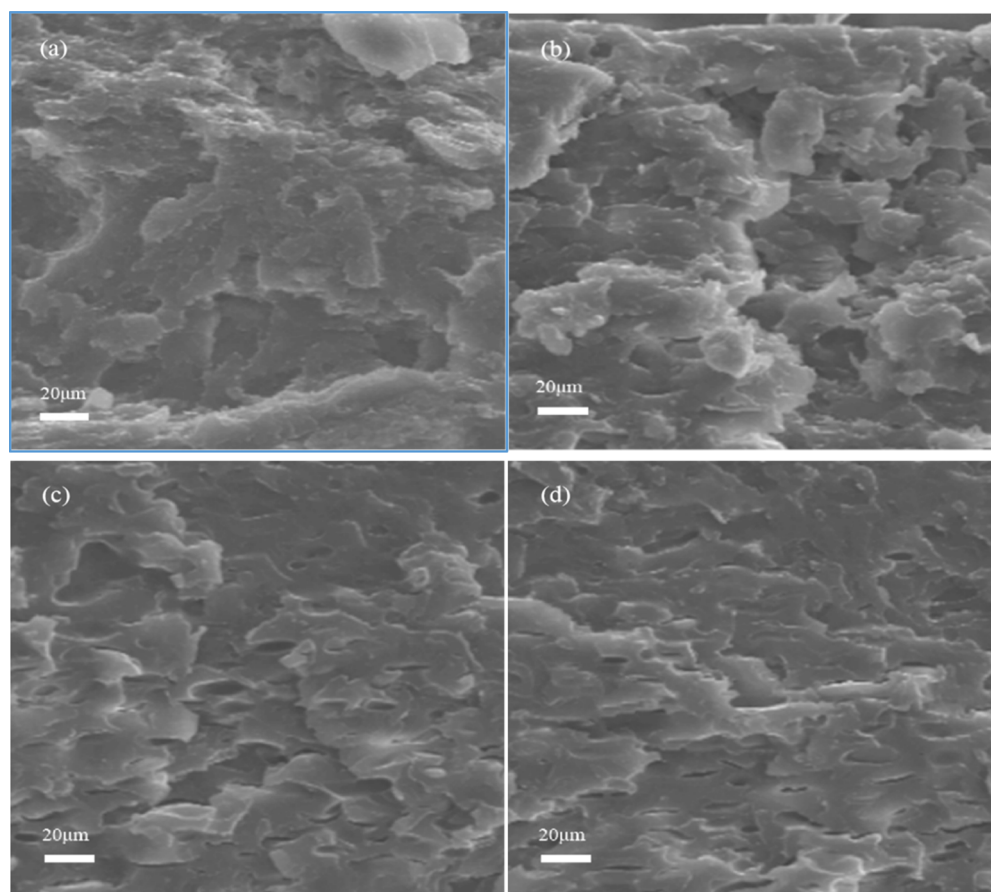


Figure 4. Cross-sectional SEM images of CA (a), CA-IL1 (b), CA-IL2 (c), and CA-IL3 (d).

(Table 2; CA-IL1, CA-IL2, and CA-IL3) were 174, 163, and 167 MPa, increased up to 1.7, 1.6, and 1.6 times, respectively, as compared with pure CA film (104 MPa), and the results indicated that the CA-ILs are grafted films. In the phenomenon shown in Table 2, given the different mechanical properties, the most possible reason is that the molecular structure of CA was changed due to the fact that the CA is grafted with ionic liquids; the molecules are covalently bonded and form strong intermolecular interactions. This eventually led to an increase in the elasticity modulus of the grafted film.

3.3. Gas Separation Properties of Films. The uniform and transparent casting solutions of pure CA and the grafted CA were achieved by stirring in THF. The casting solutions were subsequently coated on 10 cm diameter clean glass plates, the solvent was evaporated for 12 h at 25 °C, and the membranes were detached from the plates and dried in vacuo at 25 °C for 24 h to give the homogeneous membranes with similar thicknesses.

To obtain the grafted CA membrane performance in industrial applications, the mixed gas permeances and the selectivities of the obtained grafted membranes are shown in Table 3. As compared to the CO₂/CH₄ separation factors of

Table 3. CO₂ Permeabilities and CO₂/CH₄ Separation Factors of the CA Film and CA-IL Films

| sample | PCO ₂ (Barrer) ^a | PCH ₄ (Barrer) | PCO ₂ /PCH ₄ |
|--------|--|---------------------------|------------------------------------|
| CA | 32.6 | 3.52 | 9.26 |
| CA-IL1 | 65.5 | 4.21 | 15.6 |
| CA-IL2 | 105.6 | 8.38 | 12.6 |
| CA-IL3 | 88.3 | 4.60 | 19.2 |

^a1 Barrer = 10⁻¹⁰ cm³(STP)·cm·cm⁻²·s⁻¹·cmHg⁻¹.

the pure CA membrane (9.26), the CO₂/CH₄ separation factors of the CA-IL films (Table 3; CA-IL1, CA-IL2, and CA-IL3) were up to 15.6, 12.6, and 19.2, respectively. By investigating this reason, we ascribed that the imidazolium group of ionic liquid can interact with carbon dioxide, which raises the adsorption of CO₂ gas molecules and continues to undergo the penetration CO₂ in the films, ultimately resulting in higher CO₂ permeability than pure CA film. Another CH₄ gas molecule has a non-polar molecule with a regular tetrahedral structure, but the three ionic liquids added were polar substances. According to the similarity-intermiscibility theory, the solubility of CH₄ in the film was poor, which leads to a poor permeation of methane. Therefore, the CA-IL membranes show high CO₂/CH₄ selectivity.³⁷

In this study, the CA-IL films not only present high CO₂/CH₄ separation factors (12.6–19.2) but also present good CO₂ permeabilities (65.5–105.6 Barrer), and they are higher than that of pure CA membrane (32.6 Barrer). For the three kinds of CA-IL membranes, the CA-IL2 membrane exhibited the highest CO₂ permeability coefficient (105.6 Barrer) with the lowest CO₂/CH₄ separation factor (12.6), and this is due to the CA-IL2 having a long carboxyethyl spacer in the ionic liquid, which can improve the gas permeability coefficient. The CA-IL3 membrane exhibited the highest CO₂/CH₄ separation factor (19.2) with an intermediate CO₂ permeability coefficient (88.3 Barrer) (Table 3; CA-IL3), which was past the 1991 Robeson's upper bound (Figure 5).^{38,39} The separation performances of the CA-IL1 and CA-IL2 membranes were lower than that of the 1991 prior upper bound, but they were higher than that of pure CA film (Figure 5). In

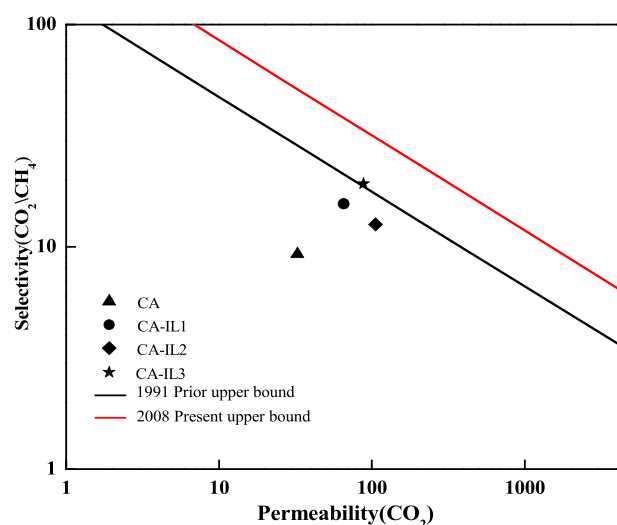


Figure 5. CO₂/CH₄ selectivities and CO₂ permeabilities of the CA film and CA-IL films in relation to Robeson's upper bound (1991 and 2008).

conclusion, the gas permeation properties of the pure CA and CA-IL films give the result CA-IL3 > CA-IL2 > CA-IL1 > CA. In general, the halogen atoms have a highly electronegative and electron-absorbing induction effect, F > Cl > Br > I.⁴⁰ In this experiment, the electron donating capacity of anions is Br⁻ > Cl⁻; the free electrons of bromide in the CA-IL3 membrane can interact with CO₂. At the same time, the imidazole group can make them more stable. As a result, the CA-IL3 film having bromide has shown the best gas separation performance.

4. CONCLUSIONS

In summary, three kinds of CA grafted with imidazole ionic liquids (CA-IL1, CA-IL2, and CA-IL3) were synthesized by cellulose acetate (CA) reaction with imidazole ionic liquids ([HO₂CMmim]Cl, [HO₂CETmim]Cl, and [HO₂CMmim]Br) via an esterification reaction, and the yields of CA-ILs were about 73.3–79.3%. The grafted CA-IL structure was characterized by FTIR and ¹H NMR. The grafting degrees of CA-ILs were 2.34–3.30% by elemental analysis. The CA-ILs exhibited good film forming ability, and their homogeneous phase compact nonporous membranes showed excellent mechanical properties. The carbon dioxide permeance (PCO₂) and CO₂/CH₄ separation factors of the CA-IL membranes were almost 2 times as compared to the pure CA film. Among the three grafted CA films, the CA-IL3 film was the best, and the permeability (PCO₂) was up to 88.3 Barrer with the highest permselectivity (PCO₂/PCH₄ = 19.2) due to the fact that the bromide ion in CA-IL3 can interact well with CO₂, which promotes CO₂ permeability. Taking the results together, the imidazole ionic liquids are useful grafting agents to raise the gas separation performances of the economical CA membranes.

■ AUTHOR INFORMATION

Corresponding Authors

Hongge Jia – College of Materials Science and Engineering, Heilongjiang Provinces Key Laboratory of Polymeric Composite Materials, Qiqihar University, Qiqihar 161006, China; Email: jiahongge@qqhru.edu.cn

Jingyu Xu – College of Materials Science and Engineering, Heilongjiang Provinces Key Laboratory of Polymeric Composite Materials, Qiqihar University, Qiqihar 161006, China; orcid.org/0000-0002-6724-9623; Email: xjy951011@163.com

Authors

Shuangping Xu – College of Materials Science and Engineering, Heilongjiang Provinces Key Laboratory of Polymeric Composite Materials, Qiqihar University, Qiqihar 161006, China

Hailiang Zhou – College of Materials Science and Engineering, Heilongjiang Provinces Key Laboratory of Polymeric Composite Materials, Qiqihar University, Qiqihar 161006, China

Liqun Ma – College of Materials Science and Engineering, Heilongjiang Provinces Key Laboratory of Polymeric Composite Materials, Qiqihar University, Qiqihar 161006, China

Yu Zang – College of Materials Science and Engineering, Heilongjiang Provinces Key Laboratory of Polymeric Composite Materials, Qiqihar University, Qiqihar 161006, China; orcid.org/0000-0001-5123-4251

Pengfei Jiang – College of Materials Science and Engineering, Heilongjiang Provinces Key Laboratory of Polymeric Composite Materials, Qiqihar University, Qiqihar 161006, China

Wenqiang Ma – College of Materials Science and Engineering, Heilongjiang Provinces Key Laboratory of Polymeric Composite Materials, Qiqihar University, Qiqihar 161006, China

Yushu Zhang – College of Materials Science and Engineering, Heilongjiang Provinces Key Laboratory of Polymeric Composite Materials, Qiqihar University, Qiqihar 161006, China

Wenwen Zhao – College of Materials Science and Engineering, Heilongjiang Provinces Key Laboratory of Polymeric Composite Materials, Qiqihar University, Qiqihar 161006, China

Xintian Wang – College of Materials Science and Engineering, Heilongjiang Provinces Key Laboratory of Polymeric Composite Materials, Qiqihar University, Qiqihar 161006, China

Shijun Zhao – College of Materials Science and Engineering, Heilongjiang Provinces Key Laboratory of Polymeric Composite Materials, Qiqihar University, Qiqihar 161006, China

Yonglan Zou – College of Materials Science and Engineering, Heilongjiang Provinces Key Laboratory of Polymeric Composite Materials, Qiqihar University, Qiqihar 161006, China

Yuxin Zha – College of Materials Science and Engineering, Heilongjiang Provinces Key Laboratory of Polymeric Composite Materials, Qiqihar University, Qiqihar 161006, China

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsomega.0c06361>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge financial support from the Fundamental Research Funds in Heilongjiang Provincial Universities (YSTSXK201867), the Natural Science Foundation of Heilongjiang Province, China (LH2019B032), and the Graduate Innovative Research Project of Qiqihar University (YJSCX2020058).

REFERENCES

- (1) Pandey, P.; Chauhan, R. S. Membranes for gas separation. *Prog. Polym. Sci.* **2001**, *26*, 853–893.
- (2) Galizia, M.; Chi, W. S.; Smith, Z. P.; Merkel, T. C.; Baker, R. W.; Freeman, B. D. 50th anniversary perspective: Polymers and mixed matrix membranes for gas and vapor separation: a review and prospective opportunities. *Macromolecules* **2017**, *50*, 7809–7843.
- (3) Basu, S.; Khan, A. L.; Cano-Odena, A.; Liu, C.; Vankelecom, I. F. J. Membrane-based technologies for biogas separations. *Chem. Soc. Rev.* **2010**, *39*, 750–768.
- (4) Guiver, M. D.; Lee, Y. M. Polymer rigidity improves microporous membranes. *Science* **2013**, *339*, 284–285.
- (5) Wang, M.; Zhao, J.; Wang, X.; Liu, A.; Gleason, K. K. Recent progress on submicron gas-selective polymeric membranes. *J. Mater. Chem. A* **2017**, *5*, 8860–8886.
- (6) Han, S. H.; Lee, Y. M. Recent high performance polymer membranes for CO₂ separation. In *Membrane Engineering for the Treatment of Gases: Volume 1: Gas-separation Problems with Membranes*; 2011; *1*, 84–124.
- (7) Du, N.; Park, H. B.; Dal-Cin, M. M.; Guiver, M. D. Advances in high permeability polymeric membrane materials for CO₂ separations. *Energy Environ. Sci.* **2012**, *5*, 7306–7322.
- (8) Wiegand, J. R.; Smith, Z. P.; Liu, Q.; Patterson, C. T.; Freeman, B. D.; Guo, R. Synthesis and characterization of triptycene-based polyimides with tunable high fractional free volume for gas separation membranes. *J. Mater. Chem. A* **2014**, *2*, 13309–13320.
- (9) Choi, S.-H.; Tasselli, F.; Jansen, J. C.; Barbieri, G.; Drioli, E. Effect of the preparation conditions on the formation of asymmetric poly(vinylidene fluoride) hollow fibre membranes with a dense skin. *Eur. Polym. J.* **2010**, *46*, 1713–1725.
- (10) Merkel, T. C.; Bondar, V. I.; Nagai, K.; Freeman, B. D.; Pinnau, I. Gas sorption, diffusion, and permeation in poly(dimethylsiloxane). *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 415–434.
- (11) Barbari, T. A.; Datwani, S. S. Gas separation properties of polysulfone membranes treated with molecular bromine. *J. Membr. Sci.* **1995**, *107*, 263–266.
- (12) Yampolskii, Y.; Alentiev, A.; Bondarenko, G.; Kostina, Y.; Heuchel, M. Intermolecular interactions: New way to govern transport properties of membrane materials. *Ind. Eng. Chem. Res.* **2010**, *49*, 12031–12037.
- (13) Pak, S.-H.; Jeon, Y.-W.; Shin, M.-S.; Koh, H. C. Preparation of cellulose acetate hollow-fiber membranes for CO₂/CH₄ separation. *Environ. Eng. Sci.* **2016**, *33*, 17–24.
- (14) Li, H.; Huang, Q.; Li, D.; Li, S.; Wu, X.; Wen, L.; Ban, C. The generation of a molecular imprinted membrane by coating cellulose acetate onto a ZrO₂-modified alumina membrane for the chiral separation of mandelic acid enantiomers. *Org. Process Res. Dev.* **2018**, *22*, 278–285.
- (15) Park, H. B.; Kamcev, J.; Robeson, L. M.; Elimelech, M.; Freeman, B. D. Maximizing the right stuff: The trade-off between membrane permeability and selectivity. *Science* **2017**, *356*, eaab0530.
- (16) Robeson, L. M. The upper bound revisited. *J. Membr. Sci.* **2008**, *320*, 390–400.
- (17) Cong, H.; Radosz, M.; Towler, B. F.; Shen, Y. Polymer-inorganic nanocomposite membranes for gas separation. *Sep. Purif. Technol.* **2007**, *55*, 281–291.
- (18) Li, J.; Wang, S.; Nagai, K.; Nakagawa, T.; Mau, A. W.-H. Effect of polyethyleneglycol (PEG) on gas permeabilities and permselectivities in its cellulose acetate (CA) blend membranes. *J. Membr. Sci.* **1998**, *138*, 143–152.

- (19) Klemm, D.; Heublein, B.; Fink, H. P.; Bohn, A. Cellulose: Fascinating Biopolymer and Sustainable Raw Material. *Angew. Chem., Int. Ed.* **2005**, *44*, 3358–3393.
- (20) Nakai, Y.; Yoshimizu, H.; Tsujita, Y. Enhanced gas permeability of cellulose acetate membranes under microwave irradiation. *J. Membr. Sci.* **2005**, *256*, 72–77.
- (21) Khan, F. Z.; Sakaguchi, T.; Shiotsuki, M.; Nishio, Y.; Masuda, T. Perfluoroacetylated Ethyl Cellulose: Synthesis, Characterization, and Gas Permeation Properties. *Macromolecules* **2006**, *39*, 9208–9214.
- (22) Bernardo, P.; Drioli, E.; Golemme, G. Membrane Gas Separation: A Review/State of the Art. *Ind. Eng. Chem. Res.* **2009**, *48*, 4638–4663.
- (23) Yang, W.; Easteal, J. A. Preparation, characterisation and gas transport properties of trifluoroacetylated ethyl cellulose. *J. Membr. Sci.* **1999**, *157*, 53–61.
- (24) Khan, F. Z.; Shiotsuki, M.; Nishio, Y.; Masuda, T. Synthesis, characterization, and gas permeation properties of *t*-butylcarbamates of cellulose derivatives. *J. Membr. Sci.* **2008**, *312*, 207–216.
- (25) Morita, R.; Khan, F. Z.; Sakaguchi, T.; Shiotsuki, M.; Nishio, Y.; Masuda, T. Synthesis, characterization, and gas permeation properties of the silyl derivatives of cellulose acetate. *J. Membr. Sci.* **2007**, *305*, 136–145.
- (26) Kim, W.-g.; Lee, J. S.; Bucknall, D. G.; Koros, W. J.; Nair, S. Nanoporous layered silicate AMH-3/cellulose acetate nanocomposite membranes for gas separations. *J. Membr. Sci.* **2013**, *441*, 129–136.
- (27) Ahmad, A. L.; Jawad, Z. A.; Low, S. C.; Zein, S. H. S. A cellulose acetate/multi-walled carbon nanotube mixed matrix membrane for CO₂/N₂ separation. *J. Membr. Sci.* **2014**, *451*, 55–66.
- (28) Moghadassi, A. R.; Rajabi, Z.; Hosseini, S. M.; Mohammadi, M. Fabrication and modification of cellulose acetate based mixed matrix membrane: Gas separation and physical properties. *J. Ind. Eng. Chem.* **2014**, *20*, 1050–1060.
- (29) Dasgupta, J.; Chakraborty, S.; Sikder, J.; Kumar, R.; Pal, D.; Curcio, S.; Drioli, E. The effects of thermally stable titanium silicon oxide nanoparticles on structure and performance of cellulose acetate ultrafiltration membranes. *Sep. Purif. Technol.* **2014**, *133*, 55–68.
- (30) Bikson, B.; Nelson, J. K.; Muruganandam, N. Composite cellulose acetate/poly(methyl methacrylate) blend gas separation membranes. *J. Membr. Sci.* **1994**, *94*, 313–328.
- (31) Rakhshan, N.; Pakizeh, M. The effect of functionalized SiO₂ nanoparticles on the morphology and triazines separation properties of cellulose acetate membranes. *J. Ind. Eng. Chem.* **2016**, *34*, 51–60.
- (32) Chen, J.; Zhang, J.; Feng, Y.; Wu, J.; He, J.; Zhang, J. Synthesis, characterization, and gas permeabilities of cellulose derivatives containing adamantane groups. *J. Membr. Sci.* **2014**, *469*, 507–514.
- (33) Andreatta, G.; Lee, L.-T.; Lee, F. K.; Benattar, J.-J. Gas Permeability in Polymer- and Surfactant-Stabilized Bubble Films. *J. Phys. Chem. B* **2006**, *110*, 19537–19542.
- (34) Tomé, L. C.; Marrucho, I. M. Ionic liquid-based materials: a platform to design engineered CO₂ separation membrane. *Chem. Soc. Rev.* **2016**, *45*, 2785–2824.
- (35) Nikolaeva, D.; Azcune, I.; Tanczyk, M.; Warmuzinski, K.; Jaschik, M.; Sandru, M.; Dahl, P. I.; Genua, A.; Lois, S.; Sheridan, E.; Fuoco, A.; Vankelecom, I. F. J. The performance of affordable and stable cellulose-based poly-ionic membranes in CO₂/N₂ and CO₂/CH₄ gas separation. *J. Membr. Sci.* **2018**, *564*, 552–561.
- (36) Li, Y.-n.; Sun, Y.; Deng, X.-h.; Yang, Q.; Bai, Z.-y.; Xu, Z.-b. Graft polymerization of acrylic acid onto polyphenylene sulfide nonwoven initiated by low temperature plasma. *J. Appl. Polym. Sci.* **2006**, *102*, 5884–5889.
- (37) Shannon, M. S.; Bara, J. E. Reactive and reversible ionic liquids for CO₂ capture and acid gas removal. *Sep. Sci. Technol.* **2012**, *47*, 178–188.
- (38) Fraga, S. C.; Monteleone, M.; Lanč, M.; Esposito, E.; Fuoco, A.; Giorno, L.; Pilnáček, K.; Friess, K.; Carta, M.; McKeown, N. B.; Izák, P.; Petrusová, Z.; Crespo, J. G.; Brazinha, C.; Jansen, J. C. A novel time lag method for the analysis of mixed gas diffusion in polymeric membranes by on-line mass spectrometry: Method development and validation. *J. Membr. Sci.* **2018**, *561*, 39–58.
- (39) Swaidan, R.; Ghanem, B.; Pinnau, I. Fine-Tuned Intrinsically Ultramicroporous Polymers Redefine the Permeability/Selectivity Upper Bounds of Membrane-Based Air and Hydrogen Separations. *ACS Macro Lett.* **2015**, *4*, 947–951.
- (40) Pathak, B.; Samanta, D.; Ahuja, R.; Jena, P. Borane derivatives: a new class of super- and hyperhalogens. *ChemPhysChem* **2011**, *12*, 2423–2428.