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KAPPA-CARRAGEENAN AS AN ATTRACTIVE GREEN SUBSTITUTE FOR POLYACRYLAMIDE IN ENHANCED OIL RECOVERY APPLICATIONS

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ABSTRACT

The rapidly growing demand for petroleum resources has become a crucial global problem. Therefore, a more realistic solution is required for oil production. Enhanced oil recovery (EOR) has become an essential technique to extract original oil content and maintain oil fields. During this process, certain viscous polymers are commonly used as mobility control agents. In this work, we introduce a new class of polymer to address the limitations of commercial EOR polymers. We successfully extracted *kappa*-type carrageenan from *Eucheuma cottonii* seaweed using demineralized water and ethanol precipitation. The amount of yield, intrinsic viscosity, and viscosity-average molecular mass of the extracted carrageenan were 18.64%, 12.77 dLg^{-1}, and 4.716×10^5 $gmol^{-1}$, respectively. Characterizations were done by dynamic viscosity and rheological measurement, along with a thermal degradation test. The measurements indicated that *kappa*-carrageenan is an attractive green substitute for polyacrylamide, as it showed relatively high resistance to temperature, shear rate, and salinity compared to polyacrylamide-based commercial EOR polymers. However, a higher concentration of carrageenan is still needed to reach the same viscosity as the commercial polymers.

Keywords: Eucheuma cottonii; *Kappa*-carrageenan; Enhanced oil recovery; Rheological measurement

1. INTRODUCTION

In order to meet increasing energy needs and lower the production demands of limited petroleum resources, enhanced oil recovery (EOR) has become an essential technique to increase sweep efficiency, i.e. to extract over half of a reservoir's original oil content and maintain the production stability of oil fields (Avarado & Manrique, 2010; Ezekwe, 2011). During this process, certain polymers are commonly used as mobility control agents that increase the viscosity of the fluid injected in the oil well, so the crude oil can easily flow towards the production well. These polymers have to fulfill the criteria of EOR polymers, such as having good stability in high temperatures, shear rates, and salinities (Sheng, 2011). In response, many researchers have worked to develop improved materials for the required polymers.

There are two main polymers which have been widely used in EOR applications: polyacrylamide (PAM) or partially hydrolized polyacrylamide (HPAM), and zanthan gum (XG)

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(Sheng, 2011). Although both polymers can form gels with very high viscosities, an important characteristic of EOR polymers, unfortunately these solutions still have serious limitations. Specifically, they have fairly low resistance against elevated temperatures, leading to polymer degradation, and a viscosity that decreases strongly with increasing salinity for PAM and remains almost constant for xanthan. The low availability of xanthan biopolymers and high economic costs also limit the practicality of these two polymers. Accordingly, we will show that the addition of some salts is actually beneficial in reaching high viscosities in the presented case, and introduce an affordable material that has enough availability, is renewable, and is ecologically safe (Iglauer et al., 2011).

In this work we address the salinity limitation of current polymers, especially PAM, and present a class of polymer featuring viscosity that increases with increasing salinity. It is the carrageenan class of polymer, a local commodity easily found in tropical waters. This biopolymer has been considered to be a good and environmentally-friendly polymer matrix (Mobarak et al., 2012). Carrageenans are anionic polysaccharides from red seaweed species of the Rhodopyceae class, usually extracted by water or alkali extraction followed by alcohol precipitation (Shanmugan et al., 2005; Zhu et al., 2008). Commonly, carrageenan is used in food industries as a stabilizer in dairy products, cosmetics, gelling agents, toothpaste, pharmaceuticals, and beverages. The structure of the carrageenan polymer is built from repeated disaccharide units (Bhattacaharyya & Tobacman, 2012), in which linear hydrophilic sulfated galactan is classified according to the 3,6-anhydrogalactose (DA) and the position and number of the sulfate groups. Carrageenans have been studied extensively in the context of food industries (Harrington et al., 2009; Gaaloul et al., 2009), but are still limited in the context of EOR applications.

There are various carrageenan types, including iota-, kappa-, and lambda-carrageenan. In this work, we extracted carrageenan from *Eucheuma cottonii* seaweed harvested from Gerupuk-Lombok, Indonesia, with a harvesting age of 30 days, and the type of carrageenan was analyzed by an FTIR spectrum. The extraction was done using demineralized water and ethanol precipitation, and we considered higher pH conditions because carrageenan undergoes hydrolysis at pH < 3.5. Intrinsic viscosities were then measured to find the optimum carrageenan. In the rheological measurement stage we investigated the heat stability of carrageenan and tested the influence of polymer concentration, shear rate, and salinity on the fluid's viscosity. We considered the dependence of the viscosity on cation types, concentrations, and temperatures, since brines in geological formations can be expected to vary significantly. A thermal degradation test was also done to investigate the aging effect on solution viscosity, and to compare it to commercial polymers used in EOR applications. The main goal of our work was to determine the potential capacity of carrageenan in EOR, and to show that carrageenan can be an attractive green substitute for PAM under high-salinity conditions.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1. Materials

Fresh *Eucheuma cottonii* seaweed was obtained from Gerupuk-Lombok, Indonesia. For extraction and characterization, potassium bromide, sodium chloride, potassium chloride, calcium chloride, and ethanol 90–95% were purchased from Merck without further purification, while demineralized water was prepared in our laboratory.

2.2. Extraction

Small pieces of dried *Eucheuma cottonii* seaweed were submerged in water (the ratio of dried seaweed to water was 1:2, w/v) and allowed to stand for 15 minutes. The wet seaweed was then collected and extracted using hot demineralized water inside an Erlenmeyer flask, placed in a water bath shaker. The seaweed was added after the solvent reached 80–90°C, and then extracted for 1 hour. The ratio of dried seaweed to solvent was 1:30 (w/v). The volume of the solvent was kept constant by adding hot water. After extraction, the filtrate was collected and then poured into ethanol 90–95% (1.5 parts with respect to the filtrate volume, v/v), stirred well, and allowed to stand for 15 minutes to produce the hydrocolloids of carrageenan. The carrageenan was then collected and added to ethanol 90–95% once again, to achieve more firm carrageenan. After 15 minutes, the wet carrageenan was collected and dried in an oven at 60°C until it reached a constant weight. The dry carrageenan was then blended into powder.

2.3. FTIR Analysis

Functional groups in the sample were analyzed by FTIR (Fourier Transform Infra Red) Prestige 21 using a KBr pellet method, and recorded at the wave number range of 400–4000 cm^{-1}. The FTIR spectrum of the sample was compared to the carrageenan FTIR spectrum in the reference, to determine the type of carrageenan based on the similarities of the functional group absorption band.

2.4. Viscosity and Rheological Measurements

All of these measurements were based on the methods and equations described in Darmayanti and Radiman (2015).

2.5. Thermal degradation test

Carrageenan solutions were placed in an oven at 70°C for 10 weeks. Commercial polymers, symbolized as PI and PII, were also used for comparison. The dynamic viscosity of all the solutions were measured and calculated every week to track the effect of aging on solution viscosity.

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis

Figure 1 displays the FTIR spectrum of carrageenan. The spectrum shows the presence of S=O in sulfate ester by having an absorption band at 1262 cm^{-1}; 1039 and 1073 cm^{-1} for the glycosidic bond; 931 cm^{-1} for 3,6-anhydrogalactose; and 843 cm^{-1} for the galactose-4-sulfate group as the specific characteristics for *kappa*-type carrageenan. There are no absorption bands at 800–805 cm^{-1} for 3,6-anhydrogalactose-2-sulfate, which is specific to *iota*-type carrageenan. Therefore, the carrageenan extracted from *Eucheuma cottonii* seaweed in this work was identified as *kappa*-type carrageenan (κC).

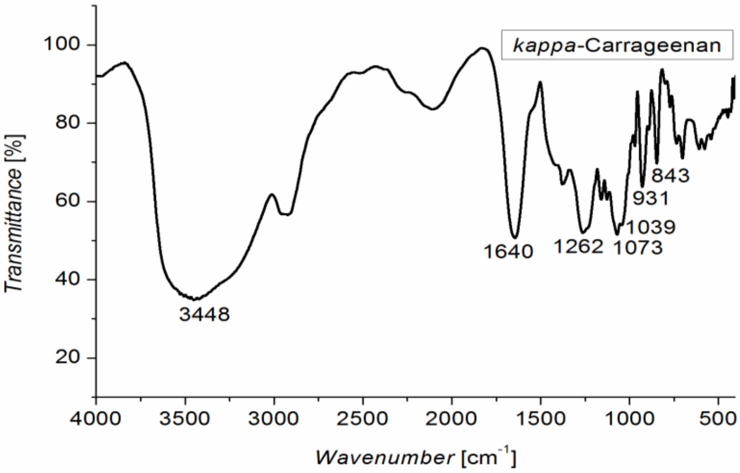

Figure 1 FTIR spectrum of carrageenan, specific for the kappa-type (κC)

3.2. Rheological Measurements

The intrinsic viscosity of the extracted κC was 12.77 dl/g, while its viscosity-average molecular mass was 4.72×10^5 g/mol. Figure 2 displays how the viscosity of 2000, 5000, 7000, and 10000 ppm κC solutions at a shear rate of 340.8 s^{-1} decreased with increases in temperature. The decreases in viscosity were not very significant at increasing temperatures, which suggests that κC has a relatively good resistance to elevated temperature. The viscosity of κC is still high at 70°C (40.22 cP for κC 10000 ppm and 16.39 cP for κC 5000 ppm), which is the target of polymers for EOR applications.

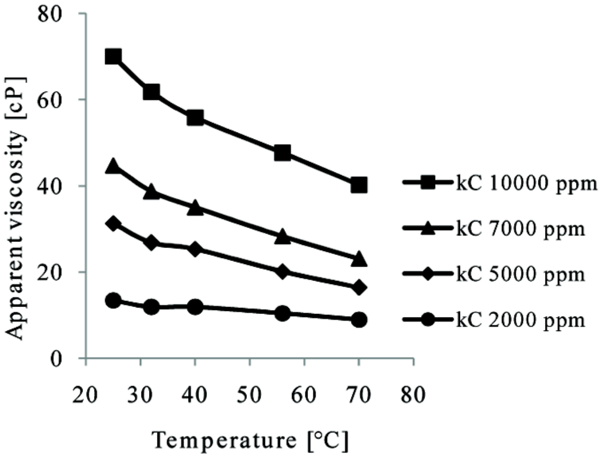

Figure 2 Effect of temperature (°C) on apparent viscosity (cP) of κC solutions at 340.8 s^{-1} for shear rate and varied concentrations

Figure 3 shows the effect of varied shear rate on polymer viscosity at elevated temperatures. It is shown that the viscosity reduction of κC is not too significant, indicating that this polymer has a relatively good resistance to shear rate, while the viscosity of 1000 ppm of PI and PII decreased drastically. Although a higher concentration of κC is still needed to reach the same viscosity as commercial polymers, κC could have great potential as an EOR polymer.

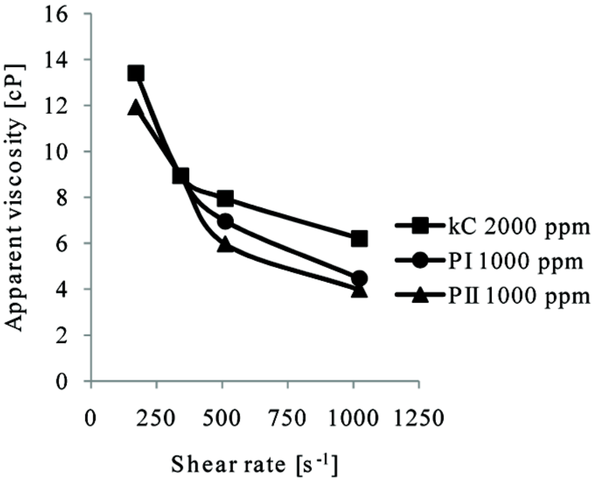

Figure 3 Effect of shear rate (s^{-1}) on apparent viscosities (cP) of the polymers at 70°C

Since κ-carrageenan (κC) is a polyanion, added salts affect its gelation behavior (Sen & Erboz, 2010). Viscosities of κC solutions with added salts in varied temperature and shear rates were analyzed, as this is industrially most relevant for EOR applications. Commonly, reservoir brines are complex mixtures of various dissolved salts of varying concentrations, and specific compositions depend on the exact geographical location. In this work, we used three cations (Na^+, K^+, and Ca^{2+}) while we kept the anion type constant (chloride) to exclude the eventual effects of anion type on viscosity or gelling.

The viscosity of the κC solutions increased with KCl concentration, especially above 15000 ppm. The reason for this viscosity increase is that the κC molecules aggregated when K^+ cations were added. The presence of K^+ cations induced the κC solution to form a firm gel phase which is thermo-reversible in high temperatures (Espinosa-Ozib et al., 2012). Gel formations occur because K^+ cations bind to the double helix (Ellis et al., 2009), which promotes helix-helix aggregation by reducing electrostatic repulsion induced by the sulfate groups between the κC molecules. This introduces an additional mechanism of crosslinking between neighboring helix chains, with the sulfate groups facing outwards (Zhu et al., 2008; Harrington et al., 2009). Most alkali metal and alkaline earth cations act in an analogous way in terms of initiating the gelling of carrageenan solutions, but *kappa*-type carrageenans are particularly sensitive towards K^+ cations. The potassium ions have a size and shape which make them fit into the carrageenan helix, so this structure is stabilized through the positively charged ions and the negatively charged sulfate groups in the carrageenan molecule. Though sodium is smaller than potassium, it has a greater hydrated radius due to its higher charge density. For this reason, sodium does not cause gelation. Therefore, in the presence of Na^+ and Ca^{2+}, the viscosities of κC solutions were not as high as in the presence of K^+.

In contrast, the comparable polyacrylamide (PAM) systems recorded a strong viscosity reduction when KCl was present. It is seen in Figure 4 that the viscosities of PI and PII commercial polymers decreased significantly with the addition of KCl. Precipitation caused neutralization of the PAM charges by cations, and not only affects the reduction of viscosity but could also lead to serious problems regarding the blockage or permeability of the pore-network structure (Iglauer et al., 2011). These high salinities reduce the EOR efficiency of PAM, but for κC higher salinities will bring higher viscosities. In this case, κC could be an alternative polymer to replace PAM in EOR applications for oil reservoirs with high salinities.

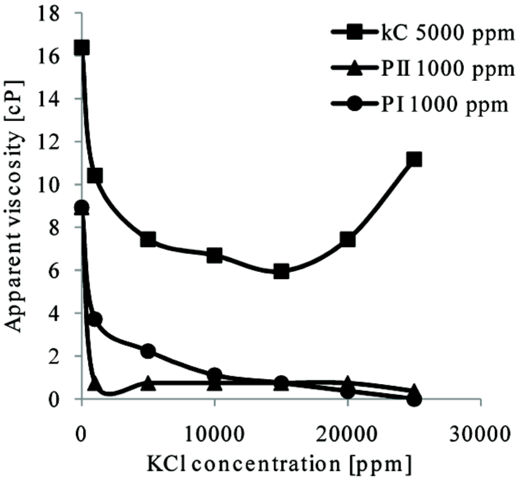

Figure 4 Effect of KCl concentration (ppm) on apparent viscosities (cP) of the polymers at 70°C and 340.8 s^{-1} shear rate

3.3. Effect of Aging on Viscosity

Further testing was done to evaluate the long-term chemical stability of κC solutions at elevated temperatures. κC was kept in an oven at 70°C for 10 weeks, and every week the dynamic viscosity of the solution was measured. An aging effect was detected in κC and the commercial PI and PII polymers, shown by the reduced viscosity every week, as displayed in Figure 5. For PI at 1000 ppm, the aging effects were very small, so it was identified to be a polymer with high resistance to thermal degradation. κC showed a much better performance than PII in terms of thermal degradation because the viscosity reduction in κC was not too significant.

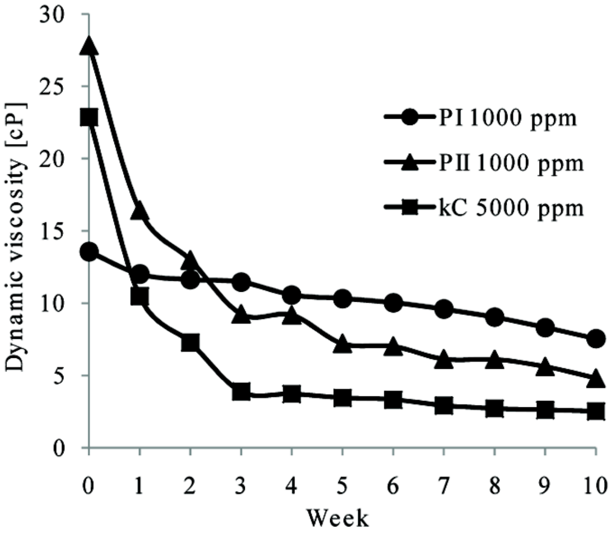

Figure 5 Dynamic viscosities (cP) of polymers kept in an oven at 70°C for 10 weeks

4. CONCLUSION

It was found that κC can reach high nominal viscosity values (above 35.75 cP at 5000 ppm), even in high salinity conditions. κC solutions also have relatively good resistance to elevated temperatures, as they can still reach high viscosities at 70°C. The shear thinning behavior of κC solutions is not as significant as commercial PAM-based polymers, giving κC high potential to substitute for those polymers in EOR applications. κC would be useful as a mobility control agent, and is recommended for use in high-salinity reservoirs that exhibit low or moderate temperatures.

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