CELLULOSE NANOCRYSTALS ADDITION EFFECTS ON CEMENT MORTAR MATRIX PROPERTIES

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Abstract- Cellulose nanocrystals (CNC) are known as stronger materials than steel. The process of cellulose nanocrystals production might be variant and complicated process, however, the end product of the cellulose nanocrystals offer new possibilities for improving cementitious composites by improving the mechanical properties. This paper focus on the relationship between density and ultrasonic pulse velocity (UPV) of the cement mortar after addition of CNC additive with the positive developments of compressive strength. The addition of CNC additives improve the formation of calcium-silicate-hydrate (CSH) gel in the cement matrix up to 0.2% of CNC concentration. Thus, this progressive formation of CSH gel in cement mortar seem to improve the strength of the cement composites up to 42-45% compared to conventional cement mortar.

Index terms- Cellulose nanocrystals, Density, Ultrasonic pulse velocity, CSH gel, Strength

I. INTRODUCTION

Cellulose known as the most abundantly available renewable organic polymer on earth that can be obtained through a lot of resources such as plants, bacteria, animals etc. where the cellulose act as the structural components in it cell wall [1]. During the development of cellulose discovery in year 1947, the cellulose nanocrystals (CNC) were discovered. However, due to the limitation of equipment to study the nanoparticle components of cellulose make the delay on it findings its true potential. Until two years after, the advanced equipment were developed to study the nanoparticles of the cellulose nanocrystals [1].

Cellulose nanocrystals known as the developing renewable nanomaterials that can contribute to many possible application such as in construction, pharmaceuticals, food, etc. The structure of CNC are known to be stronger than steel. These properties can be achieve by appropriate modification of CNC in terms of physical, chemical or biological properties based on desired improvements. The nanoparticles of CNC are stabilised in aqueous suspension during the hydrolysis process with the form of negative charges on the nanoparticles surface [2]. Furthermore, CNC nanoscale particles are promisingly can be used as reinforcing agents in composites in order to produce high performance nanocomposites. This phenomenon are due to the CNC basic physicochemical properties which content an anisotropic chiral nematic liquid crystalline phase [1].

In construction industries nowadays, there a lot of studies on developing better construction materials such as high strength cement composites, environmental friendly composites, etc. Besides that, in the production of cement mortar, the existing conventional mortar are known as non-load bearing structure. This is due to the cement mortar matrix does not contain course aggregates like concrete matrix. Reinforcing the brittle materials like mortar also become problems in finding the sufficient volume of reinforcing fibres without causing difficulties in workability, dispersion of fibre, and reinforcing costs [3]. However, with the addition of CNC into the mortar matrix can improved the strength of the mortar structure similarly to concrete without changing the workability and density of the matrix.

This research work contain the discussion of CNC incorporated in cement mortar matrix performed as reinforcing agents to strengthen the structure. With the achievement of the desired strength, the cement mortar can be use as load bearing structure later on for many possible applications in construction industries.

II. EXPERIMENTAL METHODS AND MATERIALS

Preparation of Cellulose nanocrystals

The preparation of cellulose nanocrystals started from the production of α-cellulose from the agro-wastes. However, in this study, the availability of α-cellulose in big amount can be found from the local industries in Malaysia known as Waris Nove Sdn.Bhd. The readily available α-cellulose were going through purification process which producing microcrystalline cellulose (MCC) at the end of the process. During this process, α-cellulose were reacted with boiling hydrochloric acid (HCl) solution for 15 minutes to completely purify the α-cellulose [4].
After the production of MCC, the steps continued by washing the MCC till neutral followed by drying at temperature of 60°C until constant weight and finally grinding the MCC till it passed through 60 µm sieve. The ready MCC were used to produce the crystalline cellulose by using acid hydrolysis methods. In acid hydrolysis method, 64wt% sulphuric acid (H₂SO₄) were used to break the bond between the amorphous region and crystalline region of the MCC [5]. Then, the solution were centrifuged to remove the excess H₂SO₄ solution then followed by dialysis for 5-7 days until the CNC solution were neutral. After dialysis process were complete, the CNC solution were gone through sonication process for 10 minutes to produce colloidal suspension of CNC [5] as shown in Figure 1. Flowchart for the overall extraction process of CNC are shown in Figure 2.

**Figure 1: CNC colloidal suspension**

- α-Cellulose
- Purified with boiling 0.2N HCl for 15 minutes
- Dried at 60°C until constant weight
- Grind and sieving until passed through 60μm sieve
- MCC
- Extracted with 64% wt H₂SO₄ for 1 hour
- Centrifuged and dialysis until neutral
- CNC

**Figure 2: Overall process for CNC production**

**Manufacturer and tests of cement mortar specimens**

All the manufacturing process of cement mortar were done at Structural and Material Laboratory of the Faculty of Civil Engineering of UTM. The same source of ordinary Portland cement (OPC) were used throughout the research work. The fine aggregates size used in this research were prepared by following the ASTM C778 [6] which two type of sand size were used which 20-30 sand (passed through sieve size between 850-600 µm) and graded sand (passed through sieve size between 600-150 µm). Cement mortar of 50 mm cube size were prepared by following the mix design of ASTM C109 [7]. The cube specimens were demoulded after 24 hours after casting and cured in water and tested on 7, 14 and 28 days. By following ASTM C91 [8] the cement mortar were designed to achieve target mean strength for type S mortar at age of 28 days which is 14MPa. The conventional cement mortar mix design were added with different percentage of CNC concentration starting from 0% to 0.6% with 0.2 increments. The workability of the fresh mortar were observed by using the flow table methods in ASTM C230 [9]. Ultrasonic Pulse Velocity (UPV) tests of the 50 mm cube samples were conducted by using Pundit PL-200 Ultrasonic Pulse Velocity Tester (Proceq) to measure the uniformity of mortar matrix [10]. After the UPV tests were conducted, the mortar specimens were undergoing the compressive strength test [7] by using MATEST250 equipment. Finally all the broken samples were taken to Field Emission Scanning Electron Microscope (FESEM) tests, to study the microstructure development of the cement mortar. FESEM tests were conducted by using JEOL JSM-670-1F equipment.

### III. RESULT AND DISCUSSION

**Workability of fresh mortar**

The workability of cement mortar are important to make sure that the water provide for the cement mortar hydration were sufficient to form calcium-silicate-hydrate (CSH) gel that can contributed to the strength performance of the matrix and the other hand to make sure the composites are easy to work on. The workability test of the cement mortar were conducted by following ASTM C230. Figure 3 shows the workability of cement mortar for conventional mortar and CNC cement mortar by using four types of different water/cement (w/c) ratio of 0.475, 0.50, 0.55 and 0.6. This range of w/c were chosen starting from 0.475 are due to the optimum limit given in ASTM C230 were started with 0.475. The w/c ratio used throughout this study were decided after four different types of w/c ratio were tested to fulfilled the requirement of flow table given in ASTM C230 which in between 110-115mm. When addition of the CNC liquid suspension in cement mortar mixture, the workability of the fresh mortar shows no significant
change compared to the conventional mortar. This is because of the amount of CNC liquid suspension is too small to affect the workability of the cement matrix. However, the amount of w/c ratio suggested by ASTM C230 which is 0.475 was not fully satisfied the flow table requirement. Thus, the higher amount of w/c ratio were tested and shows that, with 0.5 w/c ratio, the flow of the mortar are suitable to be used throughout the whole study with or without CNC additions.

There were several factors that need to be consider before deciding the best w/c ratio of the mortar matrix. The drying process of aggregates before apply in the mortar mix were important, this to make sure the aggregates were not over dried which can cause the absorption of water during mixing process. In this study, the aggregates used during the study were consists of two types fine aggregates which are 20-30 sand (850-600µm) and graded sand (600-150µm). Graded sand are consists of small particles sand which the concept of “the smaller the particles the larger the surface area” applied. With the larger surface area contact with water, the more the water being absorb by the aggregates. This findings also supported by [10] and [11] which they found that, the water provide during the mixing process have three different roles, which are free layer water, adsorpted layer water and filling water. The role of free layer water and filling water normally don not affect the workability of mixes, however, the adsorpted water were effected by larger surface area of the sand.

**Hardened properties of cement mortar**

Compressive strength known as the most important parameter that need to be determined in hardened cement composites specimens. Compressive strength data can be used to support other parameters such as density and ultrasonic pulse velocity (UPV) parameters. Normally, before the compressive strength were done on each samples, the samples will go through density and UPV test in order to study the relationship between the compressive strength development with the density of the structure.

In this paper, this three parameters were discuss and the relationship between it were found before and after the addition of CNC liquid suspension in the cement composites. The observation on the density and UPV were observed and the data were presented in Table 1. Based on the observation, the study on the density and UPV tests shows a definitely different pattern from the current principal which found that the increase of the density will increases the UPV value. However, in Table 1 shows that, with the increasing of CNC content the density of the cement mortar remain the same but increasing value of UPV.

This phenomenon happened due to the CNC particles that been added to the mortar composites are small and insignificant which does not affect the density or weight of the cement mortar yet increases the UPV value of the composites.

This phenomenon happened due to the same finding found by [11] and [12] which discovered that, with the addition of CNC into cement mortar structures, caused the increment of degree of hydration at the same time increase the formation of CSH gel. The good formation of the CSH gel after the addition of CNC into the mortar matrix, happened to positively improve the UPV value of the composites which resulting the dense. Figure 4 shows the comparison between cement mortar with and without addition of CNC. After the addition of CNC, the cement composites become denser with the formation of CSH gel and with the CNC nano-fibres filled in the gap in between the mortar matrix structure like appeared in Figure 4 (b). Unlike, Figure 4(a) which a gap shows in between the formation of ettringite which happened to be a micro cracks. The micro-cracks seems to become a weakness to the conventional cement mortar by decreases the strength of the composites.

### Table 1: The effect of CNC addition to cement mortar density at 28 days

<table>
<thead>
<tr>
<th>CNC content (%)</th>
<th>Density (kg/m³)</th>
<th>UPV (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2200</td>
<td>4.00</td>
</tr>
<tr>
<td>0.2</td>
<td>2200</td>
<td>4.24</td>
</tr>
<tr>
<td>0.4</td>
<td>2200</td>
<td>4.29</td>
</tr>
<tr>
<td>0.6</td>
<td>2224</td>
<td>4.31</td>
</tr>
</tbody>
</table>

Even more, the reasons of changing value of w/c might be effected by the CNC solution added during the mix. However, this study shows that, the workability of the mixes were not changes significantly after addition of different volume percentage of CNC solutions. This might due to the amount added are too small and not significant till can be effected the workability. Due to stated reasons, the w/c ratio used on this study was a little bit higher than the suggested in ASTM standard, due to materials used during the mixing process.
The basic principal of cement composites strength comes when there were improvement in CSH formation in cement matrix, the strength of the structure also increases. This phenomenon occurred because of the formation of CSH gel in cement mortar filled in the porous structure caused by uniform dispersion of aggregates and cement particles. Furthermore, the small particles of CNC reduced the inter-fibre spacing which resulting the good bonding between the CNC and the cement matrix which enhanced the composites strength [13].

Hence, with the addition of CNC into cement composites were positively developed a good bonding between the CNC and cement particles itself.

**CONCLUSION**

The following conclusion can be drawn from this study:

a) The addition of the CNC liquid suspension will not affect the existing mix design of the cement mortar. Even though, the CNC additive is in liquid form, the amount added were insignificant that affected the workability of the mortar matrix.

b) The formation of CSH gel seem to be more aggressive with the CNC appearance on the mortar structure. This formation caused the improvement in composites strength 40-45% higher than the conventional cement composites.

c) The increasing in strength of the cement mortar found to be positively developed after the addition of CNC into the cementitious composites. The existing shapes of CNC which look alike a size of nano-needle fiber assist the mortar structure to sustain more load by performed as bridging agents that holds the mortar matrix together.

d) This is good for the application of the high rise building materials, which demand the high strength cement composites at the same time lightweight.

Furthermore, the behaviour of the CNC into the cement pastes need to study more details in the future works. Since the particle size that involved in this study are nano particles which need more study on microstructure part to understand more the properties that CNC contain that can indicate the positive developments in cementitious composites properties.

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