

聚羧酸系高性能减水剂

制备、性能与应用技术新进展

Polycarboxylate superplasticizers

New progress in preparation, performance and application technology

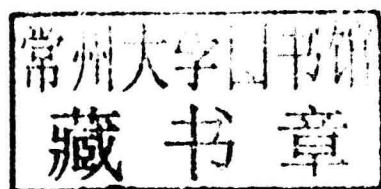
第六届混凝土外加剂应用技术专业委员会年会

中国建筑学会建材分会混凝土外加剂应用技术专业委员会 编

聚羧酸系高性能减水剂制备、 性能与应用技术新进展

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前 言

今年正值中国建筑学会建筑材料分会混凝土外加剂应用技术专业委员会成立十周年。10年来，混凝土外加剂应用技术专业委员会分别于2005年、2007年和2011年在北京成功主办了三届全国聚羧酸系高性能减水剂及其应用技术交流大会，在我国混凝土及外加剂等相关领域引起了强烈的反响，并有效地促进了聚羧酸系高性能减水剂研究的技术创新，加快了外加剂这一主流技术、主流产品的大力推广应用，对促进行业技术水平的提高起到了积极的作用。

这10年间，我国聚羧酸系高性能减水剂及其应用技术取得了令人瞩目的发展，大量的工程实践表明，聚羧酸系高性能减水剂对保证混凝土工程质量发挥了十分重要的作用，取得了一系列卓有成效的成果。如今，外加剂行业迎来了聚羧酸系高性能减水剂及其应用技术发展进程又一新的起点。

为了更好地交流国内外聚羧酸系高性能减水剂最新研究成果与应用情况，总结工程应用的实践经验，并探讨聚羧酸系高性能减水剂原材料方面的最新进展，混凝土外加剂应用技术专业委员会于2013年6月18日在北京举办“第四届全国聚羧酸系高性能减水剂及其应用技术交流会”暨“第六届中国建筑学会建筑材料分会混凝土外加剂应用技术专业委员会年会”，并特此编辑、正式出版了名为《聚羧酸系高性能减水剂制备、性能与应用技术新进展》的论文集。本届会议论文集收录了57篇具有较高学术价值的论文，内容涉及聚羧酸系高性能减水剂的综述与理论研究、合成与复配技术、应用技术、检测技术等。本论文集可供混凝土与外加剂领域的技术、生产、施工、质检、科研人员及高等院校师生等参考。

由于时间及水平有限，论文集中难免有不妥之处，谨请读者赐教指正。

混凝土外加剂应用技术专业委员会
2013年2月

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综述与理论研究

An Overview of Current PCE Superplasticizer Technology

Prof. Dr. Johann Plank

(Technical University Munich, Inorganic Chemistry Department, Munich, Germany)

Summary: Since their invention in 1981, polycarboxylate ether (PCE) polymers have attained a considerable share of the concrete superplasticizer market. This article reviews the state of art in PCE technology with respect to the chemistry being used, new promising applications and future challenges. Recently, in addition to the well-known methacrylate ester (MPEG), allyl and vinyl ether (APEG/ VPEG) types, new PCEs based on copolymers from isoprenol ether and acrylic acid (IPEG-type) with excellent dispersing performance were introduced. Also, organo-silane modified, hyperbranched and crosslinked PCEs were presented as new concepts. Major challenges for current PCE technology include their high sensitivity to different cement compositions and consumption by clay impurities. Initial results indicate that new compositions can help to reduce this sensitivity, and that PCEs with hydroxyalkyl side chains exhibit are more robust against clay. A highly promising new development is the application of PCEs as cement additive which can help to increase efficiency of the clinker mill and to produce a cement with reduced water demand.

Keywords: Superplasticizer, Polycarboxylate, Concrete, Performance, Challenge

1 Introduction

The invention of polycarboxylate comb polymers in 1981 as a novel class of concrete superplasticizers clearly represents a milestone concrete technology. With their help, it now was possible to formulate highly advanced concretes such as ultra-high strength concrete (UHPC) which can attain compressive strength values > 150 MPa, or self-compacting concrete (SCC) which no longer requires conventional compaction. Moreover, specific PCE molecules were designed which can provide long slump life (> 2 hours) for ready-mix concrete without sacrificing early strength. These few examples illustrate the extraordinary contribution of PCE admixtures to modern concrete technology.

Apart from technology, PCE superplasticizers also have been a striking commercial success. For 2010, the global volume of PCE applied in concrete was estimated at 3 mio. tons, based on

liquid with 20% (m/m) solid content. Currently, China represents the largest market for PCE products, with an annual volume of 1.27 mio. tons in 2010. Additionally, substantial volumes of PCE powder (estimates are between 60,000 and 80,000 tons) are manufactured e. g. for dry-mix mortar products such as self-leveling underlayments or machinery grouts.

This article attempts to provide an overview of the current status of PCE technology and its perspectives in the future. At first, the chemistry of the various kinds of polycarboxylates available today will be presented. This is followed by a review of more recent applications. In the third part, shortcomings and deficiencies of PCEs as evidenced in daily operations, and potential solutions for them will be discussed. Finally, an outlook will be given on what still can be expected from PCE technology in the future.

2 Chemistry of PCE Superplasticizers

As of today, a great diversity of chemically very different PCE products is on the market which includes:

MPEG-type PCEs: They constitute the first type of PCE product which was introduced into the Japanese market by Nippon Shokubai under the name 'FC 600'. MPEG-PCEs can be synthesized following two different routes:

(a) Esterification of poly (methacrylic acid) with methoxy poly (ethylene glycol) utilizing an acid catalyst (e. g. *p*-toluol sulfonic acid) and an azeotrop or vacuum to remove the water; this process produces a highly uniform comb polymer with regular (statistical) distribution of the MPEG graft chains along the polyanionic trunk chain (random copolymer, see Fig. 1). Disadvantages of this method are long reaction times and low conversion rates ($\sim 70\%$). Note that residual MPEG has been shown to present the main reason for excessive air entrainment into concrete by PCE. A practical solution to these problems is offered by trans-esterification of poly (methacrylate methyl ester) with MPEG under similar conditions as above. The advantage of this method is higher conversion rates because methanol presents a better 'exit group' than water. Disadvantages are the higher cost for the PMA methyl ester and the necessity to hydrolyse the methyl ester after grafting.

(b) Aqueous free radical copolymerisation of ω - methoxy poly (ethylene glycol) methacrylate ester macromonomer with methacrylic acid presents the second and quite common route to MPEG-PCEs (Fig. 2). This reaction is easy to carry out, composition and performance characteristics of the polymer can be controlled by the molar ratios of the monomers, and the trunk chain length is adjusted by utilizing chain transfer agents such as mercaptanes or methallyl sulfonic acid. Here, it has to be considered that the relative reactivities of both monomers may vary, depending on the pH. Notably, the macromonomer can exhibit a higher reactivity than methacrylic acid. As a consequence, in many polymerisations not uniform, but gradient polymers are attained which at the beginning of the polymerisation exhibit a higher side chain density than towards the end of the reaction. Recently, such gradient polymers possessing specific compositions have been synthesized on purpose by applying RAFT polymerisation techniques. It was found that these

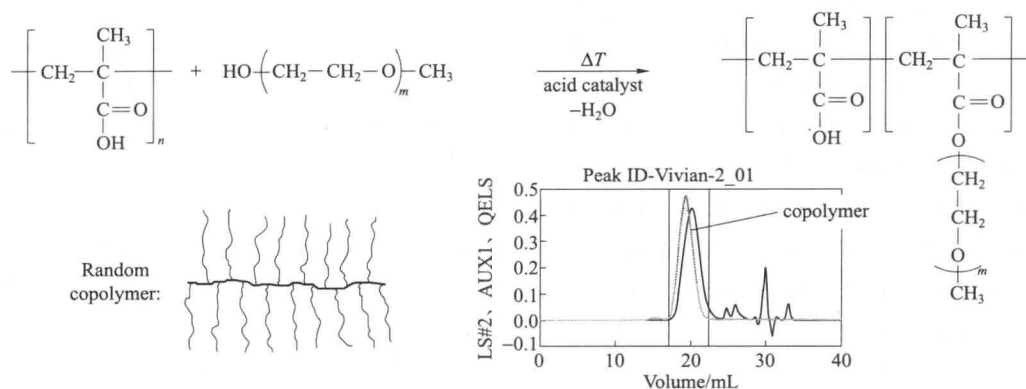


Fig. 1 Esterification (grafting) process for the synthesis of MPEG-type PCEs producing a highly uniform random (statistical) copolymer, as evidenced by GPC

polymers adsorb more strongly on cement as a result of their large anionic blocks in the trunk chain. Additionally, they exhibit higher sulfate tolerance and thus perform more robust with different cements, as they are less desorbed by SO_4^{2-} anions than comparable PCE molecules possessing random distribution of the lateral chains. Hence, these gradient PCE polymers are considered to be advantageous.

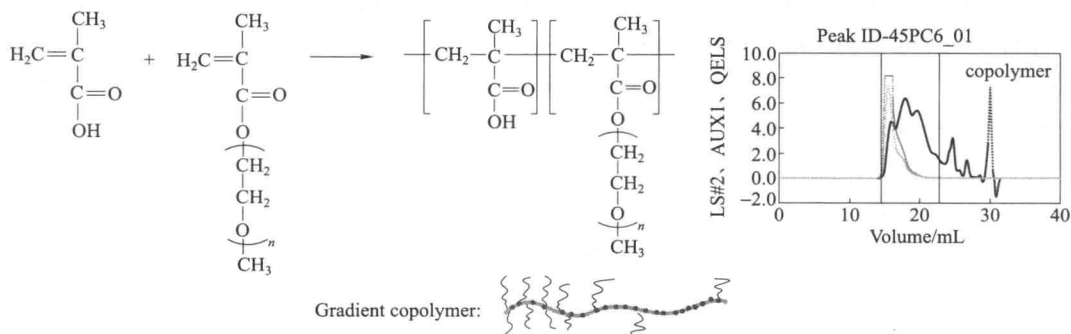


Fig. 2 Free radical copolymerisation route for the synthesis of MPEG-type PCEs producing a gradient polymer with non-homogeneous distribution of side chains

In both processes (a) and (b), attention must be given to the diol content. Commercial MPEG may contain variable amounts of PEG which presents a diol. When PEG (diol) is present in the esterification reaction, then crosslinking between two poly (methacrylic acid) backbones will occur. Such crosslinked PCE molecules, however, are known to provide very poor—if any—dispersion performance. Similarly, when PEG impurity is present in the synthesis of the macromonomer MPEG-methacrylate ester, then a diester is formed which in the subsequent copolymerisation reaction again produces a crosslinked PCE, with highly negative consequences. It has been found that the diol content present in MPEG ideally should be $< 0.5\%$, while a content of 1% already shows significant reduction in PCE performance.

APEG-type PCEs: This kind is prepared from α -allyl- ω -methoxy or- ω -hydroxy poly (ethylene glycol) ether and maleic anhydride or acrylic acid as key monomers via free radical copolymerisation either in bulk or in aqueous solution (Fig. 3). Polymerisation in bulk works well for side chain lengths of up to 34 EO units and produces a viscous PCE polymer with 100% solid content which thus requires dilution with water to obtain a pourable liquid of $\sim 60\%$ (m/m) solid content. Polymerisation in water typically yields copolymers possessing very short trunk chains ('star polymers') made of ~ 10 repeating units only, which were found to exhibit superior dispersing performance. The disadvantages of aqueous copolymerisation are longer reaction times, lower conversion rates ($\sim 85\%$) and lower concentration of finished PCE solution.

The first APEG-PCEs suffered from a reputation of causing delayed plastification (i. e. the slump of concrete increased over ~ 30 min to reach a maximum, then dropped afterwards). Such behaviour is highly unwanted as it often results in overdosing of PCE and subsequent bleeding. Meanwhile, this problem has been solved, for example by incorporation of specific comonomers as spacer molecules such as styrene which can modify the conformational flexibility of the trunk chain. This method provides PCE molecules with pronounced stiffness which can adsorb faster and thus avoid the effect of delayed plastification.

VPEG-type PCEs: Such PCEs are obtained by aqueous free radical copolymerisation of e. g. 4-hydroxy butyl-poly (ethylene glycol) vinyl ether and maleic anhydride or acrylic acid (Fig. 3). Their polymerisation must be conducted at temperatures $< 30^\circ\text{C}$ to avoid monomer degradation. As a result, a specific low temperature initiator is required. The advantage of vinyl over allyl ether technology is the much higher reactivity of vinyl ethers. VPEG-PCE technology is essentially exclusive to BASF which possesses of a huge patent portfolio.

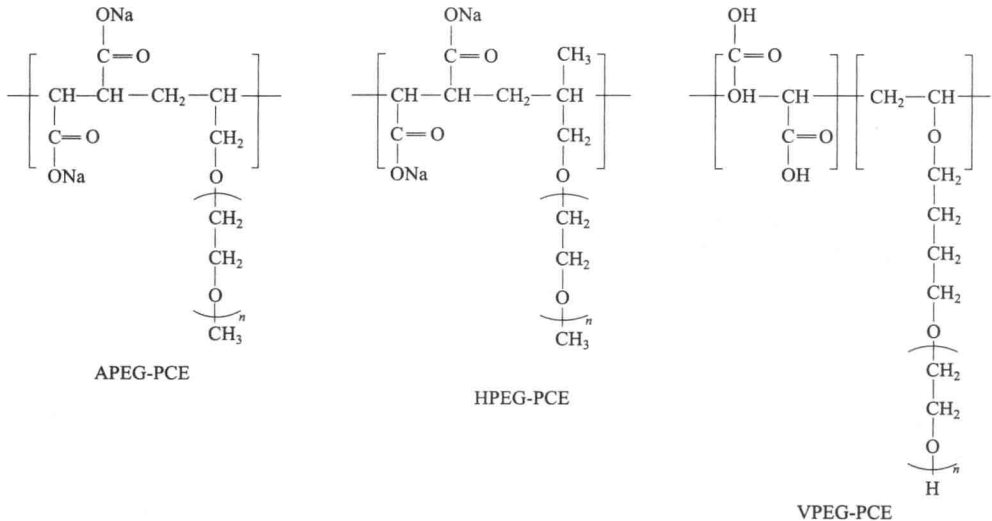


Fig. 3 Chemical compositions of typical APEG -, HPEG - and VPEG - type PCE polymers

HPEG-type PCEs: They constitute a minor modification of the APEG-based PCEs because there, instead of allyl ethers, methylallyl ethers are utilized. Their synthesis is easier compared to

APEG-PCEs because the methallyl radical does not show resonance stabilization. Unfortunately, methallyl alcohol is not listed under the REACH scheme in Europe, therefore its use in the manufacturing of PCEs is excluded at the moment.

IPEG-type PCEs: This type of PCE (sometimes also referred to as TPEG-PCE) is synthesized from isoprenyl oxy poly (ethylene glycol) ether by copolymerisation with e. g. acrylic acid (Fig. 4). In recent years, this PCE became highly popular, especially in China, because of its excellent performance which often exceeds that of any other type of PCE, and its simple preparation utilizing free radical copolymerisation. A minor drawback of IPEG-PCE technology is that macromonomers possessing very long EO chains (e. g. $n \geq 50$) appear to be difficult to make and their purity is low.

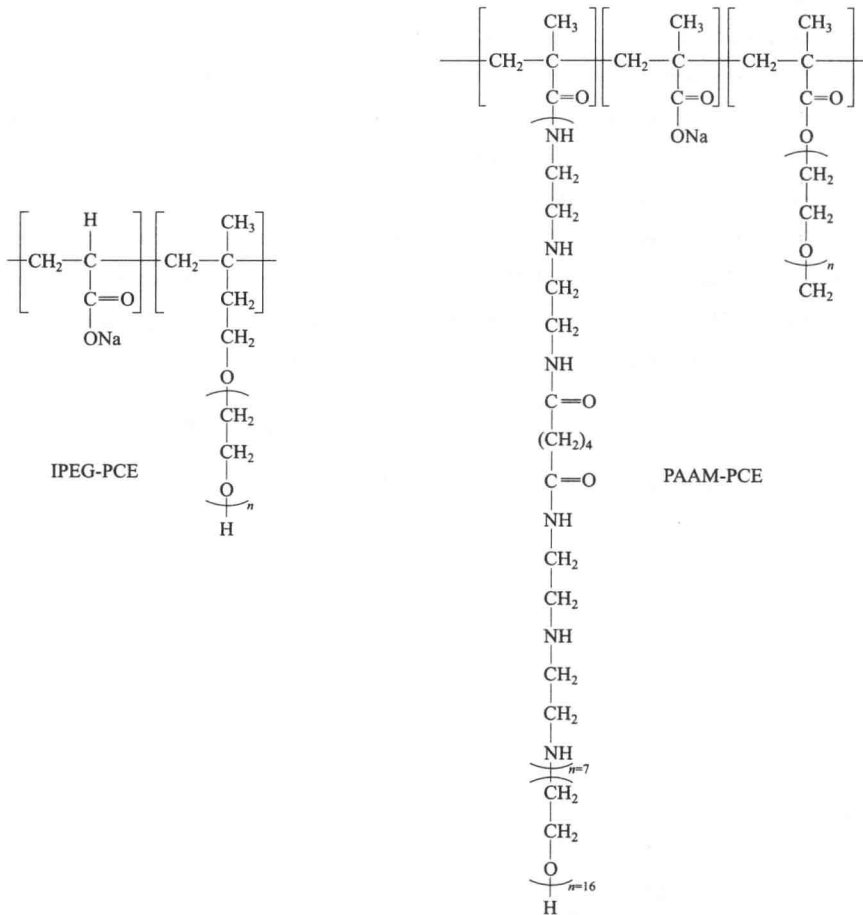


Fig. 4 Chemical structures of typical IPEG-and PAAM-type PCE polymers

Manufacturers of IPEG-PCEs should be aware that the IPEG macromonomer is relatively unstable and slowly decomposes into isoprene and MPEG. It therefore requires to keep the IPEG macromonomer as well as the finished IPEG-PCE always in aqueous solution. Similarly, powder prepared from IPEG-PCE undergoes the same reaction. This poses a significant problem, both

during the spray-drying process where isoprene constitutes a potential source for explosions, as well as during transportation, storage and application of IPEG-PCE powder which exhibits emissions. When formulated into a dry-mix mortar, then such emissions can increase the volatile organic compound (VOC) value to undesired levels.

PAAM-type PCEs: These zwitterionic PCEs possess mixed side chains composed of polyamidoamine (PAAM) and PEO segments (Fig. 4); this structural feature distinguishes them fundamentally from all other PCEs which exclusively contain PEO/PPO side chains. The PAAM-type PCE is said to fluidify cement at W/C ratios as low as 0.12. Its disadvantage is the high cost of the PAAM side chain.

In spite of the great diversity of current products, industrial and academic researchers still develop and introduce new PCE polymers with additional structural features. Those include:

Organo-silane modified PCEs: Recently, two groups independent from each other presented novel silylated PCE polymers. The first group incorporated 3-trimethoxysilyl propyl methacrylate (MAPTMS) as a new comonomer into a conventional MPEG-type PCE while the second group utilized N-maleic γ -amidopropyl triethoxy silane (MAPS) as an organo-silane modified monomer (Fig. 5). The rationale behind the introduction of a silane functionality into the PCE molecule was to obtain a chemical bond between the C—S—H surfaces and the superplasticizer, made possible through condensation of silanol ($-\text{Si}-\text{OH}$) groups present in both compounds. If formed, such a bond would anchor the PCE molecule irreversibly to the surface of cement hydrates and thus provide a molecule which cannot be desorbed e. g. by sulfate ions or anionic retarder molecules as a result of competitive adsorption. Indeed, it was found by both groups that such silylated PCE polymers exhibit high sulfate tolerance. Additionally, the MAPS modified PCE was shown to disperse cement at substantially lower dosages than the same non-modified PCE. However, clear analytical evidence

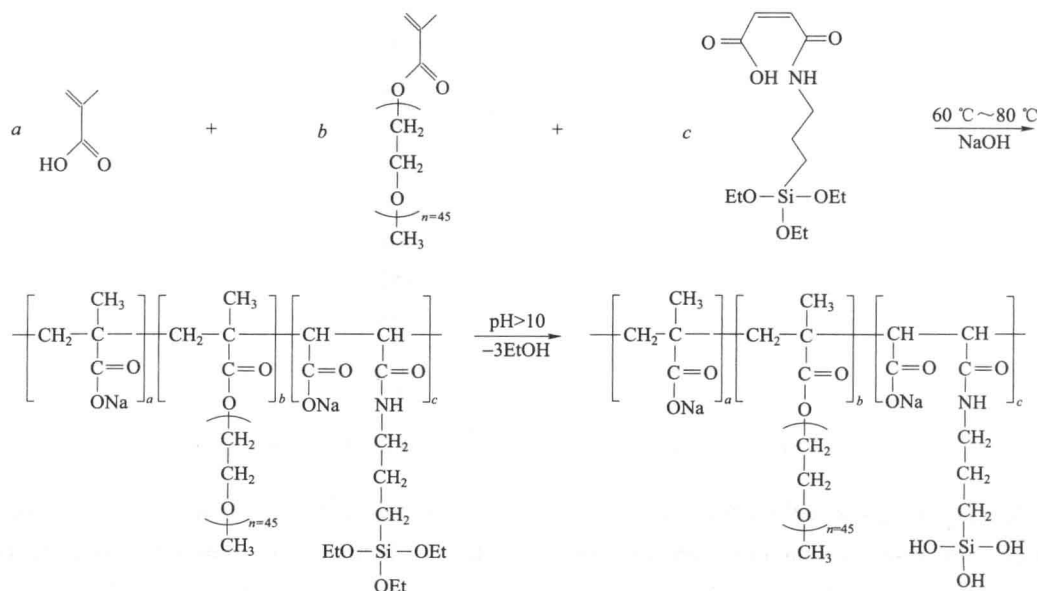


Fig. 5 Synthesis route for an organo-silane modified PCE polymer [15]

for the formation of a chemical bond between the novel PCEs and the mineral surfaces is still lacking.

Crosslinked PCE molecules (XPEG-type PCEs): It has been established before that the ability of an individual PCE molecule to cover as much surface area on cement as possible directly correlates to its dosage. Hence, polymers which stretch out on the surface are believed to present more effective PCEs. Following this concept, slightly crosslinked PCE molecules utilizing diesters (e. g. from PEG and methacrylic acid or maleic anhydride) were synthesized and shown to provide enhanced dispersion. Moreover, hyperbranched and dendrimeric PCE polymers were suggested using polycarboxylated polyglycerols. Surprisingly, they could not enhance cement dispersion when compared to conventional PCE products. Still, they present an interesting approach which perhaps requires further fine-tuning in the synthesis.

3 PCE Powder

Typically, powder products of PCEs are prepared by spray-drying of a mother liquor possessing a solid content as high as possible, to minimize the cost for energy. Manufacturers have to consider that PCE powder presents a highly flammable organic substance which exhibits self-ignition at relatively low temperature (≥ 180 °C). As a result, several explosions and fires have occurred in the spray-driers of different manufacturers in Europe. It is now recognized that a safe drying process requires the addition of certain substances (e. g. ADDITIN®) which significantly increase the self-ignition temperature. Additionally, it is common practice now to dry under an inert gas atmosphere, either CO₂ (e. g. from an exhaust gas stream) or N₂. With these two measures, safe drying of PCE is possible.

Another aspect of PCE powder is its stickiness which results from the oily or waxy EO side chains. Thus, the tendency to compact into lumps increases with increasing side chain length, side chain density and PEG/MPEG impurities contained in the PCE mother liquor. To avoid such negative behaviour, inorganic carrier materials possessing high surface area such as e. g. pyrogenic silica, foamed silica, diatomaceous earth or talcum are added during the spray-drying process. These measures result in a non-compacting powder. Its free-flowing properties (which are important when the PCE powder is mixed into a day-mortar formulation such as SLU) can be further improved by applying a flow-bed granulation step following the spray-drying.

4 Novel PCE Applications

The exceptional performance of current commercial PCE products enables to build spectacular concrete structures. A prominent example is the construction of Burj Khalifa in Dubai, with 820 m currently the tallest skyscraper in the world. Up to 650 m, its structure consists of high strength concrete incorporating VPEG-type PCEs and a retarder. This combination provided a formulation which was pumpable up to a record height of 650 m (!), and showed slump retention over 3 hours

at temperatures as high as 50 °C. Such formulations were unthinkable before the advent of PCE polymers.

Another significant and rather new application of PCE is in sprayed concrete (also referred to as shotcrete) which is applied in tunnelling e. g. for high speed railway tracks, metro lines, mining operations, etc. There, PCE polymers are utilized to reduce the water-to-cement ratio to lower values than those attainable from polycondensates which results in higher strength of concrete. This effect is highly desirable, because conventionally accelerated shotcrete exhibits poor strength development as a result of spontaneous crystallisation of cement hydrates induced by the accelerator.

Apart from concrete, PCE superplasticizers now are also used in large quantities in the manufacture of gypsum wallboards. There, the PCE products allow to substantially reduce the amount of mixing water required for the gypsum slurry. As a result, this gypsum board can be dried with much lower energy demand which reduces cost. Thus, the primary motivation for PCE used here is reduction of energy cost, while the associated gain in strength is second. Specific PCE products which are characterised by extremely fast adsorption within few seconds have been designed for this application. This use has become popular in the U. S. , the largest market for gypsum wallboards, and to some extent in Europe as well.

5 Challenges for Current PCE Technology

In spite of these many advances, PCE technology still exhibits areas where improvements are required. Those include:

Enhanced Tolerance to Different Cement Compositions: Already in the early days of PCE use, applicators noticed that most PCE products exhibit a marked sensitivity for different cement qualities. As an example, Fig. 6 displays the performance of a typical conventional PCE product with 13 different cements. While before it was known that increased C_3A contents in a cement require elevated dosages of superplasticizer to cover the more abundant surfaces of ettringite sufficiently, it was now found that additional factors influence PCE dosage. Free dissolved sulfate (e. g. from alkali sulfates) was identified as one reason for decreased cement compatibility of PCEs. While initially it was believed that the reason behind the decrease in PCE performance caused by sulfate was coiling (shrinkage) of the PCE molecule, it has been established recently that competitive adsorption between PCE and sulfate presents the main effect, whereby sulfate desorbs PCE from the surface of cement and thus prevents it from developing its dispersion power. In accordance with this model, ready-mix type PCEs which are characterised by a high grafting density (and correspondingly low anionic character) are more affected by sulfate than the more anionic PCEs used in precast concrete applications. The industry has solved the problem of sulfate sensitivity by introducing blocks of highly anionic charge into the trunk chain (e. g. in gradient polymers) or by incorporating a few, but highly surface-affine anchor groups into the PCE molecule such as e. g. dicarboxylates or phosphonates.

Still, researchers are aware that PCE performance apparently can be affected by cement