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RELEASE KINETIC POLYPHENOL OF ACTIVE EDIBLE SAGO STARCH-CHITOSAN FILM CARRYING EXTRA VIRGIN OLIVE OIL

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ABSTRACT

The kinetics of polyphenol release from active films made from sago starch and chitosan with the addition of EVOO have been studied. The purpose of this study is to determine the release kinetics of polyphenols from EVOO added to the active film. Total phenol content of 1%, 2%, and 5% EVOO added to the film was determined by the Folin-Ciocalteu method of 0.1757, 0.1868, and 0.11 mgGAE/g. The kinetic release of polyphenols was tested using three kinetic models, such as zero order, first order, and Higuchi, by comparing the active films in two solvents, namely water and 10% (v/v) aqueous ethanol solution. The highest release occurred in the active film with 2% EVOO (CHSS2) in the two solvents. The release of Polyphenol active film in 10% ethanol followed the release of Higuchi, while CHSS1 and CHSS5 in H_2O solvent followed the first-order release.

Keywords: Release Kinetic, Polyphenol, Active Film, Extra Virgin Olive Oil.

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INTRODUCTION

Currently, there is a huge interest in environmentally friendly plastics for food packaging. This is not only an alternative to plastic derived from petrochemical raw materials, which results in increased environmental pollution, although it is renewable and inexpensive.[1-3] Polysaccharides such as pullulan, carrageenan, starch, and chitosan were used to generate biodegradable films.[2] Starch, the predominant polysaccharide energy source for plants, is abundantly available and is commonly utilized as a raw material in the manufacture of plastic packaging. This is attributed to the reason that it is non-toxic, great to prepare films from, and relatively inexpensive.[4] However, because of its hydrophilic properties and limited mechanical capabilities, starch can be changed to become thermoplastics, which are then combined with other biodegradable polymers such as chitosan. Chitosan is a natural linear amino polysaccharide generated from chitin, the second most abundant polymer after cellulose. As a result, various researchers have examined and published findings related to enhancing the properties of starch–chitosan biocomposite films. The tensile strength and antioxidant activity of the films were increased by combining chitosan with sugar palm starch and extra virgin olive oil.[5] The incorporation of chitosan into a maize starch–chitosan–PVA composite film can improve its mechanical performance, transparency, UV protection, and biodegradability.[6] Corn starch-chitosan combination with grapefruit seed extract supports the films' maximum tensile strength, lowest WVP, and higher thermal stability.[7] Packaging materials which are desired by the food packaging industry are active, allowing the release of antioxidants to be modulated (controlled release).[8] A superior effect can be obtained when these active compounds are introduced in a controlled release, or supplied on specific area food surfaces. The immediate release of active chemicals (e.g., cinnamaldehyde, eugenol, and thymol) can improve their antibacterial effectiveness by enhancing their availability via interfacial interactions.[9] The antimicrobial activity of the compound is dictated mainly by the release kinetics of entrapped active ingredients from film matrices. As a result, kinetic studies to establish the efficacy of active component release in packaging films are vital. However, very little literature reported on kinetic studies of the release of active compounds like polyphenols in food packaging films. The release kinetics of polyphenol compounds from EVOO applied to the sago-chitosan starch matrix were investigated in this study. This work is the first paper on Polyphenol kinetic investigations in chitosan starch-sago films to the best of our knowledge.

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EXPERIMENTAL

Material and Methods

Materials used in this research include an active film with 1%, 2%, and 5% EVOO, Chitosan powder (particle size 200-300 mesh, MW of 102 KDa; 96.24 percent of DD), and Chimultiguna Co., Ltd. (Indramayu, Indonesia) supplied the sago starch, Gallic acid, Folin-Ciocaltue reagent, sodium carbonate, hexane, and ethanol were purchased from Sigma-Aldrich. EVOO was provided from Gautama Indah Perkasa Co., Ltd (Jakarta, Indonesia).

Determination of Total Phenol

Total phenol was determined using the Folin-Chiocalteu method referred to by Talon *et al.*[10]. Firstly, the EVOO sample was extracted by dissolving in a mixture of 1.0 mL hexane and 1.0 mL 50% ethanol, then centrifuged for 10 min. Furthermore, the ethanol fraction was diluted to a volume of 10 mL with 50% ethanol. The sample was then mixed with 0.5 mL of Folin-Chiocalteu reagent. Then 1.5 mL of 10% Na_2CO_3 and distilled water was added until the volume of the solution reached 10 mL. Then it was allowed for 2 h, and a Shimadzu UV-1800 Spectrophotometer at a maximum wavelength of 766 nm was used to confirm the absorbance of the sample. Total phenol is calculated in mg (Gallic acid equivalents) GAE/g of the sample.

Release Kinetics of Polyphenol

Sample film weighing 1.33 g was cut into small pieces and put into each of 25 mL of water and 10% ethanol at 1.5; 3; 6; 12; 24; and 48 h. After diluting the sample solution to a volume of 5 mL, 0.1 mL of the solution was used for the measurement. The sample solution was determined using the Folin-Chiocalteu method and was repeated three times.[10] The kinetic model used and its equations are summarized in Table-1. Where M_t and $M_\infty$are the amount of active substance dissolved at a specific time, t (%), and at the time of thermodynamic equilibrium, respectively. Among the three kinetic models studied, the most suitable model was determined based on the R^2 value obtained from the plot results.[11]

Table-1: Release kinetic models of Polyphenol

No.	Kinetic Models	Equations ($y = ax + b$)	Type of Linear Plot
1 2	Zero-order	$\frac{M_t}{M_\infty} = k_0 t$	$\frac{M_t}{M_\infty}$ vs. t
3	First order	$ln\frac{M_t}{M_\infty} = k_1 t$	$ln\frac{M_t}{M_\infty}$ vs t
4	Higuchi	$\frac{M_t}{M_\infty} = k_H t^{1/2}$	$\frac{M_t}{M_\infty}$ vs $t^{1/2}$

RESULTS AND DISCUSSION

Total Phenolic Content

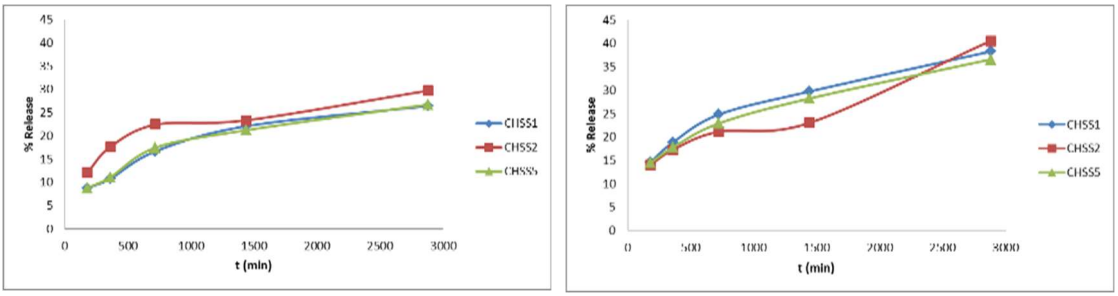
The presence of polyphenols in olive oil can protect foodstuffs' low-density lipoproteins from oxidative damage. Therefore, The European Food Safety Authority requires at least 5 mg of hydroxytyrosol and its derivatives in 20 g of olive oil (e.g., oleuropein and tyrosol).[12] The total phenolic content (TPC) in the active film samples at various EVOO contents is summarized in Table-2. Pedan *et al.* (2019)[12] reported that the TPC in the EVOO sample was 52 mgGAE/g. The results of this study are coherent with the findings of Pedan *et al.,* where at various EVOO contents in the obtained active film, the TPC was in the range of 175.7 to 201.1 mgGAE/kg sample. Most olive oils have a TPC of around 180 mgGAE/kg. TPC is also affected by cultivar, extraction system, and processing conditions.[13]

Table-2: Total Phenolic Content Data in Film Sample at Various Concentrations of EVOO

EVOO (%)	Weight of EVOO (g)	Total phenolic content (mgGAE/g)
1.0	0.08	0.176 ± 0.01
2.0	0.16	0.187 ± 0.01
3.0	0.40	0.201 ± 0.01

Release Kinetics

The mechanism for releasing the active compound from the polymer matrix involves several steps, such as molecular diffusion of water, which causes swelling of the polymer matrix, relaxation of the polymer matrix, and diffusion of the active compound from the polymer matrix into the solution until thermodynamics is achieved[10]. The rate of the active component release was evaluated, and the rate of polyphenols release from EVOO was added to the film. For 48 h, the active film was bathed in two solvents: water and ethanol 10% (v/v) aqueous solution. The total phenolic content of the sample was analyzed by carrying as much as 0.5 mL of the solution in a given duration. Fig.-1 depicts the proportion of total polyphenol film release in two solvents over a 48 h period. Fig.-1 demonstrates the profile release of all CHSS films, which originated with a quick release and progressed to a gradual release. This trend is similar to what Yemsuksawat and Liang[14] reported. For 24 h, the polyphenol release from the CHSS film was faster in a 10% (v/v) ethanol aqueous solution than in water. This phenomenon is most probably due to the interaction of polyphenols with the chitosan matrix, and Polyphenol is released from chitosan-starch films as modulated by pH and solvent polarity.[10] This observation was in line with the result reported by Yeop *et al.* [15] where polyphenol release in simulated gastric fluid (58 – 80%) is lower than in simulated intestinal fluid (72-98%) due to the difference in solubility associated with the interaction of polyphenol with either acid or base solution.



(a) (b)

Fig.-1: Profile Release of all CHSS Films

After 48 h, the CHSS2 sample had the highest total polyphenol release, with a total polyphenol content of 0.0093 mgGAE/g in water and 0.00126 mgGAE/g in 10% (v/v) aqueous ethanol solution, constituting 29.73% and 40.50% of the total phenolic antioxidants content, respectively. This limitation is due to the presence of polyphenols. The efficiency of polyphenol release is limited when incorporated into the starch and chitosan matrix. This result was in line with the observations of Perazzo *et al.*[16], who showed that adding large concentrations of green tea extract to the cassava starch matrix did not result in a high-release performance.[16] Fig.-2 shows the kinetic plot of polyphenol release in water and ethanol 10% (v/v) aqueous solution for all CHSS film samples. The release kinetics of the active substance was determined based on the highest correlation coefficient value (R^2) of the three regression analyzes of the kinetics of the active substance release model in Table-1. The correlation coefficient is obtained from the three straight line points contained in Fig.-1, namely from 180 to 720 min. The results of the kinetic analysis of the release of active substances for zero-order, first-order, and Higuchi were summarized in Fig.-2 and Table-3.

Based on the correlation coefficient results in Table-3, all films followed the Higuchi release kinetics determined with the highest correlation coefficient except for CHSS1 and CHSS5 samples in a water solvent, which follows the first-order kinetic model. The kinetics of the Higuchi model assumes that the release mechanism is dominated by diffusion[11], because the release of the active substance generally follows the release of diffusion, with the best explanation being Fickian diffusion which is characterized by the absence of swelling the polymer matrix. First-order kinetics assumes that the mechanism of the release of the active substance will be dominated by the adsorption or elimination of the active substance due to adding EVOO to the release of the active substance in the water solvent. This model is generally used to explain the release of active substances in pharmaceuticals, such as water-soluble drugs, in a porous matrix.

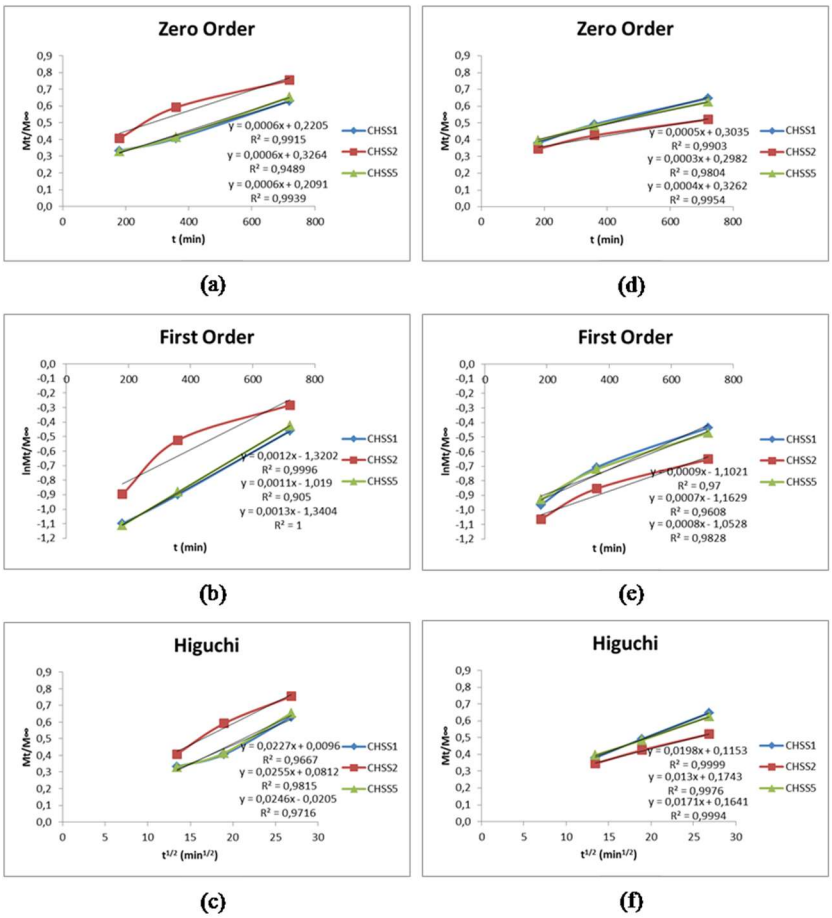


Fig.-2: Kinetic Analysis of the Release of Active Substances

Table-3: Rate Constant and Correlation Coefficient

Film Samples	Parameter	Water solvent			Ethanol 10% (v/v)		
		Kinetic model			Kinetic model		
		Zero-order	First-order	Higuchi	Zero-order	First-order	Higuchi
CHSS1	R^2	0.9915	0.9996	0.9667	0.9903	0.9700	0.9999
	k	0.0006	0.0012	0.0227	0.0005	0.0009	0.0198
CHSS2	R^2	0.9489	0.9050	0.9815	0.9804	0.9608	0.9976
	k	0.0006	0.0011	0.0255	0.0003	0.0007	0.0130
CHSS5	R^2	0.9939	1.0000	0.9716	0.9954	0.9828	0.9994
	k	0.0006	0.0013	0.0246	0.0004	0.0008	0.0170

CONCLUSION

The kinetic release of polyphenol from sago starch-chitosan film has been evaluated. The highest release occurred in the film made from sago starch - chitosan with a concentration of 2% EVOO. The release of polyphenol in ethanol 10% (v/v) aqueous solution followed the Higuchi model with the highest correlation coefficient attributed to CHSS1 which was 0.9999. While CHSS1 and CHSS5 samples in water gave a first-order release with a correlation coefficient value of 0.9996 and 1.000.

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