Intelligent pH indicator film based on PVA/Glycerol/Anthocyanin derived *Ipomoea Batatas (L.) Lam* for smart food packaging

Lámina inteligente indicadora de pH basada en PVA/Glicerol/Anocianina derivada de Ipomoea Batatas (L.) *Lam para el envasado inteligente de alimentos*

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ABSTRACT

Food safety and quality are important aspects of consumer health and wellness. The application of an intelligent pH indicator in food packaging would give significant advantages in straightforward and quick information regarding the condition of the food. This study used purple sweet potato to extract anthocyanin (ANC) as a natural pH indicator. Variation concentration of extracted ANC (1, 3, 5, and 10wt%) was incorporated with polyvinyl alcohol (PVA) and glycerol as plasticizers to produce films for pH 1 to 13 indicator. The film's characterization shows changes in the peak of FTIR spectra and surface morphology attributed to the interaction of the materials. Upon adding 1% of ANC, the films show increasing thermal stability from 188.27 ºC to 194.08 ºC with a significant decrease in tensile strength (from 39.64 MPa to 12.80 MPa) but an increase in elongation break (from 213.40 to 328.75%) compared with PVA film. Additionally, as the concentration of ANC increased, the water solubility and swelling index increased with the decreased water content. The application of the films as pH indicators shows that increasing ANC content darkens the color changes, making it more distinct. The instinctcolor changes of prepared films with ANC incorporation at wide pH range have a high potential to be use as food packaging with prompt and accurate quality information of the food condition. Any contamination and food shelf life can be monitored prior to distribution by implying this food packaging to retain the quality of the food and avoid any mishap in consumers; therefore, it will be useful information in the food industry system.

Keywords: Food packaging; pH indicator; Anthocyanin Purple Sweet Potatoes.

RESUMEN

La calidad y la seguridad de los alimentos son importantes factores para la salud y el bienestar de los consumidores. Un indicador inteligente del pH en el envasado de alimentos aportaría ventajas significativas en cuanto a información directa y rápida sobre el estado de los alimentos. El presente estudio utilizó boniato morado para extraer antocianina (ANC) como indicador natural del pH. La concentración variable de ANC extraída (1, 3, 5 y 10wt%) fue incorporada con alcohol polivinílico (PVA) y glicerol

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como plastificantes para producir películas para el indicador de pH de 1 a 13. La caracterización de la lámina muestra cambios en la concentración de ANC. La caracterización de la lámina muestra cambios en el pico de los espectros FTIR y en la morfología de la superficie atribuidos a la interacción de los materiales. Al añadir un 1% de ANC, las películas muestran un aumento de la estabilidad térmica de 188,27 ºC a 194,08 ºC con una disminución significativa de la resistencia a la tensión (de 39,64 MPa a 12,80 MPa) pero un aumento de la ruptura por elongación (de 213,40 a 328,75%) en comparación con la película de PVA.

Además, al aumentar la concentración de ANC, la solubilidad en agua y el índice de hinchamiento aumentaron al disminuir el contenido de agua. La aplicación de las películas como indicadores de pH muestra que el aumento del contenido de ANC produce un oscurecimiento de dichos cambios de color, haciéndolos más definidos. Las variaciones de color de las láminas preparadas incorporando ANC en un amplio rango de pH tienen un gran potencial para ser utilizadas como envases alimentarios que proporcionan información rápida y precisa sobre la calidad de los alimentos. Cualquier contaminación y la vida útil de los alimentos pueden ser controladas antes de la distribución mediante la implicación de este envase para conservar la calidad de éstos y evitar cualquier percance en los consumidores; por consiguiente, podrá constituir una información útil en el sistema de la industria alimentaria.

Palabras clave: Envasado de alimentos; indicador de pH; antocianina púrpura de la batata.

INTRODUCTION

Food packing plays a crucial role in safeguarding and preserving the quality and safety of food materials by acting as a protection and barrier from external environmental hazards. Beyond its primary function, it also serves other functions, including communication, convenience, and containment. Consumers can make informed decisions based on the essential information on the packaging, such as producer, food composition, storage recommendations, and expiration dates. In contrast, different sizes and shapes of packaging are available to accommodate diverse consumer preferences and requirements aligned with their lifestyles and needs [1]. However, the food quality and safety could be changed after packing due to the microenvironment within the packaging.

Consequently, there is a necessity for continuous monitoring of food quality throughout the distribution, storage, and retail stages, extending to the end consumer, which requires expertise with biological, physicochemical, and serological techniques and is time-consuming [2]. Therefore, there is a demand for straightforward, quick, dependable, and sensitive methods to monitor food quality and ensure safety. Intelligent food packaging is a new concept for protecting food quality and providing information related to the packaged food product's attributes and atmosphere inside the package. Food quality is determined by directly detecting pH changes or volatile organic compounds associated with food degradation or microbial growth [2]. Among other indicators, colorimetric pH indicators can determine the freshness of meat products based on pH variations [3]. Intelligent pH indicators can be categorized into three primary groups. In the first group, dyes are immobilized through physical adsorption on a solid support, such as an ion exchanger. The second group encompasses dyes covalently bonded to a hydrophilic support, such as cellulose or glass. The third group involves dyes physically trapped within polymer matrices [4].

For example, Choi *et al.* synthesized an intelligent agar/potato starch pH indicator film with purple sweet potato (PSP) anthocyanin extracts as natural dyes. Promising results were observed from the color changes in the pork samples over time [5]. Zeng and colleagues conducted a study on intelligent pH indicator film in 2023 using pectin/ chitosan-based incorporated with anthocyanins from black rice, resulting in positive results. However, the pH indicator is only limited to differences in pH without direct result to the pH value [20]. A similar study has been conducted by Shaikh Ahmad and colleagues. They used quinoa starch/ glycerol/ fish gelatine-based film incorporated with Butterfly pea flower, and the results showed a remarkable finding as the film detected the pH changes along with the exact pH values. Nevertheless, the presence of anthocyanin was reported to disturb the moisture film's content with increasing moisture content as more anthocyanin is present in the film [21].

These studies showed great potential for using natural dyes for intelligent pH indicators as diagnostic tools to ensure food safety and quality. Anthocyanins (ANC), derived from the Greek words "Anthos," meaning flower, and "kianos," meaning blue, are natural pigments responsible for diverse coloration in plants. The significant properties of ANC, such as water-solubility, easy incorporation in aqueous media, and antioxidant properties, make it a promising agent in the prevention of neuronal and cardiovascular illnesses; some studies also focused on the effect of ANC in cancer treatments, human nutrition, and other biological applications [6]. Besides, as a natural pH-sensitive dye, ANC has a sensitive color reaction towards a wide pH range of red or orange color under acidic conditions, purple color under neutral conditions, and blue color under alkaline conditions. This characteristic makes ANC a suitable dye for preparing intelligent pH indicators [7]. Several biodegradable polymers have been studied and used to immobilize ANC, such as polyvinyl alcohol (PVA), starch, alginate, or chitosan for food packaging applications[8]-[10]. In the study by Li *et al.* [11], sodium alginate was used as an adhesive agent to increase the mechanical strength of the glycerin films for immobilizing PSPA. Interestingly, they also demonstrated that various cooking treatments (steaming, boiling, and roasting) of PSP resulted in different total phenol, ANC, and antioxidant activity of films. Guo *et al.* synthesized blueberry ANC and hinokitiol-loaded zeolite-imidazolium framework (HIN@ZIF-8) into a sodium alginate matrix, which effectively monitored the quality of pork and extended the shelf life of cold pork for several days [8]. By comparing the temperature and light stability of ANC from different plants, PSP was better than ANC extracted from other plants [5]. Thus, PSP is a better option for fabricating intelligent pH indicators.

Polyvinyl alcohol (PVA), as a synthetic water-soluble polymer, represents a suitable candidate for the backbone of intelligent pH indicator films due to its high hydrophilicity, excellent mechanical properties, and non-toxicity [12]. However, the high hydrophilicity and high water-swelling of PVA result in instability in water [13]. A study by Pereira, de Arruda, and Stefani used chitosan blended with PVA to enhance the physical properties for incorporation with ANC [9]. PVA/starch films were crosslinked with glutaraldehyde by Mustafa *et al.* to improve the mechanical strength of intelligent pH films [10]. These studies demonstrated a few approaches to improve the mechanical properties of PVA films, which are crucial factors for immobilizing ANC in pH indicator applications. This study used glycerol (Gly) as a plasticizer for PVA. Gly was a suitable plasticizer for reducing brittleness and strengthening PVA's cohesiveness and mechanical properties [14]. Furthermore, PVA/Gly/ANC film was fabricated by extracting ANC from PSA and immobilizing it in PVA/Gly films for intelligent pH indicator application.

MATERIALS & METHOD

Materials

The PSP was purchased from a local market in Selangor, Malaysia. Analytical grades of polyvinyl alcohol were purchased from Merch KGaA, Malaysia, while ethanol (C_2H_6O, 95%), hydrochloric acid (HCl, 37%), and sodium hydroxide (NaOH, 97%) were purchased from R&M Chemicals, Malaysia. Anhydrous glycerol (99.5%), potassium chloride (KCl, 99.5%), and sodium acetate ($C_2H_3NaO_2$, 99%) were purchased from SYSTEM ChemAR, Malaysia. Deionized water was used for all dilution and sample preparation.

Anthocyanin extraction

The preparation of PSP powder and ANC extraction follows as our previously reported study. In short, the PSP was steamed and dried at 70 ºC for 48 h. Then, the dried PSP was ultrasonically mixed with 60% ethanol for 50 min. Next, the filtrate was concentrated until equilibrium was reached using a vacuum rotatory evaporator. The PSP was stored at 4 ºC for further use.

Preparation of PVA/Gly/PSPA films

The films were prepared using the solution casting method. The prepared ANC extract was mixed with 2% PVA and 1% glycerol for 10 min. Then, the solution was poured into a petri dish and dried for 48 h at 45 ºC. ANC extract concentrations were varied from 1, 3, 5, and 10%, namely PGA1%, PGA3%, PGA5%, and PGA10%, respectively. These ratios were chosen from previous studies that showed remarkable pH detection as the presence of anthocyanin increased [7], [24]. PVA/Gly (PG) with no ANC was prepared as a control.

Films characterization

Fourier Transform Infrared (FTIR) analysis was conducted from 450-4000 cm^{-1} using the ATR technique on IRTracer-100, Shimadzu, Japan. The surface morphology of the films was conducted using Field Emission Scanning Electron (FESEM) (JSM-6701F, JOEL, USA) and was sputtered with platinum before observation. The thermal stability of the film was examined from 30-350 °C at a heating rate of 10ºC/min using Differential Scanning Calorimetry (DSC-60, Shimadzu, Japan). The mechanical properties of the films were measured according to ASTM D882 using a Universal Testing Machine (AG-X plus, Shimadzu, Japan).

Water content, swelling index and water solubility

The first weight (W1) was taken after each type of film was cut (1 x 1 cm). Then, cut films were dried in an oven at 70 ºC for 24 h. The weight of the dry films (W2) was measured to calculate the initial dry matter. Then, each film sample was soaked in 30 mL of distilled water, continuously shaken for 24 h and weighed (W3). Next, the films were dried at 70 ºC for 24 h, and weighed (W4). Water content, swelling index, and water solubility were calculated using the following equation (1)-(3).

$$Water\ content(\%) = \frac{W1 - W2}{W1} \times 100 \tag{1}$$

$$Swelling\ index(\%) = \frac{W3 - W2}{W2} \times 100 \tag{2}$$

$$Water\ solubility(\%) = \frac{W2 - W4}{W2} \times 100 \tag{3}$$

pH indicator analysis

The prepared films were cut into small squares (1×1 cm) and immersed in buffer solutions having different pH (1-13) for about 10 minutes. Then, the color changes were photographed.

RESULTS & DISCUSSION

FTIR analysis

Based on Figure 1, strong stretching vibration of a hydroxyl group (O-H) was found in all films

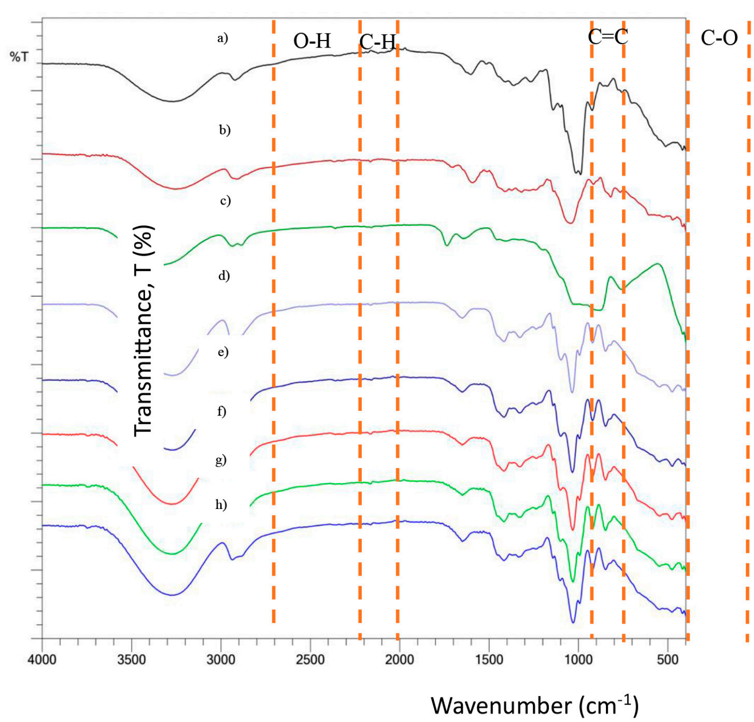

Figure 1. FTIR spectra of a) ANC, b) PVA, c) Gly, d) PVA/Gly, e) PVA/Gly/PSPA 1%, f) PVA/Gly/PSPA 3%, g) PVA/Gly/PSPA 5% and h) PVA/Gly/PSPA 10%.

composite and ANC, PVA, PG, and Gly in the range of 3100 to 3500 cm^{-1} [15]. The absorption peak between 2850-3050 cm^{-1} corresponded to the stretching vibration of an alkyl group (C-H) [16]. It was observed that the bending vibration of aromatic rings C = C was detected at the range of 1500 to 1800 cm^{-1} [15], [17]. The interactions between PSP and the polymer matrix could be attributed to this band changing as the presence of aromatic ring stretches. A weak characteristic peak at the range of 1300 cm^{-1} was assigned to the stretching of the pyran ring in flavonoid compounds, and an absorption band at the range of 1100 cm^{-1} was attributed to C–H deformations of aromatic rings [15].

FESEM analysis

FESEM analysis of PVA/Gly/PSPA 10% was conducted since it has the highest ANC concentration. As shown in Figure 2, the surface of PVA/Gly/PSPA 10% film was rough and wrinkled, indicating that ANC extract was homogeneously mixed and a strong interaction exists between PVA and glycerol. The surface structure of the thin film was contributed by the addition of phenolic compounds like ANC that promote the formation of hydrogen bonds with the polymer matrix [18].

Differential Scanning Calorimetry (DSC) Analysis

DSC analysis was conducted to understand the performance under heated conditions and the stability of the PVA/Gly/PSPA film at high temperatures. Figure 2 shows the heat flow profile as a function of the temperature of PVA/ Gly and PVA/Gly/ PSPA 10% after continuous heating from room temperature until 300 ºC. The Tg endothermic peak of the PVA/Gly film is observed at approximately 55 ºC. In contrast, the PVA/Gly/PSPA 10% film slightly shifts to a lower temperature, indicating a potential plasticizing effect of PSPA. The melting peak, Tm, of the PVA/Gly film is around 188.27 ºC, quite similar to previous literature, around 180-195 ºC [22].

In contrast, the PVA/Gly/PSPA 10% film exhibits a melting peak at a slightly higher temperature, around 194.08 ºC, suggesting enhanced thermal stability, possibly due to interactions between PVA and PSPA components. The decrease in Tg for the PVA/Gly/PSPA 10% film suggests that PSPA acts as an additional plasticizer, increasing the polymer chain mobility (Figure 3). The shift in the melting peak to a higher temperature and the change in ΔH from –169.79 J/g to –122.66 J/g indicates a modification in the crystalline structure of the PVA matrix, potentially due to the incorporation of PSPA. These changes can result in improved film flexibility and thermal stability, which are desirable traits for food packaging materials applications. Further studies could explore the mechanical and barrier properties to assess the performance of these films comprehensively.

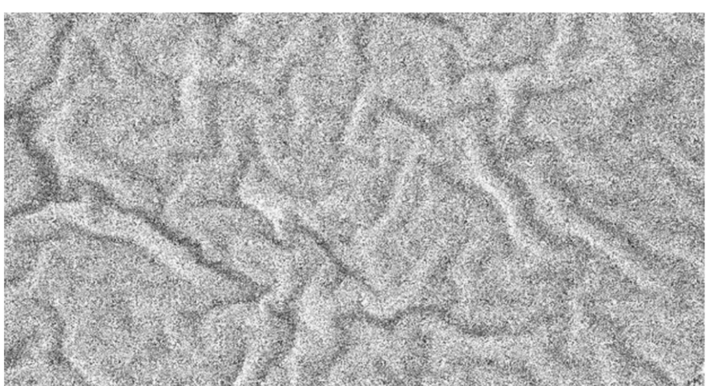

Figure 2. FESEM image of PVA/Gly/PSPA 10%.

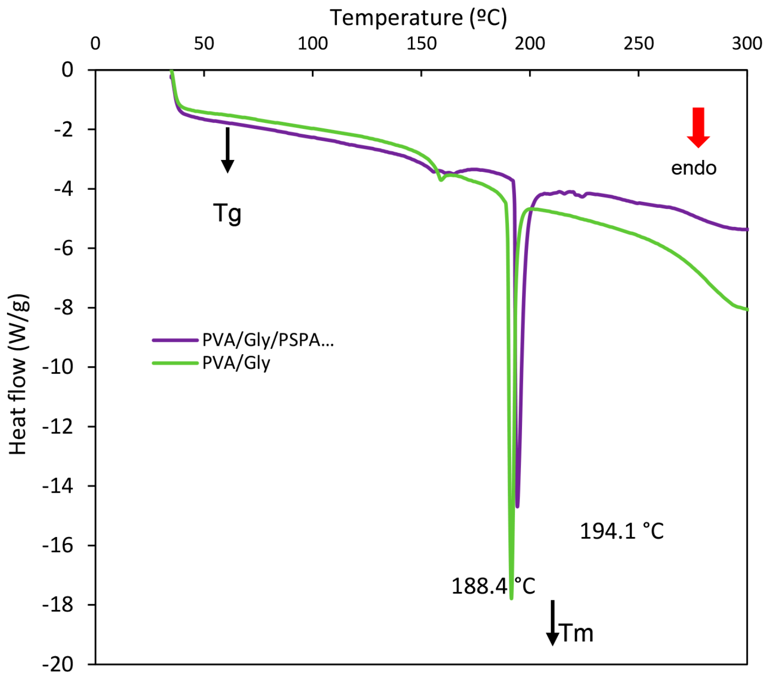

Figure 3. DSC analysis of PVA/Gly and PVA/Gly/PSPA 10% .

Mechanical properties

Based on Figure 4a and Figure 4b, the tensile strength (TS) value of PVA decreased significantly from 39.64 MPa to 12.05 MPa with increasing elongation break (EB) from 213.40 to 344.70% when adding glycerol into the film. The role of glycerol in reducing the strong intra-molecular attraction between the PVA chains and supporting the formation of H-bonds between glycerol and PVA molecules diminished the TS of plasticized biopolymers by diminishing the hydrogen bonds between PVA chains. By allowing for more chain mobility, this kind of interference and re-enactment of molecular starch chains allowed for a decrease in firmness and an enhancement in the flexibility of films.

It was reported that molecular chain mobility affected polymeric's EB [17]. In a study by Rahmadia and colleagues (2023), they prepared the indicator films using tapioca-starch based on anthocyanin extracted from purple sweet potato, similar to this study. The loading of the anthocyanin was at 5, 10, and 15 g. However, the tensile strength of the films was significantly reduced compared to this study, as shown in Figure 4a. It was concluded that the anthocyanin decreased the intramolecular interactions between the starch structure and broke down the gelatinization during the film casting [24]. Overall, the addition of anthocyanin disrupted the intramolecular structure by impairing the structure.

Nevertheless, this disturbance does not affect the potential of the smart biopolymer as a universal smart pH indicator. The EB of the films in Figure 4b was elevated by the addition of glycerol as a plasticizer, which was shown to give satisfactory flexibility, considering the incorporation of anthocyanin may disrupt the intramolecular structure as previously discussed for the tensile strength of the films, which showed a decrease in EB from 328.75 to 163.87% with an increase of the ANC concentration. This phenomenon is expected as the administering anthocyanin weakened the hydrogen molecule structure in the films [24].

Water content, swelling index and solubility analysis

Based on Figure 5a, the water content of the PVA added with glycerol as plasticizer was shown to have an increment in water content compared to PVA without the addition of glycerol from 9.09% to 21.94% due to the hydrophilic nature of glycerol

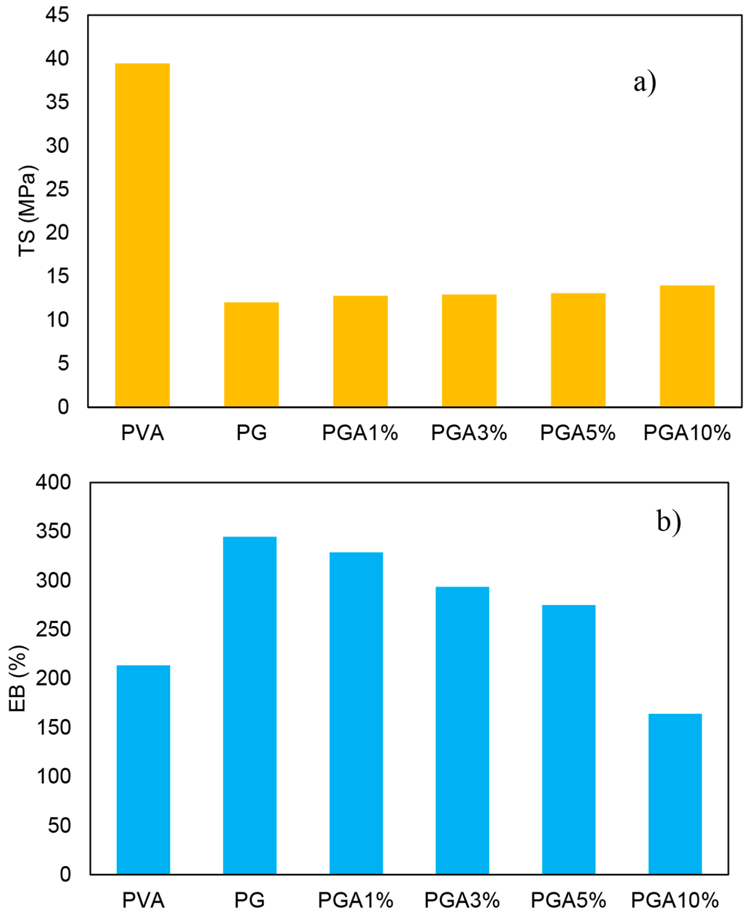

Figure 4. a) Tensile strength and b) Elongation at break analysis.

that able to intersperse among and between polymer chains, disrupting the hydrogen bonding and spread the chains apart [15], [17]. However, incorporating PSP into the PVA and glycerol films has been shown to reduce the water intake of the films. This trend decreased as PSP was added into the films from 1% to 3% at 17.83% and 17.71%. As more PSP is added, the percentage of water intake further decreases where at 5% and 10% of PSP, the water content of the films is 14.18% and 13.74%. According to [18], the interaction of the hydroxyl group in PVA, glycerol, and ANC present in PSP lowered the number of free hydroxyl groups to intermingle with water. This finding is favored compared to a previous study [22], where the film's moisture content increased as the anthocyanin loading increased between 5% and 10%. A study of the swelling index, particularly for food packaging applications, is essential for biopolymers due to their high sensitivity towards the water. This study is crucial in food packaging as high moisture content will lead to microbial growth, while having too low moisture content may lead to brittleness of the films, threatening the integrity of the food packaging.

Based on Figure 5b, the swelling index analysis, adding glycerol decreased the swelling index of PVA from 121.435% to 112.47% due to the consumption of the free hydroxyl group from the strong interaction between PVA and glycerol [19]. However, adding PSP enhanced the swelling index more than its original index. In a study by Sohany *et al.* [15] adding a hydrophilic group from ANC caused an increment in the swelling index of the films. The higher swelling index is advantageous as aqueous media, which changes pH, can penetrate the bulk matrix and increase the pH sensitivity. This condition is also in favor when moisture from the food or the environment comes in contact with the films, ensuring that the films will not disintegrate or become too fragile to handle.

Biobased polymers are known for their high-water solubility; thus, testing the newly fabricated biobased film is imperative due to its high affinity towards water. Based on Figure 5c, PGA10% shows the highest water solubility with 292.7%, and the lowest was observed to be 143.7% for PG film. The water resistance of the fabricated films is the barrier for application purposes; thus, the film solubility in water is tested for its effectiveness as food packaging. Higher water solubility is not preferred for packaging due to its restriction to aqueous foods [17]. For instance, water-soluble films should be applied for fruit coating that can easily be removed through washing, while insoluble films are more suitable for food with high moisture content. Generally, a material with a high swelling index tends to dissolve readily in water because water molecules are absorbed into hydroxyl groups, primarily through hydrogen bonding, which makes the films more soluble [19]. As a result, despite the varying parameter magnitudes, all films' swelling index and water solubility displayed a remarkably similar general pattern. The high water solubility values were accepted because all the constituents had a hydrophilic nature, including PVA, glycerol, and PSPA, consistent with other studies[15], [19].

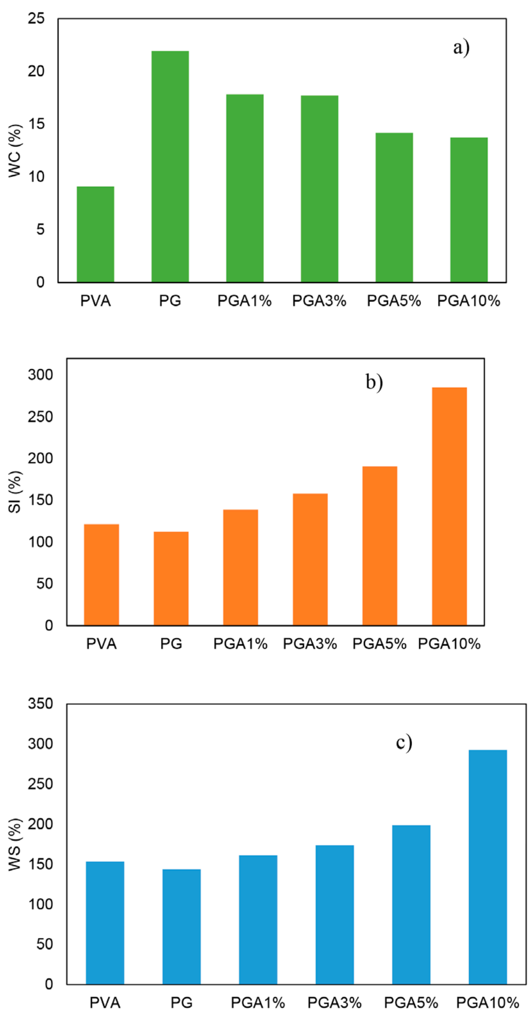

Figure 5. a) Water content, b) Swelling index and c) Water solubility.

pH indicator analysis

The color response of the films containing ANC at a wide range of pH 1 to 13 was observed, and the images are depicted in Figure 6. The change in colors was depictable and visible for all samples, even at the lowest percentage of PSP contained in the sample. PVA/Gly/PSPA 10% was darker than other films, as expected, as it has the highest amount of PSP. However, the difference in color response of films with the PSP extract might be related to the different pH of the film-forming substrate. Compared to previous studies that used anthocyanin from black rice [20], butterfly pea flower [21], and *Hibiscus sabdariffa* [23], the stability and the distinctness of the anthocyanin of purple sweet potato were proven to be sensitive towards every pH by reacting into different colors without disrupting the moisture content of the films from the water content analysis, having the lowest percent at 13.74%. It was generally expected that the indicator film would have a fast response to the immediate detection of food spoilage without contributing to the spoilage of the food [25].

CONCLUSION

In conclusion, PVA/Gly/PSPA films were successfully produced via the solution casting method for intelligent pH indicators. The effect of PSPA concentration variation was evaluated through film characterization, such as functional group, morphology observation, mechanical properties, water content, water solubility, and swelling index. Overall, Gly and PSPA content increases show a shifting of functional group peak with smooth

Figure 6. Color response images of films from pH 1 to 1.

morphology. Additional PSPA reduced the tensile strength (from 39.64 MPa to 12.80 MPa), with an increment in elongation break from 213.40 to 328.75%. However, a further increment of PSPA contents to 10% reduced the elongation break to 163.87%. Besides, the addition of Gly content improved the water contents (from 9.09 to 21.94%) with a slight decrement in the swelling index (from 121.43 to 112.47%) and water solubility (from 153.40 to 143.80).

In comparison, the increase of PSPA contents resulted in reduced water content from 21.94 to 13.74% but enhanced swelling index and water solubility of films from 112.47 to 285.30% and 143.80 to 292.70%, respectively. By using purple sweet potato anthocyanin as a pH indicator, noticeable color changes were observed for all films with darker color upon increasing in ANC concentration without entirely weakening the structure of the biopolymer, which is a significant improvement from the previous studies conducted for intelligent pH indicator food packaging films. The films have a good opportunity for food packaging, which can provide quick and fast information regarding the food condition, with appropriate mechanical properties and film integrity. Further study can be conducted on the stability of the films as food packaging on the food samples to understand the performance of the films with various food conditions.

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