Synthesis and characterization of cellulose-based graft copolymers crosslinked by gamma-irradiation for enhanced oil recovery applications

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Abstract. Cellulose-based polymers have garnered significant attention as potential candidates for use in enhanced oil recovery (EOR). The challenge in the design of EOR polymers is the need for materials with a high low critical solution temperature (LCST) and the ability to withstand harsh environmental conditions. In this study, cellulose-methylcellulose graft copolymers were prepared with different cellulose to methylcellulose weight ratios. The copolymerization was carried out using gamma radiation doses of 5, 15, and 25 kGy, respectively. The LCST of the copolymers were evaluated using differential scanning calorimetry analysis. The effect of salt addition on the LCST of the materials was studied using different phosphate-buffered saline (PBS) concentrations. The results showed that the cellulose monomer concentration increase from 0.1 to 0.5% in 2% methylcellulose dispersed in water reduced the LCST from 59 to 54°C. The hydrophobic nature of cellulose moieties induced the aggregation of the copolymers into core-shell micelles. Besides, higher gamma radiation doses lowered the LCST of the copolymers. The increase in the salt concentration in the PBS medium tended to decrease the LCST due to disrupted hydration structure of the polymer chains. This work revealed that cellulose-methylcellulose copolymers could be used in chemical EOR due to their high phase transition temperatures, preventing pore clogging and enhancing oil production in the producing wells.

1. Introduction
Thermoresponsive polymers are a type of smart material that have been widely developed due to their ability to respond to a change in temperature [1,2]. This property makes them attractive for a wide range of applications, including drug delivery, tissue engineering, and gene delivery [3,4]. These materials are also employed as carriers for radiopharmaceuticals and in radiation sterilization through their interactions with ionizing radiation [5]. Their controllable thermoresponsive properties are promising as the media in various catalytic applications. The catalytic phenomena that occur on the catalyst can be tuned through the reversible network structure of the materials [6]. Some of them are applied for environmental remediation to remove colloidal particles from wastewater [7].

In recent years, research efforts have been devoted to developing polymers for oil recovery applications [8]. Polymer materials for enhanced oil recovery (EOR) techniques are primarily implemented in the oil industry to optimize oil production from current resources [9]. The challenge in the design of EOR polymers is the need for materials with a high low critical solution temperature (LCST) value of above 40°C and the ability to withstand harsh environmental conditions [10]. With relatively high LCST value, the materials injected into a reservoir can effectively sweep and free trapped
oil in the producing well with a maintained solution viscosity, as the polymers undergo a sharp temperature rise inside the reservoir [11]. When the temperature is above the LCST, the polymers will experience a phase transition to a hydrophobic state which can clog the pores and reduce oil uptake [12].

In the search for materials with the desired properties, nanocellulose-based polymers are considered as potential candidates for use in EOR processes. Nanocellulose fibrils containing lignin segment (L-NCF) have shown an ability to form foams and possess excellent stability at bulk and bubble-scale. The L-NCF can move smoothly in porous media without plugging problems caused by the aggregation of the materials [13]. A flooding agent modified nanocellulose exhibits good 1% NaCl brine dispersion, viscoelastic properties, and pronounced shear-thinning effects. The presence of the active groups in their structure promotes microscopic recovery efficiency and emulsifiability of the nanofluid [14]. Marques et al. studied graft copolymers based on carboxymethylcellulose and thermoresponsive polyetheramines with high temperature and salinity self-assembly dependence. The copolymers have a relatively high LCST value of 60°C in saline media and show constant viscosity below their critical point [10]. Our group has also developed cellulose-methylcellulose copolymers using UV radiation to induce the crosslinking of the monomers. The characterization of the materials indicates that the copolymers have LCST range of around 38-59°C, depending on the initial concentration and the salinity of the precursors [15]. The results prompted us to synthesize cellulose-methylcellulose copolymers crosslinked with gamma radiation. The use of gamma-ray radiation is due to its higher penetrability than UV radiation that can effectively induce graft polymerization reactions [16,17].

In the present study, cellulose-methylcellulose copolymers were prepared from bacterial cellulose nanocrystals and methylcellulose monomers using different cellulose to methylcellulose ratios. The copolymerization was carried out with various doses of gamma radiation in different salinity levels of the medium. Fourier transform infrared (FTIR) spectroscopy was employed to confirm the cellulose nanocrystal synthesis. Differential scanning calorimetry (DSC) analysis was used to determine the LCST of the copolymers. To the best of our knowledge, this study is the first to report the grafting of cellulose-methylcellulose copolymers with gamma radiation as a potential candidate for EOR.

2. Materials and method

2.1. Materials
Bacterial cellulose was purchased from a local supplier (West Java, Indonesia). Sodium chloride (NaCl, ≥ 99.5%), potassium chloride (KCl ≥ 99.5%), sodium hydroxide (NaOH, ≥ 99%), disodium hydrogen phosphate (Na₂HPO₄, ≥ 99%), potassium dihydrogen phosphate (KH₂PO₄, ≥ 99.5%), sulfuric acid (H₂SO₄, 97%), and hydrochloric acid (HCl, ≥ 37%) were purchased from Merck. Methylcellulose (Metolose, SM-4000) was purchased from Shin-Etsu Chemical. Distilled water was used throughout the experiments. The sulfuric acid was diluted to a concentration of 65%. A sodium hydroxide solution with a concentration of 1% was prepared before the experiments. Other chemicals were used as received without further purification.

2.2. Synthesis of Cellulose Nanocrystals
The bacterial cellulose was rinsed with distilled water to get rid of impurities. Subsequently, the bacterial cellulose was immersed in 1% NaOH with an initial temperature of 80°C and allowed to settle for 2 h. Afterward, the bacterial cellulose was washed with distilled water and dried. The treatment was carried out to remove any remaining bacterial cells and excess acids in the bacterial cellulose matrix. The dried product was milled and hydrolyzed using 65% H₂SO₄. As much as 10 g bacterial cellulose was treated with 100 mL of 65% H₂SO₄ at a temperature of 45°C for 1 h [18]. The hydrolyzed product was then diluted with 900 mL of cold water at a temperature of 4°C. The resultant product was subsequently vacuum filtered and dried in the oven.

2.3. Preparation of Phosphate Buffered Saline
Three phosphate-buffered saline (PBS) solutions were prepared throughout the experiments: 0.5X PBS, 1X PBS, and 1.5X PBS. The salt concentration in 1X PBS solution is equivalent to the salt concentration in 0.9% NaCl. The 0.5X PBS was made from 68.5 mM NaCl, 1.3 mM KCl, 4.9 mM Na₂HPO₄, and 0.9
mM KH$_2$PO$_4$. The 1X PBS was made from 136.9 mM NaCl, 2.7 mM KCl, 9.9 mM Na$_2$HPO$_4$, and 1.8 mM KH$_2$PO$_4$. The 1.5X PBS was made from 205.3 mM NaCl, 4.0 mM KCl, 14.8 mM Na$_2$HPO$_4$, and 2.6 mM KH$_2$PO$_4$. Hydrochloric acid and sodium hydroxide were used to adjust the pH of the PBS solutions to give a final pH of 7.4.

2.4. Synthesis of Copolymers of Cellulose and Methylcellulose
The as prepared cellulose nanocrystals were suspended in 30 mL water. Three different cellulose nanocrystal suspensions were prepared: 0.1, 0.3, and 0.5%. The suspensions were stirred for 15 minutes at a rotation speed of 1500 rpm. Meanwhile, methylcellulose was dispersed in 20 mL of water, 0.5X PBS, 1X PBS, and 1.5X PBS, respectively, at a temperature of 80°C, resulting in a methylcellulose concentration of 2%. Each cellulose nanocrystal solution was then added to the corresponding methylcellulose solution. Coldwater with a temperature of 4°C was subsequently added to the mixture, reaching a final volume of 100 mL. The mixture was then kept at 4°C for 6 h. Afterward, the cellulose and the methylcellulose copolymerization was performed using gamma radiation at various doses (5, 15, and 25 kGy).

2.5. Material Characterization
FTIR spectra were acquired on an IRPrestige-21Shimadzu. The LCST of the copolymers were determined using DSC at a temperature of 30 to 60°C. The results were verified by visual observation. The high turbidity of the samples hindered the LCST measurements using the spectrophotometric method.

3. Results and discussion
3.1. Fourier Transform Infrared Spectra
The cellulose nanocrystals were prepared from the bacterial cellulose. The FTIR spectra of the cellulose nanocrystals and the methylcellulose are shown in figure 1a and 1b. In the FTIR spectra of the cellulose nanocrystals (Figure 1a), two strong bands observed at 3470 cm$^{-1}$ and 1080 cm$^{-1}$ were assigned to ─OH stretching and C─O─C stretching in anhydroglucose units, respectively. The peaks detected at 2940 cm$^{-1}$ and 1470 cm$^{-1}$ were attributed to C─H stretching of CH$_2$/CH$_3$ and C─H bending vibration of CH$_3$, respectively [19,20]. Similar peaks were observed in the spectra of methylcellulose (Figure 1b). A strong peak observed at 1435 cm$^{-1}$, which corresponds to the C─H bending vibration of CH$_3$, confirms the presence of methyl group in the methylcellulose [21,22].

![FTIR spectra of cellulose nanocrystals (a) and methylcellulose (b).]
3.2. Effect of Nanocrystal Concentrations on the LCST

The cellulose-methylcellulose copolymers were synthesized using different cellulose nanocrystal concentrations (0.1, 0.3, and 0.5%). The copolymerization was carried out with 2% methylcellulose dispersed in water using gamma radiation at a dose of 5 kGy. The relationships between cellulose nanocrystal concentrations and the LCST determined using DSC are shown in Figure 2. The values were compared with the LCST obtained from our previous study employing UV light as the source to initiate the polymerization reaction (Figure 2) [15].

![Figure 2. LCST values of the cellulose-methylcellulose graft copolymers prepared from different cellulose concentrations with gamma or UV irradiation as a polymerization initiator. The values were obtained from Abidin et al. (2017) [15].](image)

The results showed that the cellulose concentration increase contributed to the decrease in the LCST of the copolymer. The LCST decrease was likely due to the increase in the ratio of hydrophobic cellulose monomers to hydrophilic methylcellulose monomers [23,24]. With a higher fraction of the hydrophobic cellulose moieties conjugated, the cellulose-methylcellulose copolymer is more prone to aggregation into core-shell micelles. According to a study conducted by Yang et al., the LCST values of the amphiphilic polymers can be tuned by adjusting the mole ratio of hydrophilic moieties to hydrophobic units. In their study, an increase in the ratio of hydrophobic hydroxybutyl chitosan to hydrophilic deoxycholic acids leads to decreased LCST of the copolymer [25]. In another study on thermoresponsive 2-hydroxy-3-isopropyloxypropyl hydroxyethyl celluloses, the LCST of the polymers decrease from 56.1 to 21.1°C by increasing the ratio of hydrophobic isopropyl glycidil ether to hydrophilic hydroxyethyl cellulose from 2.5 to 4.5 [26].

From figure 2, the LCST values measured from the copolymers synthesized using UV-assisted polymerization were lower than gamma irradiation. The results indicated that the gamma-ray radiation was likely to induce irreversible breakage and cause more severe damage to the cellulose and methylcellulose monomers, which resulted in lower product yields. Gamma radiation is a high energy ionizing radiation that can generate radicals on the main and side chains during polymerization processes. The scission of the monomers may, however reduce polymer molecular weight that results in poor properties of the copolymerization products [27]. In addition, the interactions of gamma rays with polymer materials may cause ionizations that can lead to the formation of ions and produce fast-moving electrons. The irradiation using low-dose Co-60 gamma rays is found to trigger the degradation reactions via oxidations [28].

The LCST of the cellulose-methylcellulose graft copolymers were compared with the LCST of other materials from the literature. The LCST is however comparable to other materials, such as P(OEGMA$_{73}$-co-DEGMA$_{27}$) (59°C) [29], HPC$_{0.6}$-g-POEGMA (62°C) [29], HPC$_{0.6}$-g-P(OEGMA$_{52}$-co-DEGMA$_{48}$) (45°C) [29], POEG3A (60°C) [30], PSSP (60°C) [31], p(NIPAm-DMAa) (55°C) [32] and p(HEMA-co-DMAa) (48°C) [33].
3.3. Effect of Gamma Radiation Doses on the LSCT
The effect of gamma radiation doses on the LCST of the copolymers synthesized from 2% methylcellulose and 0.3% cellulose nanocrystals in 1.5X PBS solvent is depicted in figure 3. The results indicated that the LSCT of the copolymers decreased with the rise of gamma radiation dose during copolymerization. This was likely due to more cellulose and methylcellulose monomers ionized that subsequently crosslinked to form the cellulose-methylcellulose copolymers during copolymerization with the higher dose of gamma radiation. The results agree with a previous study conducted by Naseri et al. on the effects of gamma radiation on the microstructure and crosslink network of (styrene-butadiene rubber (SBR)/ethylene propylene diene monomer) blends in the presence of nanoclay. The study shows that the crosslink density of irradiated samples increased with the increase of absorbed dose [34]. A study on radiation crosslinking of polyurethanes also verifies that the irradiated polyurethanes possess a conjugated structure and can emit fluorescence light. The polyurethanes emit purple color where the intensity of the color amplifies with the increase of the gamma radiation doses. However, too high radiation dose (>100 kGy) may trigger the degradation reaction of the materials that can lead to a significant decrease in the degree of crosslinking [35].

3.4. Effect of Salts on the LCST
The effect of salt addition on the LCST of the copolymers synthesized from 2% methylcellulose and 0.3% cellulose nanocrystals at a gamma radiation dose of 5 kGy is shown in figure 4. The addition of salts is known to affect the phase behavior of polymers due to their tendency to disrupt the hydration structure of polymer chains. The results indicated that the LCST value measured from the cellulose-methylcellulose copolymer prepared using water as the solvent showed a comparable LCST value to the copolymer prepared in 0.5X PBS. The increase of PBS concentration led to the increase of the LCST of the copolymer. This was expected due to the reduced hydrophobicity in the system caused by the increase in the number of ions in the higher PBS concentration. Hydrophobic salts are known to bind to the polymer chains strongly, which can shift the LCST to higher temperatures. On the other hand, hydrophilic salts compete with the polymer chains to interact with water molecules, which results in lower LCST values. The lower LCST value is caused by weaker polymer-water interactions that can reduce the sol-gel transition temperature [36]. PBS solution contains Na\(^+\), K\(^+\), Cl\(^-\), HPO\(_4\)\(^{2-}\), H\(_2\)PO\(_4\)\(^-\) ions that are hydrophilic [37,38]. The findings show that the LCST value of the copolymer can be adjusted by controlling the salinity of the medium.

Zhang et al. studied the influence of salt addition on the LCST of 0.8% water-soluble polymer solutions of N-isopropylacrylamide, hydroxyethyl methacrylate, and acrylamide synthesized by free radical copolymerization. The results show that the addition of small molecules can influence the LCST of the copolymers. In their study, NaCl tends to decrease the LCST, while sodium dodecylbenzenesulfonate increases the LCST [39]. According to a study conducted by Contessi et al.,
the addition of salts into methylcellulose hydrogels lowers the LCST of the hydrogels. In the study, higher PBS and NaCl concentrations produce hydrogels with lower LCST values [40].

**Figure 4.** LCST values of the copolymers prepared from cellulose and methylcellulose monomers with various salt concentrations.

4. Conclusion

In summary, cellulose-methylcellulose graft copolymers were prepared from different cellulose nanocrystal to methylcellulose weight ratios. Gamma radiation at doses of 5, 15, and 15 kGy was used as the polymerization initiator. The increase in the cellulose monomer concentration from 0.1 to 0.5% contributed to the LCST reduction of the copolymers from 59 to 54°C. The formation of copolymers that are more prone to aggregation was caused by the increase in the ratio of hydrophobic cellulose to hydrophilic methylcellulose monomers. The decrease in the LCST of the copolymers from 53 to 51°C was observed in the materials prepared with gamma radiation doses of 5 to 25 kGy. A higher dose of gamma radiation caused more cellulose and methylcellulose fractions crosslinked during copolymerization. The presence of salts in the medium reduced the LCST of the copolymers due to their tendency to disrupt the hydration structure of the polymer chains. The graft cellulose-methylcellulose copolymers may apply in EOR processes that can withstand harsh reservoir conditions and optimize oil production.

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