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Characteristics of Nanomaterials Based on Waste Paper with Variations in Heating Temperature and NaOH Concentration

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Abstract

Cementitious materials have been attempted to achieve more environmentally friendly construction materials. Nanomaterials with smaller particle sizes than cement can enhance the hydration gel structure. This report presents the processing of prepared waste paper into nanomaterials as raw materials available in abundant resources and supports the waste recycling process. Materials were processed by alkaline treatment using 5, 10 and 15 % NaOH solutions and 2 % NaClO at heating temperatures of 100, 125 and 150 °C. Testing the characteristics of the materials aims to determine the effect of heating temperature and concentration of NaOH used in the processing of nanomaterials. Based on the XRD test results, the use of lower temperatures showed that the amorphous phase, which is the main factor in the level of reactivity of the materials, tends to increase with increasing NaOH concentration. SEM morphology analysis showed that lower heating temperature was more effective in removing lignin content after alkaline treatment. The lignin content that can cause weathering needs to be removed and achieve maximum effect in bleaching nanomaterials based on waste paper. The particle size distribution results of nanomaterials were obtained with a size of 255-513 nm. Nanomaterials prepared from recycled materials are attracting interest as a new binder in nanocomposites.

Keywords: Nanomaterials, Cementitious materials, Waste paper, Alkaline treatment

Introduction

Technological developments have encouraged progress in the industrial sectors. One of them is the construction industry which has various challenges, such as developing materials that must be innovative, energy-efficient, low cost, and environmentally friendly [1]. Population growth and infrastructure development cause the demand for cement and concrete to increase. Portland cement is the primary adhesive in the manufacture of concrete. The production of 1 ton of Portland cement requires 1, 5 tons of raw materials and releases about 1 ton of CO_2 for the manufacture of every ton of Portland cement [2]. The industrial sector generally requires a stronger building structure, higher durability, and easily renewable building materials amid sustainability concerns. The use of cementitious materials and improving the performance of concrete also have significant environmental benefits. These characteristics of pure cellulose have attracted attention as cementitious materials due to their excellent mechanical properties, high tensile strength, low density, and abundant resources [3]. In composite mixtures, the addition of nanocellulose has been shown to alter rheology, bond time, and mechanical properties, as well as compressive strength and stiffness. This mechanism provides a new ability to optimize the hydration reaction kinetics, resulting in better strength cement-based materials [4].

Nanomaterials are nano-sized materials with particle sizes less than 500 nm [5]. Nanomaterials are being developed as binders with smaller particle sizes than cement particles by improving the hydration gel to produce a denser structure [6]. The high surface area of the nano-sized particles can significantly increase the chemical reaction to accelerate the hydration reaction. The formation of nanotechnology consists of 2 methods, namely the top-down and bottom-up approaches [7]. The top-down approach makes large particles into smaller particles reduce. Waste paper is one of the materials that can be used in the manufacture of nanomaterials. In addition, cellulose waste paper into concrete at a certain percentage can improve thermal insulation properties and produce lightweight and insulated building materials [8].

Water absorption and fire resistance of concrete using waste paper as a building material is quite high and increases with the increasing use of waste paper [9].

Paper recycling has been carried out around 60 - 80 % in many countries. Waste paper can be processed into pulp before being mixed with other materials. The study reviewed the use of waste paper as a partial substitute for cement in composite mixtures. Then the characteristics of the composite using a mixture of waste paper were analyzed [10]. Waste paper is obtained from various sources such as offices, schools, and newspapers. The cut paper is then soaked in water for 3 days, and then the pulp is filtered to avoid excessive water content on the paper. After that, the waste paper is ready to be drily milled using a grinder. The increasing percentage of used waste paper causes a decrease in compressive strength. In general, the waste paper has a high absorption capacity to significantly reduce the composite density due to cavities and pore structures. The waste paper prepared into nano cellulose with alkaline solution treatment has been investigated [11]. The alkaline treatment method used is heating NaOH and $NaClO_2$, each solution for 2 h at 125 °C. The results show alkaline treatment has succeeded in removing the lignin and hemicellulose content. Research related to waste paper processing for nano-cellulose extraction has also been carried out by heating methods using alkaline solutions [12]. The waste paper used in this study was sourced from old newspapers and heated for more than 12 h, where distilled water was added periodically. The slurry was reheated and treated with 5 % NaOH and 2 % NaClO solution. The pulp is then filtered and washed with distilled water until it reaches a neutral pH. The test results of Transmission Electron Microscopy (TEM) images show that the dimensions of the resulting nano cellulose range from 100 - 300 nm.

Alkaline treatment on the properties of bleached softwood kraft pulp using NaOH at different concentrations has been investigated. The results of the XRD test showed that the crystallinity of cellulose decreased with increasing NaOH concentration. Cellulose I shifts to cellulose II. The shift can occur especially at higher NaOH concentrations, which are more than 9 %. The amorphous region displacement transformation was only seen at 12 % NaOH concentration, and this indicates that the higher the concentration of NaOH, the more dominant the amorphous structure [13]. Sodium hydroxide (NaOH) is a solid alkali in a crystalline solid, also known as caustic soda. NaOH in the heating of cellulose serves to reactivate the sample and release the ink on the paper. NaOH can penetrate the amorphous area of cellulose in the bleaching and then destroy the crystalline region [14]. Sodium hypochlorite (NaClO) is a chlorine compound often used as a disinfectant or bleaching agent in recycling waste paper to achieve a maximum effect. The use of NaClO to bleach chemical pulp is to act by destroying the phenolic groups and carbon double bonds contained therein [15].

Based on the description above, previous research has carried out processing waste paper recycling and applications in the construction industry. Then the use of NaOH with a higher concentration can increase the structure of amorphous materials. Therefore, this study aims to determine how the effect of heating temperature and NaOH concentration used in the waste paper treatment process on the characteristics of nanomaterials. The scope of the research is to analyze the characteristics of nanomaterials processed with different alkaline treatments.

Materials and methods

This study uses an experimental method. The materials used in this study include used paper from the office with the type of HVS 70/80 gsm paper. Then solid NaOH with 99 % purity, NaClO solution, and distilled water.

Extraction of cellulose from waste paper

The method used is 20 g of used paper cut into small pieces to facilitate heating the sample later. The remnants of the former clips and the like are cleaned from the paper to affect the paper recycling process. Furthermore, the scraps of waste paper are stored in water for 3 days at room temperature to encourage the decomposition of the paper into a paste-like shape. Then the sample was drained and continued with milling for 30 min. After the pulp is formed, the waste paper uses 800 mL of NaOH solution with various concentrations of 5, 10 and 15 % for 2 h with constant stirring. Samples were heated at 100, 125, and 150 °C and mixed homogeneously until a green mixture was obtained. After using NaOH solution, they are followed by heating using 800 mL of 2 % NaClO solution. Stirring was carried out continuously for 2 h. After the heating process, the next step is to wash the sample using distilled water until the sample is clean white and the pH is neutral. The next stage of treatment is drying. The sample was ready to be mechanically ground dry for 30 min and continued with the sonication process for 15 min. The next step is a sample characterization test in the form of Particle Size Analysis (PSA), X-Ray

Diffraction (XRD), Scanning Electron Microscope (SEM), and Energy Dispersive X-ray Spectroscopy (EDX). A comparison of characteristics will be carried out for all types of samples treated with Ordinary Portland Cement.

Results and discussion

XRD analysis

XRD aims to analyze the level of crystallinity of the material structure. X-Ray Diffraction (XRD) testing is done by diffracting light through a crystal slit. The results of the XRD test with variations in synthesis heating temperature and NaOH concentration as shown in **Figure 1**.

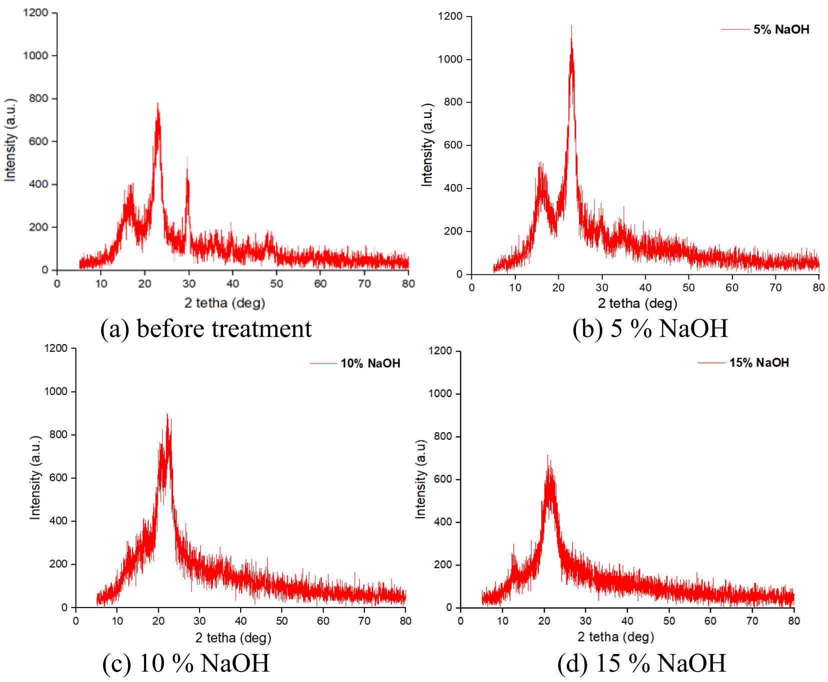


Figure 1 XRD pattern of treated materials in heating temperatures 100 °C with (a) before treatment (b) 5 % NaOH, (c) 10 % NaOH, and (d) 15 % NaOH.

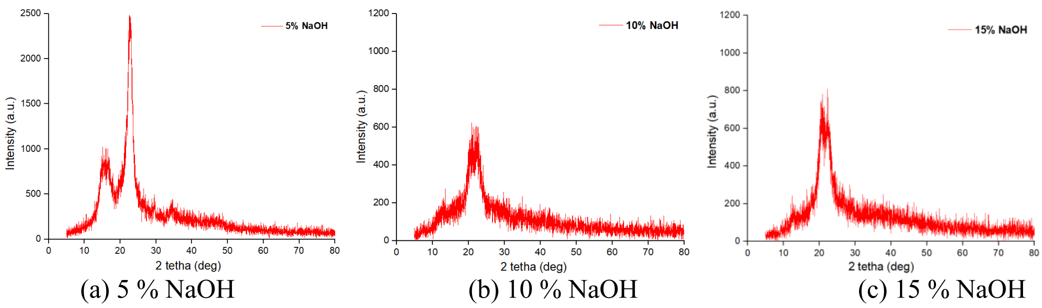
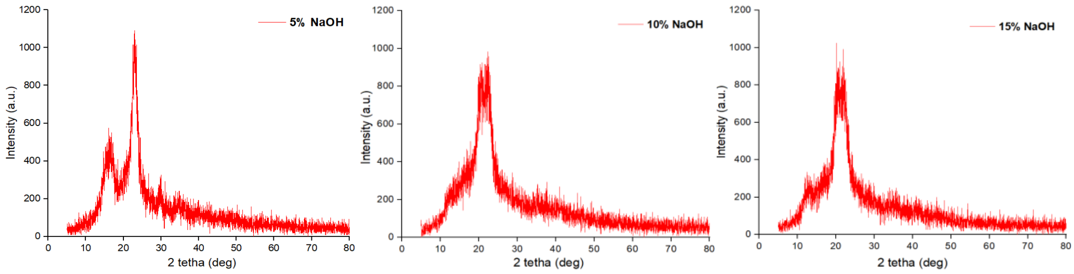


Figure 2 XRD pattern of treated materials in heating temperature 125 °C with (a) 5 % NaOH, (b) 10 % NaOH, and (c) 15 % NaOH.



(a) 5 % NaOH (b) 10 % NaOH (c) 15 % NaOH

Figure 3 XRD pattern of treated materials in heating temperature 150 °C with (a) 5 % NaOH, (b) 10 % NaOH, and (c) 15 % NaOH.

The material with variations in temperature and NaOH concentration used in the treatment process produces different diffraction patterns. Before the sample was treated, the waste paper showed a diffraction pattern with several high and sharp peaks. After the treatment process with 5 % NaOH concentration, there was a change, the sharp diffraction peak became less, while on heating at 10 % NaOH concentration, the diffraction peaks converge and widen, resulting in a reduction in the crystalline phase and an increase in the amorphous phase of the material. The following diffraction patterns with a heating temperature of 125 °C and variations in NaOH concentration are shown in **Figure 2**, and diffraction patterns with a heating temperature of 150 °C are shown in **Figure 3**. Based on the diffractogram pattern of the material with variations in the heating temperature used, there was no significant change. It was only that the heating temperature showed that the intensity seemed to increase slightly with an increase in temperature. The sharp peak pattern indicates that the sample has a semi-crystalline structure, inhibiting the amorphous phase formation due to impurities. The crystalline structure is less reactive to other materials so that the resulting structural characteristics are not good. The following is the XRD of the Ordinary Portland Cement (OPC) diffraction pattern shown in **Figure 4**.

When compared with the XRD test results of cement, it was seen that the cement has amorphous crystalline characteristics, which is characterized by the number of several high sharp peaks in the diffractogram pattern. The increased crystalline elements can cause this characteristic due to poor material storage processes. Besides CaO, amorphous silica also dominates to play a role in continuing the hydration process of the mixture to increase the strength of the structure. The amorphous percentage can be calculated using the area method [16]. From this equation, the degree of crystallinity can be calculated using the area of the fraction then obtained the amorphous phase of the material. The area of crystalline and amorphous fractions can be obtained from the origin software. The crystal area fraction value is the total number of crystal fraction area values. The following is the percentage value of the material structure with variations in heating temperature and NaOH concentration shown in **Table 1**.

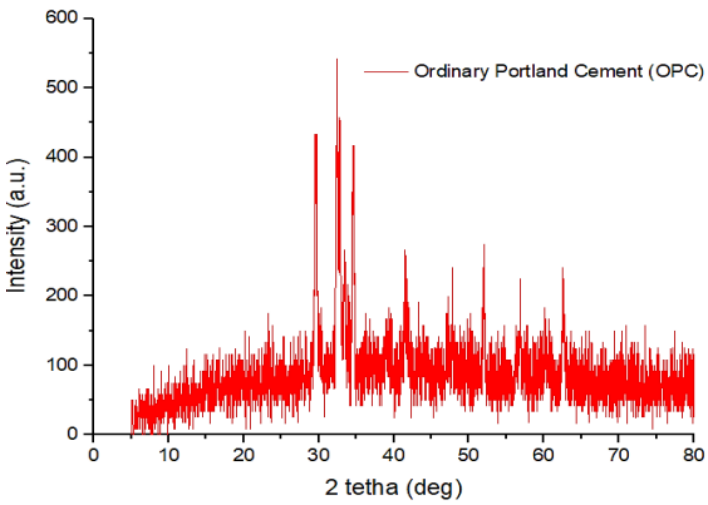


Figure 4 XRD patterns of Ordinary Portland Cement.

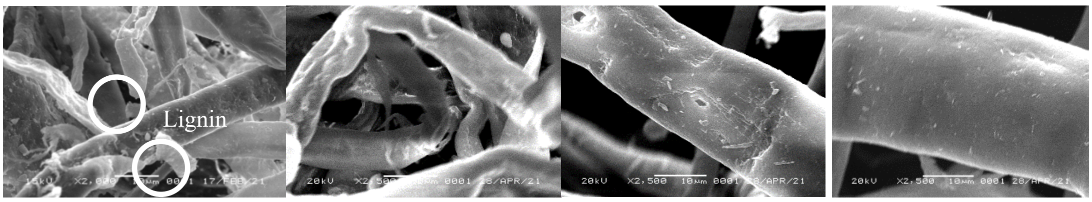
Table 1 Percentage of amorphous structure nanomaterials prepared from waste paper.

Amorphous structure (%)			
Concentration of NaOH	**Heating temperature**		
	100 °C	**125 °C**	**150 °C**
5 %	65.9	60.8	63.5
10 %	78.3	80.6	77.9
15 %	79.3	78.6	77.5

Based on the percentage of amorphous material, the lowest rate is at a concentration of 5 % NaOH 125 °C with an amorphous structure value of 60.8%. The higher content of amorphous material is the concentration of NaOH 10 and 15 %. Meanwhile, Ordinary Portland Cement (OPC) contains an amorphous structure of 52 %. The reactivity level of cement is different from that of the treated waste paper. The dominating calcium element in cement will be easily reactive if it has a crystalline structure. The amorphous structure is more reactive than the crystalline structure due to more significant movement and the location of adjacent atoms so that it can play a role in the strength of the resulting structure [17]. The percentage of amorphous material is an essential factor to see the adhesion of the material to other materials so that it will affect the strength of the composite.

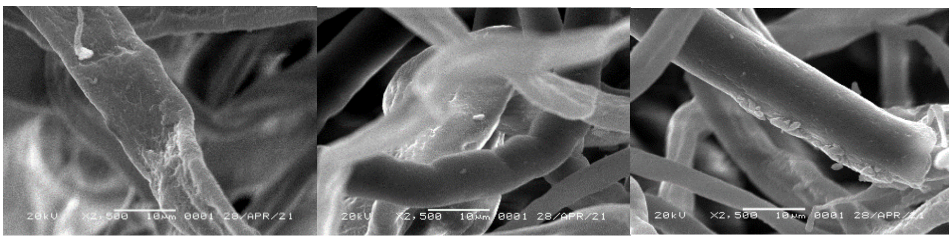
SEM-EDX analysis

SEM testing aims to determine the surface morphology by scanning it using an electron beam. The following are the SEM morphology of nanomaterials prepared from waste paper with variations in heating temperature and NaOH concentration shown in **Figures 5 - 7**. The results of SEM morphology showed that the waste paper before the treatment process still contained lignin characterized by a white structure attached to the cellulose. Based on the results, the lignin content begins to disappear after the treatment process on the waste paper materials. Lignin is a natural polymer found in plants, has a brittle nature, so that the process of using alkaline treatment helps remove the lignin content in the sample. Therefore the structure becomes stronger and cleaner.



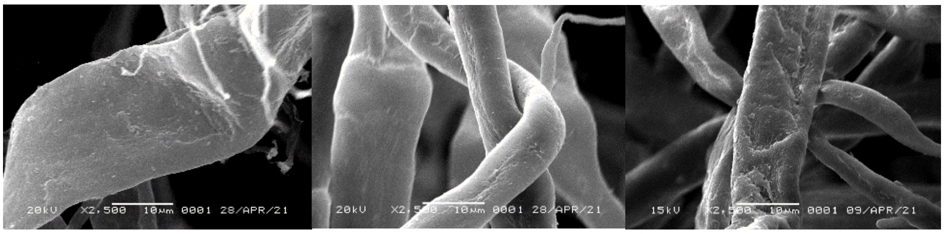
(a) before treatment (b) 5% NaOH (c) 10% NaOH (d) 15% NaOH

Figure 5 SEM images of treated waste paper in heating temperature 100 °C with (a) before treatment (b) 5 % NaOH, (c) 10 % NaOH, and (d) 15 % NaOH.



(a) 5 % NaOH (b) 10 % NaOH (c) 15 % NaOH

Figure 6 SEM images of treated waste paper in heating temperature 125 °C with (a) 5 % NaOH, (b) 10 % NaOH, and (c) 15 % NaOH.



(a) 5% NaOH (b) 10% NaOH (c) 15% NaOH

Figure 7 SEM images of treated waste paper in heating temperature 150 °C with (a) 5 % NaOH, (b) 10 % NaOH, and (c) 15 % NaOH.

Based on the surface morphology image results with a photo magnification of 2,000 - 2,500x, when heating using a 15 % NaOH solution, the structure is cleaner when compared to samples with 5 and 10 % NaOH solutions. The results related to the role of NaOH in the synthesis process, which functions to dissolve impurities in cellulose. Meanwhile, if viewed from the change in heating temperature used when the heating temperature becomes 150 °C, the structure looked more brittle. When the dissolution process uses low temperatures, the cellulose chains will more easily attract hydrated NaOH. This process can break the hydrogen bonds between the cellulose chains, eliminating the lignin and hemicellulose content. This showed that heating with a lower temperature produces have better characteristics. The following results from the EDX test, which aims to determine the mineral composition in the material with variations in heating temperature, are shown in **Tables 2 - 4**.

Table 2 Mineral composition treated waste paper at 100 °C with various concentrations of NaOH.

	Percentage (%)		
Composition	**Concentrations of NaOH**		
	5 %	**10 %**	**15 %**
CaO	54.96	23.44	23.55
SiO_2	12.49	13.30	25.48
Al_2O_3	18.99	21.04	25.36
MgO	2.80	3.30	1.22
FeO	10.76	38.92	24.39

Table 3 Mineral composition treated waste paper at 125 °C with various concentrations of NaOH.

	Percentage (%)		
Composition	**Concentrations of NaOH**		
	5 %	**10 %**	**15 %**
CaO	71.56	33.83	51.90
SiO_2	3.83	9.16	-
$Al2O_3$	16.59	10.61	47.19
MgO	8.02	9.03	0.19
FeO	-	37.37	-

Table 4 Mineral composition treated waste paper at 150 °C with various concentrations of NaOH.

Composition	**Percentage (%)**		
	Concentrations of NaOH		
	5 %	**10 %**	**15 %**
CaO	75.59	30.54	21,93
SiO_2	7.44	17.11	11,26
Al_2O_3	10.20	1.41	-
MgO	2.15	8.64	6,72
FeO	4.42	22.31	9,75

Based on the test results of the mineral composition of the nanomaterials prepared from waste paper, the samples processed using 5 % NaOH solution alkaline treatment had SiO_2 content below 10 %, CaO content was relatively high above 50 %, and Al_2O_3 ranged from 10 - 18 %. The chemical activity of the mixture in cement depends on the content of lime (CaO), silica (SiO_2), and alumina (Al_2O_3), which are the main essential compounds required for cement hydration to increase structural strength. A high enough CaO content can increase the excessive heat of hydration to cause cracks in the structure. The mineral composition of materials with the higher concentration of NaOH used, the SiO_2 content also increases. The results also show that the percentage of amorphous material increases with the increasing concentration of NaOH used. The mineral composition of the material by heating using 15 % NaOH at a heating temperature of 100 °C has a SiO_2 content that is greater than heating with 5 and 10 % NaOH concentrations. The following is the surface morphology of the OPC with a photo magnification of 2,000x, shown in **Figure 8**.

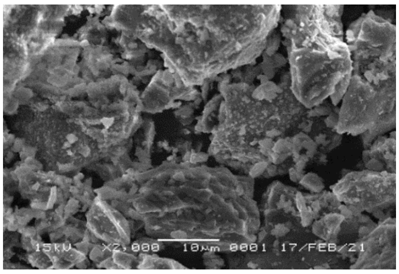


Figure 8 SEM images Ordinary Portland Cement (OPC).

Based on the morphology of the SEM Ordinary Portland Cement (OPC), there is an agglomeration of particles indicated from the XRD test results of the previous material that the amorphous structure of the material is less dominant. The process of storing cement material can also affect this. Agglomeration can be caused by the effects of air and materials becoming less reactive. OPC mineral composition test results are shown in **Table 5**.

Table 5 Composition minerals of OPC.

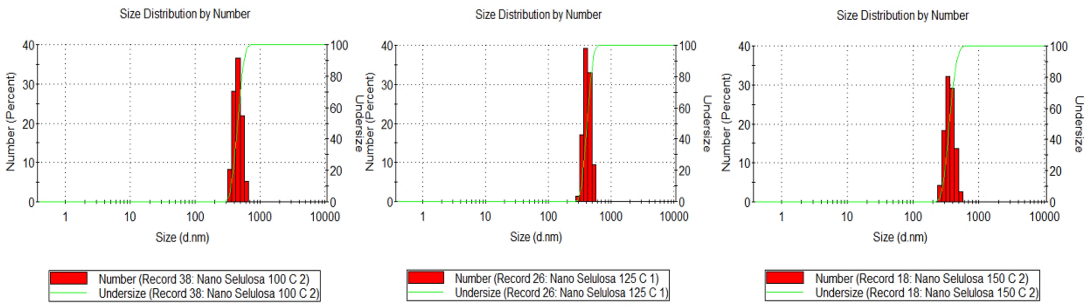
Composition	**Percentage (%)**
CaO	60.09
SiO_2	16.84
Al_2O_3	5.16
Fe_2O_3	2.73
MgO	3.20
TiO_2	0.25
MnO	0.05

Based on the results of testing the mineral composition of OPC that the main content consists of CaO, SiO_2, and Al_2O_3, nanomaterials made from waste paper have characteristics similar to cement. The results obtained are close to the results of the mineral composition test in research related to experimental investigations of the use of waste paper in the manufacture of concrete [18]. Waste paper contains 40 % CaO, 9.6 % SiO_2, 6.3 % Al_2O_3, 3.34 % MgO and Ordinary Portland Cement containing 67 % CaO, 17 % SiO_2, 50 % Al_2O_3 and 4 % MgO.

PSA analysis

Particle size analysis (PSA) testing aims to determine the particle size distribution of the materials. Smaller particle sizes can change the characteristics of the resulting structure to increase the strength of the structure. The distribution results of the particle size of the material with variations in heating temperatures at the synthesis process are shown in **Figure 9** and **Table 6**.

The particle size distribution results with variations in heating temperature obtained particle sizes measuring 255 - 513 nm. The heating temperature of the material affects the particle size results. The higher the temperature used in the treatment process, the smaller particles dominate. Nano-sized materials have better reactivity than micro-sized materials due to an increase in the surface area of the material at the nanoscale. As the surface area increases compared to the unit mass of the material, a large amount of material can come into contact with the surrounding material, thus affecting the reactivity of the materials. Based on the research in manufacturing silver nanoparticles using variations in heating temperatures, the particle size decreases by increasing reactive temperature [19]. Based on the results on the effect of the use of heating temperature during the treatment process, larger particle size dominates at the use of lower temperatures. The following is the result of the OPC particle size distribution shown in **Figure 10**.



(a)100 °C (b) 125 °C (c) 150 °C

Figure 9 Distribution of particle size nanomaterials with 5 % NaOH at heating temperatures of (a) 100 °C, (b) 125 °C, and (c) 150 °C.

Table 6 Particle size distribution nanomaterials based on a waste paper.

Percentage by number (%)			
Size (d.nm)	**Heating temperatures**		
	100 °C	**125 °C**	**150 °C**
255	0	0	4.2
295.3	0	1.4	18.2
342	8.2	17	32.1
396.1	28.1	39.3	29.1
458.7	36.6	33	13.7
513.2	21.9	9.3	2.6

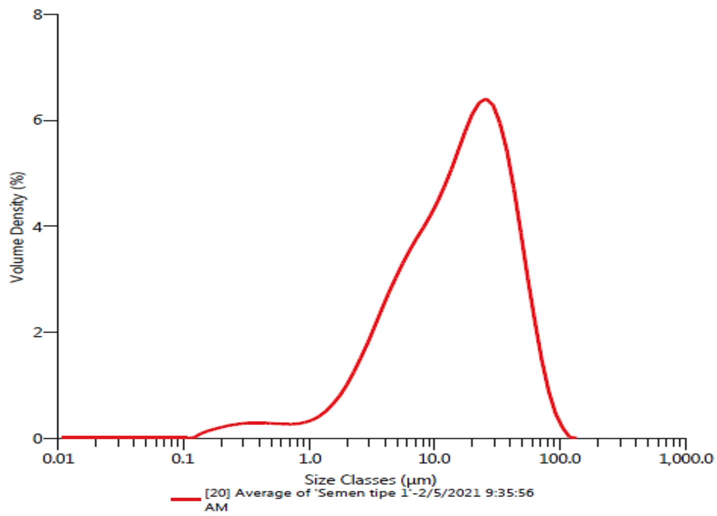


Figure 10 Distribution of particle size OPC.

The cement particle size distribution test results show that 60 % are below 30 μm in size. The fineness of Portland cement is an essential factor affecting the reaction rate between cement particles and water. The finer the Portland cement particles, the faster the hydration reaction of the cement because hydration starts from the surface of the particles. The total surface area in contact with water will be greater with a smaller cement particle size. However, if the cement particles are too small, they can react efficiently with water and calcium dioxide in the air. If the cement is very fine, it may shrink significantly during the setting process.

Conclusions

Based on the XRD test results, the percentage of amorphous material increased with the higher the percentage of NaOH concentration. In general, the waste paper contains 3 main ingredients, namely cellulose, hemicellulose, and lignin. Lower lignin content will improve the cellulose produced because lignin is brittle and can undergo weathering. The percentage of amorphous material tends to decrease with higher heating temperatures. This decrease could be because the high temperature can degrade the cellulose structure and become less effective in removing lignin. SEM morphology results showed that the role of NaOH solution in the treatment action was to dissolve impurities in cellulose. After going through the processing process, the mineral content of paper-based nanomaterials is almost the same as cement, namely the use of 15 % NaOH concentration with a heating temperature of 100 °C. Lower heating temperature and higher NaOH concentration resulted in better characteristics than the other variants. Nanomaterials based on waste paper have the possibility of being used in nanocomposites with enhanced properties. Based on the research, the processing of materials with other concentrations of NaOH can be investigated further to determine different materials characteristics.

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