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Synthesis of Nanocellulose from Durian Rinds for the Preparation of a Self-healing Smart Concrete with Augmented Mechanical Properties

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Self-healing encapsulation for concrete repair is a technology that has been in considerable attention recently. Encapsulation permits an active substance to be immobilized, protected, released, and functionalized. Herein, nanocellulose from durian (*Durio zibethinus*) rinds were prepared to encapsulate silica, the primary self-healing agent. The investigation focused on the augmentation of encapsulated self-healing material-containing concrete's mechanical properties. The synthesized durian nanocellulose (DNC) has a sheet-like morphology, whereas the encapsulated silica has a rough surface morphology based on the SEM micrographs. DNC and urea-formaldehyde (UF) were used to encapsulate silica, and the synthesized composite (DNC-UF@SiO_2) was mixed in a cementitious matrix to test its self-healing properties. Results showed that the addition of the self-healing material augmented the mechanical properties of concrete in both the pristine condition and healed samples. Notably, the DNC-UF@SiO_2 showed better mechanical performance and lower water absorption than UF encapsulated SiO_2. Hence, the prepared encapsulated self-healing material embedded in concrete showed significant healing potential concerning compressive and tensile strengths after damage, surpassing control specimens. Finally, a synthesis procedure was developed to prepare nanocellulose from durian rinds and encapsulate silica, showing a potential upcycling route of waste durian rinds for construction materials.

1. Introduction

Concrete is one of the most utilized structural materials in building and construction (Mullem et al., 2020). However, concrete composites inevitably develop cracks due to temperature fluctuations, external loads, and other external factors (Manvith Kumar Reddy et al., 2020). These concrete cracks are hard to detect (Kessler, 2007), difficult, and are costly to repair (García Calvo et al., 2018). For instance, a staggering £40 billion of annual expenditures for structural maintenance were made in the UK alone (Chindasiriphan et al., 2020). In addition, repair, maintenance, and damaged concrete infrastructure replacements cover half of the EU's infrastructure budget (Gardner et al., 2018). Consequently, cracked concrete has a significant probability of deteriorating, resulting in a decrease in the integrity and stability of a concrete infrastructure, posing a considerable threat to its durability and safety (Cui,J., 2016). The development of a material that can instantaneously repair the cracks the instant it begins to appear would be a viable solution. It would induce operational cost, structural maintenance, and repair cost and significantly increase the durability and service life of the infrastructure (Gardner et al., 2018). Its ability to heal or repair itself when the material is damaged or when its degradation initiates open several significant construction materials applications (Tan et al., 2016).
When damage is created, various smart materials can automatically heal themselves, such as bacteria-based self-healing concrete (Tan et al., 2020) and microcapsule-based self-healing concrete (Manoj Kumaar & Mageswari, 2021). For instance, microcapsule self-healing composites have gotten a lot of attention for their potential use in cement-based materials (Wang et al., 2021) and their industrial commercialization practicality (Tan et al., 2016). Various materials were used to synthesize the encapsulated self-healing composites for autogenous healing of concrete (Hassan et al., 2016). However, the amounts of the components in the

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encapsulated self-healing system and their effects on concrete's basic and self-healing capabilities necessitates further investigation (Wang et al., 2021). Consequently, there is an increase in research about composites reinforced with nanocellulose fibers from various sources. However, there is still less study on determining the potential of durian rinds as a composite reinforcement source (Rahman et al., 2016). Moreover, there is a prevalent high consumption of durian in the Philippines, especially in Davao City, which generates a high number of durian rinds wastes. For instance, Davao City is considered one of the world's largest durian producers (Lubis et al., 2018). It leads to massive quantities of unprocessed durian rinds waste which could be a potential source of a sustainable nanocellulose reinforcement material.

This study focuses on the synthesis of nanocellulose from Durian rinds and utilizes it to encapsulate concrete self-healing material. Silica acts as the self-healing agent and urea-formaldehyde augmented with durian nanocellulose (DNC) as a polymeric shell coating. The synthesized encapsulated self-healing material was used as a cement additive to prepare the self-healing concrete.

2. Materials and Methods

2.1 Materials

Sodium hydroxide (NaOH, AR ACS,Reagent Grade, Scharlau), sodium chloride (NaCl,Reagent Grade,99.5 %, Scharlau), glacial acetic acid (CH_3COOH,MW 60.05, 99.7 %, Panreac Quimica Sau, Spain), and sulfuric acid (H_2SO_4, MW 98.080, 95-97 %, AR ACS, Macron Fine Chemicals, Thailand) were used for the extraction of nanocellulose from durian husk. Durian husks were procured from a local wet market in Davao City. Sodium metasilicate (Na_2SiO_3, ERN Chemical Industry) and hydrochloric acid (HCl, 36.5-38 %, Scharlau) were used to synthesize silica. Urea-formaldehyde ($0 \leq x < 0,1$, Unicol srl, Fontanelle, Italia) and as-prepared nanocellulose were used to encapsulate silica.

2.2 Characterization

Surface morphologies of the synthesized materials were observed under Scanning Electron Microscope (ThermoScientific Quanta 250FEG SEM-EDX, USA). The SEM was equipped with an Energy Dispersive X-ray Spectrometer (EDX) for the self-healing material's elemental (C, Si, O, N) mapping. Thermogravimetric analysis (Mettler Toledo, DSC823e) was used to determine the material's stability and the actual encapsulation content.

2.3 Preparation of Raw Material

Procured durian rinds were washed to remove excess organic residue before cutting into smaller sizes. Then, the durian rinds were boiled until softened to remove the remaining durian scums. The softened durian rinds were crushed and washed, extracting the durian fibers (DF). The extracted DF were dried in a drying oven at 80 ^oC for at least two (2) days or until completely dried. Dried DF were crushed using a pulverizer (RRH-200, High-Speed Multifunction Comminutor, 28000 rpm) and were segregated according to different mesh sizes.

2.4 Synthesis of Durian nanocellulose (DNC)

The extracted DF was treated with sodium hydroxide (NaOH, 2 % solution) for four (4) hours at 100 ^oC under constant stirring (70 rpm). It was filtered and washed several times with deionized (DI) water until neutral pH was reached. The residue was then dried in a drying oven at 80 ^oC for 24 hours. The treated DF was crushed again using a mechanical pulverizer and bleached using a mixture of NaCl (22.5 g) and CH_3COOH (7.5 mL) in 1.5 L of DI water under constant mechanical stirring at 70 ^oC for two (2) hours. After the bleaching process, DF was filtered, washed several times with DI water until a neutral pH, and dried (80 ^oC for 24 hours). Bleached DF was then crushed using a pulverizer, and treated with 64 % H_2SO_4 (1 g DF/30 mL H_2SO_4) under constant mechanical stirring at 40 ^oC for 30 minutes. Subsequently, the resulting suspension was immediately diluted with DI water (10 times of H_2SO_4 solution) to cease the acid hydrolysis process. The resulting suspension was then centrifuged (Table Top Laboratory Centrifuge, Digisystem Laboratory Instruments Inc., 3200 rpm) to remove the excess acid for 10 mins. To remove the non-reactive sulfate group, soluble sugars, and salts, the treated DF underwent dialysis for 48 hours or until a neutral pH was attained. Then, the DNC produced was sonicated for 5 mins, filtered, washed, and oven-dried (80 ^oC for 24 hours).

2.5 Synthesis of DNC encapsulated SiO_2

Sodium metasilicate was dissolved in DI water (37.5 wt. %) and continuously mixed until crystal clear-like texture. Hydrochloric acid (38 wt. %) was added dropwise to the solution while constantly stirring until a stable gel-aqueous solution was achieved. The solution was then stabilized by mixing for another 15 minutes. Nanocellulose dissolved in DI water (12 wt. %) was added dropwise to the gel-aqueous mixture while stirring

(60 ^{o}C). A urea-formaldehyde (UF) solution (38 wt. %) was also added dropwise, and the final solution was stirred for 2 hours. It was then filtered, washed with DI until neutral, and oven-dried (80 ^{o}C for 12 h).

2.6 Preparation of concrete samples

Materials needed for concrete mixing were based on the ACI 211.1-91 to determine the mass weight. Coarse and fine aggregates were immersed in water for at least 24h beforehand to achieve saturated surface dry condition during batching. Cement, water, and admixture were initially added by interval to ensure homogeneous dispersion by ½ of the dry mixture for an interval of 3 minutes. After forming a cement paste, coarse and fine aggregates were hand-mixed until thoroughly blended. The freshly mixed concrete was then placed into the concrete molds. Two layers were required for less than 100mm cube and with the help of a tamping rod to allow consolidation. Lastly, the sample was dried for 24h ± 4 h before removing it from the concrete mold to start curing the concrete specimen.

2.7 Mechanical tests of concrete samples

A compressive testing machine (UTM Shimadzu, UMH100) was used to evaluate the compressive strength of concrete samples prepared in this study (ASTM C109/C109M). The minimum required curing days for compressive strength testing were 7 and 28 days in accordance with ASTM C192 / C192M-19. The calculation of the compressive strength (*fm,* MPa) is the total maximum load (*P,* N) divided by the area of the loaded surface (A, mm^2).

2.8 Water absorption test

The cracked concrete specimens were exposed to a controlled environment (temperature 25 ^{o}C, relative humidity > 95 %). Water absorption by capillarity (ASTM C1585) was performed after 28 days of exposure.

3. Results and Discussion

3.1 Characterization

Fibers were extracted from durian rinds and pre-treated before utilization for nanocellulose synthesis. The DF's surface morphology is fibrous and rod-like (Figure 1a). On the other hand, the DNC's morphology (Figure 1b) depicts nanofibrous cellulose (Mazela et al., 2020), where tangled fibers formed into thin sheet-like structures. The sheet-like morphology is beneficial for its utilization in encapsulating the self-healing material.

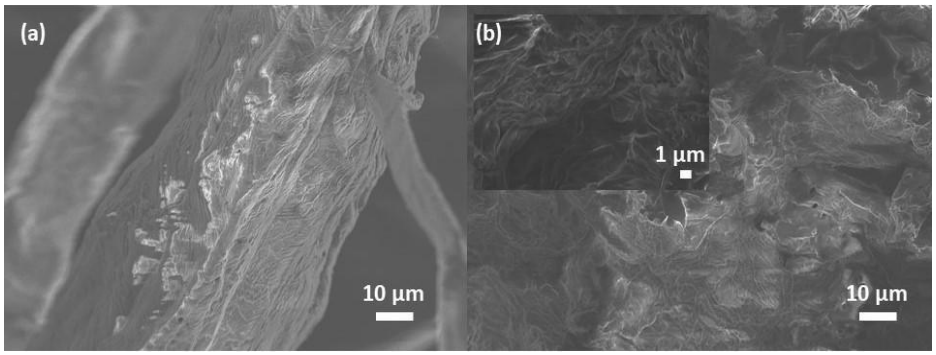

Figure 1: SEM micrographs of (a) extracted fiber and (b) nanocellulose from durian rinds.

The self-healing agent (SiO_2) encapsulation was done using urea-formaldehyde (UF) and DNC. The UF encapsulated SiO_2 (UF@SiO_2) resembles aggregated particles with a rough surface (Figure 2a). The roughness texture may help in its adherence to the cement paste. Its EDX analysis (Figure 2b) detected the presence of C, O, N, and Si. Si and O are due to SiO_2, whereas C, N, O are due to UF. Furthermore, the DNC and UF encapsulated SiO_2 (DNC-UF@SiO_2) has a morphological structure (Figure 2c) similar to that of UF@SiO_2, and EDX analysis (Figure 2d) showed an increased presence of C and O due to the added DNC. The detected Na is a by-product of the SiO_2 synthesis ($Na_2SiO_3 + 2HCl \rightarrow 2NaCl + H_2O + SiO_2$), albeit just a minimal amount.
The amount of UF and DNC that encapsulated SiO_2 can be calculated using the TGA analysis (Figure 3). The SiO_2 nanoparticles have a slight weight loss of 1.04 %, occurring at 400 ^{o}C due to some organic impurities. The UF@SiO_2 weight loss is 12.63 %, which UF accounts for 11.59 %. It is slightly lower than the actual amount of UF (13.92 %) used, which means that around 2.33% UF is lost during the encapsulation process. As for the DNC-UF@SiO_2, weight loss is 14.36 %, which entails that the actual amount of DNC and UF is 13.32 %.

Half of the amount of UF was replaced by DNC in the encapsulation process, which is more efficient, resulting in a material loss of just 0.6 %. Furthermore, mass loss below 200 ^{o}C can be attributed to moisture loss, then gradual thermal decomposition of encapsulating material (UF and DNC) above 200 ^{o}C and faster decomposition rate at above 400 ^{O}C. Nevertheless, both UF@SiO_2 and DNC-UF@SiO_2 showed thermal stability until 200 ^{o}C, which is already beneficial for application in concrete.

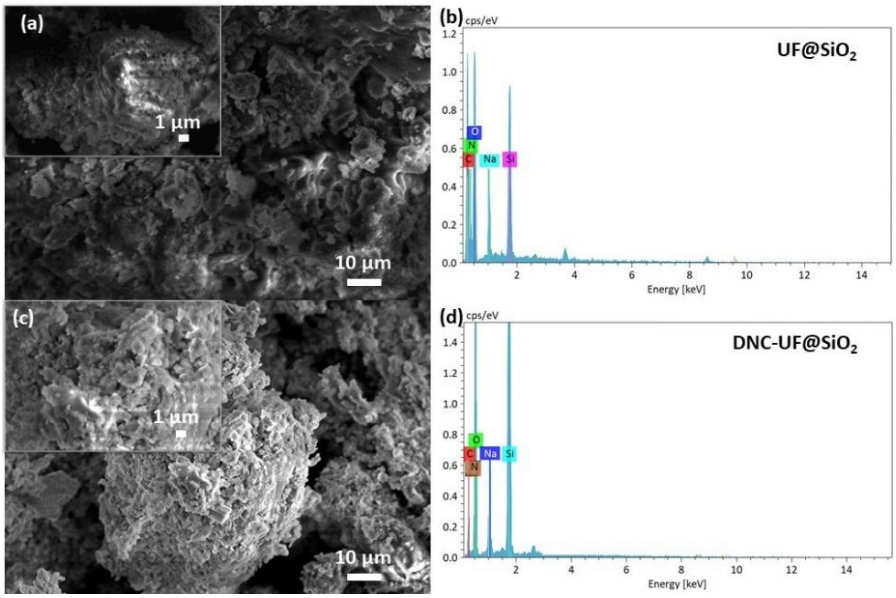

Figure 2: SEM micrographs and EDX analysis of (a, b) UF encapsulated SiO_2 (UF@SiO_2), (c, d) DNC-UF encapsulated SiO_2 (DNC-UF@SiO_2).

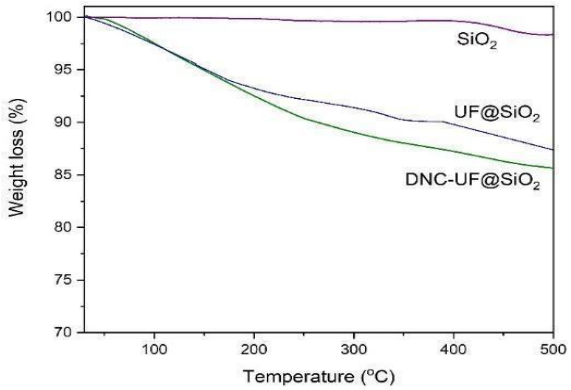

Figure 3: Thermogravimetric analysis of SiO_2 nanoparticles, UF-encapsulated SiO_2 (UF@SiO_2), and DNC-UF encapsulated SiO_2 (DNC-UF@SiO_2).

3.2 Mechanical Properties

Concrete samples were prepared using the encapsulated self-healing material (5.0 wt. % with respect to cement) and subjected to tensile (*T*) and compressive (*C*) strength test. Also, the addition of the synthesized SiO_2 in the cement mixture resulted in an increase in mechanical properties (8.2 % *T*, 32.7% C) compared to the reference samples (REF, without additive). This increase can be attributed to the reinforcing effect of silica on the cementitious matrix (Tan et al., 2016). A slight increase also is observed for UF@SiO_2 and DNC-UF@SiO_2 concrete samples, noting that the latter has a better mechanical response. The partial replacement of UF with DNC may have resulted in better adhesion to the cement mixture since DNC is inherently more hydrophilic than UF and has rough surface. A similar trend is also observed in the healed concrete samples. A slight increase was also observed in the mechanical properties of healed concrete samples with varying self-healing materials: SiO_2 (5.1 % *T*, 60.1 % *C*), UF@SiO_2 (3.9 % *T*, 4.5 % *C*), and DNC-UF@SiO_2 (5.5 % *T*, 7.1 % *C*). Hence, encapsulating the self-healing material resulted in better mechanical responses and would benefit long-term adherence in concrete before cracks may occur.

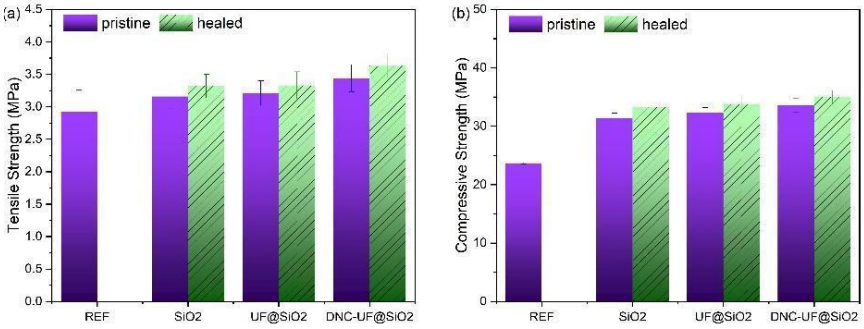

Figure 4: (a) Compressive and (b) tensile strength of pristine and healed concrete at 28 days.

3.3 Water absorption by capillarity

The water absorption results of healed concrete with self-healing materials showed lower absorption values than the reference sample. It indicates that self-healing materials improve the interaction of the hydrated compounds inherently found in concrete and form new products to heal the crack (Chindasiriphan et al., 2020). DNC-UF@SiO_2 has the lowest water absorption values indicating that the hydrophilic properties of DNC may have helped in the healing process, especially that water is critical for self-healing to occur (Hassan et al., 2016).

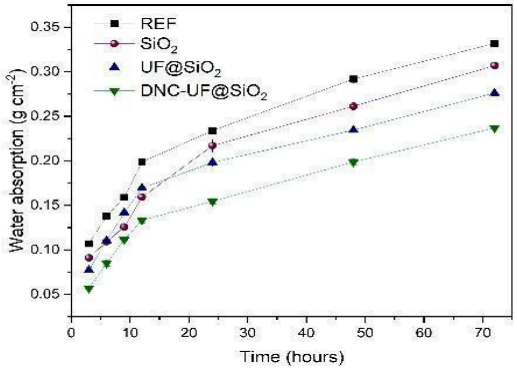

Figure 5: Water absorption by capillarity of cracked concrete samples after 28 days.

3.4 Optical microscopy of self-healed concrete

Autogenous healing of concrete due to continuous cement hydration may have occurred in the healed samples, given the improvement of their mechanical properties. As confirmed by the SEM-EDX analysis (Figure 6), healing products filled the cracked area, which resulted in an improved mechanical response. Occurrence of Na and Al are observed in the healed area (Figure 6 inset EDX result), indicating the possible presence of albite ($NaAlSi_3O_8$). Hence, there was an interaction between the encapsulated silica and the hydrated compounds in the cementitious matrix.

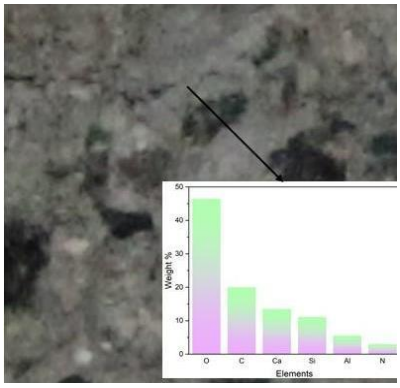

Figure 6: (a) Optical micrographs and EDX analysis of self-healed concrete with DNC-UF@SiO_2.

4. Conclusions

Encapsulation of SiO_2 using DNC was successfully done, providing better mechanical properties to the healed samples. Concrete samples with self-healing material have better mechanical properties than reference samples. Also, healed concrete has slightly better mechanical performance than pristine samples. Hence, the prepared encapsulated self-healing material augmented and healed the mechanical properties of cracked concrete. In the future, optimization of the amount of self-healing material added to the cement mixture must be done, given the successful demonstration of the healing property of DNC-UF@SiO_2. Also, elucidation on the long-term stability of DNC component in concrete must also be investigated.

Acknowledgments

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