

STUDIES ON IPN OF POLYACRYLAMIDE INVERSE EMULSION AND MODIFIED UREA-FORMALDEHYDE RESIN

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ABSTRACT

The selective water plugging agent was prepared by heating the blends of the polyacrylamide inverse latex, modified urea formaldehyde resin, crosslinking agent and catalysts. The results show that using different types of polymers and additives or changing in their proportion of the blends, the gelling viscosity, starting point of gelling and other properties of the IPN can be controlled.

INTRODUCTION

Since the geological structure and oil deposit type are very complicated and the permeability of stratum is heterogeneous, it is inevitable that there is an amount of water accompanied with oil so that the production of oil has been quite decreased. Thus the water-plugging technology plays an important role in the enhancement of oil recovery (EOR).

In this paper, a water-plugging agent adopted in complicated geological structure is introduced. It was synthesized by heating the compound of polyacrylamide inverse latex, urea formaldehyde resin, crosslinking agent and catalyst. The product prepared has the IPN structure. Some work has been done already by some authors for forming this system and in the gelation of polyacrylamide and urea formaldehyde resin. However, the formation of IPN structure in this system has not been reported. Our contribution to this system lies that the gel with IPN structure was successfully produced by using W/O/W triple emulsion, which was formed by phase-transforming W/O emulsion of polyacrylamide and the urea formaldehyde resin modified by aromatic compounds, e.g. benzene, toluene etc. Then IPN thus formed structure was studied. The effects of the type and amount of PAM and additives on the properties of IPN were investigated.

EXPERIMENTAL

1. Materials

PAM inverse latex: $\overline{M}_w = (1 \sim 8) \times 10^6$, degree of hydrolysis 20%, solid content 30%; the modified urea-formaldehyde resin: viscosity 0.5—1.0 Pa.s, solid content 60%, granted by Chemical Plant of Tianjin University. NH_4Cl , $\text{Na}_2\text{Cr}_2\text{O}_7$, hexamethylene-tetramine, polyaldehyde, 1, 3-dichloropropanol are all CP reagents.

2. Test method

Firstly, the crosslinking agent, catalyst and other additives in suitable proportion were added into a mixture of modified urea-formaldehyde resin and PAM inverse latex (phase transformed). Secondly, it was stirred and sealed in a stainless steel autoclave and placed at a given temperature for a certain period. Finally, the properties of the gel were measured after cooled.

3. Methods of determination

Starting point of gelling, gel viscosity, thermal stability and gel selectivity were determined according to the methods in reference [1].

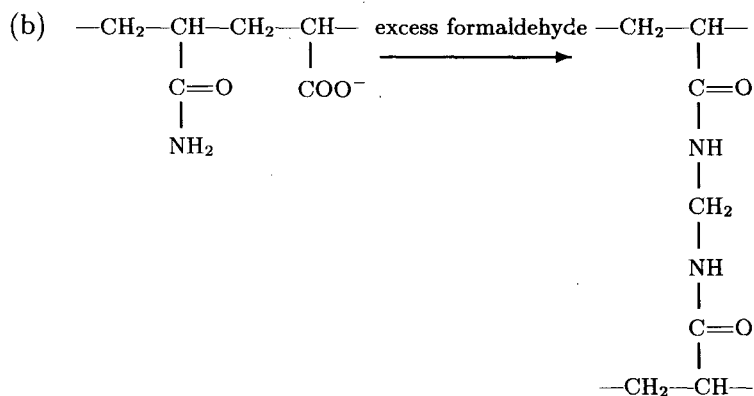
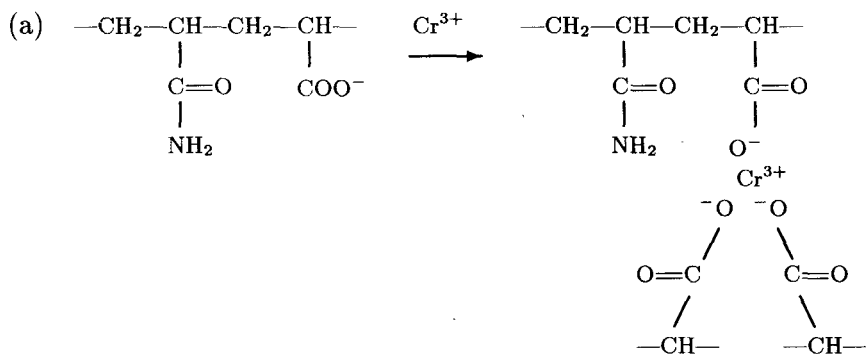
Dynamic mechanical properties were measured by TBA device (NB-1)^[2]. In the experimental data, Δ represents internal energy consumption of the material. $\ln \Delta$ is the natural logarithm of the internal energy consumption. P is the logarithm of variation periods (s). $1/P^2$ denotes the relative rigidity of the sample, whereas $\ln(1/P^2)$ is the natural logarithm of relative rigidity of samples.

Structural analysis of IPN was carried out by JEM-160 CXII transmission electron microscope.

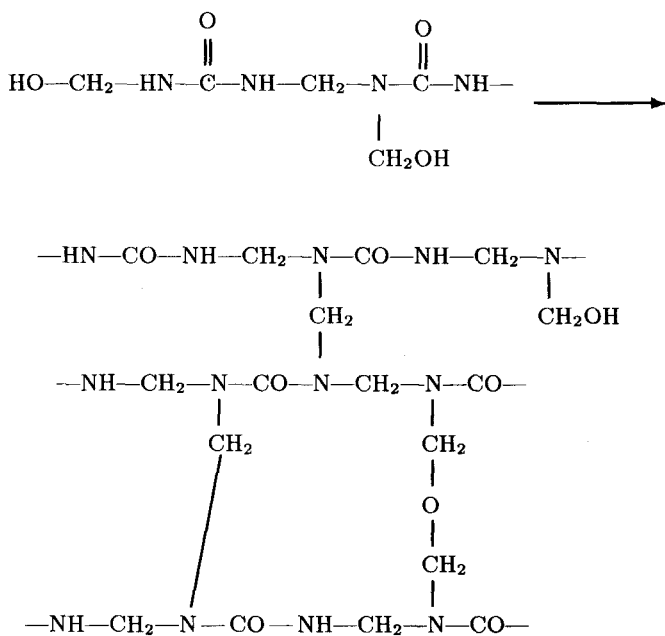
RESULTS AND DISCUSSIONS

It was found from the experiment that the gels formed individually either from urea formaldehyde resin or from polyacrylamide are both brittle, low tear resistance and low tensile strength, while the material with the IPN structure produced from these two kinds of polymers is of relatively high tensile strength and toughness. In fact, not only the molecular chains of urea formaldehyde resin or polyacrylamide can be crosslinked individually, but also the crosslinking between two polymers can occur. The reaction for crosslinking can be written as follows.

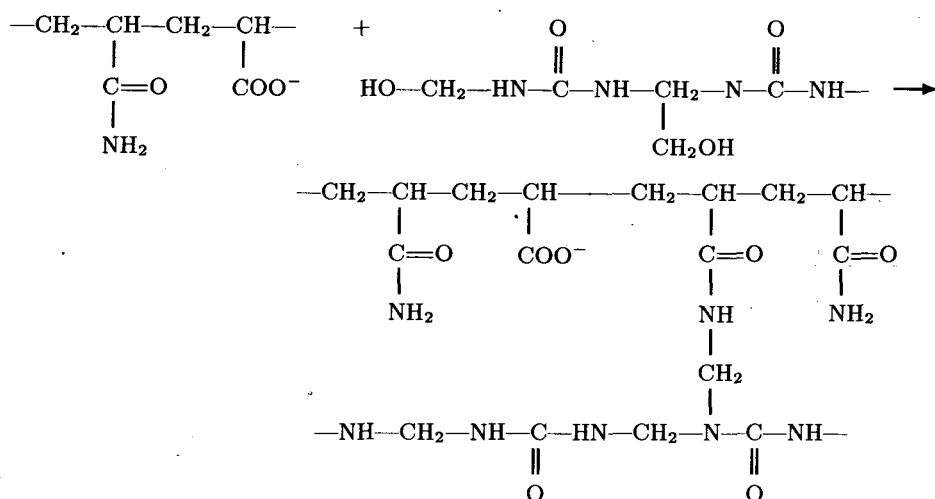
(1) Crosslinking reaction of PAM



(2) Crosslinking reaction of modified urea formaldehyde resin



(3) Crosslinking reaction between PAM and modified urea formaldehyde resin



The effects of various factors on the properties of the IPN polymers are discussed as follows.

1. Influence of molecular weight and quantity of polymer on properties of IPN

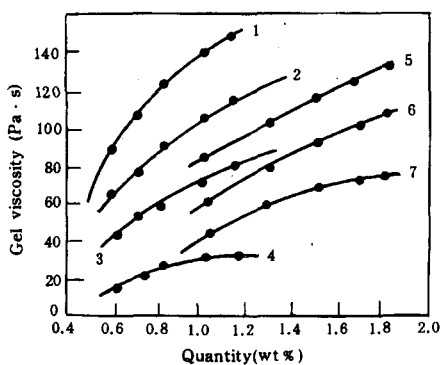


Fig. 1 Influence of molecular weight and quantities of PAM on properties of IPN
 $\text{Na}_2\text{Cr}_2\text{O}_7$: 0.06%; NH_4Cl : 0.02%;
 Temperature: 130°C, 24h

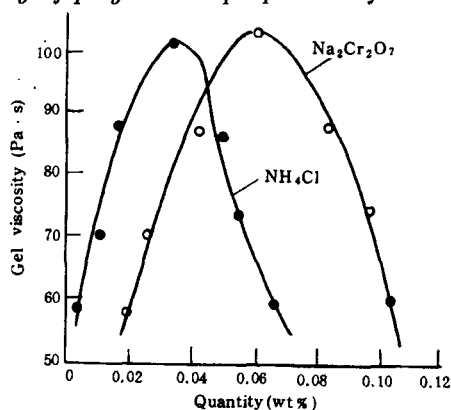


Fig. 2 Effects of crosslinking agent and catalyst on gel viscosity. Molecular weight of PAM: 4,740,000, content in blend: 1.0% Modified resin viscosity 0.8 Pa·s, content in blend: 1.8%

Fig. 1 shows that the molecular weight and quantity of polymer can exert remarkable influence on the gel viscosity of IPN. From Curve 1 to Curve 7 in the Fig. 1, the molecular weight of PAM $\times 10^{-4}$ are 596; 474; 276; 164; 520; 520 and 520 respectively, while the viscosities of the modified resins (Pa·s) are 1.0; 1.0; 1.0; 1.0; 1.0; 0.8 and 0.5 respectively. Therefore, the success rate of water-plugging and valid duration under different geological conditions can be increased by selecting suitable molecular weight and concentration of PAM.

2. Effects of crosslinking agent and catalyst on properties of IPN

Fig. 2 shows that the amount of crosslinking agent and catalyst will influence the gel viscosity notably. The crosslinking degree can be adjusted by controlling their amount. Thus, the gel with suitable starting point of gelling will be prepared.

It is found that when the crosslinking agent and catalyst which can promptly gel at 130°C can hardly react below 40°C. However if the compound which can gel well at 60–80°C is used at 130°C, the gel obtained is brittle and dehydrates seriously.

Therefore, hexamethylene-tetramine, 1,3-dichloropropanol and polyaldehyde should be used below 60°C.

3. Solidifying behavior for systems at increasing temperature

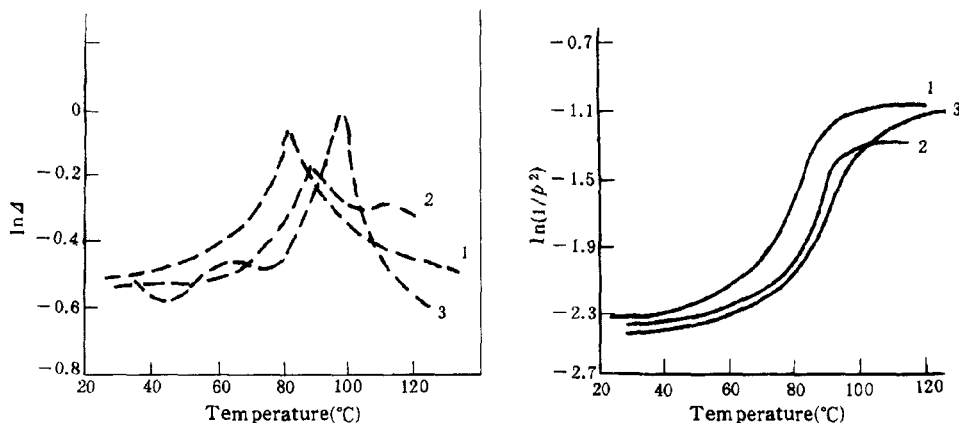


Fig. 3 TBA curves of PAM inverse latex/modified urea-formaldehyde resin system.

The conditions are the same as in Fig. 1. Molecular weight of PAM $\times 10^{-4}$:

1) 800; 2) 500; 3) 320

The structure of IPN influences its properties notably. Park et al.^[3] pointed out that the major factors for influencing the structure include: 1) compatibility of compositions, 2) crosslinking rate and form of IPN produced, 3) crosslinking density, 4) composition of IPN, 5) crosslinking degree of gel. So the structure of IPN is quite complicated. The TBA measurement can only be used to reflect the stress relaxation process from viscous-flow state to crosslinking state. Before the gelling transition, the whole molecular chain moves as an integrity before gelling, while the segment motion occurs after gelling (before the glass transition). Because of the addition of crosslinking agent and catalyst, the crosslinking density was enhanced up to or over that of the glass transition. So the glass transition point moves up or disappears. The curves in Figs. 3 and 4 only show the gelling transition for this reason.

It was clearly shown in Figs. 3 and 4 that the gelling temperatures were lowered with the increase in the molecular weight and the concentration of PAM. This is also due to the increase in crosslinking density which makes the gelling temperature

lower.

4. Thermal stability of IPN

The results are listed in Table 1.

Table 1 Thermal stability of IPN

Temperature (°C)	145	150	200	250	300	350
Gravity loss (wt%)	5.6	7.0	15.0	23.1	36.3	78.0

Elevation rate of temperature: 6°C/min; gel formed at 130°C for 24h, dehydrated

The reason for the serious gravity-loss above 150°C is mainly that the amide groups in the molecular chains of polyacrylamide can decompose easily. In addition, the thermolysis of urea formaldehyde resin can also occur.

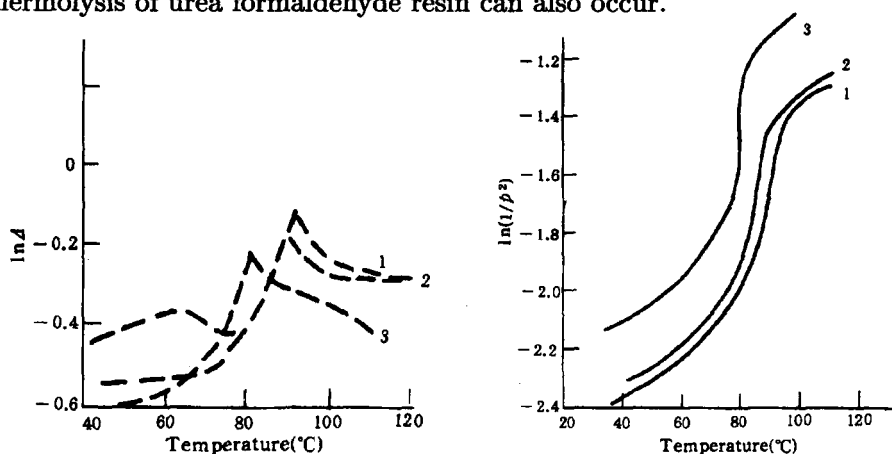


Fig. 4 TBA curve of the system during solidification at elevated temperature

The conditions are the same as in Fig. 1. Content of PAM latex in the blend (wt%):

1) 0.4; 2) 0.6; 3) 0.8

5. Selectivity of IPN

The PAM/modified urea-formaldehyde resin IPN is in swollen state in water as shown in Fig. 5. But it will shrink in various kinds of oil. So the IPN has good selectivity for water and oil and efficiency for conduction of oil.

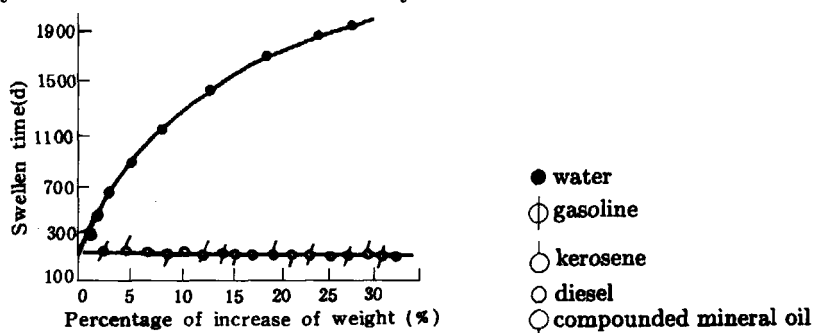


Fig. 5 State change of IPN in water or mineral oil gelling viscosity of sample: 95Pa.s (measured at room temperature)

6. Structure of IPN

It can be seen from the photos in Fig. 6. that the cell structure spread over the whole sample and the higher the crosslinking density, the larger the size of cell.

7. Practical effect

This kind of IPN has been using as water plugging agent for more than 300 examples in eight oil fields. The percentage of effectuation is from 75% to 85% and the valid duration is from half year to more than two years.

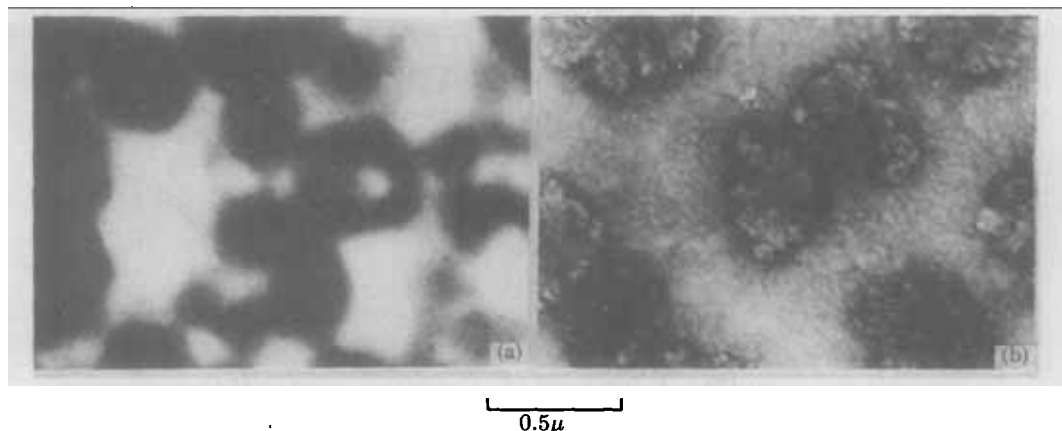


Fig. 6 Photos of IPN by electron microscope (a) gelling at 60°, 36,000 times; (b) gelling at 130°C, 36,000 times

CONCLUSION

By heating the blend of polyacrylamide inverse latex, modified urea formaldehyde resin, crosslinking agent and catalyst, the IPN can be produced. The gelling viscosity, starting point of gelling and gelling temperatures of the polymers can be adjusted with different molecular weight of polymer and different additives. Therefore various recipes can be designed to meet the needs for operating in work site and to increase the effectiveness possibility and valid duration for water plugging processes.

Keywords:

Polyacrylamide inverse latex; Modified urea-formaldehyde resin; IPN; Waterplugging agent

REFERENCES

- [1] Liu, Q.P.; Ha, R.H.; Hu, J.S., et al., *Oilfield Chemistry (in Chinese)*, **1990**, 4: 312.
- [2] Fen, P.; Gu, G.F.; Zhan, H.J., et al., *Chemistry Bulletin (in Chinese)*, **1984**, 10: 35.
- [3] Park, I.H.; Lee, J.H. and Kim, S.C., *Polym. Bull.*, **1983**, 10: 126.
- [4] Sperling, L.H., "Interpenetrating Polymer Networks and Related Materials", Plenum Press, **1981**.