Zein Protein Obtained from Maize as a Novel Biodegradable Membrane Material for Oxygen/Nitrogen Separation: Membrane Fabrication and Characterization

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Abstract
In this study, biodegradable zein protein obtained from maize was used as a novel material to prepare a membrane for oxygen/nitrogen separation. Scanning electron microscopy (SEM), thermogravimetric analysis (TGA), tensile test, X-ray diffraction (XRD) spectroscopy, differential scanning calorimetry (DSC), biodegradability test, and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy were conducted for characterizing the zein membrane, and membrane properties was compared with that of the polymeric membranes reported in the literature. The developed zein membrane showed a significantly high thermal stability. The mechanical properties of the zein membrane were higher or comparable to those of the previously reported dense membranes. In addition, biodegradation in compost was significantly higher than the other membranes reported in the literature. The developed zein membrane provided a significantly high oxygen/nitrogen selectivity at 2 bar, which was superior to most of the previously reported data on the neat biodegradable polymers with dense structure. The permeability of oxygen and nitrogen at 2 bar was 0.67 and 0.12 barrer, respectively, which brought about the selectivity of 5.45 for oxygen/nitrogen separation.

Keywords Membrane · Gas separation · Zein · Oxygen · Nitrogen · Biodegradable

Introduction
Gas separation processes are essential operations in the petroleum, gas, and some chemical industries. Gas separation using membranes is a promising technology that can be an energy-efficient method [1]. Oxygen (O2) is used in natural sewage treatment, coal gasification, glass production, and gas combustion, and nitrogen (N2) is applied in food preservation, coal extraction, and cryogenic storage [2]. Other uses of N2 are in the pharmaceutical industry, ammonia production, purging pipelines and vessels, and as a low-temperature coolant [3].

O2/N2 separation is one of the main challenges in gas separation using membranes, and this is because of the slight difference between the kinetic diameters of O2 and N2 (3.46 versus 3.64 Å, respectively) [4]. Various polymers such as polyimide (PI) [5], polysulfone (PSf) [6], polyphenylsulfone (PPSU) [7], and polyamide (PA) [8] were used in O2/N2 separation so far.

Polymeric membranes are used in gas separation applications because of their suitable mechanical property and excellent flexibility [9]. Most of the non-biodegradable polymeric membranes cause environmental issues after their service life [10]. The mentioned problem can be addressed by the application of biodegradable membranes [11]. Most of the polymers used for membrane gas separation are non-biodegradable; however, a limited number of biodegradable polymers such as cellulose acetate (CA) [12] and polylactic acid (PLA) [13] were used in O2/N2 separation. Najafi et al. [12] prepared a CA membrane and modified it using silica nanoparticles as the nanofiller. They reported that with increasing the silica loading in the membrane, the permeability of O2 and N2 decreased while selectivity did not change significantly. Jamian et al. [13] examined the effect of feed pressure on O2/N2 separation using the PLA membrane. With an increase in pressure, the permeability of gases increased, and thus the selectivity of O2/N2 decreased.
As non-commercial biodegradable polymers [13], proteins are another alternative to replace the non-biodegradable polymeric membranes. Zein is a protein (biopolymer) obtained from maize [14] and is one of the byproducts in ethanol production from corn [15]. Zein protein is biodegradable [16] and has excellent film-forming properties [17], making it suitable for the preparation of membranes. According to Shukla and Cheryan [14], zein is insoluble in water or anhydrous ethanol and is only soluble in 50–90% ethanol aqueous solution. This solubility behavior is due to a high proportion of nonpolar amino acid residues and a deficiency in basic and acidic amino acids [14]. According to Zhang et al. [18], the inherent properties in amino acid composition lead to the unique solubility of zein, which is mainly restricted to acetone, acetic acid, aqueous alcohols, and aqueous alkaline solutions. Shi et al. [19] prepared zein films by spin-coating using 0.5 (w/v) or 4% (w/v) zein solutions. In their study, zein was dissolved in 60–95% (v/v) anhydrous ethanol/water mixtures or 60–100% (v/v) acetic acid/water mixtures by magnetic stirring at ambient temperature. Spin-cast zein films prepared from an aqueous ethanol solvent was reported to lead to a rough and hydrophilic surface, while the surface of zein film produced from an acetic acid solution was smooth and more hydrophobic [19].

Zein can be applied in drug delivery, tissue engineering, and in the production of food packing, adhesives, cosmetics, and chewing gum [20–25]. A literature survey revealed just one report on the application of zein in membrane separation technology [26]. Ma et al. [26] prepared Zein single (ZS) membrane and zein composite (ZC) membrane by spin-coating zein solutions onto porous asymmetric alumina supports. They used 70% (v/v) ethanol–water for preparing zein solutions and found that 30 mg zein/mL solvent resulted in zein microspheres, while continuous films were obtained using 100 mg zein/mL solvent. Both the ZS and ZC membranes effectively removed ethanol from dilute ethanol aqueous solutions via pervaporation.

In this study, zein protein was used as a novel polymer to prepare a membrane for O₂/N₂ separation. The obtained zein membrane was characterized in terms of its morphology, thermal properties, mechanical properties, crystalline structure, biodegradability, and chemical structure. In addition, O₂ and N₂ permeability through the zein membrane, as well as O₂/N₂ selectivity, was determined in the gas permeation studies.

Materials and Methods

Materials

Zein protein was provided by Sigma-Aldrich. Glacial acetic acid (extra pure) was obtained from Dr. Mojallali Chemical Industries Complex Co., and ethanol (96 wt% purity) was purchased from Taghtir Khorasan Co. Distilled water was used in the preparation of aqueous solutions.

Membrane Preparation

According to Zhang et al. [18], the solubility of zein is mainly restricted to acetone, acetic acid, aqueous alcohols, and aqueous alkaline solutions. In the first step, various concentrations of zein were dissolved in acetic acid/water or ethanol/water solutions containing various volume ratios of the solvents. It was found that appropriate zein films can be obtained using 7 wt% zein in two solvent systems: glacial acetic acid and 80% (v/v) ethanol/water. Therefore, in the second step, these two solvent systems were considered to fabricate the zein membrane. To prepare the zein membrane using the ethanol/water solvent system, zein (7 wt%) was added to the ethanol/water solution and stirred for 30 min on a magnetic stirrer under reflex at 85 °C. Then, 6 mL of the obtained solution was poured into a plastic petri dish with a diameter of 8 cm. Solvent evaporation was achieved at room temperature for 48 h. To prepare zein membrane using acetic acid as solvent, zein (7 wt%) was added to glacial acetic acid and stirred for 5 min on a magnetic stirrer. Then, to change the hydrodynamic volume of protein [27], the zein/acetic acid mixture was sonicated for 15 min in the PS-30A Graigar ultrasonic bath (China) at 40 kHz and 40 °C. It should be noted that without ultrasonication, non-selective zein films were obtained. Ultrasonication of zein solution was also recommended in the previous literature [26, 28, 29]. Stirring was done for 2 h at room temperature to ensure the complete dissolution of zein. 6 mL of the resultant solution was poured into a plastic petri dish with a diameter of 8 cm and was kept at room temperature for solvent evaporation. The zein membrane prepared using the ethanol/water solvent system was not mechanically robust to be utilized in gas separation experiments. Therefore, glacial acetic acid was applied as the solvent in the present study.

Membrane Characterization

SEM

The morphology of the zein membrane was observed by scanning electron microscope [30, 31]. Scanning electron microscopy (SEM) images were taken via a scanning electron microscope (LEO 1450VP, Germany). Before imaging, the specimens were Au-coated using the sputtering device (SC7620, England). For cross-sectional imaging, membranes were freeze-fractured in liquid nitrogen. The thickness of the zein membrane was determined by analyzing the cross-sectional SEM images using an image processing software.
BET

The surface area and pore volume of the zein membrane were determined through Brunauer–Emmett–Teller (BET) analysis using the nitrogen gas adsorption–desorption method. The Zein membrane was cut into small pieces and degassed using the BEL PREP VAC II (BEL, Japan) degassing unit. The analysis was then carried out using BELSORP MINI II (BEL, Japan) device.

Water Contact Angle

A DP71 Olympus (Japan) electronic camera was used to image the water droplets on the membrane surface to determine the contact angle of water. Three specimens were examined, and four water droplets on each sample surface were analyzed. Finally, the average of obtained data was reported.

Thermogravimetric Analysis (TGA)

TGA was used to study the thermal stability of the zein membrane [32]. A thermogravimetric analyzer (METTLER TOLEDO, Switzerland) was applied, and the change in the weight of samples was measured in the N₂ atmosphere. The temperature increased from 25 to 800 °C at 5, 10, 15, and 25 °C/min heating rates.

Reaction type can be described by Eq. (1) [33]:

\[ A_{\text{Solid}} \xrightarrow{\text{Heat}} B_{\text{Solid}} + C_{\text{gas}} \]  

where A is the test sample, and B and C are the products of decomposition. The kinetic equation of the above solid-state reaction takes the following form [34]:

\[ \frac{da}{dt} = k(T) f(\alpha) \]  

where \( \alpha \) is the degree of decomposition, \( f(\alpha) \) is an empirical conversion function, and \( k \) is the rate constant. \( \alpha \) is described by Eq. (3) [34]:

\[ \alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \]  

where \( k(T) = Ae^{\frac{E_a}{RT}} \), \( \frac{da}{dt} = Ae^{\frac{E_a}{RT}} f(\alpha) \), and \( m_\infty \) are the initial sample mass, sample mass at the time \( t \), and final sample mass, respectively. \( k(T) \) is described by the following [34]:

\[ k(T) = Ae^{\frac{E_a}{RT}} \]  

where \( E_a[J/mol] \) is the activation energy, \( A \) is the pre-exponential factor, \( R[J/mol.K] \) is the gas constant, and \( T[K] \) is the absolute temperature. Substituting Eq. (4) into Eq. (2), the following equation is obtained [34]:

\[ \frac{da}{dt} = Ae^{\frac{-E_a}{RT}} f(\alpha) \]  

Under non-isothermal conditions, the variation of the degree of decomposition can be expressed by the heating rate (\( \phi = \frac{dT}{dt} \)). Then, the reaction rate is [35]:

\[ \frac{da}{dT} = \frac{A}{\phi} e^{\frac{-E_a}{RT}} \]  

On the integration of Eq. (6), this equation can be written in the following form [35]:

\[ g(\alpha) = \frac{A}{\phi T_0} e^{\frac{-E_a}{RT}} dT \]  

This integral has no analytical solution but has many approximation equations. One of the most famous equations in this regard is the Coats-Redfern (CR) equation. The integral form of this equation is [36]:

\[ \ln \left( \frac{g(\alpha)}{T^2} \right) = \ln \left( \frac{AR}{\phi E_a} \left( 1 - \frac{2RT}{E_a} \right) \right) - \frac{E_a}{RT} \]  

Different reaction models were investigated, as listed in Table 1. The best model was selected based on the Bayesian information criterion (BIC) and Akaike information criterion (AIC) [37] and was applied in calculating the activation energy.

Also, using the data obtained by the CR equation, the entropy of activation (\( \Delta S^* [J/mol] \)), enthalpy of activation (\( \Delta H^* [J/mol] \)), and Gibbs free function (\( \Delta G^* [J/mol] \)) were calculated [35]:

\[ \Delta S^* = R \ln \left( \frac{Ah}{K_B T_P} \right) \]  

\[ \Delta H^* = E_a - RT_P \]  

\[ \Delta G^* = \Delta H^* - T_P \Delta S^* \]  

where \( h[J.s] \) and \( K_B[J/K] \) are Planck and Boltzmann constants, respectively, and \( T_P \) is the minimum temperature of the derivative thermogravimetric (DTG) curve [35, 36].

Tensile Test

Membrane samples with the dimensions of 70 mm × 10 mm were placed in the universal testing machine (SANTAM STM-20, Iran) and were stretched at 12.5 mm/min crosshead speed.
The mechanical properties of the samples were calculated using the stress–strain data obtained for five specimens. The average of the determined values was reported.

**XRD**

X-ray diffraction (XRD) spectrum was collected in an X-ray diffractometer (Philips, PW3710, Netherlands) using Cu-Kα radiation in the 2θ range of 5.15–130° with an increment of 0.05°. Crystallite size was obtained using the Scherrer equation [38]:

\[ L = \frac{K \times \lambda}{\beta \cos \theta} \]  

(12)

where \( L \) [Å] is the crystallite size, \( \lambda \) [Å] is the wavelength, \( \theta \) [deg] is the Bragg angle, \( K \) is the shape factor, and \( \beta \) [rad] is the peak width at its half maximum. The d-spacing can be obtained using the Bragg’s law [39]:

\[ n\lambda = 2d \sin \theta \]  

(13)

where \( n \) is an integer (1, 2, 3, …), and \( d \) [Å] corresponds to the interlayer spacing. Also, the degree of crystallinity (DC) was calculated by the following equation [40]:

\[ DC(\%) = \frac{\text{Total area of crystalline peaks}}{\text{Total area of all peaks}} \times 100 \]  

(14)

**DSC**

A METTLER TOLEDO (Switzerland) differential scanning calorimeter was used under the N₂ atmosphere. The test was carried out in the temperature range of -100 to 220 °C with a 10 °C/min heating rate in the heating–cooling–heating cycle. The first heating cycle was used to eliminate the thermal history of the sample [41], and the second heating cycle was used to calculate \( T_g \) and \( T_m \). \( T_g \) was determined as the intersection of tangents on the DSC thermogram [42].

**Biodegradability Test**

The biodegradability of the zein membrane was assessed by determining the weight loss of the samples buried in compost. Three membrane samples with the dimensions of 3 cm × 3 cm and the weight of 0.0913 ± 0.0060 g were applied in the biodegradability test. Each sample was buried in 50 g compost and was put in an incubator (Shimaz Co., Iran) at the constant temperature of 30 °C. Every three days, water was sprayed on the compost. Every five days, the residual weight of the samples was measured to determine weight loss [11]:

\[ \text{Weightloss(\%) = } \left( \frac{M_0 - M_f}{M_o} \right) \times 100 \]  

(15)

where \( M_0 \) [g] is the initial weight, and \( M_f \) [g] is the residual weight of the samples.
The composition of elements in the utilized compost is as follows: N (1.45%), P (1.75%), K (1.11%), Fe (1.76%), Cu (92 ppm), Mn (660 ppm), Zn (350 ppm), organic carbon (19.6%). The pH of the compost was 8.25, and its electrical conductivity was 5.05 ds/m. The number of fecal coliform and Salmonella in the compost were lower than 1000 MPN/g dry weight and lower than 3 MPN/g dry weight, respectively.

**ATR-FTIR**

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrum of the membrane was collected on a Thermo Nicolet spectrometer (AVATAR 370, USA). The analysis was performed in the wavenumber range of 450–4000 cm\(^{-1}\) with a resolution of 4.000. The number of sample scans and background scans was each ten.

**Gas Permeation Test**

The pure gas (N\(_2\) and O\(_2\)) permeation test was carried out in a lab-scale set-up. Figure 1 shows a schematic representation of the experimental set-up. The pressure of the feed side was kept constant at 2, 4, and 6 bar, and another side of the membrane cell was maintained at atmospheric pressure. The permeability of gasses was calculated by the equation given below [43]:

\[
P = \frac{Q}{\Delta p} \times A \tag{16}
\]

where \(P\) is the permeability calculated in barrer \([1 \text{barrer} = 10^{-10} \text{cm}^3(\text{STP})/\text{cm}^2\text{cmHg}s]\), \(Q\) [cm\(^3\)/s] is the permeate volumetric flow at standard temperature and pressure, \(l\) [cm] is the membrane thickness, \(\Delta p\) [cmHg] is the partial pressure gradient between the feed side and permeate side of the membrane, and \(A\) [cm\(^2\)] is the membrane surface area.

The ideal selectivity of the zein membrane was calculated by the formula given below [43]:

\[
\alpha_{O_2/N_2} = \frac{P_{O_2}}{P_{N_2}} \tag{17}
\]

where \(P_{O_2}\) is the permeability of O\(_2\), and \(P_{N_2}\) is the permeability of N\(_2\).

Gas permeation tests were performed in three replications. The average of the obtained permeability and selectivity values was reported and compared via statistical analysis.

**Statistical Analysis**

Student's t-test was performed for comparison of means obtained in gas permeation experiments. Differences were considered significant when \(P < 0.05\).

**Results and Discussion**

**SEM and BET**

SEM characterization was used to study the morphology of the zein membrane. Figure 2 illustrates the surface and cross-sectional SEM images of the prepared membrane at different magnifications. As observed, some pores appeared on the membrane surface and cross-section during membrane formation. However, these pores were not interconnected, and thus, the obtained membrane can be used in the gas separation process.

Cross-sectional SEM images were analyzed using an image processing software to determine the thickness of the zein membrane, and the membrane thickness was obtained.
as 92.987 ± 0.348 µm. The BET surface area and total pore volume of the zein membrane were determined via the BET analysis and were obtained as 0.83598 m²/g and 0.0027983 cm³/g, respectively.

**Water Contact Angle**

The water contact angle of the zein membrane surface was obtained as 45.0 ± 4.3. The low contact angle is due to the hydrogen bonding between the polar group of the protein and water molecules [44]. Additionally, charged amino acid side chains and the N- and C-terminals, exhibit electrostatic interactions with water [44].

**TGA**

Figure 3 illustrates the TGA curves obtained for the zein membrane at different heating rates of 5, 10, 15, and 25 °C/min, and the corresponding derivative thermogravimetric (DTG) curves are shown in Fig. 4. Several parameters of the sample, such as chemical composition, density, pore size distribution, porosity, surface area, attrition rate, and reactivity affect the equilibrium state during heating [45], especially at the lower weight due to the easier heat diffusion [46], resulting in greater sensitivity [47]. According to the SEM images in Fig. 2, the pores of the zein membrane are not homogenous, varying in size and shape, which could be the reason for the different equilibrium state of each sample. Furthermore, the heating rate is an instrumental parameter that affects the equilibrium state during heating [48]. Thus, as the temperature rises at a slower rate (5 and 15 °C/min), an equilibrium state is readily achieved. In contrast, at faster heating rates (25 °C/min), due to the slow diffusion of heat, the equilibrium state is reached slowly during the thermal decomposition process and the decomposition temperature shifts towards higher values [49, 50]. A small difference in behavior at the 10 °C/min heating rate at the end of the graph may be due to the non-uniform pore size distribution caused by the heterogeneous surface chemistry of proteins [44]. Several reports have also observed the same irregular thermal decomposition at different heating rates at high temperatures [49–51].

An initial weight loss, with the Tₐ₅ of 120 °C, is observed for the zein membrane, which is generally due to the evaporation of the residual solvent and absorbed
water. Solvent evaporation and the resultant initial weight loss were reported in the previous researches [42, 52].

The DTG graphs (Fig. 4) show temperature broad peak ($T_P$) correlated to the degradation regions. This degradation temperature ($T_d$) for samples at different heating rates is listed in Table 2.

The apparent activation energy values ($E_a$) were calculated from Eq. (8) and are listed in Table 3 along with the AIC and BIC values for each model. Regarding Table 3, the Diffusion 2-D model had the minimum AIC and BIC values, so the activation energy of this model was chosen to calculate the thermodynamic properties based on Eqs. (9–11). The values of this thermodynamic property are listed in Table 4.

According to the values of activation energy in Table 4, the thermal stability and thermal degradation properties of zein membrane are acceptable compared to synthetic polymers such as poly vinyl alcohol (PVA, 127.3 kJ/mol) [53] and ethylene propylene diene monomer (EPDM, 115.8 kJ/mol) [54].

**Mechanical Properties**

The mechanical properties of the zein membrane were studied via the tensile test. The stress–strain curve of the zein membrane is shown in Fig. 5, and the corresponding values of the mechanical properties are listed in Table 5. In addition, the previous literature on biodegradable membranes with dense morphology was reviewed, and the reported values of mechanical properties are tabulated in Table 5 for comparison.

According to Table 5, the mechanical properties of the zein membrane are comparable to those of PLA [57] and are higher than those of CS/PVA (4:1) [58]. With almost equal elongation at break to PBS [55] and CA [59], the tensile strength of the zein membrane is nearly two times
and four times as high, respectively (the elastic modulus was not reported for PBS and CA). Although a significantly higher elongation at break is reported for PCL [56], the tensile strength and elastic modulus of the zein membrane are remarkably higher. The high elastic modulus of the zein membrane reflects its high elasticity, and thus, a high energy is required to change the elastic network of the zein membrane [60]. Therefore, it can be inferred that the mechanical properties of the zein membrane in the present study are superior or comparable to those of the other membranes reported in the literature. The high

![Fig. 4 DTG curves of the zein membrane at 5, 10, 15, and 25 °C/min heating rates](image)

| Table 2 Degradation temperatures ($T_d$) at different heating rates |
|---------------------------------------------------------------|
| Heating rate | 5 °C/min | 10 °C/min | 15 °C/min | 25 °C/min |
| Degradation temperature (°C) | 302.26 | 314.33 | 326.89 | 317.25 |

| Table 3 Apparent activation energy, AIC, and BIC values of degradation models |
|-----------------------------------------------|
| No model | $E_a$ (kJ/mol) at 10 °C/min | AIC | BIC |
| 1 First-order | 182.58 | 106,494.9 | 106,503.9 |
| 2 Second-order | 201.16 | 108,003.6 | 108,012.6 |
| 3 Third-order | 221.05 | 109,512.3 | 109,521.3 |
| 4 Power low 1 | 57.31 | 104,416.7 | 104,425.7 |
| 5 Power low 2 | 69.31 | 104,658.8 | 104,667.8 |
| 6 Power low 3 | 93.32 | 104,915.6 | 104,924.6 |
| 7 Diffusion 1-D | 309.35 | 104,199.7 | 104,208.7 |
| 8 Diffusion 2-D | 320.41 | 103,918.1 | 103,927.1 |
| 9 Diffusion 3-D | 170.93 | 106,780.4 | 106,789.4 |
| 10 Contracting area | 173.79 | 104,813.1 | 104,822.1 |
| 11 Contracting volume | 176.68 | 104,522.0 | 104,531.0 |
| 12 Avarami- Erofeer (A2) | 182.58 | 106,101.4 | 106,110.5 |
| 13 Avarami- Erofeer (A3) | 182.58 | 106,279.4 | 106,288.5 |
| 14 Avarami- Erofeer (A4) | 182.58 | 108,003.6 | 108,012.6 |
mechanical properties of the zein membrane is beneficial to its durability in gas separation applications.

XRD

Figure 6 illustrates the XRD pattern of the zein membrane. As observed, the XRD spectrum of the zein membrane reveals two distinct peaks at 2θ = 7.16° and 2θ = 21.18°. Similar results were reported by Vahedikia et al. [61], Oliviiero et al. [62], Nedi et al. [63], and Oliviero et al. [64]. The d-spacing and crystallite size corresponding to the peak at 2θ = 7.16° were 4.19 Å and 15 Å, respectively, and those of the peak at 2θ = 21.18° were 12.3 Å and 13 Å, respectively. These two values of d-spacing are generally attributed to the average distance of skeleton in the α-helix structure and the distance of α-inter helix in the zein protein, respectively [61]. The DC of the zein membrane, calculated using Eq. (14) was equal to 39%, which shows a lower DC compared to the polyvinylidene fluoride (PVDF) membrane [60] and a higher DC compared to the polyether block amide (PEBA) membrane [65].

DSC

Figure 7 shows the DSC curve of the zein membrane in the heating–cooling–heating cycle. The glass transition temperature (Tg) and melting temperature (Tm) of the zein membrane were detected at 142.86 °C and 181.09 °C, respectively. Pereira et al. [66] reported a similar glass transition temperature for the zein protein. This glass transition temperature implies the glassy properties [67] of the zein membrane. In glassy polymers, the diffusion of gasses and, consequently, their kinetic diameter play an essential role in O2/N2 separation [43, 68]. Accordingly, the lower kinetic diameter of O2 (dO2 = 3.46 Å) compared with that of N2 (dN2 = 3.64 Å) [68, 69] causes higher permeability of O2 than N2 through the zein membrane (Sect. 3.9).

Biodegradability

The biodegradation of the zein membrane in compost was investigated with three replicates, and its weight loss during 15 days burial is shown in Fig. 8. During the burial, the samples were taken out of compost, washed and dried, and photographed. The images of the remaining samples are represented in Fig. 8. According to the results, the zein membrane went through 80 ± 3% biodegradation in 15 days.

| Membrane material | Elastic modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) | Reference |
|-------------------|-----------------------|------------------------|-------------------------|-----------|
| Zein              | 983.82 ± 71.74        | 29.19 ± 2.15           | 4.41 ± 0.83             | This study |
| Polybutylene succinate (PBS) | –                     | 15.5                  | 5.4                     | [55]      |
| Polycaprolactone (PCL) | 2.65                  | 15.35                 | 736                     | [56]      |
| PLA               | 910                   | 34.46                 | 11.1                    | [57]      |
| Chitosan (CS)/PVA (4:1) | 906.19                | 20.38                 | –                       | [58]      |
| CA                | –                     | 6.92                  | 6.4                     | [59]      |
biodegradable polymers. The biodegradability and the plant-based nature of the zein membrane has environmental benefits including lower greenhouse gas emissions, waste reduction, reduced volume of harmful pollutants, promotion of rural investment, conserving ecosystems and biodiversity, and will help transition to the circular economy.

ATR-FTIR

Figure 9 shows the ATR-FTIR spectrum of the zein membrane. The peaks at the wavenumbers of 1042.12, 1232.12, and 1441.64 cm\(^{-1}\) are assigned to polysaccharides present in gluten [72], \(C - N\) stretching vibration in the amide-III region [73], and \(C - N\) stretching while CNH angle opens [74], respectively. The peak at 1530.85 cm\(^{-1}\) is attributed to \(N - H\) bending [73] and \(C - N\) stretching in the amide-II region [75], and the peak at 1641.59 cm\(^{-1}\) shows \(C = O\) and \(C - C\) vibrations in the amide-I region [75]. The peaks in the range of 2800–3000 cm\(^{-1}\) are related to the \(-CH_3\) and \(-CH_2\) side-chain vibrations in aliphatic groups of amino acids [75]. The peaks observed in the range of 3000–3500 cm\(^{-1}\) come from \(N - H\) stretching vibration in the amide-I region [73]. Both the \(C = O\) bond of amide-I and the \(N - H\) bond of amide-II are involved in the hydrogen bonding that takes place between the different elements of secondary structure [76]. In addition, the amide groups form hydrogen bonds with water molecules [77], which is the reason for the low water contact angle of the zein membrane (Sect. 3.2).
Gas Permeation Tests

Pure O$_2$ and N$_2$ permeability measurements were performed for the zein membrane at three pressures of 2, 4, and 6 bar. The permeability and ideal selectivity of this membrane are shown in Fig. 10. Figure 10 (a) implies that the permeability of O$_2$ was statistically higher than that of N$_2$ in all feed pressures as validated by t-test (P-values < 0.05). Solution- diffusion model explains the permeability of gases through dense polymeric membranes [68, 78]. According to Sect. 3.5, Zein protein is a glassy polymer. Because of the low chain mobility of glassy polymers [79] and low condensability of O$_2$ and N$_2$ [43], the diffusion of gases and, consequently, their kinetic diameter play an essential role in O$_2$/N$_2$ separation [43, 68]. Accordingly, the lower kinetic diameter of O$_2$ compared with that of N$_2$ (c) [68, 69] causes higher permeability of O$_2$ than N$_2$ at all pressures. With increasing pressure from 2 to 4 bar and then from 4 to 6 bar, the permeability of N$_2$ increased by twofold and 3.5-fold, respectively. The observed increase in N$_2$ permeability was statistically significant according to the results of t-test (P-values < 0.05). Increasing the pressure from 2 to 4 bar augmented O$_2$ permeability by 1.5-fold; however, a pressure increment from 4 to 6 bar dropped O$_2$ permeability slightly, i.e., by 5%. The observed increase and then decrease in O$_2$ permeability were both statistically significant according to the results of t-test (P-values < 0.05). The increase in permeability of gases with an increase in pressure can be explained as follows: as mentioned above, diffusion is dominated in this separation, and as the diffusion coefficient and mass transfer driving force increase with increasing pressure [13, 80], the permeability of gases increases.

As shown in Fig. 10 (b), the ideal O$_2$/N$_2$ selectivity of the zein membrane was 5.45 at 2 bar feed pressure, which decreased by 26% when the pressure increased from 2 to 4 bar. The difference in O$_2$/N$_2$ selectivity at 2 and 4 bar was significant (P < 0.05). The ideal O$_2$/N$_2$ selectivity of the zein membrane dropped by 72% when the feed pressure reached from 4 to 6 bar. According to the result of t-test, the observed decrease in O$_2$/N$_2$ selectivity was significant (P < 0.05).

A comparison of the results of the previous literature on O$_2$/N$_2$ separation using neat dense polymeric membranes with those of the present research is provided in Table 6. In addition, the O$_2$/N$_2$ selectivity and O$_2$ permeability of the zein membrane and other biodegradable membranes with dense structure made of neat polymers are plotted in Fig. 11.

Regarding Table 6 (non-biodegradable membranes), O$_2$/N$_2$ selectivity and O$_2$ permeability of the zein membrane is lower than that of Matrimid® 5218 [81]. Also, the O$_2$/N$_2$ selectivity of the zein membrane is almost equal to that of the polycarbonate (PC) membrane reported by Sen et al. [83], while the O$_2$ permeability of the latter is almost twice as much. However, it should be noted that the biodegradability of the zein membrane makes it a superior alternative to the mentioned Matrimid® 5218 and PC membranes in terms of enhanced waste management and reduced environmental problems. The O$_2$/N$_2$ selectivity of the zein membrane is slightly lower than that of PLA [82] but its O$_2$ permeability is twice as much. Comparing the O$_2$/N$_2$ separation performance of the zein membrane with that of the other membranes in Table 6 reveals a higher selectivity using the zein membrane.

In addition, Fig. 11 shows that the O$_2$/N$_2$ separation performance of the zein membrane is superior to most of the previously reported neat biodegradable membranes with dense structure. In addition to the excellent biodegradability of the zein membrane, zein is relatively inexpensive compared to other biodegradable polymers. In another view,
zein is the byproduct of corn industries. As a result, it has economic benefits in addition to superior performance over other biodegradable polymers.

**Conclusion**

Zein protein was applied in the preparation of a biodegradable membrane for the first time, and the performance of the developed membrane was assessed in \(\text{O}_2/\text{N}_2\) separation. Various characterizations were implemented to study the properties of the zein membrane. The obtained results are summarized below:

The developed zein membrane showed a significantly high thermal stability. The mechanical properties of the zein membrane were higher or comparable to those of the other dense membranes reported in the literature. Zein biodegradation in compost was remarkably higher than that of the previously reported membranes. The permeability of \(\text{O}_2\) and \(\text{N}_2\) at 2 bar was 0.67 and 0.12 barrer, respectively, and \(\text{O}_2/\text{N}_2\) selectivity was obtained as 5.45. The \(\text{O}_2/\text{N}_2\) separation performance of the zein membrane at 2 bar is superior to most of the previously reported data on the neat biodegradable polymers with dense structure.

**Table 6** Comparison of the results on the \(\text{O}_2/\text{N}_2\) separation performance of the zein membrane and other neat polymeric membranes with dense structure reported in the literature

| Membrane material     | Temperature (°C) | Pressure (bar) | Permeability (Barrer) | \(\text{O}_2/\text{N}_2\) selectivity | Reference |
|-----------------------|------------------|----------------|-----------------------|---------------------------------------|-----------|
| Zein                  | 25               | 2              | 0.67                  | 0.12                                  | 5.45      | This study |
| Matrimid®5218         | 25               | 1              | 1.63                  | 0.19                                  | 8.54      | [81]      |
| PLA                   | 35               | 0.5–1          | 0.336                 | 0.054                                 | 6.22      | [82]      |
| Polycarbonate (PC)    | 25               | 3.7            | 1.5                   | 0.27                                  | 5.6       | [83]      |
| CA                    | 25               | 10             | 0.95                  | 0.186                                 | 5.1       | [12]      |
| PC                    | 25               | 2              | 1.6                   | 0.33                                  | 4.8       | [84]      |
| Polyvinylchloride (PVC)| 25              | 10             | 0.023                 | 0.0066                                | 3.5       | [68]      |
| Polysulfone (PSf)     | 30               | 10             | 1.57                  | 0.5                                   | 3.17      | [85]      |
| PCL                   | 25               | 12             | 0.97                  | 0.32                                  | 3.05      | [86]      |
| Polyurethane-urea (PUU)| 25             | 6              | 5.6                   | 2.12                                  | 2.64      | [87]      |
| Polyurethane (PU)     | 25               | 10             | 7.89                  | 4.22                                  | 1.87      | [88]      |
| PBS                   | 25               | 4              | 0.2                   | 0.11                                  | 1.81      | [89]      |
| PVA                   | 35               | 8              | 2.53                  | 1.5                                   | 1.69      | [90]      |

The obtained neat zein membrane was compared with the neat polymeric membranes with dense structure reported in the previous literature, and porous membranes, as well as membranes modified through various methods, were not considered for comparison.

**Fig. 11** Comparison of the results on the \(\text{O}_2/\text{N}_2\) separation performance of the zein membrane and other neat biodegradable polymeric membranes with dense structure reported in the literature

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