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Enhanced swelling hydrogel of cellulose by adding fly ash

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Abstract

Coal combustion as a source of steam power generation produces waste in the form of fly ash, which is an environmental pollutant. Fly ash's properties are influenced by its mineral concentration, which implies that it differs significantly depending on the coal source. In this work, an environment friendly hydrogel is made from cellulose and fly ash to utilize coal waste. Environment-friendly hydrogel is used in various fields of science, such as health and agriculture. The preparation process involves two cellulose derivatives, Sodium Carboxymethyl Cellulose (CMC-Na) and Hydroxyethylcellulose (HEC), in 2% distilled water with a 3/1 ratio of CMC-Na/HEC. Citric acid (CA) is a crosslinking agent, and it is commonly used in various cellulose derivatives because it has non-toxic properties. The polymerization occurs during heating in an oven at 80°C for 8 hours. The percentage swelling ratio and FTIR measurements investigate the addition of CA variation at the range of 1.75%-5% and the variation of adding silica-based fly ash such as sodium silicate and nanosilica. The results showed that the best percentage swelling ratio with the lowest CA content and 5% nanosilica gave the highest swelling ratio at 5800%. Adding silica-based fly ash material affects the swelling ratio of the hydrogel.

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Keywords

Cellulose, Fly ash, Hydrogel, Swelling ratio

Introduction

Population growth and economic development are linearly related to the increasing need for fuel energy sources used for daily needs. Coal is a primary energy source besides petroleum, which is used in the industrial world and power plants. Burning coal as a source of steam power generation produces waste in the form of fly ash (FA), bottom ash (BA), boiler slag, and flue gas desulfurization materials, which are coal combustion products. The increase in coal consumption for energy needs, especially in countries with high coal-based power generation, produces large amounts of fly ash. According to the [1], the global capacity of coal-fired power plants has increased by 11% since 2015, with coal consumption and capacity worldwide reaching a record high in 2023. Flake ash can accumulate in landfills without proper management and pollute the environment. The characteristics of fly ash are influenced by its mineral concentration, which means that fly ash varies significantly depending on the coal source. From a chemical perspective, FA mostly comprises oxides of Si, Al, Fe, Ca, and other inorganic elements. Therefore, FA thrown away can pollute the environment and even impact air quality because its fine particles can be inhaled and cause respiratory problems. Research indicates that the components found in FA can be utilized in the construction sector as a geopolymer and concrete [2]. In addition, it is also used in agriculture to improve soil quality so that fertilizer use is reduced [3] and can be used as an adsorbent for soil processing and dye contamination control [4,5,6]. Using fly ash in various environmentally friendly applications is very important to create economic circulation and reduce the environmental impact caused by coal combustion.

FA has characteristics that make it potentially used as an additional material in making hydrogels. Hydrogel is a polymer material that can absorb and store water at least 10 times higher than its initial one. Hydrogel has a three-dimensional structure that allowhy it to bind water efficiently and release it slowly as needed. Therefore, hydrogel is often used in products that require high absorbency properties, such as agriculture applications, to increase water use efficiency. One major problem agriculture faces is water management, especially on land with a low water capacity. Hydrogel can function as a planting medium that can increase water retention in the soil so that plants can grow more optimally, even in conditions of limited water availability.

Cellulose is a natural polymer found in plants and has great potential to be developed as a hydrogel material. The selection of cellulose as a basic material for hydrogel is not only environmentally friendly but also economical and sustainable [7]. This study used cellulose derivatives such as sodium carboxymethyl cellulose (CMC-Na) and hydroxyethyl cellulose (HEC), which are very potential basic materials for making hydrogels. Both have hydrophilic properties, biodegradability, and the ability to form gels that can be adjusted for various applications. The selection of polymers is very influential because substituting hydroxyl groups with carboxyl and hydroxyl groups in cellulose significantly changes the properties of cellulose, including increasing swelling in water to solubility. Previous studies showed the ability of water uptake in hydrogels using cellulose derivatives in the form of CMC-Na / HEC compared to Methyl Cellulose (MC) and hydroxypropyl cellulose (HPC) [8]. CMC-Na/HEC is used to prevent the formation of intramolecular crosslink that can affect the level of water absorbance. In this study, citric acid (CA) is used as a crosslinker, which is considered to be able to overcome toxicity and has an affordable price. Manufacturing hydrogels based on natural materials, such as cellulose, is increasingly popular because of its environmentally friendly, biocompatible, and biodegradable properties. However, pure cellulose-based hydrogels often have limitations regarding mechanical stability, water storage capacity, and resistance to environmental changes. Therefore, researchers have developed methods to improve the properties of hydrogels by adding additional materials that can improve the material's performance. One approach being studied is the addition of FA processed into sodium silicate (Na_2SiO_3) and nanosilica as reinforcing materials in the manufacture of cellulose-based hydrogels. Cellulose-based hydrogels with fly ash and CA as a crosslinker will be characterized regarding the percentage swelling ratio and FTIR.

With its water-absorbing properties, hydrogel helps maintain soil moisture, reduces irrigation needs, and minimizes the risk of drought in plants. Therefore, the use of hydrogel in agriculture is very relevant, especially for land that has difficulty maintaining sufficient water levels. Making cellulose-based hydrogel using fly ash can be a smart solution to overcome the problem of water resistance in soil with low capacity while also contributing to more environmentally friendly coal waste management.

Method

Materials

CMC-Na (MW 700 kDa, DS 0.9 viscosity 3400 cm/s) and HEC (MW 250 kDa MS 2, viscosity 80–125 cm/s) and CA purchased from Sigma-Aldrich. FA from PLTU Paiton, Indonesia.

Preparation of Na_2SiO_3 and Nanosilica

Sodium silicate (Na_2SiO_3) was prepared according to the method [9] with some modifications. About 40 g of NaOH was added to 260 ml of Aquadest. The mixture was stirred perfectly using a magnetic stirrer at a speed of 450 rpm and a temperature of 90°C. FA were added as much as 40 grams slowly. Dissolving FA in sodium hydroxide solution was carried out for 120 minutes at a temperature of 90°C. After that, the solution was filtered from residual impurities and the liquid was taken as a sodium silicate solution. Concentrated sodium silicate solution, then diluted 200x by Aquadest.

For making the nanosilica, concentrated of Na_2SiO_3 solution is diluted twice for 2x as a primary sodium silicate (P-Na_2SiO_3) and 4x as a secondary sodium silicate (S-Na_2SiO_3). In order to strengthen the silica structure utilizing the Ostwald Ripening [10], a specific amount of P-Na_2SiO_3 : S-Na_2SiO_3 (1:1.25) is added at a specific flow rate, along with 9% sulfuric acid to maintain the pH level. Following three rounds of washing with distilled water, the resulting silica precipitate is oven-dried for twenty-four hours at 100°C.

Hydrogel Grafted of Na_2SiO_3

Hydrogel samples were synthesized by reacting CMC-Na and HEC with CA as the crosslinking agent in 50 ml of aquadest, following the method described by [11,12]. Initially, a polymer concentration of 2% by weight of aquadest was prepared using a 3:1

weight ratio mixture of CMC-Na and HEC. At room temperature, HEC was dissolved in distilled water and stirred gradually until a clear solution was obtained. After that, CMC-Na was added and stirred until a viscous solution was formed and CA was added. Subsequently, varying concentrations of CA (w/w polymer) that presented in the Table 1. were incorporated to evaluate their impact on absorbance strength. To further investigate its effect on absorbance, Na_2SiO_3 and nanosilica were also introduced as additional variables added to the variation of CA concentration of 1.75%. Na_2SiO_3 (0.01 ml) was added to the viscous solution then continuously stirring for 6 hours. The prepared samples were left at 30°C for 24 hours (aging rpocess) and then subjected to cross-linking reaction at 80°C for 24 hours, with periodic monitoring during the process.

Hydrogel Grafted Nanosilica

The preparation of the hydrogel began with dissolving nanonsilica (0.05 g) in distilled water using an ultrasonic method to enhance the dispersion and solubility of nanosilica in the solution. Subsequently, CMC-Na, HEC, and CA were added following the procedure outlined in the previous method.

Characterization

The chemical composition of the hydrogel fiber was examined using a Fourier Transform Infrared (FT-IR) spectrometer (IRSPIRIT-T with QATR-S) with a resolution of 4 cm^{-1}, covering the wavenumber range of 500–4000 cm^{-1}.

Swelling Ratio

Measurements of equilibrium swelling were performed in aquadest for every sample. Weighing the samples before and after submerged in distilled water for roughly 24 hours every two hours to calculate the swelling ratio (SR). Here is the definition of SR:

$$SR\% = (W_t - W_d / W_d) \times 100 \tag{1}$$

where W_t (g) is the weight of the swollen hydrogel at the time, and W_d (g) is the weight of the dried sample.

Results and Discussion

FTIR Result

Table 1. Sample Composition Used for 50 ml of Aquadest

Code	CMC-Na/HEC	CA (%)	Na_2SiO_3 (%)	Nanosilica (%)
A1	3/1	1.75	-	-
A2	3/1	1.75	1	-
A3	3/1	1.75	-	5
A4	3/1	3.5	-	5
A5	3/1	5	-	5

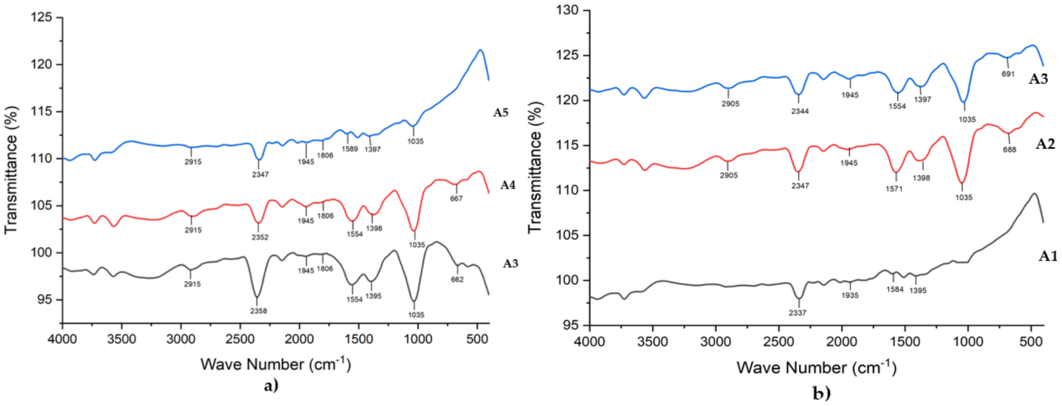

Figure 1. a) FTIR Spectra of %CA Variation, b) FTIR Spectra of Silica Introduction

The FTIR spectrum of CMC-Na/HEC without silica grafting is illustrated in Figure 1. b) sample A1 exhibits broad peaks at 1584 cm⁻¹ and 1395 cm⁻¹, corresponding to the stretching vibration of COO^- and the vibration of CH_2, respectively, as reported by [13]. For cellulose-derived (CMC-Na/HEC), the broad absorption bands characteristic of long-chain linear aliphatic compounds were observed at 2935 cm⁻¹ and 2860 cm⁻¹, followed by peaks in the range of 1470–720 cm⁻¹. The bands around 2900 cm⁻¹ and 1051 cm⁻¹ were attributed to the stretching vibrations of C-H and C-O-C groups, respectively. The band near 1320 cm⁻¹ corresponded to the bending vibrations of -OH groups. Additionally, the prominent bands at 1653 cm⁻¹ and 1423 cm⁻¹ in CMC-Na were associated with the stretching vibrations of -COO groups and their salt forms, confirming the typical absorption properties of carboxymethyl cellulose [11]. A slight shift was observed in the band corresponding to the -OH stretching vibration, which shifted from 3464 cm⁻¹[14]. Furthermore, the strong band at 1035 cm⁻¹ was linked to the stretching vibrations of Si-O-Si [9], indicating that hydrogels containing silica (A2,A3) in Figure 1. b) exhibit additional absorption bands, thereby reflecting a more complex structure.

Figure 1. a) shows the effect of CA crosslinking. Hydrogels of CA crosslinked with CMC-Na and HEC were developed for agricultural applications and the crosslinking mechanism of CA was also proposed by [11]. The possible molecular structure of crosslinked CMC-Na/HEC/Silica is shown in Figure 2. Initially, CA undergoes a condensation reaction upon heating, forming a cyclic anhydride. This cyclic anhydride then reacts with the hydroxyl groups of the cellulose chain to create an ester bond. Following the esterification step, an additional cyclic anhydride is generated during the heating process. This newly formed cyclic anhydride interacts with another hydroxyl group of cellulose, leading to the formation of a second ester bond. Through this process, CA facilitates intermolecular crosslinking via cyclic anhydride interactions between the hydroxyl groups of cellulose, resulting in ester bonds. This is evidenced by the presence of a peak at 1806 cm⁻¹ in the FTIR spectrum, which corresponds to the carbonyl (C=O) group vibration. The increased intensity of this peak at higher concentrations of CA suggests a more pronounced esterification reaction between CA and the hydrogel components [13]. With high CA concentrations, the formation of cyclic anhydrides could occur, which could potentially disrupt the interaction between the

hydroxyl groups of the polymer and the carboxyl groups of the citric acid. This could lead to changes in the morphology and functional properties of the hydrogel. The increase in the intensity of this peak at higher CA concentrations indicates a more pronounced esterification reaction between citric acid and hydrogel components. However, at high CA concentrations, the formation of cyclic anhydrides may occur, which could potentially disrupt the interaction between the hydroxyl groups of the polymer and the carboxyl groups of citric acid [15]. This may lead to changes in the morphology and functional properties of the hydrogel. On the Figure 1. a) A3, A4, A5 show that increasing CA concentration from 1.75% to 5%, the intensity of the peaks 1554 cm^{-1} related to -COO and anhydride groups decreased, indicating stronger crosslinking at A3. This suggests that higher CA concentrations are inversely related to the effectiveness of the crosslinking process.

Effect of Hydrogel Composition on Swelling

During the crosslinking process of CMC-Na/HEC hydrogels, an increase in crosslinking density leads to a reduction in equilibrium water uptake, as confirmed by FTIR analysis. Among the samples, A3 exhibited a higher swelling ratio (%SR) compared to A1 and A2, which can be attributed to the lower degree of crosslinking resulting from the reduced concentration of CA. The swelling behavior is influenced by the introduction of CA, which generates highly hydrophilic carboxylic groups that contribute to the formation of a polyelectrolyte network. Consequently, water uptake increases substantially as these carboxylic groups initially interact with the HEC chains and subsequently integrate into the gel network. Conversely, hydrogels prepared with higher CA concentrations demonstrated a lower %SR due to enhanced crosslinking density and accelerated reaction kinetics. As illustrated in Figure 3, a CA concentration of 1.75% achieved a %SR of approximately 5800%.

Figure 3 illustrates that the incorporation of silica influences the swelling capacity, as indicated by the %SR value. Sample A3, which included nanosilica and the lowest concentration of citric acid (CA), exhibited the highest %SR and superior gel strength compared to Sample A1, which displayed a decrease of %SR after 16 hours of immersion. This reduction in Sample A1 is attributed to its insufficient gel strength, leading to the breakdown and dissolution of the gel in distilled water. These findings align with previous studies, demonstrating that the addition of silica enhances the gel strength of hydrogels. The presence of silica facilitates the formation of denser cross-links, thereby improving the structural integrity of the hydrogel [16,17].

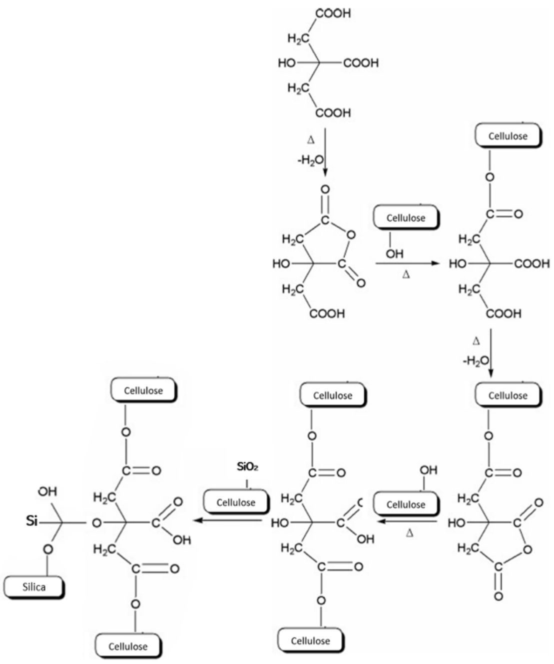

Figure 2. Crosslinking reaction mechanism of CA with cellulose [11] grafted by silica

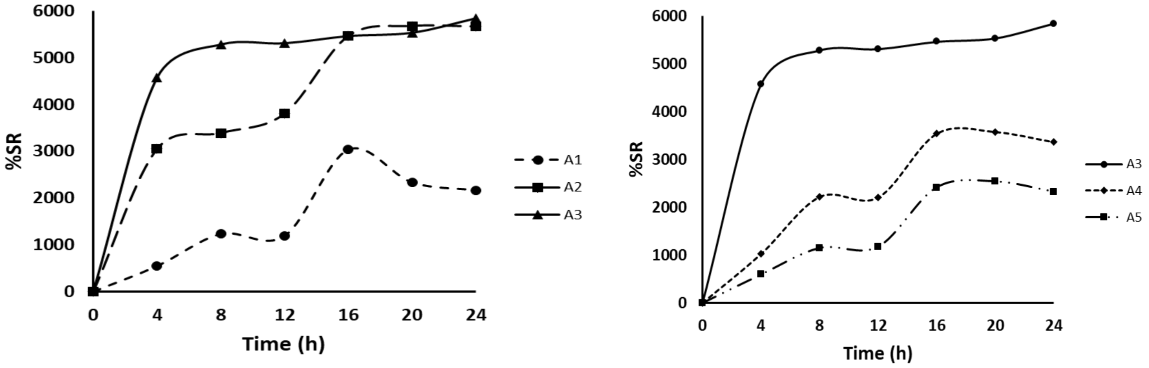

Figure 3. Swelling Ratio Versus Reaction Time of CMC-Na/HEC With Variation of CA Concentration and Introduction of Silica

Conclusion

This study demonstrated that CA can serve as an effective crosslinking agent for CMC-Na/HEC mixtures grafted with silica. The crosslinking reactions within the CMC-Na/HEC system under varying conditions, were analyzed using FTIR spectroscopy. The swelling ratio (%SR), monitored over different reaction times, corroborated the reaction mechanisms identified through FTIR analysis. An optimal swelling degree of 5800%, suitable for practical applications, was achieved at a low CA concentration. The hydrogel synthesized using the method outlined in this study offers significant advantages, including reduced raw material and production costs, as well as the elimination of toxic intermediates during the synthesis process. Future research could focus on the application of these superabsorbent hydrogels in agriculture, where optimizing water usage is critical, especially in regions facing water scarcity.

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