RESEARCH ARTICLE
doi: 10.2306/scienceasia1513-1874.2023.s006

ScienceAsia 49S (2023): **23–31**

Effects of additives on properties of PVA film for agricultural applications

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Received 17 Jan 2023, Accepted 11 Sep 2023
Available online 27 Dec 2023

ABSTRACT: This research investigates the influence of additives-namely, glycerol (20%, 30%, and 40% wt), ZnO (0 and 1 phr), and coffee extract (0%, 5%, 7.5%, and 10% phr)-on the properties of poly(vinyl alcohol) (PVA) film. The composite samples were prepared by blending using a twin-screw extruder and shaping through compression molding. The addition of glycerol yielded increased water solubility, while a higher glycerol content resulted in reduced water absorption. Concurrently, the glass transition temperature (T_g), melting temperature (T_m), and crystallinity (X_c) exhibited a decrease, leading to diminished tensile strength but elevated elongation at break. A notable linear relationship between glycerol content and film crystallinity was observed. The incorporation of ZnO reduced water solubility and absorption, enhancing tensile strength and elongation due to improved X_c and stress-transfer characteristics. Conversely, the presence of coffee extract increased water solubility and absorption, yet substantially compromised film strength and toughness by diminishing X_c and causing microstructure collapse. The findings suggest the potential use of PVA composite films for seedling planting, with tailored properties achieved through additive manipulation.

KEYWORDS: poly(vinyl alcohol), glycerol, zinc oxide, coffee extract, agricultural applications

INTRODUCTION

Currently, about 5,300 tons of plastic wastes are generated every day globally, including from agricultural applications such as seedling bags, which have been contaminating the environment, oceans, water, forests, and soil. Using biodegradable material is a better option for seedling bags. Poly(vinyl alcohol) (PVA) is a good alternative for this application because it has good physical and mechanical properties such as easily to soluble in water, good water absorption and superior toughness, etc [1]. Many researchers have considered using PVA for seedling bags for both perennial and biennial plants. The seedling bags made of PVA was decomposed naturally within a short period [2]. However, PVA has an important drawback as it has high viscosity for processing. To aid PVA processability, glycerol is used as a plasticizer. It not only increases the flowability of PVA but also improves some mechanical properties, water solubility, water absorption, and water evaporation [2]. However, adding glycerol only to PVA is not sufficient for utilizing as seedling bags; thus, non-toxic materials are considered to ameliorate its desirable material properties. Zinc oxide (ZnO) is the first choice as an inorganic additive. Not only is it a more stable compound with a potent antimicrobial effect against microorganisms, but it is also inexpensive and can be found easily in a local market. Furthermore, it has been reported that ZnO-loaded PVA has enhanced optical, electrical, dielectric, and thermal properties [2]. Additionally, Hemalatha et al [3] found that addition of ZnO as a nanofiller could modify the structural, electrical, optical, and mechanical attributes of PVA. Moustafa et al [4, 5] investigated the use of nanoparticles such as TiO_2 and Ni-ferrite to improve overall characteristics of PVA. PVA with 0.1% TiO_2 could significantly gain better tensile properties, thermal stability, and antibacterial capabilities. Moreover, the addition of only 3% Ni-ferrite to PVA could have boosted tensile strength and elongation at break when compared to plain PVA. Therefore, those PVA nanocomposite films might be utilized to maintain the integrity of the food packagings and in environmental-aspect applications.

For our past research, we studied the effect of various ZnO content, using it for improving antibacterial property on PVA film. We found that ZnO 1 wt% has an optimized content for enhancing PVA film properties including mechanical, solubility and water absorption [6]. Another additive chosen was coffee extract because of its low cost. Also, the dark color of coffee extract could be an advantage for growing the roots, which should not want to be exposed to light, and the dark color absorbs more heat, which will protect the roots on cold nights, leading to more productive plants [7]. Besides that, coffee extract consists of polyphenolic compounds, the chlorogenic acids being the main components, especially 5-caffeoylquinic acid

(5-CQA) [8]. Madkoksung et al [9] has investigated the coffee leaf extract from different coffee taxa. Different types of coffee leaves contain different amounts of phenolic and flavonoid content. Ounkaew et al [10] reported that the extracted spent ground coffee (ex-SCG) is a potential antioxidant for the development of bioactive products, which is another advantage. Many researchers have studied PVA composite filled with various coffee substances including coffee extract, spent ground coffee and instant coffee. They found that the coffee additives enhanced the mechanical properties of PVA. It also improved the UV-shielding property and thermal-oxidative stability of the PVA material [11–13].

The effects of a combination of glycerol, ZnO, and coffee extract on PVA film have not been reported in literature reviewed. In this research, glycerol, zinc oxide and coffee extract were used as additives for improving the properties of PVA film. The objective of this research was to study the effects of these additives on the physical, thermal, and mechanical properties of PVA composite films. The effects on these properties will be discussed.

MATERIALS AND METHODS

Materials

Poly(vinyl alcohol) grade RS-2117 (viscosity of 25.0–30.0 MPa-s and hydrolysis of 97.5–99.0 mol%) was provided from Kuraray Co., Ltd. (Bangkok, Thailand). Coffee extract (⩽ 177 micron) used as additive was purchased from AP Operations Co., Ltd. (Bangkok, Thailand). The main components of coffee extract are oligosaccharides and polysaccharides, chlorogenic acids, quinic acids, trigonelline, proteins, peptides, and free amino acids, as well as the formation of aliphatic acids, lactones, aroma components, and melanoidins. Compositions and fractions depended on the method and condition to obtain the extract [14]. Glycerol 99.5% was purchased from NP Chemical Supply Co., Ltd. (Bangkok, Thailand). Zinc oxide (100–200 nm) was obtained from Ajax Finechem (Bangkok, Thailand).

Preparation of PVA composite film

Poly(vinyl alcohol) mixed with glycerol, zinc oxide, and the coffee extract was dried at 70 °C for 48–72 h. Then the compounds were mixed by using a twin screw extruder at 140–190 °C, and 60 rpm. Next, the film was molded by compression molding at 190 °C, 9.30 min of preheating, 2 min of venting, 4 min of compression, and 4 min of cooling at 50 bar. The specifications for each formula are listed in Table 1.

Table 1 The compositions of the samples and their notations.

PVA (%wt)	Glycerol (%wt)	ZnO (phr)	Coffee extract (phr)	Notation
100	0	0	0	PVA
80	20	1	5	G20
70	30	1	5	G30
60	40	1	5	G40
80	20	0	5	Z0
80	20	1	5	Z1
80	20	1	0	Cof 0
80	20	1	5	Cof 5
80	20	1	7.5	Cof 7.5
80	20	1	10	Cof 10

Characterization

Characterization by Fourier Transform Infrared (FTIR) Spectrometer

Fourier Transform Infrared Spectrometer was used to analyze the functional groups of the materials. All the test samples were tested by the KBr method with a scan range from 4000–400 cm^{-1} using an FTIR spectrometer series VERTEX 70 from BRUKER.

Water solubility

The film was cut into 2×2 cm^2 pieces and weighed (m_0). Each sample was soaked in water for 24 h before being dried in an oven at 50 °C for 24 h. The dried sample was weighed (m_1). The solubility can be calculated from Eq. (1):

$$\%\,\text{Solubility} = \frac{(m_0 - m_1)}{m_0} \times 100 \tag{1}$$

Water absorption

The film was cut to 2×2 cm^2 and weighed (m_0). Then the sample was placed in a beaker containing 10 ml of water for 24 h, after which the sample was weighed again (m_1). Water absorption can be calculated from the Eq. (2):

$$\%\,\text{Water absorption} = \frac{(m_1 - m_0)}{m_1} \times 100 \tag{2}$$

Thermal properties

Differential Scanning Calorimetry (DSC) was used to analyze glass transition temperature, melting temperature, and crystallinity. The temperature was maintained between 50–300 °C with heat-cool mode and a heating rate of 10 °C/min under a nitrogen atmosphere.

Mechanical properties

The 1×4 in^2 specimens were tested for tensile strength, Young's modulus, and elongation at break by a universal testing machine according to ASTM D882 standard at a crosshead speed of 50 mm/min, a temperature of 25 °C, and a load of 5 kN.

Morphological properties

Scanning Electron Microscope (SEM) was used to analyze the distribution of encapsulated zinc oxide and coffee extract particles in the PVA matrix. The film was immersed in liquid nitrogen and then was cut so that a cross-section of the film could be observed by a SEM at a voltage of 5.0–15.0 kV. After the cross-section of the sample had been coated with gold.

Statistical analysis

Analysis of Variance (ANOVA) was used to analyze the standard variation of water solubility, water absorption and mechanical properties. It is a statistical analytic approach that compares and measures data sets to assess their relevance, the most popular of which includes comparing two means (the so-called "pairwise comparisons"). The first pairwise comparison approach is known as the least significant difference (lsd) test, in 1935. The main idea of the lsd is to compute the smallest significant difference (i.e., the lsd) between two means as if these means had been the only means to be compared (i.e., with a *t*-test) and to declare significant any difference larger than the lsd [15, 16]. In our result, the value of the water solubility, water absorption and mechanical properties were defined and included letters (a, b, c, d), which are significantly different means values at ($p \leqslant 0.05$) using Fisher's least significant difference test [17].

RESULTS AND DISCUSSION

Characteristics of PVA, glycerol, ZnO, coffee extract, and PVA/ZnO/coffee extract composite film

The functional groups of PVA, ZnO and coffee extract are shown in Fig. 1(a). For PVA, it was found that C—H stretching, C=O stretching and C—O stretching were observed at 2938 cm^{-1}, 1703 cm^{-1} and 1263 cm^{-1}, respectively, which were attributed to carbon molecules. Additionally, for the PVA functional group, the hydroxyl group (—OH, alcohol) vibrated at 3405 cm^{-1}, and the ester group appeared at 1717 and 1312 cm^{-1} corresponding to C=O and C—O, respectively. The spectrum of the ester groups in the chemical structures was found on both PVA and coffee extract indicating that the coffee extract has a similar ester functional group to PVA. They could probably have an interaction force when they were mixed. However, the vibrations at 1449 cm^{-1} and C—C stretching at 830 cm^{-1} were found only in PVA, which emphatically demonstrated that the chemical structure was composed of the methyl group (CH_3), while the vibration of ZnO was found only at a wavenumber of 510 cm^{-1}, which was attributed to Zn—O stretching.

The effects of ZnO and coffee extract on the PVA composite film are shown in Fig. 1(c,d). It was found that the hydroxyl group of the film was shifted from 3360 to 3323 cm^{-1} and C—H stretching reduced slightly from 2917 to 2912 cm^{-1} indicating that ZnO could probably form a hydrogen bonding interaction with PVA, glycerol and the coffee extract molecules. However, for the coffee extract, it was found that the wavenumbers of O—H and C—H stretching were shifted lower from 3359 to 3334 cm^{-1}, and from 2936 to 2916 cm^{-1}, respectively, when the coffee extract addition was changed from 0 phr to 10 phr. It probably made the interacting molecules more energy-consuming, despite stronger bonding. In addition, the intensities of O—H, C—H, C=O and C—O stretching were slightly increased because the coffee extract consisted of chlorogenic acid, which has a hydroxyl group, carbonyl groups, methyl groups and carboxylic groups. The possible interactions of all the additives i.e., ZnO, glycerol and coffee extract components (chlorogenic acids and melanoidins) with PVA film are shown in Fig. 2. According to Charles-Bernard et al [18], the most abundant components in coffee extract were melanoidins, chlorogenic acids, and organic acids, depending on the method (brew, dialysis, size exclusion, and ion exchange). As seen in Fig. 2, the schematic shows the chemical interaction of the functional group of chlorogenic acid with PVA, glycerol, and ZnO. It should be noted that melanoidins and other organic acids could probably interact with the hydroxyl functional group of PVA.

Effects of glycerol, ZnO and coffee extract on solubility and water absorption of PVA composite film

The solubility of the various glycerol, ZnO and coffee extract contents in PVA composite film is shown in Fig. 3. It was found that the presence of glycerol only 20 wt% in PVA composite film significantly increased water solubility (5% to 15%). It was because glycerol (21.1 $MPa^{1/2}$) has a similar solubility parameter to water (23.5 $MPa^{1/2}$) (data from Hansen solubility parameters handbook). Besides that, the glycerol is likely to migrate to film surfaces; thus, it could induce the water molecules to contact the film surfaces easily and speed up the solution process. In addition, water solubility on PVA composite film with high glycerol content increased sharply compared to low glycerol content (15% to 25%). It was because higher the glycerol content, the more hydrophilic the PVA composite and resulted in the film having free volume, as was confirmed by FTIR; therefore, the water molecules could diffuse into the PVA chain more easily, which gives the PVA film higher water solubility.

On the other hand, the presence of ZnO (Z1) led to an increase in solubility compared to that of Z0 film. When considering ZnO at 0 and 1 phr, it

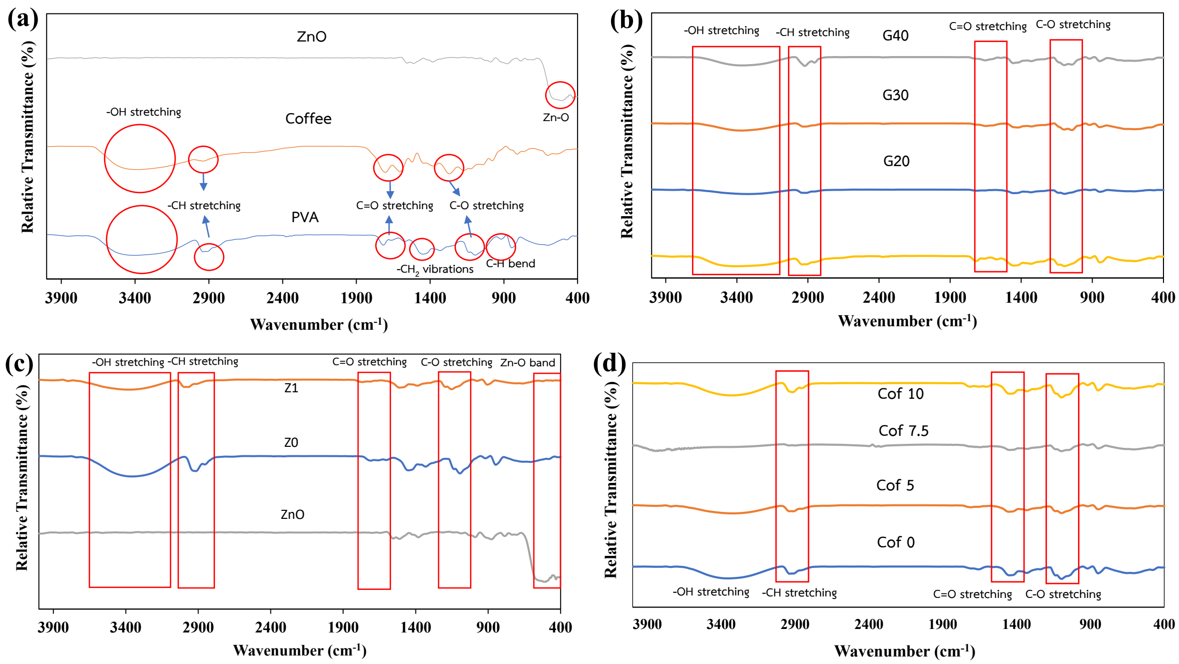

Fig. 1 FTIR spectrum of (a) PVA, coffee extract and ZnO and (b–d) film composite at various glycerol, ZnO and coffee extract contents.

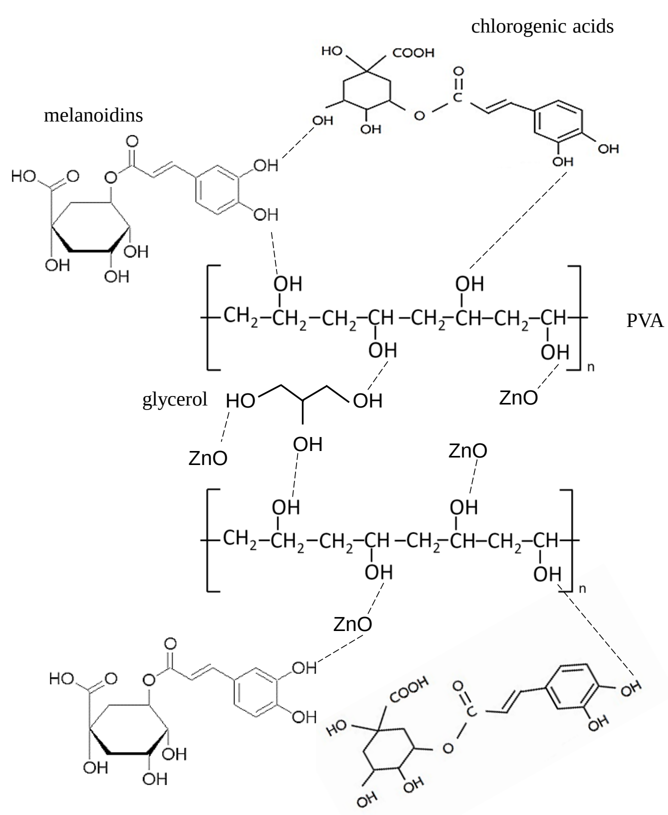

Fig. 2 The possible schematic interactions of PVA, glycerol, ZnO and coffee extract.

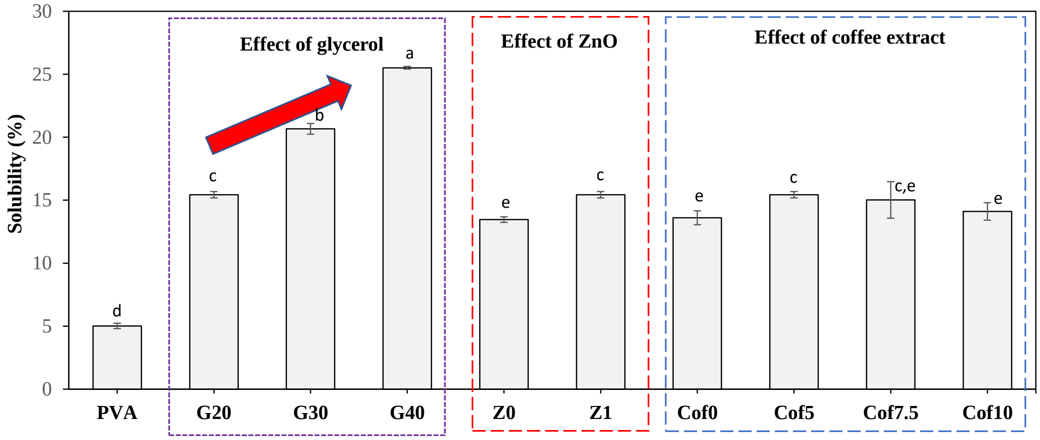

Fig. 3 Effects of glycerol, ZnO and coffee extract on solubility of PVA/ZnO/coffee extract composite films.

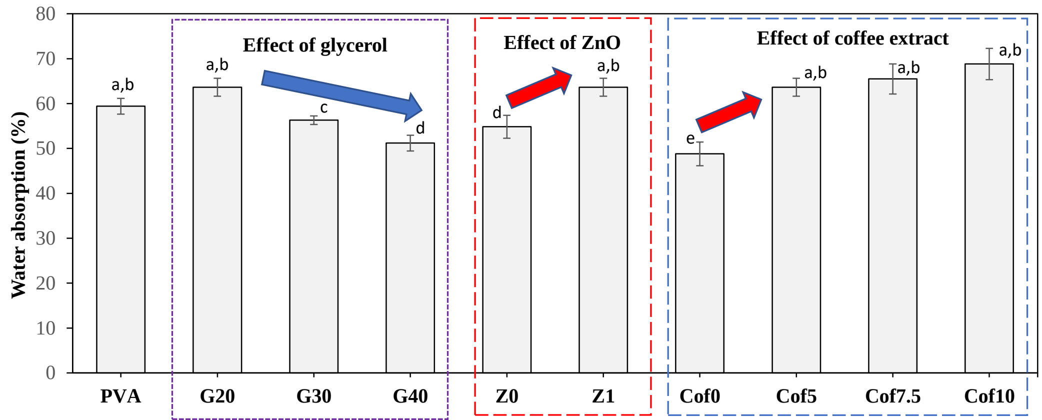

Fig. 4 Effects of glycerol, ZnO and coffee extract on water absorption of PVA/ZnO/coffee extract composite films.

was found that the solubility of PVA film composite was originally increased (13% to 15%) because the solubility parameter for ZnO was 24.4 $MPa^{1/2}$, which is close to that of PVA and glycerol. It indicated that a small amount of ZnO could disperse through PVA composite film and enhance water molecules diffusing into the film surface, resulting in higher water solubility. The effect of coffee extract content on the water solubility of PVA composite film was an initial increase from 13–15% because it contained carboxylic and ester groups, which have high polarity. However, when it compared with the presence of glycerol, the solubility of PVA composite film dropped because coffee extract has more ketone groups (C=O) and methyl groups ($-CH_3$), which have lower polarity than the hydroxyl group (−OH), hence reducing the interaction between water molecules and the PVA chain. Moreover, further increase in coffee extract on PVA composite film did not significantly change the water solubility though will a small reduction compared to 5% coffee extract content. This might be because the coffee extract could form hydrogen bonds with PVA, making it more difficult for water molecules to diffuse into the PVA chain.

The effects of glycerol, ZnO and coffee extract in PVA composite film on water absorption are shown in Fig. 4. It was demonstrated that the water absorption of PVA film increased (59% to 63%) due to the additives effect. The addition of glycerol from 20% to 40% reduced the water absorption from 63% to 51%, respectively. This was because the glycerol at high concentration could act as a plasticizer, which could be inserted between PVA chains. The addition of ZnO significantly increased the water absorption due to the adsorption of ZnO itself and molecular interaction between ZnO, PVA and water. Nevertheless, at constant glycerol and ZnO concentration, PVA composite film with increasing coffee extract gradually increased the water absorption due to the increasing number of −OH groups in the PVA film, which allowed water molecules to be absorbed absorbing PVA composite film.

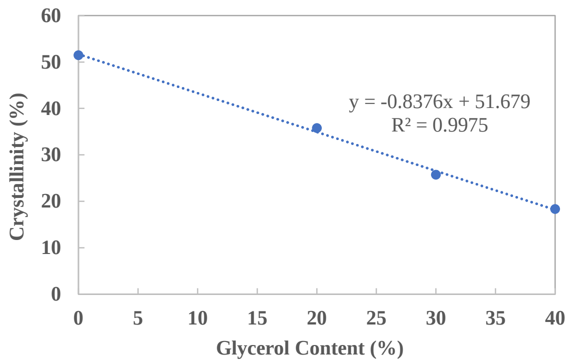

Fig. 5 The correlation between glycerol content and the percent of crystallinity.

In regards to the different contents of glycerol, the relationship between the solubility and the water absorption did not correlate well with the attempts from our investigation. It might be because the solubility mechanism of the film was different from the water absorption mechanism of the film. The solubility mechanism involves the absorption (water is absorbed on the film surface) and the diffusion (water is diffused into the film), while the water absorption mechanism focuses only on the absorption.

Effects of glycerol, ZnO and coffee extract on thermal, mechanical, and morphological properties of PVA composite films

The thermal properties of the PVA composite film are shown in Table 2. It was found that the presence of glycerol tended to reduce the melting temperature (T_m) (207 °C to 193 °C), the percentage of crystallinity (24% to 18%), and the glass transition temperature (T_g) (74 °C to 84 °C) compared to PVA without glycerol. It was probably because glycerol could act as a plasticizer to reduce the strength of the polymer chain, resulting in chain flexibility. However, PVA composite film without glycerol but containing 1 phr ZnO and 5 phr coffee extract has the lowest T_g (74 °C) because coffee extract can penetrate the PVA chain, thus causing free volume. Intriguingly, the correlation between glycerol content and the percent of crystallinity was a pathfinder, as it was inversely proportional to the linear equation for PVA, G20–G40 as shown in Fig. 5 indicating that the presence of glycerol in the film hindered the crystallization of PVA. That could be because the addition of glycerol in the film could interacte with the molecular chains of PVA to reduce the free volume of PVA chain, resulting in difficulty for the chains to move to form crystals. Note that, the DSC's data for PVA composites without glycerol (in pellet form) did not show up in this paper. PVA/ZnO/coffee extract without glycerol gives extremely high viscosity, resulting in it cannot be processed into film. This is because the component of coffee extract is mannan, which is the main polysaccharide and is responsible for its high viscosity [19].

On the other hand, it was found that the addition of ZnO significantly increased T_g of PVA composite film (from 90 °C to 105 °C), possibly due to the impediment of metal oxide particles to flowability of PVA. In addition, the presence of this metal oxide slightly increased both T_m (194 °C to 196 °C) and percent crystallinity (31% to 35%) of PVA composite film. It was because ZnO particles could act as a nucleating agent resulting in increased crystal densities. Additionally, the distributed ZnO particles increased the high surface area of composites film, leading to increase in the crystallinity of the PVA. The addition of coffee extract at 5 phr in the composite increased the percent crystallinity (26% to 35%), but T_g did not change significantly compared to the sample without coffee extract. However, further addition of coffee extract at 7.5 and 10 phr led to a decline in T_g, T_m, and percent of crystallinity. It might be because the coffee extract could act as a plasticizer in the film.

The mechanical properties test results are shown in Fig. 6. Addition of glycerol to neat PVA significantly decreased the tensile strength of the film from 50 MPa to 15 MPa or lower due to lack of crystallinity, whereas the elongation at break of PVA composite film increased from 166% to approximately 450% due to the plasticizer effect. The microstructure of PVA composite film with glycerol as shown in Fig. 7(a), indicates that the addition of glycerol into PVA composite film tended to give phase separation between the ZnO and PVA particles which a more was pronounced when the glycerol content was 40 wt%. It was because glycerol interfered with the interaction between ZnO and PVA resulting in poorly distributed ZnO.

Generally, with addition of metal-oxide, strength is inversely proportion to toughness. However, it is intriguing that the addition of ZnO doubled the tensile strength (7 MPa to 15 MPa) despited the agglomerated ZnO particles as shown in Fig. 7(b). Consequently, it raised the elongation at break (42% to 500%). It was because ZnO acts as a filler, which led to a stress-concentrated transfer from the matrix to metal-oxide particles. Besides that, ZnO could have an intramolecular interaction of hydrogen bonds with PVA. This resulted in less interaction with glycerol (much interaction with PVA) and glycerol might just be a plasticizer. However, from the morphological structure of the films with ZnO and without ZnO, it can be seen that ZnO particles were unevenly dispersed in the PVA composite film.

On the other hand, the addition of increasing amount of coffee extract tended to reduce the tensile strength (24 MPa to 5 MPa) due to loss of crystallinity. Moreover, the elongation at break was greatly reduced (600% to 32%) because the coffee extract chemical

Table 2 The melting temperature (T_m), glassy temperature (T_g) and the % crystallinity of PVA composite films.

Sample	T_g (°C)	T_m (°C)	X_c (%)	Sample	T_g (°C)	T_m (°C)	X_c (%)
PVA	102.9	212.6	51.5	Z1	105.4	196.8	35.8
G20	105.4	196.8	35.8	Cof 0	105.9	202.7	26.0
G30	106.4	199.3	25.7	Cof 5	105.4	196.8	35.8
G40	84.2	193.5	18.4	Cof 7.5	102.6	194.6	26.1
Z0	90.3	194.8	31.3	Cof 10	98.1	190.2	24.0

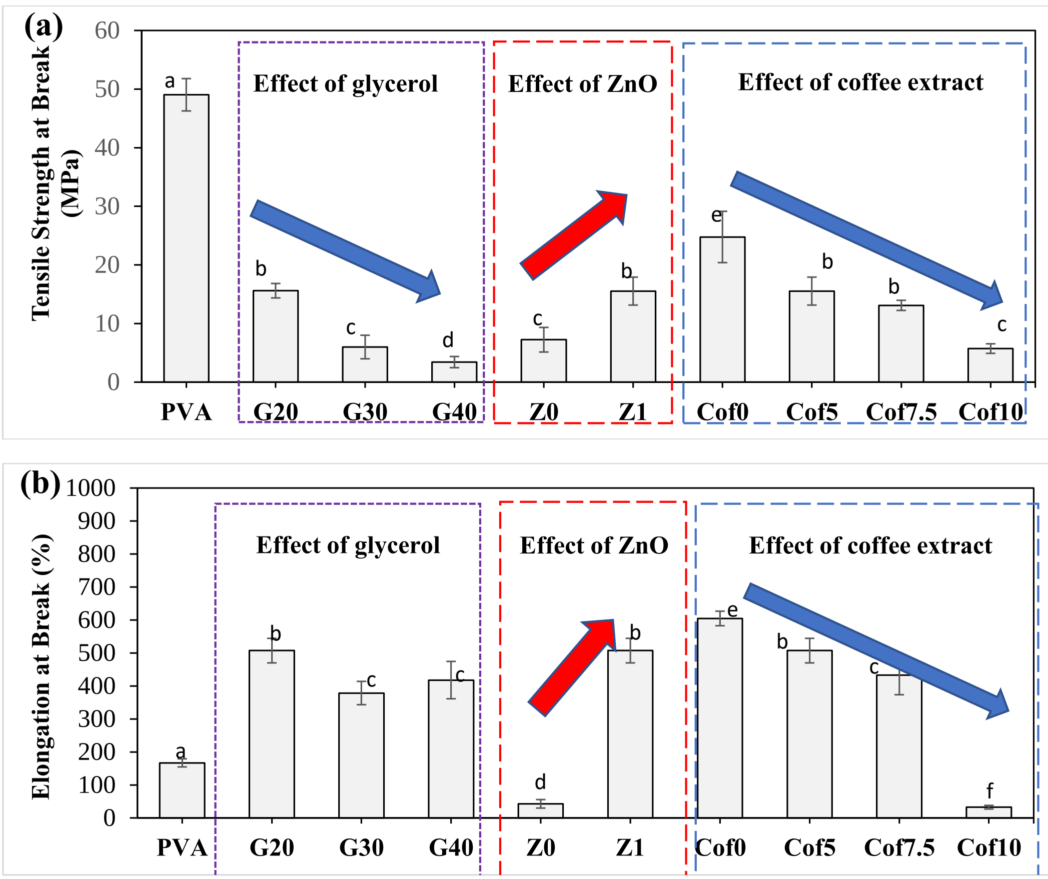

Fig. 6 Effects of glycerol, ZnO and coffee extract on (a) tensile strength and (b) elongation at break of PVA composite films.

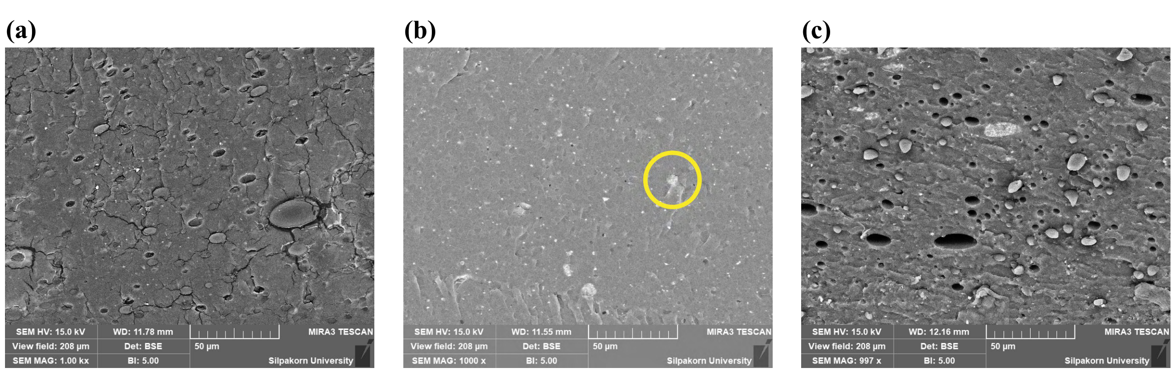

Fig. 7 Morphological cross-sections of a composite PVA films at 1000× magnification (a) G40 (b) Z1 and (c) Cof 10.

structure is a long chain hydrocarbon with much entanglement with the PVA chain; consequently, the film is less flexible when subjected to tensile loads. It should remark that the increase amount of coffee extract from 7.5 phr to 10 phr drastically dropped the elongation at break. It might be because the result of the acidic coffee extract could react with oxygen molecules of ZnO, resulting the worst dispersed phase.

In addition, the microstructures (in Fig. 7c) showed the voids and microgaps and were expanded when the amount of coffee extract was increased. It might be the presence of coffee extract which contained cyclic hydrocarbons of melanoidins and aromatic hydrocarbons of chlorogenic acids. These coffee extract could probably usurp the interaction forces of PVA, glycerol, and ZnO. They led to poor distribution of ZnO and brittleness properties of the film. Moreover, the coffee extract was consisted of non-volatile and volatile compounds. The volatile compound could probably evaporate under film processing and during the SEM test, that caused voids on the film surface. This microstructure could be evidence that the mechanical properties i.e., tensile strength and elongation at breaks of PVA composite film with high coffee extract content are drastically lower.

CONCLUSION

The potential of PVA composite film for agricultural applications, enhanced with glycerol, ZnO, and coffee extract additives, was explored. The presence of glycerol increased water solubility while reduced water absorption, attributed to the similar solubility parameters of PVA and glycerol. The trend of higher glycerol content resulting in lower water absorption and greater solubility was consistently observed. ZnO addition led to increase water solubility and absorption, facilitated by robust molecular interaction through hydrogen bonding. Coffee extract incorporation similarly elevated water solubility and absorption, possibly due to its prevalent OH groups. Thermal analyses revealed glycerol's impact on reducing glass transition temperature, melting temperature (T_m), and crystallinity (X_c), affecting mechanical properties. Tensile strength decreased, yet elongation at break slightly increased due to glycerol's plasticizer effect. A linear correlation between glycerol content and crystallinity was established. Contrastingly, ZnO augmented crystallinity, functioning as a heteronucleating agent. Despite agglomerated ZnO particles, it increased tensile strength and elongation at break through stress-concentrated transfer. Coffee extract presence, however, decreased X_c, yielding micro-voids, eruption surfaces, and phase separation in the microstructure, leading to decrease tensile strength and elongation. This study concludes that PVA composite film offers promise for seedling planting bags, with its properties being tailored through strategic additive manipulation.

Acknowledgements: The authors acknowledge the financial support of Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Thailand. The authors would also like to thank the National Metal and Materials Technology Center (MTEC) and Thailand's National Science and Technology Development Agency (NSTDA) for their instrument support.

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