

Moldable setting time evaluation between sodium alginate and bovine gelatine of glutinous rice mixture as dental putty materials

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Abstract. Putty elastomeric material is a viscous, moldable material that can be used as a dental impression to record and duplicate the tooth structure. Commercially available putty materials are hardly found in the Indonesian market. The aim of this work is to develop an alternative putty dental material from glutinous rice with two different gelling agents; sodium alginate and bovine gelatine. A commercially putty material was used as a control. The length of time required for the putty materials to set (setting time) was evaluated with compression set test. The result showed that sodium alginate and bovine gelatine gelling agents resulted in moldable putty materials that comparable to the commercial product. Glutinous rice mixed with sodium alginate gelling agent demonstrated longer setting time (more than 1 hours) compared to bovine gelatine (6 minutes). These may occur due to heat treatment applied to the bovine gelatine, while sodium alginate mixture has a chemical reaction since CaCl_2 crosslink agent had been added to the mixture. Glutinous rice with bovine gelatine mixture is a promising candidate to be used as a dental putty material. □

1. Introduction

Putty material is a moldable material that can be used as an index to record and to duplicate tooth and some other structures in the mouth, which is useful for diagnostic tooth preparation. Another advantage is that putty materials can also be used as a shell for making class IV restoration based on the recordable impression. Selection of appropriate materials will assist in the recording of impressions. Silicone indices are commonly used to help in tooth preparation and to evaluate the extent of tooth preparation. One type of silicone that is commonly used for preparation index is the condensation silicone impressions materials. This material is supplied as low, medium, high, and very high viscosity [1]. A very high viscosity material commonly referred to as "putty" was developed to overcome the large polymerization shrinkage of the condensation silicone impression materials. These putties are highly filled, contain less polymer. Hence there is less polymerization shrinkage [2, 3].

Commercially available condensation silicone putty materials are difficult to be found in the Indonesian market, so it still mostly likely to be imported. So that it is important to find an alternative materials that can substitute condensation silicon putty materials. To address this issue, we develop an



alternative putty from an easily available household material, such as glutinous rice flour. Based on the previous publications, some flour has different levels of gelatinization depending on the origin structure and compositions. Glutinous rice flour gelatinized at lower temperatures compared with other flour [4].

Currently, glutinous rice flour has been widely used in both novel and traditional foods products due to the soft, high sticky nature and easily digestible carbohydrates after it is cooked. Glutinous rice flour is also high in protein, mineral substances, and vitamins. However, poor resistance to shear force, and low elastic gel-forming ability of glutinous rice flour still appear as their negative aspects leading to its limited application in food industry. Therefore, it is necessary to enhance its inherent properties in accordance with the intended purposes as dental putty materials [5].

Rice flour can be modified in several ways, including by chemical, physical, and enzymatic methods. Physical modifications involve pre-gelatinization and heat-moisture treatment and have gained a wider application [5]. The selection of a particular hydrocolloid to be used in a specific food product depends on the characteristics of gelling agent. For example, alginate can form gels without prior heating because sodium alginate is cold water soluble and these cold-formed gels are heat stable. This makes alginate a preferred gelling agent for re-structured foods and for cold-prepared instant bakery custard that is bake-stable [6]. The rapid setting behaviour of alginate gels is also important in restructured foods that are diffusion-set [7].

Gelatine also has a wide range of functional properties. One of them is a gelling agent. Gel made from gelatine melts at low temperatures. The thermal behaviour of gels also differs because of the junction zones. Gelatine melts at much lower temperature because the junction zones are only bound by weak hydrogen bonds. Gelatine gel has a slow setting but also has good elasticity [8].

In this study, glutinous rice flour with two different gelling agents, sodium alginate and bovine gelatine, are developed as an alternative for dental putty materials which evaluated its desirable features such as demonstrate structure reproduction and setting time. Compression set test has been conducted to measure the length of time required for the glutinous rice flour putty materials to set.

2. Experimental

2.1. Commercial Condensation Silicone Putty Mixing

Putty matrix can be generated from the systems that are available, such as condensation and addition silicon. These materials are supplied with scoops for dispensing. Manipulation of the putty material is taken in a scoop, and the activator is added, which may be supplied a liquid or paste with different color from the base. The same amount of the scoop or a spoon base for every half scoop of putty combined with an appropriate amount of the accelerator. The best mechanical mixing is to knead the material with the fingers and palms until thoroughly mixed, and all streaks and stripes have disappeared. This stage is achieved when the uniform/homogeneous color appeared. Then apply the putty on the prepared tooth using the thumb and forefinger. Allow a little time (about 1-2 minutes) for the index to be polymerized perfectly on the tooth. The most important aspect at this stage is that the index should cover the entire labial and lingual surface of the tooth and the appropriate surface of at least one adjacent teeth [3, 9].

2.2. Preparation of Glutinous Rice Putty Materials

Putty materials were prepared from glutinous rice, any commercially available sodium alginate, and bovine gelatine; bovine gelatine from traditional market is ok to use. Glutinous rice was used as filler. Sodium alginate and bovine gelatine, both act as gelling and binding agents of putty materials so that it can be manipulated easily. Hot water is utilized as solvent for bovine gelatine to make this polymer dissolves or swells.

2.2.1. Preparation of Glutinous Rice Putty Materials with Bovine Gelatine

Five gram of bovine gelatine was mixed with 15 mL of hot water. This bovine gelatine mixture was then added into 30 gr of glutinous rice. They are mixed for 10 seconds by taking this mixture to the

hands and quickly knead it within 30 seconds until homogeneous. The kneaded sample was loaded into a tooth model. The sample was then allowed to set and then it was removed from the model. The detail of the resulting impression was then evaluated.

2.2.2. Preparation of Glutinous Rice Putty Materials with Sodium Alginate

Preparation of Glutinous Rice Putty Materials with Sodium Alginate was conducted using similar procedure to the preparation of glutinous rice putty materials with bovine gelatine. In this sample preparation, CaCl_2 was added as cross-linker for sodium alginate.

2.3. Surface Reproduction Examination

Both uniform/homogeneous color putty materials resulted from glutinous rice flour applied to the tooth using the thumb and forefinger. Allow the time (2-4 minutes for bovine gelatine mixed and 1-4 hours for sodium alginate mixed) for the index to set perfectly on the tooth model. The index should cover the entire labial and lingual surface of the tooth and the appropriate surface of at least one adjacent teeth. After sets, remove putty index from the tooth model. Then, visual examination for the reproduction tooth structure was checked and compared with the available condensation silicone putty materials.

2.4. Compression Set Time Test

Compression set time was evaluated based on modification of ASTM D-395-01, a standard test for rubber property [10]. Compression device consisting of two or more flat teflon plates between the parallel faces of which the specimens may be compressed as shown in Figure 1.



Figure 1. Device Used for Compression Set Test

Steel spacers for the required percentage of compression are placed on each side of the rubber specimens to control their thickness (3 mm) while compressed. Each plate shall be cleaned thoroughly and wiped dry before each test. The specimen with 6 mm thickness and 13 mm diameter sizes is placed between the plates of the compression device with the spacers on each side, allowing sufficient clearance for the bulging of the rubber when compressed. The bolts were then tightened so that the plates were drawn together uniformly until they are in contact with the spacers. The amount of compression employed shall be approximately 25 %. The test specimen shall be at room temperature when inserted in the compression device, then maintained the conditions for 5 minutes. After the time had applied, the final thickness and diameter of the specimens were then measured. The calculation of the compression set expressed as a percentage of the original deflection as follows:

$$C_B = [(t_o - t_i) / (t_o - t_n)] \times 100$$

where:

C_B = compression set (Test Method B) expressed as percentage of the original deflection,

t_0 = original thickness of specimen,
 t_i = final thickness of specimen, and
 m = thickness of the spacer bar used.

Then thickness and diameter of the test specimen of the times applied are reported after removal of the clamp.

3. Results and Discussion

An ideal impression material should have many features. It should not shrink during polymerization, shipping or storage and should have excellent flow. The colour of the impression material should be saturated enough to detect whether the prepared tooth margin is captured. An ideal impression material should also demonstrate an excellent detail of reproduction, good tear strength, and no distortion when removed from the mouth. It must be biocompatible, non-toxic and have an acceptable odour and taste. Desirable features also include long working time, short setting time, and a long shelf life. Disinfection should not reduce surface detail or accuracy. An ideal impression could be poured multiple times, without losing accuracy. No impression material meets all of these requirements, but significant improvements have been made [11].

The ability of an impression material to accurately reproduce the surface of an object is called a surface detail. This is related to the viscosity of the impression material; low viscosity produces better detail [12]. High-viscosity putty materials have poorer detail reproduction. Visually comparison of commercially putty materials and both glutinous rice putty matrix were observed on Figure 2.

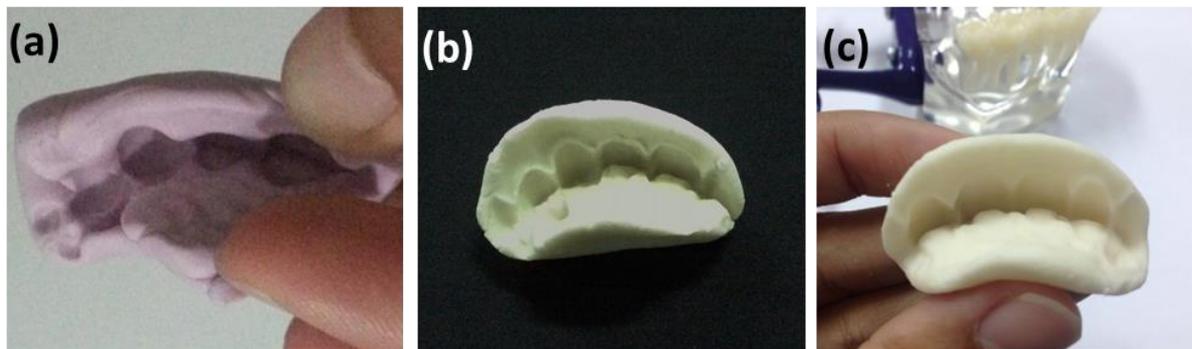


Figure 2. Surface Reproduction Result of (a) Commercially Putty Materials, (b) Glutinous Rice Putty Matrix with Sodium Alginate, and (c) Glutinous Rice Putty Matrix with Bovine Gelatine

Figure 2 shows that all samples can be used to perform the impression of tooth model. Sodium alginate mixture tends to be inaccurate and easily torn since it has an elasticity even after the matrix was removed from the tooth model, while the putty from bovine gelatine mixture perform similar properties to the commercial product and also dimensionally stable after taken out from the tooth model. The thickening agent on commercial product is used when making catalyst paste [13]. These thickening properties seem associated with gelatine performance as a thickening agent for glutinous rice mixture, which has proved popular with the general public for its uses in a wide range of food products.

The setting time of condensation silicon rubber usually 4 to 8 minutes [13, 14] which will save some chair time of the patient. Table 1 displays that glutinous rice with bovine gelatine mixture had almost same final diameter with the first measurement in 6 minutes setting time according to compression set test, which is related to existing setting time references. The bovine gelatine mixture appears to be more stable after 6 minutes as it appears to no longer expanding when subjected to compression stress. This suggests that the setting time of bovine gelatine mixture is shorter compared

to the sodium alginate. This could be caused by the similarity between a moderately high-molecular-weight-poly(dimethylsiloxane) with terminal hydroxyl groups (-OH) in condensation silicon composition with proline and 4-hydroxyproline [15] of bovine gelatine composition [13, 16]. However, alginate is a linear, anionic polysaccharide with an abundance of free hydroxyl and carboxyl groups distributed along the polymer chain backbone; it, therefore, unlike neutral polysaccharides, has two types of functional groups that can be modified to alter its characteristics compared to the parent compounds, so the setting time still need to be achieved after more than 1 hour [17, 18].

Table 1. Compression Set Test Result

Samples	t_0 (mm)	t_n (mm)	t_i (mm)	C_B (%)	d_0 (mm)	d_i (mm)
Sodium Alginate						
I (2 minutes)	6	3	3	100	13	19
II (4 minutes)	6	3	3	100	13	18
III (6 minutes)	6	3	3	100	13	15.6
IV (60 minutes)	6	3	3	100	13	19
Bovine Gelatine						
I (2 minutes)	6	3	3	100	13	17.5
II (4 minutes)	6	3	3	100	13	16.4
III (6 minutes)	6	3	3	100	13	13.9

t_0 = original thickness; t_n = thickness of the spacer bar used; t_i = final thickness of the specimen; d_0 = original diameter; d_i = final diameter of specimen; C_B = compression set test

Commercial condensation silicon rubber paste product consists of an ortho-alkyl silicate for crosslinking and an inorganic filler. A paste will contain 30-40% filler, whereas putty will contain as much as 75% filler. The catalyst paste or liquid usually contains a metal organic ester, such as tin octoate or dibutyl tin dilaurate, and an oily diluent. A thickening agent is also used when making catalyst paste. The metal organic ester catalyzes the reaction. One part of the polymerization involves chain extension by condensation of the terminal-OH group in a siloxane. The other part consists of cross-linking between chains by the ortho-alkyl silicate molecules [13].

Glutinous rice flour has a low content of amylose and a high amylopectin so it is very sticky when cooked. Flour from glutinous rice not only used as a vegetarian binder or as an adhesive [19], but can also be performed as fillers. An alginate which is found from the algae exists as an insoluble mixed salt of all the cations that are found in seawater, the main ones being sodium, magnesium, and calcium. It maintains fast ion-exchange equilibrium with the seawater. The alginate extraction process can be performed in two steps: the transformation of insoluble alginate into a soluble form, namely sodium alginate, then followed by diffusion of the soluble glycuronan into solution. Soluble sodium alginate can be cross-linked with divalent or polyvalent cations to form an insoluble alginate [20]. Since CaCl_2 was used as calcium cations, they have been reported to bind preferentially to the polyguluronic acid. Gelatine is a mixture of different polypeptide chains including α -chains, β (dimers of α -chain) and γ (trimers of α -chain) components with a molar mass of around 90, 180 and 300×10^3 g/mol respectively [21]. The well-accepted mechanism of gelatine gelation is the randomly coiled helix reversion. The amino acid-rich regions of the different polypeptide chains act as potential junction zones in that, upon cooling they take up a helical conformation resulting in the three-dimensional gel [22].

Compression set testing is used to determine the ability of elastomeric materials to maintain elastic properties after prolonged compressive stress. The test measures the somewhat permanent deformation of the specimen after it has been exposed to compressive stress for a set time period. This test is particularly useful for applications in which elastomers would be in a constant pressure/release state. The setting point of a gelatine solution is dependent on its thermal and mechanical history. Higher

setting temperatures are encountered when the solution is cooled slowly in comparison to rapid chilling; mechanical action hinders or delay setting [23].

Gelatine forms gel similar to those of carbohydrates by forming a micro-structural network that is thermo reversible gel. The amino acid-rich regions of the different polypeptide chains act as potential junction zones when the solution is heat-treated. Upon cooling, they take up a helical conformation resulting in the three-dimensional gel [22, 24]. This means that gelatine is sensitive to temperature, So that when mixed with hot water it can be gel that can easily bind to other structures. When temperature returns to normal it will then return to its stable condition.

4. Conclusions

Glutinous rice with bovine gelatine mixture had almost same final diameter with the first measurement in 6 minutes setting time according to compression set test, which is related to existing setting time references. Therefore, glutinous rice with bovine gelatine mixture is a promising candidate to be used as dental putty material.

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