

Influence of dissolved oxygen content on oxidative stability of linked polymer solution

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Abstract: The influence of dissolved oxygen content on the oxidative stability of a linked polymer solution (LPS) was studied by micro-filtration, dynamic light scattering and viscosity measurements. The results showed that at the same temperature, the degree of the oxidative degradation of the LPS increased and the rapidity of the oxidative degradation was accelerated with the increase of the dissolved oxygen content. Consequently, the size of linked polymer coils (LPCs) of the LPS became small, and the plugging capability of the LPS decreased. At a fixed content of dissolved oxygen, with increasing degradation temperature, almost the same results were observed, namely, an increased degree of oxidative degradation, accelerated rapidity of the oxidative degradation and decreased plugging capacity, with decreased oxidative stability of LPS. At 90 °C, in the presence of oxygen, LPS lost its plugging capability after having been degraded for a period of time. But at 40 °C, LPS with low dissolved oxygen content could be stable for a long time. The decreased plugging ability of LPS after oxidative degradation is mainly caused by the decreased size and number of the LPCs due to the breaking of hydrolyzed polyacrylamide (HPAM) molecule segments and the structural changing of HPAM molecules.

Key words: Linked polymer solution, HPAM, content of dissolved oxygen, degradation, stability

1 Introduction

Linked polymer solution (LPS) is defined as an aqueous solution of dispersed cross-linked polymer coils (LPCs). LPS system had been successfully applied to crude oil production as an in-depth profile control agent (Li et al, 2002) due to its low viscosity (Sun et al, 2003), suitable flow properties (Li et al, 2007; Luo et al, 2005; Shi et al, 2008) and ability of plugging pore throats in reservoirs (Sun et al, 2005a and 2005b). So far, the plugging ability (Luo et al, 2006; Zhu et al, 2006), rheological property (Sun et al, 2004), and formation conditions (Lin et al, 2007) of LPS have been well studied. It was found that the stability of LPS played a very important role in profile control and flooding. Shear stability and thermal stability of LPS have been studied, and the results showed that the plugging ability of LPS decreased under some shear stress (Lin et al, 2008a), and the degradation of LPS would be accelerated at high temperature (Lin et al, 2008b). In this paper the effects of oxygen content dissolved in the system on plugging ability of LPS, size of LPCs, viscosity of HPAM solution, and on size of HPAM coils are reported.

2 Experimental

2.1 Materials and methods

The polymer used in experiments is hydrolyzed

polyacrylamide (HPAM) produced by Pfizer company (USA), with a viscosity average relative molecular mass (M_v) of 1.80×10^7 and hydrolysis degree of 25.8%. The cross-linker aluminum citrate (AlCit) was synthesized in our laboratory. The water used in the experiments was deionized and filtered through acetate film (0.22 μm). NaCl was produced by Beijing Shuanghuan Chemical Reagent Plant (China), >99.5%, GC grade.

Linked polymer solutions were prepared by mixing HPAM solution with 10% NaCl solution, cross-linker aluminum citrate and deionized water at room temperature and the mixture was kept at 40 °C for 15 days for the cross-linking reaction to take place fully. The concentrations of HPAM and NaCl in LPS were 100 mg/kg and 500 mg/kg, respectively. The mass ratio of HPAM to Al was 20:1.

The linked polymer solutions prepared from either unprocessed HPAM solution, HPAM solution oxygenated by adding oxygen or HPAM solution deoxygenated with nitrogen were allowed to degrade at 90 °C. The oxygen content dissolved in LPS before degradation was measured with the colorimetric method.

2.2 Micro-filtration

The micro-filtration device is the same as that shown in literature (Dong et al, 2003). The micro-porous membrane used was a nucleopore membrane (supplied by China Institute of Atomic Energy) with an average pore diameter of 1.2 μm , a number of the pores per square centimeter of 5×10^6 , and a thickness of 10 μm . The LPS solution was filtered under 0.1MPa at room temperature. The filtration time was noted

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when each 1 mL of LPS passing through the membrane, and the total LPS for micro-filtration was 20 mL.

2.3 Viscosity measurement

The viscosity of HPAM solution was measured with a Ubbelode viscometer with a capillary diameter of 0.6mm. All the measurements were carried out at (30±0.1) °C.

2.4 Dynamic light scattering experiment

The average hydromechanical diameter (D_h) and size distribution of LPCs were measured by dynamic light scattering measurements with a Zetasizer-Nano-ZS (Malvern Instruments Ltd., UK). A 15 mW helium-neon laser (wave length in vacuum $\lambda=659$ nm) was used as the incident beam.

3 Results and discussion

3.1 Oxidative stability of LPS

The content of the dissolved oxygen in the deoxygenated, unprocessed and oxygen-added LPS samples was 0.3 mg/kg, 4.0 mg/kg and 12.0 mg/kg, respectively. LPS samples with different dissolved oxygen contents were allowed to degrade at 90 °C or 40 °C for micro-filtration and dynamic light scattering measurement.

3.1.1 Plugging capability of LPS

Fig. 1 shows the relationship of filtration time vs. degradation time for LPS with different oxygen contents at a degradation temperature of 90 °C. It shows that with increasing degradation time, the time of 20 mL LPS (with different oxygen contents) passing through the nucleopore membrane was shortened. For 20 mL undegraded LPS, it took 176.2 min to pass through the nucleopore membrane. For the LPS containing 0.3 mg/kg oxygen, when it was degraded for 24 h, the filtration time of which was 30 min. When it was degraded for 48 h, the filtration time was 2.1 min. For the LPS with 4.0 mg/kg oxygen, when it was degraded for 24 h, the filtration time was 5.2 min. For the LPS with oxygen content of 12.0 mg/kg, when it was degraded for 10 h, the filtration time was 1.1 min. In the both cases of 4.0 mg/kg and 12.0 mg/kg oxygen contents, LPS could not plug the membrane, indicating that the higher the dissolved oxygen content, the worse the oxidative stability of the LPS.

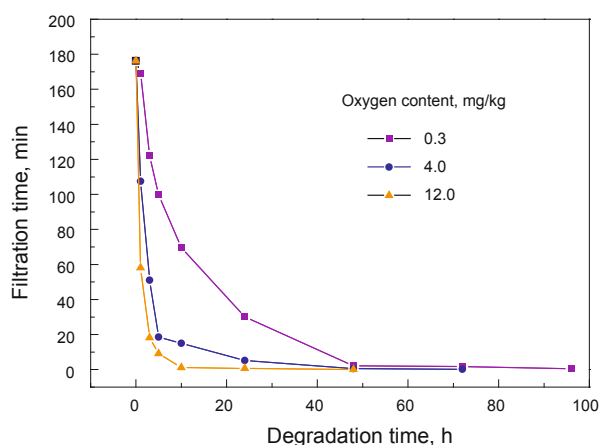


Fig. 1 Relationship of filtration time vs. degradation time for LPS with different oxygen contents (Degradation temperature: 90 °C)

Except for the oxygen content, the oxidative stability of the LPS was also affected by the degradation temperature (Fig. 2). The curves in Fig. 2 shows that after being degraded for 48 h at 40°C LPS still could plug the membrane, while after being degraded for 10 h at 90°C LPS could not plug the membrane, indicating that the LPS being degraded at lower temperature had higher oxidative stability.

Table 1 shows that the LPS, with 4.0 mg/kg and 12.0 mg/kg oxygen contents, being degraded for 120 h at 40° C, still could plug the membrane. The results further indicated that low degradation temperature can effectively improve the oxidative stability of LPS.

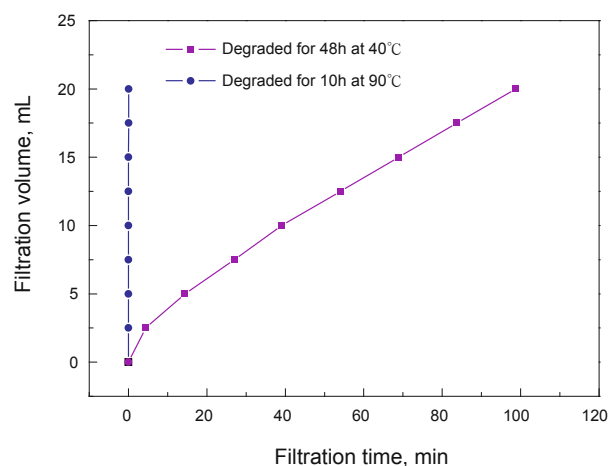


Fig. 2 Relationship of filtration volume vs. filtration time for LPS with an oxygen content of 12.0 mg/kg

Table 1 Filtration time of 20 mL LPS with different oxygen contents after being degraded at 40 °C

Oxygen contents mg/kg	Filtration time (min) after being degraded for different times (h)		
	0h	48h	120h
4.0	176.2	159.1	166.0
12.0	176.2	98.8	37.5

Table 1 also shows that the filtration time of the LPS with 12.0 mg/kg oxygen was shortened significantly with the increase of degradation time, indicating that the LPS with higher dissolved oxygen content could degrade severely at 40 °C. The degradation of the LPS led to the decrease in LPCs size hence lowered the ability to plug the membrane. The filtration time of the LPS with 4.0 mg/kg oxygen after being degraded for 120 h did not change greatly, indicating that the LPS with lower oxygen content is more oxidative stable at 40 °C.

3.1.2 Size of LPCs

Fig. 3 shows the relationship of the average hydromechanical diameter (D_h) of LPC vs. degradation time for LPS with different dissolved oxygen contents after being degraded at 90 °C. The average hydromechanical diameter (D_h) of the LPCs decreased with increasing degradation time. Before degradation, the D_h of the LPCs of all the LPS was

623nm. For the LPS with 0.3 mg/kg oxygen content, after being degraded for 48 h, the D_h of the LPCs was 52 nm. For the LPS with 4.0 mg/kg oxygen, after being degraded for 24 h, the D_h of the LPCs was 55 nm. For the LPS with 12.0 mg/kg oxygen content, after being degraded for 10 h the D_h of the LPCs decreased below 50 nm. The results indicate that degradation of the LPS was accelerated with the increase of the dissolved oxygen content. Combined with the results shown in Fig. 1, when the D_h of the LPCs decreased below 50 nm, the LPS could not plug the membrane.

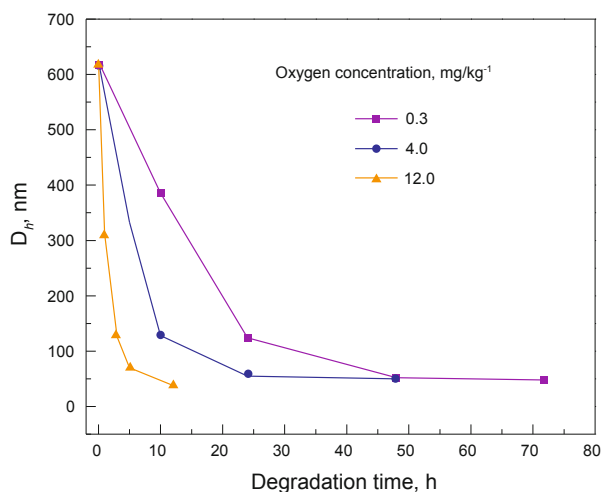


Fig. 3 Relationship of average hydromechanical diameter (D_h) of LPC vs. degradation time for LPS with different oxygen contents being degraded at 90 °C

Fig. 4 shows that size distribution of the LPCs dispersed in the LPS with 0.3 mg/kg oxygen after being degraded. With the increase of the degradation time, the size of the LPCs decreases, and the distribution became narrow. At the same time, the number of small LPCs increases. The results further indicate that the decrease in LPCs size caused by degradation is one important reason why the LPS cannot plug the membrane.

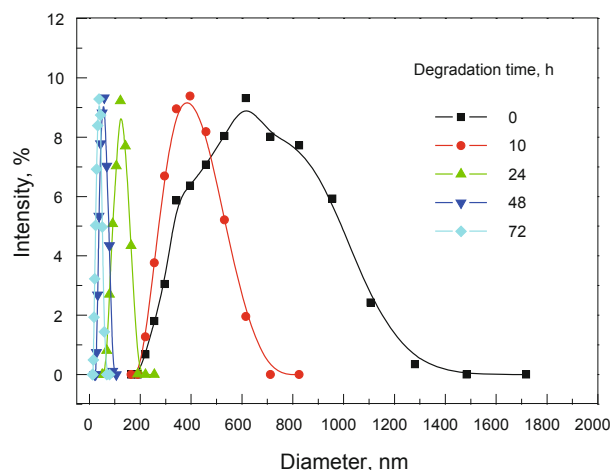


Fig. 4 Size distribution of LPCs of the LPS with 0.3 mg/kg oxygen content after being degraded for different times

3.2 Oxidative stability of HPAM solution

The dissolved oxygen contents of the deoxygenated, unprocessed, and oxygenated HPAM samples were 0.3, 4.0 and 12.0 mg/kg, respectively. The HPAM solutions with concentrations of HPAM and NaCl in the solution being 100 and 500 mg/kg, respectively, were degraded at 90 °C for investigating their oxidative stability by the viscosity method and dynamic light scattering experiment.

3.2.1 Viscosity of HPAM solution

Fig. 5 shows that the viscosity of the HPAM solutions decreases with increasing degradation time. Within the first 24 h of degradation, the viscosity decreased greatly. With further degradation, the viscosity decreased lightly, and the higher the dissolved oxygen content, the greater the viscosity changed.

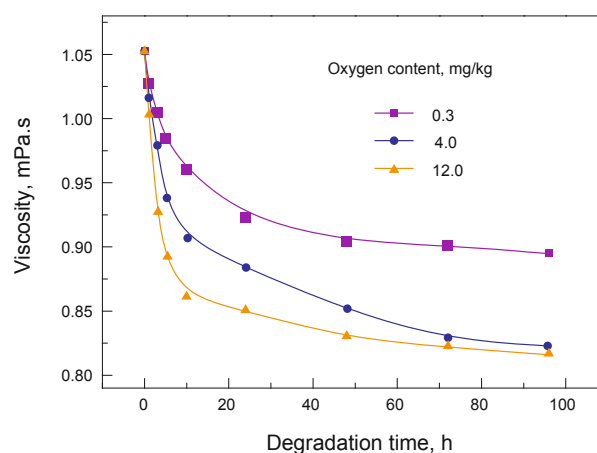


Fig. 5 Viscosity vs. degradation time for HPAM solutions being degraded at 90 °C

3.2.2 Size of HPAM coils

Table 2 shows that the average hydromechanical diameter (D_h) of the HPAM coils decreased with increased degradation time at 90 °C. The higher the dissolved oxygen content, the more rapid decrease in size of the HPAM coils. For the HPAM solution with 0.3 mg/kg oxygen, when it was degraded for 24 h, the D_h of the HPAM coils decreased from 535 nm to 71 nm. With further degradation time the decrease in size of the HPAM coils slowed down. For the HPAM solution with 12.0 mg/kg oxygen, when the degradation time was more than 10 h, the size of the HPAM coils decreased slowly. The results of dynamic light scattering measurements agreed well with those of the viscosity measurements.

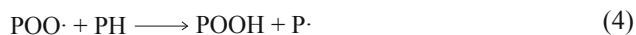
Table 2 D_h of HPAM coils in the HPAM solution with different oxygen contents after being degraded for different times at 90 °C

Degradation time of HAPM solution with 0.3 mg/kg oxygen, h	0	10	24	48
D_h of HAPM coils, nm	535	225	71	45
Degradation time of HAPM solution with 12.0 mg/kg oxygen, h	0	3	10	48
D_h of HAPM coils, nm	535	199	52	30

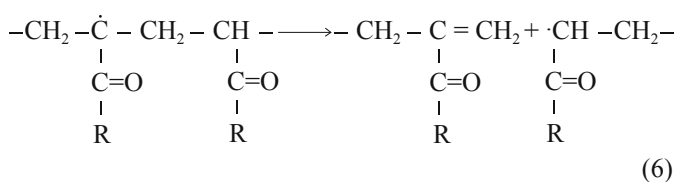
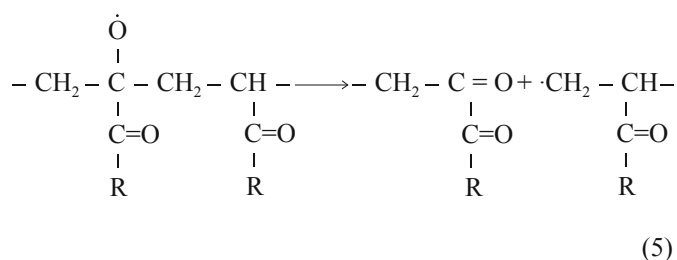
The decrease in HPAM solution viscosity was related to the oxidative degradation of the HPAM molecules at high temperature. The results above indicate that the oxidative degradation of the HPAM molecules led to the HPAM molecules becoming smaller, and the solution viscosity declined accordingly. A high dissolved oxygen content accelerated the degradation of HPAM molecules and the extent of degradation increased. Consequently, at the same degradation time, the higher the dissolved oxygen content, the smaller the HPAM coils size, and the more rapid the decrease in HPAM solution viscosity.

3.3 Results and discussion

The oxidative degradation of HPAM is a free radical reaction (Eq.1-6) initiated by peroxide within the polymer (Zhan et al, 2004). When the dissolved oxygen content in solution is enough to produce oxygen free radicals, the degradation reaction will take place. As a result the HPAM molecule segments are broken, and the size of HPAM coils becomes small. Because the HPAM concentration in the LPS was low, the cross-linking degree of LPS was also low and only 8.96% of HPAM molecular segments were cross-linked (Dong et al, 2003). Since a large amount of HPAM molecular segments did not react with Al^{3+} of cross-linker, the oxidative stability of HPAM would affect the oxidative stability of LPS.



Where, "P" represents the alkyl chain of HPAM molecules.



When LPS degraded at high temperature, firstly the HPAM molecular segments were broken, and the size of LPCs became small. At the same time, the structure of the HPAM molecules changed after degradation. The cross-link between the HPAM molecules and cross-linker was destroyed, and the

number of the LPCs decreased. Consequently, LPS lost the ability of plugging the membrane.

4 Conclusions

(1) At the same temperature, the degree of the oxidative degradation of LPS increased and the oxidative degradation accelerated with the increase of the dissolved oxygen content. Consequently, the size of LPCs became small, and the plugging capability of the LPS decreased.

(2) At a fixed dissolved oxygen content, with increasing degradation temperature, almost the same results were observed, namely, the degree of oxidative degradation increased, the oxidative degradation accelerated and the plugging capacity decreased, with decreased oxidative stability of LPS.

(3) At 90 °C, with high oxygen content, LPS lost its plugging ability after being degraded for a period of time. But at 40 °C, LPS with low dissolved oxygen content could be stable for a long time.

(4) The decreased plugging capacity of LPS after oxidative degradation is mainly caused by the decreased size and number of LPCs due to the breaking of HPAM molecule segments and the structural change of HPAM molecules.

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