Accelerated chemical degradation of polyacrylamide

Jianping Gao*, Tong Lin, Wei Wang, Jiugao Yu, Shaojun Yuan, Shaomin Wang
Department of Chemistry, Tianjin University, Tianjin 300072 , P.R.China

SUMMARY: The chemical degradation of polyacrylamide(PAM) at low temperature in aqueous medium was initiated by peroxides. The degradation degree of the polymer rose with the reaction time. The degradation degree of PAM depended not only on peroxide characteristic but also on the concentration of polyacrylamide and potassium persulfate 、 degradation temperature and original molecular weight of PAM. The results showed that the order of degradation degree of PAM in three peroxides is $K_2S_2O_8$ > $K_2S_2O_8$ – $Na_2S_2O_3$ > H_2O_2. The degradation degree of PAM grew as reaction temperature 、 molecular weight of PAM 、 concentration of potassium persulfate and PAM increased.

Keywords: chemical degradation, redox system, degradation degree, peroxide, polyacrylamide

Introduction

Polyacrylamide(PAM) is one of the important water soluble polymers and has wide applications . High molecular weight PAM is mainly used as flocculant , while the medium molecular weight PAM is used in paper as dry-fortifier , but low molecular weight PAM can be applied as disperser. So the molecular weight of PAM is the key factor to determine its application. Some researchers have tried to get a series of PAM with different medium molecular weights by chemical degradation. They found that this aim could be attained by adjusting the reaction parameters[1-2].

The use of PAM in alkaline/surfactant/polymer (ASP) flooding becomes wider and wider with the popularity of second-exploitation of oil-well, because it can improve the exploiting efficiency[3]. The main act of the polymer is to increase the density of working-liquid in ASP flooding , lower the oil-water mobility ratio and adjust the osmosis section[4]. But this technique may cause the accumulation of PAM remaining in the well. Numerical analogue computations indicated that the PAM holdup was about 25% ~ 53.6% of the PAM injected[5]. So the degradation of the aggregated PAM is significant for the removing of blockage[6-8].

 CCC 1022-1360/99/$ 17.50+.50/0

Experimental

Materials

Polyacrylamide A has a molecular weight of $12x10^6$; polyacrylamide B, $15x10^6$. Potassium persulfate ($K_2S_2O_8$) came from Tianjin East Chemical Plant. Hydrogen peroxide (H_2O_2) was provided by Beijing Chemical Plant. Sodium thiosulfate ($Na_2S_2O_3$) was from Tianjin Second Chemical Reagent Plant.

Degradation procedure

The degradation of polyacrylamide(PAM) was carried out in a D-8401 microbe cultivating case. First, a certain amount of PAM and peroxide were weighed out and put into two beakers respectively, and then distilled water was poured into the beakers to form solutions. The two solutions were poured into and mixed in a volumetric flask , which was consequently and immediately placed on a rotation-bed in the cultivating case to allow PAM to undergo degradation at a certain temperature. After a period of time of degradation. the samples were taken out to determine the molecular weight of PAM samples.

The viscosity [η] of PAM was tested with a Ubbelohde viscometer at the temperature of 30 ℃, and then the molecular weight was calculated according to Mark-houwink equation below:

$$[\eta]= K M_v^{\alpha}, \quad \text{where,} \quad K=6.31x10^{-3}, \ \alpha=0.90.$$

Degradation degree

Numeral-average molecular weight (M_n) and weight-average molecular weight (M_w) have function relationship with degradation degree(De), which is represented in the equation below:

$$M_{n(De)}= \Sigma n_{i(De)}M_{ni} / \Sigma n_{i(De)}, \qquad M_{w(De)}= \Sigma n_{i(De)}M_{ni}^{\ 2} / \Sigma n_{i(De)}M_{ni}$$

As for the random degradation of macromolecules with higher original molecular weight, the distribution of the molecular weight during degradation immediately trends to index distribution, based on which the following relationships between M_n 、 M_w and M_v exist.

$$M_w : M_v : M_n = 2 : [\ (1+\alpha)\Gamma(1+\alpha)]^{1/\alpha} \quad (1)$$

where, α is the index in Mark-Houwink equation, and the value of 0.9 is chosen in our experiment.

Again, if the molecular weight accords to index distribution, the degradation rate is represented below:

$$R = dDe/dt = -1/\varphi(De) \cdot 1/M_{w(De)}^2 - dM_{w(De)}/dt \quad (2)$$

When the equation(2) is integrated, the following equations can be obtained:

$$1/M_{w(De)} = 1/M_{w(0)} + 0.5De \quad (3)$$

or, $$1/M_{n(De)} = 1/M_{n(0)} + De \quad (4)$$

where, $M_{w(0)}$ and $M_{n(0)}$ represent the corresponding original molecular weight .

So the degradation degree is derived:

$$De = 1/M_{n(De)} - 1/M_{n(0)} \quad (5)$$

According to equation (1), the $M_{n(De)}$ and $M_{n(0)}$ can be displaced by $M_{v(De)}$ and $M_{v(0)}$ respectively.

$$M_{n(De)} = M_{v(De)} / [\ (1+\alpha)\Gamma(1+\alpha)]^{1/\alpha}, \qquad M_{n(0)} = M_{v(0)} / [\ (1+\alpha)\Gamma(1+\alpha)]^{1/\alpha}$$

$$De = 1/M_{n(De)} - 1/M_{n(0)} = [1/M_{v(De)} - 1/M_{v(0)}][\ (1+\alpha)\Gamma(1+\alpha)]^{1/\alpha} \quad (6)$$

Since α is 0.9, so $\Gamma(1+\alpha)$ becomes 0.9618 .

$$De = [1/M_{v(De)} - 1/M_{v(0)}] \times 1.954 \quad (7)$$

Therefore, the degradation degree De can be calculated from measured M_v according to equation (7).

Result and Discussion

Degradation agents

The chemical degradation of PAM was carried out at 40 ℃ in a microbe cultivation case, and the chosen degradation agents are all water-soluble peroxides.. Figure 1 shows the degradation degree of PAM during the degradation reaction under the action of three

different chemicals, at the same reaction conditions. The aqueous PAM without chemicals almost did not undergo degradation at 40 ℃, while the same sample showed an evident degradation, if it was added with degradation agents.

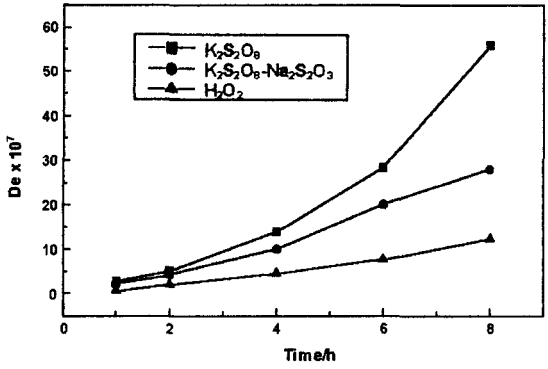

Figure1 Degradation degree of PAM in different peroxides

The degradation degree of PAM in three peroxide aqueous solutions are in the following order:

$$K_2S_2O_8 > K_2S_2O_8\text{-}Na_2S_2O_3 > H_2O_2$$

$K_2S_2O_8$-$Na_2S_2O_3$ is a redox system, and the rate of break down is the fastest, so the degradation rate initiated by the free radicals is also the fastest. On the other hand, the chance of termination among free radicals is also the highest because of the higher free radical concentration, leading to a lower degradation degree than that of $K_2S_2O_8$.

Effect of temperature on the degradation degree

Temperature is one of the key factors that affect the degradation of PAM. The degrading degree of PAM in 0.0296mol/L $K_2S_2O_8$ solution at the temperature of 30 ℃、40 ℃、50 ℃ and 60 ℃ were studied respectively, and the results are shown in Figure 2. The degradation degree of PAM increased as the temperature rose from 30 ℃ to 50 ℃, because the decomposing rate of $K_2S_2O_8$ grew. But further increase of temperature from 50 ℃ to 60 ℃ brought about slight change in the degradation of PAM. When temperature rose, the decomposing rate of the $K_2S_2O_8$ increased, so a

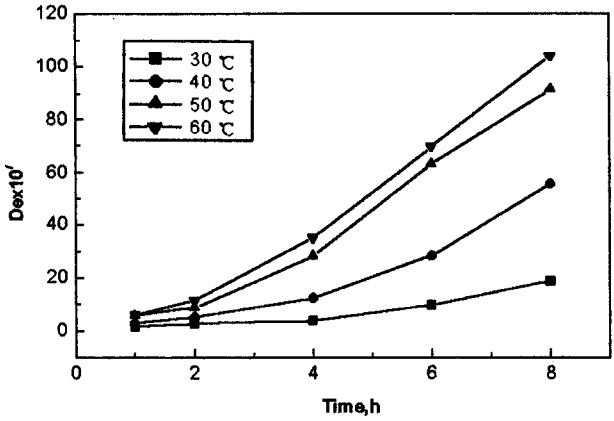

Figure2 Effect of temperature on De

larger amount of free radicals were formed that caused the increase in degradation reaction and interaction between free radicals. The two actions counteracted each other and showed the above changes. The decomposing rate k_d and $t_{1/2}$ of $K_2S_2O_8$ at different temperatures were calculated according to the following equation, and the results are listed in table I.

$k_{d2} / k_{d1} = (E_d / 2.30R)(1 / T_1 - 1 / T_2)$, $E_d = 140$ kj/mol, $R = 8.25$j/mol · K

Table I k_d and $t_{1/2}$ of $K_2S_2O_8$ at different temperatures

Temp.(℃)	30	40	50	60
$k_d \times 10^7(s^{-1})$	0.297	1.780	9.50	31.6
$t_{1/2}$ (h)	6481	1081	202	60
$k_{d(t+10)} : k_{d(t)}$	6	5.34	3.37	
$k_{d(30)} : k_{d(40)} : k_{d(50)} : k_{d(60)}$ = 1 : 3.37 : 18 : 108				

Effect of $K_2S_2O_8$ concentration

At the temperature of 40 ℃, the effect of $K_2S_2O_8$ concentration, in the range of 0.0089mol/L ~ 0.05962mol/L, on the degradation of PAM was investigated, and the results are shown in Fig.3. When $K_2S_2O_8$ concentration changes from 0.0089mol/L to 0.0148mol/L, De shows minute change. But with further increase to 0.0296mol/L or 0.0596mol/L, De changes evidently. Especially after 8 hour degradation reaction,

$K_2S_2O_8$ concentration significantly affects the degradation degree.

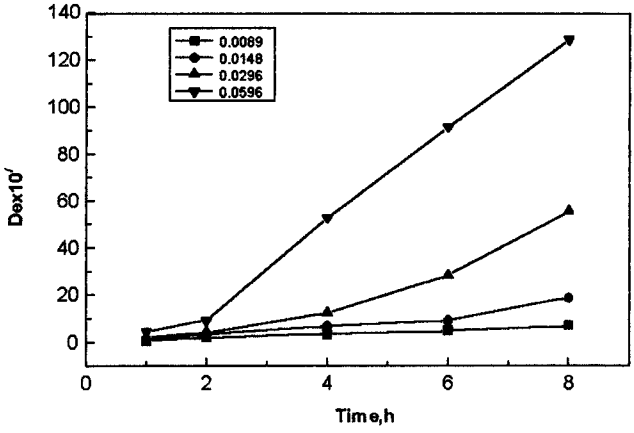

Figure 3 Effect of $K_2S_2O_8$ concentration on De

Effect of PAM concentration on De

Like $K_2S_2O_8$ concentration , PAM concentration also affects the degradation . Fig.4

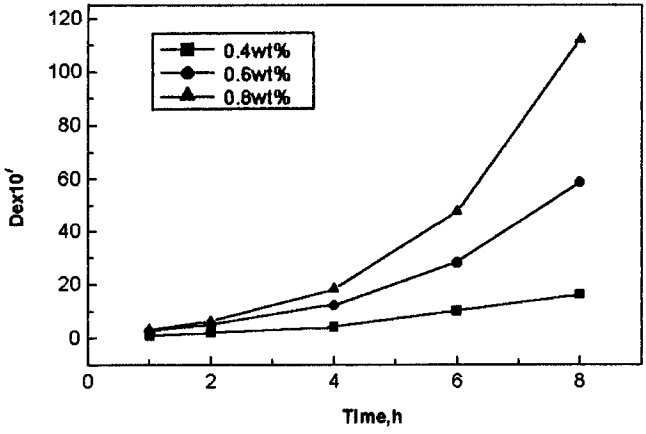

Figure 4 Effect of PAM concentration on De

shows the results at three different concentrations. De increased as the PAM concentration rose. When PAM concentration is higher, the decomposed free radicals have more chance to react with PAM molecules and cause the break down of PAM macromolecules. The difference in De between different PAM concentration became more and more obvious as the degradation reaction went.

Conclusion

1. The efficiency of three peroxides in the degradation of aqueous PAM is

$$K_2S_2O_8 > K_2S_2O_8\text{-}Na_2S_2O_3 > H_2O_2$$

2. The higher the PAM concentration is, the higher the degradation degree
3. Increasing $K_2S_2O_8$ concentration can lead higher degradation degree of PAM.
4. High temperature can cause intensive degradation of PAM.

References

[1] J. Klein, K.D.Conrad, Macromol.Chem.,178(11),1635(1978)

[2] V.F.Kurenkov, I.B.Orlova,V.A.Myagchenkov, Macromol. A28(6),1191(1986)

[3] B.Y.Wang, X.H. Cui, Oil field Chem.,11(4),327(1994)

[4] L.D. Chen ,10(3),Oil field Chem.,283(1993)

[5] G.X. Lu,F.Q. Shong, Oil field Chem.,11(3),230(1994)

[6] Y.M. Nang,T.W. Zhou, J. Daqing Petroleum Institute, 21(1),49(1997)

[7] D.S.Russel , J.Petro.Technol.,8,1513(1981)

[8] J.P.Gao, J.G.Yu, W.Wang, J.Appl.Polym.Sci., to appear.