

Synthesis and characterization of a novel amphoteric terpolymer nanocomposite for enhanced oil recovery applications

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Abstract:

Water-soluble polymers are highly applied to increase the recovery from oil reservoirs. The application of these polymers in enhanced oil recovery (EOR) has some limitations regarding chemical, thermal and mechanical degradation at harsh reservoir condition. In this research, a novel stable terpolymer has been synthesised by preparing and grafting vinylbenzyl starch with poly (acrylamide/ acrylic acid/ acrylacyloxyethyltrimethyl ammonium chloride) in the presence of silica nanoparticles *via* free radical emulsion polymerization. Different stability investigations have been applied for the synthesised polymer including temperature, salinity and shear stability analyses at harsh conditions. The chemical structure of the novel polymer has been characterized using numerous methods including proton nuclear magnetic resonance (¹H NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and high-resolution transmission electron microscope (TEM). Thermal properties have been evaluated by thermal gravimetric analysis (TGA). The rheological properties have been studied at harsh reservoir conditions in terms of formation water salinity, temperature, and shear rate. The results have shown that the introduction of vinylbenzyl starch has significantly enhanced the thermal and chemical stability of the prepared polymer. Moreover, flooding experiments conducted on sandstone core have shown that the synthesised terpolymer can enhance the oil recovery up to 43% at polymer concentration of 3 g/L.

Keywords:

Vinylbenzyl starch, Amphoteric terpolymer, Silica nanocomposite, Free radical polymerization.

1. Introduction

Starch is a biological polysaccharide that has glucose units with α -D-glycosidic bond. Although starch is an inexpensive and environmentally friendly natural polymer, it has many limitations related to industrial applications. Consequently, different chemical modifications were proposed to improve its properties [1]. Chemically modified starch derivatives that include grafted starches copolymers, pre-gelatinized starches, esterified and etherified starches have many applications such as chemical flooding and water shut off applications. Many authors reported grafting of starch with different

anionic and cationic vinyl monomers *via* free radical polymerization. These monomers 2-acrylamido-2-methyl-1-propane-sulfonic acid[2], acrylic acid, and 1-vinyl-2-pyrrolidone[3].

This research reported the synthesis of vinyl benzyl starch which is grafted with acrylamide/acrylic acid/acryloyloxyethyltrimethyl ammonium chloride terpolymer in the presence of dimethylphenylvinylsilane *via* free radical emulsion polymerization. Grafting starch with acrylamide and/acrylic acid increase polymer's capacity to absorb water. Moreover, the introduction of silica nanoparticles increases the system rigidity and thus improve salt and temperature resistance. Further, the presence of amphoteric structure presented in negatively charged carboxylate group and positively charged ammonium atom minimize interaction with bivalent cations and hence improves the polymer salt tolerance. Rheological properties of the prepared polymer composite were determined under varying conditions of temperature, salinity and shear rate. Flooding experiments conducted on sandstone core, and the volume of oil discharged by applying different polymer concentration was reported.

2. Experimental

2.1. Materials and Instrument

Commercial corn starch; Dimethyl sulfoxide (DMSO $\geq 99.9\%$); 4-(chloromethyl)styrene (90%), 4-(dimethylamino)pyridine (DMAP $\geq 98.0\%$); acrylamide (AM $\geq 99\%$); sodium dodecyl sulphate, (SDS $\geq 98.5\%$); 2-(acryloyloxy)ethyl]trimethylammonium chloride (80 wt% in water), acrylic acid ($\geq 99\%$); dimethylphenylvinylsilane (98%); potassium persulfate (KPS $\geq 99\%$); ethanol ultra-pure; acetone ($\geq 97\%$); chloroform ($\geq 97\%$). All chemicals were supplied by Sigma-Aldrich excluding starch, which was purchased from a commercial source. Deionized water was used to prepare all aqueous solutions.

FT-IR spectra was carried out on a Shimadzu Tracer 100 spectrophotometer using optical range 400–4000 cm^{-1} and 32 scans at a resolution of 6 cm^{-1} . Transmission electron microscopy (TEM) analysis was carried out on a Japanese JEOL high-resolution transmission electron microscope.

2.2. Synthesis

Typical emulsion polymerization procedure was carried out in a three-neck 250 ml reactor equipped with mechanical stirrer, thermometer, condenser, and nitrogen inlet/outlet. A 2.5g of SDS surfactant was completely dissolved in 100 ml of deionized water and charged into the reactor. The designed amount of vinyl benzyl starch, acrylamide, 2-(acryloyloxy)ethyl]trimethylammonium chloride, and acrylic acid monomers were added into the reaction mixture and stirred vigorously and purged with nitrogen for 30 min. The mixture is heated to the designated reaction temperature; then potassium persulfate and dimethylphenylvinylsilane were added to the reaction mixture. The copolymerization reaction proceed under N_2 for 12 hours. In a purpose of determining the overall monomer conversion, samples were withdrawn from polymerization reactor at different time intervals. The obtained polymer gel was precipitated by acetone, and subsequently washed with excess of ethanol and Soxhlet extraction using chloroform for 24 hr. The obtained polymer was then dried in a vacuum oven at 60°C for 24 hours.

2.3 Results and discussion

2.3.1 Characterization and structure confirmation

FT-IR spectra of starch, modified starch and polymer composite are presented in Fig. 1. It is observed that FT-IR spectrum of starch shows characteristic absorption peaks at 3283 cm^{-1} , 2929 cm^{-1} , 1159.9 cm^{-1} , and 1083.9 cm^{-1} due to (O–H), (C–H), (C–O), and (C–OH), respectively. While the IR spectra of vinyl benzyl starch shows strong peak at 1430 cm^{-1} , and 1620 cm^{-1} , which are attributed to (C–O) and (C=C), respectively. Also, a significant decrease in the intensity of (O–H) stretching band at 3400 cm^{-1} after etherification reaction can be justified by diminishing the number of hydroxyl groups

present in starch, which demonstrate a successful etherification reaction between 4-(chloromethyl)styrene and starch has occurred.

The FTIR spectrum of starch-g-terpolymer shows absorption peak at 1656 cm^{-1} and 1710 cm^{-1} due to the presence of carbonyl's stretching vibration of the amide group, $-\text{C}=\text{ONH}_2$ and unsaturated esters ($\text{CH}_2\text{CH}=\text{COO}$), respectively. The characteristic peaks at 1450 cm^{-1} assigned to methyl groups linked with ammonium, and the absorption peak at 952 cm^{-1} attributed to $\text{N}^+(\text{CH}_3)_3$ stretching vibration in 2-(acryloyloxy)ethyl]trimethylammonium chloride. The presence of these two peaks proves the incorporation of cationic moieties onto the copolymer backbone. Furthermore, the absence of characteristic band of vinyl group from $1600\text{--}1650\text{ cm}^{-1}$ confirms successful and complete polymerization. The absorption peaks 3364 cm^{-1} assigned to stretching vibrations of ($-\text{NH}$) in acrylamide, and absorption peaks at 1130 cm^{-1} and 620 cm^{-1} (Si-O-Si) in the silica network, respectively.

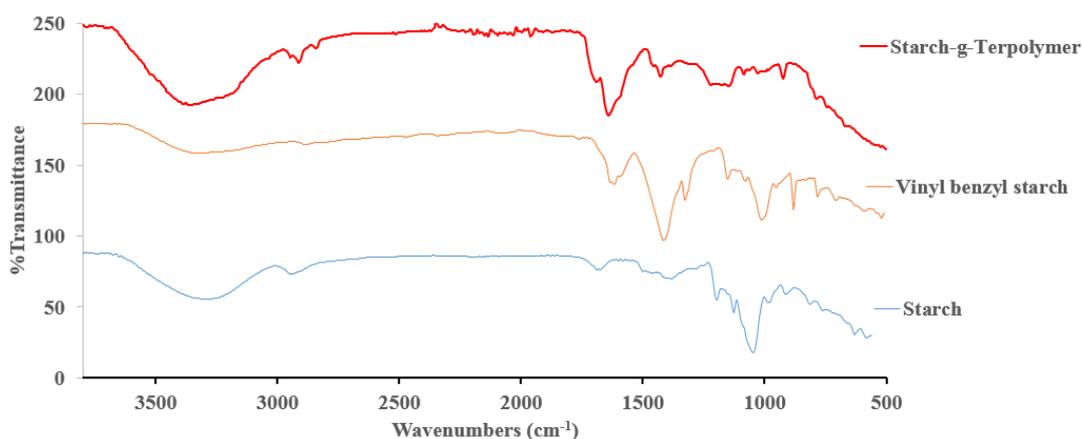


Fig. 1. Infrared spectra of starch and starch-g-terpolymer.

TEM analysis of the synthesized polymer composite as shown in Fig. 2 indicates the enclosure of inorganic silica nanoparticles in the polymer structure. The nanoparticles is represented as dark areas inserted in light colored polymer. The presence of silica nanoparticles diminish particles aggregation and hence reduce the latex size. Additionally, it increases the polymer resistance against temperature and salinity.

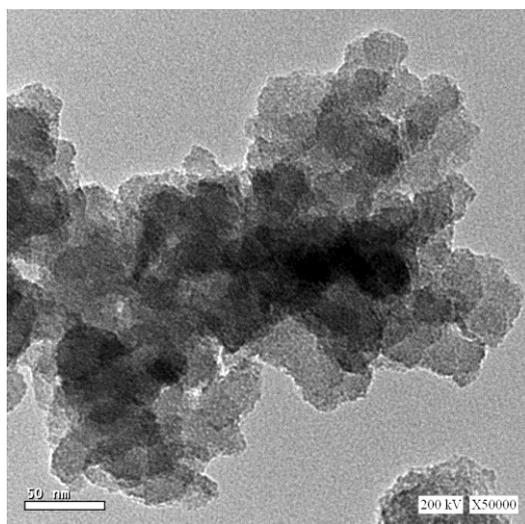


Figure 2: TEM analysis of starch-g-terpolymer

2.3.2 Rheological and solution properties

2.3.2.1 Shear resistance

The shear resistance of the synthesized starch composite was evaluated by measuring the apparent viscosity at different shear rates ranging from 0-100 s^{-1} at 25°C. As can be observed from Fig.3, the synthesized starch composite exhibits decrease in the apparent viscosity with increasing applied shear rate (shear thinning behaviour). The reported viscosity retention rate of the prepared starch composite at 100 s^{-1} was about 20%. Moreover, as the applied shear rate reduced from (100 s^{-1} –0), the viscosity of the starch composite was recovered to values slightly lower than the original viscosity. This phenomena is due to the existence of dynamic equilibrium between intermolecular association and breakage of polymer network structure formed because of shearing process[4].

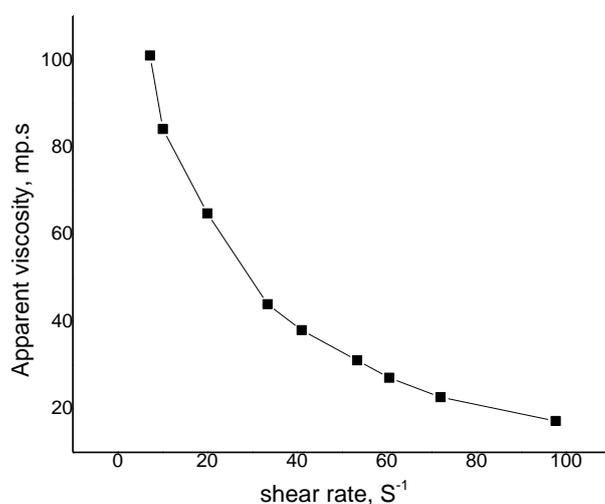


Figure 3: Effect of shear rate on apparent viscosity

2.3.2.2 Saline resistance

The rheological properties of the polymer composite was evaluated at two different saline solution concentrations. The apparent viscosity of two polymer concentrations dissolved in synthesized saline solutions at a shear rate of 7.34 s^{-1} and temperature 25 °C is presented in Fig.4. From the results shown in Fig.4, the prepared polymer composite exhibits reasonable salt resistance at different polymer concentrations. This behavior can be explained by an increase in hydrodynamic volume in aqueous solution by increasing salt concentration, which sequentially prevents curling of polymer chain and controls the viscosity reduction of polymer solution. [5]. Additionally, the presence of amphoteric polymer structure presented in negatively charged carboxylate group and positively charged ammonium atom enhance the capability of ionic exchange, and minimize interaction and precipitation with bivalent cations present in saline solution [6, 7]. Also, the hydrophobic association is greatly enhanced with increasing salt concentration where the solubility of hydrophobic moieties is lowered [5].

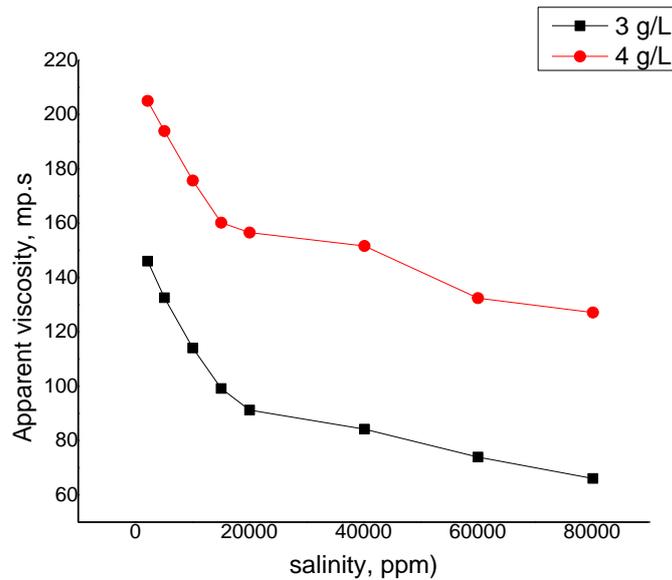


Figure 4: Effect of salinity on apparent viscosity at a shear rate of 7.34 s⁻¹

2.3.2.3 Temperature resistance

The temperature tolerance of the synthesized polymer was assisted by measuring the viscosity at different polymer concentrations (1, 3 and 4 g/L). From Fig. 5 it can be noted that initially the viscosity is gradually increased by increasing temperature till around 50°C, then decreased and became almost steady with temperature. The abrupt increase of the apparent viscosity can be explained by the presence of hydrophobic components that tend to aggregate and form hydrophobic association that result in reversible, physical, rigid molecular structures by strong van der Waal's interactions and due to starch gelation effect that occurs at elevated temperature [8, 9].

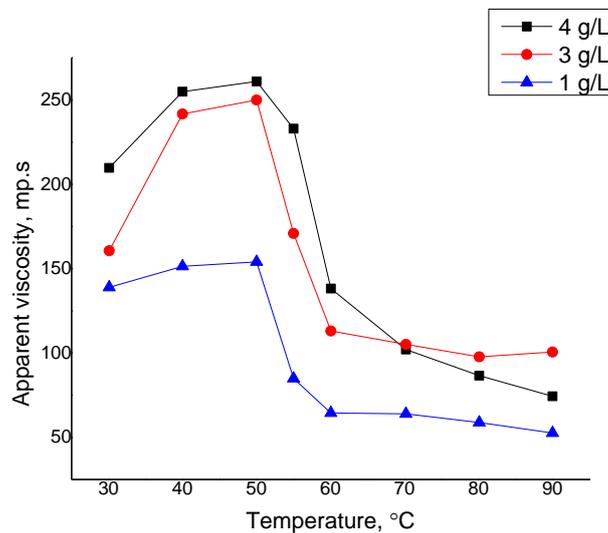


Figure 5: Effect of temperature on apparent viscosity

2.3.3 Core flooding Experiments

The core flooding experiments were carried out to investigate the effect of the synthesized polymer composite on enhanced oil recovery. A sandstone core was cleaned and prepared according to the

procedure reported in the literature [10, 11]. Flooding experiments were conducted at a temperature of 70 °C, using brine salinity of 80,000 ppm, and different polymer concentrations of (1, 2, 3 and 4 g/L). The conditions of flooding experiments and the core properties are summarized in Table 1. The percentage of oil recovery as a function of injected polymer volumes is presented in Fig. 6. As shown in Fig. 6 the maximum oil recovery of 43% was achieved by applying 3 g/L polymer concentration. Moreover, the volume of recovered oil is incrementally amplified with increasing polymer concentration. The excellent rheological properties of the polymer composite in terms of high resistance of shear, salt, and temperature result in improved sweeping efficiency and hence better enhanced oil recovery performance. Additionally, high aqueous phase viscosity due to the gelation effect attributed with the presence of hydrophobically modified starch in the polymer composite, which consequently reduce the mobility ratio and hence displacement efficiency is highly enhanced.

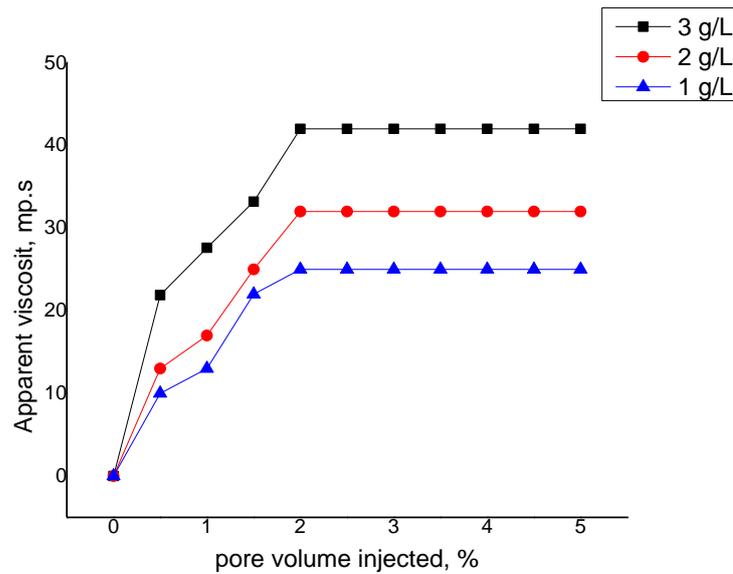


Figure 6: Oil recovery as a function of injected pore volume at different copolymer Concentration

Table 1 Flooding experiments conditions and core properties

Core flooding parameters	Value
Core material	Sandstone
Core length, cm	7.5
Core Diameter, cm	3.5
Pore volume, cc	12
Permeability, mD	50
Injection rate of brine and oil, cc/h	2
Flooding temperature, C	70
Brine salinity, ppm	80,000

4. Conclusion

Vinyl benzyl starch was successfully prepared and grafted on poly(acrylamide/acrylic acid/acrylacyloxyethyltrimethyl ammonium chloride) terpolymer using free radical polymerization in the presence of dimethylphenylvinylsilane derivative. The chemical structure of the modified starch and the polymer composite was confirmed by Fourier transform infrared (FTIR) spectroscopy and proton nuclear magnetic resonance (¹H NMR) spectroscopy. The presence of functional silica nanoparticles

significantly reduced the latex size as proved by transmission electron microscopy (TEM) and dynamic light scattering (DLS). Moreover, the measured rheological properties of the polymer demonstrate reasonable resistance to shear, temperature and salt that result from the polymer amphoteric structure. The maximum oil recovery factor from displacement flooding experiments reached 43% by applying 3 g/L polymer concentration. All these results prove that the prepared novel polymer is a promising candidate for enhanced oil recovery application at harsh reservoir conditions.

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