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酯醚型聚羧酸减水剂的制备及性能

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摘　要：采用自由基共聚法合成了酯醚共聚型聚羧酸减水剂(PCst)，红外光谱分析表明该减水剂分子结构中同时含有酯型与醚型支链。将 PCst 与酯型聚羧酸减水剂(PCes)和醚型聚羧酸减水剂(PCet)进行了性能对比研究。水泥净浆试验表明，PCet 的净浆流动度大，PCes 较小，PCst 的流动度介于两者之间；掺加 PCet 的水泥净浆易泌水，且对用水量波动和含泥量的敏感性大，PCes 与 PCst 的净浆粘聚性好，对用水量波动和含泥量的敏感性小。混凝土试验表明，PCet 的减水率大，PCes 较小，PCst 介于两者之间，但掺加 PCet 的新拌混凝土和易性略差，坍落度经时损失大，PCes 与 PCst 的混凝土拌合物不但和易性好，而且坍落度经时损失小。

关键词：聚羧酸系减水剂；酯醚共聚；分子结构；性能对比
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Synthesis and Properties of Ester Ether Copolymerization Polycarboxylate Superplasticizer

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Abstract: The ester ether copolymer polycarboxylate superplasticizer (PCst) was synthesized *via* free radical copolymerization. Based on the analysis by infrared spectroscpy, the structure of PCst contains ester and ether side chains. The properties of PCst, ester type polycarboxylate superplasticizer (PCes) and ether type polycarboxylate superplasticizer (PCet) were investigated. The results indicate that the sequence for the fluidity of cement pastes with three different polycarboxylate superplasticizers (PC) is PCet > PCst > PCes. The cement pastes with PCet are easily bleeding, which is sensitive to the change of water consumption and mud content. The cement pastes with PCst and PCes have the excellent cohesiveness, which is less sensitive to the fluctuation of water consumption and mud content. For concrete, the sequenceincreased order for the water reducing rate for different polycarboxylates is PCet > PCst > PCes. However, the workability of fresh concrete mixed with PCet is slightly worse, and the slump loss is greater. The concrete mixture with PCes and PCst has an excellent workability and a less slump loss with time.
Keywords: polycarboxylate superplasticizers; ester ether copolymerization; molecular structure; properties comparison

There are some studies on the synthesis of novel polycarboxylate superplasticizers (PC)[1–4]. As a kind of high-performance water-reducing agent with comb structure, PC becomes one of the most important concrete admixtures[5–9]. PC can be divided into ester type polycarboxylate superplasticizer (PCes) and ether type polycarboxylate superplasticizer (PCet) based on the different branched functional groups. There are a lot of macromonomers such as allyl polyethenoxy ether (APEG), methyl allyl polyoxyethylene ether (HPEG), and isopentenyl polyoxyethylene ether (TPEG). PCet can be prepared from all the above macromonomers and acrylic acid (AA) or methacrylic acid (MAA) through free radical polymerization.PCet is widely uin practice. However, compared to PCet, however, PCes has more complicated synthetic process and a lower water reducing

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rate, thus reducing its application.

PCet also has many advantages mentioned above, but it has some disadvantages such as poor compatibility with different cements, high sensitivity to mud content and water consumption. Thus, the concrete mixtures made by PCet present segregation, bleeding and exposed aggregate. Although PCes has lower water-reducing rate than PCet, it has some advantages such as good compatibility and excellent cohesiveness with different cements. The concrete mixtures made by PCes generally do not present segregation and bleeding. In this case, PCes and PCet can be used in practice to improve the property of water reducing agents by physical compounding, but the preparation of the two types of PC often complicate the process above.

In this paper, an ester ether copolymer polycarboxylate superplasticizer (PCst) was synthesized *via* free radical copolymerization. The molecular structure was characterized by infrared spectroscopy. In addition, the properties of PCst, PCes and PCet in cement paste and concrete were also analyzed.

1 Experimental

1.1 Main raw materials and reagents

Isopentenyl polyoxyethylene ether (TPEG, with M_w 2400) and polyethylene glycol methyl ether (MPEG, with M_W 1000 and 2000) were supplied by Jilin Zhongxin Chemical, China. Methacrylic acid (MAA), acrylic acid (AA), p-toluene sulfonic acid (PTSA), hydroquinone and cyclohexane were purchased from Tianjin Baishi Chemical, China. Ascorbic acid (VC), hydrogen peroxide solution (30% concentration) and thioglycolic acid (TGA) were obtained from BASF (China) Co., PCes and PCet were provided by Huizhou Clariant Chemical Co.,Ltd and Shaanxi Youbang New Material Technology Co.,Ltd, respectively.

For concrete test, cement P.O. 42.5 was supplied by Hailuo Cement Plant, Shaanxi, China. Sand and stone were used according to GB8076—2008 (concrete admixture).

1.2 Synthesis of PCst

1.2.1 Preparation of esterified macromonomers A certain amount of MPEG (M_W 1 000 and 2 000) was added into a 500 mL four-neck round-bottom flask with a stirrer, a water separator with a condenser, a thermometer and an intelligent control temperature device in an one-step process. The temperature increased to 60 ℃ in an hour under stirring and heating, and then the hydroquinone, MAA, PTSA and cyclohexane were added in sequence to the flask to ensure the uttermost esterification reaction by continually removing the produced water from reaction to the water separator. The mole ratio (MAA) : (MPEG) was1.50:1.00, the dosages of PTSA, hydroquinone and cyclohexane were 3.00%, 0.17% and15% of the total mass of monomers, respectively. The temperature increased to 105-110 ℃ and maintained for 6 hours. After the reaction, the product was cooled to room temperature, the final esterification macromonomers were M1 ($MPEG_{1000}$-MAA) and M2 ($MPEG_{2000}$-MAA).

1.2.2 Copolymerization of PCst PCst was synthesized through free radical polymerization with MPEG-MAA, TPEG and AA in water solution. In this step, a certain amount of TPEG was dissolved in deionized water and added into the flask. When the temperature increased to 60 ℃ in 30min, the aqueous solution consisting of hydrogen peroxide, M1 or M2 and AA, and the aqueous solution consisting of VC and TGA, were added dropwise into the reaction mixture for 2 h and 2.5 h, respectively. After dropping process, the reaction solution was kept 60℃ for 1 h, then cooled to room temperature and neutralized to pH value 7±1 with 30% (in mass fraction) sodium hydroxide solution.

The proportion of synthesized aqueous PCst was as follows: the mass ratio of monomers (esterification macromonomers and TPEG) and AA was 7.86:1.00, the initiator (hydrogen peroxide and VC) and chain transfer (TGA) agent were 1.05% and 0.54% of the mass of all monomers, respectively, the final solid content of polymer solution was 40% .

1.3 Characterization of PCst

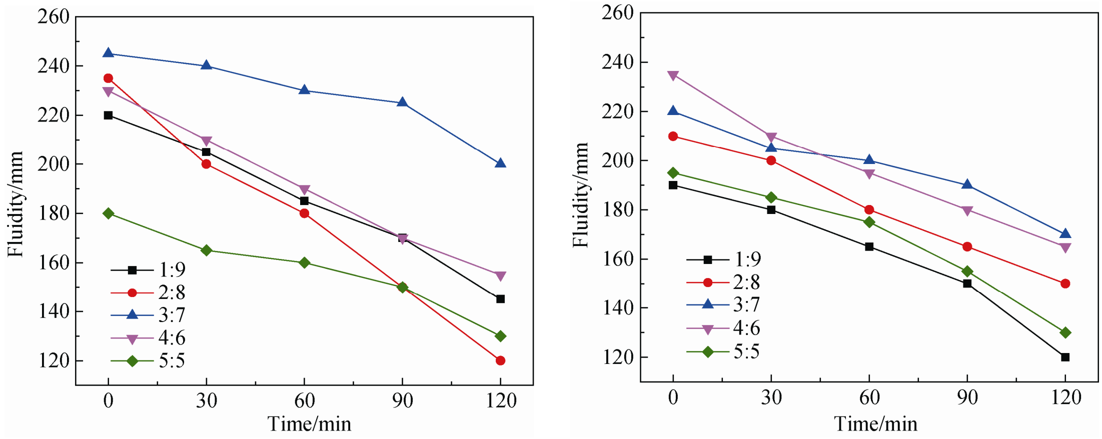
For FTIR analysis, PCst powder of 1~2 mg was mixed with KBr powder of 200~300 mg in an agate mortar. The mixture was made into a tablet for the coming measurement. For cement test, cement paste with a water-cement ratio (W/C) of 0.29 was prepared at （25±1） ℃. The dosages of three different PC (PCes, PCst or PCet) were 0.15% and 0.20% (weight percent of solid content to cement). After measuring the initial fluidity of cement paste, we sealed the paste sample in a container for 30, 60, 90 and 120 min for the subsequent measurements of the fluidity. The detailed process was based on GB/T 8077-2012 (methods for testing the uniformity of a concrete admixture). For concrete test, a concrete mixture proportion added with three different PC (PCes, PCst or PCet) was designed based on the Chinese Standard JGJ/T55—2011 (designing principles of normal concrete). The dosage of three different PCs was 0.20% (weight percent of solid content to cement). The slump of fresh concrete was measured according to GB/T50080—2002 (standard for text method of performance on ordinary fresh concrete) and GB 8076—2008: concrete admixture. The compressive strength of hardened concrete was measured at 3, 7 and 28 days of standard curing according to GB/T 50081—2002: standard for text method of mechanical properties on ordinary fresh concrete.

2 Results and discussion

2.1 Effect of ester to ether ratio on dispersibility of PCst

The influences of ester macromonomer type (M1 or

M2) and the monomer ratio (M1 or M2 to TPEG) on the dispersibility in cement paste were investigated. Figure 1 shows the fluidity and fluidity loss behavior of cement pastes with different PCst.



(a) Mass ratio of M1 with TPEG (b) Mass ratio of M2 with TPEG

Fig. 1 Effect of mass ratio of monomers on the fluidity of cement paste

In Fig. 1, the initial fluidity of cement paste is 245 mm, and the fluidity loss is 55 mm after 2 h when the mass ratio between M1 and TPEG is 3:7. The initial fluidity of cement paste is 235 mm and the flow loss is 70 mm after 2 h when the mass ratio of M2 to TPEG is 4:6,. The results indicate that PCst in which M1 and TPEG are copolymerized with a proper proportion has better dispersibility and dispersibility-maintaining ability. The specific mass ratio (M1):(TPEG):(AA) is 2.36:5.50:1.00, the initiator content and TGA dosage are 1.05% and 0.54% (mass fraction to total mass of monomers) respectively. The reaction temperature increases to 60 ℃, shortens the reaction time for 2.5 h and keeps the reaction temperature for 1 h .

Some studies on cement-water-superplasticizers system revealed that long side chains have better dispersibility and dispersibility-maintaining ability. The dispersibility is mainly attributed to steric hindrance of the side chains [10–12]. The results obtained could be explained that long side chains of TPEG form a strongly steric hindrance, thus effectively reducing the fluidity loss of cement paste. Also, short side chains of M1 can favor long-side chains uniformly distributing in main chain and easily stretching in liquid phase. Furthermore, the adsorption capacity and stability on cement particles are reinforced by short ester side chains. It could be inferred that long ether and short ester side chains play an important role in increasing the fluidity and decreasing the fluidity loss of cement paste.

2.2 Structural characteristics of PCst

Fig. 2 shows the chemical formula for the synthesis of PCst, in which m and n represent different relative molecular masses of M1 or M2 and TPEG, respectively.

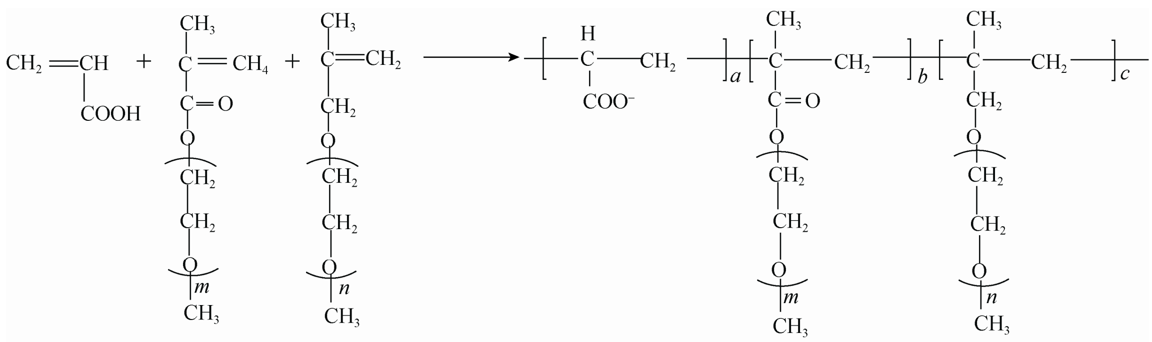
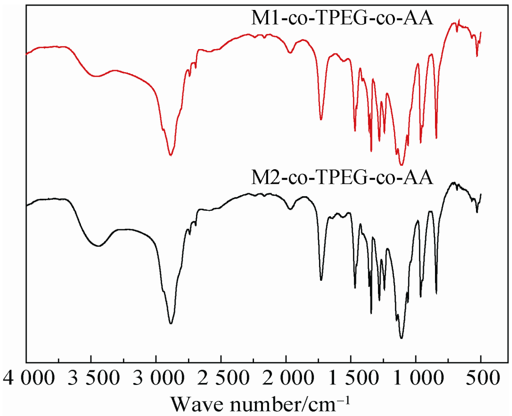


Fig. 2 Free radical copolymerization of M1 or M2, AA and TPEG

Figure 3 shows the FTIR spectra of PCst. Clearly, the wider absorption peaks at 3 300-3 650 cm^{-1} are due to the stretching vibration of the O–H(O–H, COOH stretching) bond. The stretching vibration appears at 2 850–3 000 cm^{-1} (-CH_3). The stretching vibration of C=O in ester bond appears at 1 730–1 740cm^{-1} and 1 210–1 320 cm^{-1} (C–O, COOH stretching). Those absorption peaks at 1 060-1 150 cm^{-1} are attributed to the stretching vibration of C–O–C structure, which are the typical absorption peaks of ether. The characteristic absorption peaks of the polyethylene oxide group (EO, $(CH_2CH_2O)_n$) are detected at 800–1 200 cm^{-1}. It is indicated that ester and ether groups exist in the molecular structure of PCst.



1–(M1-co-TPEG-co-AA); 2–(M2-co-TPEG-co-AA).

Fig. 3　FTIR spectra of PCst

2.3 Properties of PCst, PCes and PCet

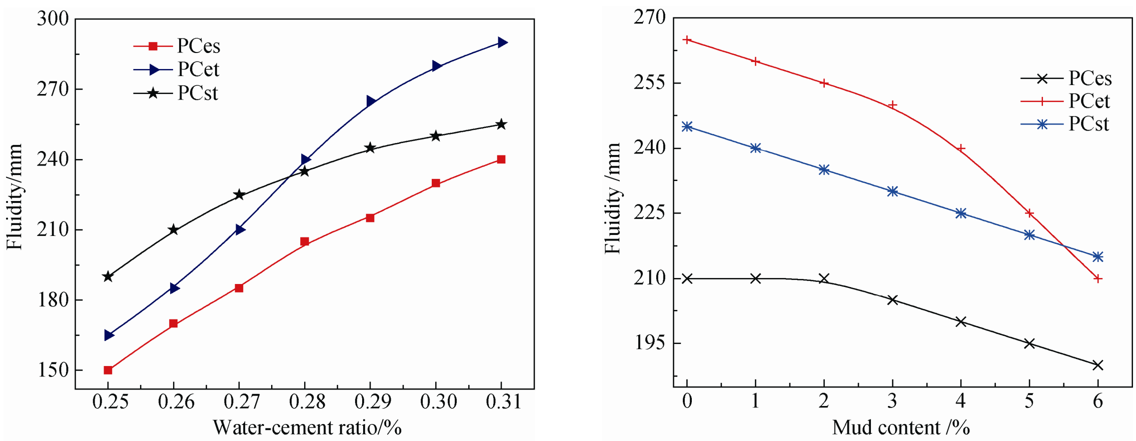
2.3.1 Workability of cement pastes with different PC Table 2 shows the fluidity and fluidity loss of cement pastes mixed with PCst, PCes and PCet. Clearly, the sequence of the fluidity of cement pastes with PC from high to low is PCet > PCst > PCes. All the cement pastes have a good fluidity retention with time. However, some cement pastes with PCet display a certain bleeding. The cement pastes with PCes and PCst have excellent cohesiveness and water-retaining ability. When ester and ether side chains are simultaneously introduced into the molecular structure, the water reducer PCst keeps a great dispersibility of PCet as well as excellent water-retaining properties of PCes. In addition, the introduction of branched chains with different functional groups and lengths leads to a more diverse molecular structure of PCst. Consequently, PCst has a greater dispersibility and a better compatibility with different cements.

Table 2　Influence of PC on fluidity of cement pastes

Cement	Time/h	PCes dosage/%		PCst dosage/%		PCet dosage/%	
		0.15	0.20	0.15	0.20	0.15	0.20
Hai luo P·O42.5	0	210	235	245	260	265	290★
	1	225	245	230	255	260	285
	2	210	220	200	245	240	280
Yao bai P·O42.5	0	175	180	250	265	260	295
	1	190	215	240	255	245	290★
	2	180	200	230	250	240	280
Ji dong P·O42.5	0	230	260	260	270	265	310★
	1	240	270	255	265	240	305★
	2	230	255	250	250	225	295

Note: ① PCst (the mass ratio of M1 and TPEG was 3:7); ② ★represents the bleeding of cement pastes.

2.3.2 Sensitivity difference among different PC at varying water consumptions and mud contents　Figure 4 shows the sensitivity difference among PCet, PCst and PCes at different water consumptions and mud contents. In the experiments, the dosages of all three PC are 0.15% (in mass fraction of solid content to cement). The sequence for the sensitivities of three different PC at different water consumptions and mud contents from high to low is PCet ,PCst , PCes. It is indicated that the sensitivity of PCst at different water consumptions and mud contents is relatively lower. The molecular structure of PCst containing ester groups is hydrolyzed in alkaline environment, and some partially hydrolyzed side chains can weaken the sensitivity of PCst at varying water consumptions and mud contents in cement paste[13].



(a) Sensitivity to water consumption　　(b) Sensitivity to mud content

Mass ratio of M1 and TPEG was 3:7.

Fig. 4　Sensitivity of PC to water consumption and mud content

2.3.3 Performance of concrete with different types of PC As is known, the importance of concrete workability cannot be overemphasized, and the slump and slump retention ability is an important index to measure the concrete workability[14]. In this study, the concrete workability without and with different PC was determined. The concrete mix proportion with cement (C), sand (S) and aggregate (G) is 360 (kg/m^3), 739 (kg/m^3), 1 108 (kg/m^3), and the dosage of PC is 0.18%. The amount of water was adjusted to control the target slump of concretes at (210±10) mm. Table 3 shows the slump variation, gas content and compressive strength of concrete.

Table 3 Performance of concrete without and with different PC

PCs type	Water amount/(kg·m^{-3})	Water -reducing rate/%	Gas content/%	Slump/mm			f_c/MPa		
				0 h	1 h	2 h	3 d	7 d	28 d
Reference	218		2.2	200			19.3	26.4	32.7
PCes	170	22.0	2.8	200	175	165	24.1	40.3	50.4
PCst	157	27.9	2.6	200	180	165	27.3	42.1	54.6
PCet	152	30.3	3.2	205※	165	120	26.5	45.5	56.8

Note: ①PCst (the mass ratio of M1 and TPEG was 3:7); ②※ represents the segregation and bleeding of concrete.

Clearly, the sequence for the water reducing rate of three different PC from high to low is PCet > PCs**t** > PCes. However, the fresh concrete mixed with PCet exhibits a poor workability and appears a certain segregation or bleeding phenomena. The water-retaining ability, cohesiveness property, and flow-ability of fresh concrete are greatly improved when PCst and PCes are added. In addition, the slump loss of fresh concrete with PCst and PCet is relatively smaller. The sequence for the compressive strength of hardened concrete prepared by three different PC from high to low is PCet > PCst > PCes, which is mainly due to the different water contents of concrete mixtures prepared by three different PC. The results indicate that the concrete mixture with PCst has a great water reducing rate and excellent slump retaining, water-retaining ability and cohesiveness property. This is since the polarity of ester molecules is greater than that of ethers, PCst provides a relatively strong hydrophilicity, thus causing that concrete mixture exhibits a good slump retention and a water retention. Also, there may be synergistic effects between side chains with different functional groups and lengths, favoring the improvement of the performance of concrete mixed with PCst.

3 Conclusions

1) A type of ester ether copolymer polycarboxylate superplasticizers (PCst) was synthesized through free radical polymerization with the MPEG-MAA, TPEG and AA in water solution.

2) Based on the comparative studies on cement paste tests on the properties of PCst, PCes and PCet, the dispersibility of PCst was slightly less than that of PCet, but more than that of PCes. The cement pastes with PCet were easily bleeding, but the cement pastes with PCst had the better cohesiveness and lower sensitivity at varying water consumptions and mud contents in cement pastes with PCes.

3) The comparative studies on concrete tests on the properties of PCst, PCes and PCet showed that the water-reducing rate of PCst was slightly lower than that of PCet, but greater than that of PCes. However, the cohesiveness and slump-retaining of concrete mixtures with PCst and PCes were clearly superior to the concrete mixtures with PCet. PCst had a great dispersibility of PCet as well as the excellent workability and compatibility of PCes.

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