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Development of Green Concrete Reinforced with Renewable Chitin Nanowhiskers

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13. Abstract
Green Concrete" is extremely important from environmental perspective, as it does not leach out toxic substances and pollutants with aging. Various renewable source based nanofillers have been added to concrete owing to their low weight, high strength and modulus, and high surface area [1]. Further, superplasticizers (SPs) or water reducers have been used to improve the fluidity of cement, because they can reduce the water-to-cement ratio [2]. However, conventional SPs are toxic and have negligible impact to reinforce concrete [3]. "Green concrete" needs adaptive green SPs, and the preparation of green SPs using modified renewable natural materials is an important pathway. So, we propose to fabricate next generation of SPs for the development of high-performance green concrete with superior strength, and improved fluidity. Thus, the focus of this study is to investigate the utilization of functionalized chitin nanowhiskers (CTNWs) as a potential green SP, in such a unique way that the NWs will offer mechanical reinforcement, while functionalization with sulfonate will provide super-plasticity to the concrete. To accomplish the objectives of this research, an experimental set up was designed to evaluate the efficiency of functionalized chitin nanowhiskers to reinforce the concrete. Tests showed that the functionalization of CTNWs with super-plasticizer influenced the fluidity and compressive strength under the conditions tested. However, the measured improvements in cement paste fluidity and compressive strength were marginal, indicating that more research is needed to optimize the type of super-plasticizer and nanoparticle. Owing to several unforeseen challenges and time constraints, evaluation of CTNWs size, particle size distribution and type of functionalization could not be evaluated in the time frame allowed for this project.

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Development of Green Concrete Reinforced with Renewable Chitin Nanowhiskers

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LTRC Project No. 21-5TIRE
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conducted for
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Louisiana Transportation Research Center

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Abstract

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Acknowledgments

We would like to acknowledge the UL Microscopy Center. Also, we would like to thank all the graduate and undergraduate student's assistance in experimental set up and experimentation.

Implementation Statement

Super-plasticizers (SPs) can be potentially considered to improve the fluidity of concrete. However, conventional SPs are toxic and negatively impact the strength of concrete. We propose to use functionalized CTNWs to tackle the cement paste fluidity and compressive strength. However, further testing needs to be conducted before drawing any definitive conclusions and incorporating the proposed and fabricated functionalized CTNWs as SPs.

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Introduction

The research on renewable or green nanofibers has experienced an explosive growth in recent years because of the unique combination of their properties including outstanding mechanical properties, rich surface chemistry, nontoxicity, biocompatibility, and abundant renewable sources. Furthermore, green nanofibers have been widely used as reinforcing materials for various construction materials [4]. However, a single pot solution to improve the strength and fluidity has never been reported earlier, and becomes a central hypothesis of the proposed work. Concretes are very useful construction materials, composed of macro and micro sized components. The size and chemical structure of ingredients influences physical properties of concrete [5,6]. Recently, cellulose fibers are used as reinforcement in cement based composites [7]. Bantia et al [8] used micro cellulose fiber to improve flexural behavior of cementitious composites. Similarly, sisal pulp nanowhiskers exhibited improved modulus and flexural strength in cement mortar [9]. More, importantly, chitin, which is derived from shrimp shell, is abundantly available natural resource, can be processed and functionalized to provide tunable solutions to industrial problems. Currently, the development of green and high-performance concrete with high strength, long service life, less nonrenewable consumption, and little pollution has become an inevitable trend. Until recently, there are no extensive utilizations of green nanofibers to reinforce concrete. However, there is a great potential for green superplasticizers in concrete research. The proposed study focuses on the development and evaluation of high performance green concrete with a novel renewable superplasticizer to improve the fluidity as well as to improve the compressive strength. Compressive strength and cement paste fluidity will be investigated along with morphological analysis of chitin nanowhiskers-concrete nanohybrid. Further, an optimum dosage will be suggested for this formulation. The developed “green concrete” will exhibit high performance and sustainability characteristics due to the following:

Superior compressive strength due to chitin nanowhiskers (High Performance, Durability, Sustainability)

Sustainable, renewable, green nanofiller based concrete with reduced carbon footprint (Green and Sustainable)

Enhanced cement paste fluidity (Durability)

Literature Review

“Green Concrete” is extremely important from environmental perspective, as it does not leach out toxic substances and pollutants with aging. Various renewable source based nanofillers have been added to concrete owing to their low weight, high strength and modulus, and high surface area [1]. Further, superplasticizers (SPs) or water reducers have been used to improve the fluidity of cement, because they can reduce the water-to-cement ratio [2]. However, conventional SPs are toxic and have negligible impact to reinforce concrete [3]. “Green concrete” needs adaptive green SPs, and the preparation of green SPs using modified renewable natural materials is an important pathway. So, we propose to fabricate next generation of SPs for the development of high-performance green concrete with superior strength, and improved fluidity. Thus, the focus of this study is to investigate the utilization of functionalized chitin nanowhiskers (CTNWs) as a potential green SP, in such a unique way that the NWs will offer mechanical reinforcement, while functionalization with sulfonate will provide super-plasticity to the concrete.

The research on renewable or green nanofibers has experienced an explosive growth in recent years because of the unique combination of their properties including outstanding mechanical properties, rich surface chemistry, nontoxicity, biocompatibility, and abundant renewable sources. Furthermore, green nanofibers have been widely used as reinforcing materials for various construction materials [4]. However, a single pot solution to improve the strength and fluidity has never been reported earlier, and becomes a central hypothesis of the proposed work.

Concretes are very useful construction materials, composed of macro and micro sized components. The size and chemical structure of ingredients influences physical properties of concrete [5,6]. Recently, cellulose fibers are used as reinforcement in cement based composites [7]. Bantia et al [8] used micro cellulose fiber to improve flexural behavior of cementitious composites. Similarly, sisal pulp nanowhiskers exhibited improved modulus and flexural strength in cement mortar [9]. More, importantly, chitin, which is derived from shrimp shell, is abundantly available natural resource, can be processed and functionalized to provide tunable solutions to industrial problems.

Table 1: Flow Test Results for all mortar mixtures

	Control	0.5% CNTW	0.75% CNTW	0.1% SIKA		0.25% CTNW-2HT-SP	0.25% CTNW-2HO-SP
Di (mm)	D25 (mm)	D25 (mm)	D25 (mm)	D25 (mm)			
102	140	143	151	205		148	117
	139	142	147	206		147	122
	141	144	152	201		149	123
	138	145	149	199		148	118
	139	157	150	201		148	119
	145	144	150	202		147	120
AVG_D25	140	146	150	202		148	120
F-Value	37.6%	43.0%	46.9%	98.4%		44.9%	17.5%

Table 2: Compressive Strength Comparison for All Mortar Mixtures

	Control (PSI)	0.5% CNTW (PSI)	0.75% CNTW (PSI)	0.1% SIKA (PSI)		0.25% CTNW-2HT-SP (PSI)	0.25% CTNW-2HO-SP (PSI)
Specimen 1	4314	5507	5552	6316		2888	1375
Specimen 2	3708	4884	5213	5880		3038	2514
Specimen 3	4173	4541	5165	6773		2948	1150
Average	4065	4977	5310	6323		2958	1680
St. Dev.	317	490	211	447		75	731
Percent Increase of compressive Strength respect to control	-	22.4%	30.6%	55.5%		-27.2%	-58.7%

Objective

The main goal is to develop new generation of high performance green concrete, using chitin nanowhiskers acting as superplasticizers (SPs), to not only improve fluidity, but also improve compressive strength of concrete. The objectives of the study are:

- Construct concrete-chitin nanowhiskers based nanohybrid.
- Evaluate the compressive strength and cement paste fluidity of this composite.
- Optimize the nanowhiskers processing conditions for optimum superplasticizer effect.

Scope

In an effort to evaluate the feasibility of a novel super-plasticizer (SPs) to fabricate green concrete, chitin nanowhiskers (CTNWs) were used to improve the fluidity and compressive strength of concrete. An experimental set up was designed to convert chitin into CTNWS and functionalize them with SP. Evaluation of plasticity was performed using cement paste fluidity and compressive strength was measured using un-functionalized CTNWs as a control. Marginal improvements in fluidity and strength were observed.

Methodology

Task 1: Literature Search- Literature search will be conducted to summarize published results for the development of renewable source based cement nanohybrids. An extensive literature search was performed to evaluate the feasibility of the synthesis of functionalized chitin nanowhiskers. After selecting the suitable methodology to fabricate chitin in to chitin nanowhiskers using probe sonication, a chemical method was used to functionalize using the SPs.

Task 2: Material Selection and Nanowhiskers Fabrication- Chitin, which is the second most abundant biopolymer on this planet (after cellulose), is commercially available. Regular Portland cement was used. Silica sand was used as an aggregate due to its consistency and uniformity. Maleic anhydride, sodium metabisulfite, sodium hydroxide, and ethanol were obtained from Fisher Scientific, USA.

Procedure: First, chitin was dissolved in concentrated hydrochloric acid by continuous stirring for 6 hours at ~ 106 °C (Figure 1). The purpose of this step is to homogenize chitin and dissolve the remnant organic residues from chitin. Further, this acid treatment will convert chitin into its nanowhiskers (CTNWs). Next, the solution was left to settle down at room temperature, followed by washing by centrifugation at 10,000 rpm for 10 minutes. This step was repeated thrice to neutralize the acid. The resulting pellet was dispersed in distilled-deionized water to check the pH. Once neutral, the solution was lyophilized to remove the water using a freeze drier. The final powder (CTNW) was collected in an air tight glass vial.

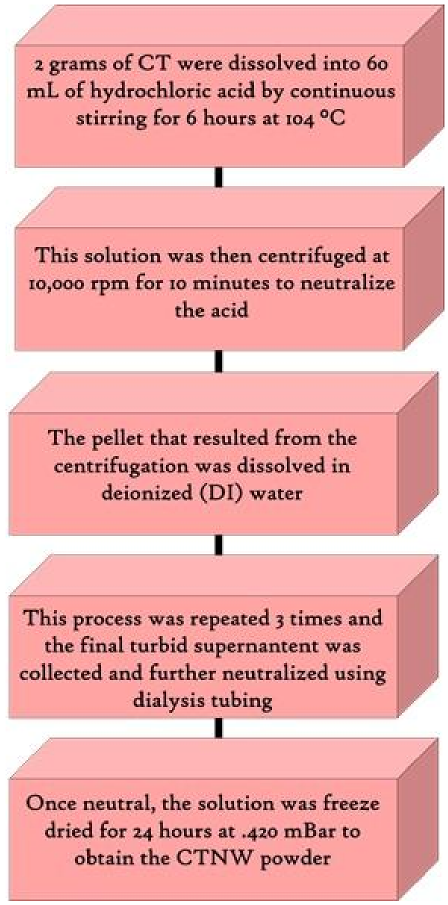

Figure 1: Schematic illustration of the conversion of chitin into chitin nanowhiskers.

Task 3: Synthesis of Functionalized Chitin Nanowhiskers- The objective of converting CTNWs into functionalized CTNWs was achieved in this step by subjecting CTNWs to sulfonation reaction using maleic anhydride and sodium metabisulfite (Figure 2).

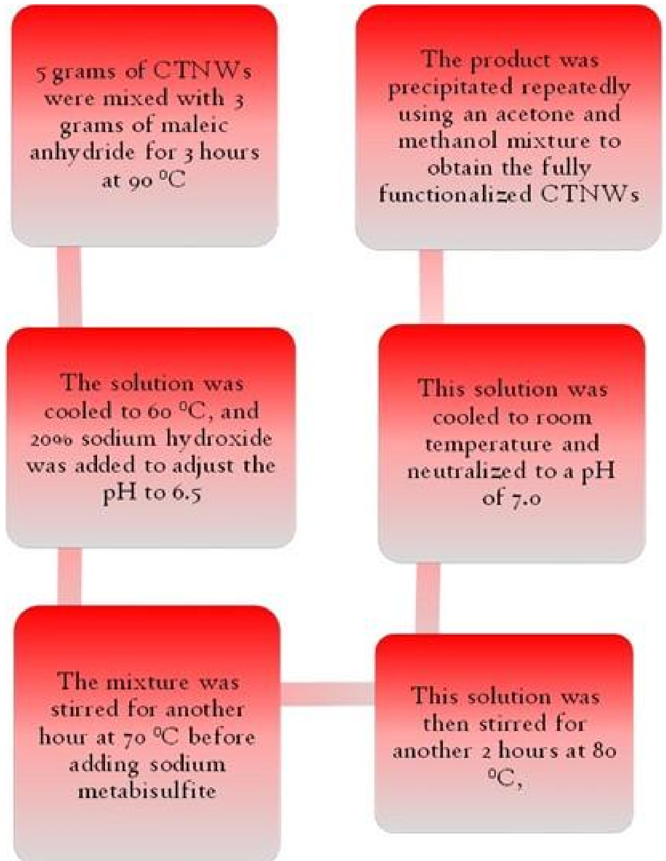

Figure 2: Schematic illustration of the conversion of CTNWs into functionalized CTNWs.

The steps and chemical reaction is given in Figure 3.

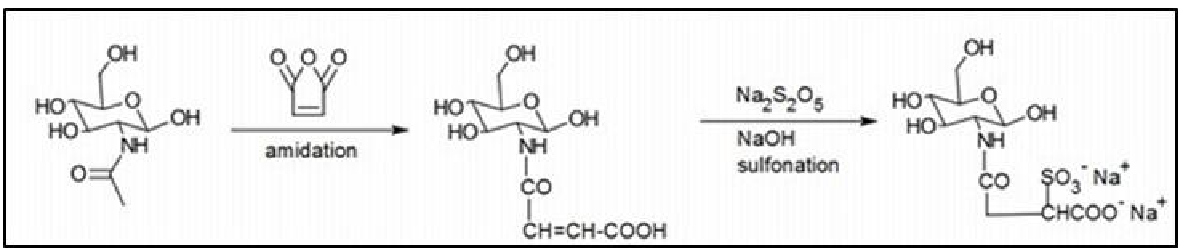

Figure 3: Chemical reactions involving amidation, followed by sulfonation of CTNWs into functionalized CTNWs.

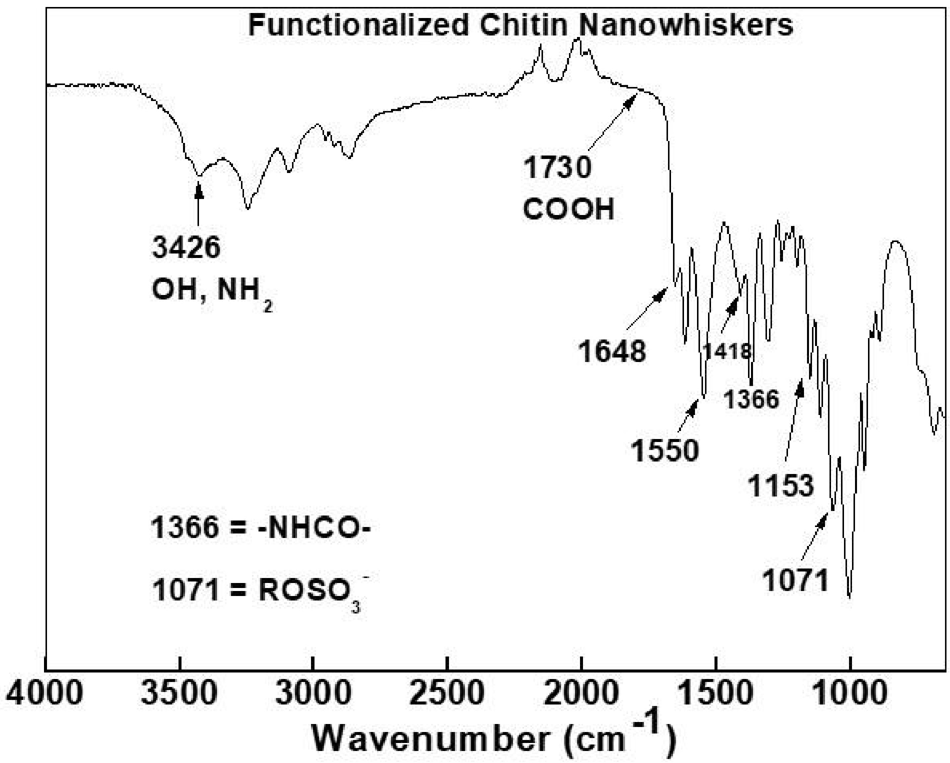

Figure 4: FTIR spectra of functionalized CTNWs.

Concrete-CTNWs Composite Preparation- Cement at a w/c ratio of 0.29 was prepared by mixing water to the overall mixture. Concrete was prepared by adding sand, stone and water by weight ratio of 3.5:7:10:2. CTNWs content by dry weight of cement will be set at 0.25, 0.5, and 1%, while keeping pure non-reinforced cement as a control. The mixes were oven-cured at respective curing temperatures for 48 h before compression tests.

Task 4: Superplasticizer Efficacy by Cement Fluidity Test- Cement fluidity test was conducted as per GB/T8077-2000. For this, a certain amount of CTNWs, 87 g of deionized water, and 300 g of cement was added to stainless steel container, followed by intermittent low and high speed stirring. Next, this mixture was poured into a vertical cone (60 mm height, 36 mm top diameter, 60 mm bottom diameter), placed on a glass plate, and the glass was vertically removed to determine cement fluidity. Another measurement at a 90 ° angle to the first was performed and averaged to give the fluidity value. Amount of CNTWs was optimized as per the fluidity and compressive strength of concrete.

To evaluate the plasticizing effect of the newly developed plasticizer CNTW, cement mortar flow test was chosen by the researchers. Also, its speculated that CNTW may affect the compressive strength of cement mortar. Hence, 28-days compressive strength of CNTW mixed cement mortar was also determined by compression test. Standard procedure of ASTM C1437-07 and ASTM C109 was followed for the flow test and compression test, respectively.

CNTW plasticizing effect evaluation

Preparing the mortar mix

From local contractors, sand passing sieve # 200 was collected. Portland Cement Type II was used for the cement mortar mix preparation. For the control mortar mix, 0.425 water-cement ratio (W/C ratio) was chosen as is provides optimum plasticity for control samples. Sand absorption ratio was estimated as 0.5% (to the weight of sand) for the entire process. Ratio of cement and sand was considered as 1:2 for all mortar mix.

To produce the control mortar mix, dry cement and sand was mixed by hand first. Water was added afterwards to be mixed by the mixing apparatus for 1 minute. Thus, the mortar slurry is prepared and ready for the flow test. For the mortar mixtures with CNTW plasticizer, the plasticizer was mixed at dry condition with cement-sand mix before adding water.

Performing the flow test

Following the standard of ASTM C1437-07, the mortar slurry was placed inside the 'flow mold' over the 'flow table' in two steps. At each step, approximately 25 mm (1 inch) of thick mortar was placed and it was tamped 20 times by tamper. After the mold is fully filled, the flow mold was lifted away 1 min after completing tamping. The initial diameter of the mortar was recoded. The flow table was immediately dropped for 25 times in 15 seconds for the flow measurement. The diameter after the 25 blow was recorded by a caliper on six different locations.

For CNTW samples, the plasticizer was mixed with the mortar before adding water at dry condition. Two groups of samples were prepared with 0.50% and 0.75% of CNTW (the percent of CNTW is calculated to the weight of cement binder). Samples with commercial plasticizer SIKA was also prepared following the same procedure for further comparison. The flow (F-Value) of the mixture is calculated by following equation:

$$F\text{-}Value = (Avg\_D_{25} - D_i) * 100 / D_i ; \qquad (1)$$

D_i, D_{25} in mm

Avg_D_{25} = Average diameter of the mortar after 25 blow

D_i = Initial diameter of the mold base at 0^{th} blow (before any blow)

Figure 5 shows example images for flow test for different mixtures. Table 1 provides the D_{25} values for all mixtures.

Figure 5: Mixture Condition After 25 Blow of Flow test

Table 1: Flow Test Results for all mortar mixtures

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AVG_D25	140	146	150	202		148	120
F-Value	37.6%	43.0%	46.9%	98.4%		44.9%	17.5%

Figure 6: Compression Samples and Sample Testing in MTS

Table 2: Compressive Strength Comparison for All Mortar Mixtures

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Discussion of Results

After converting chitin into CTNWs using a combination of probe sonication and acid treatment, the next step was to functionalize them in order to attach the super-plasticizer (SP) onto CTNWs. The size of pristine chitin flakes was highly random and was in the size range of several to hundred micro-meters. Concentrated hydrochloric acid was used to digest the organic content attached to pure chitin. Further, probe sonication provided strong ultrasonic waves to break down the fibers into nanowhiskers in the size range of 80-150 nm. The broad distribution of CTNWs could be due to the agglomeration and pellet formation of chitin during the process of acid treatment. So, further investigation is required to optimize the procedure to obtain narrow size distribution. We achieved partial success by optimizing the temperature (~105 °C), that provided uniform size and shape of CTNWs. Next, the obtained CTNWs were attached with super-plasticizer (SPs) through amidation and sulfonation reactions. First, CTNWs were subjected to maleic anhydride to facilitate amidation in order to introduce carboxyl groups and double bonds to the macromolecular chains of CTNWs, followed by sulfonation with sodium metabisulfite. These steps facilitated the macromolecular structure of CTNWs with short branched chains containing carboxyl and sulfonated groups. FTIR spectroscopy was used to ascertain the chemical structure of functionalized CTNWs. As shown in the FTIR spectra (Figure 4), the characteristic functional groups were found for peaks at 1366 cm^{-1} (−NHCO−), and 1071 cm^{-1} ($ROSO_3^-$), confirming the attachment of SPs on CTNWs.

Here, F-Value (in equation 1) indirectly measures the flowability of the mortar mix. From Table 1, it could be concluded that the control mix had 37.6% flowability where no plasticizer is used. With the addition of 0.5% CNTW plasticizer to the mix, the flowability is slightly increased to 43%. In other words, it could be seen that the Avg_D25 value increased from 140 mm to 146 mm by the insertion of the 0.5% CNTW plasticizer. If 0.75% CNTW is added, the flowability increases to 46.9%. As commercially available SIKA increases the flowability to 98.4%, we may conclude that CNTW plasticizing effect is not comparable to SIKA, even though it slightly increases the plasticity of the mix. To achieve better CNTW plasticizer, two extra different types of CNTW was made in this research: CNTW-2-HT-SP and CNTW-2-HO-SP. The first version is made by 2 percent sulfuric acid with a heterogeneous process of adding Sulphur molecule it, the second version was homogeneous process. Similar test was performed with these two new CNTW’s for only one mix. The improved fluidity of the cement paste indicated that the functionalized CTNWs has longer dispersion forces which could be due to the multiple functional groups originating from CTNWS and SPs (−COOH, $-CH_2SO_3^-$, −OH, $-NH_2$, $-NHSO_3-$). These functional groups exhibit stronger steric hindrances and electrostatic repulsion. Further, these functional groups can impart strong polarization resulting in the formation of thin and firm adsorption layer on the surface of concrete, leading to reduced frictional forces in between concrete.

Table 2 shows all compressive test results for all mortar mixtures. It could be seen that control specimen had average 28-day compressive strength of 4065 psi with standard deviations of 317 psi. With the insertion of 0.5% CNTW, the compressive strength increased by 22%; whereas 0.75% CNTW increases the strength by 31%. The standard deviation of CNTW mixtures are reasonable also. Even though the CNTW mixtures strength increase is not comparable to SIKA mixture (which is 98%), the increase of strength is more significant that the flowability. CTNW-2H-SP and CTNW-2HO-SP could not increase but rather decreases the strength. Hence, we can conclude that CNTW plasticizer has slight positive effect on plasticity on cement mortar but its strength gain to the mixture is significantly better. It is possible that CNTW could increase the compressive strength of cement concrete also, if researched.

Conclusions

Results obtained from this study under the conditions tested for the improvements in fluidity and compressive strength indicates marginal improvements due to the incorporation of functionalized chitin nanowhiskers (CTNWs). This was due to the attached super-plasticizer (SPs) onto CTNWs which imparted free volume and provided cement paste fluidity, while the nano-sized CTNWs imparted superior compressive strength. We found that a simple acid treatment of chitin can break them down into nanowhiskers shape, indicating that this method can be employed for many other natural fibers such as cellulose microfibers so that they can be used in the synthesis of green concrete. The size of chitin nanowhiskers (CTNWs) was ascertained using scanning electron microscopy (SEM), where the size of CTNWs was found in the range of 100-150 nm. Further CTNWs were attached with a superplasticizer (SP) using maleic anhydride, and sodium metabisulfite via amidation and sulfonation reactions. FTIR spectroscopy and NMR were used to confirm the attachment of SPs onto CTNWs. The presence of carboxyl and sulfonated groups were found on CTNWs. This “green SP” was then used as a nanofiller to improve the physical properties of concrete. 43% increase in fluidity was observed with the addition of 0.5% functionalized CTNWs. A slight improvement in fluidity was observed when the amount of CTNWs was increased, indicating that the particles of CTNWs attached with concrete in such a way that the overall ability of flow increases under the test conditions. This could be due to a synergistic effect of the linear long chain of attached SP on CTNWS and electrostatic repulsion in between the functional groups on SPs. Further, a 22% increase in compressive strength on a 28 days’ concrete sample was found after adding 0.5% CTNWs. This improvement in compressive strength further increased after adding 0.75% CTNWs, confirming the role of nano-sized CTNWs to improve the strength of concrete.

Recommendations

The proposed SP was synthesized and attached with CTNWs, accomplishing the experimental part of the project. Improvements in the cement paste fluidity and compressive strength confirmed the usability of this green SP, so this setup will allow evaluation of various green and natural fibers to be used for the fabrication of green concrete. However, these values were lower than the commercial SP (SIKA), indicating that further investigation on the amount of attached SPs, types, and fibers would provide highly valuable information.

Acronyms, Abbreviations, and Symbols

Term	Description
ft.	foot (feet)
in.	inch(es)
gal.	gallon(s)
LADOTD	Louisiana Department of Transportation and Development
LTRC	Louisiana Transportation Research Center
ASTM	American Society for Testing and Materials
EPA	Environmental Protection Agency

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