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学位論文全文に代わる要約
Extended Summary in Lieu of Dissertation

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学位論文題目：　Pregelatinized Waxy Rice Starch as an Emulsifier for oil–in–water emulsion
Title of Dissertation　(O/Wエマルションの乳化剤としての部分糊化もち米デンプン)

学位論文要約：
Dissertation Summary

Introduction

Emulsifiers based on natural ingredients have a significantly important role in the development of healthy food. Several types of starch are used as an emulsifier or a thickener after prior physical modification, such as pregelatinized waxy maize starch as a thickener (Bortnowska et al., 2014), and pregelatinized potato starch as a stabilizer for meat emulsion (Genccelep et al., 2015). Some gelatinized starches show the ability as an emulsifier such as waxy rice, non-waxy rice, and waxy maize starch (Kasprzak et al., 2018). In this research, the physically modified waxy rice starch (0% amylose) was used as the raw material of the emulsifier. Amylopectin, the main ingredient in waxy rice starch, is capable of hydrophobic binding guests in aqueous solution (Lundqvist et al., 2002), but its potential has not yet been explored. On the other hand, the structure of amylopectin is sensitive to shear stress (Chen et al., 2007); consequently different applied shear stress during emulsification will produce different properties of an aqueous phase and emulsion system, then next the different properties of aqueous phase influence the characteristics of emulsion, as well as its stability. In this study, the characteristics of pregelatinized waxy rice starch (PWRS) dispersion produced from the different temperature of gelatinization, and their correlation with the properties and stability of emulsion were studied. In addition, the influence of stirring speeds and types of oils was also investigated. The main objectives of this study were: to determine the appropriate gelatinization process of waxy rice starch for producing pregelatinized starch that can be used as an emulsifier; to investigate the influence of PWRS concentration on the characteristics and stability of the emulsions; to determine the appropriate emulsification process that produced stable emulsion; and to investigate the influence of the type of oils on the properties and stability of emulsions.

Materials and Methods

The study was conducted in 2 steps. Waxy rice starch (0% amylose) was used as a raw material of emulsifier. In the first of the study, the dispersed phase was 20 wt% of coconut oil. PWRS were produced at different gelatinization temperature (65, 75, and 85°C) for 10 min, then dried at 40°C, the relative humidity of 20% for 12 h. The obtained dried flake was meshed to obtain 100 mesh of PWRS. Coconut oil emulsion was made at different PWRS concentrations (3, 5, 7, and 9 wt%.) and emulsification was carried out at a stirring speed of 11000 rpm. The structural changes of waxy rice starch due to the gelatinization process were revealed by the small-angle x-ray diffraction method, the rheological properties of PWSR dispersion and emulsions was fitted by Herschel-Bulkley equation, and droplet size was obtained by measuring more than 500 droplets using ImageJ.

Hexadecane oil and coconut oil were used as the dispersed phases in the second study. Emulsification of emulsion contained 10% oil and 5% PWRS (gelatinized at 85°C) was done at the stirring speed of 8000, 11000, and 15000 rpm. The emulsion stability was investigated under two different circumstances, under the static condition and thermal treatment using differential scanning calorimetry (DSC) at −30 to 50°C for three cycles. Besides the rheological properties and stability analysis, H NMR was conducted on the PWRS, oil, and emulsions to find out the interaction between PWRS and oil.

Result and Discussion

Pregelatinized waxy rice starch characteristics

The gelatinization temperature of 65°C produced PWRS dispersion contained many granules. The presence of granule was greatly affecting the characteristics of both PWRS dispersion and emulsion. The higher degree of gelatinization resulted from the higher temperature of gelatinization produced the denser polymer network in the dispersion. Consequently, the higher the gelatinization temperature, the higher the viscosity of PWRS dispersion results in a more stable emulsion. The PWRS dispersion exhibit shear–thinning behavior, where gelatinization at 75 and 85°C produced PWRS dispersion that more pseudoplastic than those of gelatinization at 65°C at a concentration of 7wt% and lower. The SAXS profile of PWRS dispersions denoted an attractive interaction was occurred in PWRS dispersion gelatinized at 65°, while the repulsive interaction was occurred in PWRS dispersion gelatinized at 75 and 85°C.

The characteristics of emulsion with PWRS under influence temperature gelatinization and PWRS concentration

Emulsions stabilized with PWRS showed the shear–thinning character with the value of the flow behavior index ranged from 0.593 to 0.795. The yield stresses of emulsion with PWRS gelatinized at 75 and 85°C were unnoticed, while those of emulsion with PWRS gelatinized at 65°C was increased with the increased of PWRS concentration. PWRS gelatinized at 65°C produced emulsion that seems stable to creaming, but changes in droplet size occurred severely. Emulsions with PWRS gelatinized at 65 and 85°C had good creaming stability at PWRS concentrations of 5 wt% or higher, whereas emulsions with PWRS gelatinized at 75°C at all concentration showed creaming of emulsion between 0.39 and 0.58 after 21 days' storage. The stable emulsion toward coalescence was produced in emulsion with PWRS gelatinized at 85°C. The ability of gelatinized waxy rice starch was also reported by Kasprzak et al. (2018), who used gelatinized waxy rice starch at a starch concentration in the emulsion of 1–4 wt% and produce unchanged droplets size during three months of storage.

The characteristics of emulsion with PWRS under influence stirring speed, and the type of oil

The stirring speed influenced the characteristics of emulsions with PWRS during emulsification and the type of oils. The smaller droplet size has resulted from the faster stirring speed, in which coconut oil emulsion having the larger droplet size than those of hexadecane emulsions. Generally, the decrease of droplets size followed by the increase of viscosity – such as in the case of a medium chain triglyceride emulsion stabilized by a polymeric emulsifier (Pemulen TR-2 NF) (Simovic et al., 1999) and in crude oil vacuum distillation residues with a nonionic surfactant (Peralta-Martínez et al., 2004) – but in an emulsion with PWRS was the opposite, where the decrease in viscosity with the decrease in droplet size might be caused by the high sensitivity of the structure of amylopectin polymer to shear stress. The sensitivity of amylopectin polymer to shear stress has been previously reported (Chen et al., 2007; Liu et al., 2017). The stirring speed at 11000 rpm produced the highest value of consistency coefficient, while the yield stress was unnoticed at the stirring speed 11000 rpm and higher for coconut oil emulsion, and at 15000 rpm for hexadecane emulsion.

The stability of emulsion under influence stirring speed, the type of oil, and environmental condition

Stirring speed, the types of oil, and environmental conditions influenced the stability of emulsion. Th e stirring speed at 15000 rpm, result in the separation of emulsion into opaque and transparent layer for both, coconut oil and hexadecane emulsions. Under the static condition, coconut oil emulsions em ulsified at 8000 and 15000 rpm showed the lower ability to prevent coalescence than hexadecane em ulsion that showed excellent stability at all stirring speed. However, under thermal treatment, hexadeca ne emulsions were less stable than coconut oil emulsions. The irregular shape with the sharp edge of hexadecane crystal was thought of as the cause of the low ability to prevent partial coalescence. T he droplet size changes in hexadecane emulsion were signified by the shifting peak of the crystallizati on temperature peak to the higher temperature in the thermogram, while in coconut oil emulsion, the crystallization peak was not depended on droplet size. H NMR analysis shows that PWRS was better absorbed on the surface of coconut oil than on the surface of hexadecane, which was characterized by the stronger interaction. The interaction was signed from the decrease of component mobility with the increase of emulsifier concentration indicated by the increase of line-width, the shifting peak to a higher frequency, and the decrease of peak intensity. (Awad et al., 2018; Day et al., 2007; Wang et al., 2017). Emulsion instability involved complex processes influenced by several factors, such as the characteristics of the aqueous and the dispersed phase, environmental conditions, and interactions betwe en the components of the emulsion.

Conclusion

Pregelatinized waxy rice starch gelatinized at 85°C for 10 min can be used as an emulsifier for oil in water emulsion. The emulsion stability of emulsion with PWRS was influenced by the type of oil, emulsification process, and environmental condition. The low viscosity of oil, hexadecane, showed excellent stability under the static condition at all stirring speed, while coconut oil emulsion has better stability under thermal treatment than under static conditions.

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