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Natural pH Indicator from Potato Starch Films Incorporated with Curcumin

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ABSTRACT

In this work, we developed a potato starch film incorporated with curcumin to be used as a pH-sensitive smart polymeric material, which could be applied as a pH probe in food industry. The Beer-Lambert law was used to characterize curcumin which was purchased from the pharmacy of alternative medicine in the city of Benghazi. As a control experiment, the visual colour changes of curcumin powder dissolved in buffered aqueous solution were examined at the pH rage of 5-11. It was found that the colour of the solution altered from yellow to reddish-brown, as the pH of the curcumin solution changed from 7 to 8. Curcuminwas also incorporated into the starch extracted from potato before being formed into an edible film using a solution casting method. The pH-sensitivity of film was investigated at varied pH values (pH 5-11), the visual colour variations of tapioca starch-curcumin film was noted. The colour of edible film changed from pale yellow to dark orange colour by increasing the pH.But, the addition curcumin to the potato starch film did not alter mechanical properties of starch. As a result of an alteration in film colours, the potato starch-curcumin film could be applied as a natural pH indicator for monitoring food spoilage based on the acidity changes. Likewise, an environmentally friendly indicator film was too accomplished.

Introduction

The growth of the food business in recent years has necessitated the development of smart food packaging films capable of evaluating food quality and safety during packaging, storage, transportation, and distribution (Nguyet & Nguyen, 2019; Mustafa, 2016). The pH of packaged food items varies as a result of microbial deterioration during long-term storage (Nguyet & Nguyen, 2019; Mustafa, 2016; Rawat, 2015). As a result, smart packaging films that can monitor the pH of the micro-environment surrounding the packaged food items have become a hot research topic.

Safety and biodegradability are the two most important criteria for smart food packaging films. The films should be produced of natural materials that are safe for human health and do not taint food. Because of its strong film-forming capacity, low prices, good transparency, and biodegradability. However, those films have weak mechanical characteristics, are highly hygroscopic, and have a high solubility, making them rapidly dissolve when in contact with high-humidity food surfaces (Nguyet & Nguyen, 2019; Mustafa, 2016; Rattaya, 2006; Ramos, 2016).

Starch is a polysaccharide consisting of a repeat unit of glucose molecules linked by glycosidic bonds. This natural polymer is produced by most green plants as an energy store. It is the most common carbohydrate in human diets and is contained in large amounts in essential foods such as wheat, maize (corn), cassava, rice, and potatoes (Eltaboni et al, 2020). In this work starch extracted from potatoes was utilized.

Pure starch is a white, tasteless, doorless powder (Fig. 1), and soluble in warm water. It consists of two types of chains, linear amylose and branched amylopectin (see Fig. 2). According to the botanic origin, starch contains around 20 % amylose and up to 80% amylopectin by mass, but starch with 80% ofamylose could be exist(Eltaboni & Imragaa, 2017). Starch solution can be used as a thickening, stiffening or gluing agent. The biggest industrial non-food use of starch is as an adhesive in the paper making process (Tako et al, 2014).

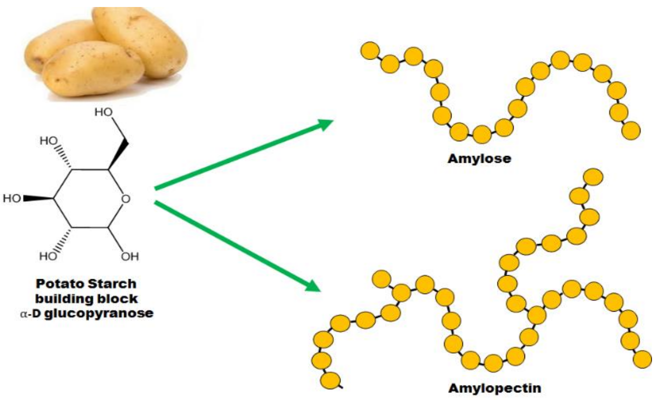

Fig. 1. Source and structure of starch.

Curcumin, a brilliant yellow substance generated by *Curcumalonga* plants, is a powerful antioxidant (Hatcher et al, 2008; Lin et al, 2000). It's the main curcuminoid in turmeric (*Curcumalonga*) (see Fig.2), which belongs to the *Zingiberaceae ginger* family. It's available as a herbal supplement, a cosmetics ingredient, a food flavouring, and a food colouring. Curcumin is a diarylheptanoid that belongs to the curcuminoids family of natural phenols responsible for the yellow colour of turmeric. It's a tautomeric molecule that exists in two forms: enolic in organic solvents and keto in water (see Fig.3). Some researchers have confirmed that curcumin cannot be used as a medicine. This is because it is difficult to study due to it is both unstable and poorly bioavailable. So that is unlikely to produce useful leads for drug development (Nelson et al, 2017).

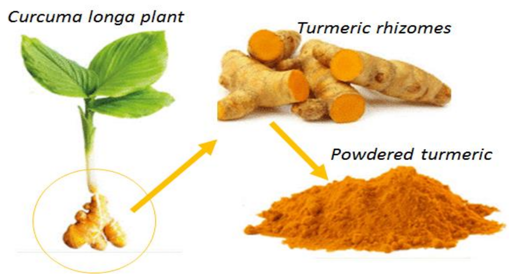

Fig. 2. Producing of Powdered Turmeric from *Curcuma* longa plants.

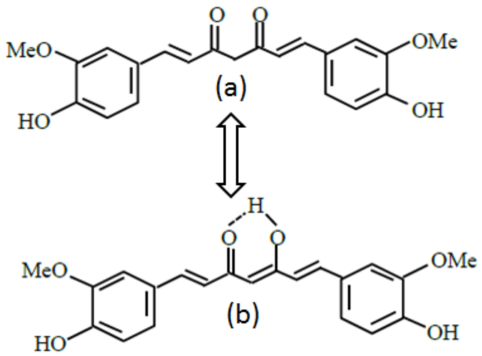

Fig. 3. Keto and enol forms of curcumin.

An acidity sensitive films are kind of intelligent packaging. These films can change their colour upon changing the pH of environment. The total volatile basic nitrogen (TVBN) like ammonia and methylamines, can be applied to specify freshness of fish, for example (Petchana, Phoopiam, & Thiraphattaraphun, 2020; Cao, 2019). The pH increasing as TVBN increasing during fish spoilage from microorganism (Petchana, Phoopiam, & Thiraphattaraphun, 2020; Cao, 2019). Ordinarily, a pH indicator contains solid support material and dye. The solid support materials with curcumin pigment have been produced by bacterial cellulose membrane (Petchana, Phoopiam, & Thiraphattaraphun, 2020; Cao, 2019)., tara gum/polyvinyl alcohol (Petchana, Phoopiam, & Thiraphattaraphun, 2020; Rodrigues, et al, 2021), gelatin (Petchana, Phoopiam, & Thiraphattaraphun, 2020; Musso, Salgado, & Mauri, 2017) and paper (Petchana, Phoopiam, & Thiraphattaraphun, 2020) But, according to our survey, there are no researches on potato starch as a solid support material with curcumin dye. Therefore, potato starch is a good substitute solid support material, because its plentifully available, low cost and biodegradable.

In this study, we are aiming to formulate edible films from potato starch, glycerol, and curcumin. Then evaluate the ability of the curcumin-starch films to change their colour with medium pH changes. And to introduce curcumin-starch film as a key player in the development of a pH-sensitive smart packaging material.

Experimental

All materials in this project have been used without further purifications unless was mentioned.

Materials:

Curcumin (Local store), potato (Local store), sodium hydroxide (Sigma), distilled water (Chemistry laboratory), hydrochloric acid (HCl) (Sigma), and glycerol (Sigma).

Preparation of Curcumin Solution:

Known molar concentration from stock solution of curcumin was prepared according to the dilution law (Fig.4).

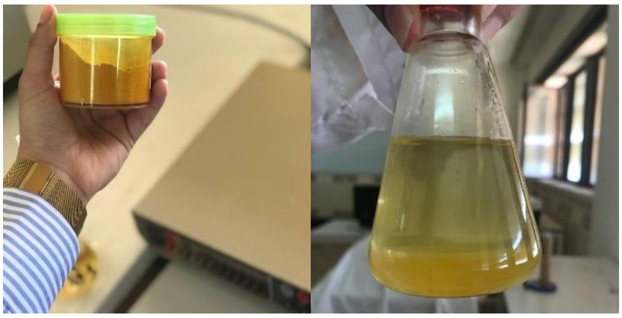

Fig. 4. Powder and solution of curcumin

Variation the pH of Solution:

The pH of sample solution was altered by adding specific portion of sodium hydroxide or hydrochloric acid and the pH was kept almost constant at the desired value by adding buffer.

Extraction of Starch:

A potato weighing of 769.09 g was washed and peeled to weight a 645.91g. Thenitwas washed, cut and put in a baker, with adding a large amount of water and left for a full day, to get a white precipitate of starch in the bottom of beaker, as depicted in Fig. 5.

Fig. 5. Extractedpotatostarch.

Preparation of the Starch Film:
Potato starch film was prepared by dissolving 2 g of potato starch in solution containing 25 ml of water, 2ml of (HCl) ((0.1M)), 2ml of (NaOH) ((0.1M)), and 2ml of glycerol. The solution was mixed up on the cold, then the solution was heated, with constant motion till homogeneous solution was observed. Similarly, dyed film of starch extracted from potato was prepared but 0.25 grams of dye was added to the film. According to the casting technique, a specific content of filmogenic solution was poured onto squared glass plates to obtain smooth and unbroken films. Finally, prepared films were dried in desiccator at room temperature for approximately 72 hours. The drying process was continued until a constant weight was obtained.

Folding Endurance
Folding strength or flexibility is a method to evaluate the mechanical properties of a film. It was measured by continually twisting prepared film strip of 2 x 2 cm, at 180° angle of the plane at the same place until it was broken. The number of times that the film could be twisted up and down without breaking is the value of folding endurance for that film. Higher folding endurance value describes the more mechanical strength of a film.

Spectrophotometry of curcumin solution:
Curcumin dye was characterized by spectrophotometric technique by measuring the absorbance of the solutions using a CECIL CE7400 spectrophotometer (Cambridge, UK). The dye molar absorptivity was estimated from the slope of the Beer-Lambert's law:

$$A = \varepsilon bC \quad \text{(Eq.1)}$$

Where C is the concentration of dye (mol /L), A is the absorbance at 460 nm, and ε is the extinction coefficient for dye (L/mol cm).

Colorimetry:
The change in solution and film colours was observed visually by taking digital photos for each sample.

Results and discussion

Fig. 6 shows the UV-vis absorption spectra of curcumin aqueous solution, from their maximum absorption Beer-Lambert's law was plotted in Fig.7. From Fig. 6was observed that the UV-visible absorbance spectra for curcumin solution, agrees with the well-known unshaped spectra for curcumin moiety (Subhan et al, 2014). And in Fig. 7 confirms that once curcumin dye is dissolved in aqueous solution, it obeys to Beer-Lambert's law with molar absorptivity equal to 952 M^{-1} cm^{-1} with good regression value (R^2 = 0.9918).
Fig. 5 represents physical appearance of starch powder extracted from potato. As was expected starch powder that extracted from potato, gives white powder which is well defined for starch that extracted from potato. Our research group have successfully extracted and characterized potato starch several times.
Fig.8displays starch film preparation process. Whereas, Fig. 9 depicts the visual appearance of dyed and undyed starch films. Fig.8 shows transition of potato starch from filmogenic solution into physically stable, solid, uncracked film, that was done via pouring solution into definite shape glassy container. On the other hand, Fig.9 proved the proper loading of curcumin molecules into starch film, since the difference in colour is obvious of dyed film compared with undyed one.

Table 1 shows mechanical properties of starch and curcumin starch films. Folding endurance data which represented in Table 1, suggested that curcumin molecule did not disturb mechanical properties of potato starch film.

Figs. 10 &11 show the change in colours of curcumin free in solution and loaded into starch films, as the pH of solution was alteredfrom pH 5 to 11). Figs. 10 &11 approved pH-sensitivity for curcumin in solution (control) and in film. In this study, we used curcumin as a sustainable and safe indicator for smart packaging materials. It is well-known that curcumin changes its colour from yellow to dark orange upon changing the pH of solution to alkaline as a result of the reaction with hydroxyl group. The gained results suggested that the curcumin-loaded-potato starch film could be applied for coating food stuff like meat that its pH rising by increasing its shelf-life time. As the pH is increasing the thin film could response to that increase by changing its colour.

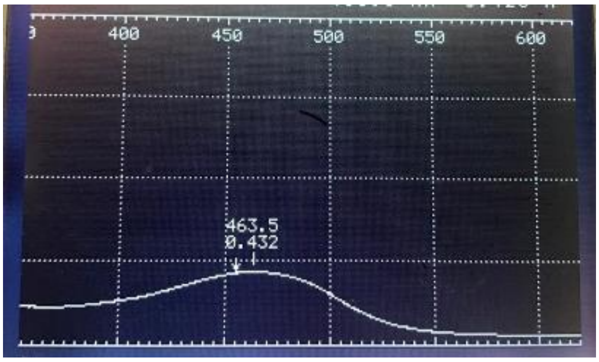

Fig.6. Absorbance of curcumin solution.

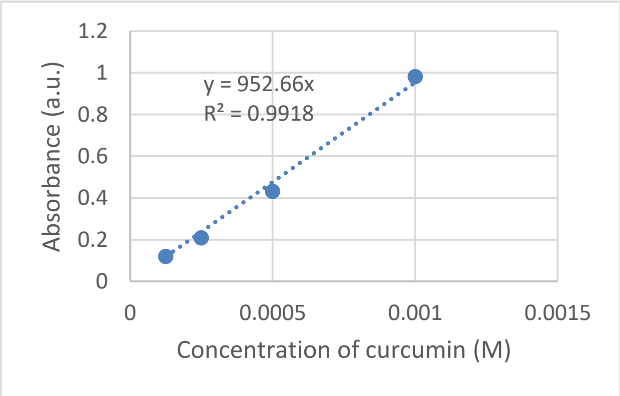

Fig.7. Beer-Lambert's law of curcumin in solution (λ_{max} = 460 nm).

Fig.8. Steps of film preparation.

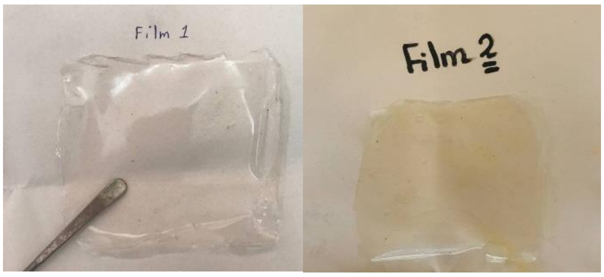

Fig.9. Colors of films; (1) potato starch film and (2) potato starch-curcumin film.

Mechanical properties of films

Table 1.folding endurance (folds) of starch and strach-curcumin films.

Film	Folding endurance
Starch	15
Starch-curcumin	13

pH sensitivity of curcumin solution

Fig.10.Zoomed photographs taken with digital camera to investigate colour changes of curcumin solution at different pH values.

pH sensitivity of starch-curcumin films

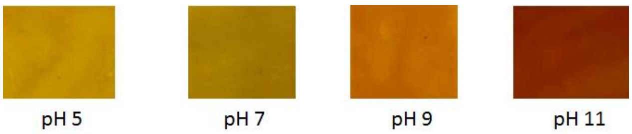

Fig.11.Zoomed photographs taken with digital camera to investigate colour changes of starch-curcumin films at different pH values.

Conclusion

The experimental results showed that the highest efficiency for curcumin-starch as a natural indicator. Since, the colour of film changed from pale yellow to dark orange colour by increasing the pH from 5 to 11.

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