The potential use of Indonesian glutinous rice flour as nanoparticles organic filler for dental impression materials

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Abstract. Indonesia as a third largest rice producer has glutinous rice as one of its natural resources, which can be used as the advantage in organic fillers production. Organic and inorganic fillers are commonly added to reinforce the mechanical properties of the polymer in impression materials. Organic fillers made from glutinous rice flour can be produced due to its high amylopectin content and unique characteristics of morphological and structural of the source plant. Moreover, it is abundant in production, low cost, non-toxic and biodegradable. However, this type of filler is not common in dental area, especially in impression materials. This study aims to exercise the probability of the use of organic fillers made from Indonesian glutinous rice as filler component of the viscosity the dental impression materials. Nano-size, morphology, and amount of glutinous rice organic filler shall affect the consistency of viscosity, which will be provided as light, medium, heavy body and putty consistency. The study can be used as a reference in the future research of Indonesian glutinous rice development for organic nanofillers production that could be used for dental impression materials reinforcement towards better mechanical properties.

1. Introduction
Indonesia’s rice crops yield by 25.9 million farmers as the country become the third-largest producer of the world. Indonesian farmers can typically grow three crops a year but it is normal to grow two crops of rice a year [1,2]. This rice production increases substantially annually and is much larger than other crop types such as potatoes, corn or wheat [3]. Rice varieties are available, and one of the most common varieties is glutinous rice (Oryza sativa var. glutinosa).

Glutinous rice, commonly known as sticky or waxy rice, is a type of short or long-grained rice, which consists almost entirely of amylopectin in its starch. Owing to the soft, high sticky nature and easily digestible carbohydrates after cooking, glutinous rice flour has been widely used in both novel and conventional foods. These properties come from the chemical compositions which contained less amount of starch (83.59%) and higher amounts of protein (7.78%), lipid (0.97%), mineral substances,
vitamins, and more nutritious than glutinous rice starch (91.78%) [4,5]. The amyllose and amylopectin ratio as well as branching degree of amylopectin are known to define the morphology and size structure of starch granules in different plant, especially of glutinous rice flour that would affect its physicochemical and functional properties, which could be beneficial also as nanoparticle filler in various applications [6].

Fillers from ceramics are still being improved organically, and it used in dentistry to enhance dispersion and biocompatibility as well as high toughness. Unlike inorganic fillers, there are advantages of organic fillers that may come from plant sources such as low density, low cost and energy consumption, renewability and biodegradability, worldwide availability of quantities, durability, non-abrasive quality, non-toxicity, and easy handling. The other implementation of organic nature is the reactive surface of the organic filler can facilitate its chemical modification and shall develop economic opportunity as well [7,8,9]. Plant body sources that have been used as biofiller are extensively studied in many applications by using it in natural or derivatives form. It becomes excellent in nanoscale fillers for polymers that improve the blending and composites [9,10].

Dental impression materials are any materials that are utilized to deliver precise copies of intra- and extra-oral tissues. Based on the clinical application of impression materials, flexible impression materials such as alginate, elastomer (polysulfide, polyether, condensation silicone, addition silicone) and agar can be extended or compressed and competent of precisely duplicating both hard and soft structures of the mouth including interproximal spaces around gingiva. In contrast, inelastic impression products, such as plaster and zinc oxide eugenol paste, are still in the right consistency and do not compress the tissue during impression tray seating. Dental impression materials, which are influenced by the composition of the fillers, should be sufficiently flexible and viscous to conform to oral tissues or in a tray, capable of being used in a fair time, biocompatible and cost-effective way. Impression materials are inserted in the mouth as viscous paste with adjustable flow behavior. Not only easy for light or medium body to free flow but also for heavy body or putty consistency to spread and retain without excess flow in the impression tray. Viscosity of the impression materials shall increase with the presence of filler proportion [11,12].

The starch or flour from the glutinous rice is very useful owing to its unique characteristics, and suitable for applications in the food or pharmaceutical industry, would have the opportunities as well to be an organic fillers for dental area, which came to the objective of this study that is to review and predict the potential use of organic nanofillers from Indonesian glutinous rice flour in order to reinforce dental impression materials.

2. Potential of Indonesian glutinous rice flour
Rice (O. sativa) is the most common crop in the world since it is used for human consumption. The three most common O. sativa subspecies are Japanese, Javanica, and Indica. Indonesia, as one of the countries that cultivated glutinous rice or sticky rice (Oryza sativa L.), has javanica varieties, which typically serve glutinous rice as traditional dishes or desserts. The production and consumption data have not been well recorded and is still generally categorized as part of total rice production data [13,14].

The starch component of glutinous rice flour contains almost no amylose, since the varieties is only about 0-2%. Mostly starch component of glutinous rice flour contain amyllopectin is a semi-crystalline highly branched polysaccharide with -1,4 backbone and -1,6 branch points. Each branch contains about 20–30 anhydroglucose units. Due to the clustered branches of amyllopectin chains that are packed together, provide its crystalline domains of the starch granules, and the aqueous solutions of amyllopectin are characterized by high viscosity, clarity, and stability as measured by resistance to gelling on aging [15,16]. The morphology of the starch granule differs not only by the source plant, but also by the different segments of the same plant [7]. Other relevant factors affecting these aspects are the degree of polymerization (DP) of amylose and amyllopectin and the potential existence of other granule components such as lipids, proteins and inorganic compounds [8,9].
Depending on the physical properties, glutinous rice included as A-type starches (most cereal starches: maize, corn, wheat) with shorter constitutive chains and a greater short-chain fraction than B-type amylopectin molecules (tuber starches as potatoes), while legumes starches usually have a C-type pattern. A-type starches also had branch points scattered in both amorphous and crystalline regions, while B-type starches had the most branch points concentrated in amorphous areas. It was concluded that the branching pattern of amylopectin played a key role in deciding the form of crystallinity [16].

Even though waxy corn/waxy maize has similar polygonal/polyhedral morphology and properties to waxy rice because its endosperm starch consists of mainly amylopectin, but its paste displays a high viscosity, stringy texture, little cloudiness, and a low tendency to gel, which is similar to tapioca starch-paste, and easy to break down under shear, which could also be affected by the granular size around 5-25 μm and its voids [6,8,17-19]. On the other hand, starches from cassava and potato produce relatively bland pastes and higher viscosity since its morphology are semi-spherical or ellipsoidal and have large granule size on the cassava or sorghum (5-35 μm) and potato (15-100 μm), which are bigger than waxy rice (5/3-8 μm) as seen in Figure 1 [6,8]. Potato starch also influenced by the presence of phosphate monoester groups in its amylopectin and posses 7.7% amylose content greater than other starches (waxy maize, rice, wheat), which is composed of essentially linear chains of -1,4 linked glucose units with approximately 200–2000 anhydroglucose units and produce amorphous region, and shall leads to retrogradation [15,20]. If water absorption took place, potato starch also showed a delay in swelling power, while white waxy wheat flour displayed higher swelling power in high temperature and pasting temperature than glutinous rice flour [21,22].

![Figure 1](image1.png)

**Figure 1.** Starches Granule Size (Yellow Line) of (a) Potato; (b) Cassava; (c) Rice [16]

Rice starch granule amylose binds up to 0.7 percent protein, which is predominantly a waxy gene protein with a large number of disulphide bonds. Protein with intact disulphide bonds makes swollen granules less likely to break down. As protein disulphide bonds were uninterrupted, the size of the rice starch granules increased, raising the degree of gelatinization and gel power. So, the low concentration of waxy gene protein on the milled waxy rice (with abundant of glutelin and prolamin rather than albumin and globulin) shall makes the waxy rice soft, smooth and develops low viscosity [14,23]. When waxy rice flours are used as the primary source of starch, consistency can be preserved for a year or longer. It doesn't show any retrograde cooking. However, this absence of retrograde is equally noticeable in other waxy grain flours and, in particular, in the distilled starches of these flours [24]. These properties are desirable for the organic filler made from glutinous rice flour to be easily to fabricate dental impression materials with variable viscosities.

### 3. Dental impression materials

Dental elastomeric impression materials contain fillers on the base and accelerator pastes. Polysulfide impression material has suitable lithopane or titanium dioxide filler on its base paste for providing the strength. Meanwhile, colloidal silica as filler is component contained in both base and accelerator pastes on polyether impression materials. On addition and condensation silicone impression materials,
both of its base and catalyst pastes are contain amorphous silica fillers which are marketed with different consistency based on the filler proportion, such as light, medium, heavy bodied and putty [11,12,25]. Figure 2 described the application of addition silicone elastomeric impression materials with light body viscosity to reproduce interproximal area and heavy body viscosity to reproduce other anatomy and for support the impression on the tray. Back to the component filler, the term is referred to as the distribution of solid particles distributed in the resin matrix to improve rigidity, strength and wear resistance and to minimize thermal expansion, viscosity polymerization, shrinkage and swelling in water and other solvents [11].

Figure 2. Dental Elastomeric Impression Materials with Light Body (Blue) and Heavy Body (Orange) Viscosities [26]

Polymers without the addition of other materials often exhibit properties that do not meet the required technical specifications. Reinforcement with inorganic fillers, which also gives surface treatment, shall influence the hardness and strength on its mechanical properties. Inorganic filler such as amorphous silica or fluorocarbons are used to add bulk and improve the properties of the paste. Surface treatment of the filler with silanated to increase filler and polymer matrix bond strength, and allows a cross-linker function [12,27]. Elastomeric materials, such as polysulfide exhibit only about 16-18% of titanium oxide or silica fillers on the composition. Since the materials are relatively costly and it has become standard practice to incorporate fillers to minimize costs, the result is to increase the elastic modulus of the cured product with minimum impact on the strength or other properties. The use of filler, which was not a mineral and had a spherical form, which was an acrylic polymer, primarily composed of methyl methacrylate, was studied in dental elastomer products. In general, this organic filler gives less affinity and less surface movement compared to elastomers. Since the filler still in large size about 50 microns, so it only gives lower tensile strength with the contribution from weak bond via Van der Waals force. Other report succeeded using glutinous rice starch as mucoadhesive polymer for controlled drug delivery, since it has the free hydroxyl groups that open possibility to be cross-linked with other polymers [28]. However, it was soon assured that very fine powders might result in a significant increase in both strength and modulus, with the amount added up to about 30 percent by volume for the reinforcement effect, and also a reduction in the size of the particles or an improvement in the structure in the propensity of the particles to form chains [9,29,30].

Different from elastomeric materials, alginate impression materials need about 60-80% of the filler because it is not marketed in paste but rather in powder. Diatomaceous earth filler shall provide the formation of firm gel surfaces and increase the strength and stiffness of alginate gel [11,31]. There is one patent in 2017 that used grain of starch or gelatinized starch from corn, glutinous rice or other starches as alginate impression filler materials, means that the organic fillers for dental impression materials could reinforce and substituted the inorganic filler that are used to, but this research did not use the nanoparticle filler [29,32].

4. Prediction on dental impression materials viscosity based on glutinous rice nanoparticle
organic filler

The using glutinous rice flour with bovine gelatin mixture in Figure 3 has been conducted on the previous research in 2017, which resulted 6 minutes setting time, with almost same final diameter with the first measurement in according to compression set test and is a promising candidate to be used as dental putty material [33]. Based on the composition result of the next research in 2019 showed that the glutinous rice with bovine gelatin and two readily marketed available lab putty have similar and comparable composition to one another, which are carbon and oxygen. Even though still agglomerated, the polyhedral morphology particles of glutinous rice flour mixture allow binding interaction between elements as seen in Figure 4. This result is like the fabricated lab putty materials that marketed available. Dental lab putty made from glutinous rice can be considered as an option of low cost and palatal matrix index [34].

![Figure 3. Dental Lab Putty Made from Glutinous Rice Flour Mixture [33]](image3)

![Figure 4. Morphological structure of Dental Lab Putty Made from Glutinous Rice Flour Mixture [34]](image4)

Both preliminary researches have not tried to use nanoparticle on the main component filler of glutinous rice flour, since those were only one type of consistency, which was putty. The presence of filler particles is important to determine the viscosity and accuracy to promote strength of the materials. Fillers that should take as considerations are filler size with its range, morphology/shapes, and filler loading as the amount of the particle that shall affect markedly the consistency of a paste, which in turn give effect on the clinical manipulation and handling properties [11,25,29].

4.1 Filler size

Nowadays, nanotechnology has a great potential in the various technological fields. Many nanotechnology applications are based on new, as well as typical, nano-structured materials. Superior nanofiller properties, such as enhanced surface area and high aspect ratio, make them highly effective structural reinforcements in elastomers. Due to the very large surface area, the required quantity of such materials is quite small [9].

Nanoparticle organic fillers made from starch have been studied quite widely using different method from one another, which resulted in 40 nm, 75.5 nm, 77 nm, 50-100 nm for waxy maize starch, cassava starch, potato starch and pea starch respectively. The average particle size of waxy rice starch is 150.4 nm using the compressed hot water process. Bio nanofilters, such as cellulose, starch and chitin, etc., are some of the nano-dimensional fillers that provide enormous reinforcement for the elastomer base systems. Rubber-clay nanocomposites exhibit outstanding properties at low clay loading levels compared to unfilled rubber compounds or conventional filled composites [9,35-38].

Another thing that needs attention on this nanosized fillers are the tendency to aggregation increases as the filler size decreases. Aggregation make the fillers have cluster structure constantly because of hydrogen bonding among fillers, which is not permanent but can lead to insufficient homogeneity, lower stiffness, and lower compressive strength of the polymer. The small size fillers
favor surface area improvement, which lead the better copy ability of smaller filler sizes to copy small spaces. That filler size is not only related to viscosity, but also to tensile strength and detailed reproduction. As stated by Shao-Yun et al., the filler size ranges from 10 nm to 80 nm to 1.3 microns to 58 microns and the tensile strength of the filler volume increases as the filler size decreases. The particle size is also important to be considered, not only for viscosity but also for the copy ability on the accuracy of the dental impression materials [25,29,37,39].

4.2 Filler morphology
There are various morphologies of SEM micrographs of filler particles, such as lathe-cut, spherical, spherical-like, sticks, and even pattern mixing. Filler particles with lathe-cut patterns are typically produced by grinding or milling glasses, while spherical patterns are created by pyrolytic or precipitation. Like inorganic filler, the morphology of organic filler also influenced by connection with the elastomer/polymer chains for the reinforcement of the materials. Wide surface fillers would have more contact area available and thus have a higher ability to strengthen the elastomer. Purity also seems to have been important for a better output of the material [25,29,30].

Morphology of starch granules are hexagonal or polyhedral in glutinous rice, tube or stick in potato, etc., but if it given the treatment to become starch nanoparticles, it could be changed to lamellar, platelet, or spherical pattern. The effect of the particles on the dental impression material intensity is important. The selection and pre - treatment of the particle is also crucial to being able to have an interaction between the filler and the printing materials. Particles are regularly surface treated to provide greater adhesion to the polymer matrix [16,25,34,37].

4.3 Filler Amount
Materials with a smaller amount of filler shall have lower viscosity, but the more filler, the thicker is the paste. Viscous materials with increased amount filler shall have higher tensile strength values and tend not to tear so easily. Meanwhile, less viscous materials will produce smaller thickness and easily tear apart. Fluid liquid monomer added with filler will become pastes and correlation between some properties of the impression materials and particle fraction as the consistency decreases as from putty to heavy, medium or light bodied materials [11,29].

On the light body materials will have less viscosity, which probably due to the larger organic matrix, which does not have the ability to impart shape to materials, only to promote the agglutination of the filler. On the other hand, this light body materials would be helpful in interproximal and subgingival area, which is very thin. Less amount of polymeric matrix is available in the composition of heavy body and putty consistency materials, which will have a major effect on elastic recovery, permanent deformation, compression strain, tear capacity, tensile strength, thermal expansion, and dimensional stability. Light body materials had a better elastic recovery than heavy body materials [11,29].

A nanoscale biofilter derived from native starch granules has been combined with several types of polymer matrices. The inherent rigidity of nanocrystal starch, special platelet-like geometry, strong interfacial interactions, and nanocrystal-organized percolation networks contribute to mechanical strength, thermal characteristics, solvent absorption, and barrier properties of the composites [10]. There are studies that prepare small-scale starch nanoparticles and minimize precipitation distribution, but also provide an approach to producing starch nanoparticles that reduces the viscosity of starch aqueous paste and does not need any high-efficiency and low-cost chemical treatment [37]. That method could be a potential of organic nanoparticle fillers that can make a different viscosity, which could be provided in light, medium, heavy body or putty consistency depends on the amount of the filler that will be going to use.

Combining the formulation of size, morphology, and amount of fillers shall be effective on having an improvement on dental impression materials with the ideal viscosity, strength, and detail reproduction of the materials.
5. Conclusions
The effect of nano-size, morphology, and amount of filler made from Indonesian glutinous rice flour shall give contribution on the viscosity for the reinforcement of dental impression materials to better mechanical properties. The study can be used as a reference for future research in conducting the development of Indonesian glutinous rice flour for organic nanofillers production towards better dental impression materials properties.

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