MECHANICAL PROPERTIES AND FORMULATION OF HYDROPHILIC FIBER AND SHRIMP SHELL COMBINATION AS A NOVEL ECO-FRIENDLY DENTAL RESTORATION MATERIAL

A. ABDILLAH

J011211022

PROGRAM STUDI PENDIDIKAN DOKTER GIGI

FAKULTAS KEDOKTERAN GIGI

UNIVERSITAS HASANUDDIN

MAKASSAR

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Artikel

Sebagai salah satu syarat untuk mencapai gelar sarjana

Program Studi Pendidikan Dokter Gigi

pada

PROGRAM STUDI PENDIDIKAN DOKTER GIGI

DEPARTEMEN ILMU KEDOKTERAN GIGI MASYARAKAT PENCEGAHAN

FAKULTAS KEDOKTERAN GIGI

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Artikel,

telah dipertahankan pada tanggal 28 November dan dinyatakan telah memenuhi syarat kelulusan pada

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Departemen Ilmu Kedokteran Gigi Masyarakat Pencegahan
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Makassar

Mengesahkan:
Pembimbing Tugas Akhir,

Nursyamsi, drg., M.Kes
NIP. 197408042005021006

Mengetahui:
Ketua Program Studi,

Muhammad Ikbal, drg., Ph.D.,
Sp.Pros., Subsp.PKIKG (K)
NIP.198010212009121002

PERNYATAAN KEASLIAN ARTIKEL DAN PELIMPAHAN HAK CIPTA

Dengan ini saya menyatakan bahwa, artikel berjudul "*Mechanical Properties and Formulation of Hydrophilic Fiber and Shrimp Shell Combination as a Novel Eco-friendly Dental Restoration Material*" adalah benar karya saya dengan arahan dari pembimbing (Nursyamsi, drg., M.Kes). Karya ilmiah ini belum diajukan dan tidak sedang diajukan dalam bentuk apa pun kepada perguruan tinggi manapun. Sumber informasi yang berasal atau dikutip dari karya yang diterbitkan maupun tidak diterbitkan dari penulis lain telah disebutkan dalam teks dan dicantumkan dalam daftar pustaka artikel ini. Apabila di kemudian hari terbukti atau dapat dibuktikan bahwa sebagian atau keseluruhan artikel ini adalah karya orang lain, maka saya bersedia menerima sanksi atas perbuatan tersebut berdasarkan aturan yang berlaku.

Dengan ini saya melimpahkan hak cipta (hak ekonomis) dari karya tulis saya berupa artikel ini kepada Universitas Hasanuddin.

Makassar, 28 November 2024

A. ABDILLAH
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UCAPAN TERIMA KASIH

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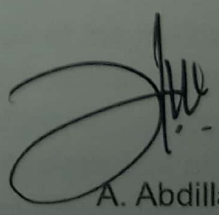

A. Abdillah
J011211022

ABSTRACT

A. ABDILLAH. **Mechanical Properties and Formulation of Hydrophilic Fiber and Shrimp Shell Combination as a Novel Eco-Friendly Dental Restoration Material.** (Dibimbing oleh Nursyamsi, drg., M.Kes)

This study evaluates the mechanical properties and formulation of dental restoration material comprised of cellulose acetate (CA) from water hyacinth and chitosan (C) from white shrimp shells. The research phases included extraction, formulation, functional group testing, antibacterial, toxicity, water absorption and solubility, compressive, shear, tensile, hardness, microleakage, thermal expansion, and shrinkage. The experimental data were analyzed using probit regression, one-way ANOVA, and Kruskal-Wallis test. The data showed CA and C had microxyl and amine groups, could inhibit S. mutans, and were non-toxic. Composite resins were divided into nine formulations with different concentrations, F1 (1% CA + 3% C), F2 (1% CA + 5% C), F3 (1% CA + 7% C), F4 (3% CA + 3% C), F5 (3% CA + 5% C), F6 (3% CA + 7% C), F7 (5% CA + 3% C), F8 (5% CA + 5% C), and F9 (5% CA + 7% C). The F9 has mechanical strength close to the control group, which has 113.33 µg/mm3 absorption, 80 µg/mm3 solubility, 32.67 Mpa compressive strength, 17.18 Mpa tensile strength, and no shrinkage. It shows that F9 has potential as an eco-friendly dental filling material. The present study completed the development of a formulation for a restoration material by combining water hyacinth fiber and shrimp skin chitosan. The outcomes of a comparative analysis of the mechanical properties of synthetic composite resins and water hyacinth fiber composites containing shrimp skin chitosan revealed that the F9 formulation (CA 5% + C 7%) exhibited the following fiber: absorption, compressive strength, tensile strength, hardness, and thermal expansion.

Keywords: *chitosan, eco-friendly, composite resin, cellulose*

1. Introduction

Caries is a global oral health problem. About 2.4 billion (36%) of the world's population have caries in permanent teeth, and more than 530 million children lose their primary teeth due to caries [1]. The prevalence rate of caries in Indonesia reached 88.8% in 2018 [2]. Untreated caries affects a patient's quality of life because they cause pain, chewing problems, stunting, and malocclusion and may affect systemic conditions [3]. The most popular caries treatment solution is composite resin fillings due to their excellent aesthetics, mechanical properties, durability, biocompatibility, non-toxicity, and practical manipulation [4, 5]. However, composite resins are non-biodegradable due to polymerization shrinkage, high water absorption, and solubility; this results in a reduction in mechanical strength and, if the monomer conversion is incomplete like BisGMA, the possibility of human exposure to the bisphenol-A compound, which is known to be responsible to increase systemic health risks such as male reproductive abnormalities [6-9]. Composite resin materials consist of an organic resin matrix, inorganic and organosilane fillers (coupling agents), and additional components such as activators, pigments, inhibitors, and ultraviolet absorbents [7]. Fillers are essential in shaping mechanical properties such as modulus, strength, fracture toughness, fatigue life, hardness, and wear resistance [9, 10]. Unfortunately, composite resin materials are nonrenewable, so more environmentally friendly materials should be proposed.

Cellulose can be an alternative to filler replacement in composite resins due to its exceptional mechanical strength [11]. Water hyacinth (*Eichhornia crassipes*) is one of the natural compounds that can be used as cellulose strands, although its highly aggressive invasive species has emerged as a significant concern and poses a threat to aquatic ecosystems in over fifty countries [12]. Water hyacinth is a weed characterized by its rapid growth and capacity to alter water salinity, reduce dissolved oxygen levels, and induce water shallowing [13]. Due to its substantial cellulose content (66.87%), water hyacinth's resistance to water and degradation, and limited application history, it shows potential as a reinforcing filler for composite resin [14, 15]. The previous study showed that this polymer is non-toxic, biodegradable and biocompatible, has a high affinity for other substances, and has excellent mechanical and regenerative properties [16]. Nevertheless, the hydrophilic nature of cellulose in water hyacinth necessitates a modification by acetylating the hydroxyl group; this process transforms cellulose into cellulose acetate [17]. Cellulose acetate has low water absorption, and is resistant to high temperatures [11].

In the context of composite resins, the water absorption capacity of the matrix is enhanced due to the absorbent properties of *bisphenol a glycidyl methacrylate* (BisGMA), *urethane dimethacrylate* (UDMA), and *triethylene glycol dimethacrylate* (TEGDMA) [18]. Because it absorbs water at a physiological pH of seven, such as in the oral cavity, chitosan can be utilized as an alternative to

matrix material [19]. Chitosan, formed through the N-deacetylation of chitin, is an inherent biopolymer known as poly-*J*-1,4-glucosamine. As evidenced by a degree of deacetylation (DD) exceeding 90%, chitosan derived from shrimp (Crustacea) is the most effective material-enhancing agent. With a degree of deacetylation of 92%, chitosan derived from the shell of the white shrimp species *Litopenaeus vannamei* contains 42.2% chitosan. The previous study showed that incorporating chitosan into composite resins enhances their adhesion to materials, biocompatibility, and has better antibacterial properties than the composite resin without the addition of chitosan without changing the flexural strength and mechanical properties of the composite [20].

This study aims to develop an advanced and ecologically sustainable dental restoration material formulation by combining chitosan derived from shrimp skin and cellulose acetate derived from water hyacinth as a matrix and filler, respectively. The formulation is designed to address tooth decay and environmental issues in alignment with the sustainable development goals, with a particular focus on goal 3, which pertains to promoting a healthy and prosperous life, and goal 15, on supporting the management and preserving of biodiversity.

2. Materials and Methods

2.1 Location and Time

This experimental research uses a group randomized design method with three replications between July 3 and September 30, 2023, in eight laboratories at Hasanuddin University and Ujung Pandang State Polytechnic, Makassar-Indonesia. Water hyacinth was obtained from Hasanuddin University Lake, while shrimp shells were purchased from PT Bomar. The research ethic was approved by the Health Research Ethics Committee of the Faculty of Dentistry Hasanuddin University and Dental Hospital of Hasanuddin University number 0120/PL.09/KEPK FKG-RSGM UNHAS/2023 on June 23, 2023.

2.2 Materials and Tool

A number of materials were utilized in this laboratory research. This includes aluminum foil, distilled water, acetic anhydride, a blue tip, a petri dish, CH3COOH glacial, DMSO, iodine salt, a measuring cup, H2SO4, HCl, pH paper, filter paper, Artemia salina shrimp larvae, methanol, methylene blue, sodium agar, NaOCl, NaOH, paper disk, polyvinyl alcohol (PVA), and a sterile swab. The control group used composite nanofiller resin (CN). An analytical balance used Fourier Transform Infrared (FTIR), Universal Testing Machine (UTM), stirring rod, petri dish, Buchner funnel, measuring cup, hot plate, incubator, Erlenmeyer flask, volumetric flask, laminar air flow, magnetic stirrer, oven, drop pipette, vacuum pump, horn spoon, spatula, and analytical balance (HVN).

2.3 Water hyacinth extraction

Sorting the stems of water hyacinth was the initial step; they were subsequently washed, cut, dried, mashed, and stored in a container [21]. Then, a 15 g sample was homogenized at 70-80 °C for 2 hours after being extracted with 4% NaOH solvent, and 3% NaOCl was used to bleach the sample at 70-80 °C for 3 hours. Following filtration, the remaining substance was dried at 105 °C for two hours [22]. Four stages comprise the acetylation process, which reduces the hydrophilic nature of cellulose: activation, acetylation, hydrolysis, and purification. To initiate the activation process, 10 g of cellulose was dissolved in a 100 ml solution containing 30% CH3COOH glacial. The mixture was stirred continuously at 200 rpm for one hour. Following this, 50 ml of acetic anhydride and 0.5 ml of sulfuric acid catalyst are added with a constant stirring at 200 rpm for 1.5 hours at 40 °C. Following this, 25 ml of distilled water and 50 ml of CH3COOH glacial, both heated to 50 °C with constant stirring at 250 rpm for 30 minutes, were added to initiate the hydrolysis process. Further, the solution was distilled and purified with water for 15 minutes, or until the pH was neutral and the CH3COOH odor had vanished, at which point it was precipitated with methanol solution. Following filtration, the precipitate was dried for 6 hours at 55 °C in an oven [23].

2.4 Shrimp shell extraction.

Deacetylation of chitin into chitosan, deproteinization, and demineralization comprise the three steps involved in chitosan extraction [24]. To accomplish deproteinization, shrimp shell powder was dissolved in a 4% NaOH solution at a ratio of 1:10 (g/ml). The solution was then heated at 70 °C for two hours before being filtered and rinsed with distilled water until the pH was neutral. The formed solid was cooled, dried for 6 hours at 80 °C in an oven, and weighed. After continuing the demineralization process, the protein-free powder was dissolved in a 1.5 M HCl solution at a 1:15 (g/ml) ratio while being stirred for one hour at room temperature. The resulting solution was filtered and rinsed with distilled water until the pH reached neutral. Subsequently, dry chitin powder was dissolved in a 1:10 (g/ml) ratio of 50% NaOH solution in distilled water and filtered. The solution was then heated at 90 °C for two hours before being rinsed with distilled water. After pouring the solid into a porcelain cup and drying it for 6 hours at 80 °C in an oven, it was weighed [25].

2.5 FTIR Analysis

The Cellulose Acetate and Chitosan was placed on Attenuated Total Reflectance (ATR) plate at a controlled ambient temperature (25 °C) and scanned using an FTIR spectrophotometer (ABB MN3000, Clairet Scientific, Northampton, UK) at wavelength of 4000-500 cm^{-1} equipped with a deuterated triglycine sulfate (DTGS) detector and potassium bromide (KBr) as the beam splitter, recorded for

32 scans at 8 cm^{-1} resolution. These spectra were recorded as absorbance values at each data point in triplicate [26].

2.6 Antibacterial test

Flying Paper Disk (FPD) testing was employed to conduct antibacterial analysis using *Streptococcus mutans* bacteria [27]. A 24-hour incubation period of 37 °C was applied to a pure culture of *Streptococcus mutans* bacteria. After suspending the isolate in 2 ml of a 0.9% NaCl solution, a sterile swab was used to evenly scratch the surface of the NA media [28]. A 50 L dripping of the acetic acid-dissolved extract onto a paper disk was followed by its evaporation and subsequent application to the agar surface. A positive control is impregnated with 30 µg amoxicillin, whereas the negative control solely comprises a solvent.

2.7 Toxicity test

In the present study, the toxicity test was carried out using the *Brine Shrimp Lethality* Test (BSLT). BSLT was performed to study the toxicity with *Artemia salina* larvae. The toxicity of the Cellulose acetate and Chitosan mixture was tested at concentrations of 62.5, 125, 250, 500, and 1000 ppm in 10 ml seawater solution and 0 ppm without the test substance as a control, which was added with 1% DMSO solvent (v/v). Then 30 Artemia salina Leach shrimp larvae aged 48 hours were used at each concentration tested. The toxic effect was obtained from observations by calculating the percentage of dead larvae at each concentration within 24 hours for each replication (three replications were used for each concentration) are tallied utilizing the following equation:

$$\% \text{ Mortality} = \frac{\text{Total death larvae}}{\text{Total larvae}} \qquad \text{Eq. (A.1)}$$

Subsequently, the data set underwent statistical analysis via probit regression, employing a 95% confidence level [29]. The results were analyzed using probit analysis so that the LC50 value was obtained using the Software Package used for Statistical Analysis (Version 26.0; SPSS Inc., Chicago, IL, USA).

2.8 Formulation preparation

After the extraction of cellulose acetate from water hyacinth and chitosan from shrimp skin, the next step is to make a composite resin formulation by mixing 2 g of PVA with 10 ml of distilled water at 80 °C. When it has thickened, chitosan (C) (3%, 5%, 7% with w/v formula) is dissolved with 5 ml of 1% CH3COOH and then added with cellulose acetate (CA) (1%, 3%, 5% with w/v formula). The three ingredients were then mixed using a hot plate at 100 °C and then moulded on a petri dish and waited to harden. Cellulose acetate (CA) with concentrations of 1%, 3%, and 5% was combined with chitosan (C) with concentrations of 3%, 5%, and 7% using the group randomised design method to obtain the formulations. In the

formulation, PVA was added as coupling agent and 1% (v/v) CH3COOH as chitosan solvent. The nine formulations were derived from the findings of this study:

Formulation	Cellulose acetate	Chitosan	Pva	Aquades	CH3COOH
F1	1% (0,15 g)	3% (0,45 g)	2 g	10 ml	5 ml
F2	1% (0,15 g)	5% (0,75 g)	2 g	10 ml	5 ml
F3	1% (0,15 g)	7% (1,05 g)	2 g	10 ml	5 ml
F4	3% (0,45 g)	3% (0,45 g)	2 g	10 ml	5 ml
F5	3% (0,45 g)	5% (0,75 g)	2 g	10 ml	5 ml
F6	3% (0,45 g)	7% (1,05 g)	2 g	10 ml	5 ml
F7	5% (0,75 g)	3% (0,45 g)	2 g	10 ml	5 ml
F8	5% (0,75 g)	5% (0,75 g)	2 g	10 ml	5 ml
F9	5% (0,75 g)	7% (1,05 g)	2 g	10 ml	5 ml

2.9 Absorption and solubility test

The sample was imprinted onto a mold measuring 25 mm in length, 2 mm in width, and 1 mm in height. The volume of the sample was determined by utilizing a digital caliper and the subsequent formula:

$$V = l \times w \times h \qquad \text{Eq. (A.2)}$$

The variables l, w, and h represent length, width, and height, respectively. Using 2,5 ml of saliva per sample, immersion was conducted for one day. The sample was drained for 15 minutes subsequent to a one-day immersion period prior to absorption measurement, which was conducted utilizing the aforementioned formula:

$$Sp = \frac{m2-m3}{V} \qquad \text{Eq. (A.3)}$$

The symbols Sp (Sorption or absorption), m2 (mass after soaking in µg), m3 (mass after drying in µg), and V (volume of the sample) are denoted (mm^3). The solubility of composite resins is determined through the utilization of samples that have undergone absorption testing. After one day of drying on silica gel, the samples were placed in a desiccator. The mass of the dried samples was

determined by weighing them on an analytical balance. The following formula was used to determine solubility:

$$SL = \frac{m1-m3}{V} \qquad \text{Eq. (A.4)}$$

SL represents solubility; m1 denotes initial mass in µg; m3 signifies mass in µg after drying; and V signifies sample volume in mm^3 [30].

2.10 Micro-leakage test

The sample was imprinted onto a mold measuring 2 mm in height and 5 mm in diameter. Following that, 1 ml of methylene blue was drip-treated onto the sample, which was left undisturbed for a duration of 24 hours. The sample was divided in half in equal portions. The specimen underwent examination through the measurement of the penetration rate of methylene blue. The dye penetration metric was utilized to assess the test outcomes. The dye penetration score is classified into three categories: score 0 (zero) indicates the absence of dye solution penetration; score 1 (one) signifies dye solution penetration on half of the surface; and score 2 (two) indicates dye solution penetration on more than half of the entire surface [31].

2.11 Compressive strength test

An UTM was employed to perform compressive strength tests. Load was applied at a crosshead speed of 1 mm/min while the specimen was affixed to the lower jaw of the UTM; the specimen remained broken throughout. Using the following formula, the compressive strength (Mpa) was determined:

$$CS = \frac{F}{\text{Area of a cross-section}} \qquad \text{Eq. (A.5)}$$

The maximum breaking load, denoted in newtons, is F. For the calculation of the cross-sectional area, see Equation (A.2) [32].

2.12 Shear strength test

UTM-based shear strength testing. The shear strength of a material refers to its highest capacity to endure loads that induce shear deformation within the material prior to its release [33].

2.13 Tensile strength test

Evaluation of tensile strength using UTM. The material is subjected to the tensile test by laying it on top of the UTM until it is severed. The value and maximum strength of the material will then be displayed via parameter value display [34].