Synthesis of Cellulose Fiber from Coconut Coir as Potential Application of Dental Flowable Composite Filler

Twi Agnita Cevanti[1,2], Mahardika F. Rois[3], Nur Shiyama Purnama Sari[3], Steella Ilham Isnaini[3], Sella Ramadhani Alya Sasono[3], Ghaly Muhammad Bahreisy Firdaus[3], Heru Setyawan[3], Adioro Soetojo[2]*, Ira Widjiastuti[2]

1. Department of Dentistry, Hang Tuah University, Kampus UHT AR Hakim Surabaya 60111, Indonesia.
2. Department of Conservation Dentistry, Faculty of Dental Medicine, Universitas Airlangga, Surabaya 60132, Indonesia.
3. Faculty of Dental Medicine, Universitas Airlangga, Surabaya 60132, Indonesia.

Abstract

Natural fibers should be further developed for natural fiber technology as a composite reinforcement in the field of dental. But natural fibers have relatively poor interaction with the matrix and low durability. The adhesion becomes weaker between the highly hydrophilic natural fibers and the hydrophobic matrix.

This study aims to explore the potential of coconut coir to substitute the existing synthetic fiber as a dental flowable composite filler. A low modulus elasticity and crosslinking ability material required for the basis material would be fulfilled by coconut coir.

Cellulose fiber from coconut coir was synthesized through delignification using an organic solvent, bleaching by peroxide in alkali, dissolve using alkali and crosslinking agent, and nucleating process through freeze-drying. The variation observed in this study was the concentration of ethanol as an antisolvent agent and the rate of nucleation. Among the concentration studied, ethanol 96% showed the best nucleation ability of the cellulose, followed by 70% and 50%. Observing the SEM images, it was also found that the increase in nucleation rate caused the fiber became thinner and stronger. In contrast, the low nucleation rate caused the cellulose fibers tended to have a flake-like shape.

XRD patterns of the samples showed the change in the crystalline phase of cellulose from amorphous (1b-cellulose) to crystalline (1a-cellulose) during chemical treatment. The coconut coir has high potential as raw material to be engineered as filler in a dental flowable composite.

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Introduction

The dental composite reinforcement materials used today consist of various synthetic materials such as crystalline silica and lithium/barium-aluminum glass. Synthetic fillers are currently the main choice for filling materials in composites for dental restorations. However, there are still some drawbacks in using the synthetic materials. They tend to cause severe ecological problems because the production process relies on fossil fuels and is quite expensive. In addition, the manufacturing process has higher risk for the labors than that of materials from natural resources.[1,2]

The use of composites in restoration of posterior teeth is currently increasing due to the improvement of their physical and mechanical properties. Based on a clinical review by Brunthaler et al., it was shown that early failure of composite restorations in posterior teeth is closely related to bulk fracture. Da Rossa et al., & Pallesen & Qvist also demonstrated in their long-term study (10 years of follow-up) that failure of posterior composite restorations was more often caused by fracture than caries. Restorations in posterior teeth receive a high masticatory load. Therefore, the composite resin used must have resistance to fracture and mastication. Fiber-reinforced composite (FRC) technology continues to develop as an innovative solution to overcome these problems. Fibers in FRC play a

Corresponding author:
Adioro Soetojo,
Faculty of Dental Medicine, Universitas Airlangga
St. Mayjen. Prof. Dr. Moestopo No. 47, Surabaya, Indonesia.
E-mail: adioro-s@fkg.unair.ac.id

role in providing better transverse strength, reducing shrinkage in a certain direction, and providing lower residual stress than particulate reinforced composites (PRC).[3,4]

The current weakness of FRC is the interfacial bond between inorganic fibers and organic matrices. Intraoral hydrolysis and degradation weaken this interfacial bond so failure can still occur. Laboratory studies have shown that the use of a bilayered structure consisting of a fiber-reinforced composite substructure combined with a surface layer of a conventional restoration composite increases the fracture load on the restoration. Currently, fiber-reinforced composites still have the disadvantage of several failures, possibly due to the selection of fibers that are too short, so that they cannot increase the strength and toughness of the composite resin. Fiber orientation may also have an important role in the load-bearing capacity of the restoration. Fibers with random orientation provide a stiffer structure that slows down the ability to resist crack propagation.[5,6,7,8,9] Finally, the higher cost is a factor that should be considered for the global evaluation of FRC materials.

Today the whole world is faced with environmental and cost problems. The cost required is very large for the synthetic fiber production process. The depletion of fossil resources is a critical problem for fiber composite resins today.[10,11,12] Polymer products based on green materials such as agricultural and plantation crops are the basis for forming products that are eco-efficient, sustainable and competitive with synthetic materials. Natural materials are easily degraded which is not possible with synthetic materials. The advantages of natural fibers are low density, corrosion resistance, and non-abrasive. In addition, it is also abundant and has a high specific strength compared to synthetic fibers.[13,14]

Natural fibers are currently being developed as filler raw materials for the polymer composite industry. But natural fibers have relatively poor interaction with the matrix and low durability. The bond or adhesion becomes weaker between the highly hydrophilic natural fibers and the hydrophobic matrix. These properties of natural fibers preclude the use and industrial production of composites. But natural fibers can be modified so that the physical, mechanical, and chemical properties can be as required. The development of natural-based materials such as natural fibers also directly supports ecosystems, leading to socio-economic development for cultivation, agriculture, and remote or rural areas. Therefore, it should be further developed for natural fiber technology as a composite reinforcement in the field of dental materials.[11,12]

Coconut coir with the Latin name Cocos nufirera L (coir) is a by-product and the largest part of the coconut fruit. There are several characteristics possessed by coconut fiber, namely resistant to organisms and decay, light and strong, elastic, not affected by moisture and humidity, high water absorption capacity, and also easy to obtain. Coconut coir is very abundant and has important pharmacological effects with low toxicity. The superior characteristics of coco fiber are that its elastic modulus is quite low and its elongation at break is very high. The nature of the fiber is not stiff, very flexible, and the most ductile. The surface structure of the fiber is hollow like foam/sponge.[15,16,17] Another advantage is that it is strong, lightweight, heat resistant, salt water resistant, weather resistant and inexpensive.[18] Seeing the characteristics, properties and structure of coconut coir fiber can meet as one of the requirements for restoration materials in dentistry. Judging from its characteristics, coconut fiber has a high potential to replace synthetic fiber-based composites.

This study explores the potential of coir fiber as a substitute for synthetic fiber as a filler or reinforcement for composite resin restorations. A low modulus of elasticity and strong cross-linking ability are expected to occur between the coir fibers and the resin matrix. The purpose of this study was to obtain cellulose from coir fiber which has the potential to be used as reinforcement for composite restorations by knowing its characteristics.

Materials and methods

Research Samples

Coconut coir (CC) used in this work was the outer husk of coconut collected at keputih market, Surabaya City (East Java, Indonesia). Fresh CC was oven at 60^{o}C for 24 h to remove the moisture. Then the CC ground to a fine powder. The reagents employed were: ethanol (C_2H_5OH) (Merck), sodium hydroxide 4% w/w

(NaOH) (Merck), hydrogen peroxide (H_2O_2), urea (PT. Petrokimia Gresik), and demineralized.

Research Methods

Here the fine fiber, coconut coir, was digested in 60% wt of ethanol solution with hydrothermal reactor at a temperature of 150° C for 4 hours. The digestion was conducted with a volume ratio of 20 mL per gram of coconut coir. This process is expected to break down lignin from coconut coir, to obtain pulp cellulose. After that, pulp cellulose was washed by demineralized water. The bleaching step was carried out with alkaline treated pulp cellulose by H_2O_2 3% (w/w) and NaOH 4% (w/w) at 50° C for 180 min used Rotary vacuum evaporator. The same procedure was repeated three times and oven-dried at 80° C for 24 h.

The nucleation step begins with extracting cellulose from coconut coir with a mixture of NaOH solution, urea, demin water (1gr:1gr:4gr:14ml). Then the nucleation process is carried out by adding ethanol to the cellulose filtrate using a sirring pump. In this study used 70% w/w and 96% ethanol with the additian of ethanol varied rate 5ml/min, 10ml/min, 15ml/min and 20ml/min. After that slurry cellulose was clotted with temperature freezer of -25°C. And then freeze dried at a temperature of -45° C and pressure of 5 mTorr until dry particles are formed. The crystallinity of the material during chemical treatment were characterized using X-ray diffraction (XRD; PANalytical, X'Pert Pro) analysis with Cu radiation over an angle range of 5°- 90°. The morphology of nanoshet cellulose from coconut coir was characterized using a SEM with type Hitachi FlexSEM 1000.

Results

Figure 1a, 1b. Pulp Delignification and 1b. Pulp Bleaching.

Delignification and bleaching have changed the structure and color of coconut coir. In Figure 1a the results of the delignification show that the coconut coir structure is softer with a dark color. After bleaching, the color of the coconut coir is brighter, and its shape is like pulp (Fig. 1b).

An XRD analysis performed on each chemical treatment, to gain insight into the changes in the structure of cellulose fiber formation. Figure 2 presents the results of the XRD analysis, (a) the delignification process, (b) the bleaching process, and (c) the nucleation process for 96% ethanol at a rate of 20 ml/min. The XRD pattern for the delignified cellulose (Figure 2a) have 2 characteristic peaks at 16.668° the (110) plane and 22.983° the (200) plane where the structure of the cellulose is identical to 1b-cellulose which is amorphous.

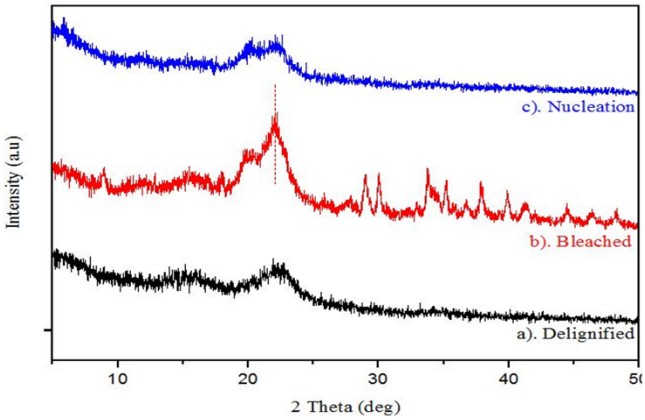

Figure 2. XRD pattern of celluloce a). Delignification, b). Bleaching, and c). Nucleation.

After bleaching, a shift to the left and to form sharper peaks become 15.421° and 21.803° (Figure 2b). The pattern is indicated as 1α-cellulose. In addition, a new pattern of planes (110) appears which is clearly visible at 19.154° belonging to Poly(trimethylcellulose). As a result of the bleaching process, many new patterns appear which are indicated as impurities from the mixing of NaOH and H_2O_2. Among the (002) plane and the (310) plane at the peaks of 30.147^0 and 35.236^0 are Sodium Carbonate. The (402) plane and the (-511) plane peaks at 28.990° and 33.866° are patterns belonging to Sodium Hydrogen Carbonate Hydrate. The synthesis process was carried out by dissolving cellulose into a solution of NaOH and Urea followed by nucleation with 96% w/w ethanol. This mixing process resulted in identical C-N bonds with nitrocellulose and a double peak (020) plane and (110) plane appeared on the main peak of cellulose at 20.28° and 21.803°

(Figure 2c). Prior to nucleation, ion exchange was carried out so the impurities that appeared in the bleaching results did not appear in the nucleation results.

The morphological characterization of the formed nanosheets was carried out through SEM analysis. SEM images provide useful insight into the morphological aspects of nanosheets produced from the synthesis process with varying ethanol concentrations and cellulose addition rates. The yellow circle in Figure 3 indicates the fibers formed in the nanosheet. At low rates for all concentrations, the formed nanosheets tend to flake and do not lead to 2 dimensions. While at a higher rate, a 2-dimensional nanosheet is formed and looks like a fiber.

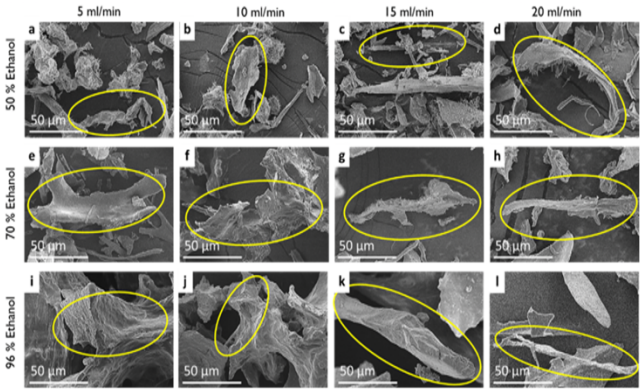

Figure 3. SEM images of cellulose nucleated by 50 % ethanol at (a) 5 ml/min, (b) 10 ml/min, (c) 15 ml/min, and (d) 20 ml/min; nucleated by 70 % ethanol at (e) 5 ml/min, (f) 10 ml/min, (g) 15 ml/min, and (h) 20 ml/min; nucleated by 96 % ethanol at (i) 5 ml/min, (j) 10 ml/min, (k) 15 ml/min, and (l) 20 ml/min.

Discussion

Coconut coir is a lignocellulosic biomass whose main components consist of lignin, cellulose, and hemicellulose. Coconut coir contains 46% lignin (weight base) so that it makes coconut coir hard.[19] Nanocellulose synthesis process of coconut coir begins with the breakdown of lignin that is composed of a phenolic polymer network. Solving lignin done mechanically using a grinder and chemically with delignification. The delignification process was digested using a 60% ethanol solution at 150°C for 4 hours. Figure 1a shows that the delignification process did not change the color of the coconut coir pulp. However, alkaline treatment in bleaching makes the pulp lighter in color (Figure 1b). This indicates that the delignification process accompanied by thermal pretreatment above 120°C weakens the lignin adhesion which is characterized by a softer pulp structure.[20] The presence of ethanol which is an organic solvent can extract lignin from coconut fiber, leaving cellulose, hemicellulose, and a little lignin (dark in color).[21] The bleaching process is carried out using an alkaline solution and hydrogen peroxide. In Figure 1b, the color of the bleached sample becomes brighter and has a smoother structure. the use of H_2O_2 in bleaching makes the pulp surface smooth.[22] Alkali treatment can remove natural and artificial impurities by dissolving the ligno-cellulosic material between the fibers.[23] The use of alkali causes an increase in the degree of polymerization and decreases the breaking strength of the fiber, resulting in a fiber with high tensile strength. Alkali also has the advantage could damage the hydrogen bonds in cellulose hydroxyl groups of the fiber, thus making it more reactive functional groups adjuvant.[23]

Synthesis of cellulose fiber from coconut coir has been successfully carried out. The best results are shown in the use of a concentration of 96% ethanol rate of 20ml/min. This cellulose fiber has an amorphous crystalline structure. In terms of shape, it resembles a roll of thin paper. The concentration of ethanol and the speed of adding ethanol in the nucleation process play an important role in the fiber formation process. The higher the concentration of ethanol used and the faster the increase, the greater the possibility of formation. The success of the formation of fibers from coconut fiber can be used as a reference for further research on the formation of composite fibers in teeth as an application.

Conclusions

The coconut coir has high potential as raw material to be engineered as filler in a dental flowable composite.

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Declaration of Interest

The authors declare that there are no conflicts of interest.

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