Improvement of the functional properties of cellulose acetate film by incorporating with glycerol and n-propanol

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Abstract  Cellulose acetate (CA) was used for the preparation of food packaging film. Glycerol and n-propanol were introduced, as plasticizer and transparent agent, respectively for evaluating the possible changes of the film functional properties on tensile strength and transparency. The transmittance, haze value, tensile strength and flexibility were acquired by using optical and mechanical analyses, respectively. The presence of glycerol improved the functional properties of films by increasing their extensibility, flexibility and elasticity; however transparency of the films deteriorated with the inclusion of plasticizer. Therefore, the addition of n-propanol as transparent agent into the films enhanced the transparency. Moreover, morphological changes and gas barrier property were confirmed by scanning electron microscopy and water vapor transmission rate analyses. The results suggest that CA films incorporated with plasticizer and transparent agent have good functional properties in isolating water vapor, mechanical performance and optical properties, demonstrating that the optimal film has a potential in the application for food packaging.

Graphical abstract

High strength transparent cellulose acetate film (CAF) was prepared with glycerol as plasticizer and n-propanol as transparent agent. The addition of glycerol and n-propanol has a significant influence on film mechanical performance, optical properties, water vapor barrier property and physical behavior, such as pore structure.
Keywords  Cellulose acetate · High-strength transparent film · Plasticizer · Transparent agent · Food packaging

Introduction

The petroleum-based plastic for food packaging is omnipresent in the modern life due to its excellent performance of extensibility and flexibility. However, most of them are non-biodegradable, and accumulate as waste after use, bringing serious ecology and environmental problems to soil, marine and river (Chae and An 2018; Haward 2018; MacLeod et al. 2021; Stubbins et al. 2021). Therefore, the focus of the current study is to find alternative sustainable solutions to the production of biodegradable packaging plastic using renewable materials (Lambert and Wagner 2017; Li et al. 2021). Cellulosic biomass has been extensively studied as the raw material for fabricating fibers, films and composite materials (Credou and Berthelot 2014; Klemm et al. 2005). Although cellulose-based materials exhibit environmentally friendly characteristics, cellulose solvents have their own disadvantages, such as poor solubility and difficulty in solvent recovery (Kostag et al. 2019; Lopatina et al. 2020; Tu et al. 2020). For this reason, cellulose derivatives have aroused wide interest among the researchers worldwide due to their good solubility, flexibility and important physico-mechanical properties (Heinze et al. 2018; Oprea and Voicu 2020; Shaghaleh et al. 2018).

Cellulose acetate (CA), as one of the earliest cellulose derivatives, has been widely used in different applications, including membranes for water treatment, gas separation, and films for packaging (Assis et al. 2020; Lee and Kang 2020; Mubashir et al. 2021). According to the material performance requirements and customer orientation for food packaging, the commercially applicable films mainly depend on their mechanical and optical properties, lipid and water solubility, and functional properties to act as a barrier to water vapors (Assis et al. 2020; Liu et al. 2021; Tedeschi et al. 2018). As a raw material, the properties of cellulose acetate are mainly affected by the preparation strategies, including solvent system, additives and film-forming process.

Owing to the amorphous or semi-crystalline structure, cellulose acetate can be dissolved in solvent systems, including acetone, acetic acid, metal-complex solutions, ionic liquids, N,N-Dimethylformamide (DMF)/N,N-Dimethylacetamide (DMAc), and trichloromethane (Ferrarezi et al. 2013; Gomez-Hermoso-de-Mendoza et al. 2020; Kim et al. 2016). Since the structure and properties of films can be controlled by using different film-making technologies, casting method is usually adopted to obtain homogeneous dense CA polymeric films for the manufacture of food packaging. However, its mechanical properties should still be improved. Extensive research has been made to evaluate and demonstrate the applications of plasticizer additive with the purpose of improving the film properties of flexibility and extensibility by decreasing the intermolecular forces between polymer chains (Charvet et al. 2019; Teixeira et al. 2021). Among all the plasticizers, glycerol is one of the most commonly used material in biopolymers due to its positive qualities, such as hydrosoluble, polar, non-volatile, low molecular weight and multiple hydroxyl groups’ structure (Prézélus et al. 2021; Suderman et al. 2018). Nevertheless, the addition of glycerol has a significant influence on film physical behavior, such as pore structure by altering the intermolecular forces between polymer and glycerol interactions, which may affect the gas permeability and optical properties (Faradilla et al. 2018; Hong et al. 2020).

This work focuses on the dissolution and regeneration of cellulose acetate for producing high-strength and transparent cellulose acetate film (CAF) for their potential applications in packaging. Plasticizer of glycerol was incorporated to improve the film mechanical performance. Moreover, transparent agent was introduced for the first time to alter the polymeric characteristics desired. The effect of glycerol and transparent agent addition on the mechanical, optical, hydrophilic and hydrophobic, crystallinity properties, and water vapor transmission rate of CA films was studied in detail and depth.

Methods and materials

Materials

Cellulose acetate (CA), with 39.8 wt% acetyl and 3.5 wt% hydroxyl groups (degree of substitution is 2.67), was obtained from the Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Reagents such as
tetrahydrofuran, methanol anhydrous, ethanol anhydrous, n-propanol, n-butanol and n-pentanol were purchased from the Hengxing Chemical Reagent Co. Ltd. (Tianjin, China). Sodium chloride (NaCl) and calcium chloride (CaCl2) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Glycerol was supplied by the Tianjin Jinbei Fine Chemical Co. Ltd. (Tianjin, China). Distilled water was used in all of experiments. All reagents used in this work were of analytical grade.

Preparation of films

CA based films were prepared using the casting method, according to the reference (Goncalves et al. 2019) with modifications. The CA powder was solubilized in tetrahydrofuran (1:7.5 w/v) and held for 4 h under magnetic stirring to form homogeneous solution. Glycerol was added into the formed solution in different concentrations (0, 5, 10 and 15%) (g Glycerol /g CA). For the transparent films preparation, proposal transparent agents (methanol, ethanol, n-propanol, n-butanol and n-pentanol) were added into the solution. The volume ratio of transparent agent to solvent was set to be 0, 0.6, 1.2, 1.8 and 2.4%.

The solution prepared according to the experimental design was poured into a clean and dry glass template and spread with the help of a glass rod. The solvent was volatilized under controlled temperature (25 ± 2 °C) and humidity (45 ± 5 RH%) conditions for 120 min. Afterwards, the films were detached from the glass templates, packed in a vacuum, and stored for further analysis. The films thickness (μm) was obtained with the aid of a digital micrometer (DL321025S, Deli group, China). Measurements were taken at five points for each film.

The control film was made with 0% glycerol and transparent agent. The obtained samples are labeled CAF (pure cellulose acetate film), CAF-5G (5% glycerol in CAF), CAF-10G (10% glycerol in CAF), CAF-15G (15% glycerol in CAF), CAGF-0.6P (5% glycerol and 0.6% n-propanol in CAF), CAGF-1.2P (5% glycerol and 1.2% n-propanol in CAF), CAGF-1.8P (5% glycerol and 1.8% n-propanol in CAF), CAGF-2.4P (5% glycerol and 2.4% n-propanol in CAF). The compositions of cast solution for prepared films were listed in Table S1.

Visual properties

The prepared films were appraised for color using Commission International Eclairage (CIE) Lab scale (L*: lightness, a*: red-green, b*: yellow-blue) to obtain the luminosity degree L* and chromaticity a* and b*. The sample (5×5 cm) was placed on white control plate (L*: 96.54, a*: −0.43 and b*: 1.19) for determination with a 3nh colorimeter (SR64, Shenzhen 3nh Technology Co., Ltd., China). The colors for each film were detected by the average of three readings.

Optical properties

The opacity properties (luminous-transmittance data and haze value) of the films were detected by 3nh Hazemeter (YH1200, Shenzhen 3nh Technology Co., Ltd., China) according to ASTM D1003 (ASTM, 2013) with three different kinds of light source (light source C, A and D65), which was determined according to the amount of light the films can be absorbed and the degree of cloudiness. The reading of opacity was performed at random points by the average of three times throughout the films.

Scanning electron microscopy (SEM)

The surface morphologies of the films were observed by the Scanning Electron Microscope (Zeiss Sigma 300, Germany). The sample was cut into small strips (about 8 × 4 mm) and adhered to the conductive adhesive, which was fixed on the sample table. Samples were sprayed with nano gold by ion sputtering apparatus. The SEM observation was conducted under low vacuum condition with 5.00 kV of acceleration voltage. The samples were observed on the surface and fracture region, and the samples were sudden broke by liquid nitrogen for fracture region analyses.

Fourier transform infrared spectroscopy (FTIR)

The structural chemical analysis of the films was revealed by Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 6700, Thermo Fisher, America) under attenuated total reflection (ATR) mode. The spectra were obtained in the wavelength range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹ resolution and a total of 32 scans for each sample.
X-ray diffraction (XRD)

The crystal characteristic measurement was performed to reveal any changes in cellulose acetate films with X-ray diffraction (XRD) equipment (Bruker AXS D8 Advance, German). The X-ray diffraction patterns were obtained using Cu-Kα radiation at the accelerating voltage and the applied current 40 kV and 40 mA, respectively, and the diffractograms were collected in the range of 5°–30° (2θ angle range) with a scan speed of 5° per minute.

Mechanical properties

The mechanical properties of prepared films including tensile strength (TS), elongation at break (EB), and Young’s modulus (YM) were measured at room temperature using an universal testing machine (i-Strentek1510, Labthink, China) with load cell of 500 N, operating according to the standard ISO1184-1983. Samples with dimensions (10 cm long and 2.5 cm wide) were fixed to the claws in a speed of 100 mm/min. The tensile strength was defined as the tensile prior to the breaking of the sample. The EB was given by the deformation at the moment the sample was ruptured by the initial length of the sample. The modulus of elasticity (YM) was calculated as the slope of the curve in the elastic zone. The average value and standard deviations of each sample were determined using three parallel specimens.

Water vapor transmission rate (WVTR) measurement

WVTR of prepared films was evaluated according to the gravimetric method (ASTM E96-2016) with modifications (Gökkaya Erdem et al. 2021). The films were fixed and sealed on top of capsules which were used to hold the anhydrous calcium chloride (CaCl₂) in the glove box with dry condition (0% RH). The capsules were then placed in an airtight glass desiccator containing saturated potassium chloride solution (KCl aq.) under controlled conditions of temperature (25 ± 2 °C) and humidity (75 ± 2 RH%). The water vapor permeability of the films was determined by linear regression of the constant mass transfer region between the weight gain (W) and the time (t) that is correlated with the exposed area, obtained according to the equation:

\[ \text{WVTR} = \frac{W}{t \cdot A} \]

where WVTR: Water vapor transmission rate (g m⁻² day⁻¹)W: Weight gain after permeation (g)t: permeation time (day)A: surface area of exposed film (m²)

Hydrophobic and hydrophilic performance

The surface contact angle between prepared films and water was analyzed by a contact angle measuring instrument (JY-PHa, Shanghai Zhongchen, China). First, the syringe is pumped repeatedly and quickly with distilled water to ensure that the syringe is filled with distilled water and no bubble exist; Then the films are cut into small pieces, and pasted them on the sample table flatly; Finally, the speed of injection needle to inject water is set, and start measuring.

Results and discussion

Visual aspect of the films

All the prepared solutions were homogeneous and transparent. However, the films prepared based on CA presented different features after casting depending on the additives used in the casting solution. The effect of the incorporation of plasticizer and transparent agent on the color of the films based on is shown in Fig. 1 and Fig S1, S2. As shown in Fig. 1(a–d), the film color was varied and gradually increased in intensity according to the glycerol concentration added. When the concentration exceeds 10%, the glycerol starts to overflow to the surface (Fig. S1). In this manner, varies of monohydric alcohols, as proposed transparent agents, associated with the discrepancy of their aliphatic chain were introduced to enhance the transparency of the CAF. As shown in Fig. S2, the CAF prepared with the addition of methanol and ethanol still presented a white color. By contrast, the films with n-propanol, n-butanol or n-pentanol showed a high opacity. Therefore, n-propanol, n-butanol or n-pentanol could be used as the transparent agent. Since n-propanol is more commonly used reagent which has lower toxicity and viscosity, we
chose it as the transparent agent for the subsequent experiment. Moreover, according to the amount of n-propanol added (Fig. 1e–h), an apparent weakening of color intensity was observed in the films, while only 0.6% of n-propanol can lead to the presentation of the white color.

Further inspection of the color analysis was presented in Table 1, demonstrating that the glycerol and n-propanol added into the cellulose acetate films caused the differences on the luminosity parameter (L*), red coloration (a*) and yellow color (b*). Before starting the test, all samples were placed on the white control plate. It can be seen from Table 1 that the luminosity (L*) of the films decreased with the increase of the amount of glycerol from 5 to 15% compared with the pure CA film. The trend was reversed with the addition of n-propanol, in which the luminosity (L*) of the films increased with the increasing amount of n-propanol.

As can be seen from the above results (Fig. 1), the color intensity of the films increases with the addition of glycerol, and decreases with n-propanol. It can be predicted that the changes caused an variation in the values of the parameters a* and b*, and the obtaining of coloring films ranging from light yellow to orange as well as the significant difference (p < 0.05) in the ΔE of the films compared with the control film. Cellulose acetate films with increasing amount of glycerol as plasticizer showed a reduction in the red coloration (a*), while causing an increase in the yellow color (b*). However, when the n-propanol was added as the transparent agent, the films presented an increase of the red color and a reduction of the yellow color. It is worth noting that the film color represents an important parameter for packing materials due to its ability to impart higher opacity.

**Optical properties evaluation**

The opacity properties of the films were detected by using three different kinds of light source (light source C, A and D65). Table 2 presents the transmittance and haze value of the investigated films. There are no significant differences of measurement among

**Table 1** Color analysis of biodegradable cellulose acetate films with the addition of different concentrations of glycerol and n-propanol, for the parameters the luminosity (L*), chromaticity (a* and b*).

| Samples   | L*       | a*      | b*      | ΔE      |
|-----------|----------|---------|---------|---------|
| Control   | 96.54 ± 0.40 | −0.43 ± 0 | 1.19 ± 0.05 | −       |
| CAF       | 97.81 ± 0.17 | −0.14 ± 0.07 | 0.95 ± 0.4 | 1.59 ± 0.11 |
| CAF-5G    | 97.25 ± 0.07 | −0.23 ± 0.07 | 1.26 ± 0.15 | 0.96 ± 0.05 |
| CAF-10G   | 97.19 ± 0.30 | −0.30 ± 0.05 | 1.38 ± 0.22 | 0.82 ± 0.09 |
| CAF-15G   | 96.84 ± 0.45 | −0.36 ± 0.35 | 1.36 ± 0.35 | 0.6 ± 1.05 |
| CAGF-0.6P | 97.17 ± 0.17 | −0.21 ± 0.12 | 1.17 ± 0.12 | 0.97 ± 0.06 |
| CAGF-1.2P | 97.68 ± 0.40 | −0.09 ± 0.07 | 0.85 ± 0.07 | 1.57 ± 0.17 |
| CAGF-1.8P | 97.84 ± 0.07 | −0.05 ± 0.10 | 0.85 ± 0.10 | 1.70 ± 0.08 |
| CAGF-2.4P | 97.74 ± 0.45 | −0.09 ± 0.20 | 0.85 ± 0.20 | 1.61 ± 0.25 |

Different superscripts letter within the same columns indicate statistically significant different values (p < 0.05).
the light resource A, C and D65, indicating that the prepared films have similar transmittance to those kinds of light resources. Therefore, the subsequent analysis is implemented based on the light source C. The transparency and haze value of pure CA film is 93.64 and 0.86%, respectively. For the films incorporated with glycerol, the transparency is decreased from 92.53% with 5% of glycerol to 84.29% with 15% of glycerol. The corresponding haze degree is sharply increased from 4.91% with 5% of glycerol to 91.69% with 15% of glycerol. On the contrary, several differences can be detected for the CA films with 5% of glycerol at various concentrations of n-propanol. All of them displayed higher transparency compared with the films only with the addition of glycerol and an increased transmittance value from 92.80% with 0.6% of n-propanol to 93.92% with 2.4% of n-propanol.

Not surprisingly, the corresponding haze degree is significantly decreased from 3.06% with 0.6% of n-propanol to 0.45% with 2.4% of n-propanol. Therefore, the addition of either glycerol or n-propanol can affect the transparency of the designed materials, thereby improving the optical properties. This phenomenon is in good agreement with the corresponding digital images (Fig. 1 and Fig. S1, S2) explained above, which is because that an increase in opacity usually leads to the decrease in color and haze degree.

The obtained results indicate that the addition of glycerol and n-propanol has a significant influence on film optical behavior. It is known that the opacity of the polymer films can be strongly related to their internal structure formed during the drying process. Moreover, the formed structure is strongly influenced by the composition of the initial solution (Kim et al. 2016). Therefore, higher opacity may be related to the presence of film structure due to the differences in refraction of the phases, as well as the pore size and roughness. However, in this work, the raw materials and reagent used in the film preparation process include cellulose acetate, propanol, n-propanol and tetrahydrofuran. All these materials are of hydrophilic nature, and characterized by miscible dispersion formed by CA, solvent and additives, presenting a possible chemical interaction between their chains. It is remarkable, however, that the volatility difference was presented among propanol, n-propanol and tetrahydrofuran. In that case, the volatilized process of solvent and additives justifies the maintenance of opacity by the films.

### Table 2 Optical properties analysis of biodegradable cellulose acetate films with different alcohols

| Samples    | C       | A       | D65     |
|------------|---------|---------|---------|
|            | T       | H       | T       | H       | T       | H       |
| CAF        | 93.64   | 0.86    | 93.66   | 0.9     | 93.68   | 0.88    |
| CAF-5G     | 92.53   | 4.91    | 92.55   | 4.7     | 92.57   | 4.93    |
| CAF-10G    | 87.35   | 91.27   | 87.16   | 91.19   | 87.39   | 91.32   |
| CAF-15G    | 84.29   | 91.69   | 84.02   | 91.51   | 84.33   | 91.74   |
| CAGF-0.6P  | 92.80   | 3.06    | 92.83   | 3.02    | 92.84   | 3.08    |
| CAGF-1.2P  | 93.75   | 1.42    | 93.77   | 1.43    | 93.79   | 1.44    |
| CAGF-1.8P  | 93.78   | 0.73    | 93.80   | 0.78    | 93.82   | 0.75    |
| CAGF-2.4P  | 93.92   | 0.45    | 93.95   | 0.52    | 93.96   | 0.47    |

C, A, D65: Light resources; T: Transmittance value; H: haze value

Figure 2 shows the SEM images of the prepared films based on CA. The control film without the addition of glycerol and n-propanol presented a smooth and homogeneous surface (Fig. 2a1-a2). This behavior is closely related to the casting method used under the suitable drying conditions. Besides, cellulose acetate presented good solubility in tetrahydrofuran, and the formed films was transparent without roughness and good distribution of pores in the polymer matrix. With the addition of glycerol, the surface image (Fig. 2b1 and b2) of the film containing 5% of glycerol was beginning to present micropores with a diameter ranging from 80 to 360 nm. Moreover, the scanning electron microscopy demonstrates that there were many small pores with the diameters ranging from 1000 to 2000 nm and uniform depressions on the surface of films incorporated with 10 and 15% of glycerol (Fig. 2c and d), respectively. Although the pores present similarity in terms of number and diameter in both CAF-10G and CAF-15G, there was
a considerable reduction in the depth of pores for CAF-15G compared with CAF-10G. As can be seen from Fig. 2, the fracture images of the films start to present small pores after the introduction of glycerol (Fig. 2a3-a4, b3-b4, c3-c4 and d3-d4). With the increase of glycerol content, the number and diameter of pores on the film cross section increased. Therefore, the existence of glycerol may modify the polymer network by interacting with the polymer molecular, causing internal morphological changes reflected by the appearance of pores with different number and diameter.

When using tetrahydrofuran as the solvent, the pore size and porosity of the film surface increased with the increase of glycerol content in the casting solution. This is mainly due to the influence of thermodynamic properties and kinetic behavior of the film-forming system. As evaporation of the solvent with low boiling point (tetrahydrofuran) proceeds, instantaneous phase separation occurs and polymer-poor nucleus are formed, i.e., the spherical microbubbles, which is the necessary conditions for the formation of film pores. The spherical microbubbles get close to each other until the formation of gel (Gomez-Hermoso-de-Mendoza et al. 2020). At low glycerol concentration, the glycerol molecules interacting with cellulose acetate played a plasticizing role, and the film has low porosity. However, the higher the glycerol content, the faster the gel, and the larger the average pore size, resulting in open pores on the surface and inside the film. The glycerol molecules are separated from the casting solution in the form of microbubbles (Thiangtham et al. 2019).

As can be seen from the results in visual aspect of the films, n-propanol could be used as the transparent agent to enhance the opacity of films. Figure 3 shows the SEM images of the cellulose acetate films with 5% glycerol and 0.6–2.4% n-propanol. With the addition of 0.6% n-propanol, the film presented
a rough surface with uniform depressions (Fig. 3c1-e2). With the increase of n-propanol from 1.2 to 2.4% (Fig. 3f1-f2, g1-g2, h1-h2), it was noted that the surface gradually became smooth even at high resolution. The fracture image of the film with 0.6% n-propanol (Fig. 3e3-e4) shows the micropores with diameters ranging from 90 to 150 nm. It is worth noting that porous cross section starts to change when the concentration of n-propanol is increased to 1.8% (Fig. 3f3-f4, g3-g4 and h3-h4). In addition, the pores disappeared with the addition of n-propanol at the concentration of 1.8 and 2.4%. It can be seen from the results that glycerol and n-propanol have a strong influence on film structure behavior. The analyses results of SEM images show that the surfaces of the films incorporated with glycerol and n-propanol were characterized by pore-like structures with different size, which may have significantly affected the visual and optical properties.

Fourier transform infrared spectroscopy (FTIR-ATR) measurement

The FT-IR spectra of the prepared films based on CA are shown in Figs. 4 and 5. It can be seen from the IR spectra in Fig. 4 that the spectrum for pure CAF has a broad peak around 3434 cm\(^{-1}\) in CAF, which is related to the stretching vibration of O–H. The peaks at 2943 and 2884 cm\(^{-1}\) are assigned to the asymmetric stretching vibration of C–H in alpha-saturated methyl groups and methylene groups, respectively. While the sharp peak presented at 1733 cm\(^{-1}\) is assigned for C=O stretch of the acetate function. And the characteristic peak at 1370 cm\(^{-1}\) could be assigned to the symmetric bending of C–H. Besides, the peaks at 1220 cm\(^{-1}\) and 1032 cm\(^{-1}\) are attributed to the asymmetric stretching of C–O in C–O–H and C–O–C from the pyranose ring, respectively (Candido et al. 2017; Chen et al. 2016).
It is observed in Fig. 4 that the addition of glycerol resulted in an increase of intensity in the bands 3434 cm\(^{-1}\) (stretching vibration of O–H) and 2943 cm\(^{-1}\) (stretching vibration of C–H). Due to the existence of C–H and O–H groups in the chemical structure of glycerol, glycerol was successfully integrated into cellulose acetate film, which may cause an increase of the interactions by hydrogen bonds between glycerol and CA molecular chain. However, not all of the three O–H groups in glycerol molecular can be available for the formation of hydrogen bonds. Therefore, the O–H prominent band may also be related to the higher amount of O–H present in the film with the increase of the amount of glycerol.
Similar tendency was observed in Fig. 5, showing the similarity of the FT-IR analyses with the presence of different amount of n-propanol and glycerol in CA film. The main reason for this phenomenon is that the positions of characteristic peaks of O–H and C–H in n-propanol overlapped with those in glycerol.

X-ray diffraction (XRD) determination

Figure 6(a) shows the XRD patterns of the films based on CA without and with glycerol. For the sample of CAF, the broad diffraction peak at 2θ = 7–13° was stacked by the peaks at 2θ = 8.3° and 10.4°, which is assigned to the principal characteristic of semi-crystalline region caused by acetylation of CA. The wide and diffuse diffraction peak around 2θ = 18.8° is attributed to the less ordered region of CA. Since the cellulose acetate substitution degree has reached 2.67, it means that most of the hydroxyl groups in cellulose are replaced by acetyl groups. As a result, the presence of acetyl group in cellulose acetate, to some extent, may cause disruption in the formation of a regular crystal structure between the molecular chains (Chen et al. 2016; Zhou et al. 2021).

Mechanical properties estimation

Table 3 charted the data for the mechanical property analyses of the prepared films. It can be seen from the results that the acetate films incorporated with glycerol received a unidirectional increase in the tensile strength, reaching 18.2 N at the concentration up to 15% in comparison with the control film of 14.9 N. However, it is worth noting that the film with the addition of n-propanol presented a reduction of the resistance values for the parameter evaluated. The tensile strength of the film with 5% glycerol and 0.6% n-propanol reached 17.0 N, which was, however, reduced to 15.2 N when n-propanol amount increased to 2.4% in the film (but still higher than that of the control film). The value changes for tensile strength of the films may have been influenced by their thickness. Combined with the SEM results, it was demonstrated that the addition of glycerol contributed to the increase of the thickness of the cellulose acetate films. On the one hand, the presence of the glycerol as plasticizer may have triggered a certain disarrangement of the CA structure by the intra and intermolecular interactions with CA molecular chains; besides, the glycerol, as a nonsolvent in casting solution, enhanced the

| Samples     | TS (N) | YM (MPa) | EAB (%) | Thickness (μm) |
|-------------|--------|----------|---------|----------------|
| CAF         | 14.9   | 67.73    | 2.26    | 22             |
| CAF-5G      | 16.7   | 64.23    | 2.93    | 26             |
| CAF-10G     | 17.9   | 57.74    | 3.63    | 31             |
| CAF-15G     | 18.2   | 60.67    | 3.44    | 30             |
| CAGF-0.6P   | 17.0   | 70.83    | 3.55    | 24             |
| CAGF-1.2P   | 16.4   | 68.33    | 3.48    | 24             |
| CAGF-1.8P   | 15.4   | 70.00    | 3.52    | 22             |
| CAGF-2.4P   | 15.2   | 69.09    | 2.89    | 22             |

TS Tensile strength; YM Young’s modulus; EAB Elongation at break
formation of pore structure in the film (Zhang et al. 2020). In this way, it was manifested as an increase in the thickness of the films. With the addition of n-propanol as a transparent agent, the thickness of the cellulose acetate films decreased. The mutual solubility of n-propanol and glycerol was used to remove the excessive plasticizer from the film because neither of them is the solvent for cellulose acetate.

The Young’s modulus of the cellulose acetate films with the incorporation of glycerol leads to the decrease of stiffness compared with CAF (67.73 MPa), and the minimum value was 57.74 MPa from CAF-10G. This demonstrates that although the glycerol is sufficient to plasticize the films, the morphologically porous structure on the surfaces and in fracture regions of the prepared film are without resistance to the tensile force. It has been reported that the presence of plasticizer may cause the disarrangement of the polymer structure, leading to greater flexibility of the material but consequent reduction of the tensile strength. However, at larger final amount of plasticizer in the polymeric material, there may be excessive interactions between the polymer networks. Therefore, with the addition of n-propanol, the mutually soluble non-solvents (excessive glycerol and n-propanol) for acetate cellulose are extruded out from the film due to the contraction of cellulose acetate (Fig. S1), resulting in a gradual decrease of film thickness and pore structure but increase of stiffness compared with the sample of CAF-5G.

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The elongation at break (EB) reflects the degree of flexibility of the films. It was observed in Table 3 that there was an increasing tendency of this parameter due to the incorporation of glycerol with the amount ranging from 5 to 10% into the cellulose acetate film, and it drops slightly when the amount of glycerol reaches 15%, indicating that flexibility of the films may have been influenced by the porous structure. Therefore, the presence of these micropores on the surface and in the fracture region may provide profusion space for the stretching operation, making the material more flexible. This may also explain the mechanical behavior of the addition of n-propanol with which, in the films, 0.6–2.4% of n-propanol can cause EAB reduction. It can be seen from the SEM results, films with the addition of n-propanol showed fewer pores and an increasingly compact structure. Therefore, the flexibility of the films depends on the intermolecular forces between polymer and plasticizer additive interactions on the one hand, and its pore structure on the other hand.

Hydrophobic and hydrophilic performance

The wettability of the prepared films was quantitatively characterized by the contact angles of the water dropped on the surface of samples. As shown in Fig. S3 and Table 4, the static contact angle of pure CAF (70.8°) was decreased to 64.26°, 68.40°, and 69.44° after the addition of 5, 10, and 15 wt% glycerol, respectively, indicating a better wettability of modified films with plasticizer. However, the contact angle was gradually enhanced with the increase of glycerol amount from 5 to 15%. It is worth noting that the addition of glycerol caused changes of surface morphology, reflected by the appearance of pores (Fig. 2), which is related to hydrophilic properties (Hou et al. 2019).

After the addition of n-propanol, the water contact angle with the surface of modified films was further decreased to 60.93° and 64.27° after the addition of 0.6 to 2.4% n-propanol, respectively, indicating that the films incorporated with glycerol and n-propanol had better wettability than the original CAF and CAF with glycerol. The improved wettability of the modified films was attributed to the polarity of the hydroxyl group of glycerol and n-propanol. As mentioned previously, according to Fig. 3, the surface of the modified films gradually became smooth with the addition of n-propanol. This indicates that the interaction between n-propanol and glycerol resulted in

| Samples     | WCA (°) | WVTR (g·m⁻²·day⁻¹) |
|-------------|---------|---------------------|
| Control     | –       | 338.27              |
| CAF         | 70.80   | 176.89              |
| CAF-5G      | 64.26   | 178.72              |
| CAF-10G     | 68.40   | 180.31              |
| CAF-15G     | 69.44   | 189.88              |
| CAGF-0.6P   | 60.93   | 179.89              |
| CAGF-1.2P   | 61.21   | 183.40              |
| CAGF-1.8P   | 62.41   | 188.60              |
| CAGF-2.4P   | 64.27   | 193.09              |

WVTR Water vapor transmission rate; WCA Water contact angles
changes in surface morphological properties of the CA film, thus affecting the hydrophobic and hydrophilic performance of the films.

Water vapor transmission rate (WVTR) detection

The water vapor permeability of the prepared films was determined. As shown in Table 4, the capsule without sealing film has a water vapor transmission rate of 338.27 g·m⁻²·day⁻¹, which can be explained by the fact that water vapor was directly absorbed by the anhydrous calcium chloride (CaCl₂). Based on the barrier properties of films, water vapor penetration process was obstructed and restricted. For example, the rate of water vapor passing through the pure CAF was sharply decreased to 176.89 g·m⁻²·day⁻¹. The addition of glycerol to the cellulose acetate film led to an increase in WVTR compared with the control film. This might have occurred due to the pore-forming effect caused by the incorporated glycerol, which is conducive to water vapor permeability due to the porous structure on film surface and inside it. Moreover, the hydrophilic property of glycerol containing three hydroxyl groups will also contribute to the interaction with water molecules (Wan et al. 2018). In general, the hydrophilic properties of films are mainly determined by the surface physical structure and chemical composition. Due to the cellulose acetate and glycerol both are of hydrophilic nature, the glycerol may cause an increasing the hydrophilicity of the films. However, the presence of the additives may have provoked an internal morphological changes reflected with the appearance of micropores, which improved the microstructure roughness of the film surface and further affected the film hydrophilicity.

Similar tendency was observed in Table 4, showing the similarity of the WVTR analyses with the presence of different concentrations of n-propanol and glycerol in CA film. The WVTR of CAGF was increased from 179.89 g·m⁻²·day⁻¹ to 193.09 g·m⁻²·day⁻¹ after the addition of 5 and 15% n-propanol, respectively. According to the morphological analysis results, the surface of modified films gradually became smooth, and the pores disappeared with the addition of n-propanol. However, the raw material of cellulose acetate has good hydrophilicity and moisture permeability, and the additives of glycerol and n-propanol are chemicals with hydroxyl groups. Moreover, the thickness of modified films with the addition of n-propanol was decreased (Table 3), which also enhanced the water vapor transmission. Therefore, the hydrophilic properties of films are depending on the physical structure and chemical composition.

Conclusion

In this study, the high-strength and transparent film was successfully prepared by the incorporation of cellulose acetate (CA) with glycerol as plasticizer and n-propanol as transparent agent by using casting method. It can be seen from the results that the addition of glycerol and n-propanol had a strong influence on the film functional properties of tensile strength, transparency, morphological behavior including pore structure, and barrier properties for water vapor. Combined with the analyses of the main parameters, CAGF-1.2P showed good performance. Firstly, the tensile strength of CAGF-1.2P reached 17.0 N, while that of the control film was 14.9 N. The Young’s modulus and elongation at break were 68.33 MPa and 3.48%, respectively, which are higher than the CA of 67.73 MPa and 2.26%, respectively. It also obtained a high transmittance value and low haze degree of 93.75 and 1.42%, respectively. Secondly, CAGF-1.2P presented a smooth surface and compact internal structure in the film, conferring a good functional property as a barrier to water vapor. Therefore, given the properties shown, the films incorporated with glycerol and n-propanol have the potential of application in food packaging.

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Declarations

Conflict of interest The authors confirm that this article content has no conflict of interest.
**Ethical approval**  This article does not contain any studies with human participants or animals performed by any of the authors.

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