

Effect of Temperature and Alkali Solution to Activate Diethyl Carbonate for Improving Rheological Properties of Modified Hydroxyethyl Methyl Cellulose

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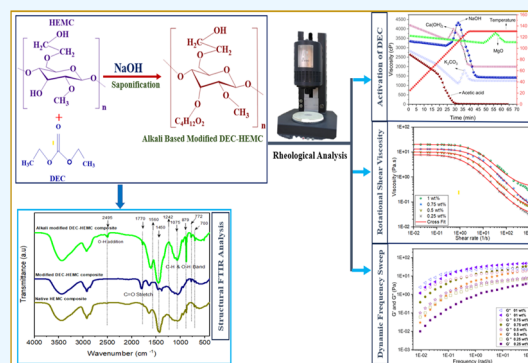


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ABSTRACT: The applications of cellulose ethers in the petroleum industry represent various limitations in maintaining their rheological properties with an increase in both concentration and temperature. This paper proposed a new method to improve the rheological properties of hydroxyethyl methyl cellulose (HEMC) by incorporating diethyl carbonate (DEC) as a transesterification agent and alkali base solutions. Fourier transform infrared (FTIR) analysis confirmed the grafting of both composites onto the HEMC surface. The addition of sodium hydroxide (NaOH) improved the stability of the polymeric solution as observed from ζ -potential measurement. Shear viscosity and frequency sweep experiments were conducted at concentrations of 0.25–1 wt % at ambient and elevated temperatures ranging from 80–110 °C using a rheometer. In the results, the increase in viscosity at specific times and temperatures indicated the activation of DEC through the saponification reactions with alkali solutions. All polymeric solutions exhibited shear-thinning behavior and were fitted well by the Cross model. NaOH-based modified solution exhibited low shear viscosity compared to the DEC-HEMC solution at ambient temperature. However, at 110 °C, its viscosity exceeded that of the DEC-HEMC solution due to the activation of DEC. In frequency sweep analysis, the loss modulus (G'') was greater than the storage modulus (G') at lower frequencies and vice versa at higher frequencies. This signifies the viscoelastic behavior of modified solutions at 0.50 wt % and higher concentrations. The flow point ($G' = G''$) shifted to a low frequency, indicating the increasing dominance of elastic behavior with the rising temperature. At 110 °C, the NaOH-based modified solution exhibited both viscous and elastic behavior, confirming the solution's thermal stability and flowability. In conclusion, modified HEMC solution was found to be effective in controlling viscosity under ambient conditions, enhancing solubility, and improving thermal stability. This modified composite could play a significant role in optimizing viscoelastic properties and fluid performance under challenging wellbore conditions.



1. INTRODUCTION

Cellulose ethers make up a significant and valuable class of chemical compounds derived from natural cellulose through etherification. Cellulose ethers are soluble in water and possess a combination of biodegradability, nontoxicity, and renewable sourcing, making them environmentally friendly choices for various applications.^{1,2} Cellulose ethers act as thickeners, texture modifiers, emulsion and suspension stabilizers, binders, adhesives, film formers, protective colloids, and structuring agents.^{3,4} Due to their unique and versatile rheological properties, cellulose ethers find applications in various industries such as food, pharmaceuticals, construction, painting, and particularly the oil and gas sector.^{5–8} Hydroxyethyl cellulose (HEC), hydroxyethyl methyl cellulose (HEMC), methyl cellulose (MC), hydroxypropyl methyl cellulose (HPMC), and carboxymethyl cellulose (CMC) are the widely used classes of cellulose ether to be used in petroleum industry applications encompassing drilling fluid,

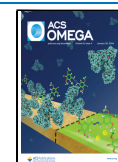
cementing, and polymer flooding for enhanced oil recovery (EOR).^{9,10} These cellulose ethers serve as viscosifying agents that enhance viscosity, prevent fluid loss, mitigate gas migration, and improve the fluid's ability to suspend particles during drilling and cementing operations,^{9,11} where the polymer is added in designed drilling mud and cement slurry to improve the flowability and properties of fluid. However, in polymer flooding for EOR applications, cellulose ethers improve sweep efficiency and mobility, ultimately enhancing oil recovery.¹² In all these operations, the fluids are displaced

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from the surface to the wellbore and reservoir, requiring a high shear rate for displacement.¹³ Furthermore, these fluids encounter formation fluid and an elevated thermal reservoir temperature. The mechanical shear rate, along with high reservoir temperature and salinity, affects the rheology in terms of viscosity of polymers. As the flow behavior of the displacing fluid plays a vital role in drilling and flooding operation, it becomes imperative to regulate the viscosity of cellulose ethers under specific salinity and temperature conditions, especially with high shear rates.^{12,14–16}

The combined effect of shear rate, salinity, and reservoir temperature affects the rotational flow behavior and viscoelastic properties of polymers. At a high shear rate and temperature, the polymer exhibited thermal and shear thinning, which is undesirable for drilling operation and flooding operations.^{17,18} The loss of viscosity in the polymer at elevated temperature renders it incapable of achieving the required objective of improving fluid properties and displacement of the reservoir fluid. As the viscosity of the polymer is lost at elevated temperature, the polymer becomes unable to achieve the required objective. Simultaneously, the viscoelastic behavior of the polymer is affected by these factors, transforming the liquid solution into a gel type solid, thereby reducing its fluidity, which can pose challenges for displacement of fluid.¹⁹

The influence of the temperature on the rheology of cellulose ether is a crucial parameter that progressively intensifies with increasing wellbore depth during drilling operation. The polymers exhibit a behavior of thermal thinning at elevated temperature linked with shear rate, underscoring the significance of this aspect in understanding and optimizing its performance in drilling and flooding operation, where polyalkylamine (PAM) tends to precipitate at temperatures higher than 80 °C.²⁰ Similarly, hydrolyzed polyacrylamides (HPAM) and HEC lose viscosity over 70 and 60 °C, respectively.^{21,22} Xanthan gum also exhibits decreased viscosity when exposed to 85 °C,²³ while starch and CMC undergo severe deterioration at temperatures exceeding 90 °C.²⁴ To address the issue of temperature-induced polymers, various approaches have been explored and utilized to synthesize and regenerate polymers.²⁵ Solvents and ionic liquids have been utilized to synthesis and improve the thermal characteristics of polymers.²⁶ However, the synthesis through toxic ionic liquids is considered problematic, requiring additional catalysts for reaction, along with numerous derivatization stages and high temperatures.²⁷ Furthermore, the utilization of ionic solvents links to significant environmental pollution that poses economic and environmental challenges. Blending of various cellulose ethers such as HEC, starch, CMC, and xanthan has been adopted to extend the thermal degradation range. Nevertheless, combination of polymers affects the ζ -potential of the solution.²⁸ Another effective method for extending the degradation temperature range is to increase the concentration of the polymer. This enhancement depends on interactions between polymer molecules, the chemical structure, and the molecular weight of the polymer.²⁹ At higher concentrations, intermolecular forces and polymer–polymer interactions become more pronounced, rendering the polymer more resistant to degradation at high temperatures. As a result, an increased polymer concentration can lead to an increase in thermal degradation temperature. For petroleum industry applications, utilization of high concentrations and combinations of polymers also enhances the fluid viscosity under

surface conditions and at ambient temperature.³⁰ The high viscosity of polymeric solutions affects the rheology under the surface condition, which requires a high shear rate and pump pressure for displacement in the wellbore.³¹ Furthermore, elevated fluid viscosity, pump pressure, and shear rate become the cause of formation fracture and wellbore damage. To address the challenges posed by ionic liquids, increased viscosity under surface conditions, and shear and thermal thinning, there has been a search for modifying cellulose ether to improve its thermal and rheological properties. In such circumstances, it becomes necessary to modify the polymer to reduce the viscosity under surface conditions and compensate the viscosity loss caused by thermal and mechanical factors.³² An ideal approach to mitigate viscosity loss is to incorporate polymers along with cosolvents through transesterification reactions that enhance the viscosity of polymers at a specific time and temperature.

Organic carbonates have been investigated as cosolvents for modification. Due to their environmental friendliness and safety, organic carbonates are considered as an excellent option to replace ionic solvents.³³ There has been limited research in the literature focusing on the modification of cellulose ether using organic carbonate as a transesterification agent to enhance viscosity. The modification of cellulose ether through organic carbonates as a transesterification agent has been found to increase the molecular weight and improve the thermal characteristics as concluded from our previous article.³⁴ This improvement in the characteristics of the cellulose ether is of significant interest in the context of rheological measurements. Variation in molecular weight, polymer structure, morphology, and thermal stability can lead to changes in their flow behavior properties.^{35,36} Such modification can impact the material's ability to withstand shear forces and maintain its structural integrity under different conditions. Rheology plays a crucial role as a parameter that requires careful consideration before field implementation of cellulose derivatives in the oil and gas industry. Controlling the viscosity of the polymer is essential for polymer flooding in EOR and drilling operation projects, as it entails maintaining polymer viscosity within predetermined salinity and temperature ranges.

The rheological behavior of polymeric solutions has been studied to evaluate the effects of shear rate, salinity, and temperature. Higher shear rates cause the solution to become less structured, which causes the polymer molecules to spread out and lose their molecular bonds. The reduction in viscosity was due to the increased force disrupting their orderly arrangement. Polysaccharide solutions and synthesized cellulose ether exhibit pseudoplastic behavior. They become less viscous when subjected to shear stress (shear-thinning). However, when the shear stress is removed, their initial viscosity rapidly returns to normal.¹⁴

The higher salinity in the reservoir has an adverse effect on the gelling capability of the polymer. Petroleum reservoirs typically exhibit mineral concentration ranging from 40,000 to 10,000 ppm, depending on the depth and producing layer.¹⁹ When reservoir formation brine encounters high salinity and hardness, the injected polymer undergoes chain breakdown. In this process, the carbon chain attempts to conform and precipitate out of the solution, ultimately reducing the viscosity.³⁷ The introduction of salt resulted in a lower shear viscosity compared to that of a salt-free solution, but a significant increase in salt concentration had minimal impact.

When salt is added, it triggers a shift from a disordered state to an ordered state in the polysaccharide polymer backbone. During this transition, the polymer backbone takes on a helical shape, while the charged trisaccharide side chains collapse onto the backbone due to charge screening effects, thus stabilizing the ordered conformation.¹⁴ The presence of salts in polymeric solutions reduces the repulsion among the carbonyl groups found in cellulose derivatives, leading to a decrease in solution viscosity. The salts also cause the elongated polymer molecules to aggregate, resulting in further reduction in viscosity.¹⁵ In general, the increase in viscosity when dissolving polymers in water is primarily due to the specific arrangement of the polymer's large molecular structures. For charged polymers, the repulsion between charged groups additionally contributes to the higher solution viscosity. However, salts do not significantly impact noncharged polymers. In the case of charged polymers, the addition of salt reduces the repulsion between molecules, resulting in decreased solution viscosity.³⁸

Chatterji and Borhardt investigated the temperature and viscosity dependence of water-soluble polymers. They confirmed that viscosity of cellulose derivatives, including HEC, decreases with temperature.³⁹ The trend suggests that as the temperature rises, the viscosity of solutions decreases. Elevated temperatures have the effect of diminishing the structural integrity of polymers within the solution, resulting in disruption of the bonds between polymer molecules (polymer degradation). In the case of HEC polymer solutions, an increase in temperature leads to a significant reduction in viscosity due to the weakening of both intermolecular bonds and the polymer's structure.⁴⁰ The functional groups responsible for dissolving the polymer in water become disrupted, causing the polymer to dissolve in water and ultimately decreasing the solution's viscosity.

Castelain examined the viscosity of cellulose ethers within various concentration ranges and characterized the viscosity at a minimum shear rate and above the critical concentration.⁴¹ Laschet evaluated the effect of intermolecular interaction on hydrophobically modified cellulose ether solutions.⁴² Wang et al. studied the impact of solvent substitution on cellulose rheological properties and gelation in high pH water solvents, finding that temperature decreases both intrinsic viscosity and gelation time.⁴³ The literature provides valuable insights into the viscosity dependence of cellulose ether. However, research focusing on the rheology of modified solutions especially in the context of temperature and behavior during viscoelastic region has been relatively limited.^{1,44,45} Therefore, understanding the rheology of modified composites in terms of shear rate, viscosity, concentration, and temperature is essential for implementing them in petroleum industry applications.

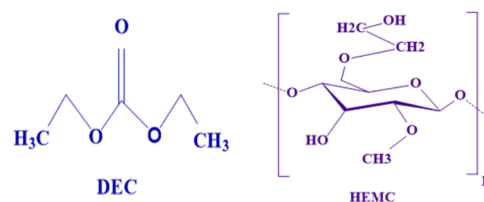
This research work presents the use of diethyl carbonate (DEC) (an organic carbonate) as a transesterification agent to modify and improve the rheology of the HEMC (cellulose ether) solution. The alkali solution has been used as a trigger during the modification of HEMC. The novelty of this research lies in assessing the rheology of modified HEMC solutions and the impact of alkali solutions as triggers to activate the transesterification agent DEC. Experimental work was carried out to modify and characterize the modified composite through Fourier transform infrared (FTIR) and ζ -potential measurement. The activation of DEC in modified DEC-HEMC solution using various alkali base solutions was assessed through viscosity analysis as a function of the temperature and time. The viscosity of the modified solution

was also determined using acetic acid (acidic pH). Further in this frame, multiple formulations of modified solutions were examined to study various rheological parameters, including shear viscosity, storage modulus (G'), loss modulus (G''), flow point ($G' = G''$), and loss tangent ($(\tan \delta) = G''/G'$). The investigation involved steady shear rotational experiments to analyze viscosity versus shear rate and shear stress, as well as oscillatory testing in frequency sweeps to evaluate viscoelastic behavior. Furthermore, the Cross model for nonlinear regression analysis was also employed to evaluate the rheological behavior of solution and relevant fluid parameters. The findings of this study provide important insights into the viscoelasticity and flow properties of modified solutions for optimizing fluid properties in petroleum industry applications.

2. MATERIALS AND METHODS

2.1. Materials. Hydroxyethyl methyl cellulose (HEMC) polymer in powder form was provided by GANTRADE Corporation, China, with the following characteristics: particle size (mesh) = 80, molecular weight = 9×10^4 g/mol, degree of substitution (DOS) = 1.4, and molar substitution (MO) = 0.2. Organic carbonate, i.e., DEC ($C_5H_{10}O_3$), sodium chloride (NaCl), sodium hydroxide (NaOH), potassium carbonate (K_2CO_3), magnesium oxide (MgO), calcium hydroxide ($Ca(OH)_2$), and acetic acid (CH_3COOH) were purchased from Daejung Chemicals & Metals, Korea. The chemical structures of DEC and HEMC used in this study are depicted in Scheme 1.

Scheme 1. Chemical Structure of DEC and HEMC



2.2. Methods. The experimental setup of polymer modification and relevant analysis employed in this study are provided in Figure 1. HEMC was modified through the wet and dry method. Modification of the polymer composite is depicted in the Supporting Information. The chemical functional groups in the modified composites were examined using a PerkinElmer FTIR spectrophotometer. The FTIR spectra of composites were collected with 32 scans at a resolution of 4 cm^{-1} in the 500 to 4000 cm^{-1} wavenumber range.³⁴ The optimal concentration of DEC for modification was based on FTIR analysis (Figure S1). Further, the ζ -potential of polymer solutions was analyzed using the Zetasizer Nano ZS (Malvern Instruments, U.K.).

2.3. Polymeric Solution Preparation. The modified composite in powdered form was mixed with deionized water and stirred using a hot magnetic plate stirrer to prepare polymer solutions for rheology measurement. The polymeric solution of 0.25 to 1 wt % concentration was prepared by changing the weight ratio concentration in deionized water. Alkaline and acidic solutions of NaOH, MgO, K_2CO_3 , and acetic acid, each with a molarity 01, were prepared and added in polymeric solution separately. Additionally, modified polymer solutions were prepared by mixing 0.50 wt % modified polymer with prepared brine (1–10 wt %) to

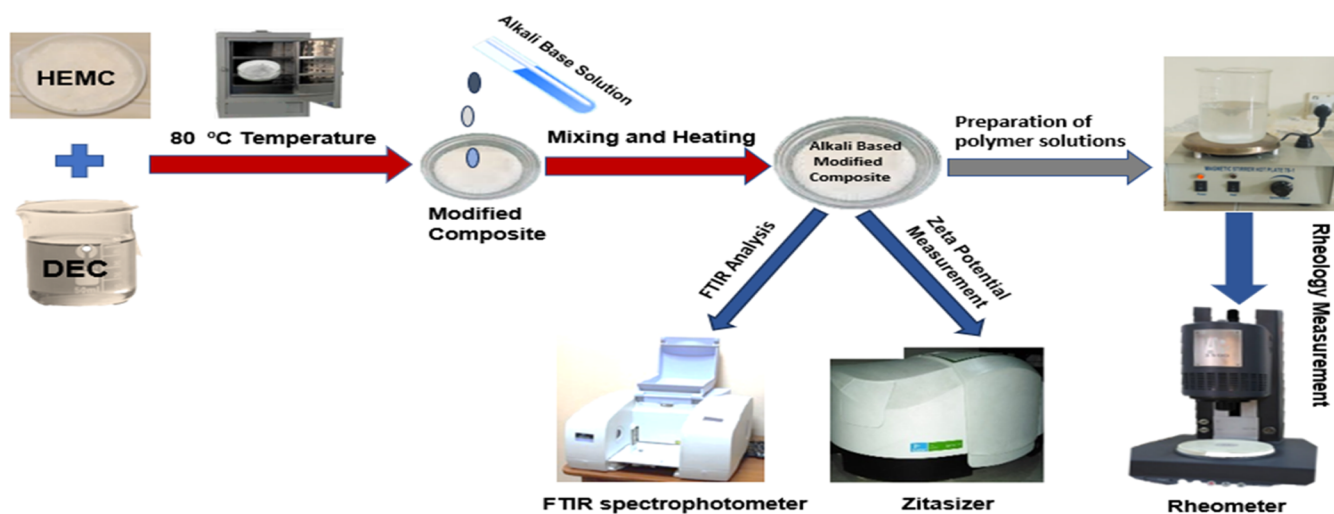


Figure 1. Schematic representation of polymer modification and experimental analysis.

evaluate the salinity effect on polymeric solutions, resembling the concentration found in reservoir.

2.4. Rheological Measurements. The rheological measurements of the prepared polymer solutions were conducted using a rotational rheometer (AR1500, TA Instruments) equipped with a Peltier heating system. The measurements utilized a cone–plate measuring configuration with a 40 mm diameter cone having an angle of 2° (CP40/2 $^\circ$) and a truncation gap was set at 0.1 mm. The same geometry was used in all rheologically related experiments.

First, the activation of DEC in the presence of different alkali solutions was studied by measuring the viscosity of polymeric solutions at a 10 (1/s) constant shear rate as a function of time and temperature. The test temperature ranged from 30 to 130 $^\circ\text{C}$. Next, rotational viscosity experiments were conducted by increasing the shear rate from 0.01 to 1000 (1/s). The measurements were made in the automatic acquisition time mode, which required a minimum of 1.8 s for each data point. The obtained flow curve data provide viscosity as a function of shear rate and shear stress, which will be used to determine relevant parameters by using the Cross model. The viscoelastic behavior was analyzed by evaluating the storage modulus (G') and loss modulus (G'') across a frequency ranging from 10^{-2} to 10^2 radius per second (rad/s), under a constant stress. The measurements were carried out three times for each sample by using different samples. The deviation in viscosity and modulus between the polymeric solutions was found to be less than 15% (standard deviation).

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis. The FTIR analysis was conducted to identify the possible interaction of DEC and NaOH with the functional groups present in the HEMC. Figure 2 displays the FTIR of both native HEMC and modified HEMC composites. The FTIR spectrum of the HEMC composite revealed six prominent peaks at 632, 1061, 1432, 1634, 2923, and 3433 cm^{-1} . In the range from 600 to 900 cm^{-1} , the transmittance peaks belong to the fingerprint region and are associated with cellulose, representing the characteristics of methyl and alkyl groups.⁴⁶ The band at 1432 cm^{-1} corresponds to the stretching of C–O and C=O bonds within the secondary hydroxyl function group. A broad transmittance band at 1061 cm^{-1} corresponded to the stretching of the C–O bond, connecting

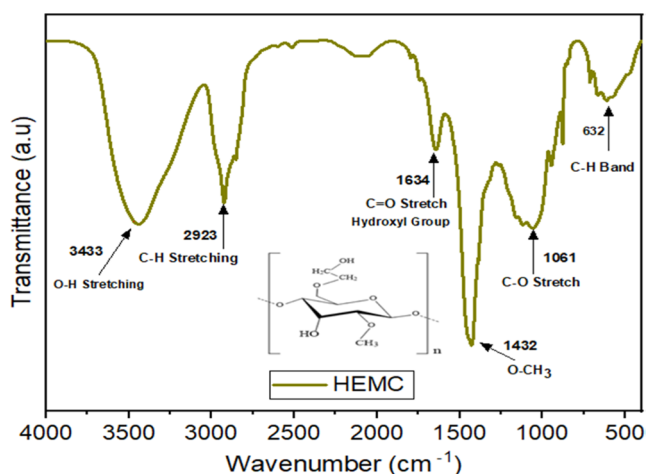


Figure 2. FTIR spectrum of the HEMC composite.

anhydro-glucose components in cellulose.⁴⁷ In the region from 1643 to 1898 cm^{-1} , there were moderate to weak transmittance peaks that were attributed to the C=O stretching vibration of the secondary hydroxyl group.⁴⁸ The high-intensity peak at 3433 cm^{-1} also corresponds to the moderate stretching of OH in functional groups and signifies the presence of free O–H in molecular structure.⁴⁹ The bands at 2853 and 2923 cm^{-1} are attributed to a strong stretching vibration of C–H aliphatic groups indicating the crystalline structure.⁵⁰ Finally, the weak peak observed at 2512 cm^{-1} represents the C \equiv C stretch of the alkyne group and is linked to SP_3 C–H stretching.⁴⁸

Figure 3 depicts the FTIR spectrum of both unmodified and modified HEMC composites. It was observed that a weak symmetrical band in the C–H band region shifted to 772 cm^{-1} in the spectrum of the modified DEC–HEMC composite. Similarly, in the C=O hydroxyl group region, a strong transmittance peak changed in intensity to a weak transmittance peak at 1420 cm^{-1} . Furthermore, a new transmittance peak at 1770 cm^{-1} was identified in C=O stretch vibration of the secondary hydroxy function group region of the DEC–HEMC polymer sample.³⁴ The addition of NaOH altered the FTIR spectra in the fingerprint region of the modified composite, where a new and high-intensity transmittance

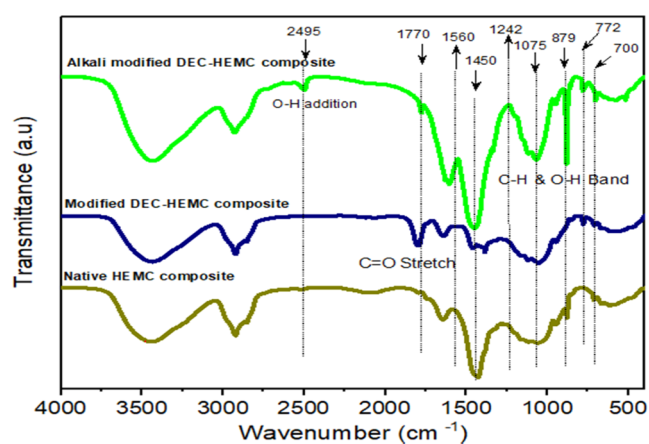


Figure 3. FTIR spectra of unmodified and modified HEMC composites.

peak was observed at 879 cm^{-1} wavenumber. Additionally, a moderate transmittance peak at 1770 cm^{-1} wavenumber changed in intensity from moderate to low due to the replacement of a methyl group through an OH functional group. Another weak transmittance peak was observed at the 2495 cm^{-1} wavenumber, indicating the addition of a hydroxyl group from sodium hydroxide to the modified composite. Hence, the FTIR spectral analysis confirms the presence of NaOH and DEC on the HEMC surface.

3.2. ζ -Potential Measurement and Analysis. ζ -potential quantifies the surface charge carried by particles within a solution. This electrokinetic property is considered an important parameter for determining the solution's stability. A high ζ -potential value, whether positive or negative, indicates good particle stability in solution, whereas low values, resulting from van der Waals associations, indicate poor stability of particles in the solution.⁵¹ ζ -potential varies with changes in concentration and the alkali pH solution, particularly in polymeric solution with altered functional groups. The ζ -potential results of the polymeric solutions are provided in Figure 4. The native HEMC solution exhibits a low ζ -potential

value -12 mV , indicating weak electrostatic colloidal stability of the suspension in an electrolyte environment. In contrast, the modified composite demonstrates an improved ζ -potential of -44.5 mV , achieved through modification via diethyl carbonate. This high value of ζ -potential is attributed to the attachment of negatively charged carbonate groups on the cellulose surface. These negative charges on the function group prevent the fluctuation of particles and enhance the particle stability in aqueous solution.^{10,35}

The zeta value decreases with an increasing concentration of polymer composites in the aqueous solution. A reduced ζ -potential value was observed by increasing the concentration of the DEC-HEMC modified composite, as presented in Figure 4. At high concentrations, the ionic strength of the solution increases due to the release of ions from the polymer's ionizable groups, and the molecules in the polymer chain come close together.⁵² Therefore, this increase in ionic strength and electrostatic shielding reduces the ζ -potential of the solution with increasing concentration. The ζ -potential of the polymeric solution increased by the addition of NaOH solution, which was added for modification. The ζ -potential value of this alkali-based modified polymer was -52.4 mV , indicating good stability of particles in aqueous solution. The increased ζ -potential value was due to the complete dissociation of NaOH in the solution.⁵³ The addition of the alkali increases the concentration of OH^- ions and raises the pH, leading to an increased quantity of hydroxyl groups on the surface of cellulose particles, consequently enhancing the surface charge repulsion and increasing the particle stability by reducing fluctuation.

3.3. Solubility and Activation of the Modified HEMC Composite. The viscosity of modified DEC-HEMC solution was determined to assess the impact of organic carbonate on HEMC solubility with respect to time at a constant shear rate and $25\text{ }^\circ\text{C}$ temperature. The viscosity of the modified DEC-HEMC solutions was found to be greater than that of the unmodified HEMC solution, as shown in Figure 5. The increase in viscosity of polymeric solution is attributed to the higher molecular weight of the modified composite.

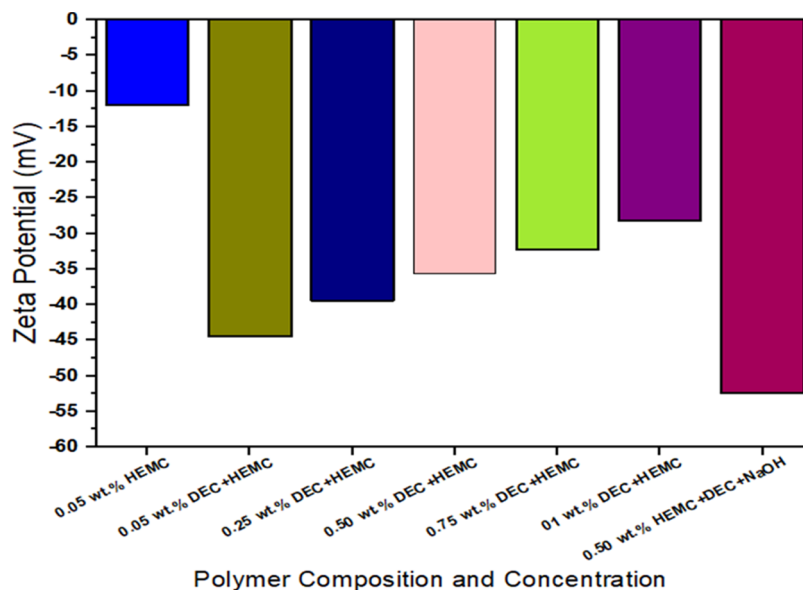


Figure 4. ζ -Potential of modified HEMC solution by changing the composition and concentration.

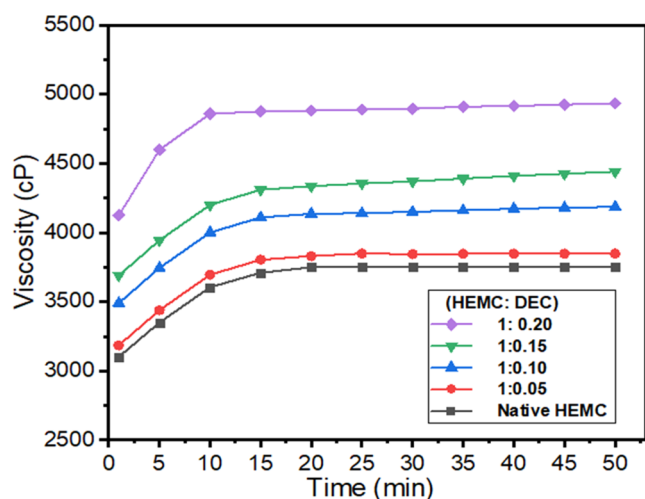


Figure 5. Viscosity with respect to time of native and modified HEMC solution at various weight ratio concentrations.

Furthermore, an increase in the concentration of DEC in terms of the weight ratio enhances solubility and viscosity. The modified DEC-HEMC having 1:0.20 weight ratio concentration achieved its maximum viscosity in 10 min, explaining the improved solubility of HEMC through DEC modification.

The activation of the DEC in the modified composite was evaluated through viscosity measurement using time and temperature sweep analysis of polymeric solutions. Figure 6a illustrates the viscosity profiles of native and modified solutions by changing the temperature over time. Both native and unmodified solutions showed a gradual decrease in viscosity as the temperature increased 25–130 °C. This decrease in viscosity continued until the vaporization temperature was reached. Beyond the vaporization temperature, a significant change in viscosity reduction was observed, as shown in Figure 6a. The substantial change in viscosity occurred at 83 °C for HEMC and at 101 °C for modified DEC-HEMC polymeric solution. This change was due to the breakdown of the molecular chain and degradation above the vaporization temperature confirmed through DSC analysis (Figure S2).

The impact of basic and acidic pH solutions as a trigger for initiating hydration is depicted in Figure 6b. The presence of

acidic solution did not show any acceleration effect on the hydration rates of modified DEC-HEMC solution. However, the introduction of alkaline led to a significant reduction in the time and temperatures required for hydration to begin. The onset of hydration was influenced by the strength of the alkali and its solubility. It was observed that the addition of NaOH reduced the viscosity of the polymeric solution. The initial viscosity of the solution was 3964 cP, and this viscosity was reduced to 3352 cP by the addition of NaOH. The alkali base solution acts as a trigger and thermally activated the DEC in modified solution, increasing its viscosity to 110 °C. The maximum viscosity for the NaOH-based polymeric solution was 4325 cP, achieved within 32 min hydration time at 110 °C.

Furthermore, the addition of hydrated lime ($\text{Ca}(\text{OH})_2$) to the modified polymeric solution increased the initial viscosity of the solution to 4189 cP. The activation temperature for hydrated lime-based polymeric solution was 103 °C, where it reached maximum viscosity of 4008 cP in 29 min. Additionally, the inclusion of potassium carbonate (K_2CO_3), another alkali solution trigger, reduced the initial viscosity of the polymeric solution. However, upon thermal activation at 123 °C, it reached a maximum viscosity of 1812 cP in 36 min. In contrast, magnesium oxide (MgO) with large particle size was the only time-dependent activator. It activates the DEC and enhances the viscosity of polymeric solution after 55 min. The increase in viscosity was attributed to the temperature-based saponification reaction of the free hydroxyl group with diethyl carbonate. This reaction resulted in the elongation of the structure chain of HEMC, leading to enhanced viscosity during reaction and activation. NaOH reduces the initial viscosity of HEMC and restricts early thermal viscosity reduction, as observed in Figure 6b. Furthermore, the viscosity of the NaOH-based modified solution upon activation was greater than all other alkaline-based solutions. Based on temperature and time sweep viscosity analysis, NaOH is considered more promising as a trigger for delayed viscosification than other alkaline solutions.

3.4. Rotational Flow Properties of Modified Solution.

3.4.1. Concentration Effect and Shearing Action. Figure 7a shows the rotational viscosity profile as a function of shear rate for modified DEC-HEMC solutions at 25 °C. Viscosity measurements were conducted at concentrations of

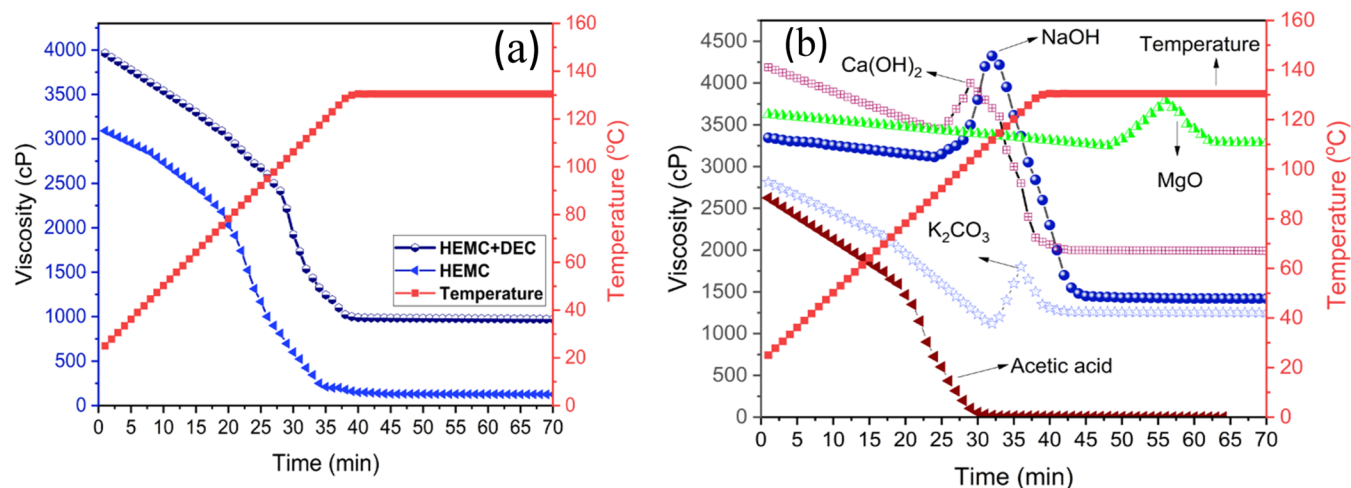


Figure 6. Viscosity of solution as a function of time and temperature: (a) native and modified HEMC, (b) alkaline and acidic solution-based modified HEMC solution to activate DEC.

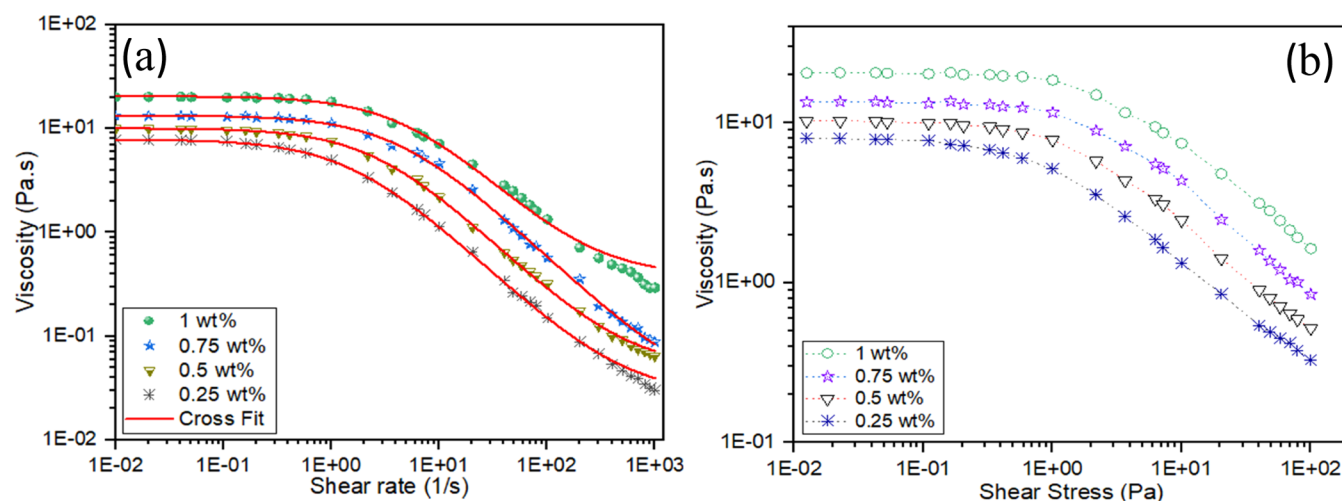


Figure 7. Steady-state viscosity profile of modified DEC-HEMC solutions by change in concentration at 25 °C temperature: (a) viscosity with respect to shear rate and (b) viscosity with respect to shear stress.

0.25, 0.50, 0.75, and 1 wt %. The viscosity of the solution increased from 7.82 to 10.14 Pa·s at a minimum shear rate of 0.01 (1/s) when the solution concentration changed from 0.25 to 0.50 wt %. The viscosity of solution continued to increase with further concentration increments, reaching a viscosity of 13.19 Pa·s for a concentration of 0.75 wt % and 20.34 Pa·s for a concentration of 1 wt %. At lower concentrations, the polymer chains have more space between the molecules, allowing them to move relatively freely, resulting in lower viscosity. Concentration increases viscosity across the entire shear rate range due to the presence of many micelle-like aggregates. These aggregates facilitate the formation of bridges and enhance the network.⁵⁴ The increased viscosity was attributed to the greater frequency of intermolecular interactions as well as entanglements among the cellulose chains. Furthermore, the viscosity data decrease as the shear rate increases for all concentrations of DEC-HEMC solutions. The high viscosity and large critical shear rate for shear thinning in concentrated polymer solution reveal the complex rheological behavior. The increase in viscosity due to increasing concentration is attributed to the greater number of polymer molecules confined within the aqueous solution in which they dissolve.⁵⁵ The polymer molecules are densely packed, leading to frequent interactions and entanglements. As the polymer concentration increases, these interactions and entanglements become more pronounced, effectively restricting the mobility of individual polymer chains. Consequently, the viscosity increases. Additionally, at higher concentrations, van der Waals forces and interactions between polymer chains become more prominent. These interactions act as physical cross-links, contributing to the overall network structure of the solution. They effectively bind the polymer chains together, further increasing viscosity.⁵⁶ The increased viscosity of a modified DEC-HEMC polymeric solution is crucial for elevating the residue resistance factor and enhancing sweep efficiency in polymer flooding applications for enhanced oil recovery. It was observed that all of the solutions exhibit Newtonian behavior at low shear rates and transition to high shear-thinning behavior at high shear rates. The viscosity of 0.25 wt % modified DEC-HEMC solution was decreased from 7.82 to 0.03 Pa·s by changing the shear rate 0.01 (1/s) to 1000 (1/s). Similarly, the viscosities of all polymer solutions also

decreased with an increasing shear rate. The shear thinning behavior is attributed to the disentanglement of polymer coils in solution and the alignment of particles in the flow direction.^{57,58} In the petroleum industry, particularly for applications involving drilling fluids, the essential characteristic of polymeric solutions is their ability to exhibit shear thinning behavior. The shear thinning property of polymeric solutions is essential as it enables the suspension of drilling cutting under low shear rates while imposing minimal resistance to flow during a high shear rate.¹⁴ Further, modified DEC-HEMC polymer molecules arrange themselves into an ordered structure in an aqueous solution. The substantial entanglement and aggregation of these large molecules in the aqueous solution contribute to a heightened viscosity at low shear rates. Subsequently, as the shear rate increases, the polymer chains uncoil and partially align in the high shear rate region, resulting in a reduction in the viscosity of the polymeric solution.^{59,60} The shear thinning behavior (pseudoplastic fluid) of the modified DEC-HEMC solution can be regarded as a potential candidate for polymer flooding project and cementing, given its ability to reduce pumping resistance at the wellhead. This behavior is attributed to the gradual decline in molecular entanglement at higher shear rates.

The impact of shear stress on viscosity of modified DEC-HEMC solution is provided in Figure 7b. It was observed that increasing the shear stress leads to a decrease in the viscosity of polymeric solution. The reduction in viscosity is due to the alignment and relaxation of the polymer chain induced by the shearing force within the cellulose solution.⁶¹ The most significant change in behavior and viscosity of the solutions occurred from a shear stress of 0.55 Pa, which is considered critical shear stress for modified DEC-HEMC solutions.

The experimental results and flow curves of modified solutions are fitted using the non-Newtonian Cross model, as expressed in eq 1.

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{1}{1 + \lambda\dot{\gamma}^n} \quad (1)$$

where η represents the viscosity at a given shear rate ($\dot{\gamma}$), and η_0 and η_{∞} represent the viscosities at low and high shear rates, respectively. The characteristic time constant is denoted by λ , and n is a dimensionless power index constant. The parameters

of polymeric solutions through the Cross model are given in Table 1 and Figure S3. The increase in both zero and infinite

Table 1. Cross Model Parameters of Modified DEC-HEMC Solutions

concentration wt %	η_0 (Pa.s)	η_∞ (Pa.s)	λ (s)	n	R^2
0.25	7.8777	0.0260	0.1968	0.8725	0.982
0.50	10.090	0.0544	0.2249	0.9014	0.994
0.75	13.413	0.0206	0.3648	0.9147	0.985
1	20.556	0.3818	0.3819	0.9211	0.975

shear viscosity, along with a decrease in characteristic time constant (relaxation time) with increasing polymer concentration, is attributed to the increase in segment density and the creation of three-dimensional network structure. Relaxation time values less than one indicate a faster response to external force in terms of stress and shear rate. The modified solution will respond more rapidly to changes in shear rate at higher concentrations. At 0.50 wt % and higher concentrations, the increasing relaxation time is attributed to the entanglement and interaction between the polymer chain due to increased viscosity. This improvement in entanglements in terms of Cross model parameters is considered as an important element affecting the rheological behavior of modified DEC-HEMC solutions. The power index constant and characteristic time constant of all polymeric solutions were less than unity, which also indicates the shear thinning behavior of modified cellulose ether. Based on the Cross model, a good fit with R^2 value of 0.994 was achieved for the 0.50 wt % concentration. This polymeric concentration exhibited a power index value (n) of 0.9014 and relaxation time of 0.2249, indicating a significant transition to shear thinning behavior at a higher shear rate.

3.4.2. Temperature Effect. Figure 8 illustrates the effect of temperature on the flow behavior of the modified DEC-

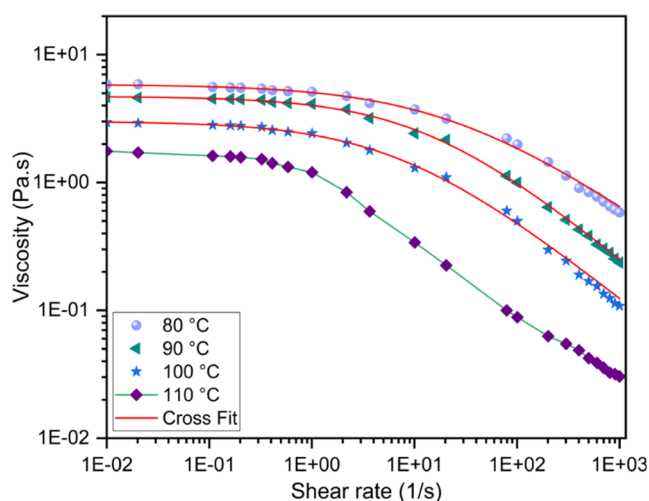


Figure 8. Steady-state viscosity profile of modified DEC-HEMC solutions at elevated temperatures.

HEMC solution. The shear thinning behavior of solution at elevated temperatures was also evaluated, and the corresponding parameters are depicted in Figure S4. The viscosity of the 0.50 wt % solution was evaluated with respect to shear rate at elevated temperatures ranging from 80 to 110 °C, based on the vaporization temperature of HEMC. A decrease in the viscosity of the solution was observed at 80 °C as compared to the

viscosity at 25 °C. The shear viscosity of a 0.50 wt % solution decreased from 5.846 to 3.725 Pa·s as the temperature increased from 25 to 80 °C at a 10 (1/s) shear rate. In total, the viscosity of the polymeric solution decreased by 36% between 25 and 80 °C. Furthermore, the viscosity of the modified solution decreased to 2.424 and 1.152 Pa·s at 90 and 100 °C, respectively. It was noted that up to 100 °C, the viscosity of solution decreased gradually, losing 80% of its viscosity at a shear rate of 10 (1/s). A significant change and reduction in viscosity occurred at 110 °C compared to the preceding temperature and viscosity profiles. The viscosity of solution was 0.342 Pa·s at 110 °C, indicating a 70% reduction in viscosity as the temperature increased from 100 to 110 °C. The reduction in viscosity was due to the increase in the mobility of polymer chains within the solution induced by temperature. The decrease in intermolecular interactions occurs because of the thermal motion of molecules with increasing temperature. The variation in viscosity was linked to a conformational shift from an ordered, rod-like structure of cellulose to a more flexible disordered structure as the temperature increased. This shift occurred due to the progressive reduction in rigidity of the (1-4)- β -D-glucan chain within the temperature range of 80–110 °C.^{14,62} Further, this increased mobility allows the polymer chains to move more freely, reducing their resistance to flow and subsequently lowering viscosity. Beyond 100 °C, thermal degradation of the polymer was initiated, leading to a substantial reduction in viscosity. At low shear rates, a continuous decrease in viscosity was observed, but at high shear rates, a sudden decrease in viscosity occurred due to dehydration. The reduction in viscosity is attributed to thermal thinning and a decrease in the degree of hydration. The water molecules associate less tightly with polymer chains, diminishing interactions between the water and polymer, which leads to a reduction in viscosity.

3.4.3. Salinity Effect. The shear viscosity of a salt-based modified polymeric solution was measured as a function of the shear rate for different salt concentrations at 25 °C to investigate the impact of salinity as shown in Figure 9. The addition of 1 wt % salt made the shear viscosity lower than that of a without salt solution. The viscosity of solution reduced 9.80–8.52 Pa·s at a shear rate of 0.1 (1/s). The viscosity of the solutions displayed a gradual decrease with an increase in salt concentration, reaching values of 7.28, 6.88, 6.43, and 5.91 Pa·s

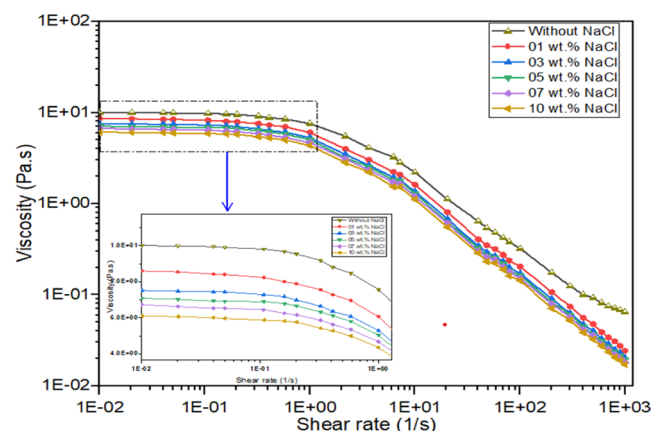


Figure 9. Shear viscosity profile of modified DEC-HEMC solutions by change in salt concentration at 25 °C temperature.

at 3, 5, 7, and 10 wt % salt additions in the polymeric solution, respectively, measured at 0.1(1/s). The maximum percentage of viscosity is reduced by the addition of 1 wt %, and for the remaining concentration, further salt addition had little as compared to 1 wt % salt. The viscosity of solution decreased by 24% at a maximum salt concentration of 10 wt % in solution. The reduction in viscosity of modified HEMC solution was attributed to the interaction of free-flowing ions and oxygen atoms contained in the functional groups.⁶³ Furthermore, a decrease in viscosity of the polymeric solution is observed across all shear rates due to the addition of salt, which restricts the complete hydration of HEMC in the aqueous solution. In the presence of salt, there is insufficient water available for the complete expansion of cellulose, leading to a reduction in viscosity.⁴⁰ The polymer chain degradation and viscosity of the modified DEC-HEMC polymer are significantly influenced by saline solutions with various ionic compositions. The structure of the HEMC polymer incorporates carboxylate groups to augment hydrodynamic volumes and increase solution viscosity, essential for applications in the drilling fluid and polymer flooding process.⁶⁴ When present in saline solutions, Na⁺ ions have the capacity to enter the hydration layer and tend to distribute between two oxygen atoms. Positive ions play a pivotal role in the polymer backbone structure, leading to a reduction in hydrodynamic volume and a subsequent decrease in viscosity.⁶⁵ In petroleum application, for drilling and flooding operations, it is necessary that the viscosity of polymeric solution should be low, and reduced viscosity requires a low shear rate and pump pressure during displacement under surface conditions. Therefore, the viscosity of the modified DEC-HEMC polymeric solution showed reduced viscosity and can be considered an effective solution that requires a low shear and pump rate for displacement in drilling and polymer flooding applications.

Additionally, the shear viscosity of a 10 wt % salt-based modified solution was determined at high temperatures to assess the solution behavior under high reservoir conditions. The viscosity of the salt-based solution was determined at 100 and 110 °C, as depicted in Figure 10.

The viscosity of the solution decreased from 2.824 to 2.256 at 100 °C and 1.621 to 1.276 Pa·s at 110 °C at a 0.1 (1/s) shear rate due to addition of salt to the polymeric solution. The reduction in viscosity was 20–22% at elevated temper-

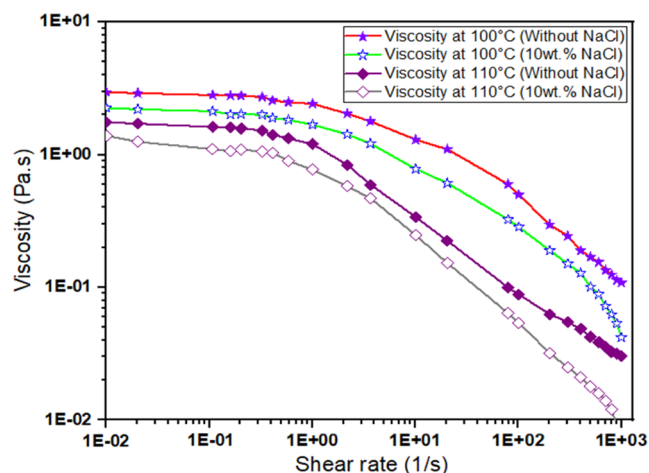


Figure 10. Steady-state viscosity profile of salt-based DEC-HEMC solutions at elevated temperatures.

atures with addition of 10 wt % NaCl salt in the polymeric solution. The salt is less effective in reducing viscosity under high thermal conditions compared to ambient conditions, primarily due to the presence of DEC as a transesterification agent in the HEMC polymer. The presence of Na⁺ ions and temperature activate the DEC, and the Cl⁻ ion of salt becomes less effective in reducing viscosity. Salt-based modified solution maintains its viscosity at elevated temperatures and can effectively improve the fluid properties for drilling and polymer flooding in petroleum applications, especially under thermal wellbore and reservoir conditions.

3.4.4. Rotational Flow Properties of Alkali-Based Modified Solution. The flow properties of trigger-activated modified DEC-HEMC were evaluated at 25, 100, and 110 °C to investigate the impact of NaOH alkali solution on viscosity. The viscosity flow curves with Cross-model fits at ambient and elevated temperatures as a function of shear rate are shown in Figure 11. Additionally, the Cross-model fits with parameters at each temperature are depicted in Figure S5.

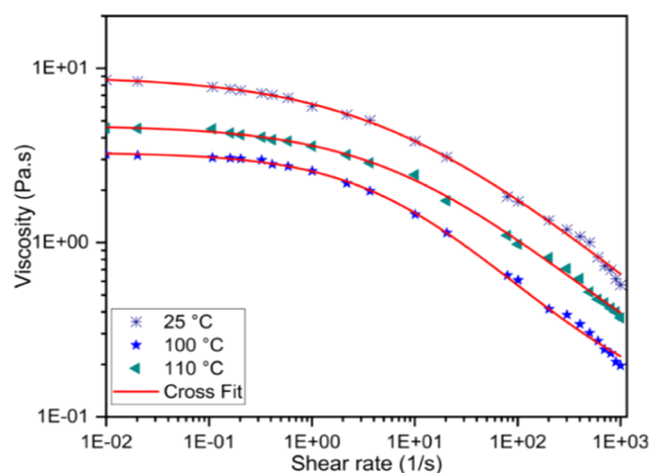


Figure 11. Steady-state viscosity profile of NaOH-based modified DEC-HEMC solutions at ambient and elevated temperatures.

The NaOH-based modified DEC-HEMC solution exhibited a similar shear thinning behavior at 25 °C. However, the initial viscosity of the solution was lower than that of the modified DEC-HEMC solution. The viscosity of solution decreased from 10.14 to 8.58 Pa·s at a shear rate of 0.01(1/s) by addition of NaOH in 0.50 wt % DEC-HEMC solution. Reduced viscosity was also observed at all shear rates, with a minimum viscosity of 0.571 Pa·s recorded at a maximum shear rate of 1000 (1/s). The addition of a strong base, such as NaOH, to the polymeric solution reduces the initial viscosity of the solution at ambient temperature. This delayed and reduced viscosity at ambient temperature was due to the disruption in the intermolecular structure of HEMC, making it more soluble in the solvent.^{43,66} As a result, the molecules disperse in the solvent, leading to a reduction in initial viscosity. At an elevated temperature of 100 °C, the polymeric solutions exhibited thermal thinning behavior. The shear viscosity of the solution decreased across all shear rates, ranging from 0.01 (1/s) to 1000 (1/s), in comparison to the viscosity observed at 25 °C. Upon increasing the temperature to 110 °C (above the degradation temperature of the DEC-HEMC composite), an increase in viscosity was recorded in polymeric solution as observed in Figure 11. The viscosity of

solution escalated from 3.218 to 4.525 Pa·s at a shear rate of 0.01 (1/s) and from 0.187 to 0.370 Pa·s at the maximum shear rate of 1000 (1/s) at 110 °C. DEC acts as a transesterification agent that becomes activated at specified temperature, enhancing the viscosity of the HEMC. Activation of DEC extends the thermal stability of HEMC where increased and enhanced viscosity was observed at 110 °C.

3.4.5. Viscoelastic Properties of Modified Solution. The suitability of the polymer for petroleum industry applications strongly depends on its viscoelastic properties, particularly the amount of elastic (solid-like) behavior quantified by the storage modulus (G') versus viscous (fluid-like) behavior quantified by the loss modulus (G''). The viscoelastic properties were investigated by evaluating the modulus (G' and G'') through frequency sweep at constant shear stress by varying concentration and temperature. The behavior in terms of loss and storage modulus of modified DEC-HEMC solutions is shown in Figure 12.

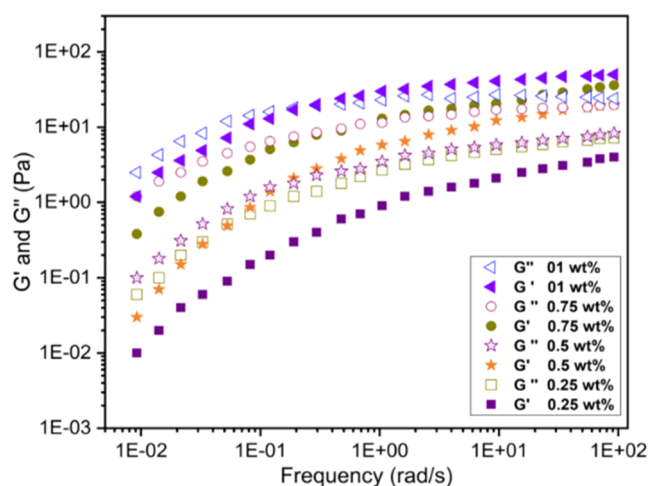


Figure 12. Dynamic frequency sweep curves of modified DEC-HEMC solutions for different concentrations at ambient temperature.

It was observed that the loss modulus (G'') for the 0.25 wt % concentration polymeric solution was greater than the storage modulus (G'), indicating that the polymer solution was more liquid-like. At higher concentrations, 0.50, 0.75, and 1 wt %, the modulus was distinguished by two regions. At low frequencies, the loss modulus was dominant, while at high frequencies, the storage modulus took precedence, indicating the transition of the viscous behavior. The change in viscoelastic behavior indicated that at higher concentrations, the polymer cross-linking network in terms of hydrogen bonding or entanglement of polymer chains was not permanent and rearranged its molecular structure in response to the frequency.^{54,67} The characterization of rheological properties of polysaccharide solutions in oscillatory shear usually focuses in the linear viscoelastic (LVE) region where the applied strain amplitude is sufficiently small.¹ The behavior of the cellulose ethers and their derivatives is affected by the change in frequency in the linear viscoelastic region under constant low stress,⁵⁴ where the rheological behavior is independent of the shear strain and only depends on the microstructure and temperature.^{53,68} By increasing concentration from 0.50 to 1 wt %, the elastic modulus becomes dominant, which shows the gel-like behavior of modified DEC-HEMC solution. The cellulose ethers and other polymers

exhibited a similar pattern due to the interlocking of polymer coils.^{69,70} The point of intersection in the transition corresponds to the flow point [$G' = G''$] that becomes more complex with increasing concentration due to higher density of the solutions.^{58,71}

It is observed that the flow point (crossover point) was not consistent across all concentrations as it shifted toward higher frequencies. This crossover point specifies the transition between the concentrated network and semidilute network solution. In Figure 13, a clear transition from viscous to elastic

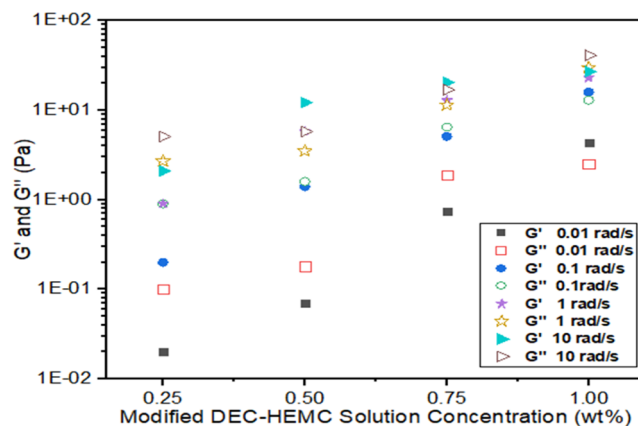


Figure 13. Variation in modulus as a function of concentration at different frequencies.

behavior was observed at 0.1 rad/s of 0.50 wt % modified DEC-HEMC solution. In contrast, other concentrations of the solution exhibited complex transitions across all frequencies. Therefore, the polymeric solution of 0.50 wt % concentration, denoted as the critical concentration of the modified DEC-HEMC composite. Additionally, low loss tangent ($\tan \delta$) for polymeric solution was observed, which also showed the degree of viscoelasticity as shown in Figure 14. A lower value of ($\tan \delta$) indicates high predominance of elastic behavior over viscous behavior and thus high viscoelasticity.⁵⁵ The ($\tan \delta$) values of 0.50 wt % concentrated solution was lower than 1 in between the frequency range 0.1 and 10 rad/s (in the range of critical concentration), reflecting the high dominance of the elastic component in the sample.

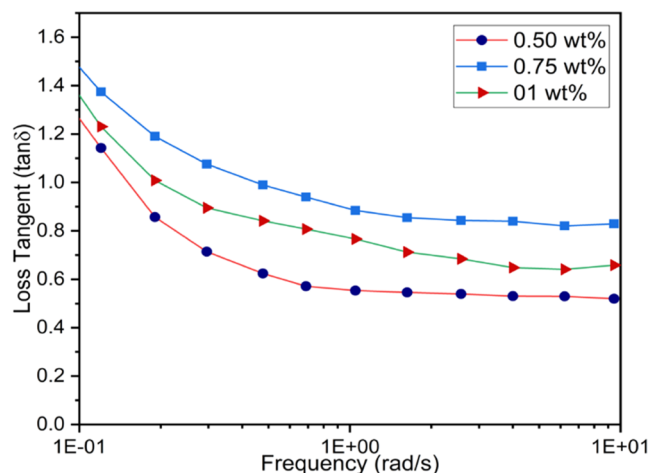


Figure 14. Loss tangent as a function of frequency of the modified DEC-HEMC solution for different concentrations.

The impact of temperature on viscoelastic behavior was evaluated by determining the loss and storage modulus of 0.50 wt % modified DEC-HEMC solution within the range of 80–110 °C. As shown in Figure 15, a decrease in storage and loss

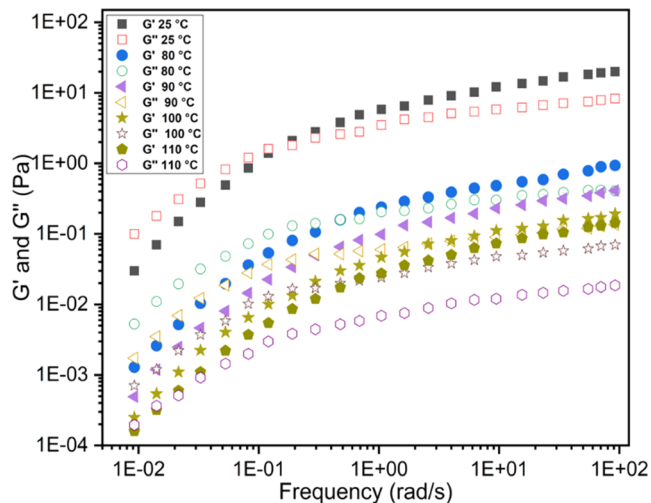


Figure 15. Dynamic frequency sweep curves of 0.50 wt % modified DEC-HEMC solutions at ambient and elevated temperatures.

modulus values was evident as the temperature increased from 80 to 110 °C. This decrease in modulus values with increasing temperature was attributed to the thermal thinning behavior of polymeric solution.⁷² At 80 °C, the solution displayed viscoelastic behavior, with the loss modulus being predominant at low frequencies, while the storage modulus dominated at high frequencies. It was observed that as the temperature exceeded 80 °C, the flow point [$G' = G''$] gradually shifted toward lower frequencies. The flow point of polymeric solution was shifted to 0.30 rad/s at 90 °C and 0.18 rad/s at 100 °C. This shift indicated a transition toward more pronounced elastic behavior at higher temperatures. The temperature rise initiated a dehydration process within polymeric solution, reducing the water content in solution and leading to the formation of gel-like structure with increased density.^{53,68} Furthermore, at 110 °C, the flow point shifted to 0.01 rad/s, and the storage modulus entirely dominated over the loss modulus. This shift indicated that the polymeric solution exhibited more solid-like behavior than liquid-like behavior. At that temperature, the polymeric solution underwent complete degradation, forming a gel emulsion in the solution, rendering it unable to flow.^{55,73}

3.4.6. Viscoelastic Properties of Alkali-Based Modified Solution. The viscoelastic properties of sodium hydroxide-based modified polymeric solution are shown in Figures 16 and 17. The addition of NaOH to DEC-HEMC solution decreased the storage and loss modulus of solution and shifted the flow point toward higher frequency. This transition led to the loss modulus becoming dominant over the storage modulus, as observed in Figure 16. Consequently, these alkali-based polymeric solutions remained in the liquid state and were considered pumpable at low frequencies due to the prevalence of viscous behavior over elastic behavior. The high loss modulus of the polymeric solution was due to the polymer structure, concentration of HEMC, and solvent used in solution at 25 °C ambient temperature. Furthermore, the elastic modulus increases continuously with increasing

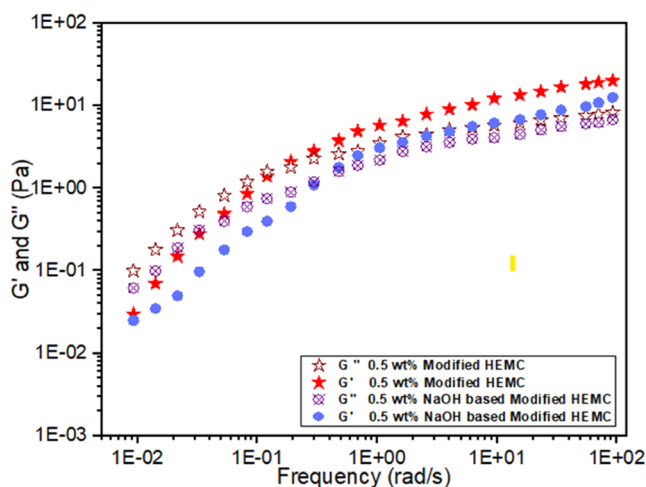


Figure 16. Dynamic frequency sweep curves of modified solutions (with and without alkali base solution) at ambient temperature.

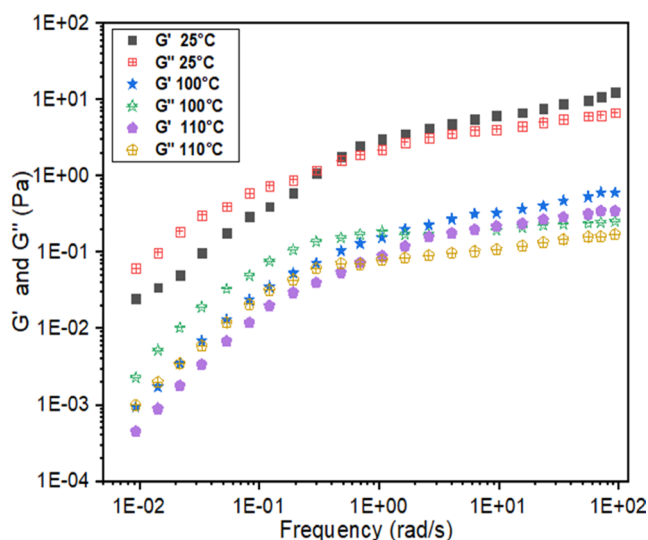


Figure 17. Dynamic frequency sweep curves of NaOH-based modified solutions at ambient and elevated temperatures.

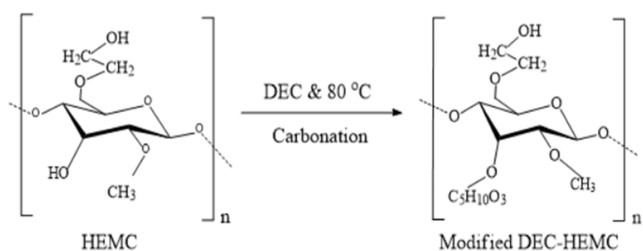
frequency, and the storage modulus becomes dominant over loss modules. Based on these results, the NaOH-based modified DEC-HEMC solution exhibits viscoelastic behavior at ambient temperature.

The effect of temperature on the viscoelastic properties of NaOH-based modified DEC-HEMC was investigated by determining the loss and storage modulus at 100 and 110 °C. Figure 17 illustrates that as the analysis temperature increased from 25 to 100 °C, both the storage and loss modulus values decreased. The reduction in each modulus was due to the thermal thinning behavior of HEMC. Similar viscoelastic behavior of NaOH-based polymeric solution was observed at both 100 and 110 °C, with the loss modulus being dominant at low frequencies and the elastic modulus dominating at higher frequencies. Notably, the flow point shifted toward a lower frequency when the analysis temperature was increased from 100 to 110 °C. This shift indicates that the elastic modulus begins to dominate earlier at low frequency, and this change is attributed to the greater polymer chain mobility. This increased mobility can result in more efficient chain entanglements and a higher tendency for the

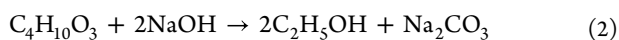
polymer chains to resist flow. As a result, the material exhibits a more elastic response. The NaOH-based polymeric solution exhibited viscoelastic behavior at elevated temperature, where viscous behavior was dominant at low frequency and the elastic behavior was raking preference at high frequency. At this temperature, the DEC was activated, which increased the viscosity and elevated the degradation temperature, allowing the solution to remain in a liquid state and be pumpable. In contrast, the modified DEC-HEMC solution without NaOH exhibited elastic behavior, where polymeric solution transformed into gel, rendering it nonpumpable at 110 °C.

3.4.7. Chemical Reaction and Proposed Mechanism to Activate the Modified Composite. The carbonation process was involved in the modification of HEMC by a green solvent DEC. The modification of HEMC was confirmed through FTIR analysis, revealing distinctive peaks and substitution of new functional groups in the HEMC spectrum. The modification process followed a consistent route, where HEMC reacted with DEC at specified temperature.³⁴ The modification process led to the breakdown of supramolecular structure of cellulose, increasing the accessibility of hydroxyl groups for the reaction.⁷⁴ In this context, a dual reaction occurred between the monomer rings of the hydroxyl functional group and diethyl carbonate molecules through intra and inter annular interactions.³¹ The possible chemical reaction of HEMC carbonation with diethyl carbonate is presented in Scheme 2. Further saponification and hydrolysis

Scheme 2. Chemical Reaction and Structure of the Modified DEC-HEMC Composite

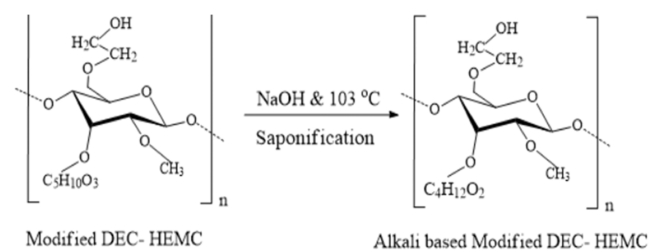


reaction initiated upon introducing alkali solution in the modified DEC-HEMC composite. The saponification process involves the hydrolysis or cleavage of ester bonds in the presence of a strong base.⁷⁵ Saponification reaction of DEC-HEMC with NaOH initiates the cleavage of the ester bond in DEC by the hydroxide ion from the alkali solution. The hydrolysis reaction exploits the DEC and NaOH. The formation of a new chemical structure of HEMC confirmed through H NMR analysis where DEC as a transesterification agent grafted on the free hydroxyl group at the third position (3-OH) of the anhydro-glucose unit as shown in Figures S6 and S7. The chemical reaction of NaOH with DEC is presented in eq 2, and the complete chemical structure after activation is shown in Scheme 3.



The formation of a new chemical structure of the modified composite increases the hydrogen molecules. The increase in hydrogen molecules becomes the cause of viscosity reduction.⁷⁶ Therefore, initial viscosity of solution was reduced by addition of NaOH in modified DEC-HEMC solution. Furthermore, the increased temperature initiates the dehydration process, reducing the number of hydrogen molecules

Scheme 3. Chemical Reaction and Structure of the Alkali-Based Modified DEC-HEMC Composite



from structure.⁶¹ At elevated temperature above 100 °C, the dehydration and saponification process leads to an increase in the effective size of the polymer chain. Moreover, this interaction created a meshlike structure that delayed the movement of the chain. As a result, carbonation and saponification reactions of HEMC with NaOH altered properties in terms of viscosity.

4. CONCLUSIONS

Based on the experimental results and extensive analysis, it was concluded that the DEC and NaOH successfully grafted onto the free hydroxyl group of the HEMC surface. This modification significantly improved the electrokinetic properties and overall stability of the polymeric solution. Increased viscosity with respect to time of different alkali-based polymeric solutions showed the activation of DEC in polymeric solution. Sodium hydroxide has emerged as a superior trigger compared to other alkaline solutions, exhibiting more promising results to activate DEC and increase the thermal stability of the modified composite.

In-depth analysis of the rotational flow behavior revealed that the modified polymeric solution exhibits pseudoplastic behavior at all temperature ranges. The Cross model effectively described shear viscosity data, with a power index of 0.94 at 0.50 wt %, confirming significant shear thinning behavior at high shear rates. Sodium hydroxide addition remarkably improved solubility, with impressive thermal stability at 110 °C, resulting in increased viscosity due to activation of DEC by NaOH solution as a trigger in polymeric solution. In contrast, solutions without NaOH exhibited lower and decreased viscosities at the same temperature.

Frequency sweep oscillatory measurement revealed that the behavior of modified solution depended on concentration, transforming from viscous to elastic behavior by increasing concentration. The 0.50 wt % modified DEC-HEMC solution emerged as the critical concentration across all concentration ranges due to its viscoelastic behavior, having a flow point at 0.04 rad/s and low loss tangent compared to other concentrations. The elastic behavior of the solution at 110 °C temperature indicated that the modified DEC-HEMC solution had degraded, transformed into gel-like structure, lost viscosity, and become unable to flow, while the NaOH-based modified DEC-HEMC solutions exhibited viscoelastic behavior at that temperature, confirming thermal stability and flowability.

Based on the results of this study, it is recommended to use 0.50 wt % concentration of NaOH-based modified cellulose for polymer applications in the petroleum industry. The reduced viscosity of the polymeric solution at ambient temperature will require a low shear rate and pump pressure for fluid and polymer displacement. Additionally, observed viscoelastic

behavior and enhanced viscosity at high temperature ensure that the fluid remains in a liquid state, ultimately improving the fluid and polymer properties under thermal reservoir conditions.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c07451>.

Modification process of HEMC, FTIR spectra of HEMC by changing concentration of DEC, DSC curve for unmodified and modified HEMC composites; cross model fitting curve and parameters of modified solution at ambient temperature at 0.25, 0.50, 0.75, and 1 wt % concentration; cross model fitting curve and parameters of 0.50 wt % modified solution at 80, 90, 100, and 110 °C elevated temperatures; cross model fitting curve and parameters of NaOH-based modified solution at 25 °C ambient and 100 and 110 °C elevated temperatures; H NMR spectrum of the HEMC composite and structure, and H NMR spectrum of the modified DEC-HEMC composite (PDF)

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Notes

The authors declare no competing financial interest.

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