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STARCH NANOPARTICLES SYNTHESIZED BY THE MICROEMULSION METHOD: CHARACTERIZATION AND THEIR APPLICATION AS BIOPLASTICS

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ABSTRACT

Starch-based bioplastic is a material that breaks down naturally and is designed to address environmental and health concerns caused by the usage of petroleum-based plastics. Modified starch, including nano-sized forms, provides improved functional characteristics to the original. In this study, cassava starch nanoparticles (CSNPs) were produced and used as bioplastics. CSNPs were prepared utilizing the precipitation in water-in-oil microemulsion method with different surfactants, including Span 60 and Tween 80. Furthermore, bioplastic was manufactured using the casting method, with the inclusion of glycerol. The results revealed that CSNPs treated with Span 60 had a smaller particle size of 127 nm and a higher gelatinization temperature of 99.35 ºC than Tween 80. Bioplastics produced from CSNPs/Span 60 were also more hydrophobic and mechanically stable than bioplastics made from native cassava.

Keywords: Bioplastics, Cassava Starch, Micro-Emulsion, Modification, Nanoparticles.

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INTRODUCTION

Plastic is a waterproof, lightweight, inexpensive, and multipurpose material that is widely utilized in medical, furniture, electronics, transportation, heat insulation, and food packaging.[1] On the other hand, plastic has significant drawbacks, including the fact that it is non-biodegradable, creating environmental pollution; it can migrate to the bodies of animals and humans in the form of micro/nanoplastics, causing health concerns; and its combustion can produce a carcinogenic compound, namely dioxin.[2-3] Therefore, the goal of this research is to develop bioplastics based on cassava starch nanoparticles (CSNPs) that can be used to substitute plastic. Nano-sized starch, measuring 50-200 nm, has the features of renewability, biocompatibility, low density, and high biodegradability,[4] Making it appropriate for various applications. In prior research, sago and maize starch nanoparticles were successfully produced utilizing the microemulsion method[5-7] and used for drug delivery. However, studies on the physicochemical characteristics of starch nanoparticles (SNPs) and their application as bioplastics are currently limited. Hence, in this study, CSNPs will be synthesized via precipitation in a water-in-oil (W/O) microemulsion process with Span 60 and Tween 80 as the surfactant and then evaluated for the amylose content, physical characteristics, thermal stability, particle size, and morphology.

The best-performing CSNPs will be utilized for manufacturing bioplastics. In addition to CSNPs, glycerol is also utilized to make bioplastics. The created bioplastic is further evaluated for physicochemical and mechanical qualities to determine the efficacy of SNPs in increasing the quality of cassava starch-based bioplastic.

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EXPERIMENTAL

Materials

Cassava starch, oleic acid, sodium hydroxide (Merck), absolute ethanol (Merck), Span 60 (Sigma Aldrich), Tween 80 (Merck), amylose (Sigma Aldrich), acetic acid (Merck), glycerol (Sigma Aldrich), and distilled water.

Preparation of Starch Solution

This study produced two different types of cassava starch solutions. The first type (N) was created by combining cassava starch with 0.5 M NaOH (1:10), then heating and stirring (80 °C, 900 rpm, 1 h). The second type was created by combining cassava starch and NU solution (ratio 1:10), then heating and stirring (80 °C, 900 rpm, 1 h). The NU solution was made by reacting 0.5 M NaOH with 0.5 M urea (0.8:1). Both types of starch solutions were determined by the particle size using PSA and functional groups using FTIR. The best results will be used for cassava modification by a microemulsion method.

Precipitation in Water-in-Oil Microemulsion System

The methodology of CSNP manufacturing refers to Chin et al.[5] with modification. Briefly, cassava starch solution type N was dripped into the oil phase (ratio 1:20, which is the oil phase consisting of absolute ethanol and oleic acid (ratio 3:1) and also 3% of surfactant) while stirring (900 rpm, 1 h), and then the modified cassava was separated from the supernatant using centrifugation. The modified cassava can be dried using a freeze dryer. The surfactants utilized in this study include Span 60 and Tween 80. The best-performing modified starch will be utilized to produce bioplastics.

Preparation of Bioplastics

One gram of native or modified cassava and 15 ml of distilled water were heated while stirred until gelatinized. Add the 3 % glycerol, then heat and stir (85 °C, 900 rpm, 15 min) until homogenous. The bioplastic was poured into a mold and dried at room temperature for 24 hours.

Characterization of CSNPs and Bioplastics

The CSNPs was characterized of the particle size using a PSA (Microtrac MRB), shape and surface morphology using a FESEM (Thermo scientific), functional group using a FTIR (Perkin Elmer), amylose content using spectrophotometer UV-Vis (Shimadzu spectrophotometer UV-1800), water solubility and swelling power using gravimetric method, and also thermal stability using a DSC (Perkin Elmer). Moreover, the analyses conducted to determine the characteristics of bioplastics include surface morphology using SEM (Thermo scientific), hydrophobicity (water solubility, swelling power, contact angle (Dino-lite, digital microscope pro)), and mechanical properties (thickness using digital caliper, tensile strength and elongation at break using UTM (Shimadzu AG-IS 50 KN)).[8]

RESULTS AND DISCUSSION

Preparation of Cassava Starch Solution

The starch solution is prepared by heating and stirring because the swelling and gelatinization processes precede the starch dissolution. The presence of water, as well as heating, can cause swelling. Heating will break the intermolecular bonds, allowing water to enter the starch granule and produce swelling.[9] To speed up the swelling process, the heating temperature should be higher than the gelatinization temperature. Stirring could accelerate the reaction by increasing the amount of energy transmitted into the solution, allowing the hydrogen bond breaking to proceed more quickly and reducing the particle size of starch.[10] According to Chin *et al*.,[5] the optimal stirring is 900 rpm; stirring at higher speeds causes bubbles and splashing of the solution. The starch solution was produced with two types of solvents: N and NU. The solvent dissolves the cassava starch by breaking down the starch granules through heating and stirring, allowing the starch molecules to be released into the solution. Solvent N can also break intermolecular and intramolecular hydrogen bonds in starch by replacing hydrogen atoms in the hydroxyl group with Na atoms, resulting in sodium alkoxide (-ONa), as illustrated in Fig.-1. Intermolecular hydrogen bonding in starch is created by interaction between amylose-amylose, amylose-amylopectin, and amylopectin-amylopectin, whereas intramolecular hydrogen bonding is created by interaction between water and starch molecules. The process of breaking hydrogen bonds and forming sodium alkoxide in starch can improve its solubility

in water. Furthermore, the purpose of urea in the NU solution is to prevent self-association of starch molecules, leading to improved solubility of native starch.[11] Moreover, the kind of solvent affects the particle size of the starch. Cassava starch dissolved in solvent N has smaller particle sizes than solvent NU, measuring 245 and 262 nm, respectively. This is most likely due to urea's bigger molecular size compared to NaOH, which means that the starch-NU reaction produces a larger result than starch-N. As a result, the next step is to prepare a cassava starch solution using solvent N.

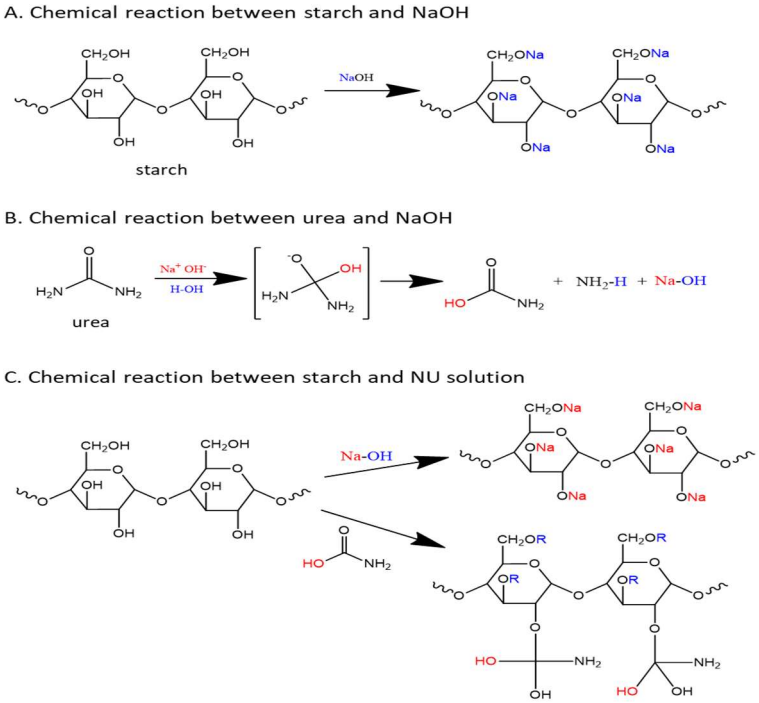

Fig.-1: Chemical Reaction between Starch and the Types of Solution

Preparation of CSNPs by Precipitation in Water-in-Oil Microemulsion System

In the preparation of CSNPs using the precipitation method in a water-in-oil microemulsion system, cassava starch that has dissolved in N solvent is then added to the organic solvent while homogenized, causing the nanoparticles to settle in the microemulsion system,[12] As shown in Fig.-2. the organic solvents utilized included ethanol as co-stabilizers, oleic acid as the oil phase, and Span 60 and Tween 80 as surfactants. Ethanol was chosen as a co-stabilizing agent because it is low in toxicity and has short carbon chains that can produce starch nanoparticles with smaller particle sizes than methanol and acetone. Furthermore, oleic acid can disperse starch nanoparticles more effectively than other oil phases, such as cyclohexane, hexane, palm oil, and sunflower oil, because it is a hydrophobic monounsaturated fatty acid.[5] The two surfactants utilized in this study are non-ionic, specifically Span 60 ($C_{24}H_{46}O_6$, Mw = 430.62 g/mol, HLB = 4.7) and Tween 80 ($C_{64}H_{124}O_{26}$, Mw = 1310 g/mol, HLB = 15). Surfactants are applied to reduce interfacial tension between the oil and water phases and stabilize the resulting dispersed phase.[12]

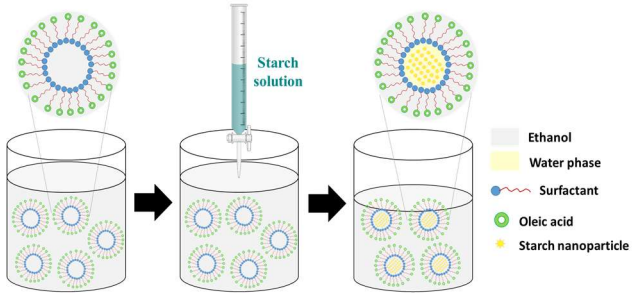

Fig.-2: Illustration of Water-in-Oil Microemulsion System in the CSNPs Production

Characteristics of CSNPs

The particle size of native and nanoparticle cassava was assessed by particle size analyzer (PSA), where 1% sample solution was analyzed using the Dynamic Light Scattering (DLS) method. As a result, native cassava, CSNPs/Tween 80, and CSNPs/Span 60 had particle sizes of 966 nm, 141 nm, and 127 nm, respectively. These findings provide that the kind of surfactant influences the particle size of CSNPs. Tween 80 is a surfactant having a Hydrophilic-Lipophilic Balance (HLB) greater than Span 60, indicating that it is more hydrophilic. Generally, surfactants with higher HLB can create smaller droplets in a microemulsion system, resulting in smaller nanoparticles.[11,6] In contrast, this study found that the particle size of CSNPs/Tween 80 is greater than that of CSNPs/Span 60. Some possible causes consist of a high sample concentration, causing the particle size read by the PSA tool to be larger than it is, and the effect of water phase concentration, which determines the chemical interaction between the surfactant and the synthesized nanoparticles. However, more research is needed to verify this.

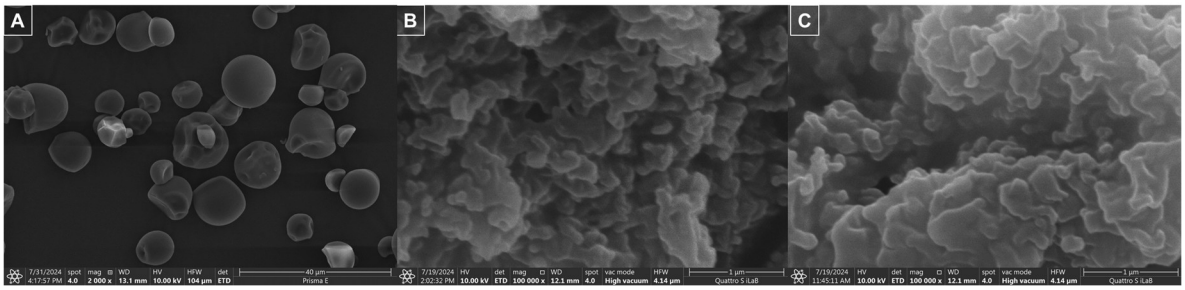

Fig.-3: Morphology of A) NC B) CSNPs/Tween 80 and C) CSNPs/Span 60

The morphology of native and nanoparticle of cassava starch can be seen in Fig.-3, where the native cassava (NC) starch, which was previously solid spherical, has transformed into nano-sized particles with a non-uniform shape due to agglomeration. Meanwhile, Chin *et al.*[5] reported that sago starch nanoparticles prepared using the nanoprecipitation method with a microemulsion system are spherical and have a homogenous particle size distribution. The difference was influenced by the drying procedure used in this study, which involved a freeze dryer. The drying process can cause particles to agglomerate. Furthermore, agglomeration is affected by stirring speed, starch injection rate, and starch solution to ethanol ratio.[5,6] The FTIR spectra of native and cassava starch nanoparticles, as demonstrated in Fig.-4, reveal that the spectra of CSNPs/Span 60 and CSNPs/Tween 80 are more closely related to Span 60 and Tween 80, respectively, when compared to native cassava. This suggests that a reaction occurs between cassava starch and surfactant during the modification process, such as the entry of a carbonyl group (C=O) from surfactant into cassava starch, as confirmed by the presence of intake at wave numbers 1735 and 1709 cm^{-1} in CSNPs/Span 60 and CSNPs/Tween 80, respectively. Furthermore, CSNPs/Span 60 exhibits a higher intensity of C-H absorption at 2956-2849 cm^{-1} and methylene (-CH_2-) absorption at 1467 cm^{-1} than native cassava starch. Similarly, with CSNPs/Tween 80, the intensity of C-H absorption at 2924-2854 cm^{-1} and methylene (-CH_2-) absorption at 1457 cm^{-1} is higher than native cassava starch. This indicates that C-H and -CH_2- groups from surfactants are able to substitute into cassava starch.

The main components of starch granules, including cassava starch, are amylose and amylopectin. Amylose is a straight-chain glucose polymer through α-1,4-glycosidic linkages, unbranched, amorphous, and soluble in hot water, and its composition is crucial for gelatinization, retrogradation, pasting, and starch texture.[13-14] Figure-5 demonstrates that native cassava starch has a higher amylose content than CSNPs, which is 23.376%. The amylose composition of native cassava starch varies between 20-35%, depending on the variety, extraction method, starch grade, and purity.[15-16]

Apart from amylose content, native cassava starch has higher water solubility and swelling power than CSNPs (Fig.-5). Water solubility refers to starch's ability to absorb water, while swelling power relates to starch's ability to hold water.[15] The mechanism of water entrance into starch granules is as follows: when starch is heated in a lot of water, the intermolecular hydrogen bonds (between starch molecules) break down, allowing water to penetrate and interact with starch molecules through intramolecular hydrogen bonds. As more water enters the starch granule, its size increases (indicating high swelling power), finally causing amylose to leach out.[13,17] Water is absorbed more readily through the amorphous region (amylose

and amylopectin branches),[9] which means that the water solubility and swelling power are directly correlated with amylose concentration.[18] Differential Scanning Calorimetry (DSC) can be utilized to determine the thermal properties of native and cassava starch nanoparticles. It provides the T_{onset} (initiation temperature of gelatinization), T_{peak} (highest temperature of the reaction), T_{end} (finishing temperature of the reaction), and ΔH (enthalpy of melting or needed energy for the gelatinization process).[8,13]

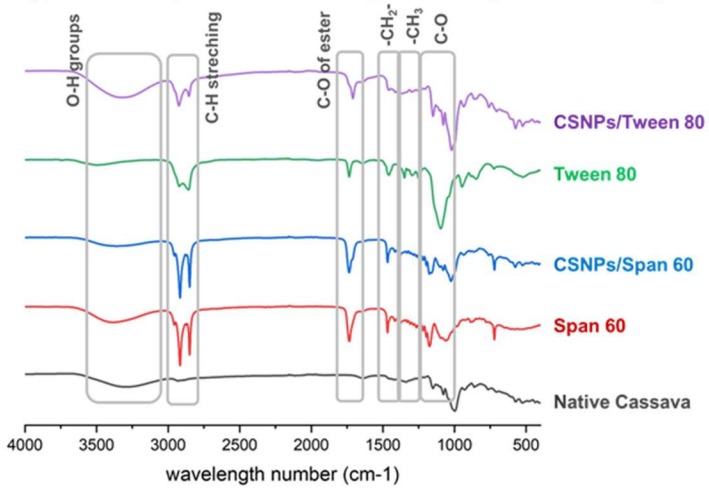

Fig.-4: Spectra FTIR of Native and CSNPs

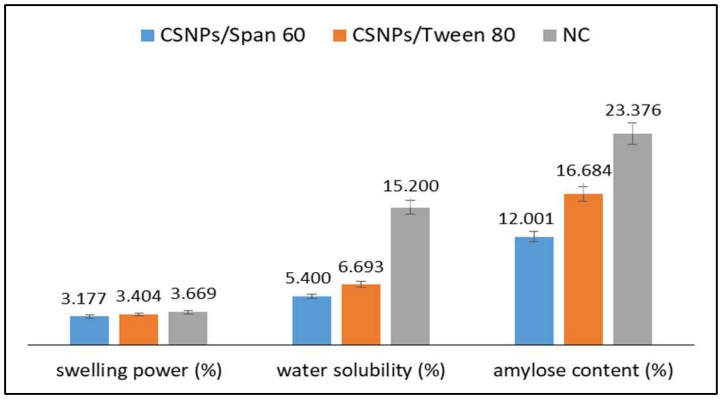

Fig.-5: Physicochemical Characteristics of Native and CSNPs

Table-1: Thermal Characteristics of Native and CSNPs

Sample	T_{onset} (ºC)	T_{peak} (ºC)	T_{end} (ºC)	Enthalpy (J/g)
NC	50.47	58.98	68.64	26.63
CSNPs/Tween 80	93.61	94.40	96.89	1.21
CSNPs/Span 60	99.35	105.55	110.54	342.38

Based on Table-1, native cassava has a lower T_{onset}, T_{peak}, and T_{end} than CSNPs, indicating that it gelatinizes faster. The gelatinization process is directly related to swelling power, which encourages starch swelling, allowing gelatinization to take place at less temperature and consequently reducing T_{onset}, T_{peak}, and T_{end}. Table-1 also reveals that CSNPs/Span 60 has the highest enthalpy, followed by native cassava, and finally (the lowest) by CSNPs/Tween 80, indicating that CSNPs/Span 60 requires more energy to complete the gelatinization process than NC and CSNPs/Tween 80. High enthalpy reflects the amount of energy needed to convert starch crystals into amorphous during the gelatinization process.[19] Starch crystals can form as a result of amylopectin breakdown, which causes re-association of the double helix, making disruption more difficult.[20]

Preparation and Characterization of Bioplastic

There are two kinds of bioplastics produced in this study, namely bioplastics made from native cassava as a control and bioplastics from CSNPs/Span 60. Glycerol, which serves as a plasticizer, is added to

bioplastics during the manufacturing process. Glycerol binds to starch through intermolecular bonds, resulting in bioplastics that are more elastic, not brittle, smooth, and transparent.[21-22] Figure-6 demonstrates that the control bioplastic has a more uneven surface than the CSNPs/Span 60 bioplastic, as well as cracks. Native cassava has a larger particle size than CSNPs, so when blended with glycerol, some native cassava particles may remain undissolved and appear as tiny clumps on the surface of bioplastics. The cracks in the bioplastic control are induced by the high amylose content in native cassava, which affects its brittleness.[23] As a food packaging material, the hydrophobicity of bioplastic is an important factor to consider. Table-2 demonstrates that the control bioplastic has lower hydrophobicity (swelling power and water solubility) than the modified bioplastic (that is, CSNPs/Span 60). Swelling power is a phenomenon in which water particles penetrate the starch granules and create swelling. The more water that can be absorbed into starch-based bioplastics, the higher the swelling power value and solubility in water, because the swelling process is always followed by amylose leaching.[17] The hydrophobicity of bioplastic can also be determined by the contact angle test findings. The control bioplastic has a greater contact angle than the CSNPs/Span 60 (Fig.-7), indicating that the latter is more hydrophobic than the former. Control bioplastics exhibit higher tensile strength and lower elongation than CSNPs/Span 60 bioplastics (Table-2). This is because cassava starch utilized in the production of control bioplastics contains more amylose than CSNPs/Span 60. Hirpara and Dabhi[14] reported that as amylose content increased, native starch films showed decreased elongation at break as well as higher ultimate tensile stress and Young's modulus. Amylose is known to retrograde into starch crystal structures following gelatinization, reaching a high ultimate crystallinity in dried films.[24] The hydrophobic and mechanical characteristics of starch-based bioplastics are strongly influenced by the starch cultivar, modification or substitution degree, and amylose-amylopectin ratio.

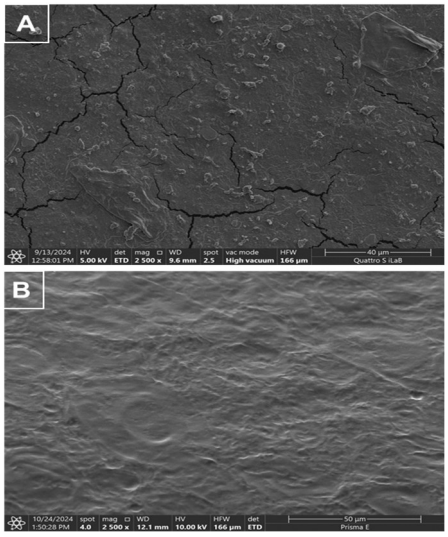

Fig.-6: Surface Morphology of Bioplastic from (A) Native Cassava and (B) CSNPs/Span 60

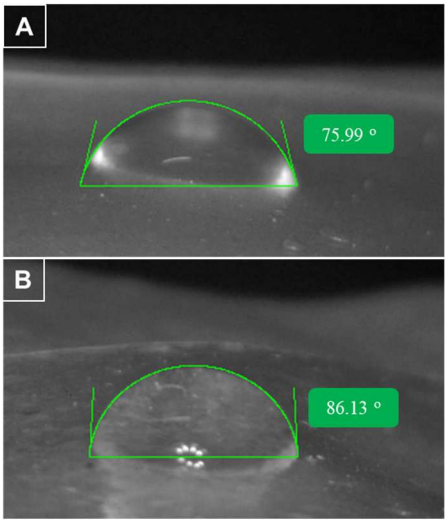

Fig.-7: Contact Angle Analysis of Bioplastic from (A) Native Cassava and (B) CSNPs/Span 60

Table-2: Physical and Mechanical Characteristics of Bioplastics

Parameters	Bioplastic Control	Bioplastic CSNPs/Span 60
Swelling power (%)	74.78 ± 0.05	50.46 ± 0.02
Water solubility (%)	37.25 ± 0.01	8.809 ± 0.01
Thickness (mm)	0.125 ± 0.01	0.240 ± 0.01
Tensile strength (MPa)	2.593 ± 0.42	0.128 ± 0.02
Elongation (%)	21.22 ± 17.01	30.71 ± 13.32

CONCLUSION

The precipitation in the water-in-oil microemulsion method successfully reduced the size of native cassava starch to nano-sized, decreased amylose content, swelling power, and water solubility, and enhanced gelatinization temperature. When used for food packaging, nanoparticle starch-based bioplastic provides higher hydrophobicity and elasticity properties than native cassava-based bioplastic.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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