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Improved rheological properties and stability of multi-walled carbon nanotubes/polymer in harsh environment

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Abstract

This work aims to improve the rheological properties and stability of multi-walled carbon nanotube (MWCNT)/acrylamide base skeleton polymer blends at harsh environment of high salinity-high temperature (HS-HT) or various pH. Different co/ter-polymers have been accomplished to modify the structure of acrylamide polymer by free-radical copolymerization of acrylamide based monomers. Anionic, cationic and hydrophobic functional groups were used for synthesis of polyelectrolyte, polyampholytic and partially hydrophobic acrylamide polymer types. The conversion, molecular weight and poly dispersity of co/ter-polymers have been evaluated by ^{1}H-NMR, GPC and DSC analysis. The effects of sonication power, concentration of polymer and concentration of MWCNTs were also investigated on rheological behaviour of co/ter-polymers. The results show that negative polyelectrolyte and polyampholytic polymers are the best candidates for the improvement of MWCNTs/polymer stability and viscosity at HS-HT and alkali environment respectively.

Keywords

Polyelectrolyte polymer; Polyampholytic polymer; Partially hydrophobic polymer; Multi-walled carbon nanotubes; Rheological behaviour; Stability.

Introduction

In the last decade, nanoparticle (NPs) dispersions have attracted great attention in oil industries due to the significant different properties of NPs compared to the same fine or bulk molecules.[1,2] One of the current state of the art techniques for increasing the amount of crude oil from an oil field (known as enhanced oil recovery-abbreviated EOR) involves improvement of polymer characteristics such as rheological behaviour with the help of NPs.[3-5] Polymer flooding is a robust chemical flooding method with more than 40 years' precedent.[6] Several research studies and field practices have shown an increasing recovery in the range of 5-30% of original oil in place (OOIP) by improving the mobility ratio inside porous media with the help of polymers.[7] Moreover, polymers are used widely as acid mud for drilling, fracturing and acidizing during oil exploration, since they can increase viscosity, filtration loss, flow regulation, and have other functions.[8, 9] Polyacrylamide (PAM) is the most often-used polymer in oil industry applications because of the promising rheological properties of polymer solution and the relatively low price.[10-12] However, the efficiency of conventional polymers e.g. PAM significantly is reduced at harsh environment of high salinity-high temperature or variate pH because of degradation or precipitation.[13, 14]

In recent years, improvement of polymers stability by modification of structure or by nanoparticles has gained a great interest.[15, 16] Cheraghian *et al.*, showed that the addition of nanoclay to PAM had positive effects on the viscosity properties of polymer solution.[15] In another study, Hu *et al.*, concluded that the formation of a bridge between free NPs and polymer after the addition of SiO_2 NPs (higher than a critical concentration) to partially hydrolyzed polyacrylamide (HPAM) solution led to a sharp increase in effective viscosity.[16] However, the stabilization of NPs in polymer solution is still a challenge, especially at harsh environment. Modification of polymer structure is also a versatile method to improve the properties of NPs/polymer dispersions. Some "grafts" can be incorporated onto the hydro-soluble backbone chain to improve the tolerance of polymer or coated NPs at harsh environment of reservoir. Therefore, both stability and rheological behaviour of the NPs/polymer solution could be enhanced this way. Some recent research studies have been reviewed here.

Hussein *et al.*, concluded that amphiphilic copolymer including a proportion of the hydrophobic branch incorporated in the hydrophilic polymer-based skeleton improved the viscosity of polymer solution. They improved the flow behaviour of developed associating ionic polymers based on diallylammonium salts containing single-, twin-, and triple-tailed hydrophobes, especially for EOR application.[17] Li *et al.*, synthesized a series of new thermoviscosifying polymers by co-polymerization of acrylamide monomers with thermosensitive monomer based on N-(1,1-dimethyl-3-oxobutyl)-acrylamide.[11] Moreover, the ability of new polymers was assessed for oil recovery efficiency in sand packed porous media. It was found that viscosity of thermoviscosifying was higher than that of PAM after aging at 45 or 85 °C for one month. Core-flooding tests also demonstrated higher oil recovery of 16.4 and 15.5% by applying the thermoviscosifying polymer at 45 and 85 °C, respectively, while oil recovery for PAM was only 12%. Ranka *et al.*, proposed that polyampholytes sulfobetaine methacrylamine have a better resistance in high salinity-high temperature conditions compared to polyelectrolytes, which qualifies them as a potential candidate for stabilizing NPs in a hard condition.[18]

Based on small-angle neutron scattering results, Ranka *et al.*, illustrated that a polyelectrolyte shrank while poly ampholytes swelled under high ionic media and high temperature.[18]

Earlier studies have demonstrated the potential of carbon nanotubes (CNTs) for EOR.[19-21] However, the tendency of CNTs to establish strong Van der Waals and π-π interactions, results in immiscibility with most media and forms tight bundles.[22, 23] Han *et al.*, investigated the transport behaviours of polymeric stabilized MWCNTs through a saturated quartz sand column in the presence of electrolytes, model clays, and humic acid as a natural organic matter.[24] A breakthrough (C/C_0) ranging from 0.69 to 0.90 at ionic strength from 0.3 to 10 mM was obtained for MWCNTs. The results showed that non-stabilized MWCNTs were much less transportable and were vulnerable to electrolyte effects, compared to polymeric stabilized MWCNTs. Functionalizing of CNTs with nitrene cycloaddition reaction has been used for the modification of CNTs to increase stability and solubility in aqueous solution.[20, 25]

In current work, MWCNTs hybrid modified acrylamide co/ter-polymers are introduced as novel materials with unique stability and rheological properties at harsh environment and have potential applications not only in oil industry application but also in other engineering fields e.g. heat transfer application by elastic turbulence improvement. A series of polyelectrolyte, polyampholytes and partially hydrophobic PAM have been synthesized via free-radical copolymerization. The negative sulphonic acid, positive trimethyl ammonium chloride and hydrophobic alkyl in acrylamide base monomers were used for modification of the PAM polymer.

Experimental

Chemicals

Monomer of acrylamide (AA), isopropyl acrylamide (IAA), 2-acrylamido-2-methyl-1-propanesulfonic acid (APSA), (3-acrylamidopropyl) trimethylammonium chloride (ATAC), 4-4'-azo-bis-4-cyanopentanoic acid (ACPA), sodium chloride, magnesium chloride, calcium chloride and MWCNTs were purchased from Sigma-Aldrich.

Polymer synthesis

Different mixtures of monomers including AA, IAA, APSA and ATAC with mass percent according to Table 1 were separately dissolved in a round-bottomed flask containing 180 ml deionized water. 10 mg of ACPA was added as an initiator for free-radical polymerizations and the flask was stirred using a magnetic stirrer for 6 h under reflux at 80 °C in a water bath. The polymerisation solution was carried out under nitrogen gas as shown in Figure S1 in electronic supplementary information.

Table 1. Different mixture of AA monomers during polymerization process

Sample number	AA (g)	IAA (g)	APSA (g)	ATAC (g)
1	7.5	0	0	0
2	3.75	0	3.75	0
3	3.75	0	0	3.75
4	3.75	0	1.875	1.875
5	3.75	1.875	1.875	0

In the next step, MWCNTs were dispersed in water, API brine (plus 2 wt% $MgCl_2$) or variant pH solution (acidic pH=3 or alkali pH=11) and MWCNTs de-agglomerated by ultrasonic probe (Fisher scientific) mixed with amplitude of 25 out of 100 for 5 min. Then polymer was added and mixed in the MWCNTs suspension with a magnet stirrer for 24 h. The acidic pH of 4 and alkali pH of 10 for polymer solution were adjusted with hydrochloric acid and sodium hydroxide, respectively, using a pH meter (Seven Compact Mettler Toledo, UK). The API brine samples were kept in an oven at constant temperature of 80 °C. The analysis of stability was performed for immobile samples after one week.

Characterization

The conversion of co/terpolymers was evaluated by ^{1}H-NMR analysis using Nuclear magnetic resonance (NMR) analysis on a Bruker Avance 500 spectrometer (resonance frequency of 400 MHz for proton). The co/ter-polymers were also analysed by gel permeation chromatography (GPC), using 0.1 M $NaNO_3$ as the mobile phase for measurement of polydispersity and molecular weight of polymers. The analysis was performed on an Agilent Technologies Infinity 1260 MDS instrument equipped with differential refractive index (DRI), light scattering (LS), viscometry (VS) and UV detectors. The type of column set was Tosoh TSKGel GPWXL columns operated at 40 °C with a flow rate of 1 ml/min. Poly (ethylene oxide) standards (Agilent Easy Vials) were used for calibration between 106-1,368,000 g/mol. The samples were filtered through a hydrophilic GVWP membrane with 0.22 µm pore size before injection. Experimental molar mass and dispersity values of synthesized polymers were determined by conventional calibration using Agilent GPC/SEC software.

The nature of surface functionality species of synthesised polymers was explored using Attenuated total reflection (ATR)-Fourier-transform infrared spectroscopy (Nicolet iS10 FT-IR spectrometer). The transition glass temperature (T_g) of polymers were evaluated using differential scanning calorimetry (DSC, Mettler Toledo Ltd.). Viscosity of NPs/polymers solution was measured using a Physica Anton

Paar rheometer (Cone plate CP75-1, model MCR 301) at a shear range of 10-1000 s^{-1} at 22 °C. Dynamic measurements were performed with frequencies ranging between 1 and 100 rad/s (i.e., 0.159 to 15.92 Hz). The morphology of dispersed MWCNTs was analysed by transmission electron microscope (FEI Tecnai TF20 TEM). The stability of MWCNTs over flocculation and sedimentation was characterized by recording the transmission of near-infrared light during the centrifugation of MWCNTs/polymer solution by a dispersion analyser centrifuge (LUMiSizer, Lum GmbH, Germany).

Results and discussion

Co/ter-polymers characterization

The co/ter-polymers, which were synthesised by free radical polymerization in this study, have a structure of hydrophilic molecular main chains with anionic, cationic or hydrophobic neutral random side chains (Figure 1). The conversion of monomer to polymers was estimated using ^{1}H-NMR analysis.

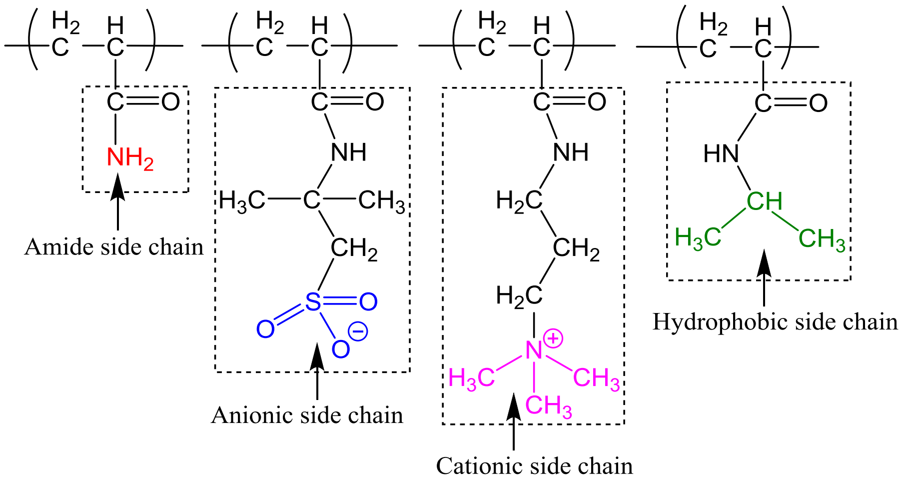


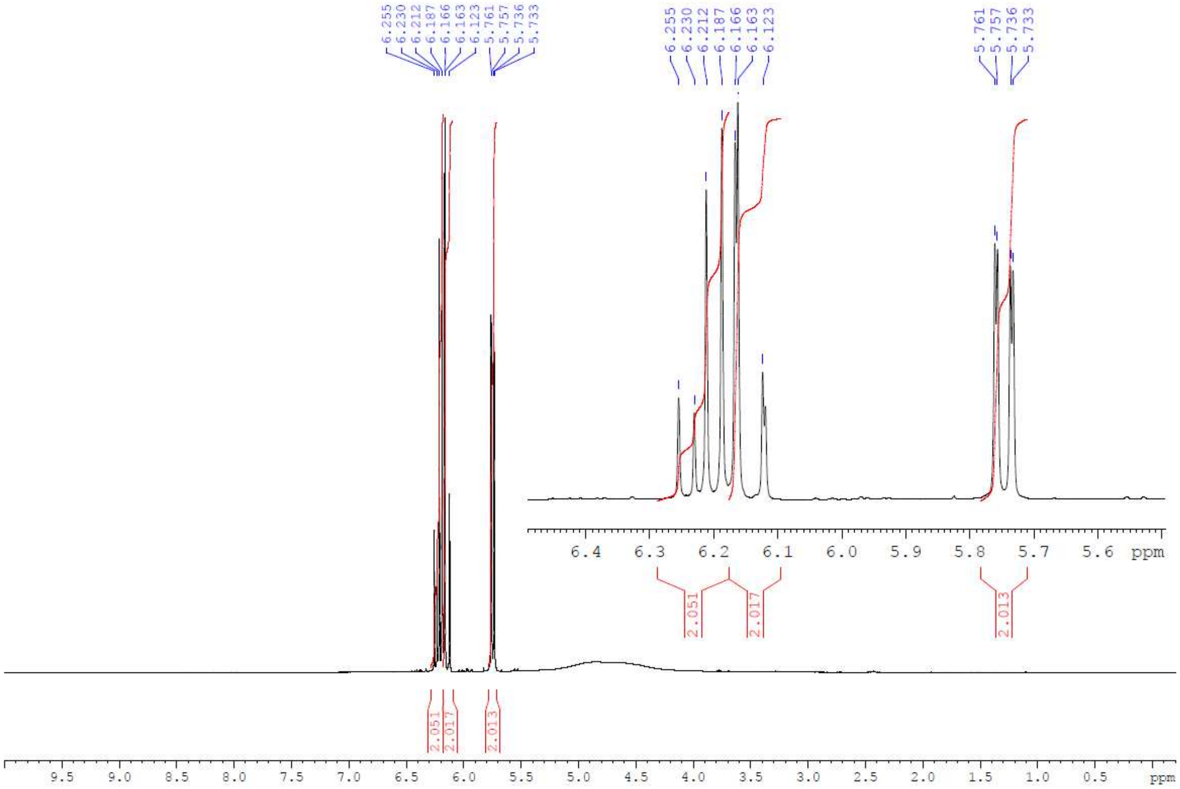
Figure 1. Schematic of side chains in co/ter-polymers molecular structure.

^{1}H-NMR spectra of co/ter-polymers were recorded for polymer solution containing 10 wt% of deuterium oxide (D_2O) and 10000 ppm polymer concentration at 25 °C. Figure 2 shows the ^{1}H-NMR spectra for monomer and polymer of sample 1 and 2. For brevity, the ^{1}H-NMR analysis of other samples are given in Figure S2 in electronic supplementary document. The conversion of co/ter-polymers was determined by using the ratio between the ^{1}H-NMR resonances of monomers and polymer units, according to following equation:[26]

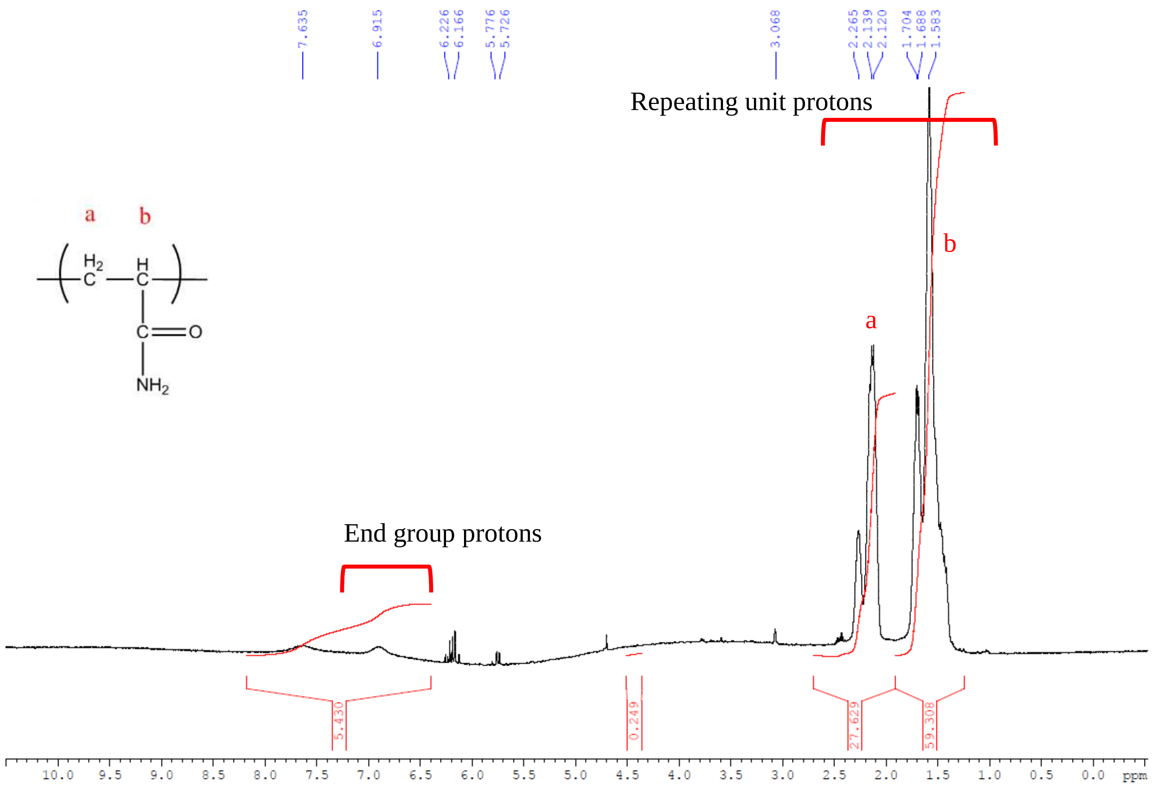
$$Conversion = \frac{S_p}{S_p+S_m} \qquad \text{Eqn.(1)}$$

where S_p is the peak area of the obtained polymer, and S_m is the peak area of the monomer. The conversions at the end of co/ter-polymerization have been reported in Table 2. By comparing the spectrum of sample 2 with sample 1, the extra peak c appeared, which were attributed to the negative side chain protons. Integration of peaks contributed for amide branches and other functional groups were measured using MastReNova software (version 6.0.2, Mestrelab research S.L.) and were used to calculate the substitution percent.[27] For example, after reacting APSA with AA monomers, the integration of peaks equal to 3.2 and 3.41 (48.4 and 51.6 substitution percent) were appeared for functional groups of AA and APSA in ^{1}H-NMR spectra of sample 2, respectively (Figure 2e). Substitution percent of other samples have been illustrated in Table 2.

(a)



(b)



7.635
6.915
6.226
6.166
5.776
5.726
3.068
2.265
2.139
2.120
1.704
1.688
1.583
Repeating unit protons
a
b
H2
C
H
C
C
O
NH2
b
a
End group protons
5.430
0.249
27.629
59.308
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
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0.5
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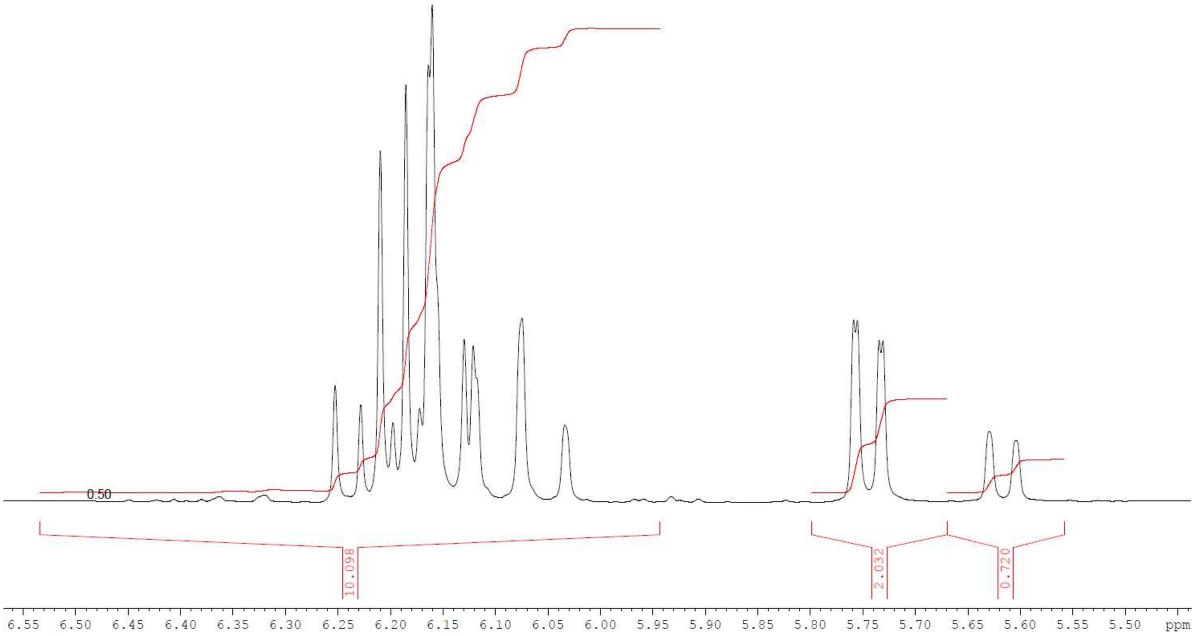
ppm

(c)



0.50
10.098
2.032
0.720
6.55
6.50
6.45
6.40
6.35
6.30
6.25
6.20
6.15
6.10
6.05
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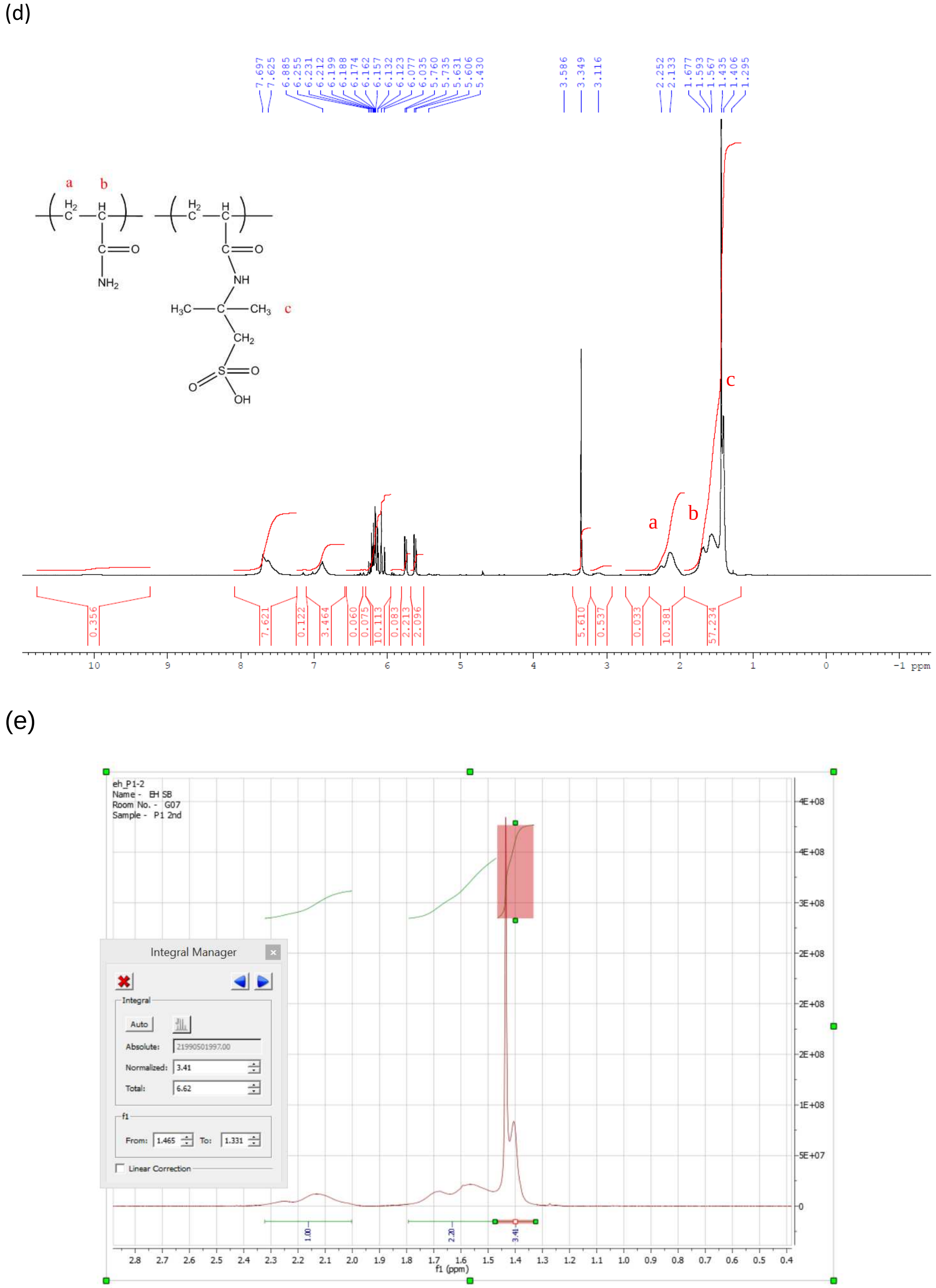


eh_P1-2
Name - EH SB
Room No. - G07
Sample - P1 2nd

Absolute: 21990501997.00
Normalized: 3.41
Total: 6.62
From: 1.465 To: 1.331
☐ Linear Correction

Figure 2. ^{1}H-NMR spectra for different sample 1: (a) AA monomer, (b) PAA, and sample 2: (c) AA-APSA monomers blend, (d) AA-APSA copolymer, (e) integration of peaks for sample 2.

The ATR-FTIR spectra of different co/ter-polymers are shown in Figure 3. It can be seen that the peak of APSA anionic polymer containing SO_3 group appeared at 1040 cm^{-1}.[28, 29] The bands observed at 1037, 1320 and 1435 cm^{-1} for copolymers containing APSA (sample 2, 4 and 5) decisively shows the existence of anionic monomers in the structure of copolymer, which is corresponded to the stretching vibrations of SO_3 group. The vibrations observed in 967 cm^{-1} in sample 3 and 4 is attributed to the quaternary ammonium group in ethoxylated group of ATAC cationic polymer.[30, 31] The bands at 1649 cm^{-1} and 2930 cm^{-1} were attributed to the carbonyl group (C=O) in amide group and $-CH_3$ stretching vibrations, respectively.

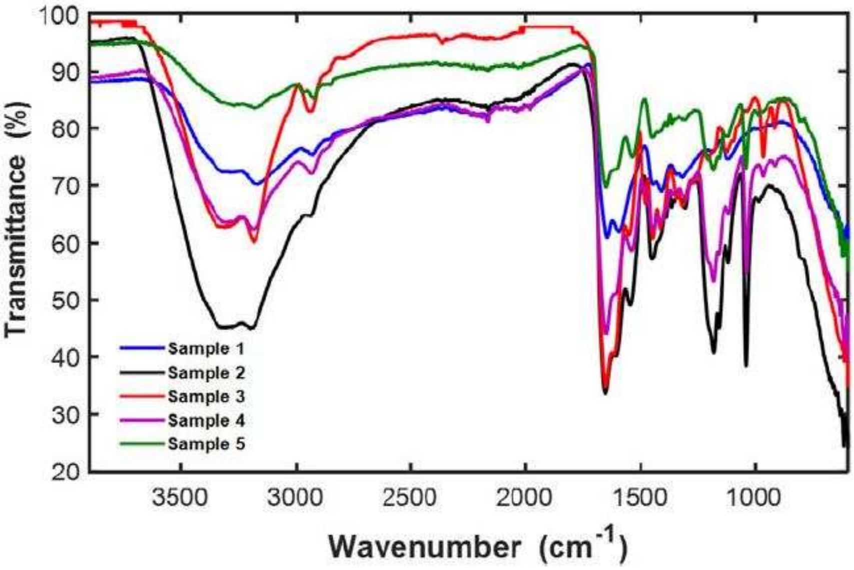


Figure 3. FTIR spectra for co/ter-polymer samples.

The results of GPC spectrums for the molecule weight distribution of all polymer samples are shown in Figure 4a. The average molecular mass (M_n), the weight average molecular mass (M_w) and the polydispersity index (PDI) of the polymers obtained by GPC are also summarized in Table 2. The results show that the polydispersity of polymers increased when different monomers were used during polymerization. The minimum and maximum PDI belong to pure acrylamide polymer and partially hydrophobic polymers respectively. The higher M_w and PDI for partially hydrophobic polymer implies that the high weight polymer chains fraction in sample 6 which has a significant influence on M_w.

In order to strengthen the co/ter-polymer structure confirmation after reaction of different monomers, a DSC analysis was also performed. At transition glass (T_g) the polymer goes from a hard, glass-like state to a rubber-like state. Probably the transition temperature at DSC could indicate if blend of two polymers (two T_g's) or a random co/ter-polymer was formed (one T_g) during polymerization. According to Figure 4b just one T_g appeared for each co/terpolymer with a little difference in values. Moreover, only a single GPC peak was appeared for each polymer solution that each peak shows the bands of one co/ter-copolymer in solution. The combination of GPC (single peak) and DSC (single T_g) results imply the formation of random co/ter-polymer instead of homopolymers with high degree of certainty.

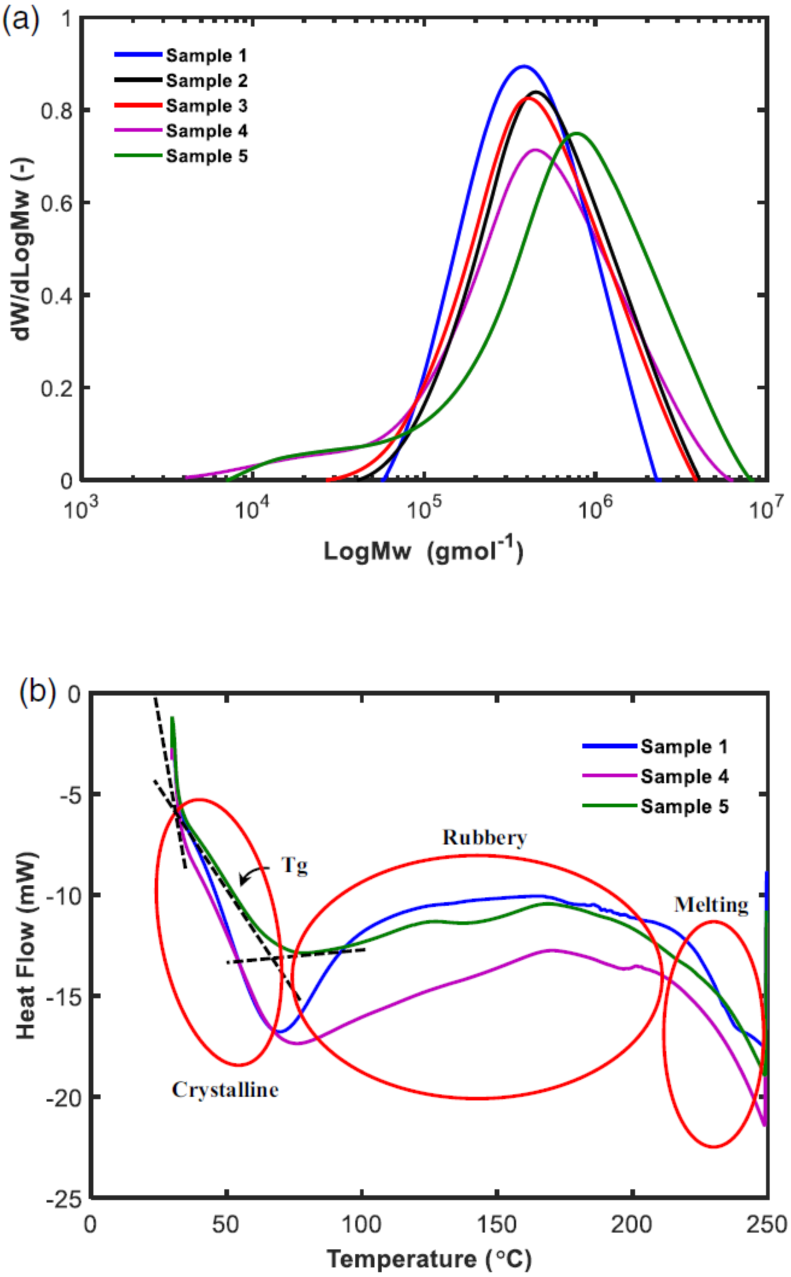


Figure 4. (a) GPC spectra for the molecule weight distribution of polymer samples, (b) DSC curves of co/ter-polymers.

Table 2. Different mixture of AA monomers during polymerization process

Sample number	Conversion %	$M_{n,GPC}$ (g/mol)	$M_{w,GPC}$ (g/mol)	PDI	Substitution ratio (%)
1	100	295696	499573	1.68	AA:100
2	85	343140	696575	2.03	AA:48.4-APSA:51.6
3	83	297457	636557	2.14	AA:46.1-ATAC:53.9
4	81	157055	721406	4.59	AA:38.4-APSA:32.9-ATAC:28.7
5	91	216920	1106656	5.11	AA:44.1-APSA:25.3-IAA:30.5

MWCNTs/polymer characterization

Rheological analysis of MWCNT/polymers dispersion

Rheological behaviour is one of the most important criteria of an injected chemical fluid in porous media. A proper viscosity of the displacing fluid is required to ensure a favourable mobility control in order to achieve higher oil recovery. The effects of temperature and salinity on viscosity of PAM have been investigated before for aqueous solutions.[13, 14, 32, 33] Briefly, the viscosity of PAM solution would be reduced at an elevated temperature and/or in the presence of salinity, whilst the mechanisms of temperature and salinity effect are different.

The higher mobility of the copolymer chains at elevated temperature results in the weakening of the hydrophobic effect between polymer chains and increasing polymer solubility as schematically shown in Figure 5a. Moreover, the solvent viscosity decreases at higher temperature. All these factors lead to easier molecular movement of the polymer versus shear force and hence a decrease in viscosity of polymer solution. No degradation of molecular weight was observed at elevated temperature since the PAM backbone remained stable at high temperature for a long time.[14, 32]

In the presence of salinity, the ionic shielding on the amide groups ($-CONH_2$) in the chemical structure of PAM reduces the chains' repulsion of the PAM backbone. As a result, the polymeric coils collapse and the molecular coil size is reduced, while viscosity decreases (Figure 5b).[32, 33] At significant concentrations of salinity (especially divalent ions), the highly hydrolysed PAM could start to precipitate which limits its potential for many EOR applications in reservoirs with harsh environment (Figure 5b).

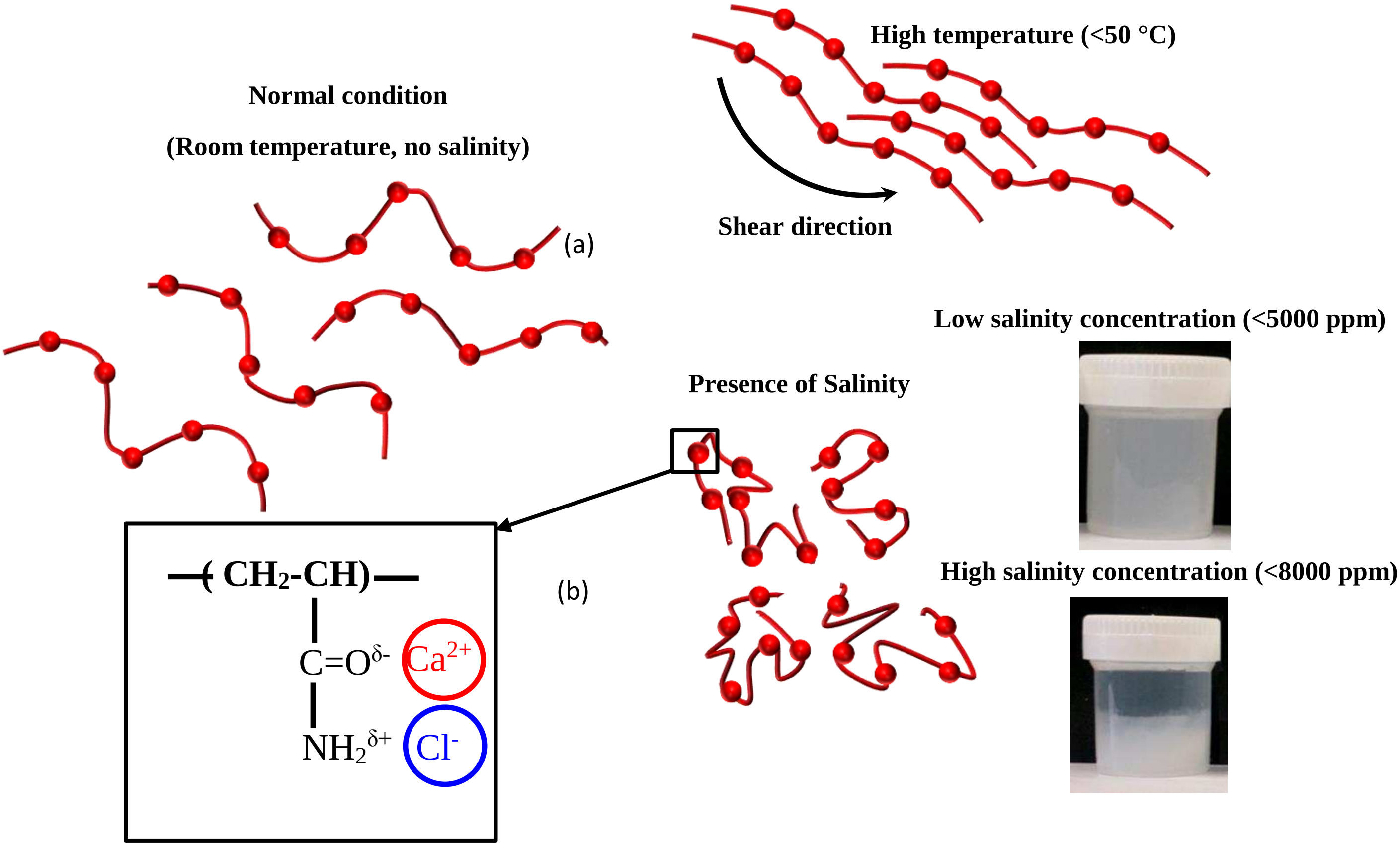


Figure 5. Schematic mechanisms of viscosity reduction of PAM at (a) high temperature (<50 °C) and (b) high salinity (<8000 ppm).

Figure 6a and b displays the variation of viscosity of a 1000 ppm co/ter-polymers solution at various shear rates in pure water at 25 and 60 °C. The reason for selection of 1000 ppm is discussed in detail in "stability analysis" section. The plots reveal the improvement of viscosity after incorporation of hydrophobic chains in the polymer structure. The increase in the viscosity value would be attributed to the intermolecular hydrophobic association between the polymer chains. The hydrophobic chains tend to associate to minimize their exposure to the aqueous medium which results in an increase of solution viscosity. However, based on results of earlier studies, it should be noted that a limit for hydrophobic fraction in polymer structure exists that improve the viscosity.[17, 34] Highly hydrophobic branches in polymer's backbone lead to effective association and thickening properties.[27] These hydrophobic groups can associate to form temporal physical networks, so the viscosity of solutions can be improved.[17] Previous studies indicated that the distribution of hydrophobic branches along the polymer chain significantly affects the associative properties of those polymers with a flexible skeleton.[34, 35] However, a higher fraction of hydrophobic chains reflects to the increasing compactness of physical cross-links of polymers in an aqueous media which leads to viscosity diminishing.[17, 34]

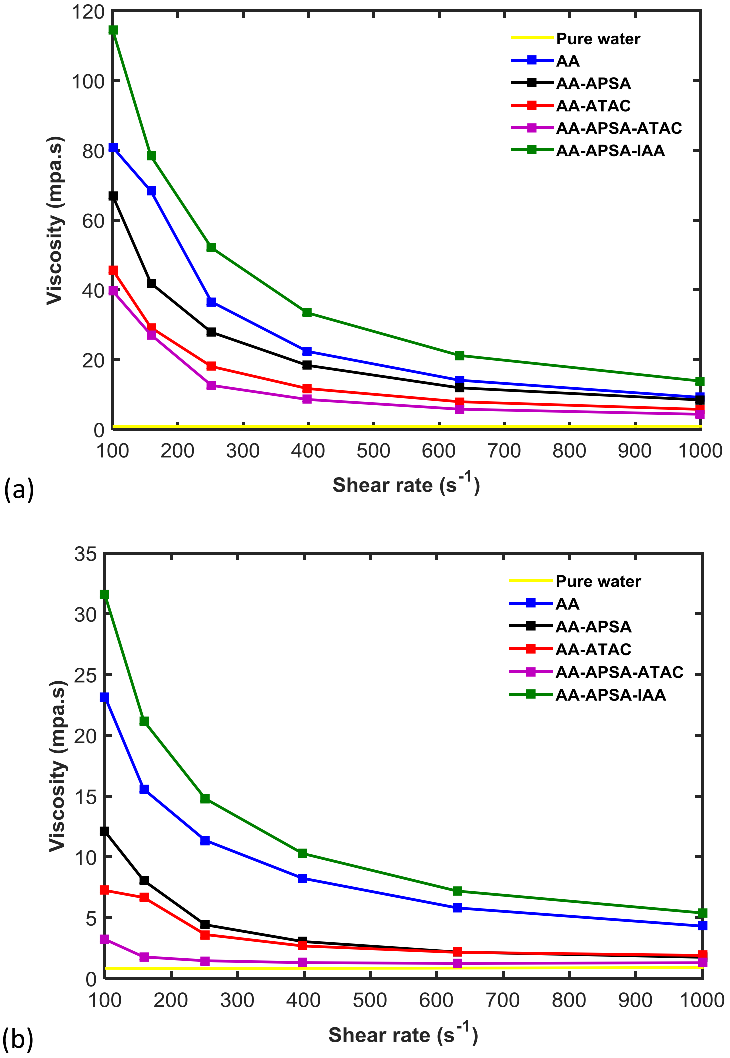


Figure 6. Viscosity of pure co/ter-polymers (1000 ppm) in pure water at (a) 25 and (b) 60 °C.

Figure 7 shows the viscosity of MWCNTs/polymers (1000-1000 ppm) in pure water measured at 25 and 60 °C as a function of shear rate. The viscosity of solutions is significantly boosted in presence of MWCNTs compared to pure polymer solutions.

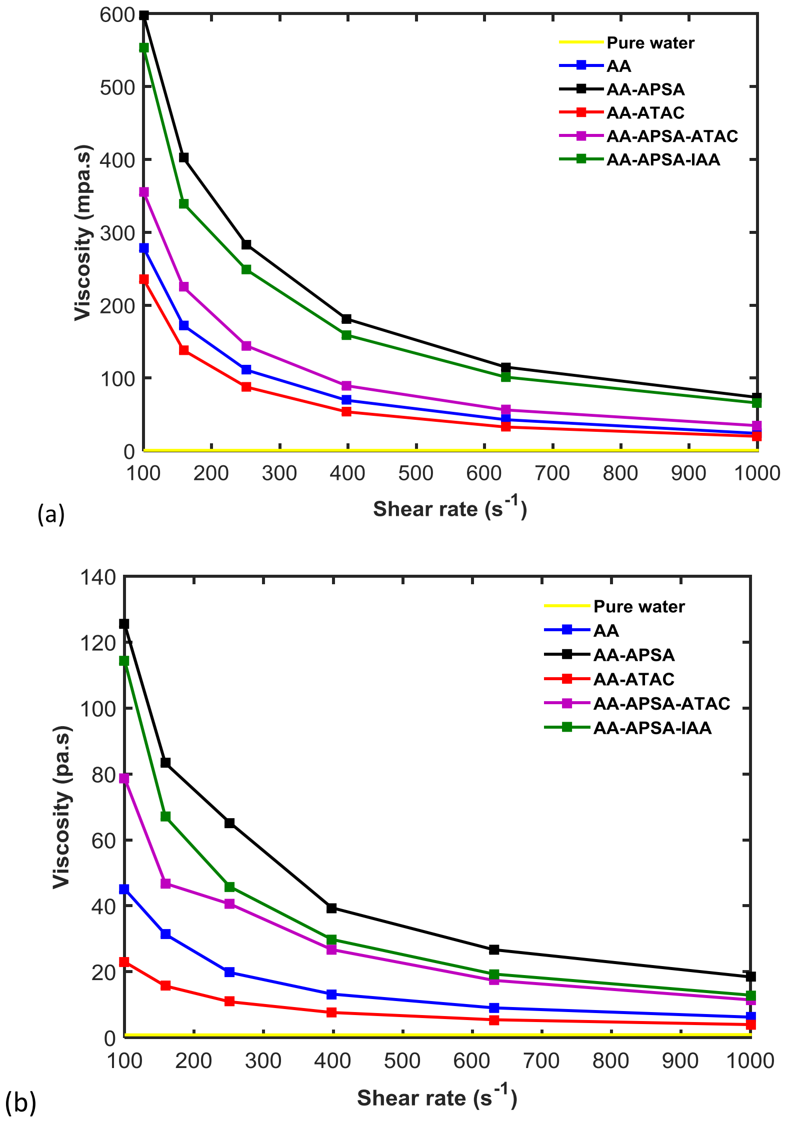


Figure 7. Viscosity of MWCNTs/polymers (1000-1000 ppm) in pure water at (a) 25 and (b) 60 °C.

The different strategies including covalent linking, complexation via π-π, CH-π, NH-π, interactions and wrapping were proposed for functionalizing of carbon nanotubes (CNTs) with polymers.[36, 37] The advantage of noncovalent functionalization is that it is a simple procedure suitable for production of NPs/polymer solution on a large scale for example EOR application. However, the disadvantage of noncovalent surface modifications is weak interaction (e.g. Van der Waals, π-π and hydrophobic interactions) between CNTs and polymer molecules which reduces the stability of NPs/polymer solution.[38] In-depth investigation of strength bond between different functional groups of co/ter-polymers and MWCNTs with experimental characterization or by molecular dynamic (MD) simulation is beyond the scope of current research. However, interested readers could refer to related studies to find useful information.[37-39] Usually non-covalent bonds are formed on multi-point interaction between polymers and the surface of the CNTs (Figure 8).[40] These multi-point interactions reinforce the polymer chains which results in higher internal friction between the polymer chain and the surrounding solvent molecules and improvement of viscosity.

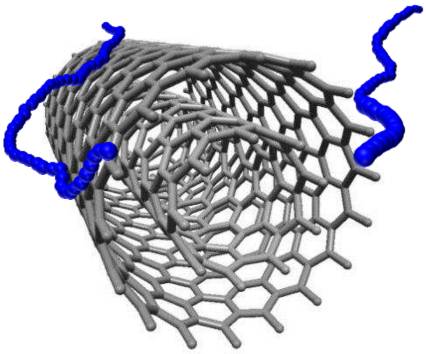


Figure 8. Different routes for MWCNTs functionalization: noncovalent polymer wrapping or π-π, CH-π and NH-π interactions.[41]

Table 3 represents the ratio of average polymer solution viscosity with and without MWCNTs at different temperatures. According to Table 3, the ratio of viscosity is higher for polymer containing negative group (sample 2 and 4) which are bolded in the Table 3. Based on our observation, the intermolecular interaction between MWCNTs surface and polymer containing negative sulfonate group is higher compared to other functional groups. This interaction is stronger especially at higher temperature which produces higher internal friction. The proper resistance of sulfates and sulfonates groups against high temperature has been reported by several other researcher.[42, 43]

Table 3. The ratio of average polymers solution viscosity with and without MWCNTs at different temperatures.

Sample number	**1**	**2**	**3**	**4**	**5**
Viscosity (25 °C)	38.59	29.26	19.73	16.37	52.25
Viscosity (25 °C-with MWCNTs)	116.45	275.52	94.66	150.8	244.63
Viscosity ratio	3.01	**9.41**	4.79	**9.21**	4.68
Viscosity (60 °C)	11.41	5.24	4.04	1.71	15.07
Viscosity (60 °C-with MWCNTs)	20.78	59.74	11.08	36.92	48.02
Viscosity ratio	1.82	**11.37**	2.74	**21.59**	3.18

Figure 9 shows the viscosity variation of MWCNTs/polymers (1000-1000 ppm) in alkali solution (pH=11) measured at 25 and 60 °C as a function of the shear rate. Table 4 also represents the average viscosity ratio of MWCNTs/polymer in alkali solution and pure water.

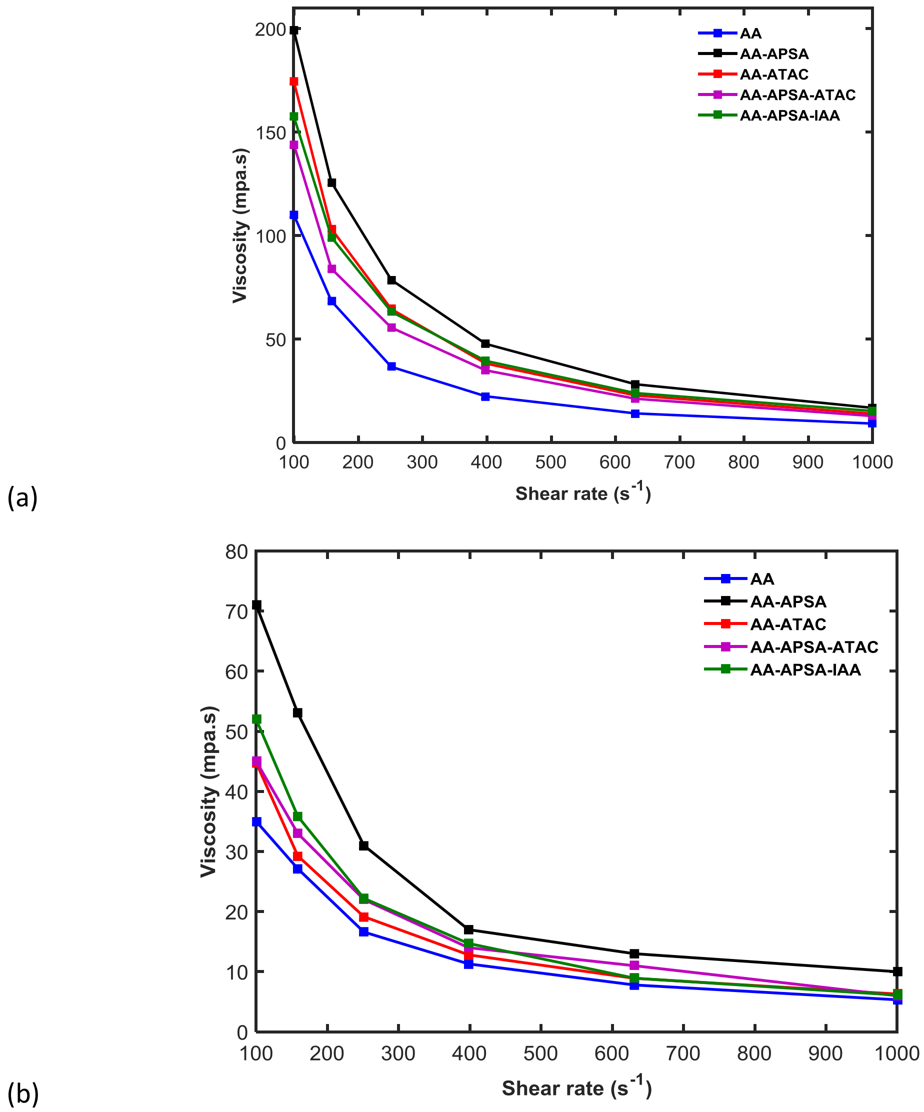


Figure 9. Viscosity of MWCNTs/polymers (1000-1000 ppm) in alkali solution (pH=11) at (a) 25 and (b) 60 °C.

Table 4. Average viscosity ratio of MWCNTs/polymer in alkali solution and pure water.

Sample number	**1**	**2**	**3**	**4**	**5**
Viscosity (25 °C-with MWCNTs)	116.45	275.52	94.66	150.8	244.63
Viscosity (25 °C-with MWCNTs-pH=11)	43.44	82.68	69.51	58.75	66.44
Viscosity ratio	0.37	0.30	**0.73**	0.39	0.27
Viscosity (60 °C-with MWCNTs)	20.78	59.74	11.08	36.92	48.02
Viscosity (60 °C-with MWCNTs-pH=11)	17.19	32.5	20.19	21.83	23.29
Viscosity ratio	0.82	0.54	**1.82**	0.59	0.48

Based on Table 4, the viscosity ratio is significantly reduced for all polymers at alkali solution (pH=11) due to a high degree of hydrolysis in the presence of OH^- ions. Earlier studies investigated the mechanism of polyacrylamide hydrolysis at either alkaline or acidic conditions.[13, 44, 45] The alkali or acidic environments assist the process of hydrolysis as shown in Figure 10.

During polyacrylamide hydrolysis a fraction of amide groups convert to either carboxylic acid (acid conditions) or to carboxylate ones (basic conditions). The electrostatic repulsion of the carboxylate group leads to the extension of molecular chains of PAM inside solution and increasing viscosity.[46] Although the hydrolysis of acrylamide polymer chains has a positive effect on viscosity, there is a limitation for degree of hydrolysis. Martin and Sherwood proposed the degree of polyacrylamide hydrolysis up to 35 mol% displays the most viscous solutions.[47] If the degree of hydrolysis is too low, the polymer has relatively weaker polyelectrolytes due to lower carboxylate groups in the polymer skeleton resulting in a weaker repulsive force on the latter chains. The PAM converted to polyacrylic acid (PAA) when the degree of hydrolysis was completed or when the amide groups were totally replaced by the carboxyl groups. PAA is also a relatively weak polyelectrolyte in comparison to hydrolysed PAM with optimum degree of hydrolysis. The reason is that the hydrolysis degree is higher than the optimum threshold (or complete hydrolysis), decreasing the effective electrostatic repulsion of negative carboxylate groups. [48, 49]

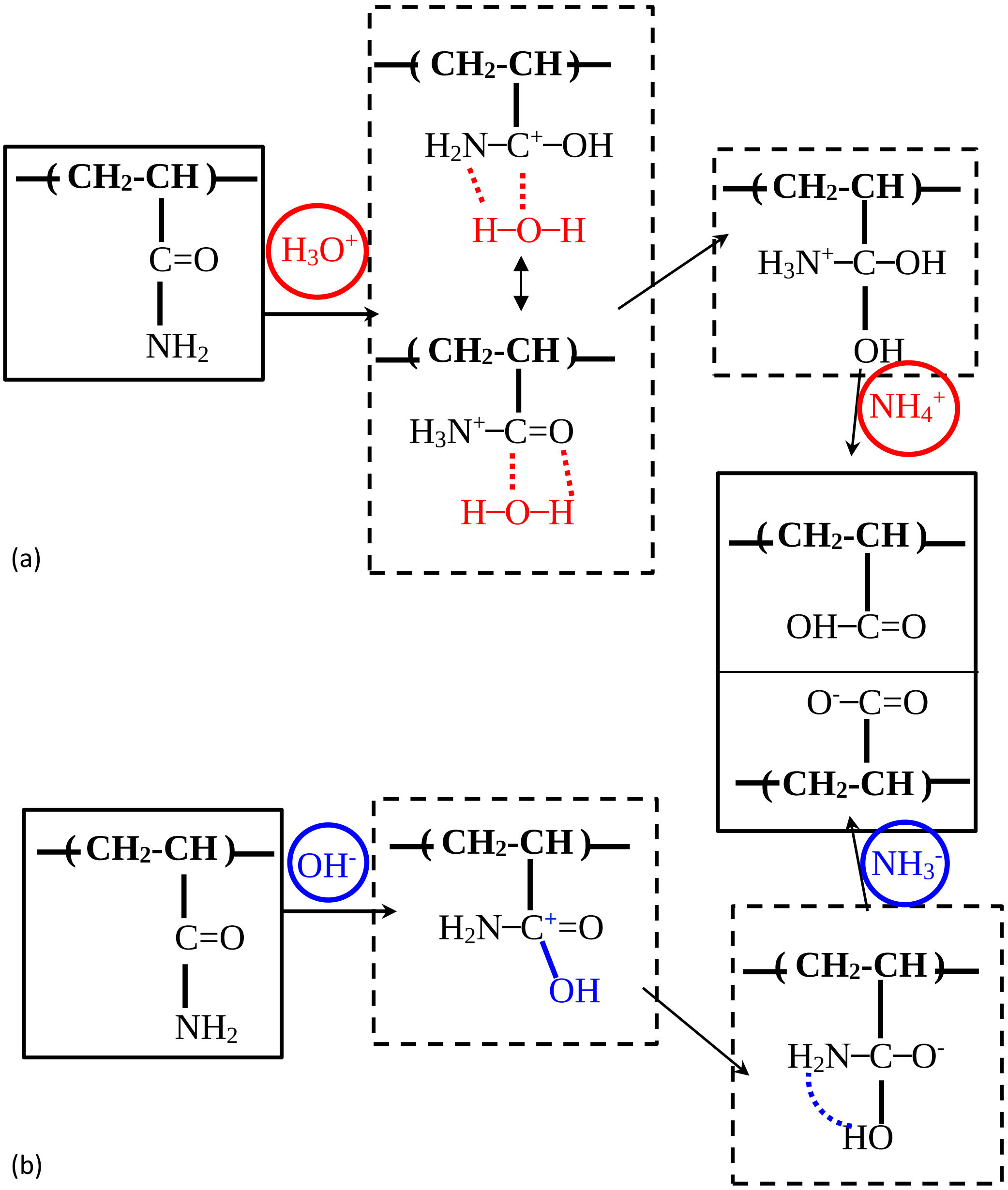


Figure 10. Proposed reaction pathways of the amide hydrolysis under assisted (a) acidic and (b) alkali conditions.

Another conclusion from Table 4 is a lower decreasing of viscosity ratio for cationic polymer compared to other samples. Figure 11 proposes the controlling mechanism of PAM hydrolysis including positive chains. The positive quarterly ammonium group adsorbs OH^- ions of environment and control the hydrolysis fraction of amide groups which is the main reason for lower viscosity ratio diminishing.

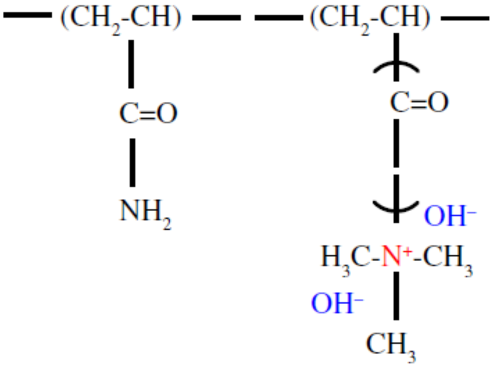


Figure 11. Proposed controlling mechanism of PAM hydrolysis including positive chains.

Figure 12 illustrates the rheological results of salinity influence on MWCNTs/polymer solutions at 25 and 60 °C. Table 5 represents the ratio of average polymer solution viscosity with and without MWCNTs for API brine. As discussed in previous sections, the viscosity of polymers in brine solution is lower than in pure water (Figure 5b). Similarly the decreasing of viscosity ratio is lower for cationic polymer. The reason is compatibility of positive group to mono and divalent cationic ions (Na^+, Mg^{+2} and Ca^{+2}) which shield the negative or amide groups in the chemical structure of co/ter-polymers.

It should be noted that although the sensitivity of positive acrylamide polymer against high pH and salinity is less compared to other samples, the average viscosity of polymer including positive chains is also much lower than polymer containing negative and hydrophobic groups.

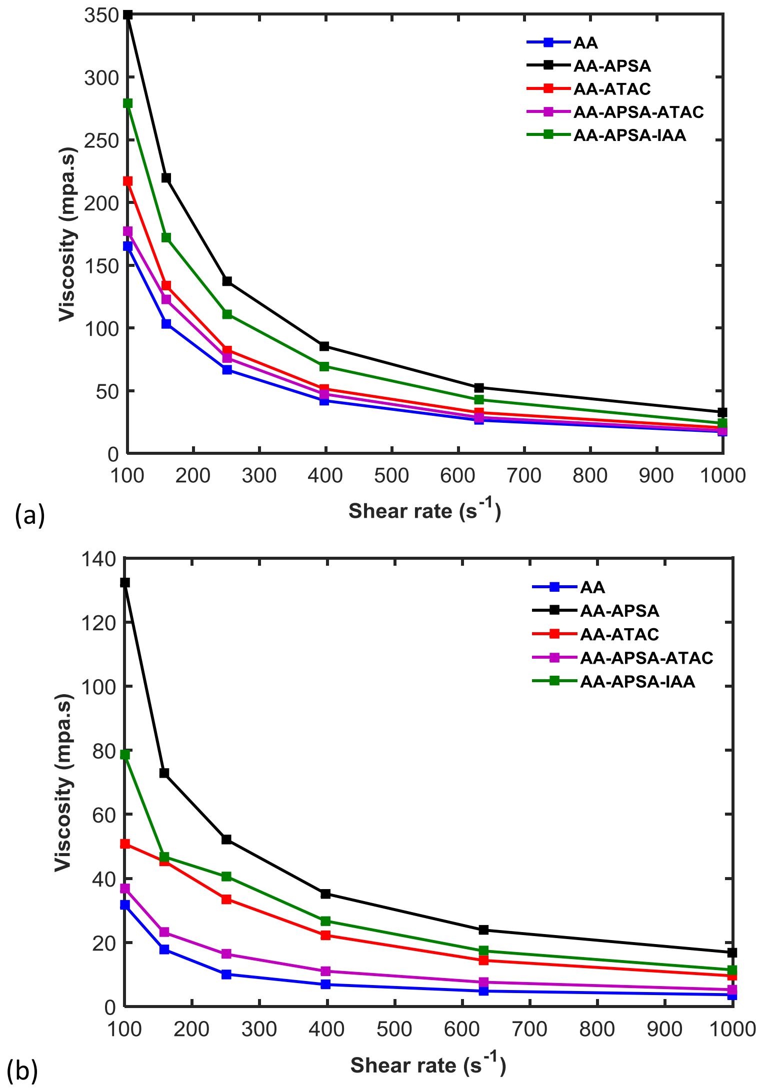


Figure 12. Viscosity of MWCNTs/polymers (1000-1000 ppm) in API brine solution plotted at (a) 25 and (b) 60 °C.

Table 5. The ratio of average polymer solution viscosity with and without MWCNTs for API brine.

Sample number	**1**	**2**	**3**	**4**	**5**
Viscosity (25 °C-with MWCNTs)	116.45	275.52	94.66	150.8	244.63
Viscosity (25 °C-with MWCNTs-API)	70.24	146.22	89.61	78.36	116.45
Viscosity ratio	0.60	0.53	**0.94**	0.51	0.47
Viscosity (60 °C-with MWCNTs)	20.78	59.74	11.08	36.92	48.02
Viscosity (60 °C-with MWCNTs-API)	12.5	45.5	29.3	16.7	36.9
Viscosity ratio	0.60	0.75	**2.64**	0.45	0.76

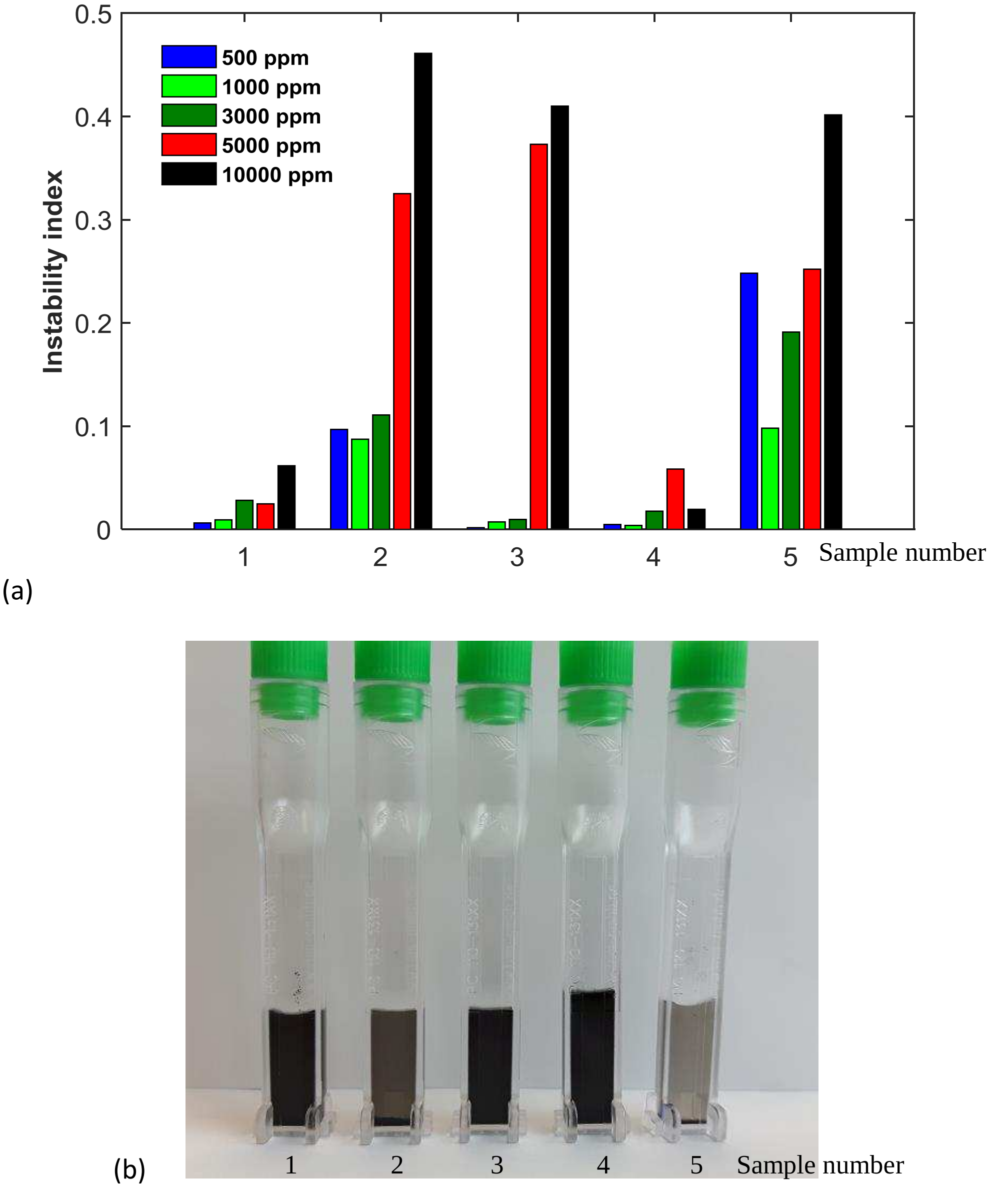
Stability analysis

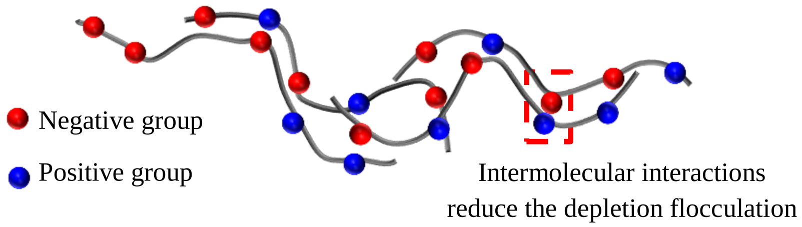
Physically adsorbed polymer (wrapping or non-wrapping) could stabilize the CNTs via steric repulsion among polymer function which has been reported experimentally[18, 38, 50] or by MD modelling.[51, 52] The solvation of the polymer side chains by the aqueous phase and the electrostatic repulsion between polymer chains in presence of counter ions are two main factors which affect the stability of MWCNTs. In many cases, nanotubes coated with polymeric stabilizers flocculate under harsh conditions which finally cause phase separation in an aqueous medium. Na^+, Ca^{+2}, and Mg^{+2}, are common cations existing in the oil reservoirs, which have an effect on intermolecular association between polymer chains by reducing the hydration shell volume of the polymer chains.[14] Flocculation and polymer phase separation in saline water take place when the interactions between the polymer side chains with the water molecules are not strong enough compared to the chains-chains interactions. In the current study, the analytical centrifugation dispersion analyser (LUMiSizer 6110) were performed to evaluate the stability of functionalized MWCNTs with co/ter-polymers at harsh condition as a direct and absolute technique. [53, 54]

LUMiSizer is a proper technique for analysis of long-term stability of particles in suspension and of de-mixing phenomena. [55, 56] LUMiSizer measurement of the transmitted near infrared light intensity by sensors arranged linearly across the sample from top to bottom during centrifugation. The shape of transmission profiles over the entire sample length at different times contains information about the kinetics of the separation process and instability of samples. The centrifugal sedimentation method used with this equipment allows a fast instability analysis of samples in min/h instead of months/years.[57] The MWCNT/polymer dispersion (0.5 ml) was filled in a polycarbonate capillary cell and centrifuged for about 36 min at 3000 rpm which is equivalent to 1 month in real conditions. [57] At first the effect of polymer concentration was evaluated on stability of MWCNT (1000 ppm) to select the optimum polymer concentration. Figure 13a shows the final instability index of MWCNT/polymer dispersion for pure water. The instability index is measured based on the clarification (increase in transmission due to MWCNT sedimentation) at a given separation time, divided by the maximum clarification of samples. The instability index is a dimensionless number and ranges from 0 (more stable) to 1 (more unstable). In fact, for the same total clarification, samples with high clarification rates tend to be more unstable. [55, 58]

According to Figure 13, the concentration of polymer higher than 3000 ppm leads to de-stability of MWCNTs because of depletion flocculation.[59, 60] If full coverage of the MWCNTs is achieved, surplus polymers can lead to dispersion destabilization through depletion flocculation. This phenomenon happened when a concentration of polymers exceeded the critical concentration.

It seems, dispersion containing PAM and ampholytic ter-polymer produce weaker depletion flocculation results in higher stability in pure water. Presumably weaker depletion flocculation is due to lower repulsion interaction between amide groups or negative/positive chains of ampholytic ter-polymer that is schematically shown in Figure 13c. Based on Figure 13, 1000 ppm of polymer concentration was selected as a proper concentration for stabilization of MWCNTs for the next part of the experiments. For brevity, the photos of test tubes containing different concentration of MWCNTs/polymer dispersions have been shown in Figure S3 in electronic supplementary information at the end of the centrifuge operation.

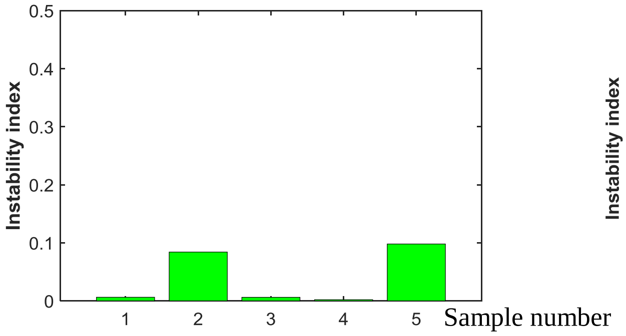




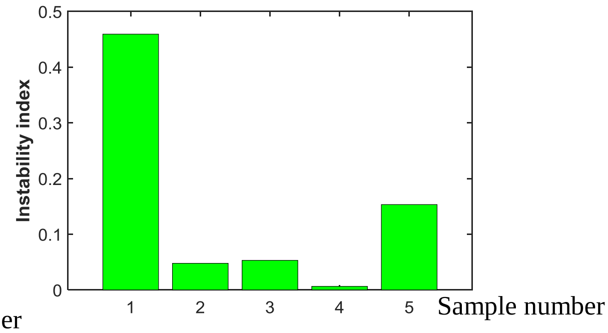
(c)

Figure 13. (a) Effect of polymer concentration on final instability index of MWCNTs/polymer dispersion in pure water (b) samples test tubes at the end of centrifuge operation (1000 ppm polymer concentration), (c) the reason of lower depletion flocculation for ampholytic polymer.

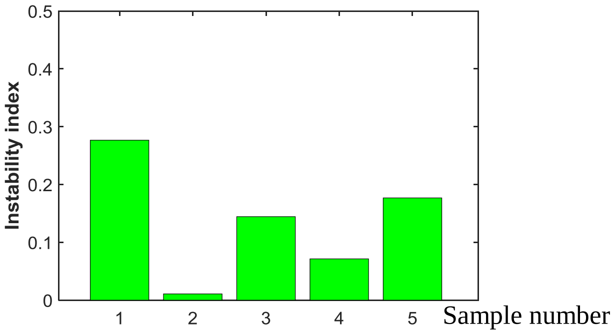
Figure 14a and b shows the final instability index and trend of instability index versus time for test tubes of samples containing 1000 ppm of polymers, respectively. The stability of MWCNTs (1000 ppm)/polymer samples (1000 ppm) were evaluated at harsh environment of high salinity-high temperatures or various pH which is denoted by number 1 to 3. The higher instability index confirmed more agglomeration and sedimentation rate of MWCNT in polymer solution.



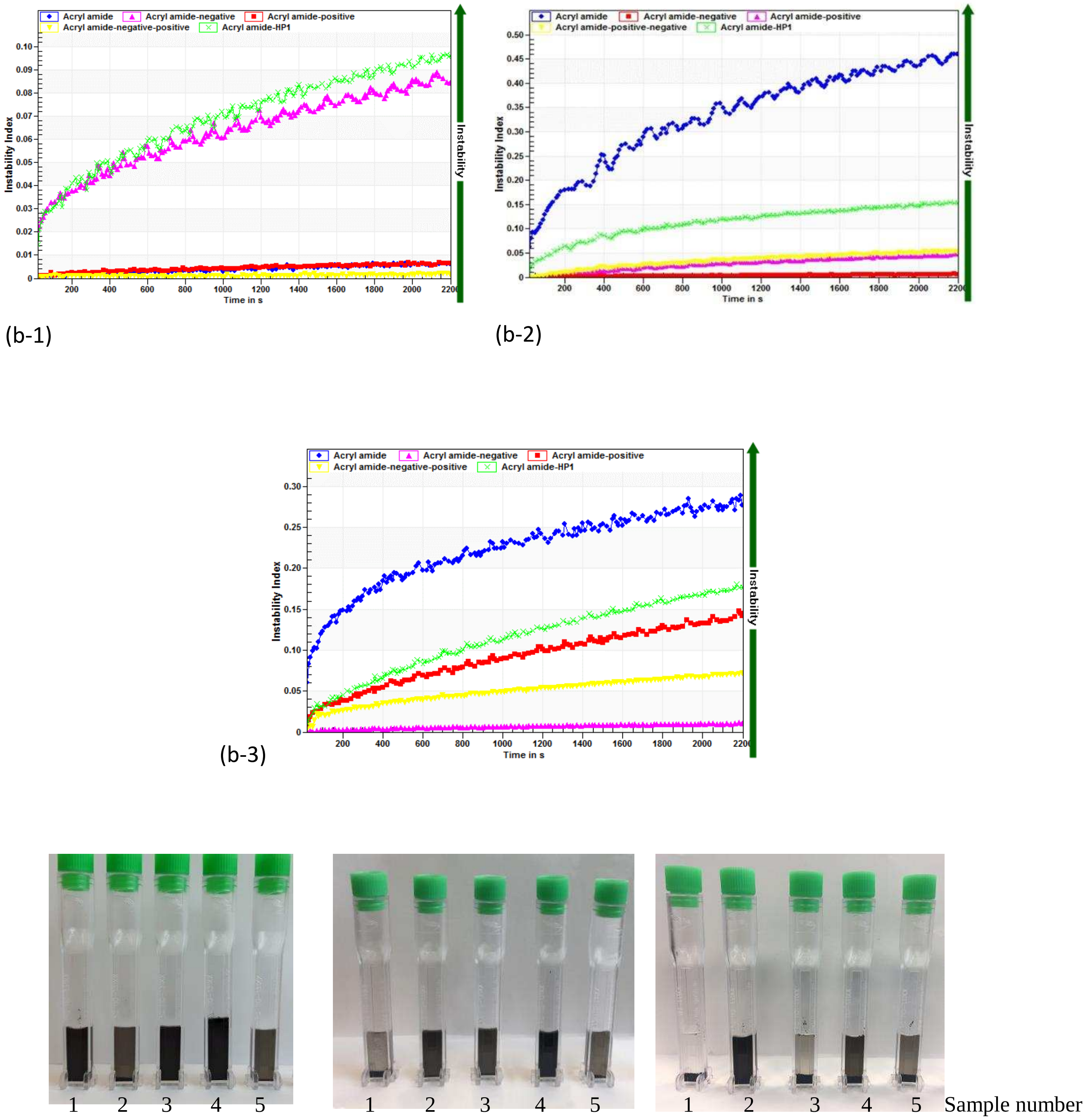
(a-1)



(a-2)



(a-3)



(b-1)

(b-2)

(b-3)

(c-1)

(c-2)

(c-3)

Figure 14. (a) Final instability index of MWCNTs (1000 ppm)/polymer (1000), (b) trend of instability index versus time and (c) samples test tubes at the end of centrifuge operation (1000 ppm polymer concentration), at (1) pH=4, (2) pH=11, (3) API brine.

According to Figure 14 (a-1, 2 and 3), the stability of MWCNTs in PAM was proper in an acidic condition (a-1) while the rate of sedimentation is increased drastically in an alkali solution and API brine [Figure 14 (a-2, 3) and (b-2, 3)]. The reason is possibly due to amide groups of PAM have compatibility at acidic pH in compare to alkali pH and high salinity.[13] Another observation is that the stability of MWCNTs in copolymer solution containing negative sulfonate-functional was lower at acidic pH (a-1) and (b-1) which is probably due to the effect of positive molecular hydrogen (H^+) on the sulfonate groups. At alkali pH, the sulfonate groups of copolymer were deprotonated more intensely than acidic pH which provide stronger repulsive electrostatic force between functionalized MWCNTs. On the contrary, positive groups of copolymer containing quarterly ammonium side chains were protonated more effectively at acidic environment results in higher stability at low pH (a-1) and (b-1). Variation of pH has the least effect on stability on MWCNTs in polyampholytic solution (a-1, 2) and (b-1, 2). The existence of positive-negative side chains in the structure of polyampholytic polymer counteract the variation of pH on the instability of MWCNTs. Moreover, the best stability at high temperature-high salinity condition was obtained for copolymer containing negative sulfonate function. Copolymer containing sulfonate group has higher resistance against divalent ions which maintain the solubility of skeleton acrylamide at high salinity concentration and the steric repulsion force between polymer branches (a-3) and (b-3).[42, 61, 62] The negative sulfonate group attracted mono and divalent ions inside API brine and prevented the collapse of the polymer backbone by protecting the chains repulsion of the acrylamide chains. The amount of MWCNT sedimentation could be observed from sample test tubes by naked eye at the end of centrifuge operation (c-1, 2 and 3). Clearly lower sedimentation of nanotube happened for samples containing ampholytic polymer and negative polyacrylamide in alkali and high salinity condition respectively. The dispersion and microstructure of the sample 2 in API brine solution were examined by TEM (Figure 15). It can be seen in Figure 15b that the MWCNTs exhibits good dispersibility in the API brine solution as individual nanotubes and the length of the MWCNTs is about several micrometres.

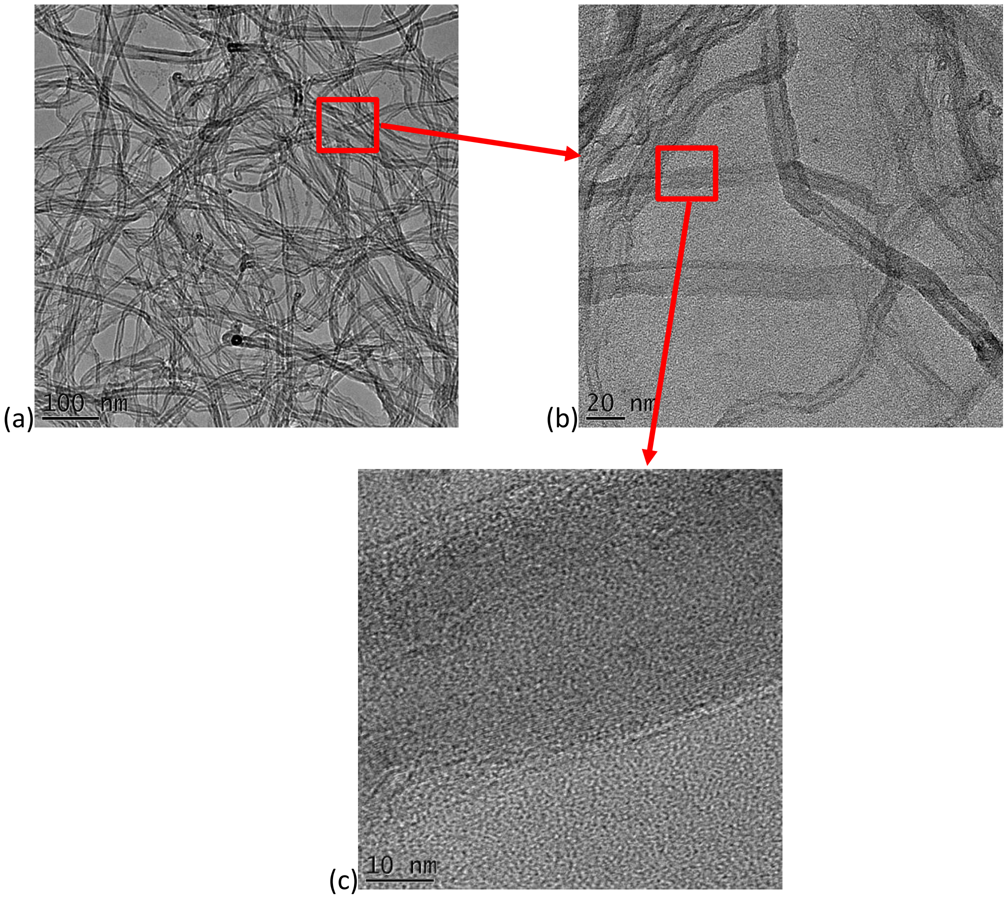


Figure 15. TEM photo of MWCNTs/polymer (sample 2) in API brine at different magnification.

Selection of proper samples

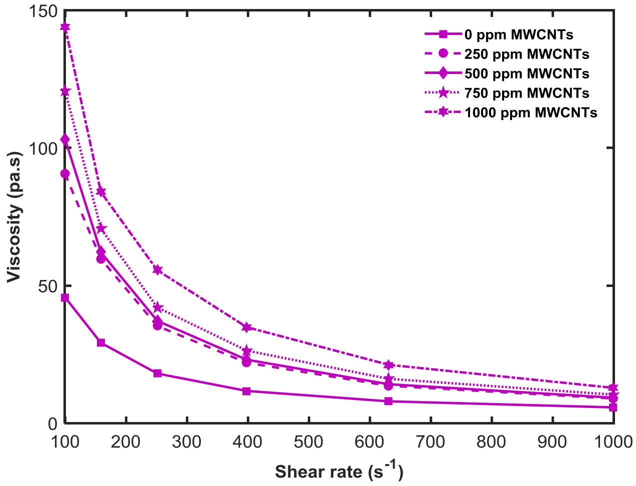
Table 6 briefly represents the viscosity and stability evaluation of different MWCNTs/polymers.

Table 6. Viscosity and stability evaluation of different MWCNTs/polymers.

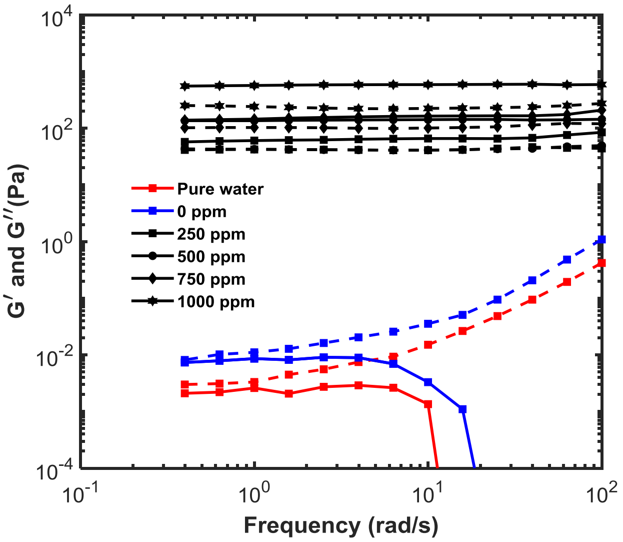
Sample type / Solution		AA	AA-APSA	AA-ATAC	AA-APSA-ATAC	AA-APSA-IAA
Pure water	Viscosity (T=TR)	**Weak**	**Good**	**Weak**	**Tolerable**	**Good**
	Stability (T=60 °C)	**Good**	**Tolerable**	**Good**	**Good**	**Tolerable**
Alkali environment (pH =11)	Viscosity (T=TR)	**Weak**	**Tolerable**	**Tolerable**	**Tolerable**	**Tolerable**
	Stability (T=60 °C)	**Weak**	**Tolerable**	**Tolerable**	**Good**	**Weak**
API brine	Viscosity (T=TR)	**Weak**	**Good**	**Tolerable**	**Weak**	**Tolerable**
	Stability (T=60 °C)	**Weak**	**Good**	**Weak**	**Tolerable**	**Weak**

Based on results of this study, the polyampholytic ter-polymer and polyelectrolyte copolymer containing the negative sulfonate group are good candidate in alkali and API brine solution respectively for improving the viscosity and stability of MWCNTs/polymer solution. Figure 16 shows the effect of MWCNTs concentration on rheological behaviour of selected candidate at room temperature. As shown in Figure 16b, d, both storage (G′) and loss (G″) moduli increase after addition of MWCNTs. The linear regime regardless of strain amplitude, is clearly observed due to an increase of rubberlike behaviour of polymer solution in the presence of MWCNTs. Four different types of interactions including (a) MWCNT-MWCNT network due to overlap of two nanotubes, (b) MWCNTs/polymer network where the polymer could be entangled or adsorbed on the nanotube, (c) MWCNTs bridging by polymer, and (d) polymer network formation in the polymer matrix through temporary entanglements, are responsible for viscoelastic behaviour of solution.[63]

In the viscoelastic diagram of polymer/nanotubes, the crossover of modulus (where G′ > G″) is representative of characteristic relaxation time, which corresponds to the time for a nanotube to diffuse a distance equal to its length.[64, 65] Basically, at low concentrations of nanotubes the relaxation time could be detected from modulus curves cross section while by increasing the concentration of nanotubes the characteristic relaxation time commence to increase and at a specific concentration tent to infinity (maximum packing fraction).[65] The increase of characteristic relaxation time is due to slowing down of nanotube diffusivity and the tendency of solution to behave like an elastic solid. Both nearly constant moduli and G′ > G″ in Figure 16b, d confirm the increasing of MWCNTs/polymer network tendency to behave as an elastic solid compared to pure polymer solution. Indeed, the diffusion time of a single nanotube is slowed down due to entanglement with neighbouring nanotubes. Because of dominance of G′ over G″ the relaxation time of MWCNTs/polymer solution is longer than experimentally accessible frequency domain of current study.



(a)



(b)

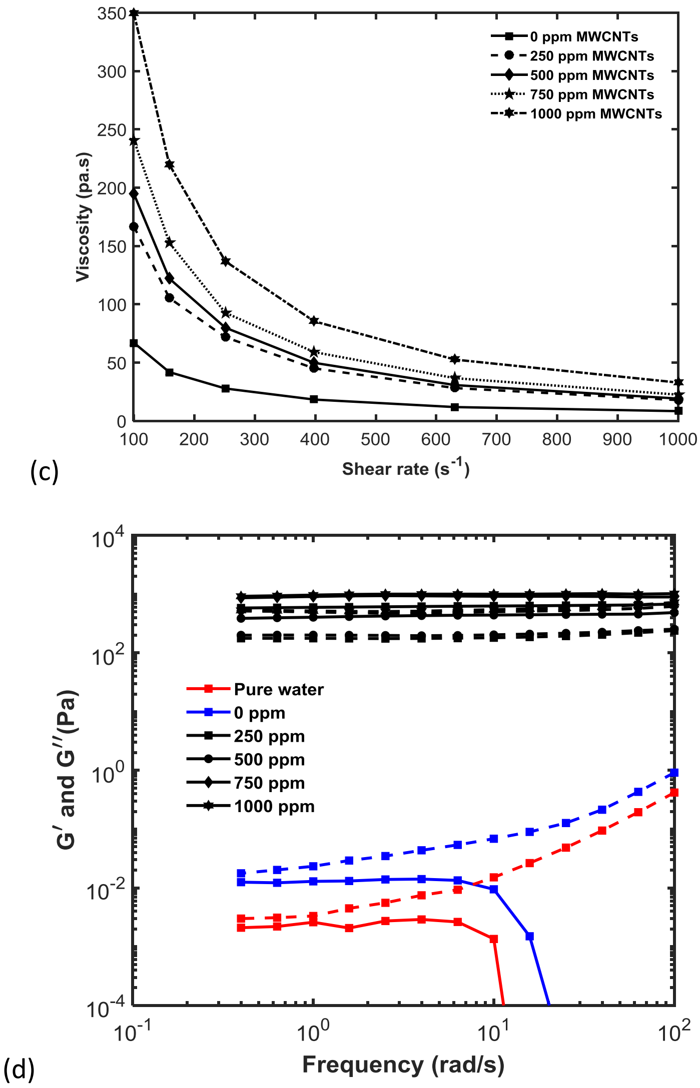


Figure 16. Effect of MWCNTs concentration on rheological behaviour of selected candidate (a) viscosity and (b) viscoelastic values of polyampholytic ter-polymer at alkali solution, (c) viscosity and (d) viscoelastic values of copolymer containing negative sulfonate group at API brine, G′ (–), and loss modulus, G″ (--) in (b) and (d).

As mentioned in previous sections, two-step method (same as current study) is the simplest and proper method for preparation of MWCNTs/polymer solution on a large scale in which MWCNTs disperse into a polymer fluid. The mixing step and de-agglomeration of MWCNTs in polymer solution is vital for preparation of a stable solution. However, the detrimental effect of mixing strength on polymer structure should also be considered. Figure 17 shows the viscosity of MWCNTs/polymers (sample 2) which were produced with following procedures:

1-Addition of MWCNTs to polymer solution and mixing by ultrasound probe (amplitude of 25 out of 100) for 5 min.

2-Addition of MWCNTs to pure water and de-agglomeration of particles by ultrasound probe (amplitude of 25 out of 100) for 5 min. Then addition of polymer to MWCNTs suspension and mixing with magnet stirrer for 24 h.

A drastically decreasing of viscosity is observed due to rupture of polymer base skeleton during ultrasound mixing. Therefore the procedure 2 is advised for preparation of MWCNTs/polymer solution with two step method.

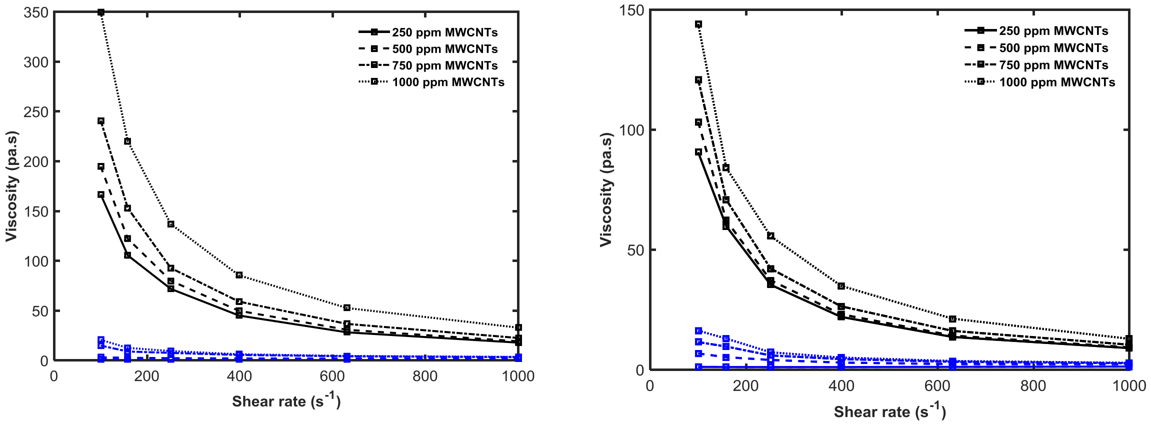


Figure 17. Effect of sonication on viscosity of MWCNTs/polymer solution (blue lines: procedure 1, black lines: procedure 2)

Conclusions

A series of co/ter-acrylamide based skeleton polymers have been synthesised and characterized. A systematic study of the effects of polymer structure, polymer concentration, nanotubes' concentration on viscosity and stability of MWCNTs/polymer solutions was conducted in this work. The following conclusions have been drawn:

- The polydispersity of co/ter-polymers was increased when different monomers were used during polymerization. The viscosity of pure PAM solution was increased around 35% of initial value after incorporation of hydrophobic chains in the its structure due to intermolecular hydrophobic association between the polymer chains.
- The acrylamide base skeleton polymers viscosity diminished between 70-80 percent at higher temperature of 60 °C. The huge amount of viscosity reduction shows that the acrylamide co/ter-polymers alone are not an effective chemical agent for subsurface application. The viscosity of polymer solutions was significantly boosted in presence of MWCNTs compared to pure co/ter-

polymer solutions. The highest increasing of viscosity happened for co/ter-polymer containing negative sulfonate-functional group around nine times. The effect of negative sulfonate group is especially noticeable to avoid decreasing of polymer viscosity at high temperature. Therefore MWCNT/polymers could be used as a potential agent for application in harsh environment of subsurface.

- In alkali condition, the maximum and maximum instability index equal to 0.28 and 0.006 was appeared for MWCNTs in polyacrylamide and polyampholytic ter-polymer respectively. On the other hand, the maximum and maximum sedimentation rate of MWCNTs (instability index equal to 0.27 and 0.01) was occurred in API brine containing polyacrylamide and copolymer containing negative sulfonate group respectively. High variation of particles stability after functionalizing of nanotube with co/ter-polymers highlighted the importance of polymer's structure modification especially for application in harsh environment.

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