A novel kind of concrete superplasticizer based on aryl isocyanate polycondensates

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Abstract. A novel superplasticizer was synthesized by polycondensation of Alkyl phenol phosphate and toluene diisocyanate grafting with methoxy polyoxyethylene ether (MPEG). The chemical structure and molecular weight of polycondensates molecules were determined by 'H nuclear magnetic resonance (NMR) and gel permeation chromatography respectively. The experimental results indicated that the polycondensates of Alkyl phenol phosphate and toluene diisocyanate grafting with MPEG not only exhibited good water-reducing properties but also demonstrated effective anti-clay abilities alone. Furthermore, the polycondensates showed good fluidity maintaining abilities within 1–3 h and good workability of concrete. The results of T500 Time experiments show that lower plastic viscosity of the polycondensates leads to fresh concrete much “looser” than conventional PCEs in self-compacting concrete.

Keywords: superplasticizer, polycondensation, isocyanate, phosphoric acid group, plastic viscosity

1. Introduction

Polycarboxylate superplasticizers (PCEs) are widely used in different industrial fields to improve the performance of concrete. With the development of the construction industry and requirements of environmental protection, modern concrete technology aims towards minimizing the needs for Portland cement without sacrificing the important engineering properties of hardened concrete [1-3]. PCEs reduce the dosage of water to increase the strength of hardened concrete. However, it can be observed that some PCEs lead to fresh concrete with a very “sticky” and cohesive consistency [4]. In china, there has been a growing dependency on manufactured and dramatic decline of availability of naturally local sands as fine aggregates for concrete and mortar because of environmental and resource pressures. The sands used in concrete and mortar are getting less and less pure. The presence of clay as impurities increasing the water demand to provide a concrete or mortar of given workability, compromising the rheological property of concrete or mortar after absorbing water and swelling, weakening the bond between the cement and aggregates, and dramatic increasing the dosage of PCEs especially [5-8].

In this work, we synthesized and characterized a novel superplasticizer by polycondensation of Alkyl phenol phosphate and toluene diisocyanate grafting with methoxy polyoxyethylene ether (MPEG) and compare it with commercially available conventional PCEs. The backbone of this superplasticizer consists of benzene ring structure which is the same as poly(β-naphthalene sulfonates) (BNS).
2. Experimental investigation

2.1. Materials
The chemicals were used without further purification: Methoxy polyoxyethylene ether (MPEG, Mw=1000, Clariant corporation), Toluene-2,4-diisocyanate (TDI, Kumho Mitsui Chemical Inc.), Polyphosphoric acids (85%, Shanghai ziyi-reagent corporation), Phenoxyethanol (Shanghai Zihibio corporation), Formaldehyde (37%, Ningbo Xingye corporation), Montmorillonite (MMT, Aladdin Reagent corporation), the effective content $\geq$95%, average particle size=1.52µm, specific surface area=10.86 m$^2$/g.

2.2. Measurements
NMR spectra were performed on Bruker Avance DPX 400 MHz for $^1$H NMR. The residual solvent signals were used as reference; chemical shifts are given on the TMS scale (D$_2$O: $\delta$=4.79 ppm). Molecular weight was determined by gel permeation chromatography (GPC) measurements. The samples were analyzed using a 0.1mol/L NaNO$_3$ aqueous solution as eluent at a flow of rate of 0.5 mL/min.

2.3. Cement paste tests
An ordinary Portland cement (52.5, Jiangnan Onoda Co., China), which meets the requirements of GB8076 standard was used throughout all the experiments. The cement fluidity tests were conducted with the following procedure. The fresh cement pastes were prepared at 20°C~25°C, the water to cement ratio (w/c) is 0.29. The amount of 87g water containing the defined amount of polymer was added to 300g cement and mixed for 2 min at low speed and a further 2 min at high speed. The cement fluidity took the average of two measurements.

2.4. T$_{500}$ Time of self-compacting concrete [9]
This test is used to assess the flow rate of self-compacting concrete (SCC). The slump cone with above described dimensions was filled with fresh concrete. Upon lifting the cone, the time for the concrete to flow to diameter of 500 mm is recorded. The concrete mixture proportions are shown in table 1.

|        | Cement | Fly ash | Sand  | Gravel | Water |
|--------|--------|---------|-------|--------|-------|
| kg/m$^3$| 360    | 195     | 840   | 835    | 178   |

Table 1. Concrete mixture proportions (kg/m$^3$).

2.5. Polycondensates synthesis

2.5.1. Preparation of Phenoxyethanol Phosphate. Preparation of Phenoxyethanol Phosphate was according to the preparation method of literature[10]. Phenoxyethanol was esterified azeotropically in the presence of polyphosphoric acids in toluene on a water separator at 120°C~125°C. The reaction product which precipitated on cooling was filtered off, washed with petroleum ether and dried to give a white powder. The structure of Phenoxyethanol Phosphate was shown as figure 1.

![Figure 1. The reaction of preparation of phenoxyethanol phosphate.](image-url)
2.5.2. *Grafting of toluene diisocyanate with methoxy polyoxyethylene ether (MPEG-TDI).* Toluene-2,4-diisocyanate was reacted with MPEG (Mw=1000) at 80°C ~ 85°C for several hours. The reaction product was diluted by water. The structure of MPEG-TDI was shown as figure 2.

![Chemical structure](image1.png)

**Figure 2.** Reaction of preparation of MPEG-TDI.

2.5.3. *Polycondensation of Phenoxyethanol Phosphate and MPEG-TDI.* Phenoxyethanol Phosphate, MPEG-TDI, water and H₂SO₄ were uniform mixing, formaldehyde in the form of a 37% aqueous solution were added dropwise to the solution formed in this way. The polycondensation reaction is complete at 105°C. After the end of the reaction, the reaction mixture is brought to a pH of 7.5 by means of 32% aqueous NaOH solution. The structure of Polycondensates was shown as figure 3.

![Chemical structure](image2.png)

**Figure 3.** Reaction of preparation of MPEG-TDI.
3. Results and discussion

Polycondensates of phenoxyenthanol phosphate and MPEG-TDI were synthesized and characterized by $^1$H-NMR. The performance of polycondensates was investigated by cement paste and T500 time of fresh concrete.

3.1. Structures of the polycondensates

Figure 4 shows the 1H NMR spectrum of the typical polycondensates of phenoxyenthanol phosphate and MPEG-TDI. (a)-(c) peaks are ascribed to methylene protons in –O-CH$_2$- group, - (CH$_2$)$_2$- protons, (d) are ascribed to the chemical shift value of CH$_3$O- proton characteristic peaks in the MPEG chain segment moiety.

The characteristic properties of polycondensates obtained from GPC are shown in figure 5. The results indicate that the polycondensates have molecular weight 18336, with the PDIs are 1.22.

![Figure 4. $^1$H NMR spectrum of the polycondensates.](image1)

![Figure 5. Gel permeation chromatography.](image2)

3.2. Cement dispersion test

Cement dispersion test evaluates the dispersing performance of synthesized compounds. In figure 6, the results indicated that polycondensates demonstrated good water-reducing effects compared with conventional PCEs, despite the dosage of polycondensates is higher about 30% than conventional PCEs. The fluidity of polycondensates reached 200 mm at a 0.2 wt.% and 240 mm at a 0.25wt.% dosage. Impressively, the spread flow decreased only from 200 to 165 mm for polycondensates after 1 h, even maintained at 130 mm after 3 h. The loss of polycondensates was obviously less than conventional PCE used here (from 205 to 100 mm after 3 h). The polycondensates showed good fluidity maintaining abilities within 1~3 h here.

![Figure 6. Dispersion properties.](image3)

![Figure 7. Fluidity loss of cement paste.](image4)
3.3. Effect of clays on cement fluidity

Figure 8 indicates the impact of MMT on the conventional PCE and polycondensates. As shown in figure 8, in the cement/MMT system, the conventional PCE exhibited a strong decrease in performance caused by the addition of MMT. With approximately 1 wt.% MMT, the spread flow decreased by 36% and became less than 155 mm at 0.2 wt. % dosage, compared with figure 6. The newly synthesized polycondensates demonstrated good resistance property of MMT under the same condition. With approximately 1 wt.% MMT, the fluidity decrease from 200 mm to 180 mm at 0.2 wt.% dosage, the spread flow reductions were 10%, respectively.

![Figure 8. Effect of clays (MMT) on cement fluidity.](image)

3.4. T\textsubscript{500} time of concrete

Concrete viscosity can be assessed by the T\textsubscript{500} time during the slump-flow test. The time value of concrete fluidity with 500 mm is recorded to describe the rate of flow. Concrete with a low viscosity will have a very quick initial flow and then stop. Concrete with a high viscosity may continue to creep forward over an extended time. T\textsubscript{500} time test results were described in table 2. There were the same slump and spread of fresh concrete with PCEs and polycondensates by adjusting the dosage of admixture. T\textsubscript{500} time of polycondensates was only 7.8s. Compared with 11.4s of PCEs at the same spread flow, the spread flow velocity of polycondensates increased by 36%. It means fresh concrete with polycondensates has lower plastic viscosity than concrete with PCEs at the same plastic stress.

| admixture      | Slump /mm | Spread flow /mm | T\textsubscript{500} /s | Admixture dosage (%) |
|----------------|-----------|-----------------|------------------------|----------------------|
| PCEs           | 270       | 625             | 11.4                   | 0.45                 |
| Polycondensates| 268       | 630             | 7.8                    | 0.80                 |

4. Conclusions

A novel kind of concrete superplasticizer has been synthesized based on aryl isocyanate polycondensates. The chemical structure and molecular weight of desired products have been determined by \textsuperscript{1}H NMR and GPC, respectively. The results of cement fluidity tests indicate that the polycondensates of Alkyl phenol phosphate and toluene diisocyanate grafting with MPEG not only exhibit good water-reducing properties but also demonstrate effective anti-clay abilities alone. Furthermore, the polycondensates show good fluidity maintaining abilities within 1–3 h and good
workability of the concrete. The results of T500 Time experiments show the lower plastic viscosity of the polycondensates than conventional PCEs at the same plastic stress.

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