SYNTHESIS RESEARCH OF NEW POLYETHER POLYCARBOXYLATE SUPERPLASTICIZER

Xiuxing Ma, Feiyu Yu, Xinqi Guo

Xiamen Academy of Building Research Group

1. INTRODUCTION

At present, the ecumenic polycarboxylate superplasticizer was produced by a copolymerization reaction under a certain temperature from some olefin unsaturated monomers and the polyethylene glycol unsaturated carboxylic acid esters, which were prepared by the esterification reaction of polyethylene glycol with the over-dosaged unsaturated carboxylic acid. But, because the present domestic product craft for unsaturated carboxylic acid esters is not mature, to engender certain influence to the industrialization manufacture. Further more, the mass fluctuation from the unsaturated carboxylic acid esters extremely influenced the next step copolymerization reaction, so its industrialization production need further strengthens.

In recent years, the polyether polycarboxylate superplasticizer became one of luminescent spots in polycarboxylate superplasticizer synthesis research area. Because the big monomer of allyl alcohol polyethylene glycol covers the active unsaturated duplet chemical bond, the synthesis of polycarboxylate superplasticizer may realize with a comparatively simpler craft. This article digests the domestic and foreign correlation research results, combines response activeness and the characteristic from the big monomer of allyl alcohol polyethylene glycol, carries through the massive synthesis research, so obtained unprecedented progress on the synthesis technical of the polycarboxylate superplasticizer with the basis radical polymerization response principle.

This article has studied systematically synthetic method of the polyether polycarboxylate superplasticizer and the influence to the performance of polycarboxylate superplasticizer from the factors of raw material allocated proportion and craft parameter. This synthesis craft has the succinct operation. At the reaction process, the method did not need to deaerate with the nitrogen, and enhanced the response conversion rate, the response efficiency and the product quality, reduced the energy consumption. The synthesis craft has met the industrialization production requirement.
2. EXPERIMENTAL PART

2.1 Main raw material
Allyl alcohol polyethylene glycol (XPEG), from Shanghai, the molecular respectively include 1200, 1600, 2400;
Maleic anhydride ( MAn ), from Jiangsu;
Methacrylic acid sulfonic sodium (MAS), from Shandong.

2.2 Synthesis methods
Firstly unsaturated monomer was mixed with the four meatus bottle by a certain way. The faint yellow clarifies the liquid were prepared by a copolymerization reaction under a certain temperature, inverse proportion and concentration in a water solution system with instillment for a radical initiator and a certain time for reaction through the neutralization of NaOH.

The ideal molecular structure as shown in Figure 1:

```
          SO₃H
          \   \   
     CH₂   \   \   
   (CHCH)x(CH₂CH)y(CH₂CH)z
          HOOC COOH CH₃ CH₂(OCH₂CH₂)ₙ OH
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Figure 1: The ideal molecular structure

2.3 Infrared spectra (IR)
The sample for infrared spectra was prepared with the KBr sheeting through vacuum drying after deposition and lavation 4-5 time in aether. The instrument is Nicolet Avatar 360 in Xiamen University.

2.4 Test methods of the performance
The methods according to the GB/T8077-2000 (Concrete Admixture Uniform Nature Testing method), W/C is only 0.29, the cement JianFu P.O 42.5R was used.

3. RESULTS AND DISCUSSION

3.1 Orthogonal design of experiment results and analysis
By fixing the reaction temperature, the system concentration, the amount of the radical initiator, the throwing methods of the materials and so on, considering various monomers amount used and the XPEG molecular weight, performance influence of polycarboxylate superplasticizer is given in Table 1. The superplasticizer dosage (to convert solid) was 0.2%, W/C=0.29.
Table 1: Orthogonal design of experiment results

<table>
<thead>
<tr>
<th>NO.</th>
<th>XPEG (mol)</th>
<th>MAn (mol)</th>
<th>MAS (mol)</th>
<th>Molecular weight of XPEG</th>
<th>Initial cement paste fluidity (mm)</th>
<th>60min cement paste fluidity (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>3</td>
<td>1.0</td>
<td>1200</td>
<td>268</td>
<td>267</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>4</td>
<td>1.5</td>
<td>1600</td>
<td>288</td>
<td>278</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>5</td>
<td>2.0</td>
<td>2400</td>
<td>275</td>
<td>258</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>3</td>
<td>1.5</td>
<td>2400</td>
<td>282</td>
<td>262</td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
<td>4</td>
<td>2.0</td>
<td>1200</td>
<td>278</td>
<td>279</td>
</tr>
<tr>
<td>6</td>
<td>2.0</td>
<td>5</td>
<td>1.0</td>
<td>1600</td>
<td>281</td>
<td>268</td>
</tr>
<tr>
<td>7</td>
<td>2.5</td>
<td>3</td>
<td>2.0</td>
<td>1600</td>
<td>262</td>
<td>257</td>
</tr>
<tr>
<td>8</td>
<td>2.5</td>
<td>4</td>
<td>1.0</td>
<td>2400</td>
<td>254</td>
<td>232</td>
</tr>
<tr>
<td>9</td>
<td>2.5</td>
<td>5</td>
<td>1.5</td>
<td>1200</td>
<td>266</td>
<td>264</td>
</tr>
</tbody>
</table>

Table 2: Range analysis to the result of initial fluidity

<table>
<thead>
<tr>
<th>XPEG</th>
<th>MAn</th>
<th>MAS</th>
<th>Molecular weight of XPEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>831</td>
<td>811</td>
<td>803</td>
</tr>
<tr>
<td>K2</td>
<td>841</td>
<td>820</td>
<td>836</td>
</tr>
<tr>
<td>K3</td>
<td>782</td>
<td>810</td>
<td>815</td>
</tr>
<tr>
<td>R</td>
<td>59</td>
<td>10</td>
<td>33</td>
</tr>
</tbody>
</table>

Table 3: Range analysis to the result of 60min fluidity

<table>
<thead>
<tr>
<th>XPEG</th>
<th>MAn</th>
<th>MAS</th>
<th>Molecular weight of XPEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>803</td>
<td>786</td>
<td>767</td>
</tr>
<tr>
<td>K2</td>
<td>809</td>
<td>789</td>
<td>804</td>
</tr>
<tr>
<td>K3</td>
<td>753</td>
<td>790</td>
<td>794</td>
</tr>
<tr>
<td>R</td>
<td>56</td>
<td>4</td>
<td>37</td>
</tr>
</tbody>
</table>

From Table 2, which is range analysis to the result of initial fluidity, we can see that the influence factor of initial dispersibility from large to small in turn is: XPEG, MAS, XPEG molecular weight, MAn. From Table 3, which is range analysis to the result of 60min fluidity, we can see that the influence factor of dispersive conservation from large to small in turn is: XPEG molecular weight, XPEG, MAS, MAn.

The mole number of XPEG direct of PEO side chain has been introduced into molecular structure. In a certain scope, the more the quantity of side chain are, the stronger steric hindrance function is. So the reducing efficiency and the dispersion ability was good. Because the mole number was excessively high, which cause the principal chain to shorten, the conversion rate has been cause to reduce with excessive system concentration. So the initial dispersible ability and dispersive conservation have been cause to weaken. The mole number of Methacrylic acid sulfonic sodium (MAS) was also obvious to influence the dispersible ability of superplasticizer. The more amount was increased, the more -SO₃H groups were...
introduced, which can enhance the dispersible ability. But the mole number of Methacrylic acid sulfonic sodium surpassed the ration, the influence to dispersible ability of superplasticizer was not palpable, even the dispersible ability reduced possibly because of the reducing of the molecular weight for excessive reaction of chain transfer. The molecular weight of XPEG is one of the important influence factors about combs structure. when the molecular weight of XPEG was 1200, the initial cement paste fluidity was comparatively small and the fluidity conservation was good; When the molecular weight of XPEG was 1600, the initial cement paste fluidity and the fluidity conservation have been enhanced; When the molecular weight of XPEG was 2400, the dispersible ability was good but the fluidity conservation was not as well as the lower molecular weight because of reducing to the side chain density for the longer side chain affecting the copolymerization reaction.

Synthesizes above analysis, the best raw material proportion to synthesize the new polyether polycarboxylate superplasticizer was as follows: XPEG:MAN:MAS was 2:4:1.5, XPEG molecular weight was 1600.

3.2 Effect of product performance from the radical initiator

3.2.1 Effect from batch feeding way of the radical initiator

According to the action mechanism of the radical initiator, its half-life is different under the different temperature. The feeding way greatly affected the monomer conversion rate and the copolymer molecular structure, thus the dispersible ability got some Effect, which have been shown in Table 4:

<table>
<thead>
<tr>
<th>batch feeding way</th>
<th>one batch feeding</th>
<th>Two batch feedings</th>
<th>Three batch feedings</th>
<th>Adds by drops continuously</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial fluidity mm</td>
<td>270</td>
<td>285</td>
<td>300</td>
<td>314</td>
</tr>
<tr>
<td>60min fluidity mm</td>
<td>280</td>
<td>295</td>
<td>310</td>
<td>320</td>
</tr>
</tbody>
</table>

From Table 4, the dispersible ability of superplasticizer obtained the enhancement with increasing along with the batch feeding number of times. With the reaction time was increasing, the radical initiator lose activeness because of its density to lower, which cause the polymerization to difficulty. Compared with readying the materials at different times, adding by drops can guarantee the uniformity of the polymer structure. This is as a result of the dispersible ability of superplasticizer becoming better, therefore the best batch feeding way of radical initiator was adding by drops continuously.

3.2.2 Effect of the dosage of the radical initiator
Figure 2: Effect of the dosage of the radical initiator

From Figure 2, when the radical initiator has been used less, the copolymer molecular weight was larger, and then its surface activity reduced. When the dosage of the radical initiator used increased, the copolymer molecular weight reduced, polymerizing power enhancing and the dispersible ability also correspondingly increasing. On the other hand, when the dosage of the radical initiator was too large, system polymerization speed excessively was quick, which possibly cause the gelatin effect, cause the molecular weight sharp to grow. As a result, its disperser ability got lower with cement paste fluidity reducing. Therefore, the best dosage of the radical initiator was 2.0% of all monomers gross weight.

3.3 Effect of product performance from the system concentration

Figure 3: Effect of product performance from the system concentration

From Figure 3, along with the system concentration increasing, the dispersible ability of superplasticizer also rised. This was because the polymerization effect got better along with
the concentration increasing, the copolymerization conversion rate to be good and the
dispersible ability to be good. But when the concentration surpassed 60%, the solution has
reached the saturated condition, the monomer cannot dissolve completely, greatly reducing
the response activeness of the unsaturated duplet bond. So the dispersible ability of
superplasticizer has been reduced greatly. Therefore, the best concentration was 50%.

3.4 Effect of product performance from the Reaction temperature

From Figure 4, when the temperature was low, the dispersible ability was very bad. Along
with the temperature increasing, the dispersible ability of superplasticizer obviously rised. But
the dispersible ability dropped with the temperature increasingly. At the lower temperature, the
copolymerization was very difficult to occur, and the conversion rate was low. So that, the
performance of superplasticizer was bad with undertone. When too high temperature, the
system produced the massive hot free radicals, which cause the side reaction to increase with
difficulty control response. So the reaction produced other by-products, deepened the products
color, reduced its dispersible ability. Therefore, the best reaction temperature was between 70
C and 75C.

Figure 4: Effect of product performance from the Reaction temperature
3.5 Effect of product performance from the Reaction time

From Figure 5, we can see that at the initial reaction period, because of the few polymerization product, the larger monomer concentration, the lower conversion rate, the water-reducing effect was not very good. Along with the time increasing, the monomer concentration reduced gradually, the polymer concentration increased gradually, the conversion rate of monomer elevated gradually, so the water-reducing effect of product also increased. But after arrived certain time (5h), the initiator effect is weaken, the amount of free groups dropped. When the conversion rate achieved a certain degree, the conversion rate did not increased really, moreover possibly some side reactions occurred. Therefore, the best reaction time was five hours.

3.6 Infrared spectrogram analysis

Figure 6: Infrared spectrogram of the polyether polycarboxylate superplasticizer
Shown as Figure 6, 1100cm$^{-1}$ was the characteristic absorption band of ether linkage, 1562cm$^{-1}$ was the stretching vibration of the carboxylic groups, 3401cm$^{-1}$ was the characteristic absorption band of the hydroxyl, 1346cm$^{-1}$ was the characteristic absorption band of sulfonic groups. The results indicated that product structure was consistent with the ideal molecular structure designed.

4. CONCLUSIONS

(1) Through the orthogonal design of experiment, the best raw material proportion to synthesize the new polyether polycarboxylate superplasticizer was as follows: XPEG:MAN:MAS was 2:4:1.5, XPEG molecular weight was 1600.

(2) By analyzing the influences of several factors on the reaction process and the product performance influence, we confirmed the best reaction conditions.

(3) Through infrared spectrogram analysis to the molecular structure of synthetic product, the results indicated that high performance polycarboxylate superplasticizer product has been achieved with the ideal molecular structure including the ether groups, the sulfonic groups, the carboxylic groups and so on.

REFERENCES

