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Research Article

Poly (vinyl alcohol) and casein films: The effects of glycerol amount on the properties of films

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Abstract

The aim of the present work was to investigate the effect of glycerol (GLY) concentration on the properties of poly (vinyl alcohol) (PVA)/casein (CAS) blend films. The films were prepared by solution casting method at the different concentrations of GLY. The structural, mechanical, thermal, barrier and hydrophilic-hydrophobic properties of the films were determined by various methods. The structural analysis indicated that there were some interactions between the components. Tensile test results release that tensile strength of the film decreased with the addition of GLY while strain at break values increased. According to thermogravimetric analysis (TGA) results, the GLY included films exhibited lower thermal stability than GLY-0 film. The residual weight decreased by increasing GLY content. The contact angle measurements showed that all films were hydrophilic structure. Also, the water vapor barrier property of the GLY-0 film was developed with the addition of GLY.

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1. Introduction

In recent years, there has been an increasing interest in the development of biodegradable packaging materials due to the environmental concerns, renewability and cost-effectiveness. The polymers obtained from natural and biodegradable sources are an attractive alternative for the petroleum-based synthetic polymers.

Biodegradable polymers can be classified their raw materials and production methods: (1) directly obtained from biomass with extraction, such as polysaccharides (starch, pectin), lipids and proteins (milk proteins, soy protein). (2) The chemically synthesized polymers from bio-based monomers or mixing of petroleum and biomass such poly (vinyl alcohol) and polylactic acid. (3) The polymers produced by microorganisms such as poly (hydroxyl butyrate) [1–4]. Among the first group, proteins frequently used and studied for the food packaging applications due to the their nutritive value, abundance and film forming properties [4–6]. Especially, the bovine milk protein casein (CAS) previously investigated because of its film forming properties, high barrier to gases and transparency [6–8]. In addition, CAS based films are flavourless, odorless, colorless and smooth [8,9]. These properties make it appropriate for the food packaging, protecting and edible film applications. On the other hand, the mechanical properties (brittle) and water vapor permeability of CAS films restrict the usage area [10]. The addition of plasticizer and blending with biodegradable polymers can be used to develop these limitations.

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Poly (vinyl alcohol) (PVA) is a biodegradable, water soluble, nontoxic and biocompatible polymer. It produces by the hydrolysis of poly (vinyl acetate). PVA has good mechanical and thermal property, chemical resistance and good barrier to gases and aroma [3,11,12]. Due to the its good film-forming property and water solubility PVA is a suitable polymer to blend with natural polymers and proteins. Different PVA/ natural polymer studies have been reported in the literature such as soy protein, myofibrillar protein, tara gum, alyssum homolocarpum seed gum, whey protein isolate which were produced by solution casting method. Generally, these blends have been prepared to use in the packaging, protecting and agricultural mulching film applications [5,12–17]. Also, in the literature PVA/CAS films have been prepared by electrospinning method for the wound dressing material [18] and enzyme substrate [19]. According to the best of authors knowledge, there is no PVA/CAS solution casting film study in the literature.

PVA has many hydroxyl groups in its structure and can form hydrogen bonds with protein molecules. These strong interactions restrict the molecular, chain movement and processability of the blends [12,15,19,20]. Besides that, casein has brittle film structure. In this sense, to overcome this processability and mechanical limitations plasticizers can be used. The plasticizers are low molecular weight non-volatile organic compounds. A plasticizer decreases the second order transition temperature and increases the flexibility of the materials by increasing the free volume of polymer. Furthermore, suitable amount plasticizer obstructs the crack formation during the transportation and packaging and improve the tear resistance and toughness of films. The polarity and molecular weight of plasticizer affects the efficiency. In addition, compatibility is important factor [10,21,22]. The natural based plasticizers generally used for PVA and CAS films. The most common plasticizers include different types of polyols (glycerol, poly (ethylene glycol)), sorbitol, lipids, oligosaccharides and sucrose [22]. Among these, glycerol is efficient and most widely used plasticizer. Because, it has more hydrophilic nature compared to sorbitol and also glycerol molecules are small [23–25]. Glycerol (GLY) was used as the plasticizer in our study. GLY is a high boiling point, water soluble, sweet taste liquid compound [26]. It is a good choice for the food packaging films due to the non-toxic property.

In this study, we aimed to develop a biodegradable, environmentally friendly material instead of non-biodegradable petroleum-based materials. The preparation of such a material will be an important development for both of the environment and living health. Additionally, it is a great advantage that casein used in the study is obtained from an edible and renewable source and cheap. This study proposes a new material produced by traditional method from cheap and renewable raw materials. It is believed that this material can be used in particular for packaging purposes. It is also important to find the optimum amount of plasticizer that affects many properties of the material obtained. So with this motivation, plasticized PVA/CAS films were prepared. Firstly, CAS was plasticized with different amount of GLY and blended with PVA as the ratio of 20:80. The effects of different loading levels of GLY in the film properties were investigated.

2. Experimental setup

2.1. Materials

Bovine milk casein powder (C3400) was obtained from Sigma Aldrich. High molecular weight poly (vinyl alcohol) (degree of hydrolysis = 86.7-88.7 mol%) was supplied from Kuraray Co. Ltd. as trade name of Kuraray Poval 47-88. Plasticizer glycerol ($C_3H_8O_3$, $d=1.26\text{kg/l}$) was supplied from Merck. Triethanolamine (TEA) (Purity: 99%, $d= 1.12\text{kg/l}$) was also supplied from Merck which was used as solvent for the CAS. The structures of materials are given in Fig. 1.

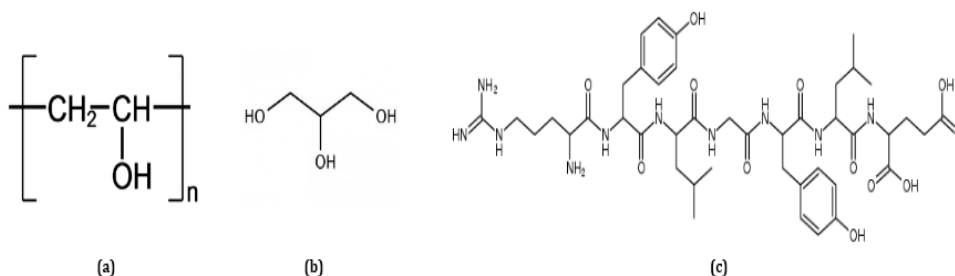


Fig 1. Chemical structures of materials (a) PVA, (b) GLY, (c) CAS

2.2. Preparation of films

The PVA/CAS/GLY films were prepared by solution casting method. Firstly, PVA was dissolved in distilled water under continuously stirring for 1h at 80 °C to obtain 6 wt.% solution. CAS and GLY were dissolved in the 5% TEA solution under magnetic stirring for 1h at 35°C to prepare a 6% plasticized CAS solution. The GLY/CAS ratio was changed as 0:100, 10:90, 15:85, 20:80 and 25:75. Then, plasticized CAS which includes different amount GLY and PVA were blended at the ratio of 20:80 (v/v). The mixed solution was continuously stirred for 15 min at room temperature to prepare homogeneous solution. The total solid content was kept at 6 g to obtain uniform film thickness. Finally, the film-forming solutions were casted onto the polystyrene petri plate (120mm x120mm) and dried at room conditions for 2 days. The prepared films were denoted according to different ratios of GLY as shown in Table 1.

Table 1 Formulations of prepared PVA/CAS films

Sample Code	Dosage			PVA (g)	Total solid (g) (in 100 ml)	Number of produced specimens
	Plasticized CAS (g)		GLY Percentage			
	CAS (g)	GLY (g)				
GLY-0	1.20	0	0%	4.8	6	3
GLY-10	1.08	0.12	10%	4.8	6	3
GLY-15	1.02	0.18	15%	4.8	6	3
GLY-20	0.96	0.24	20%	4.8	6	3
GLY-25	0.90	0.3	25%	4.8	6	3

2.3 Characterization

The structural analysis of the film was characterized by Fourier transform infrared spectroscopy (FTIR). A Perkin Elmer Spectrum 100 testing machine was used for the analysis. Spectra were obtained in the ranging from 650 to 4000 cm^{-1} wavelength.

The tensile test was used to determine the mechanical properties of the films. The test was applied according to ASTM-D 882 standard by using computer controlled Instron universal testing machine. The samples were cut into 20 mm x 80 mm rectangle pieces and measurement were conducted with 10 mm/min crosshead speed. The elongation at break and tensile strength values was determined.

The surface hydrophobicity of the films was determined by the sessile-drop method using Attention Theta Lite contact angle measurement instrument. The distilled water was dropped on the surface of film and the contact angle was recorded. To obtain the average contact angle value at least 10 measurements were made for each specimen.

Thermogravimetric analysis (TGA) (Mettler Toledo TGA 1) was conducted to measure the thermal stability of the PVA/CAS blend films. Measurements was carried out at temperatures ranging from 25 °C to 600 °C at the heating rate of 20 °C/min under nitrogen atmosphere. The sample weight was approximately 8-10 mg. The residual mass at 600°C, the onset temperature (T_{onset}), the end temperature (T_{end}) and the temperature at maximum rate of weight loss (T_{max}) were determined.

The water vapor permeability (WVP) of films was determined through the modified gravimetric method according to the ASTM E96 standard at 35% RH and 23°C.

3. Results and Discussions

3.1. FTIR analysis

The FTIR spectra of the pure and blend films can be seen at Fig. 2. The broad peaks at the range from 3282-3294 cm^{-1} are associated to the stretching of the hydroxyl (OH) groups of CAS and PVA from the intermolecular and intramolecular hydrogen bonds [18]. The -OH peak of GLY-0 (unplasticized PVA/CAS) film was shifted higher wavelength region and intensity of peak decrease on the GLY-25 spectrum. These are the evidence of interactions between PVA/CAS and GLY. GLY may cause destroyed the crystalline regions of polymers and random chain rearrangement [26].

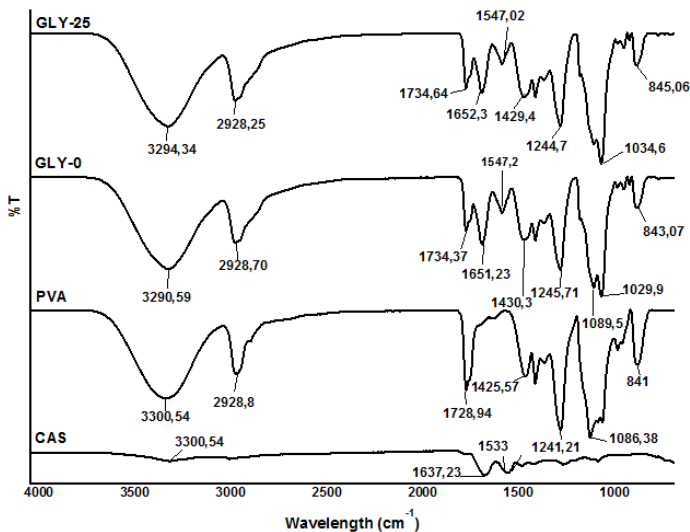


Fig. 2 FTIR spectra of pure PVA, CAS, GLY-0 and GLY-25

The absorptions bands of CAS at 1637 cm^{-1} indicate the -CONH vibration. Also, 1533 and 1515 cm^{-1} peaks are -NH bending vibrations of CAS structure. All these peaks indicate that the protein network structure of casein. These peaks were also seen in the spectra of PVA/CAS blend films and shifted high wavelengths. In the pure PVA film spectrum, a broad band at 3300 cm^{-1} which is attributed to the -OH groups, stretching vibration of C-H was seen at 2928 cm^{-1} , carbonyl group (C=O) vibration at 1728 cm^{-1} , C-O stretching vibration at 1086 cm^{-1} [15,18,26]. These bands were shifted at high or low wavelengths with

incorporation of CAS and GLY in the PVA structure. These results attributed to the interaction between the CAS, GLY and PVA materials.

3.2. Mechanical Properties of Films

The effects of plasticizer GLY amount on the mechanical properties of PVA/CAS film were evaluated and obtained results were given in Fig. 3-4.

The tensile strength results of blend films are given in Fig. 3 as a function of the amount of GLY. Tensile strength can be defined as the resistance of the film to the elongation under the applied stress [25]. The tensile strength value of unplasticized PVA/CAS film (GLY-0) was measured as 38 MPa. This value decreased by adding plasticizer and the reduction is about 22% for GLY-10 and GLY-15. As the amount of GLY increased, the tensile strength decreased. The maximum reduction observed for the GLY-25 as %50. The reduction of tensile strength is the result of the plasticization effect of GLY which destruct the hydrogen bonds and crystalline region in the film structure and resulted reduced the film strength and hardness too. The plasticizing ability of GLY may be the result of asymmetry and branched OH groups that increase the free volume [10,26,27]. Similar plasticizer effect was also observed different studies in the literature for the sodium caseinate [25], PVA-GLY [26], PVA-Sorbitol [27], PVA/SPI film [12] and sodium caseinate/GLY films [9].

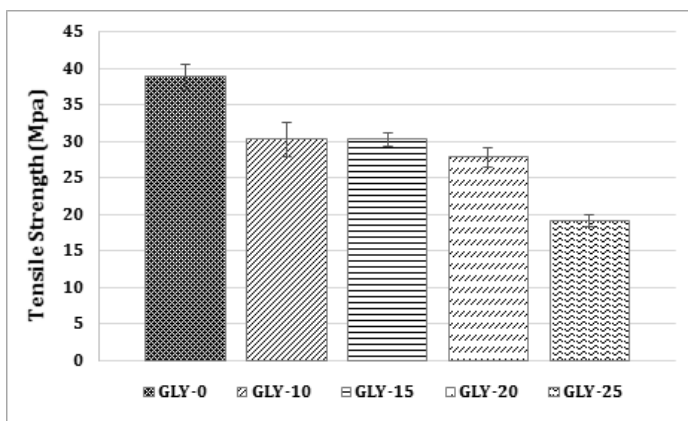


Fig. 3 Tensile strength values of the PVA/CAS films with different GLY amount

The percentage elongation value gives the information about the stretching capacity of the films. It is defined as maximum elongation a material can sustain before breaking [28]. Fig. 4 shows the elongation values (%) of the films as a function of GLY amount. The elongation value of GLY-0 was measured as 207%. With the increase of GLY percentage, the elongation prominently enhanced. The maximum increment was seen at GLY-15 as 36%. The GLY addition destruct the hydrogen bonds and increase the chain mobility and also free volume of PVA. And also decreases the interaction between the protein chains CAS. Eventually, flexibility of the films increases.

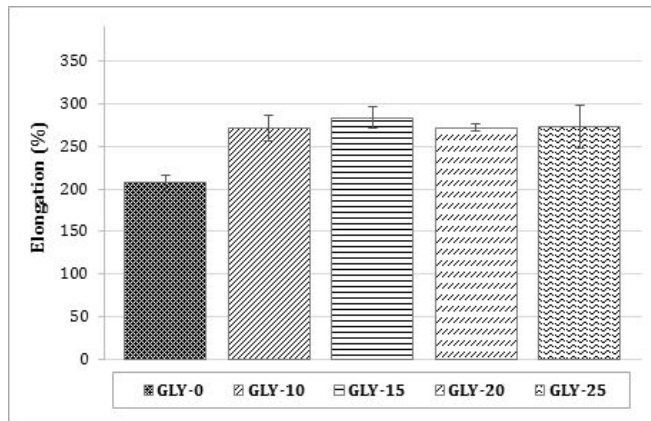


Fig. 4 Elongation values of the PVA/CAS films with different GLY amount

3.3. Contact Angle

The surface hydrophilicity-hydrophobicity characteristics of the films can be directly determined with the water contact angle (θ). The contact angle values of hydrophilic films are $0 < \theta < 90$. The hydrophobicity increased with the increasing θ value [29].

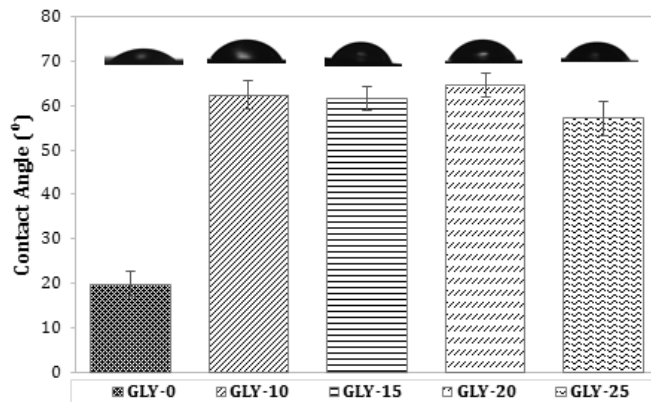


Fig. 5 The water contact angle values of the films

The water contact angle values of each film surface were illustrated in Fig. 5. All films exhibited hydrophilic character ($\theta < 70$). The unplasticized GLY-0 film has lowest θ value as 19° and this value increased with the addition of glycerol about % 65-70. The maximum contact angle was observed for the GLY-20 sample. The hydrophilic groups such as hydroxyl on the film surface, impurity and roughness of the surface affect the contact angle of the materials [15]. The increasing of contact angle by increasing GLY content may be due to the consumption of hydrophilic $-OH$ groups on the film surface. The FTIR spectra of the samples support this result. A plasticizer decreased the number of free $-OH$ group in the structure which causes decreasing the hydrogen bonds between the PVA and water molecules [27]. The contact angle values of PVA/CAS/GLY blends are higher than in the reported biodegradable film studies on the literature. According to Su et al., the θ values of soy protein isolate/PVA/GLY films are lower than 50° [17].

3.4. Thermogravimetric Analysis (TGA)

The thermal properties of the samples were determined with TGA. The thermal stability of the polymers is related with the degradation of macromolecules and low molecular weight molecules for a specific time and temperature. The stability of these molecules depends on the interactions like hydrogen, van der Waals bonds, dipole dipole. When the thermal energy given to the material is higher than the bond energy, chain scission and bond dissociations of related bonds begin [26,30].

The results of studied samples were given in Fig. 6 and Table 2. As illustrated in Fig. 6 all samples exhibited multiple degradation. This is explained by the presence of several molecular weight molecules. The first degradation stage was shown in the range of 110-121 °C for all samples. This weight loss is assignable to the water or moisture vaporization from the film structure [18,30]. Biranje et al. reported that the PVA/CAS blends exhibited initial weight loss about 100 °C due to the hydrophilic structure of the films. $T_{\text{onset-1}}$ value of the pure PVA is 113.8 °C which increased with the incorporation of casein in the structure to 121.6 °C. After that $T_{\text{onset-1}}$ value of GLY-0 decreased with the increasing content of GLY. The second weight loss was started at 335 °C for the pure PVA due to the main polymer chain scission and acetate group decomposition. This is followed by a third smaller weight loss approximately at 395 °C due to the decomposition of polymer backbone [27]. As for the GLY-0 blend film $T_{\text{onset-2}}$ decreased to the 287 °C and this reduction continued with increasing GLY content according to data listed in Table 2. This may be due to the plasticizing effect of GLY and the boiling point of GLY is about 290 °C. GLY might have been eliminated from the film structure about this temperature. On the other hand, the residual weight of pure PVA was 0.75% and it increased with the addition of casein to the 7.7%. However, this value decreased by adding GLY. The minimum residual weight at 500 °C was observed for the GLY-25 film. So, GLY accelerated the degradation of the films.

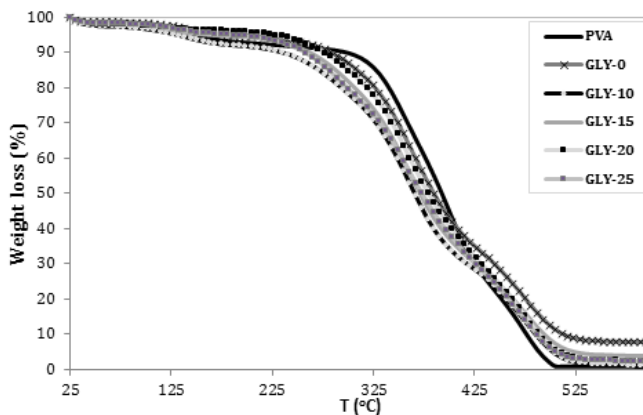


Fig. 6 TGA curves of the samples

Table 2 Thermal properties of the films obtained from TGA

Samples	T _{onset-1} (°C)	T _{endset-1} (°C)	T _{onset-2} (°C)	T _{endset-2} (°C)	T _{max} (°C)	Residue _{500 °C} (wt%)
PVA	113.8	159.9	335.0	504.1	398.3	0.75
GLY-0	121.6	158.3	300.1	508.3	362.6	7.7
GLY-10	120.8	163.1	279.4	496.9	358.4	1.2
GLY-15	114.7	142.7	277.6	502.2	358.8	3.8
GLY-20	113.5	126.3	275.7	495.2	357.6	2.4
GLY-25	110.2	141.8	266.4	479.5	357.6	0.75

3.4. Water Vapor Permeability (WVP)

The WVP is the amount of the transferred vapor between the film and ambient. It is important property which determines the usage are of the films and product shelf-life of the packaged material. The water vapor barrier property of the films depends on several factors such as ambient conditions, thickness, the composition of the structure and crystallinity of the polymer [3,15]. The hydrophilic-hydrophobic nature of the materials controls the barrier properties. PVA is the water soluble, hydrophilic polymer and casein is also hydrophilic structure. Thus, their WVP is higher than the other polymers. The hydrophilic polar groups interact with the water and causes increased permeability [3,17].

The WVP values of selected films were given in Table 3. The water barrier property of the pure PVA is higher than CAS. The blend film (GLY-0) exhibited lower WVP than both of components PVA and CAS as $6.413 \times 10^{-11} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$. This may be due to the interaction (hydrogen bonds) between the casein and PVA molecules. By contrast, the WVP value of the PVA-CAS film increased to $7.798 \times 10^{-11} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ for the GLY-25. It was because plasticization effect of GLY. The film structure has become more porous and hydrophilic. Also, the plasticizers increase the free volume of the polymer matrix and protein network [6]. By increasing free volume and pore size of the film, water molecules can permeate easily in the structure. Wagh et al. reported that, the WVP values of casein and whey protein concentrate films increased with the increasing plasticizer content [6].

Table 3 The WVP values of selected films

Samples	Water Vapor Permeability $\text{g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1} (\times 10^{-11})$
PVA	13.288
CAS	10.971
GLY-0	6.413
GLY-25	7.798

4. Conclusions

The development of new biodegradable materials instead of petroleum-based products attracts attention with the increased sensitivity to health and environmental problems. The milk protein casein and biodegradable synthetic polymer PVA blend films were produced by using solution casting method in our study. To improve the mechanical properties of the films glycerol was used as plasticizer at different concentrations.

The FTIR results indicated that there were interactions between the components via hydrogen bonding due to the hydroxyl groups. The tensile strength decreased by increasing GLY content. The flexibility of the films developed with the addition of GLY. The maximum increment was observed for the GLY-15 film as 33%. The TGA gave the

information about the thermal properties of the films. It was showed that all films exhibited multiple degradation stage. Firstly, the water in the structure was eliminated about 110 °C and then polymer chain scissions and degradations occurred. The $T_{\text{onset-1}}$ value decreased with the increasing content of GLY. Also, it was observed that the GLY accelerated the degradation of the PVA-CAS films. The contact angle values revealed that the all films were hydrophilic because of hydrophilic nature of the components. The WVP property were enhanced by adding GLY. Based on the data obtained from this study, it is planned to perform cross-linking to these films in order to further improve the properties of the films.

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