Asian Journal of Science, Engineering and Technology (AJSET)
eISSN: 3006-6980 (online)
https://ideapublishers.org/index.php/ajset
Vol. 4, No. 1 (January-June), 2025, pp. 1-18
https://doi.org/10.47264/idea.ajset/4.1.1
Original Research Article

Enhancing thermal stability and viscosity of cellulose ether using propylene carbonate as a transesterification agent for oilfield applications

Ghulam Abbas*[1] | Faisal Hussain Memon[1] | Abdul Samad Shaikh[1] | Tariq Ali Chandio[2] | Khalil Rehman Memon[3] | Abdul Haque Tunio[3]

1. Mehran University of Engineering & Technology, S.Z.A.B Campus, Khairpur Mir's, Sindh, Pakistan.
2. School of Chemical and Energy Engineering, Universiti Teknologi Malaysia, Johor Bahru, Malaysia.
3. Mehran University of Engineering and Technology, Jamshoro, Sindh, Pakistan.

*Corresponding Author Email: engr_abbas@muetkhp.edu.pk

Article History

Received:
10-Nov-2024

Revised:
15-Dec-2024

Re-revised:
11-Jan-2024

Accepted:
13-Jan-2025

Published:
20-Jan-2025

Abstract: This study presents the utilisation of Propylene Carbonate (PC), along with an alkali-based solution, to modify the Hydroxyethyl Methyl Cellulose (HEMC) polymer to mitigate the thermal degradation of cellulose ether. The experimental results from FTIR and XRD analysis confirmed the addition of a new function group to the HEMC backbone and the formation of a new organic carbonate-based cellulose ether. Shear viscosity experiments were conducted at concentrations of 0.50-wt.% to 2-wt.% at ambient and elevated temperatures ranging from 80°C-110°C using a rheometer. All polymeric solutions exhibited shear-thinning behaviour, and the viscosity of polymeric solutions was enhanced by increasing the concentration of modified HEMC solutions. The modified HEMC solutions exhibited higher viscosity at 1000 s-1 shear rate at 110ºC compared to the native HEMC solutions, confirming the enhanced thermal stability of the PC-based modified HEMC solution. Alkali-based modified HEMC solution exhibited low shear viscosity at ambient temperature. The alkali-based polymeric solution's viscosity was increased by 48% at a high shear rate at 110ºC. In conclusion, 0.50-wt.% and 01-wt.% concentration of alkali-based PC-modified HEMC solution proved efficient in maintaining viscosity under ambient conditions, increasing solubility and exhibiting improved thermal stability at geothermal conditions for oil field applications.

Keywords: Propylene carbonate, Cellulose ether, Viscosity, Organic carbonate, Concentration, Thermal degradation, Rheological properties, Hydroxyethyl methyl cellulose.

How to Cite: Abbas, G., Memon, F. H., Shaikh, A. S., Chandio, T. A., Memon, K. R., & Tunio, A. H. (2025). Enhancing thermal stability and viscosity of cellulose ether using propylene carbonate as a transesterification agent for oilfield applications. *Asian Journal of Science, Engineering and Technology (AJSET), 4*(1), 1-18. https://doi.org/10.47264/idea.ajset/4.1.1

1. Introduction

Cellulose ethers are valuable chemical compounds derived from natural cellulose through etherification. Their water solubility, biodegradability, non-toxicity and renewable sourcing make these compounds environmentally friendly with versatile applications (Lopez & Richtering, 2021). These applications include thickening, improving texture, stabilising emulsions and suspensions, serving as binder and adhesive, forming films, protecting colloids and functioning as structural agents (Zheng *et al.*, 2019). Based on their unique characteristics and rheological properties, cellulose ethers are widely used in various industries, including coatings construction, food pharmaceuticals, and oil and gas sector (Sun *et al.*, 2018; Wei *et al.*, 2020). In the petroleum industry, cellulose ethers serve as indispensable materials for applications that include drilling, cementing, enhanced oil recovery, fracturing, and workover operations. During drilling operations, the cellulose ether is a viscosity modifier and fluid loss control agent to optimise the drilling fluid properties (Khan *et al.*, 2024). For enhanced oil recovery, they are employed to improve the oil displacement efficiency by modifying the viscosity of the injected fluid (Xiong *et al.*, 2024). In hydraulic fracturing, they act as gelling agents to suspend proppants, facilitating better fracture propagation and conductivity (Sun *et al.*, 2024).

Additionally, during workover operations, cellulose ethers contribute to effective wellbore cleaning and the prevention of formation damage, thereby maintaining the integrity and productivity of oil and gas wells. Cellulose ethers and their derivates like Methylcellulose (MC), Carboxymethyl Cellulose (CMC), Hydroxyethyl Cellulose (HEC), Hydroxyethyl Methyl Cellulose (HEMC) and Hydroxypropyl Methylcellulose (HPMC) play crucial roles in cement slurries. In cement slurries, these biopolymers serve as multifunctional additives that improve slurry performance and decrease the quantity of other chemical additives. These biopolymers enhance slurry performance by increasing viscosity, reducing permeability, controlling fluid loss and preventing free water separation through cement slurries. However, at high temperatures, their chemical structure degrades their viscosity and diminishes their effectiveness (Abbas *et al.*, 2013; Sabzian mellei *et al.*, 2022). For instance, Hydrolysed Polyacrylamides (HPAM) and HEC lose their viscosity at 70 °C and 60 °C, respectively (Pope, 2011). Starch and CMC degrade significantly above 90 °C, whereas xanthan gum weakens at temperatures above 85 °C (Abbas *et al.*, 2020). Moreover, Polyalkylamine (PAM) precipitates at temperatures higher than 80 °C (Hamza *et al.*, 2019).

Various strategies have been researched and implemented to synthesis and regenerate polymers to solve their heat deterioration. To improve the thermal stability of polymers, ionic liquids and solvents have been investigated (Xia *et al.*, 2020). However, toxic ionic liquids pose challenges as they require multiple derivation steps, additional catalysts and high temperatures reactions, making the process more complex (Ojogbo *et al.*, 2020). Blending and mixing of high molecular weight polymers have been utilised to increase thermal stability. The range of thermal degradation has been expanded by blending different cellulose ethers, including HEC, starch, CMC and xanthan. However, combining polymers influences the solution's zeta potential (Lashari & Ganat, 2021). Increasing the concentration of the polymer is another efficient way to increase the degradation temperature range. Higher polymer concentrations strengthen intermolecular forces and enhance polymer-polymer interactions, increasing the polymer's thermal degradation resistance (Chandio *et al.*, 2021; Qi, 2014). The higher concentrations and polymer combinations increase fluid viscosity at ambient temperature and surface conditions, optimising their performance for petroleum industry applications (Abbas *et*

al., 2015). However, the increased viscosity requires higher shear rates and pump pressures to effectively displace polymer and fluid in the wellbore at the surface and ambient temperature conditions. High viscosity during fluid displacement at ambient and surface conditions can affect rheology and may lead to wellbore damage or formation fractures due to excessive pump pressure and shear stress (Reddy *et al.*, 2012). As a result, there is currently no widely used polymer solution that effectively enhances the fluid characteristics in geothermal settings during the drilling and cementing of oil and gas wells.

Organic carbonate is a green co-solvent regarding environmental impact and safety. Organic carbonates are considered an alternative to previously used ionic liquids (Dutta *et al.*, 2020). Researchers have explored using organic carbonates as co-solvents to modify and enhance polymer properties. However, the utilisation of organic carbonate to modify the cellulose ether and other polymers is an unexplored area as found in the literature. In our previous study, the organic carbonate was utilised to modify the polymer composite. The utilisation of organic carbonate effectively improves the characteristics of cellulose ether, as concluded in our previous study (Abbas *et al.*, 2023a). The molecular weight of cellulose ether increased, where zeta potential and thermal stability of the polymer composite was enhanced (Abbas *et al.*, 2023b). The change in cellulose ether properties is expected to impact the material's resistance to shear stress and enhance its rheology in geothermal conditions. Therefore, it is crucial to investigate the impact of temperature and polymer concentration on rheology at various shear rates to use cellulose ether and its derivatives in cement and drilling fluid for oil and gas applications.

Propylene Carbonate (PC), Ethylene Carbonate (EC), Diethyl Carbonate (DEC), and Dimethyl Carbonate (DMC) are organic carbonate solvents, both cyclic and acyclic, that are biodegradable and exhibit low toxicity. These solvents have been explored as eco-friendly co-solvents for modification processes and are regarded as safer and more environmentally conscious alternatives to traditional ionic liquids. Their green chemistry attributes make organic carbonates highly promising candidates for use as sustainable solvents and effective transesterification agents in modification applications (Dutta *et al.*, 2020). This research used PC, an organic carbonate, as a transesterification agent to modify the HEMC solution. This research aims to determine the optimal concentration and temperature range for utilising modified HEMC solutions in oilfield applications. The study expects to identify a modified HEMC formulation with improved rheological properties and enhanced thermal stability for high-temperature environments.

This study aims to evaluate the viscosity at various concentrations and temperature ranges to determine the ideal concentration and maximum temperature of degradation for utilising modified HEMC solution in drilling fluid and cement slurry. The novel aspect of this research is to modify the HEMC and determine the impact of organic carbonate and NaOH on the rheological properties of the polymeric solution. The modified HEMC composite was characterised using FRIR and XRD analysis. Next, the modified solution's rheology in terms of viscosity was determined at a concentration of 0. 50 wt.%, 01 wt.%, 1.50 wt.%, and 2 wt.%. To assess the maximum temperature of thermal degradation of modified HEMC, the effect of temperature at both ambient and elevated temperatures 80 ºC to 110 ºC was also determined. It is expected that PC based modified HEMC solutions will exhibit enhanced thermal stability compared to unmodified HEMC. Further, adding NaOH will further improve the viscosity and thermal stability of the modified HEMC solution.

2. Materials and methods

2.1. Materials

In this study, Hydroxyethyl Methylcellulose (HEMC) was obtained as a white to off-white powdered material, characterised by an 80-mesh particle size, Degree of Substitution (DS) of 1.4, molar substitution (MS) of 0.2 and molecular weight $9x10^4$ g/mol from GANTRADE Corporation, China. Propylene Carbonate (PC) ($C_4H_6O_3$) of GR grade, with a specific gravity of 1.20, boiling point of 240 ºC and flash point of 123 ºC was purchased from Daejung Chemical & Metals, Korea. Sodium Hydroxide (NaOH) white pellets of GR grade of 98 % purity and a density of 2.13 g/cm^3 used to activate the PC for cellulose ether modification were purchased from Daejung Chemical and Metals, Korea.

2.2. Methods

2.2.1. Synthesis of polymer composite

To modify and graft HEMC, the powder was spread in a thin layer, and the organic carbonate (PC) was applied directly to the polymer surface. The mixed composite was placed in the roller oven at 80 ºC for 12 hours to initiate the chemical reaction. The dry and wet method was used to mix and synthesis the sample. The optimal concentration ratio of HEMC to PC composite, 1:0.2 was used for modification and confirmed through FTIR analysis.

2.2.2. Characteristics measurement of polymer composite

In characteristics measurement, a PerkinElmer FTIR spectrometer determined the functional group of polymers composite. The spectrum was recorded across 500-4000 cm^{-1} wavenumber range, having 32 scans at a resolution of 4 cm^{-1} (Memon *et al.*, 2023). Furthermore, the structural analysis was evaluated using PANalytical X-ray diffraction (XRD). The structure was analysed at 2 theta diffraction angle range of 10º to 40º. In structural analysis, the crystallinity index of the composite was determined using the deconvolution method using crystallinity equation (Owi *et al.*, 2016).

$$\mathrm{CI} = \left[\frac{\mathrm{Icr}-\mathrm{Iar}}{\mathrm{Icr}}\right] * 100\% \quad (1)$$

I_{cr} denotes the intensity of the highest peak of the crystalline region, and I_{ar} represents the intensity of the amorphous region in the XRD spectrum.

2.2.3. Rheology measurement

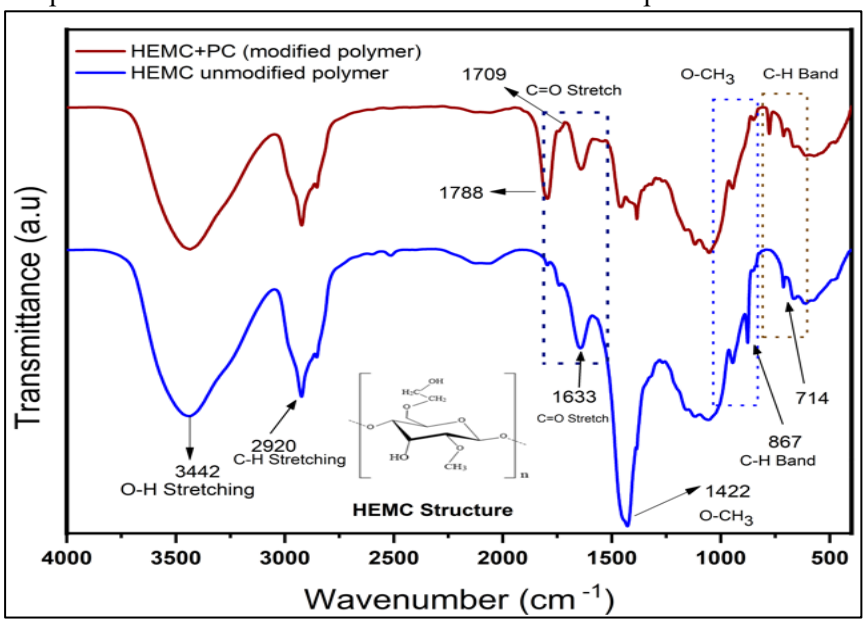
The polymer solution was initially prepared for rheology measurement. The solution was prepared by mixing modified and unmodified HEMC composite in deionised water using magnetic plate stirrer separately. The polymer solution ranging 0.50 wt.% to 2 wt.% was prepared by changing the quantity of polymer composite in deionised water. The rheology of prepared polymeric solutions was determined by measuring viscosity at different shear rates of 0.01 s^{-1} to 1000 s^{-1}. The effect of temperature was evaluated across a range of conditions, including ambient temperature at 25 °C, as well as elevated temperatures of 80 °C, 90 °C, 100 °C, and 110 °C. A rheometer (AR 1500, TA Instruments-USA) with a 40 mm cone and plate geometry at 2° angle was used for the evaluations.

3. Results and discussion

3.1. Functional group analysis

The FTIR spectra of the native and modified HEMC polymer samples reveal significant functional group characteristics as presented in Figure 1. The molecular structure contains free hydroxyl groups indicated by the broad band at 3442 cm^{-1} corresponding to O-H stretching (Yusuf *et al.*, 2022). Aliphatic group C-H stretching, frequently linked to crystalline cellulose, is responsible for vibrations between 2920 cm^{-1} and 2517 cm^{-1} (Parid *et al.*, 2018). A weak intensity peak at 2517 cm^{-1} due to the vibration of the cellulose unit corresponds to sp^3 C-H stretching. A definite transmittance peak observed at 1422 cm^{-1} represents the availability of amorphous crystalline structure in cellulose ether. Furthermore, a moderate band at 1633 cm^{-1} corresponds to C=O stretching vibration, and is associated with the secondary hydroxyl group (Indran *et al.*, 2014). In Figure 1 print region, the weak intensity band at 714 cm^{-1} and 898 cm^{-1} represents the alkyl and methyl group, which represents the unique characteristics of HEMC (Figueiredo *et al.*, 2021).

Figure 1: FTIR Spectrums of unmodified and modified HEMC composite



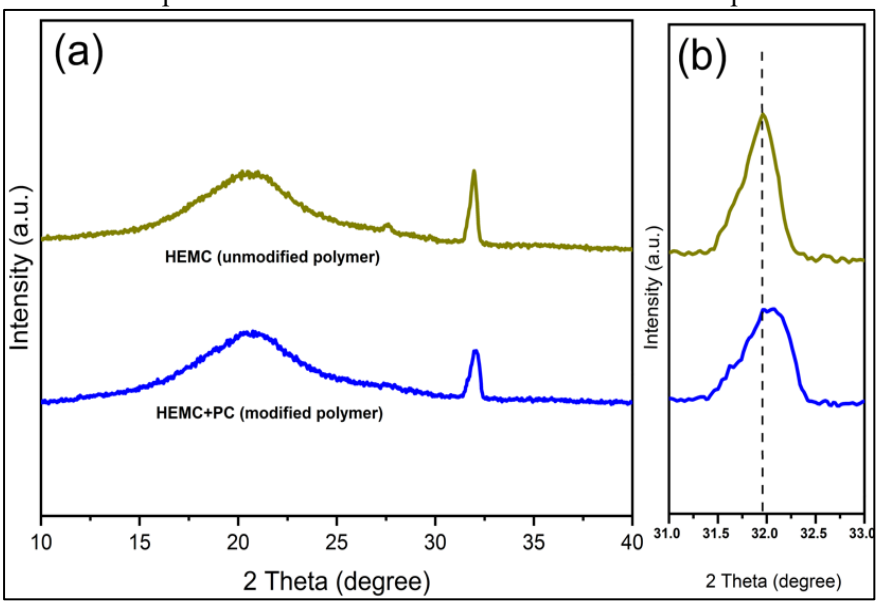
The modified HEMC composite's FTIR spectrum shows distinctive bands connected to the organic carbonate in carbon-hydrogen bond, methoxy group and carbonyl group stretching regions. A weak symmetric peak at 867 cm^{-1} in unmodified HEMC composite was observed to move to a weaker transmittance in the C-H band region of the modified HEMC composite. This new peak in structural isomer generation within the alkyl structure confirmed the chemical modification of HEMC composite. Furthermore, in the spectral region corresponding to the methoxy group ($O\text{-}CH_3$) of the native polymer, a distinct and strong transmittance peak was observed at 1422 cm^{-1}. This peak signifies the characteristic vibrations associated with the methoxy functional group, underwent a notable change in intensity in the modified polymer samples. This change implies that new functional groups have been added to the HEMC backbone. Moreover, a clear new peak in the C=O stretching region at 1804 cm^{-1} appeared in the modified polymer sample, confirming that PC successfully substituted and modified the HEMC polymer surface. Additional transmittance changes in the C-H stretching region and

changes in the intensity of the C=O bands highlight the structural transformation caused by organic carbonates. For instance, changes in the stretching regions of O-H and C-H show that the modifying agents have successfully interacted chemically. Alterations in the transmittance bands linked to the C=O and O-CH_3 groups representing structural changes in the cellulose ether support these changes. The elemental analysis confirmed the successful grafting of PC onto the polymer by revealing an increased carbon content.

3.2. Structural analysis

In XRD analysis, the native and modified HEMC composite shows the diffractogram peaks at 20.5º, 27.5 º and 32 º regions of 2 theta, as observed in Figure 2. The humps in XRD profile shows that the polymeric composite is semi-crystalline in nature as it has crystalline and amorphous broad hump (Santos *et al.*, 2013). The sharp peak at 32 º regions shows the semi-crystalline nature of HEMC. The shape of the modified HEMC composite remains the same after modification through PC. However, the intensity of the hump was slightly reduced and shifted to 31.6 º as observed in Figure 2. Moreover, the diffraction peak at 20.5 º in the PC modified HEMC sample becomes broader, indicating the amorphous content in the polymeric composite. In contrast, the native HEMC sample showed a higher crystalline-to-amorphous ratio as analysed through the sharp peak at 32 º. The solubility of the polymeric solution is associated with reducing crystallinity. Therefore, the decreased crystalline of the modified HEMC aligns with their enhanced solubility. The change in structure to the amorphous phase of the modified HEMC composite is attributed to the disruption of the cellulose crystalline region during the modification process.

Figure 2: XRD structural pattern of unmodified and modified HEMC composite



The Crystalline Index (CrI) of polymer samples was determined using the deconvolution method. The crystallinity index of the native HEMC sample was 54.8%. Removing hemicellulose becomes easy by alkaline conduction during modification process, and it helped reduce the crystallinity. Further, the CrI of the modified HEMC sample was 52.3 % due to the change in the composite structure towards amorphous in nature. The reduced CrI in the PC based modified sample was due to the disruption in crystalline structure, including cellulose molecule distortion and dissociation (Fang *et al.*, 2002). The reduction in the crystallinity index

confirms the successful incorporation of PC on the native HEMC surface, validating the findings.

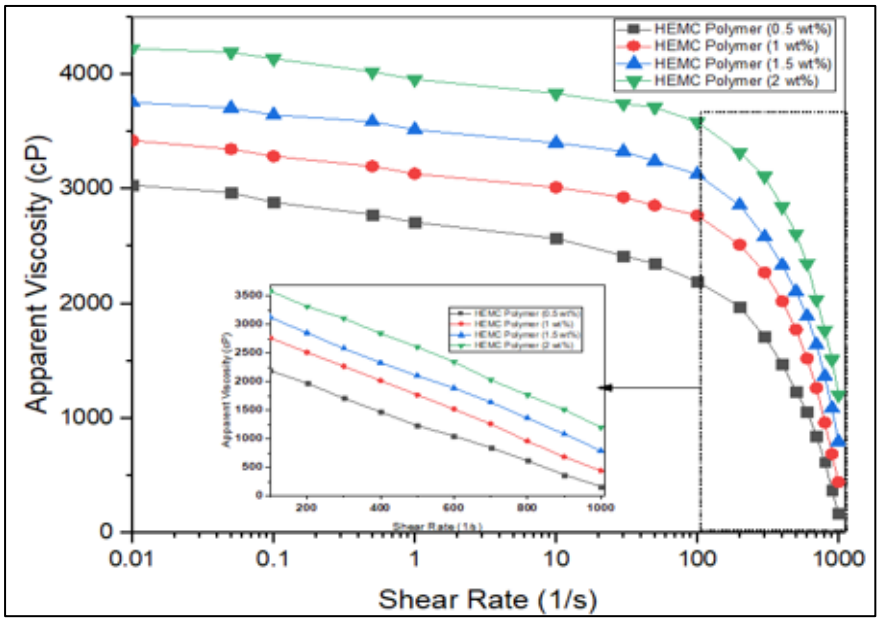
3.3. Rotational flow properties

The flow properties of native and modified HEMC solutions were determined by changing the concentration, temperature and shear rate. The flow properties of the polymer solutions were determined in terms of viscosity analysis by changing the shear rate of each polymer solution separately.

3.3.1. Effect of concentration on viscosity

The impact of concentration on the viscosity of all polymeric solutions were determined by changing the shear rate from 0.01 s^{-1} to 1000 s^{-1} at ambient temperature. The viscosity of both native and modified HEMC solutions was determined at 0.50 wt.%, 1 wt.%, 1.5 wt.% and 2 wt.% concentrations as shown in Figure 3 and Figure 4. It is observed that the viscosity of all polymer solutions increased with increasing polymer concentration from 0.50 wt.% to 2 wt. %. At a minimum shear rate of 0.01 s^{-1}, the viscosity of the native HEMC solution was 3032 cP as observed in Figure 3. Viscosity increased with the concentration of the polymer, reaching 3421 cP at a concentration of 1 wt.%. Similarly, the viscosity further increased to 3750 cP and 4226 cP for HEMC concentrations of 1.5 wt.% and 2 wt.%, respectively. At the maximum shear rate of 1000 s^{-1}, the viscosities were reduced to 170 cP, 440 cP, 797 cP, and 1206 cP for the same concentrations. Similarly, the PC-modified HEMC solutions exhibited a viscosity of 4432 cP at 0.5 wt.% concentration, which increased to 4693 cP, 5039 cP, and 5708 cP for 1 wt.%, 1.5 wt.%, and 2 wt.% concentrations, respectively, at the minimum shear rate.

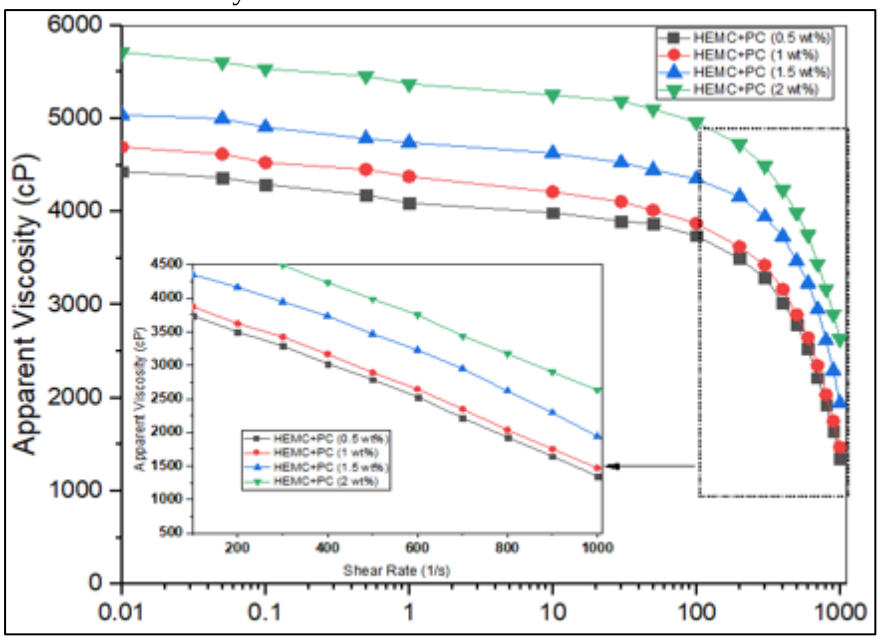
Figure 3: Shear rate vs viscosity of native HEMC solutions at different concentrations



The higher density of polymer molecules in solutions, which results in improved intermolecular interactions and entanglements, is responsible for increased viscosity with concentration. Higher concentrations cause the polymer chains to be packed closer together, which limits their mobility and raises their viscosities. The solutions network structure is further enhanced by the

development of micelle-like aggregates and the predominance of van der Waals forces, which fortify intermolecular bonds and raise viscosity (Martínez *et al.*, 2022).

Figure 3: Shear rate vs viscosity of modified HEMC solutions at different concentrations

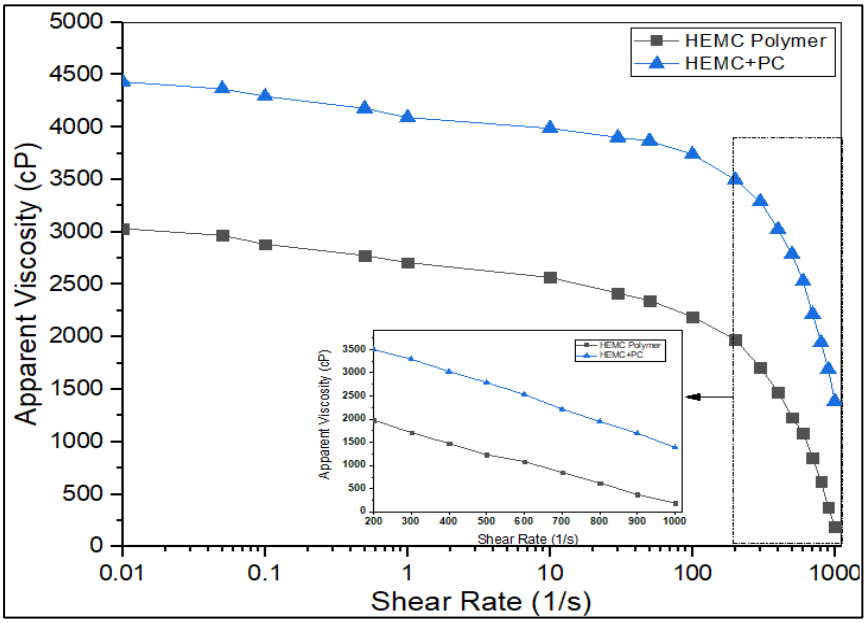


Both the native and modified polymer solution's viscosity profiles showed shear-thinning behaviour at all concentrations, with viscosities falling as the shear rate rose. For instance, when the shear rate is 1000 s^{-1}, the viscosity of the native HEMC solution (0.5 wt.%) dropped from 3033 cP to 170 cP, and the PC-modified HEMC solution dropped from 4432 cP to 1347 cP. The viscosity decreased due to the polymer chains disentangling and aligning in the flow direction at higher shear rates. Pseudoplastic fluids exhibit shear-thinning behaviour (Clasen & Kulicke, 2001; Yeun *et al.*, 2005). By lowering flow resistance at high shear rates, shear-thinning enables polymer solutions to provide high viscosity at low shear rates, which aids in suspending drilling cuttings while lowering pumping pressure and energy needs (Jang *et al.*, 2015). The significant aggregation and entanglement of polymer chains in aqueous solutions is responsible for the increased viscosity of the PC-modified HEMC solutions, especially at low shear rates. Higher shear rates cause these chains to partially align and uncoil, lowering viscosity (Taylor & Nasr-El-Din, 1998; Xu *et al.*, 2013). Given that maintaining ideal rheological characteristics is essential for operational efficiency in well-cementing and polymer flooding projects, the modified solution's pseudoplastic nature raises the possibility that they could be good candidates.

The viscosity comparison of unmodified and PC-modified HEMC solutions at different concentrations (0.5 wt.%, 1 wt.%, 1.5 wt.%, and 2 wt.%) at ambient temperature was also analysed. Across all concentrations, the modified HEMC solutions exhibited significantly higher viscosities than their unmodified solutions. At a concentration of 0.5 wt.% and a shear rate of 0.01 s^{-1}, the viscosity of the modified HEMC solution was approximately 46% higher than that of the unmodified solution, as shown in Figure 5. The chemical reaction during the modification process results in the grafting of new functional groups, as observed in FTIR analysis on the cellulose ether backbone. Further, In the reaction process, hydroxyethylation of cellulose typically enhances solubility, while inter- and intra-annular intrachain formation increases the molecular weight of the polymer (Abbas *et al.*, 2023a). Therefore, the

enhancement in viscosity can be attributed to the increased molecular weight of the modified HEMC polymer composites, which is higher than the unmodified polymers.

Figure 4: Viscosity comparison of native and modified HEMC solution



The addition of structural complexity brought about by the organic carbonate-based modification results in improved rheological characteristics and stronger intermolecular interactions. The impact of concentration on viscosity was consistent across higher concentrations, with modified solutions at 1 wt.%, 1.5 wt.%, and 2 wt.% also display significantly higher viscosities than their unmodified counterparts, as analysed from Figures 3 and Figure 4.

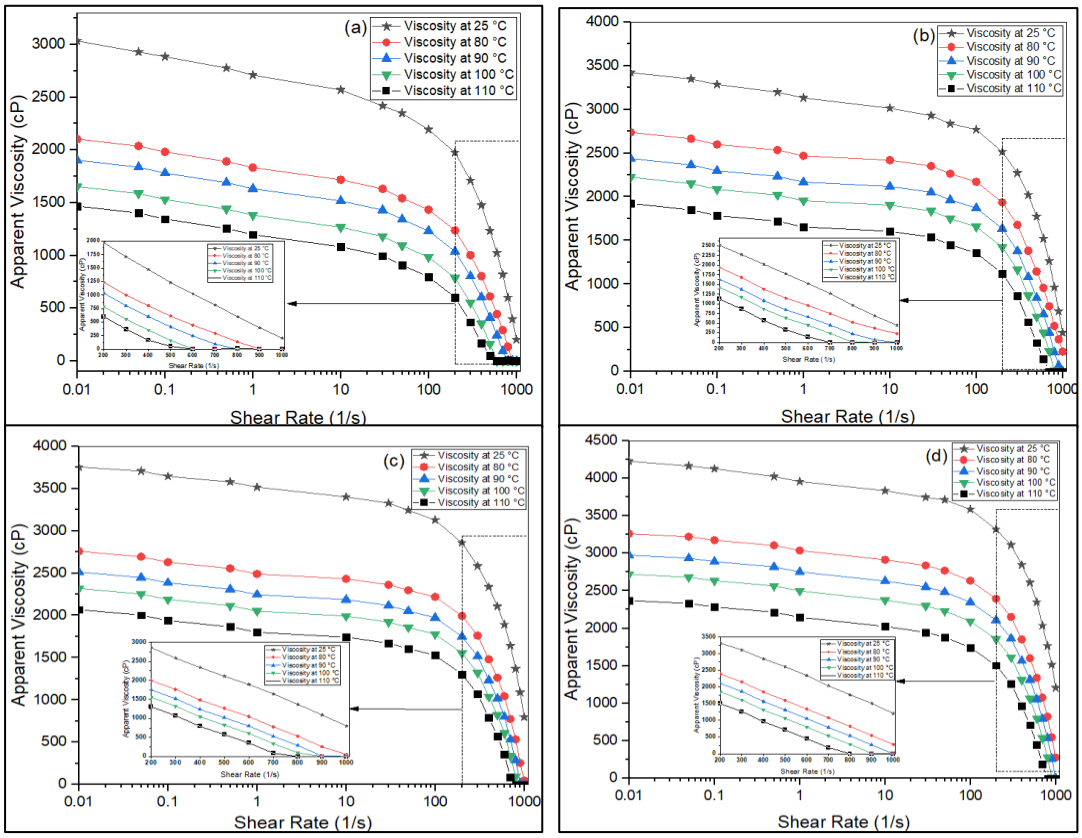
The greater viscosity of the modified solutions can be attributed to the increased polymer concentration in the aqueous solution. The presence of organic carbonate in the modified HEMC increases the density and interaction of the polymer molecules, which enhances the entanglement and aggregation of the polymer chain. As a result, the network structure becomes stronger, raising the solutions' viscosity.

3.3.2. Effect of temperature on viscosity of polymer solution

The thermal behaviour of unmodified and PC based modified HEMC solutions were evaluated at different concentrations across different temperatures (25 °C and 80 °C to 110 °C). The temperature-dependent viscosity profiles of native and modified HEMC solutions are shown in Figures 6 (a-d) and Figure 7 (a-d).

All solutions, irrespective of the concentration or modification, showed a general trend of decreasing viscosity with increasing temperature. For unmodified HEMC solutions, viscosity at 0.5 wt.% decreased from 3035 cP at 25 °C to 1467 cP at 110 °C under the shear rate of 0. 01 s^{-1} as shown in Figure 6. At a higher shear rate of 1000 s^{-1}, viscosity approached negligible values at elevated temperatures, highlighting the shear-thinning nature of the polymer. Similar trends were observed for higher concentration (1 wt.%, 1.5 wt.%, and 2 wt.%), with significant reductions in viscosity as temperature increased.

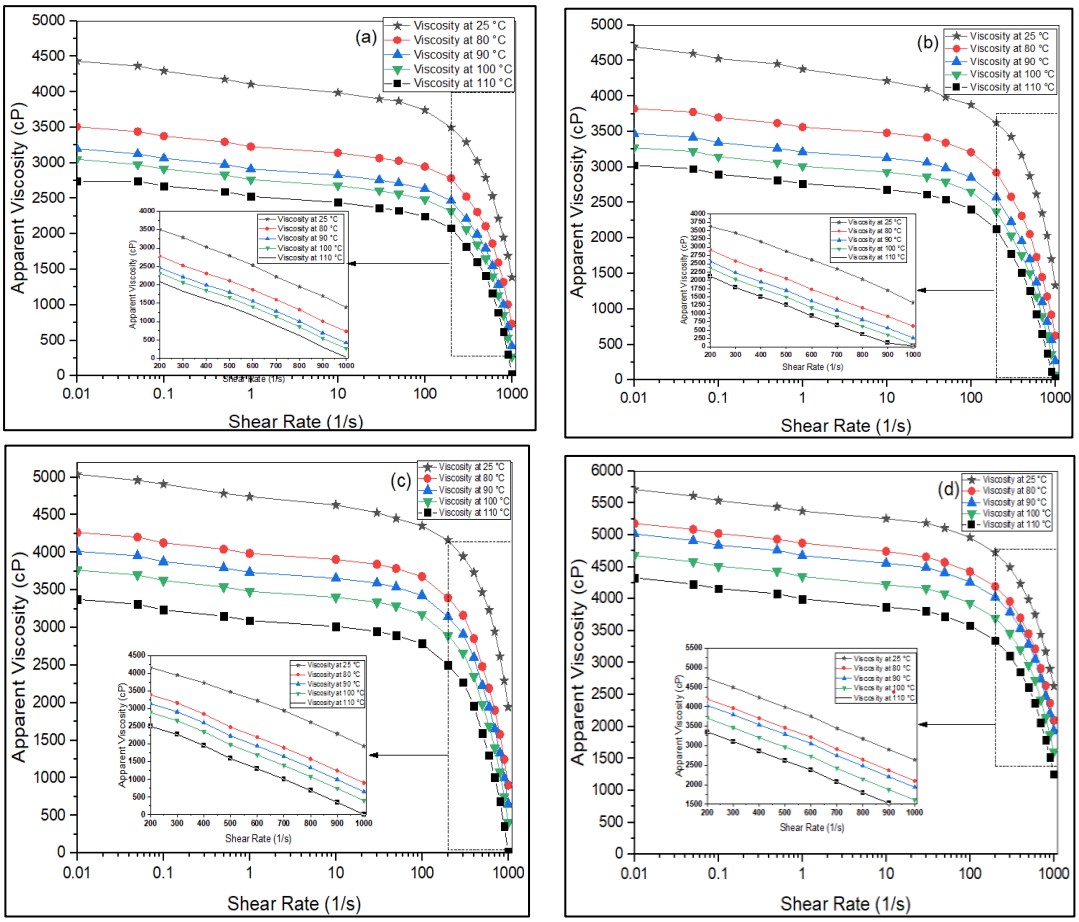
Figure 5: Shear rate vs viscosity at ambient and elevated temperatures of native HEMC solution, (a) 0.50 wt.% concentration, (b) 0.50 wt.% concentration, (c) 0.50 wt.% concentration, (d) 0.50 wt.% concentration



It was observed that at 110 °C the 2 wt.% solution have viscosity of 2371 cP at low shear rate of 0. 01 s^{-1}, indicating the influence of polymer concentration on viscosity retention under thermal stress. In next, the viscosity of PC-based modified HEMC also decreased with increasing temperature however at the same conditions these solutions showed noticeably higher viscosities than their unmodified counterparts. For instance, at 0.5 wt.% concentration, the viscosity at 110 °C was 2745 cP at a shear rate of 0.01 s^{-1}, which is notably higher than the corresponding unmodified solution as observed in Figure 7. Similarly, modified HEMC solutions at concentrations of 1 wt.%, 1.5 wt.%, and 2 wt.% displayed enhanced viscosity, as depicted in Figure 7.

A shift from a rod-like ordered molecular structure to a more flexible disordered configuration that lessens the glucan chain's rigidity is responsible for the observed decrease in viscosity with increasing temperature (El-hoshoudy, 2019). The increased molecular mobility, which permits polymer chains to move more freely and lowers flow resistance, caused a gradual decrease in viscosity up to 100 °C. However, a sudden drop in viscosity at 110 °C indicates the start of thermal deterioration, which is worsened by dehydration effects at higher shear rates. Remarkably, the PC-modified HEMC solutions demonstrated exceptional thermal stability, especially at low concentrations. For instance, the 0.5 wt.% modified solution retained a significant portion of its viscosity at 110 °C temperature, indicating resistance to complete thermal decomposition. This enhanced thermal stability is attributed to improved intermolecular interactions and the formation of cross-linked networks facilitated by the PC modification.

Figure 6: Shear rate vs viscosity at ambient and elevated temperatures of modified HEMC solution, (a) 0.50 wt.% concentration, (b) 0.50 wt.% concentration, (c) 0.50 wt.% concentration, (d) 0.50 wt.% concentration



3.3.3. Viscosity of alkali activated modified HEMC solution

The flow behaviour of the alkali-activated modified HEMC solution was evaluated at 25 °C, 100 °C, and 110 °C. At an ambient temperature of 25 °C, the NaOH-modified solution exhibited shear-thinning behaviour like that of the PC-modified HEMC solution, as depicted in Figure 8. However, the initial viscosity was lower in the NaOH-modified solution. Specifically, when NaOH was added, the viscosity was 0.50 wt.% PC-based HEMC solution decreased from 4432 cP to 4105 cP at a shear rate of 0.01 s^{-1}. At the highest shear rate of 1000 s^{-1}, the viscosity dropped to a minimum value of 1068 cP.

The disruption of HEMCs intermolecular structure brought on by adding NaOH is responsible for decreased initial viscosity at room temperature. Due to improved molecular dispersion and a resulting decrease in viscosity, this disruption makes the polymer more soluble in the solvent (Wang *et al.*, 2015). The viscosity of the alkali-activated solutions decreased at all shear rates at 100 °C in contrast to values at 25 °C, indicating thermal thinning behaviour at higher temperatures. However, when the temperature was raised to 110 ° C, viscosity significantly increased, as shown in Figure 9. When the shear rate was 0. 01 s^{-1} the solution's viscosity rose from 2939 cP to 3121 cP, and when the shear rate was 1000 s^{-1} it increased from 154 cP to 327 cP. PC activation in the polymer system is responsible for this increase in viscosity at 110 °C. PC improves the interaction between polymer chains by acting as a transesterification agent,

which increases viscosity at high temperatures. By maintaining increased viscosity at high temperatures, the thermal activation of PC increases the HEMC systems' thermal stability and qualifies it for demanding applications.

Figure 7: Shear rate vs viscosity of alkali activated modified HEMC solution at ambient temperature

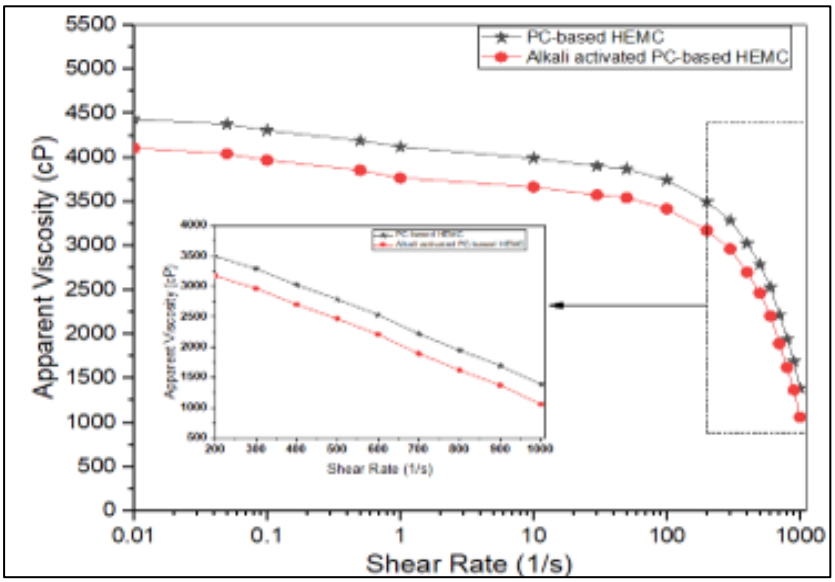
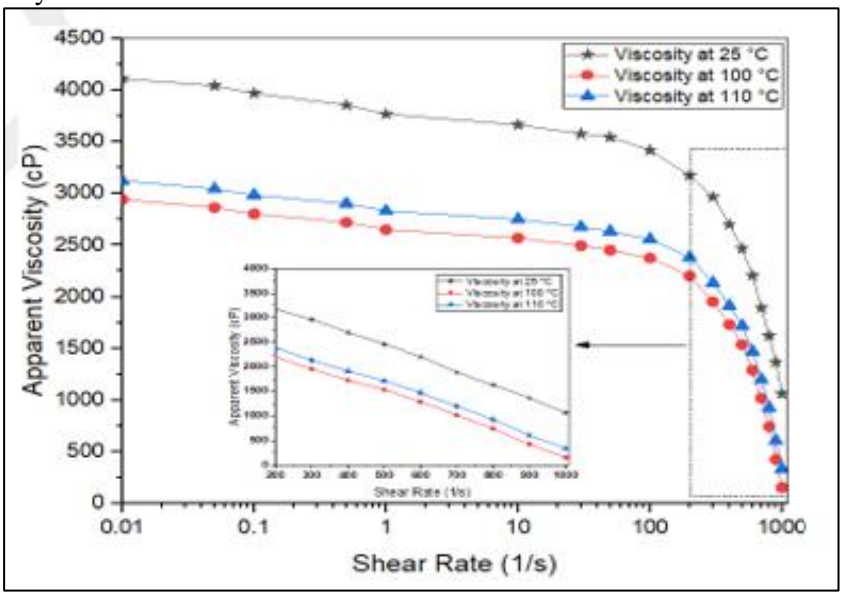


Figure 8: Viscosity vs shear rate of alkali activated solutions at ambient and elevated temperatures



4. Conclusions and recommendations

This study investigated the effect of PC organic carbonate and NaOH alkali solution as a trigger to in HEMC solution was investigated. Overall, the rheology in terms of shear viscosity of native and modified HEMC solution containing PC and NaOH were measured at 0.50 wt.%, 1 wt%,1.5 wt.% and 2 wt.% at ambient and elevated temperatures. The main conclusions could be drawn as follows:

- FTIR analysis revealed the appearance of new peak corresponding to the free hydroxy group of cellulose ether, confirming the successful grafting of PC on HEMC surface.

The modification achieved using PC as a transesterification agent proved to be an important parameter to enhance the thermal characteristics of cellulose either.

- XRD analysis confirms the semi-crystalline nature of HEMC composite, with the modified HEMC exhibiting significantly improved solubility in aqueous solution compared to the native HEMC. This enhancement is attributed to the reduced crystallinity index achieved by incorporating PC as a transesterification agent.
- Viscosity measurement at varying concentrations revealed a positive correlation between viscosity and concentration, indicating enhanced intermolecular interaction at high concentrations. The PC based modified HEMC solution exhibited significantly higher viscosity at 100 °C and 110 °C due to grafting of new functional groups and inter- and intra-annular intrachain formation, underscoring its improved thermal stability compared to the unmodified HEMC solution.
- At ambient temperature, the viscosity of alkali based modified HEMC solution was lower than that of the modified PC-modified HEMC solution at ambient temperature, which showed the optimal approach for minimising the surface viscosification of cellulose ether. The viscosity of alkali-PC based modified HEMC solution was notably higher at an elevated temperature of 110 ºC than the native and PC modified HEMC solution. This increase in viscosity revealed that the addition NaOH based solution trigger activate the PC in an aqueous solution of HEMC, demonstrating the enhanced thermal stability of the polymer solution.

Based on viscosity analysis conducted at various concentrations and temperature conditions, it is revealed that 0.50 wt.% and 1wt.% concentration of PC modified HEMC solution is optimal. The recommended concentrations not only resolve the issue of surface viscosification but also demonstrate enhanced viscosity at geothermal conditions. This improvement in viscosity contributes to better fluid properties, making the solution more suitable for further utilisation in drilling fluid and cementing applications within the oil and gas industry.

Declaration of conflict of interest

The author(s) declared no potential conflicts of interest(s) with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) received no financial support for the research, authorship and/or publication of this article.

ORCID iD:

Ghulam Abbas https://orcid.org/0009-0008-6625-9249

Abdul Samad Shaikh https://orcid.org/0009-0001-2464-1959

Tariq Ali Chandio https://orcid.org/0000-0003-2745-2421

Abdul Haque Tunio https://orcid.org/0009-0009-8196-7654

Publisher's Note

IDEA Publishers Group (AJSET IDEA-PG) stands neutral with regard to the jurisdictional claims in the published maps and the institutional affiliations.

References

Abbas, G., Irawan, S., Kumar, S., & Elrayah, A. A. I. (2013). Improving oil well cement slurry performance Using Hydroxypropylmethylcellulose Polymer. *Advanced Materials Research*, *787*, 222–227. https://doi.org/10.4028/www.scientific.net/amr.787.222

Abbas, G., Irawan, S., Memon, M. K., Kalwar, S. A., & Kumar, S. (2015). Hydroxypropylmethylcellulose as a free water and settling control agent in oil well cement slurry. In *ICIPEG: Proceedings of the International Conference on Integrated Petroleum Engineering and Geosciences 2014* (pp. 121–128). Springer. https://doi.org/10.1007/978-981-287-368-2_11

Abbas, G., Irawan, S., Memon, K. R., & Khan, J. (2020). Application of cellulose-based polymers in oil well cementing. *Journal of Petroleum Exploration and Production Technology*, *10*(2), 319–325. https://doi.org/10.1007/S13202-019-00800-8/FIGURES/4

Abbas, G., Tunio, A. H., Memon, K. R., Mahesar, A. A., & Memon, F. H. (2023a). Effect of temperature and alkali solution to activate diethyl carbonate for improving rheological properties of modified hydroxyethyl methyl cellulose. *ACS Omega, 9*(4), 4540–4554. https://doi.org/10.1021/acsomega.3c07451

Abbas, G., Tunio, A. H., Memon, K. R., Mahesar, A. A., Memon, F. H., & Abbasi, G. R. (2023b). Modification of cellulose ether with organic carbonate for enhanced thermal and rheological properties: characterisation and analysis. *ACS Omega* 8(28), 25453–25466. https://doi.org/10.1021/acsomega.3c0297

Chandio, T. A., Manan, M. A., Memon, K. R., Abbas, G., & Abbasi, G. R. (2021). Enhanced oil recovery by hydrophilic silica nanofluid: experimental evaluation of the impact of parameters and mechanisms on recovery potential. *Energies*, *14*(18), 1–18. https://ideas.repec.org/a/gam/jeners/v14y2021i18p5767-d634588.html

Clasen, C., & Kulicke, W. M. (2001). Determination of viscoelastic and rheo-optical material functions of water-soluble cellulose derivatives. *Progress in Polymer Science*, *26*(9), 1839–1919. https://doi.org/10.1016/S0079-6700(01)00024-7

Dutta, S., Yu, I. K. M., Tsang, D. C. W., Fan, J., Clark, J. H., Jiang, Z., Su, Z., Hu, C., & Poon, C. S. (2020). Efficient depolymerisation of cellulosic paper towel waste using organic carbonate solvents. *ACS Sustainable Chemistry and Engineering*, *8*(34), 13100–13110. https://doi.org/10.1021/acssuschemeng.0C04102

El-hoshoudy, A. N. (2019). Synthesis of acryloylated starch-g-poly acrylates crosslinked polymer functionalised by emulsified vinyltrimethylsilane derivative as a novel EOR agent for severe polymer flooding strategy. *International Journal of Biological Macromolecules*, *123*, 124–132. https://doi.org/10.1016/j.ijbiomac.2018.11.056

Fang, J. M., Fowler, P. A., Tomkinson, J., & Hill, C. A. S. (2002). The preparation and characterisation of a series of chemically modified potato starches. *Carbohydrate Polymers*, *47*(3), 245–252. https://doi.org/10.1016/S0144-8617(01)00187-4

Figueiredo, L. R. F., Nepomuceno, N. C., Melo, J. D. D., & Medeiros, E. S. (2021). Glycerol-based polymer adhesives reinforced with cellulose nanocrystals. *International Journal of Adhesion and Adhesives*, *110*, 102935. https://doi.org/10.1016/J.IJADHADH.2021.102935

Hamza, A., Shamlooh, M., Hussein, I. A., Nasser, M., & Salehi, S. (2019). Polymeric formulations used for loss circulation materials and wellbore strengthening applications in oil and gas wells: A review. *Journal of Petroleum Science and Engineering*, *180*(February), 197–214. https://doi.org/10.1016/j.petrol.2019.05.022

Indran, S., Edwin Raj, R., & Sreenivasan, V. S. (2014). Characterisation of new natural cellulosic fiber from Cissus quadrangularis root. *Carbohydrate Polymers*, *110*, 423–429. https://doi.org/10.1016/J.carbpol.2014.04.051

Jang, H. Y., Zhang, K., Chon, B. H., & Choi, H. J. (2015). Enhanced oil recovery performance and viscosity characteristics of polysaccharide xanthan gum solution. *Journal of Industrial and Engineering Chemistry*, *21*, 741–745. https://doi.org/10.1016/J.JIEC.2014.04.005

Khan, M. A., Li, M. C., Lv, K., Sun, J., Liu, C., Liu, X., Shen, H., Dai, L., & Lalji, S. M. (2024). Cellulose derivatives as environmentally-friendly additives in water-based drilling fluids: A review. *Carbohydrate Polymers*, *342*, 122355. https://doi.org/10.1016/J.CARBPOL.2024.122355

Lashari, N., & Ganat, T. (2021). Synthesised graphene oxide and fumed aerosil 380 dispersion stability and characterisation with partially hydrolysed polyacrylamide. *Chinese Journal of Chemical Engineering*, *34*, 307–322. https://doi.org/10.1016/J.CJCHE.2020.09.035

Lopez, C. G. & Richtering, W. (2021). Oscillatory rheology of carboxymethyl cellulose gels: Influence of concentration and pH. *Carbohydrate Polymers*, *267*. https://doi.org/10.1016/j.carbpol.2021.118117

Martínez, S., Espert, M., Salvador, A. & Sanz, T. (2022). The role of oil concentration on the rheological properties, microstructure, and in vitro digestion of cellulose ether emulsions. *Food Hydrocolloids*, *131*. https://doi.org/10.1016/j.foodhyd.2022.107793

Memon, F. H., Tunio, A. H., Memon, K. R., Mahesar, A. A. & Abbas, G. (2023). Unveiling the diagenetic and mineralogical impact on the carbonate formation of the Indus Basin, Pakistan: implications for reservoir characterization and quality assessment. *Minerals 13*(12), 1474. https://doi.org/10.3390/MIN13121474

Ojogbo, E., Ogunsona, E. O., & Mekonnen, T. H. (2020). Chemical and physical modifications of starch for renewable polymeric materials. *Materials Today Sustainability*, *7–8*. https://doi.org/10.1016/J.MTSUST.2019.100028

Owi, W. T., Lin, O. H., Sam, S. T., Chia, C. H., Zakaria, S., Mohaiyiddin, M. S., Villagracia, A. R., Santos, G. N., & Akil, H. M. (2016). Comparative study of microcelluloses

isolated from two different biomasses with commercial cellulose. *BioResources*, *11*(2), 3453–3465. https://doi.org/10.15376/biores.11.2.3453-3465

Parid, D. M., Aliaa, N., Rahman, A., Baharuddin, A. S., Mohammed, A. P., Johari, A. M., Zubaidah, S., & Razak, A. (2018). Synthesis of CMC. *BioResources*, *13*(1), 535–554.

Pope, G. A. (2011). Recent developments and remaining challenges of enhanced oil recovery. *Journal of Petroleum Technology*, *63*, 136. https://doi.org/10.2118/0711-0065-JPT

Qi, L. (2014). The application of polymer mud system in drilling engineering. *Procedia Engineering*, *73*, 230–236. https://doi.org/10.1016/J.PROENG.2014.06.192

Reddy, B., Patil, R., & Patil, S. (2012). Chemical modification of biopolymers to design cement slurries with temperature-activated viscosification-a laboratory study. *SPE Drilling & Completion*, *27*(2), 94–102. http://www.onepetro.org/mslib/servlet/onepetropreview?id=SPE-141005-PA

Sabzian mellei, A., Madadizadeh, A., Riahi, S., & Kaffashi, B. (2022). Synergetic effects of PVP/HEC polymers on rheology and stability of polymeric solutions for enhanced oil recovery at harsh reservoirs. *Journal of Petroleum Science and Engineering*, *215*(PA), 110619. https://doi.org/10.1016/j.petrol.2022.110619

Santos, R. M. dos, Flauzino Neto, W. P., Silvério, H. A., Martins, D. F., Dantas, N. O., & Pasquini, D. (2013). Cellulose nanocrystals from pineapple leaf, a new approach for the reuse of this agro-waste. *Industrial Crops and Products*, *50*, 707–714. https://doi.org/10.1016/J.INDCROP.2013.08.049

Sun, C., Liu, R., Sheng, H., Wang, R., Zhang, Z., Zhao, J., & Zhang, M. (2018). Effect of microparticulation and xanthan gum on the stability and lipid digestion of oil-in-water emulsions stabilised by whey protein. *Food & Function*, *9*(9), 4683–4694. https://doi.org/10.1039/C8FO00182K

Sun, J., Wen, Z., Khan, M. A., Lv, K., Shen, H., Dai, L., Li, Y., Ding, Y., Liu, C. & Li, M. C. (2024). A review of cellulose nanomaterial-stabilised Pickering foam: Formation, properties, and emerging oilfield applications. *International Journal of Biological Macromolecules*, *281*, 136274. https://doi.org/10.1016/J.IJBIOMAC.2024.136274

Taylor, K. C., & Nasr-El-Din, H. A. (1998). Water-soluble hydrophobically associating polymers for improved oil recovery: A literature review. *Journal of Petroleum Science and Engineering*, *19*(3–4), 265–280. https://doi.org/10.1016/S0920-4105(97)00048-X

Wang, W., Li, F., Yu, J., Navard, P., & Budtova, T. (2015). Influence of substitution on the rheological properties and gelation of hydroxyethyl cellulose solution in NaOH–water solvent. *Carbohydrate Polymers*, *124*, 85–89. https://doi.org/10.1016/J.CARBPOL.2015.01.065

Wei, Y., Cai, Z., Wu, M., Guo, Y., Tao, R., Li, R., Wang, P., Ma, A., & Zhang, H. (2020). Comparative studies on the stabilisation of pea protein dispersions by using various

polysaccharides. *Food Hydrocolloids*, *98*, 105233. https://doi.org/10.1016/J.FOODHYD.2019.105233

Xia, Z., Li, J., Zhang, J., Zhang, X., Zheng, X., & Zhang, J. (2020). Processing and valorisation of cellulose, lignin and lignocellulose using ionic liquids. *Journal of Bioresources and Bioproducts*, *5*(2), 79–95. https://doi.org/10.1016/J.JOBAB.2020.04.001

Xiong, P., Niu, Y., Meng, F., Ma, Q., Song, C., Zhang, Q., & Che, Y. (2024). Grafted copolymers based on HPMC with excellent thermo-viscosifying and salt-tolerant properties at low concentration for enhanced oil recovery. *Geoenergy Science and Engineering*, *233*, 212566. https://doi.org/10.1016/J.GEOEN.2023.212566

Xu, L., Xu, G., Liu, T., Chen, Y., & Gong, H. (2013). The comparison of rheological properties of aqueous welan gum and xanthan gum solutions. *Carbohydrate Polymers*, *92*(1), 516–522. https://doi.org/10.1016/J.CARBPOL.2012.09.082

Yeun, S. G., Regnier, L., & McClements, D. J. (2005). Influence of environmental stresses on stability of oil-in-water emulsions containing droplets stabilised by β-lactoglobulin-ι-carrageenan membranes. *Journal of Colloid and Interface Science*, *286*(2), 551–558. https://doi.org/10.1016/j.jcis.2005.01.051

Yusuf, S. M., Junin, R., Muhamad Sidek, M. A., Agi, A., Ahmad Fuad, M. F. I., Rosli, N. R., Rahman, N. A., Yahya, E., Muhamad Soffian Wong, N. A., & Mustaza, M. H. (2022). Screening the synergy of sodium dodecylbenzenesulfonate and carboxymethyl cellulose for surfactant-polymer flooding. *Petroleum Research*, *7*(3), 308–317. https://doi.org/10.1016/j.ptlrs.2021.11.002

Zheng, X., Huang, F., Chen, L., Huang, L., Cao, S., & Ma, X. (2019). Preparation of transparent film via cellulose regeneration: Correlations between ionic liquid and film properties. *Carbohydrate Polymers*, *203*, 214–218. https://doi.org/10.1016/j.carbpol.2018.09.060